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Block Copolymer Electrolytes: Thermodynamics, Ion Transport, and Use in Solid-
State Lithium/Sulfur Cells

By

Alexander Andrew Teran

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

Doctor of Philosophy

in

Chemical Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Nitash P. Balsara, Chair

Professor Elton Cairns

Professor Andrew Minor

Fall 2013

Block Copolymer Electrolytes: Thermodynamics, Ion Transport, and Use in Solid-State Lithium/Sulfur Cells

©

By Alexander Andrew Teran

Abstract

Block Copolymer Electrolytes: Thermodynamics, Ion Transport, and Use in Solid-State Lithium/Sulfur Cells

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Alexander Andrew Teran

Doctor of Philosophy in Chemical Engineering

University of California, Berkeley

Professor Nitash P. Balsara, Chair

Nanostructured block copolymer electrolytes containing an ion-conducting block and a modulus-strengthening block are of interest for applications in solid-state lithium metal batteries. These materials can self-assemble into well-defined microstructures, creating conducting channels that facilitate ion transport. The overall objective of this dissertation is to gain a better understanding of the behavior of salt-containing block copolymers, and evaluate their potential for use in solid-state lithium/sulfur batteries. Anionically synthesized polystyrene-*b*-poly(ethylene oxide) (SEO) copolymers doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt were used as a model system. This thesis investigates the model system on several levels: from fundamental thermodynamic studies to bulk characterization and finally device assembly and testing.

First, the thermodynamics of neat and salt-containing block copolymers was studied. The addition of salt to these materials is necessary to make them conductive, however even small amounts of salt can have significant effects on their phase behavior, and consequently their ion-transport and mechanical properties. As a result, the effect of salt addition on block copolymer thermodynamics has been the subject of significant interest over the last decade. A comprehensive study of the thermodynamics of block copolymer/salt mixtures over a wide range of molecular weights, compositions, salt concentrations and temperatures was conducted. The Flory-Huggins interaction parameter was determined by fitting small angle X-ray scattering data of disordered systems to predictions based on the random phase approximation (RPA). Experiments on neat block copolymers revealed that the Flory-Huggins parameter is a strong function of chain length. Experiments on block copolymer/salt mixtures revealed a highly non-linear dependence of the Flory-Huggins parameter on salt concentration. These findings are a significant departure from previous results, and indicate the need for improved theories for describing thermodynamic interactions in neat and salt-containing block copolymers.

Next, the effect of molecular weight on ion transport in both homopolymer and copolymer electrolytes were studied over a wide range of chain lengths. Homopolymer electrolytes show an inverse relationship between conductivity and chain length, with a plateau in the infinite molecular weight limit. This is due to the presence of two mechanisms of ion conduction in homopolymers; the first mechanism is a result of the segmental motion of the chains surrounding the salt ions,

creating a liquid-like environment around the ion while the second mechanism of ion conduction is attributed to diffusion of the entire polymer chain with coordinated ions.

Equilibrated block copolymer electrolytes exhibit a non-monotonic dependence on molecular weight, decreasing with increasing molecular weight in the small molecular weight limit before increasing when molecular weight exceeds about 10 kg mol^{-1} . Conductivity in annealed electrolytes was shown to be affected by two competing factors: the glass transition temperature of the insulating polystyrene block and the width of the conducting poly(ethylene oxide) (PEO) channel. In the low molecular weight limit, all ions are in contact with both polystyrene (PS) and PEO segments. The intermixing between PS and PEO segments is restricted to an interfacial zone of width of about 5 nm. The fraction of ions affected by the interfacial zone decreases as the conducting channel width increases. Furthermore, the effect of thermal history on the conductivity of the block copolymer electrolytes was examined. Results suggest that long-range order impedes ion transport, and consequently decreases in conductivity of up to 80% were seen upon annealing.

The effect of morphology on ion transport was studied by conducting simultaneous impedance and X-ray scattering experiments as the block copolymer electrolyte transitioned from an ordered lamellar structure to a disordered phase. The ionic conductivity increased discontinuously through the transition from order to disorder. A simple framework for quantifying the magnitude of the discontinuity was presented.

Finally, block copolymer electrolytes were examined specifically for use in high energy density solid state lithium/sulfur batteries. Such materials have been shown to form a stable interface with lithium metal anodes, maintain intimate contact upon cycling, and have sufficiently high shear moduli to retard dendrite formation. Having previously satisfied the concerns associated with the lithium metal anode, the compatibility of the sulfur cathode was explored. The sulfur cathode presents many unique challenges, including the generation of soluble lithium polysulfides (Li_2S_x , $2 \leq x \leq 8$) during discharge. The solubility of such species in block copolymers and their effect on morphology was examined. The lithium polysulfides were found to exhibit similar solubility in the block copolymers as in typical organic electrolytes, however induced unusual and unexpected phase behavior in the block copolymers.

Inspired by successful efforts to physically confine the soluble lithium polysulfides via nanostructured carbon-sulfur composites in the cathode, our nanostructured block copolymer electrolytes were employed in full electrochemical cells with a lithium metal anode and sulfur cathode. Different cathode compositions, electrolyte additives, and cell architectures were tested. Surprisingly, the polysulfides diffused readily from the cathode through the block copolymer electrolyte, and the normally robust SEOLi metal interface was detrimentally affected their presence during cycling. The polysulfides appeared to change the mechanical properties of the electrolyte such that intimate contact with the lithium metal was lost. Several promising strategies to overcome this problem were investigated and offer exciting avenues for improvement for future researchers.

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List of Symbols

A	attempt frequency, $S\text{ cm}^{-1}\text{ K}^{-1/2}$
A_c	sample area (cm^2)
A_{eff}	effective sample area (cm^2)
a	statistical segment length (nm)
B_i	x-ray scattering length density ($\text{nm}^{-2}\text{ mer}^{-1}$)
b_i	x-ray scattering length (nm mer^{-1})
d	domain spacing (nm)
D	periodicity
E_a	activation energy (kJ mol^{-1})
E_c	Coulombic efficiency (%)
f	morphology factor
FWHM	full width at half maximum (nm^{-1})
I	scattering intensity (cm^{-1})
I_{Dis}	disordered copolymer scattering intensity (cm^{-1})
I_{Bgd}	background scattering intensity (cm^{-1})
I_{Ord}	ordered copolymer scattering intensity (cm^{-1})
i	current density (A cm^{-2})
$i_{C,i}$	current density upon i^{th} charge (A cm^{-2})
$i_{D,i}$	current density upon $(i + 1)^{\text{th}}$ discharge (A cm^{-2})
K	molecular weight dependent contribution conductivity ($\text{S kg mol}^{-1}\text{ cm}^{-1}$)
L	thickness (cm)
M_{PEO}	number averaged molecular weight of the poly(ethylene oxide) block (kg mol^{-1})
M_{PS}	number averaged molecular weight of the polystyrene oxide block (kg mol^{-1})
M_{SEO}	number averaged molecular weight of the SEO copolymer (kg mol^{-1})
M_S	molar mass of styrene (kg mol^{-1})
M_{EO}	molar mass of ethylene oxide (kg mol^{-1})
M_i	molar mass of species i (kg mol^{-1})
m	mass (g)
m_S	mass of sulfur (g)
N	number averaged degree of polymerization (sites chain^{-1})
N_{avg}	Avogadro's number
N_i	number averaged degree of polymerization of block i (sites chain^{-1})
N_{PEO}	number averaged degree of polymerization of PEO block (sites chain^{-1})
N_{PS}	number averaged degree of polymerization of PS block (sites chain^{-1})
N_{SEO}	number averaged degree of polymerization of SEO copolymer (sites chain^{-1})
P	pressure (psi)
PDI	polydispersity index
q	scattering vector (nm^{-1})
q_{max}	scattering vector at highest intensity scattering (nm^{-1})
q^*	scattering vector at the primary scattering peak (nm^{-1})
$q_{\{hkl\}}$	scattering vector at reflection plane hkl (nm^{-1})
R	ideal gas constant ($\text{kJ mol}^{-1}\text{ K}^{-1}$)
R_b	bulk resistance (Ω)
R_g	radius of gyration (nm)

$R_{g,0}$	radius of gyration of neat copolymer (nm)
r	molar salt concentration ($[\text{Li}^+] [\text{EO}]^{-1}$)
$S_{C,i}$	specific capacity upon i^{th} charge (mAh g^{-1})
$S_{D,i}$	specific capacity upon $(i + 1)^{\text{th}}$ discharge (mAh g^{-1})
S_{ideal}	ideal capacity (mAh)
T	temperature (K)
T_g	glass transition temperature (K)
T_m	melting temperature (K)
T_{ODT}	order-disorder transition temperature (K)
T_0	reference temperature (K)
V	potential (V)
v_{EO}	molar volume of ethylene oxide ($\text{cm}^3 \text{mol}^{-1}$)
v_{LiTFSI}	molar volume of LiTFSI ($\text{cm}^3 \text{mol}^{-1}$)
v_{ref}	reference volume ($\text{nm}^3 \text{site}^{-1}$)
v_s	molar volume of styrene ($\text{cm}^3 \text{mol}^{-1}$)
w	weight fraction of salt in copolymer
X	number of hours to charge/discharge cell (h)
x_{av}	molar average length of the polysulfide anion
Y_{LiTFSI}	volume fraction salt in PEO/salt microphase

Greek

α	interfacial zone width (nm)
ΔH_m	enthalpy of melting (J g^{-1})
θ	scattering angle
ρ_c	density of cathode matrix (g cm^{-3})
ρ_i	density (g cm^{-3})
ρ_{PEO}	density of polyethylene oxide (g cm^{-3})
ρ_{PS}	density of polystyrene (g cm^{-3})
λ	wavelength (nm)
χ	interaction parameter
χ_{eff}	interaction parameter of salt-containing copolymer
χ_0	interaction parameter of neat copolymer
σ	ionic conductivity (S cm^{-1})
σ_c	ionic conductivity during cooling (S cm^{-1})
σ_{dis}	ionic conductivity of disordered copolymer (S cm^{-1})
σ_{H}	ionic conductivity during initial heating (S cm^{-1})
σ_n	normalized conductivity
σ_{ord}	ionic conductivity of ordered copolymer (S cm^{-1})
σ_{VTF}	ionic conductivity from VTF fit to data (S cm^{-1})
σ_0	ionic conductivity from segmental motion (S cm^{-1})
ϕ_{EO}	volume fraction of PEO microphase
$\phi_{\text{EO/salt}}$	volume fraction of PEO/LiTFSI microphase

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Chapter 1 - Introduction

1.1 Block Copolymer Self-Assembly

Block copolymers are a class of materials in which a chain of identical molecules is covalently bonded to a chain of a different molecule. The most basic version of a block copolymer is a linear diblock copolymer, shown in Figure 1-1a, where two chemically distinct chains, or blocks, are linked end-to-end. Using this strategy, one can create materials with many blocks bonded together into as many different molecular architectures as current synthetic strategies will allow. This work focuses exclusively on nearly monodisperse, diblock copolymers. The classic battle between entropy and enthalpy, coupled with the geometric constraints on phase separation, cause these materials to self-assemble into nanostructured morphologies with length scales on the order of 5 - 100 nm. These ordered morphologies include stacked lamellae (LAM), bicontinuous gyroids (GYR), and hexagonally packed cylinders (HEX) among others and are shown in Figure 1-1b. At sufficiently high temperature, entropy dominates, resulting in the formation of a disordered phase (DIS) where the two blocks are homogeneously mixed; the nature of concentration fluctuations in the disordered phase has been studied in considerable detail.⁶ This self-assembly, or lack thereof, is controlled by the volume fraction of one component, ϕ , and the degree of segregation χN , where N is the overall degree of polymerization and χ is the Flory-Huggins interaction parameter, which is a measure of thermodynamic compatibility between the blocks. The classic diblock copolymer phase diagram is shown in Figure 1-1c. By tuning these parameters appropriately, it is possible to obtain nanostructured materials that combine the material properties of the constituent blocks. This has led researchers to use block copolymers as solid membranes for selective transport of various species, typically with one transporting block and one structural block.

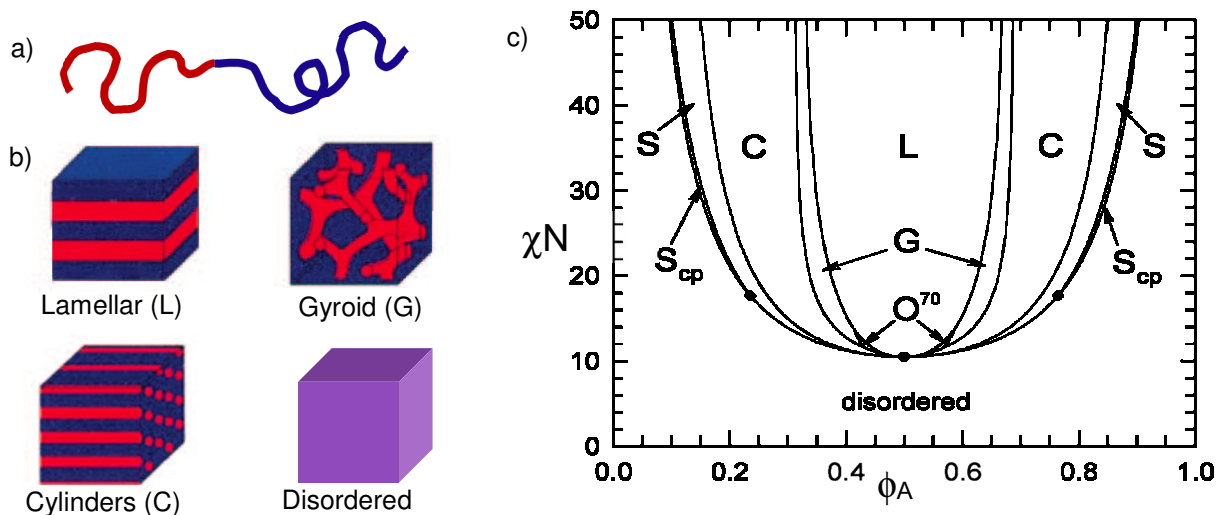


Figure 1-1 Block copolymer self assembly.

Schematics of (a) a linear diblock copolymer and (b) selected block copolymer morphologies. (c) Theoretically predicted block copolymer phase diagram from ref¹

1.2 Polymer Electrolytes

Lithium metal batteries hold great promise to dramatically increase the energy density compared to current lithium ion batteries. The thermodynamic instability of traditional organic electrolytes against lithium metal and the tendency for lithium dendrites to form within the cell have prevented the successful commercialization of lithium metal rechargeable batteries. Polymer electrolytes offer a solution to both these problems by forming a stable interface with the lithium metal and, if the modulus of the polymer is high enough, preventing the formation of lithium dendrites.⁷

Of particular interest in recent years are block copolymers with added ions that selectively dissolve in one block for applications such as solid-state electrolytes in rechargeable lithium batteries. Such materials can offer high conductivity, stable electrochemical characteristics, and excellent mechanical properties. One commonly studied system is polystyrene-*b*-poly(ethylene oxide) (SEO).^{8,9} Polyethylene oxide (PEO) has been studied for several decades as a solid-state electrolyte due to its ability to dissolve alkali salts,¹⁰⁻¹² and polystyrene (PS) is a mechanically rigid polymer. Previous work in our group has successfully shown that nanostructured block copolymer electrolytes, specifically polystyrene-*b*-poly(ethylene oxide) (SEO) doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), have high ionic conductivity at elevated temperature and sufficiently high modulus to prevent the formation of dendrites.⁸ Additionally, the system has been shown to form a stable interface with lithium metal anodes as well as maintain intimate contact upon cycling in symmetric¹³ and full electrochemical cells.¹⁴

1.3 Outline of Dissertation

The remainder of this dissertation is organized as follows. Chapter 2 describes the synthesis of the block copolymer using anionic techniques. A description of the polymerization characterization and purification techniques is presented along with a list of the synthesized and characterized polymers. In Chapter 3 we study the thermodynamics of block copolymers with and without salt by fitting the random phase approximation (RPA) to small angle x-ray scattering results. The effect of molecular weight on ion transport in homopolymer electrolytes is discussed in Chapter 4. In Chapter 5, we extend the molecular weight study to symmetric block copolymer electrolytes. We also discuss the role thermal processing and long-range order on ion transport. In Chapter 6 we examine the effect of nanostructure on ion transport by performing simultaneous conductivity and x-ray scattering experiments of a block copolymer electrolyte as it undergoes an order-disorder transition. Chapter 7 marks the beginning of our work investigating the compatibility of block copolymer electrolytes with the lithium/sulfur chemistry. To begin, we examine the solubility of lithium polysulfides in the block copolymers and observe unexpected changes in morphology. In Chapter 8 we use these block copolymers as solid polymer electrolytes in full Li/S electrochemical cells and examine the ability of the nanostructured electrolyte to confine the sulfur in the cathode matrix. When our initial strategy proves unsuccessful, several different strategies for cell improvement are investigated, including electrolyte additives, polymer-ceramic hybrid electrolytes, and sulfur-carbon composite active material. Finally, Chapter 9 provides a summary of the study.

Chapter 2 - Block Copolymer Electrolyte Synthesis and Characterization

ABSTRACT

Polystyrene-*block*-poly(ethylene) oxide was synthesized by means of living anionic polymerization. Removal of residual cryptand catalyst from the copolymers was achieved using a packed column of neutral alumina. The molecular weights and molecular weight distributions were determined via gel permeation chromatography while the relative block lengths were determined using nuclear magnetic resonance. Salt-containing copolymer samples were freeze-dried from solution with rigorous drying procedures. Small angle x-ray scattering and electrochemical impedance spectroscopy are used extensively for morphological and ion transport characterization, respectively, of the polymer electrolytes

2.1 Anionic Polymerization

Anionic polymerization allows the synthesis of polymers with well-defined molecular weights and narrow polydispersities, and is conducive to the creation of sequentially grown blocks to form block copolymers. This technique requires extremely pure solvents and monomers, since the presence of water or other proton donors can cause chain termination and oxygen can cause coupling of the chains. Great care is taken to remove contaminants by rigorous purification of the solvents and monomers as well as thorough degassing of the reaction vessels to remove oxygen. All of the synthetic steps are performed on a high-vacuum line or in an argon-filled glove box. Reaction glassware is cleaned by soaking in a saturated KOH/isopropanol bath for several hours followed by extensive rinsing using a sequence of tap water, distilled water, and alternating methanol and tetrahydrofuran before being dried overnight in a convection oven.

The following is a description of the anionic synthesis, characterization, and purification of polystyrene-*block*-poly(ethylene oxide) (SEO), whose structure is shown in Figure 2-1. First the polystyrene block is grown using *sec*-butyllithium as an initiator. The polystyrene block is then end-capped by a single ethylene oxide moiety to yield an oxyanion, functionalizing the chain end for ethylene oxide polymerization. A cryptand catalyst is then added to the polymerization reactor before to enable propagation of the polyethylene oxide block. The synthetic methods have been adopted from ¹⁵ and ¹⁶ and the ethylene oxide was purified according to a patent by Eitouni et al.¹⁷

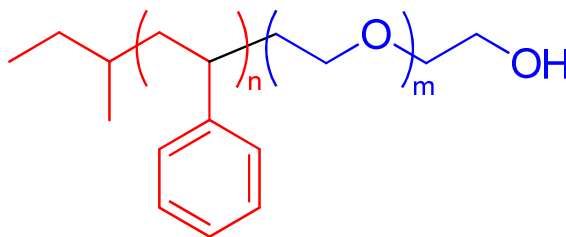


Figure 2-1 Structure of polystyrene-*block*-poly(ethylene oxide).

2.1.1 Benzene Purification

One liter of benzene from the solvent columns (MBraun SPS) was added to an evacuated, flame dried 2-L reactor. The reactor was returned to the vacuum line, frozen using liquid nitrogen, and degassed for at least 15 minutes to remove trace oxygen. After the degassing was complete, the benzene was allowed to thaw completely before being brought into the glove box. An appropriate quantity of *sec*-butyllithium in cyclohexane was added to the benzene as a water-scavenger; in general 0.035 mol of *sec*-butyllithium per 1000 mL of solvent should be sufficient to remove all traces of moisture. Styrene was then added in a roughly 10:1 molar ratio with *sec*-butyllithium in order to ensure styrene oligomers grow which are heavy enough to prevent any possibility of entrainment in the subsequent solvent distillation. The mixture was allowed to stir in the glove box for 24 hours at room temperature. The solvent was determined to be clean if the bright red color characteristic of polystyryl lithium species appeared and persisted without fading. The purification reactor was then removed from the glove box and returned to the vacuum line, and once again frozen, degassed, and thawed. A polymerization reactor and a waste reactor were added to the vacuum line, degassed, and flame dried. Approximately 50 mL was then distilled from the purification reactor into a waste reactor in order to remove the undesired cyclohexane from the mixture. Clean benzene was then distilled from the purification reactor to the polymerization reactor.

2.1.2 Styrene Purification

A fresh bottle of styrene was opened in the glovebox and filtered through a column of neutral alumina packed on glass wool into a flame dried reactor, using a volume of alumina equal to the volume of styrene to be purified. The neutral alumina removes inhibitor and the as-received styrene should be sufficiently anhydrous. The styrene was then removed from the glovebox and added to the vacuum line where it was frozen, degassed, and thawed before being returned to the glovebox.

2.1.3 Styrene Polymerization

The polymerization reactor containing pure benzene was brought into the glovebox. The desired amount of *sec*-butyllithium initiator was carefully added to the rapidly stirred polymerization reactor, followed by the desired amount of styrene monomer. The reaction mixture will rapidly change from colorless to bright yellow, orange or red, depending on the concentration of chain ends. The intense colors are characteristic of the growing polystyrene chain capped by polystyryl lithium anions. The reaction scheme for the initiation and propagation of the styrene polymerization is shown in Figure 2-2. The reaction was allowed to stir in the glovebox for at least eight hours. After complete consumption of the styrene monomer, an aliquot for

analysis was removed. The aliquot was terminated by the addition of degassed isopropanol, and the sample was analyzed by gel permeation chromatography (GPC) to determine its molecular weight.

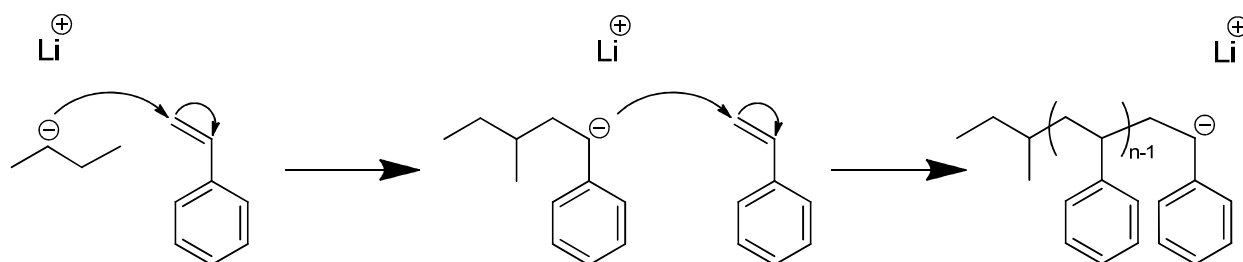


Figure 2-2 Styrene polymerization initiation and propagation scheme.

2.1.4 Ethylene Oxide Purification

Extreme caution is required for working with ethylene oxide. It is an acutely toxic gas and all precautions should be taken to avoid exposure. The first purification stage consists of a long neck, round bottom flask with freshly powdered calcium hydride and a “football” stir bar. The flask was placed on the vacuum line and degassed, first at room temperature and then on liquid nitrogen. An excess of ethylene oxide was distilled from the cylinder into the liquid nitrogen-cooled flask. The ethylene oxide/calcium hydride mixture was then slowly warmed from liquid nitrogen temperature (-196 °C) to the temperature of a dry ice/isopropanol mixture (-78 °C) and stirred overnight to remove moisture.

The second purification stage consisted of *n*-butyllithium dissolved in ethylbenzene. One liter of ethylbenzene was added to an evacuated, flame dried 2-L reactor using a funnel in the glovebox. Approximately 0.075 mol of *n*-butyllithium in heptane was added to the reactor as a water-scavenger. The mixture was allowed to stir in the glove box overnight at room temperature before being placed on the vacuum line and subsequently frozen, degassed, and thawed. A waste reactor was added to the vacuum line and degassed. Approximately 50 mL was then distilled from the *n*-butyllithium purification stage into the waste reactor in order to remove the undesired heptanes from the mixture.

Ethylene oxide was then distilled from the calcium hydride purification stage to the *n*-butyllithium purification stage. The source flask was cooled on a mixture of salted ice water (-10°C), and the destination reactor was cooled on a mixture of dry ice/isopropanol. The distillation was stopped once the ethylene oxide was completely removed from calcium hydride. At this point, the *n*-butyllithium purification stage was thawed to room temperature and stirred for two hours to remove trace moisture. The reactor can be kept at room temperature for up to three weeks, however over time a small amount of white solids will appear. These solids are slowly propagating ethylene oxide polymers and oligomers which precipitate from the mixture due their low solubility in ethylbenzene. The presence of these solids does not affect the purification step, and the stage will continue to yield ethylene oxide monomer of high purity.

2.1.5 Polystyrene Endcapping

A graduated ampoule was added to the vacuum line, degassed, and flame dried and the polymerization reactor was returned to the vacuum line, frozen and degassed. A few milliliters (< 5 mL) of ethylene oxide were distilled from the *n*-butyllithium purification stage to the graduated

ampoule, and then subsequently to the polymerization reactor. The polymerization reaction mixture was allowed to thaw slowly. One ethylene oxide moiety will react with each styryl anion, end-capping the chain with an oxygen anion as shown in Figure 2-3. Propagation of ethylene oxide polymerization is suppressed by the strong association of the oxyanion and the lithium cation. The end-capping reaction was allowed to proceed at room temperature with stirring for 24 hours. At the conclusion of the end-capping reaction, the polymerization reactor should be colorless, as evidence of the elimination of all carbanions. The reactor was then returned to the glove box where the cryptand catalyst *tert*-butyl phosphazene (P_4 -*t*-Bu) in hexane, shown in Figure 2-4, was added to the reactor with 5% stoichiometric excess relative to the number of chain ends calculated from the GPC results of the polystyrene aliquot. The *tert*-butyl phosphazene associates selectively with the lithium cation, which allows the oxyanion to propagate by reacting with additional ethylene oxide monomer. The polymerization reactor was then allowed to stir at room temperature in the glove box overnight.

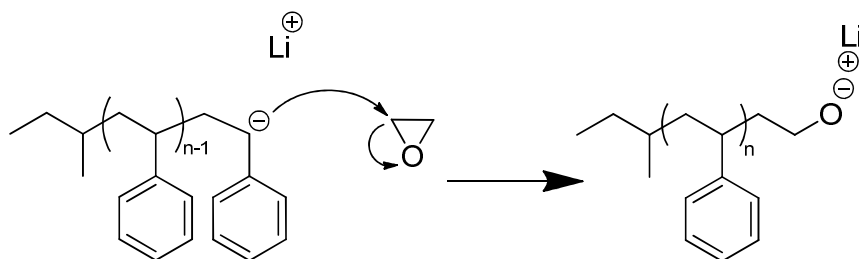


Figure 2-3 Styrene end-capping scheme.

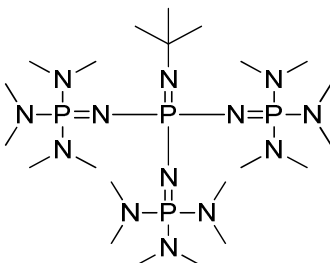


Figure 2-4 *tert*-butyl phosphazene structure.

2.1.6 Ethylene Oxide Polymerization

The polymerization reactor was returned to the vacuum line, frozen, degassed, and maintained in a frozen state. Since a small quantity of ethylbenzene inevitably becomes entrained in the ethylene oxide, a 10% excess of ethylene oxide monomer was distilled from the *n*-butyllithium purification stage to the ampoule. The ampoule was then warmed to -10 °C and the desired quantity of ethylene oxide was distilled to the polymerization reactor by difference. An additional milliliter of ethylene oxide was distilled to compensate for any monomer that did not reach its final destination. Once the distillation was complete, the polymerization reactor was thawed and heated to 45 °C using a silicone oil bath on a hot plate with temperature feedback control. The polymerization reactor was stirred at temperature for four days. Depending on the concentration of growing polyethylene oxide chain anions, the polymerization reactor may develop a blue-purple color. Finally the polymerization reactor was brought into the glove box and the chains terminated with isopropanol. The ethylene oxide polymerization propagation and termination scheme are shown in Figure 2-5. The structure of polystyrene-*block*-poly(ethylene oxide) is shown in Figure 2-1.

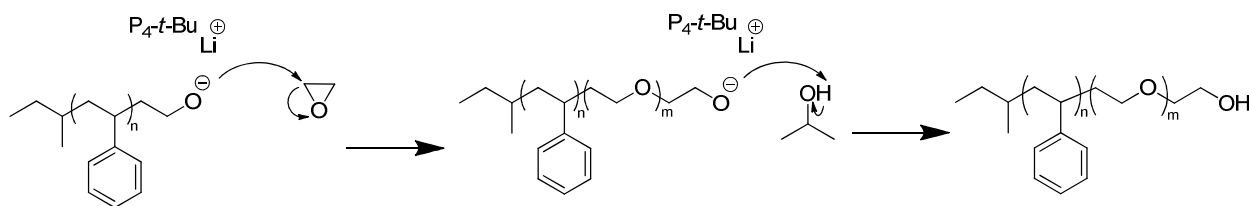


Figure 2-5 Ethylene oxide polymerization propagation and termination scheme.

2.2 Purification

Residual salts and catalyst were removed by three cycles of precipitation in hexanes, redissolution into benzene, and filtration through a cellulose membrane. Low molecular weight copolymers were filtered through neutral alumina to remove the phosphazene base until no evidence remained when the polymer was examined using ^1H nuclear magnetic resonance (NMR) spectroscopy. Figure 2-6 shows NMR spectra for a low molecular copolymer before and after it was filtered through neutral alumina. Protons from the phosphazene base are located at 2.6 – 2.8 ppm, indicated by the letter ‘d’. All copolymers were freeze-dried from benzene in a lyophilizer (Millrock LD85) to remove solvent. Properly cleaned neat copolymers are completely transparent and colorless.

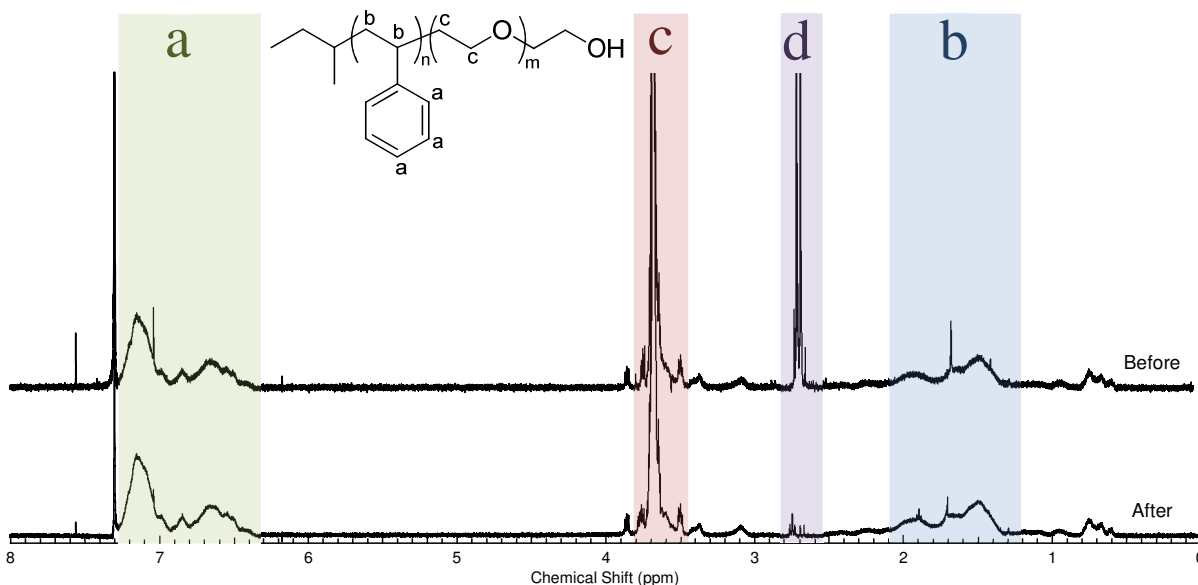


Figure 2-6 NMR spectra of SEO copolymer before and after phosphazene removal.

It is important that copolymers be thoroughly cleaned before final characterization, particularly for small molecular weight copolymers. During synthesis, one phosphazene molecule is added for each polymer chain. Therefore, a given quantity of low molecular weight copolymer will contain a far greater concentration of residual phosphazene molecules than the same quantity of high molecular weight copolymer. This is evident in Figure 2-7a, which shows the integrated NMR signal from the phosphazene protons as a function of the molecular weight of the polystyrene block, M_{PS} . For reasons not completely clear, the apparent molecular weight of the poly(ethylene oxide) block, M_{PEO} , determined from ^1H NMR spectroscopy can decrease significantly once the

phosphazene base has been fully removed from the polymer. The relative magnitude of the decrease in M_{PEO} seems to be strongly related to the M_{PS} , as shown in Figure 2-7b.

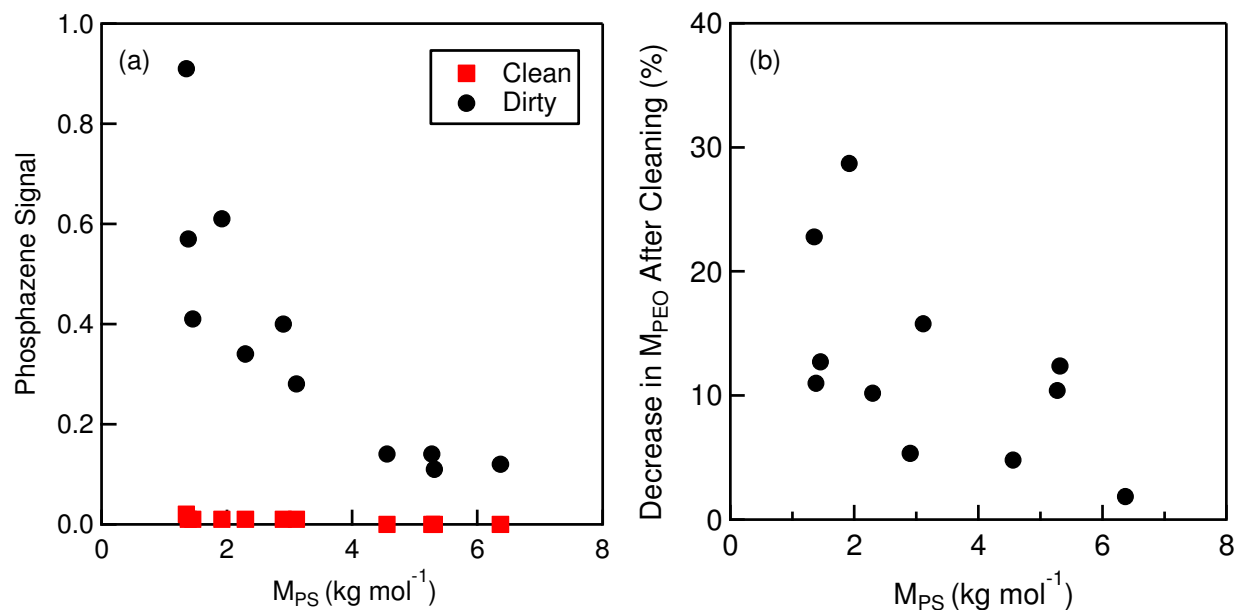


Figure 2-7 Results of phosphazene removal on small molecular weight SEO copolymers.

(a) Integrated phosphazene signal from NMR spectra and (b) decrease in the apparent molecular weight of the poly(ethylene) oxide block, M_{PEO} , versus the molecular weight of the polystyrene block, M_{PS} for all of the small molecular weight SEO copolymers.

2.3 Characterization

2.3.1 Molecular Weight Characterization using GPC

The terminated aliquot of the polystyrene block was characterized using GPC to determine the molecular weight of the first block of the copolymer. A Viskotek VE 2001 Separations Module and a Viscotek TDA 302 Triple Detector were used to determine the number- and weight- averaged molecular weights and the polydispersity indices of the homopolymer. The instrument was run at room temperature with tetrahydrofuran as the mobile phase. Samples were prepared by dissolving 5 mg of dried polymer in 10 mL of tetrahydrofuran removed from the reservoir. The samples were allowed to dissolve thoroughly and filtered before loading into the GPC. The calculations were performed by the OmniSEC software provided by Viscotek using a series of polystyrene standards purchased from PolymerSource.

It was not possible to determine the block copolymer total molecular weight, M_{SEO} , using GPC alone, however this method could be used to determine the polydispersity index, PDI , of the block copolymer. The samples were prepared and performed similarly to that of the homopolymer, however dimethylformamide was used as the solvent to dissolve the polymer and as the mobile phase in the GPC.

2.3.2 Characterization of Polymer Composition using ^1H NMR

NMR characterization of the block copolymers was performed on an AVB-400 Spectrometer (Bruker Biospin Corporation). Samples were prepared by dissolving approximately 10 mg of dried polymer in 1.0 mL of deuterated chloroform. In the SEO copolymer, there are three primary chemical environments in which the protons may reside: the aromatic ring (6.3 - 7.3 ppm), the alkyl backbone (1.3 - 2.1 ppm), or the ether backbone (3.4 - 3.8 ppm). These are indicated clearly in Figure 2-6 by letters a, b, and c respectively. For low molecular weight copolymers, it is possible to observe smaller peaks arising from end-group protons. Assuming no homopolymer was present in the block copolymer, the ratio of the peak integration of the ether backbone protons to that of the aromatic ring protons was used to calculate the weight percent of each block. The molecular weight of the polystyrene aliquot, determined using GPC, was then used to calculate the molecular weight of the poly(ethylene oxide) block.

The polymers used in this study are called SEO(xx-yy) where xx and yy are the number averaged molecular weights of the polystyrene (PS), M_{PS} , and poly(ethylene oxide) (PEO), M_{PEO} , blocks in kg mol^{-1} respectively. The volume fraction of the PEO block, ϕ_{EO} , is given by

$$\phi_{\text{EO}} = \frac{v_{\text{EO}}}{v_{\text{EO}} + \frac{M_{\text{PS}}M_{\text{EO}}}{M_{\text{S}}M_{\text{PEO}}}v_{\text{S}}} \quad (2-1)$$

where v_{EO} and v_{S} are the molar volumes of ethylene oxide monomer units and styrene monomer units, respectively, and M_{S} and M_{EO} are the molar masses of styrene ($104.15 \text{ g mol}^{-1}$) and ethylene oxide (44.05 g mol^{-1}), respectively. Molar volumes are calculated by

$$v = \frac{M}{\rho} \quad (2-2)$$

In this work, $\rho_{\text{PEO}} = 1.139 - 7.31 \times 10^{-4}T$ and $\rho_{\text{PS}} = 1.0865 - 6.19 \times 10^{-4}T + 1.36 \times 10^{-7}T^2$ for the densities of the PEO block and PS block respectively.¹⁸

2.3.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is used to study the thermal transitions of materials. In the case of polymers, it can be used to determine the glass-transition temperature, melting temperature, and heat of melting. The heat of melting can be used to calculate the percent crystallinity of the sample.

Samples were sealed in aluminum hermetic pans in the glovebox. DSC scans consisted of at least two heating/cooling cycles and were conducted over the range -30 to 150 °C (or -80 to 150 °C, depending on the instrument) at a rate of 5 °C/min. The data presented is always obtained from the final heating run.

2.4 Library of Copolymers

Table 2-1 lists the polystyrene-*block*-poly(ethylene oxide) copolymers synthesized by the author. Table 2-2 lists the polystyrene-*block*-poly(ethylene oxide) copolymers synthesized by former students that were re-purified and re-characterized by the author.

Lab Name	Polymer	M _{PS} kg mol ⁻¹	M _{PEO} kg mol ⁻¹	φ _{EO}	PDI	Morphology	Chapter Reference
SEO.AT.1	SEO(47-45)	47	45	0.48	1.04	LAM	-
SEO.AT.2	SEO(1.7-1.4)	1.7	1.4	0.44	1.05	DIS	3, 5, 6, 7
SEO.AT.3	SEO(4.9-5.5)	4.9	5.5	0.52	1.04	DIS	3, 5, 7, A
SEO.AT.4	SEO(60-63)	60	63	0.50	1.03	LAM	5
SEO.AT.5	SEO(1.9-0.8)	1.9	0.8	0.29	1.05	DIS	3, B
SEO.AT.6	SEO(1.4-1.6)	1.4	1.6	0.45	1.03	DIS	3, A, B
SEO.AT.7	SEO(2.9-3.3)	2.9	3.3	0.52	1.05	LAM	3, 5, A
SEO.AT.8	SEO(113-105)	113	105	0.46	-	LAM	-

Table 2-1 Characteristics of copolymers synthesized by the author.

Lab Name	Polymer	M _{PS} kg mol ⁻¹	M _{PEO} kg mol ⁻¹	φ _{EO}	PDI	Morphology	Chapter Reference
SEO11	SEO(6.4-7.3)	6.4	7.3	0.52	1.04	LAM→DIS	3
SEO12	SEO(1.4-2.3)	1.4	2.3	0.61	1.04	DIS	A, B
SEO13	SEO(2.3-4.2)	2.3	4.2	0.64	1.04	DIS	B
SEO17	SEO(240-269)	247	116	0.52	1.26	LAM	8
SEO18	SEO(5.7-2.6)	5.7	2.6	0.30	1.05	DIS	B
SEO19	SEO(5.6-3.3)	5.6	3.3	0.36	1.04	DIS	5
SEO20	SEO(4.9-3.6)	4.9	3.6	0.41	1.04	DIS	5
SEO22	SEO(1.5-1.2)	1.5	1.2	0.43	1.05	DIS	5

Table 2-2 Characteristics of copolymers synthesized by former students.

2.5 Electrolyte Preparation

In order to use the copolymers as electrolytes, charge carriers must be introduced in the form of dissolved lithium salts. The following procedure describes how these salt-containing copolymers were prepared: The copolymers were dried at 100 °C under vacuum in a glovebox antechamber for at least 24 h, and then brought directly into an argon-filled glovebox. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt (Novolyte) was received under argon, opened in the glovebox, and then dried at 120 °C under vacuum in a glovebox antechamber for three days. The electrolytes were prepared by mixing an SEO/benzene solution with the necessary amount of a LiTFSI/tetrahydrofuran solution. Benzene and tetrahydrofuran were purified using a solvent purification system (MBraun SPS) to remove water and other impurities. The solution was freeze-dried in a lyophilizer (Millrock LD85) without exposure to air, then subsequently dried under vacuum in a glovebox antechamber for at least 12 h to remove residual solvent. Due to the hygroscopic nature of the salt, argon-filled gloveboxes (MBraun) with oxygen and water at sub-ppm levels were used for all sample preparation.

The salt concentration in our electrolyte is quantified by the molar ratio of lithium atoms to ethylene oxide (EO) moieties, r . The number of EO units in the copolymer is calculated from the molecular weight of the PEO block without correcting for end groups. We assume that the salt

resides almost exclusively in the PEO domain.³ The volume fraction of the new PEO/salt microphase, $\phi_{EO/salt}$, which we will refer to as the conducting phase, by

$$\phi_{EO/salt}(r) = \frac{v_{EO} + rv_{LiTFSI}}{v_{EO} + rv_{LiTFSI} + \frac{M_{PS}M_{EO}}{M_S M_{PEO}} v_S} \quad (2-3)$$

where v_{LiTFSI} is the molar volume of LiTFSI (141.9 cm³ mol⁻¹).

2.6 Small Angle X-Ray Scattering

Small-angle x-ray scattering (SAXS) is a commonly used technique to probe the microstructure of block copolymer systems. The typical set-up for such experiments is shown schematically in Figure 2-8. In this technique, high-energy incident x-rays strike the sample and scatter due to differences in electron scattering length density of the blocks. The scattering vector is given by

$$q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad (2-4)$$

where λ is the wavelength of the incident x-rays and θ is the angle between the scattered and incident x-rays.

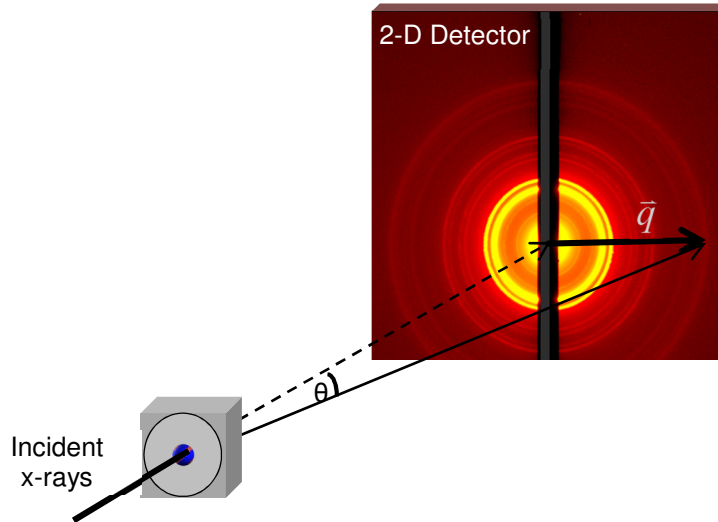


Figure 2-8 Schematic of small angle x-ray scattering experiment.

The 2-D scattering pattern is captured on a charge-coupled device (CCD) detector and can be integrated azimuthally to obtain 1-D scattering profiles. The scattering profiles can be used to determine characteristics of the sample such as morphology, domain spacing and even the interaction parameter. Block copolymer morphologies are most commonly identified by their 1-D SAXS profiles, with each morphology having different peak shape or different spacing between peaks. Figure 2-9a shows a scattering profile with a single, broad peak, which is characteristic for

a disordered block copolymer. Figure 2-9b shows a scattering profile with multiple, sharp peaks with integer spacing, which is characteristic of an ordered lamellar phase.

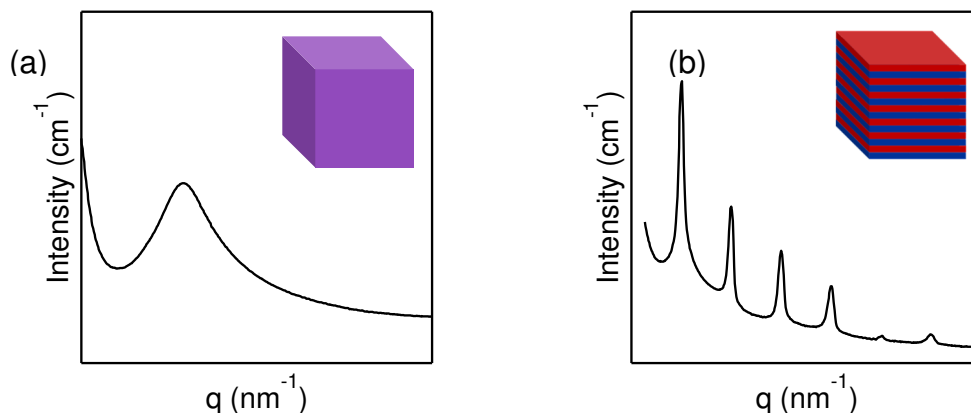


Figure 2-9 Characteristic SAXS profile of (a) disordered and (b) ordered lamellar copolymers.

Domain spacing can be calculated by

$$d = \frac{2\pi}{q^*} \quad (2-5)$$

where q^* is the magnitude of the scattering vector at the primary scattering peak. For most ordered structures, this corresponds to the {100} family of reflection planes. The one exception is the gyroid (GYR) morphology, where it corresponds to the {211} family of reflection plane. For disordered block copolymers, where no reflection planes are present, ‘correlation hole’ scattering creates a single broad peak. Additional analysis is required to determine the interaction parameter from the scattering profile, and will be discussed in more detail in Chapter 3. The 2-D scattering patterns contain additional information such as the sample alignment or orientation with respect to the beam.

Small angle X-ray scattering (SAXS) samples were prepared by pressing/melting the polymer into aluminum spacers. The samples were sealed with Kapton windows in custom-designed airtight holders and mounted in a custom-built 8-sample heating stage. Actual sample thicknesses were measured after experiments were completed. SAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Silver behenate was used to determine the beam center and sample-to-detector distance. The scattered intensity was corrected for beam transmission, empty cell scattering, as well as for unavoidable air gaps in the system. Glassy carbon was used to determine the scaling calibration to obtain the absolute intensity scattering. Two-dimensional scattering patterns were integrated azimuthally using the Nika program for IGOR Pro to produce 1-D scattering profiles.¹⁹

2.7 Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) can be used to determine the ionic conductivity of polymer electrolytes. Impedance measurements were performed on a Bio-Logic VMP3 potentiostat over a $0.1 - 10^6$ Hz frequency range at an amplitude of 50 mV. Figure 2-10a shows

an equivalent circuit for an ionically conductive sample between blocking electrodes where Q_b and Q_{int} are constant phase elements associated with the sample and sample-electrode interface respectively, and R_b is the bulk resistance of the sample. Figure 2-10b shows a typical Nyquist impedance plot, where R_b is determined, by the low-frequency minimum. Ionic conductivity can be calculated by

$$\sigma = \frac{L}{R_b A_c} \quad (2-6)$$

where A_c is the area of the spacer and L is the thickness of the sample.

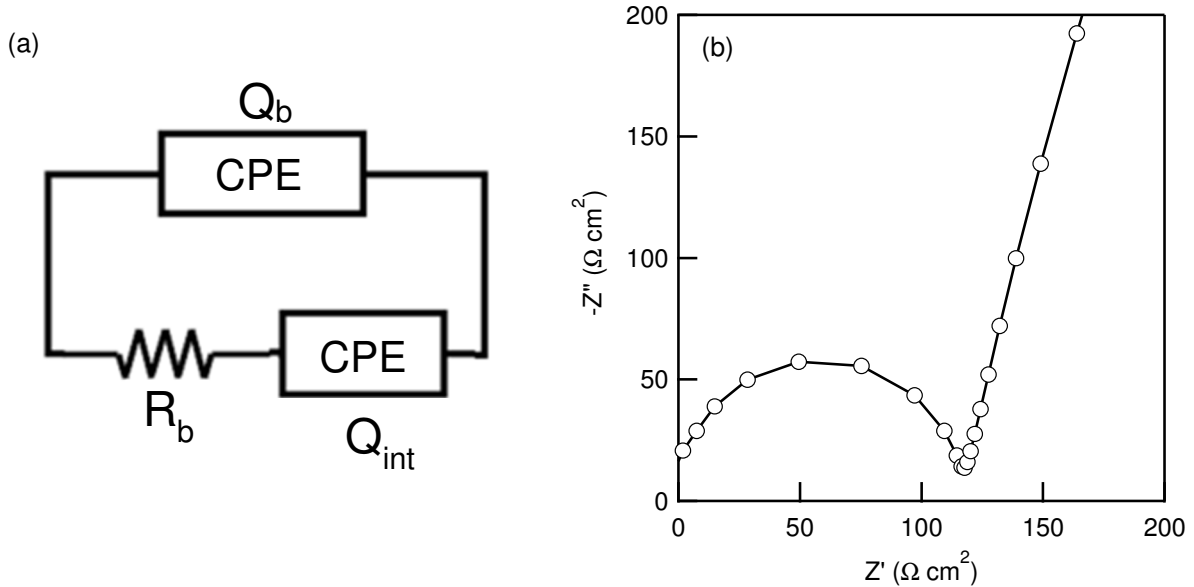


Figure 2-10 Typical impedance spectroscopy results for a polymer electrolyte.

(a) Equivalent circuit for ion conductor with blocking electrodes and (b) Nyquist plot for SEO(240-269) with LiTFSI at $r = 0.085$.

Freeze-dried samples were placed into Garolite G-10 spacers and pressed between two aluminum foil current collectors (17 μm) using a hand press at room temperature. Initial sample thicknesses were measured with a micrometer. Aluminum tabs were attached to the current collectors using Kapton tape. The entire assembly was sealed under vacuum in Showa-Denko pouch material with tabs exposed. This configuration allowed us to maintain an air-free environment for the electrolyte upon removal from the glovebox. The sealed samples were loaded into a custom heating stage. Temperature control was implemented by a feedback temperature controller operated by a custom LabVIEW control program that enabled consistent temperature history control across multiple experiments.

After the experiments were performed, the sample was carefully disassembled and the final thickness was measured again. Finally, the aluminum shims were removed to inspect the sample for defects. In some cases, samples experienced bubble formation that decreased the effective area and voided conductivity results.

Chapter 3 - Thermodynamics of Block Copolymers with and without Salt¹

ABSTRACT

This chapter describes a comprehensive study of the thermodynamics of block copolymer/salt mixtures over a wide range of molecular weights, compositions, salt concentrations and temperatures. The Flory-Huggins interaction parameter was determined by fitting small angle X-ray scattering data of disordered systems to predictions based on the random phase approximation (RPA). Experiments on neat block copolymers revealed that the Flory-Huggins parameter is a strong function of chain length. Experiments on block copolymer/salt mixtures revealed a highly non-linear dependence of the Flory-Huggins parameter on salt concentration. These findings are a significant departure from previous results, and indicate the need for improved theories for describing thermodynamic interactions in neat and salt-containing block copolymers.

The thermodynamic properties of block copolymers with and without added salt have been the subject of several investigations.²⁰⁻²⁸ Most of the work in this field is built on the assumption that the interaction parameter of the neat copolymer, χ_0 is independent of N despite comprehensive studies by Mori et al.²⁰ and Lin et al.²¹ that demonstrate that χ_0 between PS and polyisoprene (PI) in symmetric block copolymers decreased with increasing N . We are not aware of any study wherein χ_0 was measured as a function of N and shown to be independent of N .

It has been observed that the addition of salt to such copolymers, which is necessary to imbue them with ionic conductivity, can have a substantial effect on their material properties. Even small amounts of salt can change the phase behavior of the copolymer. Current work suggests that this is due to an increase in the effective interaction parameter, χ_{eff} , between the structural block and the salt-containing block.²⁹ Both the ion transport and mechanical properties of these materials are affected by the morphology and degree of segregation. It is therefore of great practical interest to understand this effect. All of the previous theoretical and experimental work, including work from our laboratory, suggests that χ_{eff} increases linearly with increasing salt concentration. The exception to this is the work of Huang et al.²² who showed that the relationship between χ_{eff} and salt concentration is distinctly non-linear, with a steep slope at low salt concentrations and plateau-like behavior at high salt concentration. The theoretical work of Nakamura and Wang indicates

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that non-linear χ_{eff} versus salt concentration data are a signature of incomplete dissociation.²⁷ In the limit of complete dissociation, their theory predicts a strong linear increase in the dependence of χ_{eff} on salt concentration.

The purpose of this study is to present a comprehensive study of block copolymer thermodynamics over a wide range of block copolymer molecular weights, compositions, salt concentrations and temperatures. The value of χ_{eff} for a series of SEO copolymers with lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) salt was measured directly by fitting random phase approximation (RPA) theory to small angle X-ray scattering profiles of disordered SEO/LiTFSI mixtures. Our data overwhelmingly reaffirms that χ_0 is a strong function of N ; ignoring this effect has a profound impact on the interpretation of thermodynamic data from salty samples. In particular, complex non-linear dependencies of χ_{eff} on salt concentration are presented and we even show data wherein the addition of salt leads to a decrease in χ_{eff} .

3.1 Sample Preparation

The SEO copolymers in this study were synthesized, purified, and characterized using methods described in Chapter 2. A list of the polymers' characteristics can be found in Table 3-1. The neat copolymers are completely transparent and colorless.

Polymer	M _{PS}	M _{P_{EO}}	M _{SEO}	N _{PS}	N _{P_{EO}}	N _{SEO}	PDI	ϕ_{EO}	Morphology	T _{ODT} °C
	kg mol ⁻¹			at 140 °C						
SEO(1.9-0.8)	1.9	0.8	2.7	30	12	42	1.05	0.29	DIS	-
SEO(1.4-1.6)	1.4	1.6	3.0	22	24	46	1.03	0.52	DIS	-
SEO(1.7-1.4)	1.7	1.4	3.1	27	21	48	1.05	0.44	DIS	-
SEO(2.9-3.3)	2.9	3.3	6.2	46	50	96	1.05	0.52	DIS	-
SEO(4.9-5.5)	4.9	5.5	10.4	78	83	161	1.04	0.52	DIS	-
SEO(6.4-7.3)	6.4	7.3	13.7	101	111	212	1.04	0.52	LAM → DIS	107.5

Table 3-1 Characteristics of the copolymers used in Chapter 3.

The overall degree of polymerization was calculated by

$$N_{\text{SEO}} = N_{\text{PEO}} + N_{\text{PS}} \quad (3-1)$$

where

$$N_i(T) = \frac{M_i}{\rho_i(T)N_{\text{Avg}}v_{\text{ref}}} \quad (3-2)$$

and v_{ref} is a reference volume that was fixed at 0.1 nm³.

The salt-containing copolymers were prepared using methods described in Chapter 2. A full list of salt-containing samples used in this study can be found in Table 3-2.

Polymer	r [Li ⁺]/[EO]	$\phi_{EO/salt}$	Morphology	T _{ODT} °C
SEO(1.9-0.8)	0.03	0.31	DIS	107.5
	0.05	0.32	DIS	
	0.085	0.34	DIS	
	0.10	0.35	LAM→DIS	
	0.125	0.37	LAM	
	0.15	0.38	LAM	
	0.20	0.41	LAM	
	0.25	0.43	LAM	
SEO(1.4-1.6)	0.03	0.55	DIS	62.5 107.5
	0.05	0.56	DIS	
	0.085	0.59	DIS	
	0.10	0.60	DIS	
	0.125	0.61	HEX→DIS	
	0.15	0.63	HEX→DIS	
	0.20	0.65	HEX	
	0.25	0.67	HEX	
SEO(1.7-1.4)	0.01	0.45	DIS	82.5 107.5 117.5
	0.03	0.47	DIS	
	0.04	0.47	DIS	
	0.065	0.49	LAM→DIS	
	0.075	0.50	LAM→DIS	
	0.085	0.51	LAM→DIS	
	0.10	0.52	LAM	
	0.125	0.53	LAM	
	0.15	0.55	LAM	
	0.17	0.56	LAM	
	0.20	0.57	GYR	
	0.25	0.60	GYR	
SEO(2.9-3.3)	0.005	0.53	DIS	62.5 107.5 132.5
	0.01	0.53	DIS	
	0.015	0.54	LAM→DIS	
	0.02	0.54	LAM→DIS	
	0.025	0.54	LAM→DIS	
	0.03	0.55	LAM	
	0.04	0.56	LAM	
	0.05	0.56	LAM	
	0.085	0.59	LAM	
	0.10	0.60	LAM	
	0.125	0.61	LAM/GYR	
	0.15	0.63	GYR	
	0.20	0.65	HEX	
SEO(4.9-5.5)	0.0025	0.52	LAM→DIS	102.5
	0.005	0.52	LAM→DIS	137.5
	0.01	0.53	LAM	
	0.03	0.54	LAM	
	0.05	0.56	LAM	
	0.085	0.58	LAM	
	0.10	0.59	LAM	
	0.125	0.61	LAM	
	0.15	0.62	LAM	
	0.20	0.65	LAM	
	0.25	0.67	HEX	
SEO(6.4-7.3)	0.085	0.59	LAM	

Table 3-2 Characteristics of the electrolytes used in Chapter 3.

3.2 Chi of Pure Copolymer

Figure 3-1 shows the scattering intensity as a function of wave vector q , of four nearly symmetric SEO copolymers in the neat state at 110 °C. All four polymers are in the disordered state, indicated by the single, broad scattering peak. The arrows indicate the location of the primary scattering peak, q^* . The location of q^* shifts to higher values as the molecular weight of the copolymers decreases, representing a corresponding decrease in the characteristic length scale of the copolymer. The intensity of the scattering also decreases as the molecular weight decreases. The intensity of SEO(1.7-1.4) in Figure 3-1d is so low that at first glance it is difficult to locate the primary scattering peak; the inset shows the primary scattering peak on a magnified scale. The peak at approximately 0.3 nm⁻¹ is the result of imperfect background subtraction of the Kapton windows used to prepare the sample. Similarly, the baseline intensity observed at high values of q is an artifact of imperfect background subtraction of the empty cell. These effects are most pronounced in Figure 3-1d due to the extremely low scattering observed from this sample.

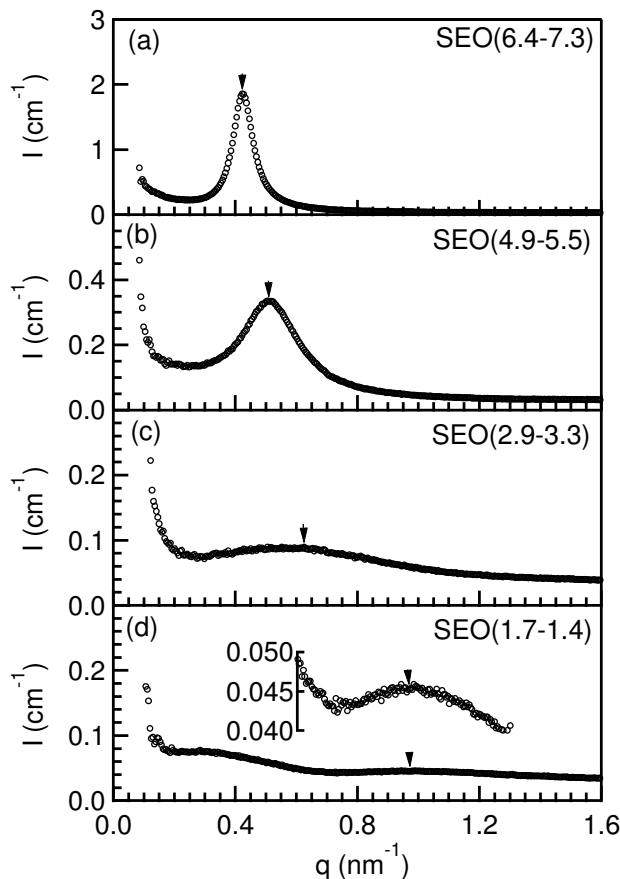


Figure 3-1 SAXS profiles of neat copolymers.

SAXS profiles of a series of neat, symmetric SEO copolymers at 110 °C: (a) SEO(6.4-7.3), (b) SEO(4.9-5.5), (c) SEO(2.9-3.3), and (d) SEO(1.7-1.4).

The scattering theory of monodisperse, disordered block copolymers was developed by Leibler.³⁰ The scattering function $I(q)$ proposed by this theory for a perfectly monodisperse AB diblock copolymer with degree of polymerization N can be written as:

$$I_{Dis}(q) = v_{ref} \left(\frac{b_A}{v_A} - \frac{b_B}{v_B} \right)^2 \left[\frac{S(q)}{W(q)} - 2\chi \right]^{-1} \quad (3-3)$$

where b_A and b_B are the x-ray scattering lengths of blocks A and B respectively, v_A and v_B are the monomer volumes of A and B respectively. $W(q)$ and $S(q)$ are the determinant and sum of the elements respectively, of the structure factor matrix $\|S_{ij}\|$. In this work, the reference volume is 0.1 nm^3 . The expressions $W(q)$ and $S(q)$ are given by:

$$W(q) = S_{AA}(q)S_{BB}(q) - S_{AB}^2(q) \quad (3-4)$$

$$S(q) = S_{AA}(q) + S_{BB}(q) + 2S_{AB}(q) = Ng(1) \quad (3-5)$$

with

$$S_{AA}(q) = Ng(\phi) \quad (3-6)$$

$$S_{BB}(q) = Ng(1 - \phi) \quad (3-7)$$

$$S_{AB}(q) = (N/2)[g(1) - g(\phi) - g(1 - \phi)] \quad (3-8)$$

$$g(\phi) = (2/x^2)[\phi x + \exp(-\phi x) - 1] \quad (3-9)$$

and

$$x = q^2 R_g^2 \quad (3-10)$$

$$R_g^2 = Na^2/6 \quad (3-11)$$

where S_{AA} , S_{AB} , and S_{BB} are the pairwise elements of the structure factor matrix, $g(f)$ is the form factor for a Gaussian chain, and R_g is the radius of gyration of the copolymer.

The polydispersity of a copolymer has been shown to affect its scattering. Since our copolymers are not perfectly monodisperse, the expression $I(q)$ was modified to reflect their non-ideality by assuming a Schultz-Zimm distribution for total molecular weight.²⁰ In this case, Equation (3-9) is replaced by

$$g(\phi) = (2/x^2)\{\phi x - 1 + [k/(k + \phi x)]^k\} \quad (3-12)$$

where

$$k = 1/(PDI - 1) \quad (3-13)$$

and N in Equations (3-5) - (3-8), and (3-10) is the number averaged degree of polymerization. More detailed discussion of limitations, assumptions, and justifications for using the particular form of the scattering equations shown above can be found in Mori et al.²⁰ A k value of 28.5 was

used for all fitting done, which corresponds to *PDI* of approximately 1.04. Our results are not sensitive to the exact value of k used in the calculations over the range of *PDI*s in Table 3-1. In the discussion below, all values of N are number-averaged and all values of χ are obtained by fitting experimental scattering curves from disordered samples to Equation (3-3).

The only adjustable parameters for fitting the absolute scattering of a neat copolymer to the scattering function $I_{Dis}(q)$ in Equation (3-3) are R_g and χ . Figure 3-2 is as an example of the fitting performed in this study, showing the absolute intensity scattering of SEO(6.4-7.3) at 110 °C. The open symbols show the data and the solid line represents a fit to the equation

$$I(q) = I_{Dis}(q) + I_{Bgd}(q) \quad (3-14)$$

where $I_{Bgd}(q)$ is an exponential decay to compensate for the imperfect background subtraction that occurs near the beamstop. The fit shows excellent agreement with the data over the entire range. Figure 3-3a and Figure 3-3b show the sensitivity of the fit to R_g and χ respectively, confirming the accuracy of the values determined by this procedure.

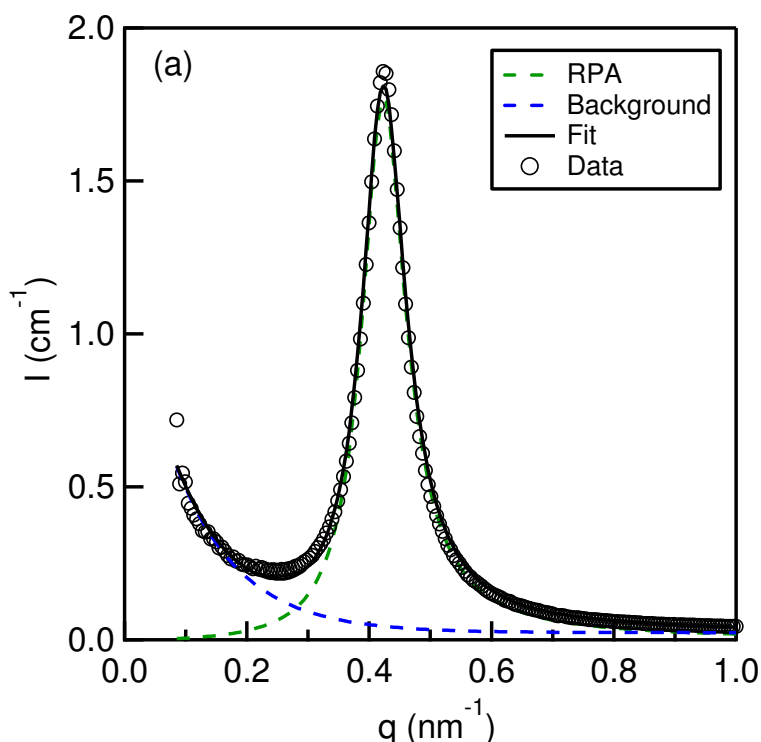


Figure 3-2 Fitting of RPA results to SAXS profiles of neat, disordered copolymer. Comparison of the experimental and calculated SAXS profiles for neat SEO(6.4-7.3) at 110 °C. The calculated fit is the sum of the exponentially decaying background and the theoretical random-phase approximation results.

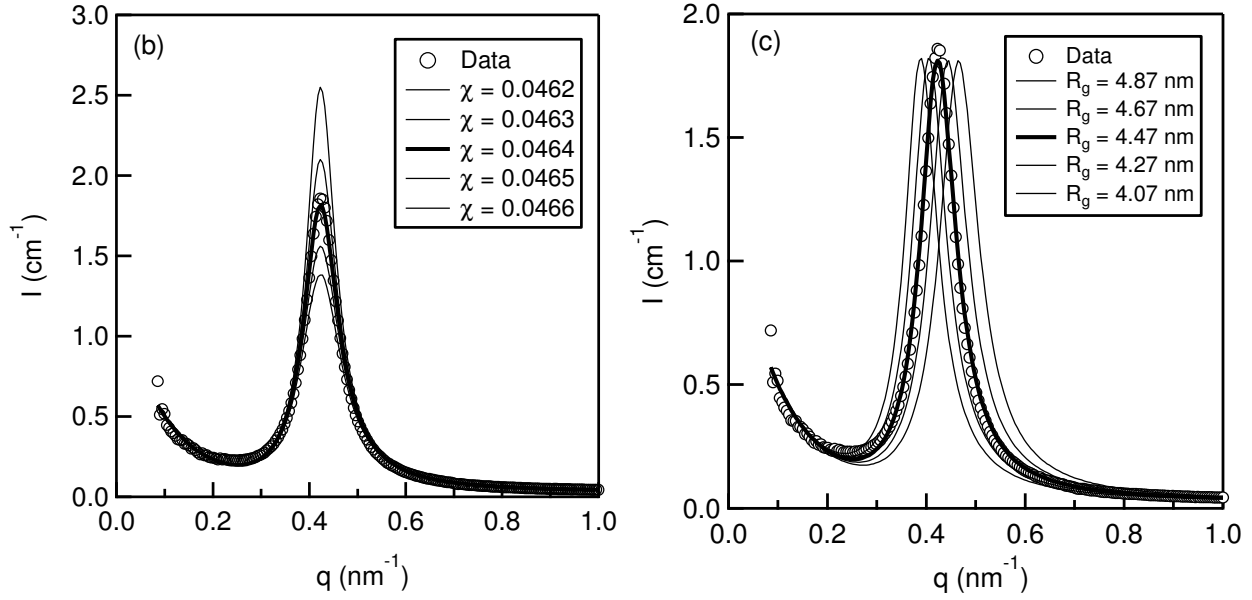


Figure 3-3 Sensitivity analysis of RPA fitting results.

Comparison of the experimental and calculated SAXS profiles for neat SEO(6.4-7.3) at 110 °C. The calculated fit is the sum of the exponentially decaying background and the theoretical random-phase approximation results. Plots (a) and (b) demonstrate the sensitivity of the calculated fits to small changes in the interaction parameter, χ and the radius of gyration, R_g , respectively.

Figure 3-4 shows the temperature dependence of χ_0 for the neat block copolymers. These values were obtained from the fit of Equation (3-3) to the 1-D scattering profiles of disordered samples. SEO(6.4-7.3) is ordered at $T < 105$ °C, preventing values of χ_0 from being obtained for those temperatures. The scattering from SEO(1.4-1.6) and SEO(1.9-0.8) at all temperatures as well as SEO(1.7-1.4) at $T > 105$ °C is indistinguishable from the background, preventing values of χ_0 from being determined; this is a consequence of small degree of polymerization of the copolymers and the relatively low scattering contrast between blocks. The dotted lines indicate a fit of the data to

$$\chi_0 = \frac{\Psi}{T} \quad (3-15)$$

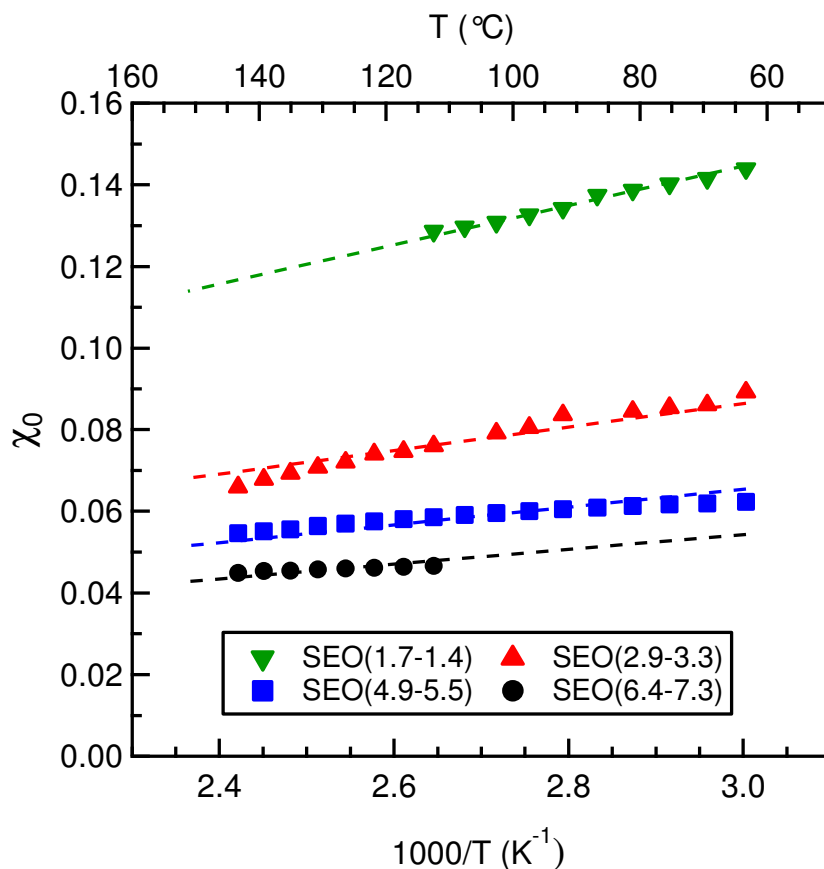


Figure 3-4 Temperature dependence of chi parameter for neat copolymers.

Temperature dependence of χ_0 for a series of neat, symmetric SEO block copolymers. The dashed lines are fits of the data to Equation (3-16).

It is clear that χ_0 is not independent of chain length. While this dependence is often ignored, it has been reported in polystyrene-*b*-polyisoprene (PS-*b*-PI) copolymers.^{20, 21} Figure 3-5 shows χ_0 as a function of $1/N$ for the neat copolymers at 60 and 140 °C. The dotted lines represent a fit to

$$\chi_0 = A(T) + \frac{B(T)}{N} \quad (3-16)$$

where $A(T) = 10.2 \cdot T^{-1}$ and $B(T) = 1.85 \times 10^3 \cdot T^{-1}$. This functional form implies that at infinite N , χ_0 becomes a simple function of $1/T$. It also indicates that even at $N \sim 10^3$, a 10% difference in χ_0 is expected compared to χ_0 at infinite N . Several other functional forms were tested, however no other expression resulted in as good a fit to the data.

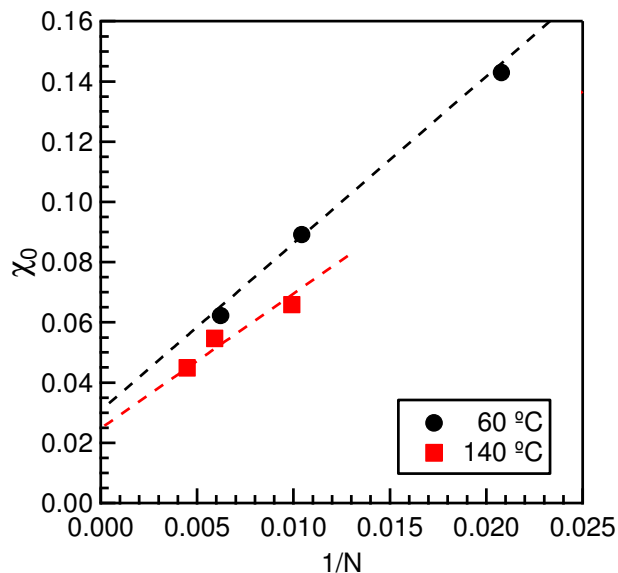


Figure 3-5 Molecular weight dependence of chi parameter for neat copolymer.

Molecular weight dependence of χ_0 for a series of neat, symmetric SEO block copolymers at 60 and 140 °C. The dashed lines represent fits to Equation (3-16).

3.3 Chi of Ion-Containing Copolymers

3.3.1 Symmetric Copolymers

Figure 3-6a shows the SAXS profiles of SEO(2.9-3.3) at 60 °C in the neat state and at selected salt concentrations. In the neat state, the polymer exhibits a single broad, low-intensity peak at $q^* = 0.658 \text{ nm}^{-1}$, corresponding to a domain spacing of 9.6 nm. At $r = 0.01$, the copolymer is still disordered, but the peak has become much more pronounced and the q^* peak has shifted to lower q . The addition of more salt in the $r = 0.10$ sample results in the appearance of a sharp primary scattering peak with higher order reflections at $q/q^* = 1, 2, 3$, and 4 indicating the presence of well-ordered lamellae (LAM). The $r = 0.15$ sample exhibits peaks at $q/q^* = 1, \sqrt{4/3}, \sqrt{7/3}, \sqrt{15/3}, \sqrt{16/3}, \sqrt{19/3}, \sqrt{20/3}, \sqrt{21/3}, \sqrt{23/3}, \sqrt{24/3}, \sqrt{25/3}$ indicating the bicontinuous gyroid phase (GYR) while the $r = 0.20$ sample shows peaks at $q/q^* = \sqrt{4}, \sqrt{7}, \sqrt{12}$, and $\sqrt{13}$ indicating hexagonally packed cylinders (HEX). Experiments similar to those reported in Figure 3-6a were repeated at temperatures between 60 – 140 °C. These results are summarized in Figure 3-6b, which shows the overall phase behavior of SEO(2.9-3.3) as a function of salt concentration. The open circles indicate observed coexistence between adjacent phases, the dashed lines represent boundaries between phases, and the shaded areas represent regions of coexistence. In the neat state and at low salt concentrations, the copolymer is disordered. As salt is added to the copolymer, χ_{eff} and $\phi_{\text{EO/salt}}$ begin to increase and the sample gains a weakly ordered lamellar morphology with accessible order-disorder transitions (ODTs). The order-disorder transition temperature, T_{ODT} , of the electrolyte increases as the salt concentration increases from $r = 0.015$ to $r = 0.025$. At salt concentrations from $r = 0.03$ to $r = 0.10$, the copolymer retains the lamellar morphology over the entire temperature range. At $r = 0.125$, we observe coexistence of the lamellar and gyroid phases before observing the pure gyroid phase at $r = 0.15$. At the highest salt concentration tested for this copolymer, $r = 0.20$, hexagonally packed cylinders (HEX) are observed at all temperatures.

Phase boundaries in Figure 3-6b were placed at the midpoint between different observed morphologies. For example, the sample with $r = 0.15$ was GYR while that with $r = 0.20$ was HEX.

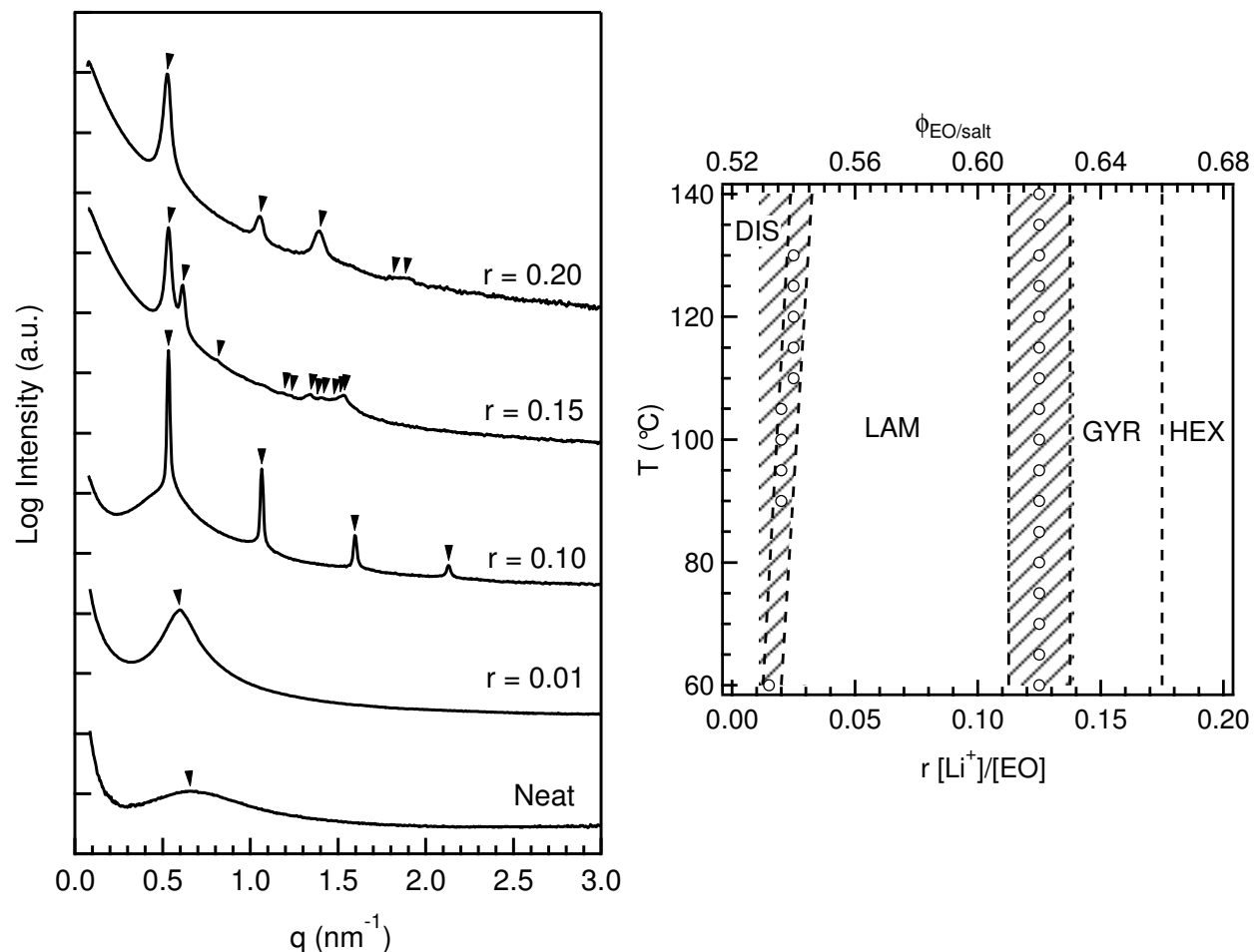


Figure 3-6 Phase behavior of a salt-containing copolymer.

a) SAXS profiles at 60 °C for SEO(2.9-3.3) at several salt concentrations. Profiles are offset vertically for clarity. b) Phase diagram of SEO(2.9-3.3)/LiTFSI as a function of salt concentration, r . Dashed lines mark phase boundaries and open circles indicate observed coexistence.

The effect of salt addition on χ_{eff} between the blocks can be measured directly via RPA fitting of SAXS profiles obtained from disordered electrolytes; however introducing salt to the copolymer presents two minor complications:

(1) The first is that it predicates coexistence between phases, as is required by the Gibbs phase rule for binary mixtures. This means that the transition from order to disorder, or the transition between ordered phases, is expected to occur continuously over a region of coexistence. This is observed experimentally by the apparent superposition of scattering profiles from the two phases. This is illustrated in Figure 3-7, which shows the absolute intensity scattering profile of SEO(2.9-3.3) with $r = 0.02$ at 105 °C. The open symbols show the experimental data and the solid black line shows the fit to

$$I(q) = I_{Dis}(q) + I_{Ord}(q) + I_{Bgd}(q) \quad (3-17)$$

where $I_{ord}(q)$ is an additional term to account for the scattering from the ordered phase:

$$I_{ord}(q) = K \exp\left(\frac{-(q - q_0)^2}{\sigma^2}\right) \quad (3-18)$$

where K , σ , and q_0 are fitting parameters. The contribution from the exponential background decreases substantially once salt is introduced to the copolymer as a result of the larger scattering contrast between phases, and concomitant higher scattering intensity.

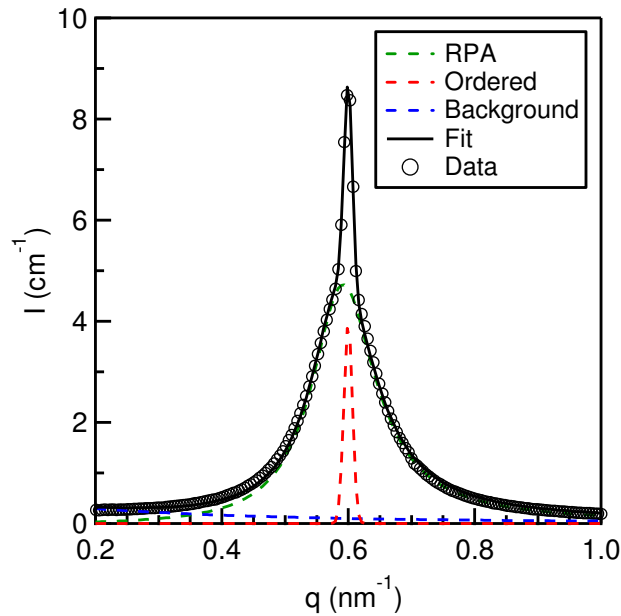


Figure 3-7 Fitting of SAXS profiles of ordered, salt-containing copolymer.

Comparison of the experimental and calculated SAXS profiles for neat SEO(2.9-3.3), $r = 0.02$ at 105 °C. Coexistence between the ordered and disordered state is observed. The calculated fit is the sum of the background, the theoretical random-phase approximation predictions, and the ordered peak.

(2) The second minor complication is that since the PEO phase is no longer pure, its scattering length density, $B_{EO/salt}$, must be adjusted accordingly. Assuming ideal mixing (no volume change of mixing) and perfect localization of salt in the PEO phase, the new scattering length density of the PEO/LiTFSI phase can be calculated by:

$$B_{EO/salt}^{ideal} = Y_{LiTFSI} B_{LiTFSI} + (1 - Y_{LiTFSI}) B_{EO} \quad (3-19)$$

where

$$B_i = \frac{b_i}{v_i} \quad (3-20)$$

and Y_{LiTFSI} is the volume fraction of LiTFSI in the PEO/LiTFSI microphase calculated by

$$Y_{LiTFSI}(r) = \frac{r\rho_{EO}M_{LiTFSI}}{r\rho_{LiTFSI}M_{EO} + r\rho_{EO}M_{LiTFSI}} \quad (3-21)$$

It is well known that salt solutions do not obey the ideal mixing rule. For this reason, we left $B_{EO/salt}$ as an additional fit parameter to achieve the best fit to the data. The scattering length density obtained from this fit is called $B_{EO/salt}^{fit}$. This means that for a fully disordered, salt-containing copolymer, the number of fit parameters was increased by one relative to the pure copolymer.

We can calculate the density of the PEO/LiTFSI microphase, $\rho_{EO/salt}^{fit}$, using

$$\rho_{EO/salt}^{fit} = B_{EO/salt}^{fit}(\rho_{EO/salt}^{ideal}/B_{EO/salt}^{ideal}) \quad (3-22)$$

where

$$\rho_{EO/salt}^{ideal} = \frac{1 + (rM_{LiTFSI}/M_{EO})}{(1/\rho_{EO}) + (rM_{LiTFSI})/(\rho_{LiTFSI}M_{EO})} \quad (3-23)$$

Figure 3-8a shows the values for $\rho_{EO/salt}^{fit}$ of all the disordered samples at 140 °C. The solid black line represents the calculated density of the microphase based on the assumptions mentioned above. Deviations from ideal mixing are shown clearly in Figure 3-8b, which presents the ratio of $\rho_{EO/salt}^{fit}$ to $\rho_{EO/salt}^{ideal}$ for all disordered samples as a function of r . At low salt concentration, the fitted density is greater than expected and at high salt concentration, the fitted density is lower than expected with a crossover salt concentration of about $r = 0.085$. It is interesting to note that the cross-over value of $r = 0.085$ coincides with the salt concentration at which maximum conductivity is observed in this system.⁹ The values of $\rho_{EO/salt}^{fit}$ never varied by more than $\pm 5\%$ of the ideal value. These seemingly insignificant deviations in $\rho_{EO/salt}$ are important during the calculation of the scattering contrast because the electron density of the two phases of interest are similar: a 5% increase in $\rho_{EO/salt}$ results in a 100% increase in $(B_{EO/salt} - B_{PS})^2$ while a 5% decrease results in a 27% decrease.

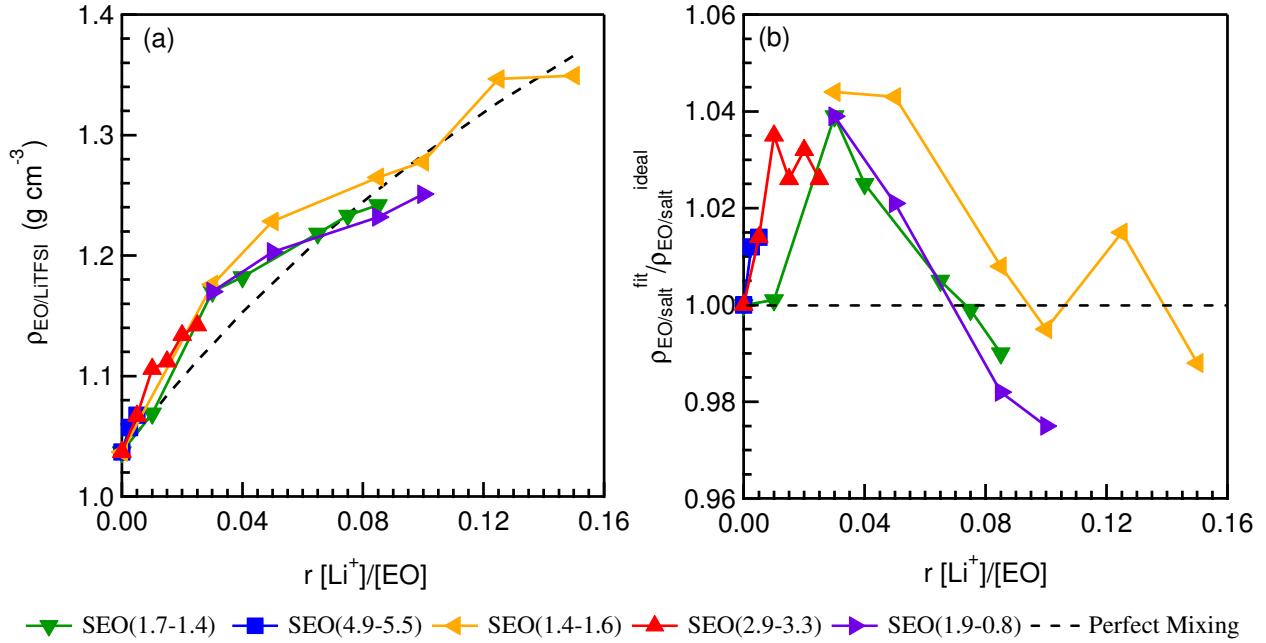


Figure 3-8 Concentration dependence of conductive microphase density. a) Fitted density of PEO/salt microphase, $\rho_{\text{EO/salt}}^{\text{fit}}$, and b) ratio of fitted to ideal density of PEO/salt microphase, $\rho_{\text{EO/salt}}^{\text{fit}} / \rho_{\text{EO/salt}}^{\text{ideal}}$, versus salt concentration, r , for all disordered electrolytes at 140 °C. The dashed lines represent the density under perfect mixing conditions.

The fitting procedure described above was used to measure the effect of r on χ_{eff} for each of the polymers in this study. The salt concentration for each polymer was increased in small increments from zero until the concentration at which an ODT was no longer accessible in the experimental temperature window. The salt concentration at which this occurred depended on N and ϕ_{EO} of the polymer. Figure 3-9 shows χ_{eff} versus inverse temperature for the series of symmetric copolymers over the full range of salt concentration. The volume fraction $\phi_{\text{EO/salt}}$ of all samples shown here are between 0.44 and 0.54. The full symbols indicate the sample was fully disordered while the open symbols denote that coexistence was observed at this temperature, such as in Figure 3-7. Figure 3-9a shows the χ_{eff} values for SEO(4.9-5.5) at $r = 0, 0.0025$ and 0.005 . The pure copolymer has a relatively high χN value and needs only a small quantity of salt to induce ordering; it exhibits an ODT at very small concentrations and becomes permanently ordered at $r = 0.01$. Figure 3-9b shows the χ_{eff} values for SEO(2.9-3.3) at $r = 0, 0.005, 0.01, 0.015, 0.02$, and 0.025 . There is a large increase in χ_{eff} between $r = 0$ and $r = 0.005$, especially at higher temperatures. As the value of r increases, the subsequent increases in χ_{eff} decrease in magnitude. Figure 3-9c shows the χ_{eff} values for SEO(1.7-1.4) at $r = 0, 0.01, 0.03, 0.04, 0.065, 0.075$, and 0.085 . Once again we observed a large increase in χ_{eff} values at low salt concentrations and smaller increases in χ_{eff} as the value of r increases. At the highest salt concentrations, χ_{eff} is nearly independent of r .

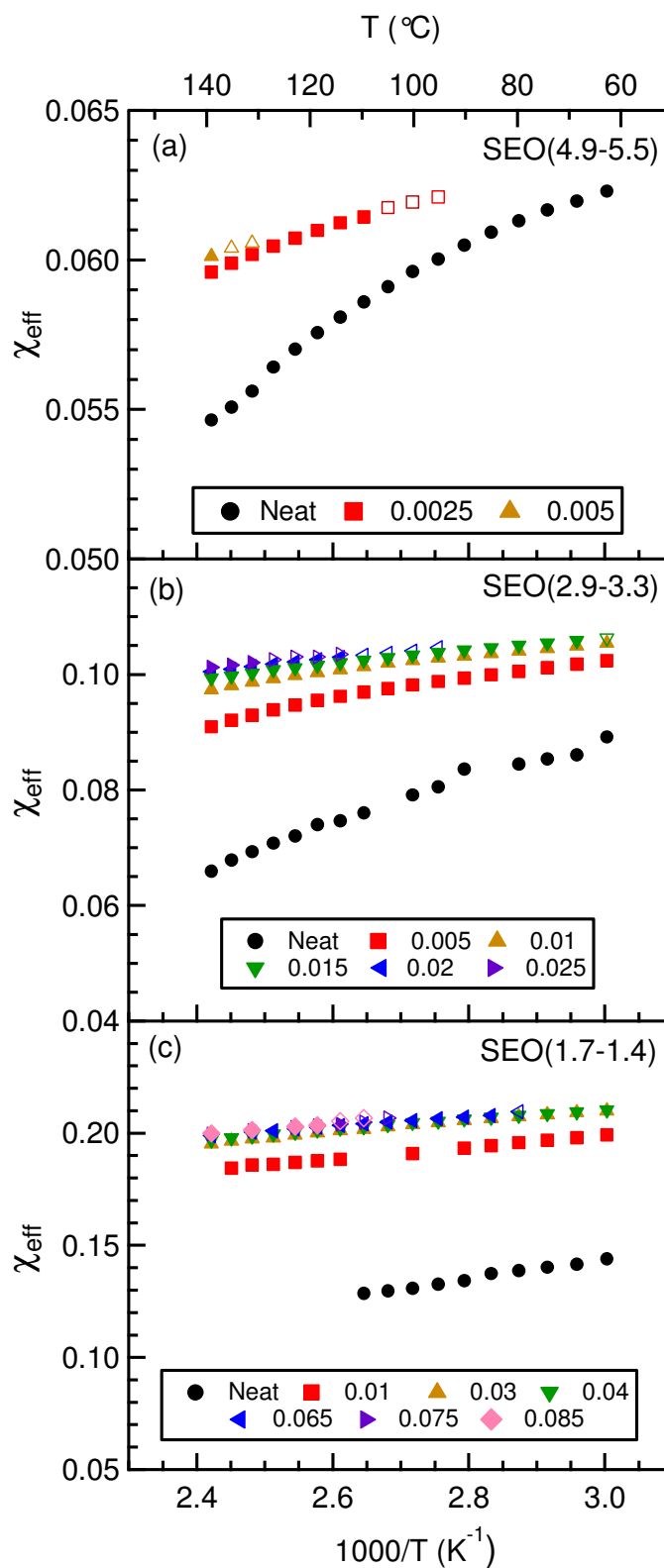


Figure 3-9 Chi parameter for salt-containing symmetric copolymers.

Effective interaction parameter, χ_{eff} , versus inverse temperature for a) SEO(4.9-5.5), b) SEO(2.9-3.3), and c) SEO(1.7-1.4) at a series of salt concentrations. The full symbols indicate the sample was fully disordered while the open symbols denote that coexistence was observed at this temperature

We show χ_{eff} obtained from different symmetric copolymers as a function of salt concentration at 60 and 140 °C in Figure 3-10a and Figure 3-10b, respectively. There are several things worth noting in these plots: (1) The lack of collapse of the data in these plots indicates that χ_{eff} is a strong function of chain length, N , as first described in Figure 3-4 and Figure 3-5 in the context of χ_0 for salt-free samples. (2) The relationship between χ_{eff} and r is highly non-linear, with a sharp initial increase at low salt concentration followed by an apparent saturation. (3) The magnitude of the increase in χ_{eff} with r depends strongly on the chain length of the copolymer. This complex behavior can be captured by an extension of Equation (3-16) to

$$\chi_{\text{eff}} = A(T) + \frac{B(T)}{N} + \frac{C(T)}{N} \left[1 - \exp\left(\frac{-D(T)r}{N}\right) \right] \quad (3-24)$$

where $C(T) = 1.01 \times 10^{-2} \cdot T$ and $D(T) = 22.4 \cdot T$. The dotted lines in Figure 3-10c and Figure 3-10d are the results obtained by plotting Equation (3-24) with N values given by Equation (3-1) at 60 and 140 °C, respectively. This remarkably simple expression, with four adjustable parameters, accurately captures the behavior seen by all the symmetric copolymers at all temperatures and salt concentrations. Several other functional forms were tested, however no other expression resulted in as good a fit to the data. It is important to note that because our approach for measuring χ requires disordered samples, the window over which χ can be measured in our approach closes rapidly with increasing molecular weight. The extent to which Equation (3-24) applies to molecular weights that are not covered explicitly in our study remains to be established. Nevertheless, Equation (3-24) implies that in the high molecular weight limit, the addition of salt to the copolymer is expected to have a negligible effect on χ_{eff} .

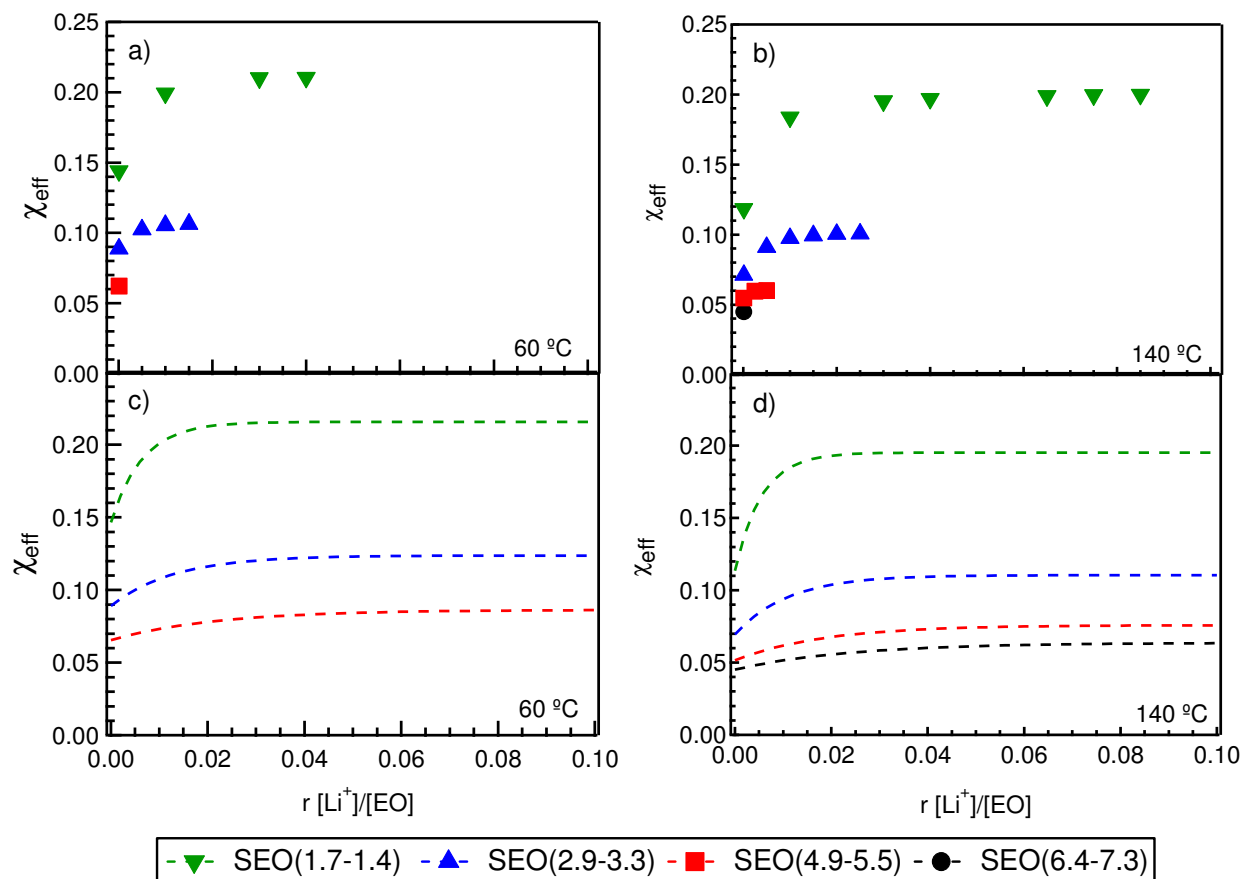


Figure 3-10 Concentration dependence of chi parameter for symmetric copolymers.

Effective interaction parameter, χ_{eff} , versus salt concentration, r , for a series of symmetric diblock SEO copolymers at a) 60 and b) 140 °C. The dashed lines represent fits to Equation (3-24) at c) 60 and d) 140 °C.

3.3.2 Asymmetric Copolymers

Two additional polymers examined in this study were asymmetric. Figure 3-11a shows χ_{eff} versus inverse temperature for SEO(1.4-1.6) at a range of salt concentrations, where $\phi_{\text{EO/Salt}}$ ranges from 0.55 to 0.63. The full symbols indicate the sample was fully disordered while the open symbols denote that coexistence was observed at that temperature. The value of χ_{eff} increases with increasing salt concentration with small variations in slope. Figure 3-11b shows χ_{eff} versus inverse temperature for SEO(1.9-0.8) at a range of salt concentrations, where $\phi_{\text{EO/Salt}}$ ranges from 0.31 to 0.35. The most noteworthy feature of this plot is that χ_{eff} decreases as the salt concentration is increased. To our knowledge, this is the first experimental data showing that the addition of salt can induce mixing in diblock copolymers.

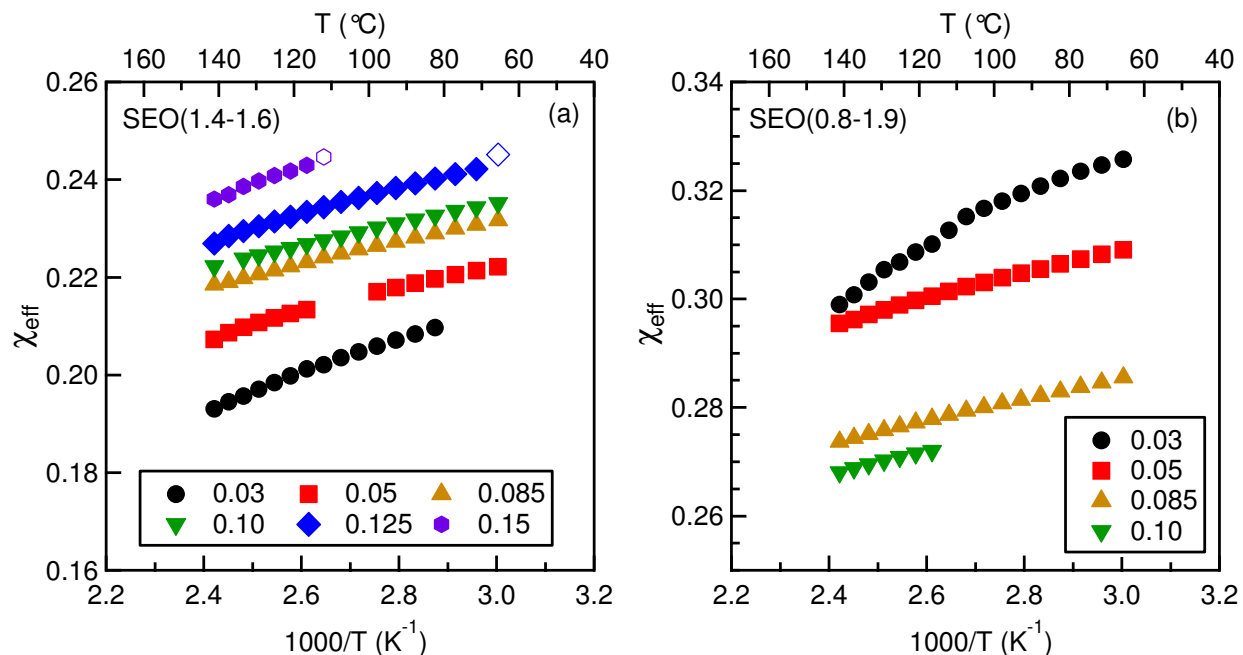


Figure 3-11 Chi parameter for salt-containing asymmetric copolymers.

Effective interaction parameter, χ_{eff} , versus inverse temperature for a) SEO(1.4-1.6) and b) SEO(1.9-0.8) at a series of salt concentrations. The full symbols indicate the sample was fully disordered while the open symbols denote that coexistence was observed at this temperature.

Figure 3-12 shows χ_{eff} as a function of r for the asymmetric SEO copolymers. The values of χ_{eff} for SEO(1.4-1.6) increase steadily as a function of r while they decrease for SEO(1.9-0.8). The dotted lines are the results obtained by plotting Equation (3-24) with N values given by Equation (3-1). Not surprisingly, the data from SEO(1.9-0.8) are qualitatively different from predictions based on Equation (3-24). We offer no explanation for the departure of the data in Figure 3-12 from Equation (3-24).

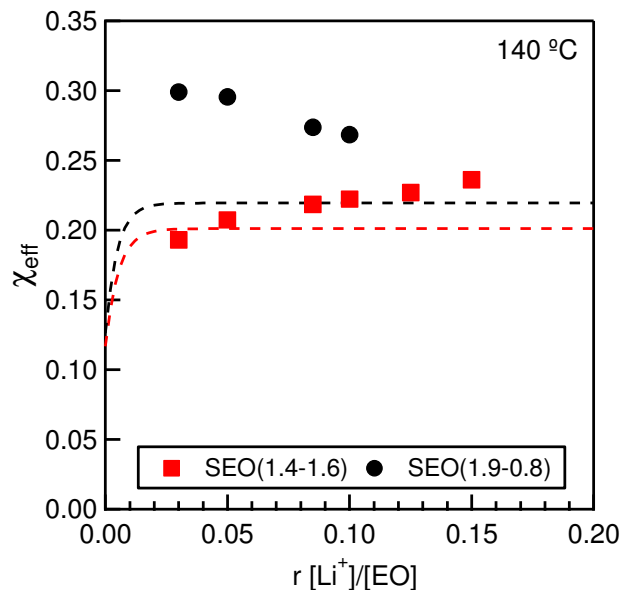


Figure 3-12 Concentration dependence of chi parameter for asymmetric SEO copolymers.

Effective interaction parameter, χ_{eff} , versus salt concentration, r , for SEO(1.4-1.6) and SEO(1.9-0.8) at 140 °C. The dashed lines represent a fit to Equation (3-24).

3.4 Phase Behavior

The data collected in this study are summarized in Figure 3-13 by plotting all the disordered samples onto a diagram that resembles a conventional block copolymer phase diagram. The abscissa in Figure 3-13 is the volume fraction of the ion-containing phase, $\phi_{\text{EO/salt}}$, and the ordinate is $\chi_{\text{eff}}(N, r)N$. Each sample is represented by three open symbols representing $T = 60, 100$, and 140 °C connected by a line. The values for $\phi_{\text{EO/salt}}$ are calculated by Equation (2-3) and the values for χ_{eff} are determined using Equation (3-14). It is worth noting that, due to the choice of a fixed v_{ref} , as T increases from 60 to 140 °C, N increases while χ decreases. Depending on the magnitude of the change in χ with T , the value χN of a given sample may change very little in Figure 3-13 or in some cases even increase as T increases. The filled symbols show χN at the ODT for all the neat and salty copolymer samples. These data points appear to reconstruct the expected parabolic shape of the diblock copolymer phase envelope, confirming the veracity of our approach. Numerous such plots of phase envelopes exist in the literature.^{31, 32} In all cases, observations of phase behavior are used to determine χ . Figure 3-13 is unique because: 1) χ is determined independently from disordered state scattering profiles and 2) χ is an explicit function of N .

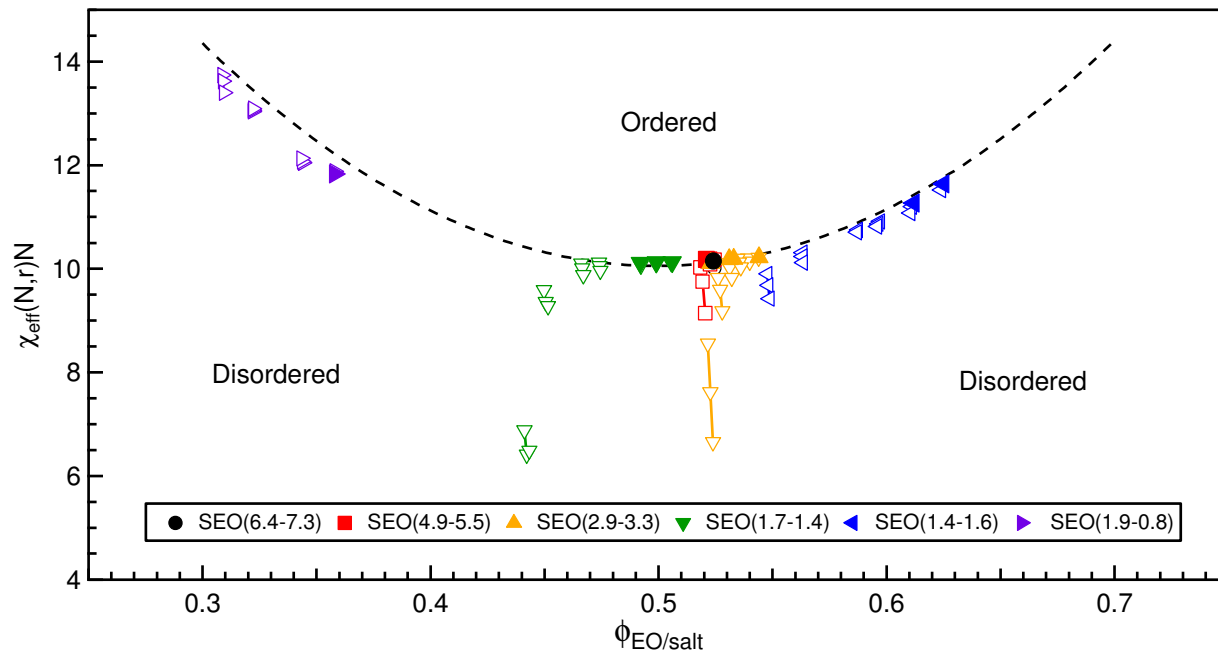


Figure 3-13 Experimental SEO/LiTFSI phase diagram.

Values of $\chi_{\text{eff}}N$ versus $\phi_{\text{EO/salt}}$ for all disordered samples in this study. Each sample is represented by three open symbols representing $T = 60, 100,$ and 140 °C connected by a line. The filled symbols show $\chi_{\text{eff}}N$ at T_{ODT} for each ODT observed. The dashed line is merely a guide for the eye.

The multitude of morphology data collected in this study are summarized in Figure 3-14 by recasting the results onto a diagram that resembles a conventional block copolymer phase diagram, using the same axes as Figure 3-13. Each of the samples listed in Table 3-1 and Table 3-2 is represented by three symbols representing $T = 60, 100,$ and 140 °C connected by a line. The values for $\phi_{\text{EO/salt}}$ are calculated by Equation (2-3) and the values for χ_{eff} are calculated using Equation (3-24). Circles represent the disordered state, square symbols represent a lamellar morphology, a cross denotes the gyroid morphology, and the triangles denote hexagonally packed cylinders. Open symbols signify that coexistence was observed at that temperature. Phase boundaries, represented by dashed lines, are meant to guide the eye. Samples of SEO(1.4-1.6) and SEO(1.9-0.8) have been omitted due to their lack of conformity to Equation (3-24). This diagram marries the experimentally observed phase behavior with the expected $\chi_{\text{eff}}(N,r)N$ and $\phi_{\text{EO/salt}}$ values obtained from the fitting equations.

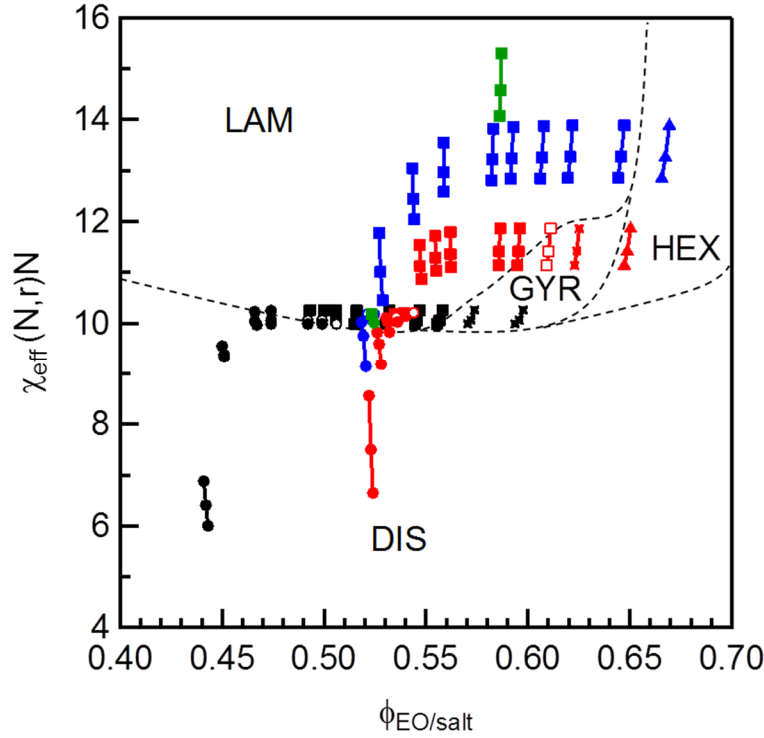


Figure 3-14 Calculated SEO/LiTFSI phase diagram.

SEO/salt phase diagram calculated from Equation (2-3) and (3-24). Each sample is represented by three symbols representing $T = 60, 100,$ and 140 °C connected by a line. Circles represent DIS, squares represent LAM, crosses denote GYR, and triangles denote HEX. Open symbols signify that coexistence was observed. Phase boundaries, represented by dashed lines, are meant to guide the eye.

3.5 Domain Spacing

In addition to measuring χ , the fitting of the scattering data also yields values of R_g for each sample. The domain spacing for the disordered sample can be determined by

$$d = DR_g \quad (3-25)$$

where D is the periodicity of the copolymer and is a function of ϕ . For monodisperse samples, the dependence of D on ϕ is given in ref. 30. The domain spacing for the ordered samples can be determined by Equation (2-5). Figure 3-15 is a comprehensive set of data showing the temperature dependence of the domain spacing for each of the polymers and salt concentrations with an accessible ODT measured in this study. The full symbols indicate the disordered domain spacing while the open symbols denote the ordered domain spacing. At temperatures for which two domain spacings are reported for a single sample, coexistence was observed. In almost all circumstances, the domain spacing increased monotonically as a function of salt concentration and decreased as a function of temperature.

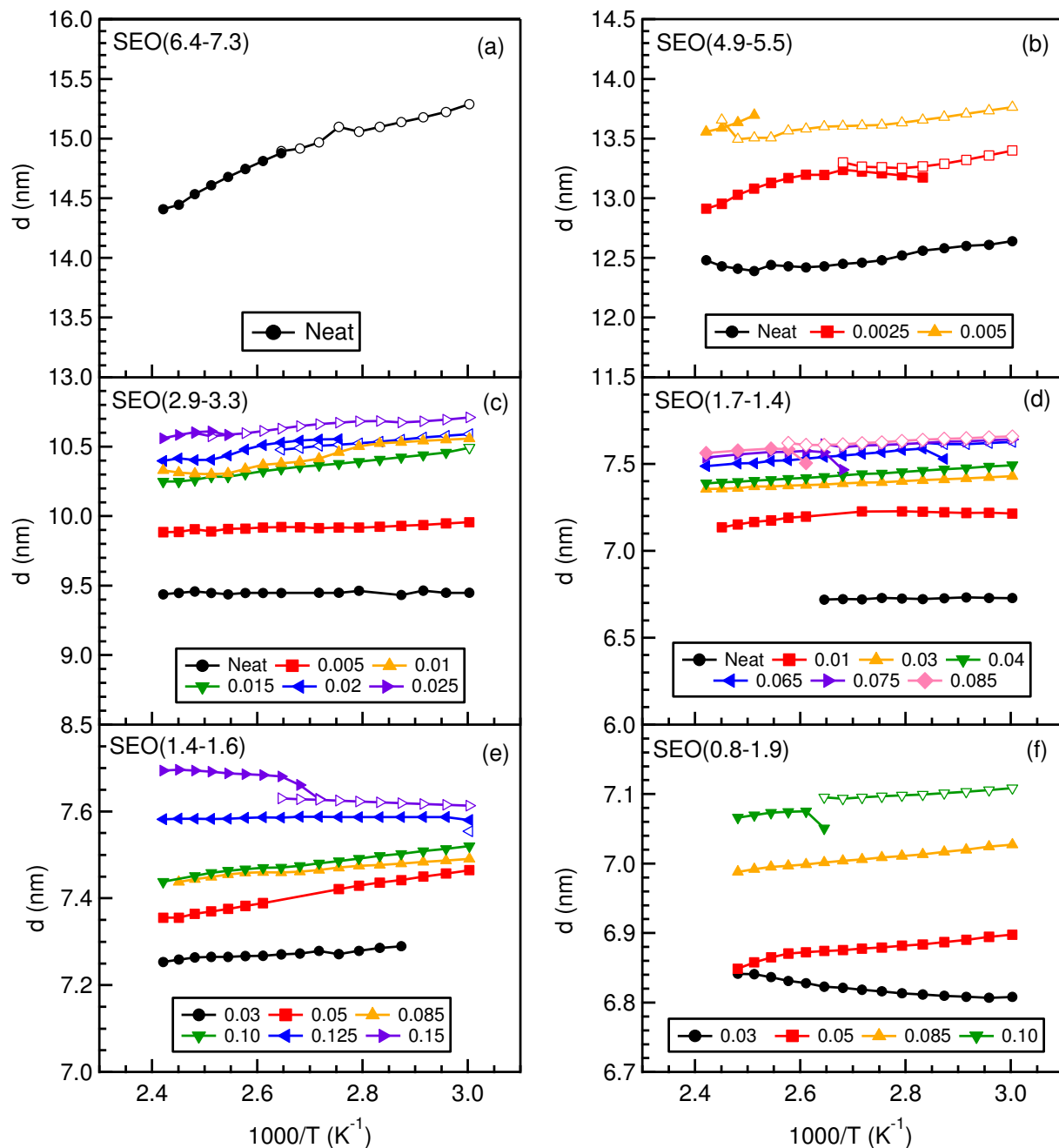


Figure 3-15 Domain spacing of salt-containing copolymers.

Domain spacing, d , versus inverse temperature for (a) SEO(6.4-7.3), (b) SEO(4.9-5.5), (c) SEO(2.9-3.3), and (d) SEO(1.7-1.4) at a series of salt concentrations. Filled and empty data points indicate disordered and ordered domain spacings respectively. Temperatures for which there exists both a disordered and an ordered domain spacing for a given salt concentration indicate that a coexistence of phases was observed.

Figure 3-16a shows the normalized domain spacing, $d/R_{g,0}$, for all the copolymers and salt concentrations in this study at 80 °C, including those without an accessible disordered state, where $R_{g,0}$ is the calculated radius of gyration of the neat diblock. An analogous plot featuring the absolute values of d for each of the electrolytes is shown in Figure 3-16b. It is clear that the

normalized domain spacing is a non-linear function of r , increasing steeply when r increases from 0 to 0.05 followed by a more gradual increase when r increases from 0.05 to 0.25. The functional form of $d/R_{g,0}$ versus r in Figure 3-16 is similar to that of χ_{eff} versus r in Figure 3-10. However, $d/R_{g,0}$ increases from about 3.7 to 5.7 for SEO(4.9-5.5) when r increases from 0 to 0.25 and only increases from 3.7 to 4.6 for SEO(1.7-1.4) over the same range of r . Thus the polymers with longer chain length show the largest increase in normalized domain spacing with salt loading. This is in contrast to the trends seen with χ_{eff} in Figure 3-10; polymers with the shortest chain length show the largest increase in χ_{eff} with salt loading.

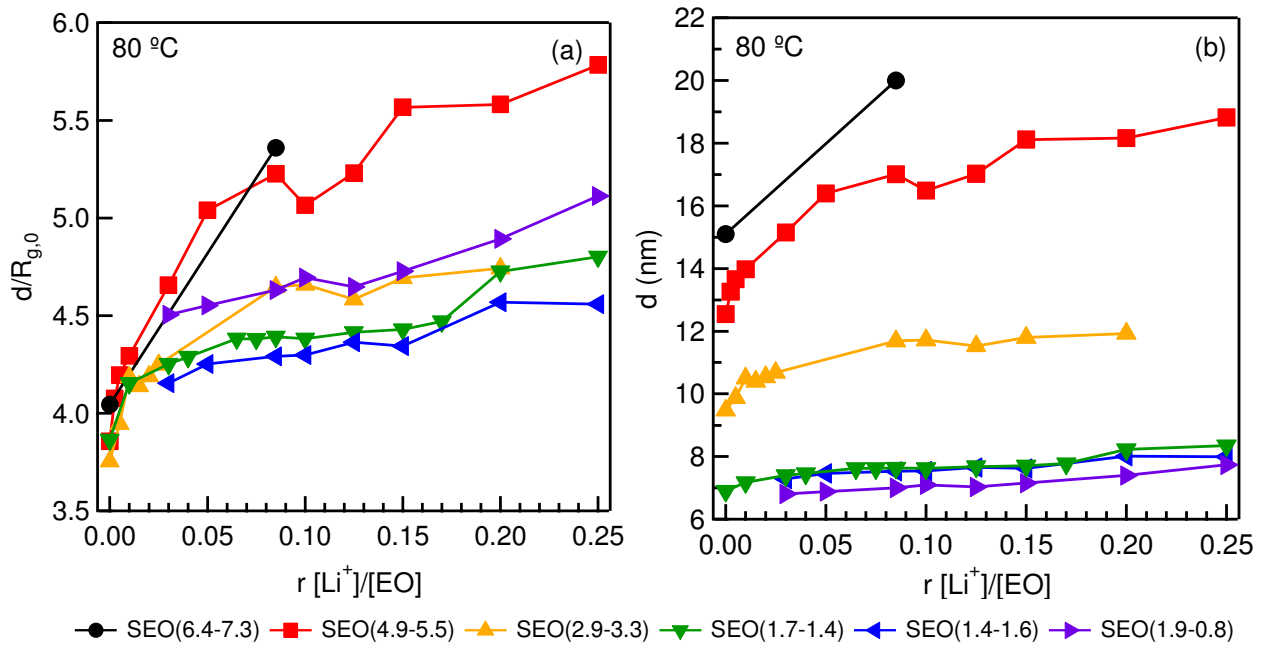


Figure 3-16 Domain spacing versus salt concentration for SEO/LiTFSI mixtures.

(a) Normalized domain spacing, $d/R_{g,0}$, and (b) absolute domain spacing, d , versus salt concentration, r , for all samples in this study at 80 °C.

Empirically we found that the dependence of domain spacing on salt concentration obtained for most samples collapsed when $d\chi_{\text{eff}}^{2/3}$ was plotted versus r as shown in Figure 3-17. The collapse was observed for all samples with the exception of the SEO(1.9-0.8), the polymer with the lowest value of ϕ_{EO} . The data in Figure 3-17 suggest that the product $d\chi_{\text{eff}}^{2/3}$ at a given salt concentration is constant, which in turn suggests that d and χ_{eff} are inversely related to each other. It is evident from Figure 3-16 and Figure 3-17a that the relationship between χ_{eff} and d is not simple and that traditional relationships between d and χ cannot be used. Figure 3-17b shows explicitly that the oft-cited $N^{2/3}\chi^{1/6}$ versus d relationship does not hold for salt-containing samples; It is thus not possible to estimate values of χ_{eff} from measurements of d .

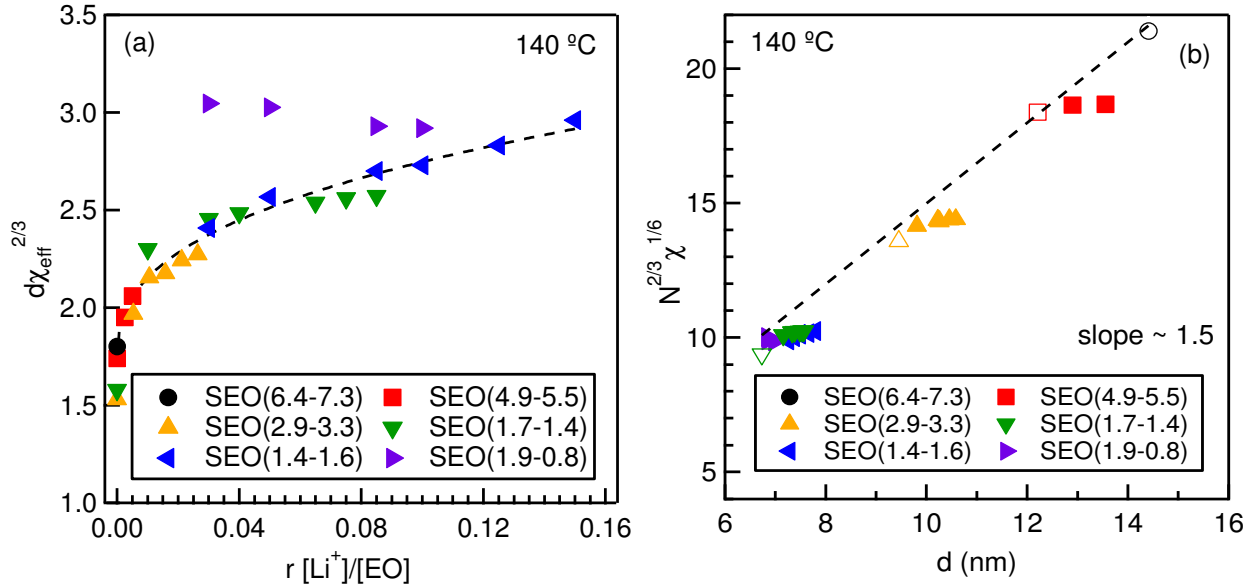


Figure 3-17 Chi analysis for SEO/LiTFSI mixtures.

(a) $d\chi_{\text{eff}}^{2/3}$ versus salt concentration, r , for electrolyte at 140 °C. The dashed line is a guide for the eye. (b) $N^{2/3} \chi^{1/6}$ versus d at 140 °C. Open symbols are neat SEO and full symbols are salt-containing SEO. The dotted line is a fit to the expression $d \sim N^{2/3} \chi^{1/6}$ through the neat SEO data.

3.6 Comparison with Previous Work

Significant experimental and theoretical effort has been undertaken to understand and quantify the effect of salt addition on χ_{eff} . Wang et al.²⁹ used small angle neutron scattering (SANS) to directly measure χ_{eff} on a polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) copolymer complexed with lithium chloride while Naidu et al.²⁴ used SAXS to measure χ_{eff} on a polystyrene-*b*-poly(2-vinyl pyridine) (PS-*b*-P2VP) copolymer doped with lithium perchlorate. Young et al.²³ and Huang et al.²² used domain spacing as a proxy to study χ_{eff} in an SEO copolymer mixed with several lithium salts, and a poly(ϵ -caprolactone)-*b*-poly(ethylene oxide) (PCL-*b*-PEO) complexed with lithium perchlorate, respectively. The effect of salt on χ_{eff} was determined from order-disorder transition (ODT) measurements by Wanakule et al.²⁶ using a series of SEO copolymers complexed with LiTFSI and by Gunkel et al.²⁵ using both an SEO copolymer and a PS-*b*-P2VP copolymer complexed with lithium triflate, respectively. Nakamura et al.^{27, 28} and Wang et al.³³ and have published a series of theoretical papers studying the problem using self-consistent field theory and the Born energy of solvation.

The results presented in Figure 3-10 appear contrary to almost every other study, both experimental and theoretical, that has attempted to determine the relationship between χ_{eff} and r . All previous studies assume that χ_{eff} was a linear function of r , i.e. $\chi_{\text{eff}} = \chi_0 + mr$. Indeed, if one conducts measurements on one polymer and a few salt concentrations, it is easy to see how the relationship may appear linear. The work in refs. 22, 24, and 29 is limited to a single block copolymer and a few salt concentrations. Our work clearly shows that the assumptions that were the basis of the analysis in refs. 23 and 25 are not valid. In previous work from this lab (ref. 26), we ignored the N dependence on χ_0 . Surprisingly, the only experimental study to show any indication of the non-linearity of the relationship contains no comment on the novelty of this

observation.²⁴ The theoretical work by Nakamura et al.²⁷ suggests that such non-linear behavior might be expected if ion pairing of the salt species were occurring in the copolymer. The lack of ion-pairing in dilute homopolymer PEO/LiTFSI mixtures ($r < 0.10$) is well established³⁴ and the ionic conductivity of high molecular weight SEO/LiTFSI mixtures also does not show evidence of ion pairing.⁹ However, ion transport in low molecular weight SEO copolymers is considerably more complex and the data do not rule out the possibility of ion-pairing in these systems.³⁵

3.7 Conclusion

Understanding the effect of salt addition on the thermodynamics of block copolymers remains an active area of research with implications for both fundamental understanding of salt/polymer miscibility as well as applications such as solid-state electrolytes. However, before this is done, it is important to quantify thermodynamic interactions in neat diblock copolymers. Our results reaffirm that the Flory-Huggins interaction parameter in neat SEO copolymers, χ_0 , is a strong function of N (Figure 3-5). Conventional wisdom suggests that the intrinsic Flory-Huggins parameter should be independent of N . Several theoretical papers have attempted to explain the origin of the difference between the χ measured from scattering experiments and the intrinsic Flory-Huggins parameter.^{6, 36-50} For example, the 'intrinsic' Flory-Huggins parameter between PS and PEO in neat block copolymers might be given by $A(T) = 10.2 \cdot T^{-1}$ (see Equation (3-16)), i.e. χ_0 in the limit of N tending to infinity. Ignoring the N dependence on χ_{eff} has a profound effect on the interpretation of thermodynamic data from salty samples.

Our experiments on salt-containing block copolymers reveal that the relationship between χ_{eff} and r is highly non-linear, with a sharp initial increase at low salt concentration followed by an apparent saturation (Figure 3-10) and that the magnitude of the increase in χ_{eff} with r depends strongly on the chain length of the copolymer. We present a relatively simple expression that captures the behavior of χ_{eff} as a function of salt concentration and chain length for symmetric electrolytes; however the behavior of asymmetric electrolytes remains poorly understood. In the case of a copolymer with PEO as the minor component, the addition of salt promotes mixing in contrast to all other reports in the literature, which indicate that the addition of salt promotes demixing. These findings reveal a much more complex relationship between χ_{eff} and salt concentration in block copolymers and represent a significant departure from previous results that asserted a simple linear relationship existed. Additionally, we demonstrate that changes in domain spacing do not correlate in the expected manner with changes in χ_{eff} for salty copolymer samples.

The results presented in this study are a significant step forward in understanding the effect of salt on block copolymer thermodynamics; yet many questions remain to be answered. Additional experimental and theoretical work is needed to better understand the origin of the data presented in this chapter.

Chapter 4 - Effect of Molecular Weight on Conductivity of Homopolymer Electrolytes²

ABSTRACT

The ionic conductivity, σ , of mixtures of poly(ethylene oxide) (PEO) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) was measured as a function of molecular weight of the PEO chains, M_{PEO} , over the range 0.2 – 5000 kg mol⁻¹. Our data are consistent with an expression $\sigma = \sigma_0 + K/M_{\text{PEO}}$ proposed by Shi and Vincent [Solid State Ionics 60 (1993)] where σ_0 and K are exponential and linear functions of temperature respectively. Explicit expressions for σ_0 and K are provided.

Solid polymer electrolytes remain the subject of continual interest in the scientific community for their potential use in high specific energy, solid state batteries.⁵¹ These materials are formed by the complexation of a low lattice-energy salt with solvating polymers^{10,52}. Poly(ethylene oxide) (PEO) has been the most widely studied solvating polymer due to its ability to solvate a wide variety of salts through interaction of its ether oxygens with cations.

It is widely believed that ion conduction in an amorphous homopolymer above the glass transition temperature takes place through two mechanisms.^{53, 54} The first mechanism is a result of the segmental motion of the chains surrounding the salt ions, creating a liquid-like environment around the ion. Ions migrate by hopping between adjacent liquid-like environments. This mechanism is dependent on labile interactions between the ion and the polymer chain, and is thus affected by chemical composition of the polymer and temperature. It is, however, independent of the molecular weight of the chain. The second mechanism of ion conduction is attributed to diffusion of the entire polymer chain with coordinated ions. This mechanism is similar to diffusion of salts in traditional low molecular weight electrolytes such as water and alkyl carbonates wherein ions diffuse with "shells" of coordinated solvent molecules. Since polymer diffusion coefficients decrease rapidly with increasing molecular weight⁵⁵⁻⁵⁷ the second mechanism is only applicable in low molecular weight polymers. A thorough study of these mechanisms requires studies of ion transport as a function of chain length over a wide range of molecular weights. Further, these studies should be conducted on nearly monodisperse model polymers synthesized by techniques such as anionic polymerization. In simple amorphous polymer melts, it has been shown that the motion of long chains in the presence of a small concentration of short chains is profoundly different from that in their absence due to entanglement dynamics.^{58, 59} Upon the addition of salt to the system, such entanglement dynamics are coupled to the formation of dynamic cross-links between the salt and the polymer.⁶⁰

²Reprinted from *Solid State Ionics*, 203, Alexander A. Teran, Maureen H. Tang, Scott A. Mullin, and Nitash P. Balsara, "Effect of molecular weight on conductivity of polymer electrolytes." 18–21, Copyright (2011), with permission from Elsevier.

The effect of polymer molecular weight on transport in polymer electrolytes has, to our knowledge, only been addressed in three prior studies. In a pioneering publication, Shi and Vincent⁶¹ determined the lithium cation diffusion coefficient, D_{Li} , as well as steady state current, I_s^+ , of mixtures of lithium triflate and PEO as a function of the PEO molecular weight, M_{PEO} . Pulsed field gradient (PFG) nuclear magnetic resonance (NMR) was used to measure D_{Li} while DC measurements on the polymer/salt mixtures sandwiched between two lithium foils were used to measure I_s^+ . They proposed equations for the transport coefficients based on theories of polymer dynamics such as the Rouse model for diffusion of short chains and the reptation model for the diffusion of long chains. In a subsequent publication, Hayamizu et al.⁶² determined D_{Li} and ionic conductivity, σ , in mixtures of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and PEO as a function of M_{PEO} . Impedance spectroscopy was used to measure σ . More recently, Diddens et al.⁶³ used molecular dynamics simulations to determine D_{Li} in PEO/LiTFSI mixtures as a function of M_{PEO} . They demonstrated excellent agreement between simulation results⁶³ and experiments.⁶²

The goal of this paper is to augment the existing experimental data on the effect of M_{PEO} on σ in PEO/LiTFSI mixtures. In previous studies, our group has reported on the molecular weight dependence of conductivity and salt diffusion coefficient in PEO-based block copolymer electrolytes over a wide range of molecular weights.^{3, 5, 8} The data presented here provides a baseline for analyzing the effect of polymer molecular weight on ion transport in these more complex systems.

4.1 Polymer Electrolyte Preparation

Poly(ethylene oxide) samples were obtained from Polymer Source, Inc. The polymers used in this study can be found in Table 4-1 and are labeled PEO(X), where X indicates the number averaged molecular weights of the samples in kg mol^{-1} . A high molecular weight PEO sample which we label PEO(5000) was obtained from Aldrich. The polydispersity index of this sample was not provided but we expect it to be significantly higher than 1.15. PEO(5000) was dissolved in acetone and recrystallized. The other polymers were used as received. Argon gloveboxes (MBraun and Vacuum Atmospheres Company) with oxygen and water at sub-ppm levels were used for all sample preparation and testing steps. All polymers were dried at 100 °C under vacuum in a glovebox antechamber for at least 24 h, except PEO(0.2) which was received in an ampule under argon, opened in the glovebox, and used as received. LiTFSI salt, obtained from Novolyte, was transferred from its air-free packaging into a vial inside of a glovebox, and then dried at 120°C under vacuum in a glovebox antechamber for three days.

Polymer	M_{PEO} kg mol ⁻¹	PDI	[EO]/chain
PEO(0.2)	0.19	1.01	4
PEO(0.6)	0.64	1.03	15
PEO(1.0)	1.0	1.10	23
PEO(2.0)	2.0	1.10	45
PEO(4.0)	4.0	1.03	91
PEO(10)	10	1.05	2.3 x10 ²
PEO(20)	20	1.10	4.5 x10 ²
PEO(50)	50	1.19	1.1x10 ³
PEO(360)	360	1.12	8.2x10 ³
PEO(5000)	5000	-	1.13x10 ⁵

Table 4-1 Characteristics of the polymers used in Chapter 4.

LiTFSI salt was added directly to PEO(0.2) and PEO(0.6) and stirred at 90 °C for about 12 h. The rest of the electrolyte samples were prepared by blending a PEO/benzene solution with the necessary amount of a 25 wt % solution of LiTFSI salt in tetrahydrofuran (THF). Benzene and THF were purified using an MBraun solvent purification system to remove water and other impurities. For PEO(10), PEO(20), PEO(50), PEO(360), and PEO(5000), methyl ethyl ketone was added to the benzene/THF mixture to achieve a homogenous solution. The solutions were mixed at 50 °C for 72 h, then placed inside an air-tight desiccator, transferred into a Millrock LD85 lyophilizer, and freeze-dried without exposure to air for one week. The concentration of salt in the electrolytes is specified by r , the molar ratio of Li⁺ ions to ethylene oxide moieties, $r = [\text{Li}^+] [\text{EO}]^{-1}$, without accounting for the -OH end groups on each of the chains. The concentration r was held fixed at 0.085 for all samples. The ionic conductivity of PEO/LiTFSI mixtures is peaked in the vicinity of this salt concentration.^{5, 8} It is customary in the literature of solid electrolytes to use the term n , the molar ratio of EO to Li⁺ ions, to describe salt concentration. The value of n in our samples, with no end group corrections, is 11.76

4.2 Electrochemical Measurements

Conductivity cells, similar to those designed by Lascaud et al.⁵, were built of stainless steel to enable examination of samples with a wide range of viscosities. An important difference is that the diameters of the upper and lower electrodes in our cells were 8 and 10 mm, respectively. A schematic of the conductivity cell is shown in Figure 4-1. The unequal area electrodes were useful for loading samples with widely different mechanical properties, from watery liquids to semi-crystalline solids.

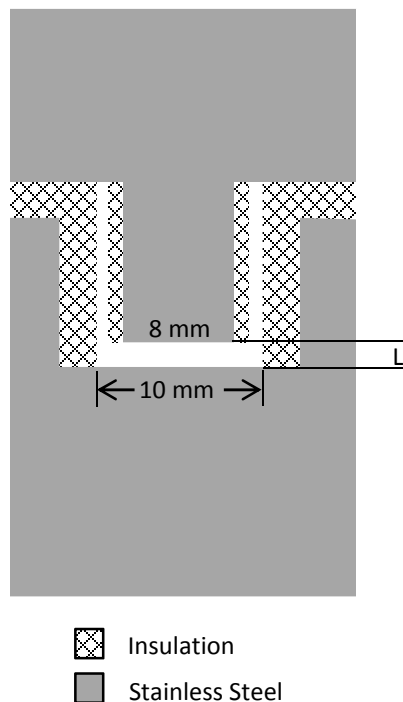


Figure 4-1 Schematic of liquid conductivity cell.

To facilitate sample loading, the electrolyte was placed on the bottom electrode and heated to 100 °C in the glovebox. In most cases, this resulted in a sample of uniform thickness on the electrode. PEO(360)/LiTFSI and PEO(5000)/LiTFSI showed too great a resistance to flow even at elevated temperature. They were pressed into pellets of appropriate size and loaded into the conductivity cells. Sample thicknesses ($\pm 1\mu\text{m}$) were determined by subtracting the thicknesses of the lower and upper electrodes from the overall assembled cell thickness. The thicknesses ranged from 0.8 to 2.2 mm.

A home-made temperature controlled box was used to house the cells during the electrochemical experiments. The AC impedance spectroscopy measurements, performed using a 16-channel Bio-Logic VMP3 potentiostat, were made across the frequency range 1 MHz to 10 Hz at a peak-to-peak amplitude voltage of 20 mV. A characteristic Nyquist impedance plot of a polymer electrolyte is shown in Figure 2-10b; the electrolyte resistance, R_b , was determined by the low-frequency minimum. Measurements were made at a series of temperatures with a minimum of 3 h equilibration at each temperature. All data presented in this work are from cooling.

Calculating the sample conductivity from the measured resistance R requires knowledge of both the electrode separation, $L[\text{cm}]$, and the effective cross-sectional area, $A_{\text{eff}}[\text{cm}^2]$. To find the effective area of a conductivity cell with two unequally sized electrodes, the experimental set-up was modeled in COMSOL Multiphysics. Solving Laplace's equation for the primary current distribution in the polymer electrolyte yielded the steady state current, I , through the electrodes as a function of applied voltage, V and assumed value of electrolyte conductivity, σ_{model} . These were used to calculate the effective cross-sectional area by $A_{\text{eff}} = LI/(V\sigma_{\text{model}})$. The linearity of Laplace's equation means that A_{eff} depends only on geometry and is independent of V and σ_{model} . The numerical data were found to obey the empirical equation,

$$A_{eff} = 2.3L^3 - 2.91L^2 + 1.35L + 0.498 \quad (4-1)$$

Sample conductivity, σ , was calculated using $\sigma = L/(A_{eff}R_b)$. Three samples from each electrolyte were tested, with error bars of data points representing the standard deviation. The exception was PEO(5000)/LiTFSI, for which only one sample was run. The accuracy of our procedure was verified using an aqueous KCl conductivity standard. Conductivity measurements were made between 330 and 368 K. The PEO/LiTFSI mixtures are in the amorphous state in this temperature range and concentration.⁶⁴ Volel et al. have shown that the conductivity of amorphous PEO/salt mixtures is not dependent on sample preparation details such as the solvent used to create the mixture and thermal history.⁶⁵

4.3 Conductivity Results

Figure 4-2 shows the ionic conductivity, σ , of PEO/LiTFSI mixtures with $r = 0.085$ at temperatures (T) between 330 and 368 K. Following Shi and Vincent,⁶¹ we assume that the relationship between σ and M_{PEO} is of the form

$$\sigma = \sigma_0 + \frac{K}{M} \quad (4-2)$$

where σ_0 represents transport due to segmental motion, and the K/M_{PEO} term accounts for transport of coupled polymer chains and coordinated ions. The M_{PEO}^{-1} dependence of the second term accounts for the increase in friction experienced by diffusing polymer chains with increasing molecular weight based on the Rouse model.⁶⁶ The curves in Figure 4-2 represent least-squares fits of our data to Equation (4-2). Figure 4-3a and Figure 4-3b show σ_0 and K as a function of $1/T$. Over the limited temperature window of our measurements, the data are consistent with the following expressions:

$$\sigma_0 = A * \exp\left(\frac{-B}{T}\right) \quad (4-3)$$

and

$$K = C + \frac{D}{T} \quad (4-4)$$

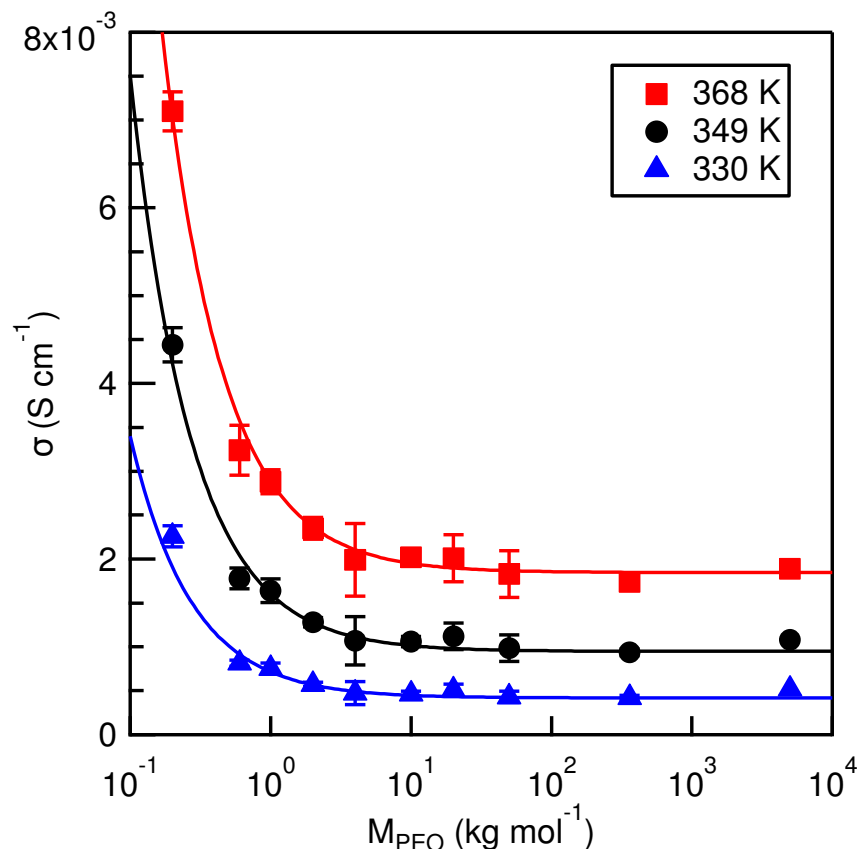


Figure 4-2 Conductivity as a function of molecular weight of PEO/LiTFSI at $r = 0.085$.

Ionic conductivity, σ , as a function of molecular weight, M , of PEO/LiTFSI electrolytes with $r = 0.085$ at three temperatures. The curves represent the fit to Equation (4-2).

The Vogel-Tamman-Fulcher (VTF) equation, originally developed to describe the temperature dependence of the viscosity of glass-forming liquids, is a stretched exponential expression typically used to describe the temperature dependence of σ over a wide temperature window. We use a simple Arrhenius expression because our temperature window is limited. In the standard models for polymer dynamics such as the Rouse and reptation models, the temperature dependencies of both segmental and molecular motion arise due to the temperature dependence of the monomeric viscous friction constant.⁶⁷ This implies that if the two terms σ_0 and K/M_{PEO} arose from segmental and molecular motion respectively, then their temperature dependencies would be identical. In other words, one would expect the temperature dependence of K to also follow the Arrhenius expression. The temperature dependence of K is, however, not consistent with the Arrhenius expression. We have thus used an empirical expression for describing the temperature dependence of K [Equation (4-4)]. Least-squares fits, shown by lines in Figure 4-3a and Figure 4-3b, give $A = 590 \pm 250 \text{ S cm}^{-1}$, $B = (4.66 \pm 0.15) \times 10^3 \text{ K}$, $C = (7.3 \pm 0.4) \times 10^{-3} \text{ S kg mol}^{-1} \text{ cm}^{-1}$, and $D = -2.3 \pm 0.1 \text{ S K kg mol}^{-1} \text{ cm}^{-1}$.

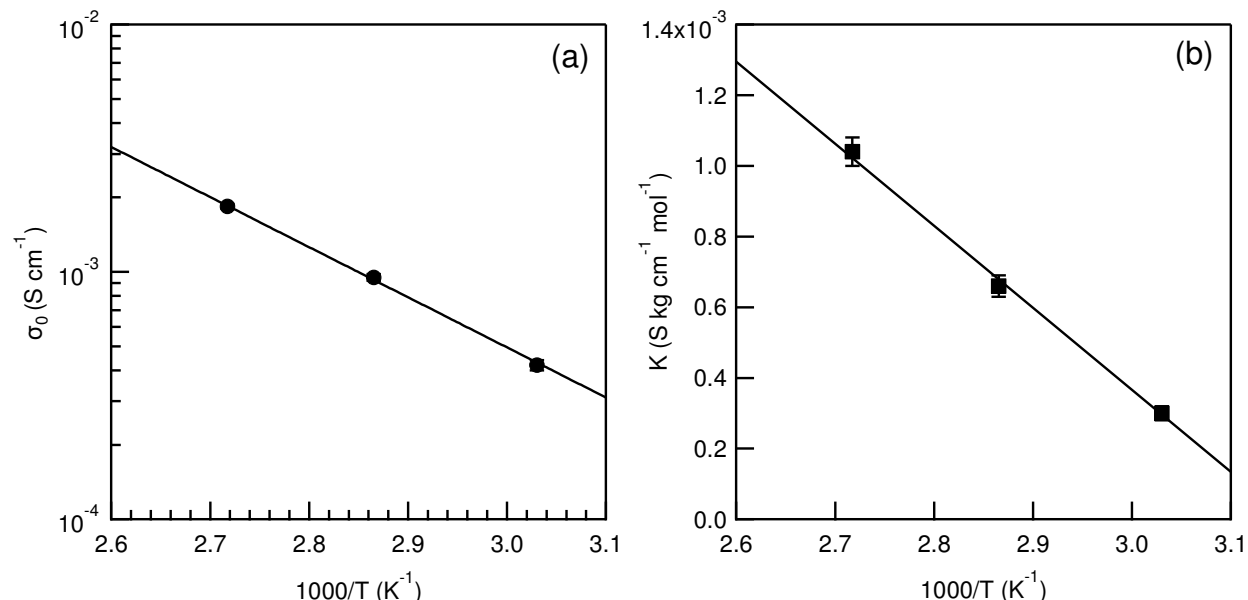


Figure 4-3 Fitting parameters σ_0 and K .

Fitting parameters (a) σ_0 and (b) K as a function of inverse temperature. The curves represent the fit to Equations (4-3) and (4-4) respectively.

It is, perhaps, important to distinguish the present work from the two previous experimental studies on the effect of polymer molecular weight on ionic conductivity.^{61, 62} The study of Shi and Vincent covered a wide range of PEO molecular weights from 0.4 to 4000 kg mol⁻¹ but 9 out of the 10 samples had molecular weights lower than 10 kg mol⁻¹. In addition, the salt used in this study was lithium triflate which is not optimal for PEO-based electrolytes. PEO/LiTFSI mixtures have significantly higher conductivities than PEO/lithium triflate mixtures. Hayamizu et al. studied PEO/LiTFSI electrolytes but their work was limited to molecular weights below 2.5 kg mol⁻¹. Both Shi and Vincent and Hayamizu et al. used PEO samples with unspecified polydispersity. In contrast, the present study on PEO/LiTFSI electrolytes uses nearly monodisperse samples that are more-or-less evenly spaced along the log(M_{PEO}) axis in the 0.2 to 360 kg mol⁻¹ range. Figure 4-4 compares the PEO/LiTFSI conductivity from this study with several others.^{5, 62, 68} There is good agreement between the different measurements with the exception of the $M_{\text{PEO}} = 0.5$ kg mol⁻¹ data point of ref. 62. A potential reason for the exception at such low molecular weight is the presence of -CH₃ end groups used in ref. 62. Our study is based on PEO chains with -OH end groups.

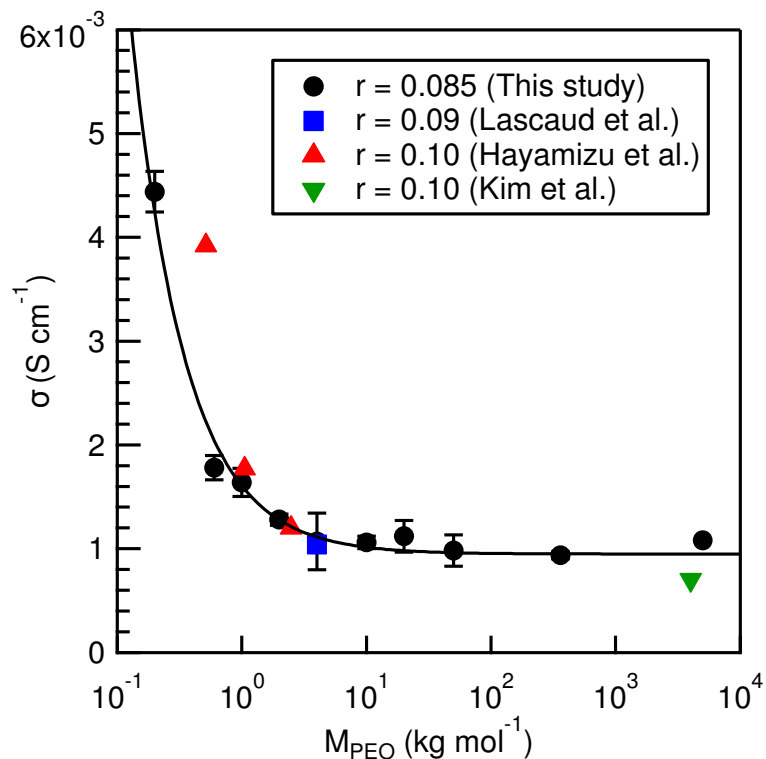


Figure 4-4 Literature comparison of PEO/LiTFSI conductivity.

4.4 Conclusion

The ionic conductivity of PEO/LiTFSI electrolytes was measured using AC impedance spectroscopy as a function of molecular weight of the host polymer over the range 0.2 – 5000 kg mol⁻¹. The data are captured by two empirical temperature-dependent parameters σ_0 and K , originally proposed by Shi and Vincent⁶¹.

Chapter 5 - Effect of Molecular Weight on Conductivity of Block Copolymer Electrolytes³

ABSTRACT

The ionic conductivity and glass transition temperatures of nanostructured block copolymer electrolytes composed of polystyrene-*b*-poly(ethylene oxide) (SEO) doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were studied in the small molecular weight limit (between 2.7 and 13.7 kg mol⁻¹). In this range, the annealed conductivity exhibits a non-monotonic dependence on molecular weight, decreasing with increasing molecular weight in the small molecular weight limit before increasing when molecular weight exceeds about 10 kg mol⁻¹. We show that annealed electrolyte conductivity is affected by two competing factors: the glass transition temperature of the insulating polystyrene block and the width of the conducting poly(ethylene oxide) (PEO) channel. In the low molecular weight limit, all ions are in contact with both polystyrene (PS) and PEO segments. The intermixing between PS and PEO segments is restricted to an interfacial zone of width, α . Our experiments suggest that α is about 5 nm. The fraction of ions affected by the interfacial zone decreases as the conducting channel width increases. We also study the effect of thermal history on the conductivity of the block copolymer electrolytes. Our data suggest that long-range order impedes ion transport.

Nanostructured block copolymer electrolytes containing an ion-conducting block and a modulus-strengthening block are of interest for applications in solid-state lithium metal batteries.^{12, 69} These electrolytes are designed to have high shear moduli to prevent dendrite formation at the anode while maintaining good ionic conductivity.¹³ An example of such an electrolyte is polystyrene-*b*-poly(ethylene oxide) (SEO) doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).⁸ With the appropriate ratio of styrene to ethylene oxide units, this system self-assembles into a well-defined lamellar microstructure, creating channels of poly(ethylene oxide) (PEO) that facilitate ion transport.

Previous work by our group has demonstrated that the ionic conductivity of symmetric SEO mixed with a given concentration of LiTFSI salt increases with increasing molecular weight of the PEO block.⁸ Coarse-grained simulations of block copolymer electrolytes ascribe this trend to

³Adapted with permission from Yuan, Rodger, Alexander A. Teran, Inna Gurevitch, Scott A. Mullin, Nisita S. Wanakule, and Nitash P. Balsara. 2013 "Ionic Conductivity of Low Molecular Weight Block Copolymer Electrolytes." *Macromolecules*, 46 (3), pp 914–921. doi: 10.1021/ma3024552. Copyright 2013 American Chemical Society.

decreased diffusivity near the interfacial zone between blocks coupled with decreasing volumetric density of interfacial regions with increasing M_{PEO} .⁷⁰ This effect is further accentuated by the fact that lithium salt is increasingly localized near the middle of the PEO lamellae in SEO electrolytes as M_{PEO} increases.³ However, experimental data available in the literature are limited to SEO polymers with M_{PEO} greater than 5 kg mol⁻¹.⁸

In contrast, homopolymer PEO mixed with LiTFSI salt shows an exponential decrease in ionic conductivity as a function of molecular weight, reaching a plateau at about 5 kg mol⁻¹, above which it becomes independent of molecular weight.⁶¹ Ion conduction in PEO is believed to be dependent on both local segmental motion of polymer chains and the long-range diffusion of polymer chains with coordinated ions.^{53, 54} While the former mechanism is independent of molecular weight, the latter contributes significantly to ionic conductivity only at chain lengths below the entanglement threshold of PEO (3 kg mol⁻¹).

The purpose of this study is to extend our previous work on nanostructured block copolymer electrolytes³ to the low molecular weight limit. The conductivity of a series of nearly symmetric SEO block copolymers mixed with LiTFSI salt was measured as function of total molecular weight, M_{SEO} , in the range 2.7 – 13.7 kg mol⁻¹. Our experiments allow us to elucidate the factors that govern ionic conductivity in this regime.

5.1 Sample Preparation

SEO block copolymers were synthesized, purified, and characterized as described in Chapter 2 of this dissertation. SEO/LiTFSI mixtures were also prepared as described in Chapter 2. A list of the polymers' characteristics can be found in Table 5-1. The neat copolymers are completely transparent and colorless. The salt concentration in our electrolyte, quantified by the molar ratio of lithium atoms to ethylene oxide (EO) moieties, r , was set to 0.085 for all samples. This concentration has been shown to produce the highest ionic conductivity for SEO electrolytes.³ The new volume fraction of the salt-containing PEO block, which we will refer to as the conducting phase, $\phi_{EO/salt}$, can be calculated using Equation (2-3). Sample morphologies and glass transition temperatures were determined via SAXS and DSC, respectively, as described in Chapter 2.

Polymer	M_{PS} kg mol ⁻¹	M_{PEO} kg mol ⁻¹	M_{SEO} kg mol ⁻¹	$\phi_{EO/salt}$	PDI	Morphology	d nm
SEO(1.5-1.2)	1.5	1.2	2.7	0.49	1.05	LAM→DIS	7.4
SEO(1.7-1.4)	1.7	1.4	3.1	0.49	1.05	LAM→DIS	7.7
SEO(2.9-3.3)	2.9	3.3	6.2	0.57	1.05	LAM	11.6
SEO(4.9-3.6)	4.9	3.6	8.5	0.46	1.04	LAM	13.4
SEO(5.6-3.3)	5.6	3.3	8.9	0.41	1.04	LAM	13.8
SEO(4.9-5.5)	4.9	5.5	10.4	0.57	1.04	LAM	16.8
SEO(6.4-7.3)	6.4	7.3	13.7	0.57	1.04	LAM	20.0
SEO(60-63)	60	63	123	0.55	1.03	LAM	90.6

Table 5-1 Characteristics of electrolytes with $r = 0.085$ used in Chapter 5,

Electrochemical Impedance spectroscopy experiments were performed as described in Chapter 2. The samples were heated from 30 to 130 °C and then cooled back to 30 °C, all in 10 °C intervals with 1 h equilibration at each temperature. After the experiments were performed, the sample was

carefully disassembled and the final thickness was measured again. Sample thicknesses decreased 7% on average after annealing.

5.2 Morphological and Thermal Characterization

We begin this section by reminding readers that all of our discussion relates to SEO/LiTFSI mixtures with $r = 0.085$. We will refer to the salt-containing copolymer samples as electrolytes. In order to compare directly with previous work,³ all the electrolytes used in this study are roughly symmetric with lamellar (LAM) morphologies. Figure 5-1a shows 1-D SAXS profiles for all of the small molecular weight electrolytes listed in Table 5-1 at 90 °C. Sharp scattering peaks and higher order peaks at $q/q^* = 2, 3, 4$, etc., confirms the presence of well ordered, lamellar morphologies at this temperature. Two of the electrolytes, SEO(1.5-1.2) and SEO(1.7-1.4), exhibit order-to-disorder transitions (ODTs) at 95 and 105 °C respectively. It's worth noting that all of the copolymers in this study are disordered (DIS) in the neat state, with the exceptions of SEO(6.4-7.3) and SEO(60-63), which are lamellar. Several studies on ion-containing block copolymers have shown that the addition of salt induces changes in the phase behavior and domain spacing due to an increase in the effective interaction parameter, χ_{eff} , between the two blocks.^{25, 27, 71, 72} If we were to decrease M_{SEO} further, the copolymers would either not order at the salt concentration of interest or exhibit ODTs at unacceptably low temperatures. We have thus reached the lower limit of M_{SEO} for the purposes of studying the effect of molecular weight on conductivity for nanostructured symmetric SEO electrolytes.

The shift of the primary scattering peak to lower q values in Figure 5-1a indicates that the domain spacing, d , increases with M_{SEO} . The scaling of d with M_{SEO} for all small molecular weight copolymers at $r = 0.085$ is shown in Figure 5-1b. The curve through the data represents a least-squares power law fit assuming that $d \sim M_{\text{SEO}}^{\nu}$, where the experimental value of ν is 0.65 ± 0.06 .

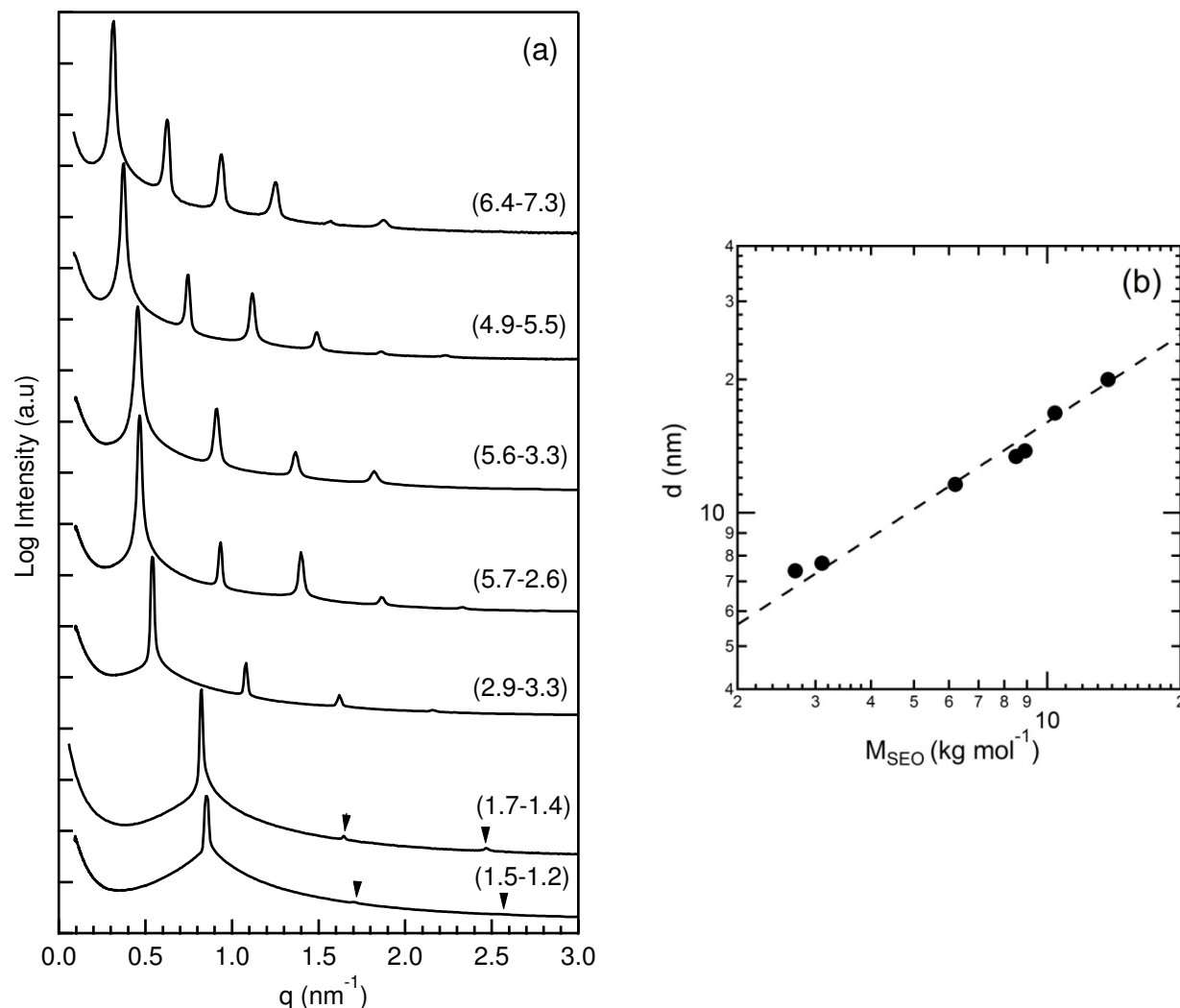


Figure 5-1 SAXS profiles and domain spacing of SEO/LiTFSI electrolytes.

(a) SAXS intensity versus scattering vector, q , and (b) domain spacing, d , versus total molecular weight, M_{SEO} , at 90 °C of all small molecular weight copolymer electrolytes, $r = 0.085$, used in this study. The intensity of the profiles in the dashed box in (a) have been magnified to make the higher order peaks more visible. The dotted line represents a power law fitting through the data where $d = 3.6M^{0.65}$

For microphase separated block copolymers, a glass transition temperature for each of the constituent blocks is expected. DSC measurements of all the electrolytes showed a glass transition temperature corresponding to the PS block, T_g^{PS} , and another at a lower temperature corresponding to the PEO block, T_g^{PEO} . DSC measurements also confirmed that all small molecular weight electrolytes used in this study are amorphous at all temperatures. SEO SEO(60-63) at $r = 0.085$ shows a melting peak of the PEO block at 42.3 °C. Figure 5-2 shows T_g^{PS} and T_g^{PEO} of the electrolytes as a function of M_{PS} and M_{PEO} respectively. Figure 5-2a shows that T_g^{PS} is strongly dependent on the length of the PS block. Also shown in Figure 5-2a is the T_g of PS homopolymer as a function of molecular weight, taken from the literature.² Close examination shows that the difference in T_g^{PS} between the block copolymer electrolyte and the neat PS homopolymer

decreases as the block length increases, shown in the inset. The difference has a maximum value of about 19 °C for one of the shortest chains and approaches zero at the high molecular weight limit. We attribute this to the broad interfacial zones between the microphases, where PEO and PS segments are mixed in the low molecular weight limit. We expect the interface to become sharper as molecular weight increases.^{73, 74} Our data is consistent with this expectation. Figure 5-2b shows the dependence of T_g^{PEO} in the electrolyte on M_{PEO} . Also shown in Figure 5-2b is the dependence of T_g^{PEO} on molecular weight of neat homopolymers.⁴ There is a dramatic difference between the homopolymer and block copolymer electrolyte data shown in Figure 5-2b. The T_g^{PEO} of the block copolymer electrolytes is nearly independent of block length, not changing by more than 5 °C over the molecular weight range studied. A large change in T_g is expected over this range of molecular weights for neat homopolymer PEO (-40 to -15 °C). The values of T_g^{PEO} of the copolymer electrolyte agree with homopolymer PEO with an equivalent concentration of the same salt, shown by an open square in Figure 5-2b.⁵ It is obvious that the presence of LiTFSI in the PEO affects the very nature of the glass transition.

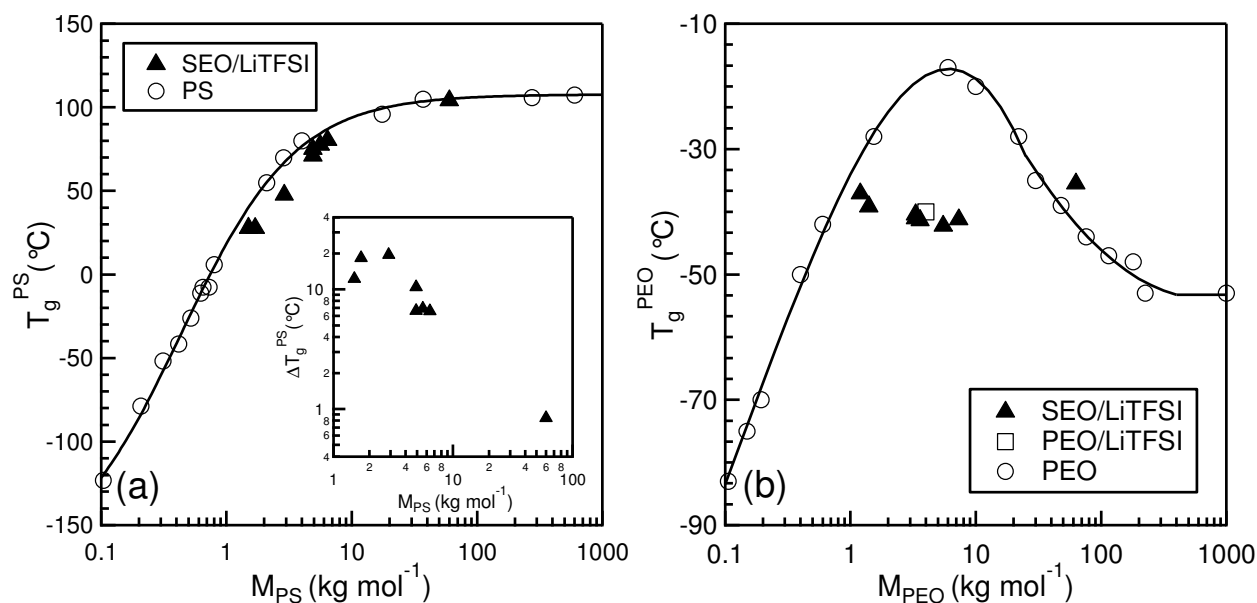


Figure 5-2 Glass transition temperatures of SEO/LiTFSI electrolytes. (a) Glass transition temperature of the PS block, T_g^{PS} , versus M_{PS} and (b) glass transition temperature of the PEO block, T_g^{PEO} versus M_{PEO} for the SEO/LiTFSI copolymer electrolytes. Open circles denote the T_g of the neat PS and PEO homopolymers taken from references ² and ⁴ respectively. Inset in (a) shows the difference in T_g^{PS} between the copolymer electrolyte and neat homopolymer, ΔT_g^{PS} . Open square in (b) is T_g of a PEO/LiTFSI mixture taken from reference ⁵. Solid curves are meant to guide the eye.

5.3 Conductivity

For the purposes of this study, it is useful to define a normalized conductivity, σ_n , as

$$\sigma_n(T) = \frac{\sigma_{SEO}(T)}{f \phi_{EO/salt} \sigma_{EO}(T)} \quad (5-1)$$

where σ_{EO} corresponds to the conductivity of homopolymer PEO at the same salt concentration and molecular weight and f is a morphology factor that accounts for constraints imposed by the geometry of the conducting phase. In previous work, we have argued that f should have a value of $2/3$ for randomly oriented lamellar grains. Figure 5-3 shows a schematic clarifying the origins of the morphology factor values for different morphologies. At such low molecular weights, ion transport from both vehicular and segmental motion of the polymer chains is expected in homopolymer PEO. However polymer chains in ordered block copolymers are trapped within microphases, and therefore unable to exhibit the vehicular contribution to conductivity. Thus we have used only the segmental motion contribution of the PEO conductivity i.e. σ_{EO} in Equation (5-1) is the conductivity of PEO in the high molecular weight limit. Normalized conductivity provides a metric to compare the observed conductivity with the idealized case: if the conducting phase of the block copolymer electrolyte behaved exactly like its homopolymer electrolyte counterpart, it would result in a normalized conductivity of unity. Normalizing also accounts for the fact that $\phi_{EO/salt}$ is not identical in all samples (see Table 5-1).

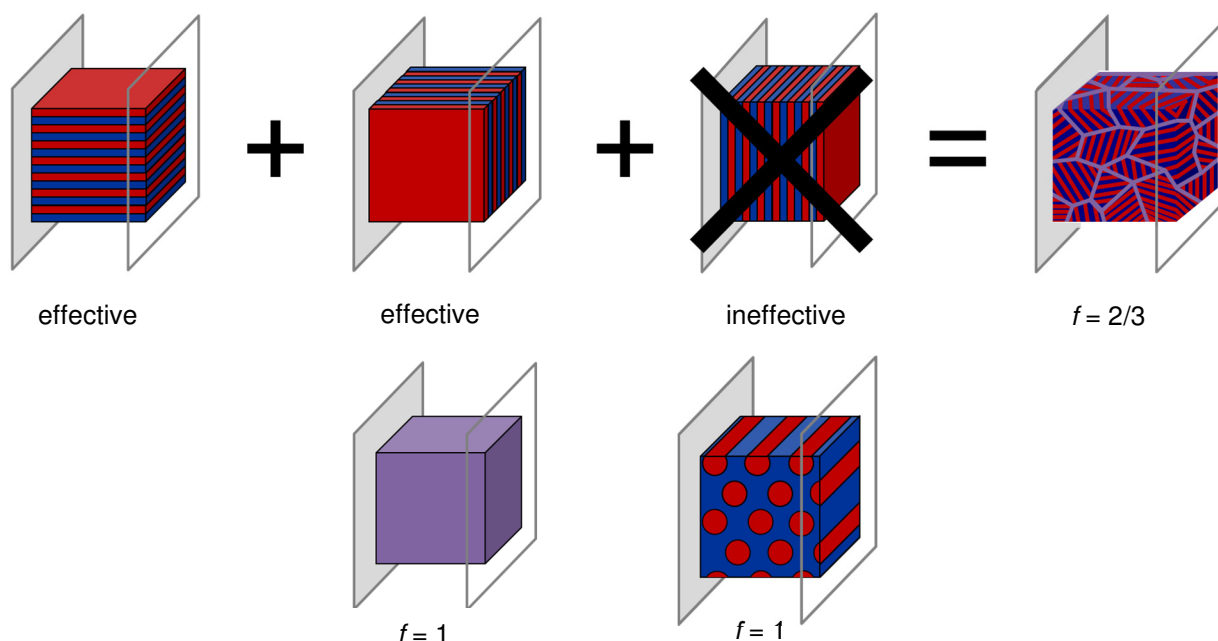


Figure 5-3 Morphology factor schematic.

Figure 5-4a shows σ_n of the electrolytes during cooling at 90 °C as a function of M_{SEO} . The normalized conductivity shows a maximum at lowest molecular weight and decreases monotonically until $M_{SEO} \sim 10 \text{ kg mol}^{-1}$ before rebounding sharply. Figure 5-4b shows the same

data plotted alongside results from ref. 3, providing a wider context. The non-monotonic dependence of σ_n on M_{SEO} suggests that conductivity is affected by two opposing effects: 1) the glass transition temperature of the insulating PS block and 2) the width of the conducting PEO channel.

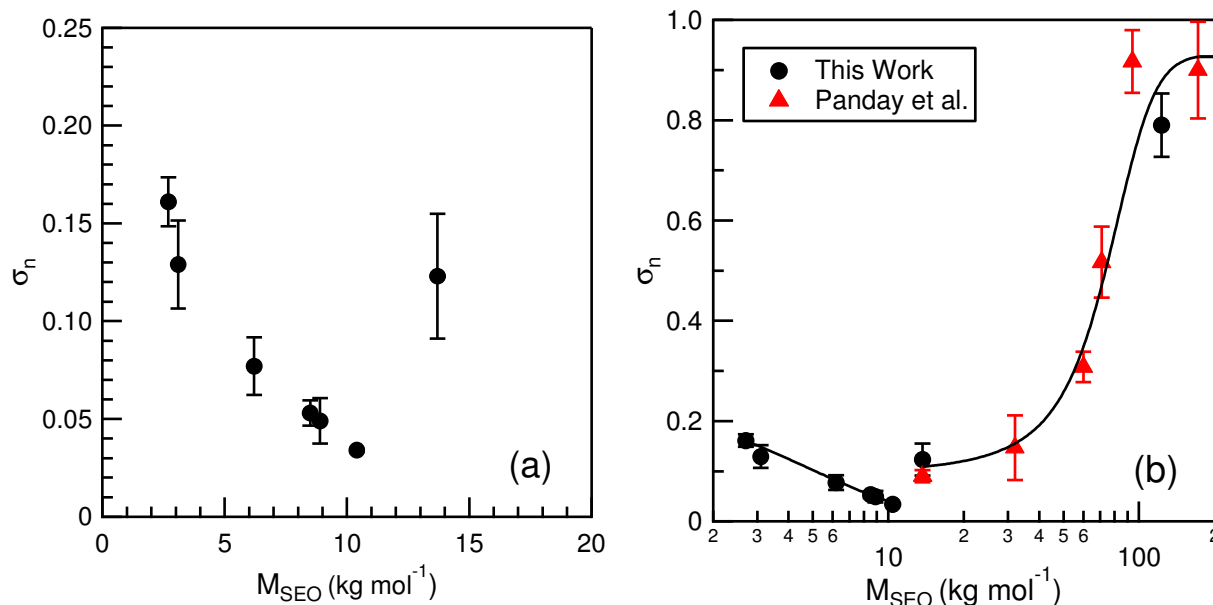


Figure 5-4 Normalized conductivity of SEO/LiTFSI electrolytes.

Normalized conductivity, σ_n , versus total molecular weight, M_{SEO} at 90 °C of (a) the small molecular weight copolymers used in this study and (b) the copolymers used in this study as well as those from Panday et al.³ The solid curves are meant to guide the eye.

Many studies have shown that conductivity of electrolytes is affected by the glass transition temperature of the conducting phase.^{75, 76} The glass transition temperature of the conducting phase in our electrolytes is unaffected by changes in M_{SEO} (see Figure 5-2b). We are proposing that the conductivity of block copolymer electrolytes in the low molecular weight regime is in fact affected by T_g^{PS} , the glass transition temperature of the non-conducting block. The T_g^{PS} in our electrolytes increases substantially with increasing chain length (Figure 5-2a); this is expected to change the dynamics of the PEO segments in the vicinity of the PS-PEO interface. Therefore, as the molecular weight of the copolymers increases and thus T_g^{PS} increases, the retardation of PEO chain dynamics is intensified, contributing to a decrease in σ_n . It is worth noting that the σ_n values in Figure 5-4a are far below unity, indicating that the PEO channels in the block copolymer are much less effective at transporting ions compared to bulk PEO.

Previous work on this system has suggested that the increase in σ_n with increasing molecular weight is related to the increase in the channel width of the conducting PEO block.³ As the channel width increases, the interfacial area per unit volume decreases and a smaller fraction of PEO segments reside in the PS-PEO interface, where segmental motion is significantly hindered. At sufficient distance from the interface, the PEO segments behave more like homopolymer PEO. Based solely on this hypothesis, a monotonic increase in normalized conductivity would be expected as molecular weight increases.

Let us assume that the interfacial region in which the PEO has reduced mobility as a result of its proximity to the glassy PS block has a fixed width, α . In this case, when $2\alpha > d\phi_{\text{EO/salt}}$, all PEO

segments are affected by the glassy PS segments. Therefore, there is a threshold channel width, below which we assume that the entire channel is comprised of interfacial region. However when $2\alpha < d\phi_{\text{EO/salt}}$, a sudden increase in conductivity would be expected due to the presence of unconstrained PEO segments in the middle of the channel. Such a sudden increase is observed in the σ_n versus M_{SEO} data shown in Figure 5-4 between M_{SEO} of 10.4 and 13.7 kg mol⁻¹. Using d values reported in Table 5-1 for these polymers, we estimate that $4.8 < \alpha < 5.7$ nm. Our assumption of a fixed α may be considered a first approximation – in reality, the interfacial width will decrease with increasing M_{SEO} .⁷⁷

We note in passing that in their classic study of block copolymer electrolytes, Soo et al. proposed that the conductivity in the strong segregation limit was affected by the glass transition temperature of the non-conducting block.⁷⁸ To the contrary, our data indicate that the glass transition temperature of the non-conducting block is only important in the weak segregation limit.

5.3.1 Annealing Effects

Figure 5-5a shows the conductivity, σ , of SEO(4.9-3.6) at $r = 0.085$ versus inverse temperature during the initial heating and cooling scan. The dotted vertical line indicates the T_g^{PS} of the sample and the solid curve represents a fit of the cooling data to the Vogel-Tamman-Fulcher (VTF) relation.¹² The VTF relation is an empirical expression commonly used to describe the temperature-dependence of conductivity in polymer electrolytes and takes the form

$$\sigma_{\text{VTF}}(T) = AT^{-1/2} \exp\left(\frac{-E_a}{R(T - T_0)}\right) \quad (5-2)$$

where σ_{VTF} is the fitted ionic conductivity, A and E_a are fitting parameters, R is the universal gas constant, and T_0 is a reference temperature typically associated with the glass transition temperature of the conducting polymer. In this work, we fix $T_0 = T_g^{\text{PEO}} - 50$ K where T_g^{PEO} is the glass transition temperature of the PEO block of the respective electrolyte.

As the sample is initially heated, the conductivity increases steeply until it reaches the T_g^{PS} , at which point the slope of the conductivity versus inverse temperature decreases significantly before resuming at a more moderate slope. Upon cooling, the conductivity decreases smoothly with temperature. After the initial heating and cooling run, conductivity from subsequent temperature scans superimposes perfectly upon the cooling run. Figure 5-5b shows the same data as Figure 5-5a, but with the normalized conductivity, σ_n , as the ordinate. The heating scan data is characterized by a sharp maximum at $T = T_g^{\text{PS}}$. In contrast, normalized conductivity upon cooling is a weak function of inverse temperature. Figure 5-5 shows that the sample undergoes an annealing process during the initial heating run that is strongly dependent on T_g^{PS} , and that the freeze-dried state is more conductive than the annealed state. No abrupt changes in σ are evident at T_g^{PS} for any of the annealed samples (e.g. Figure 5-5a).

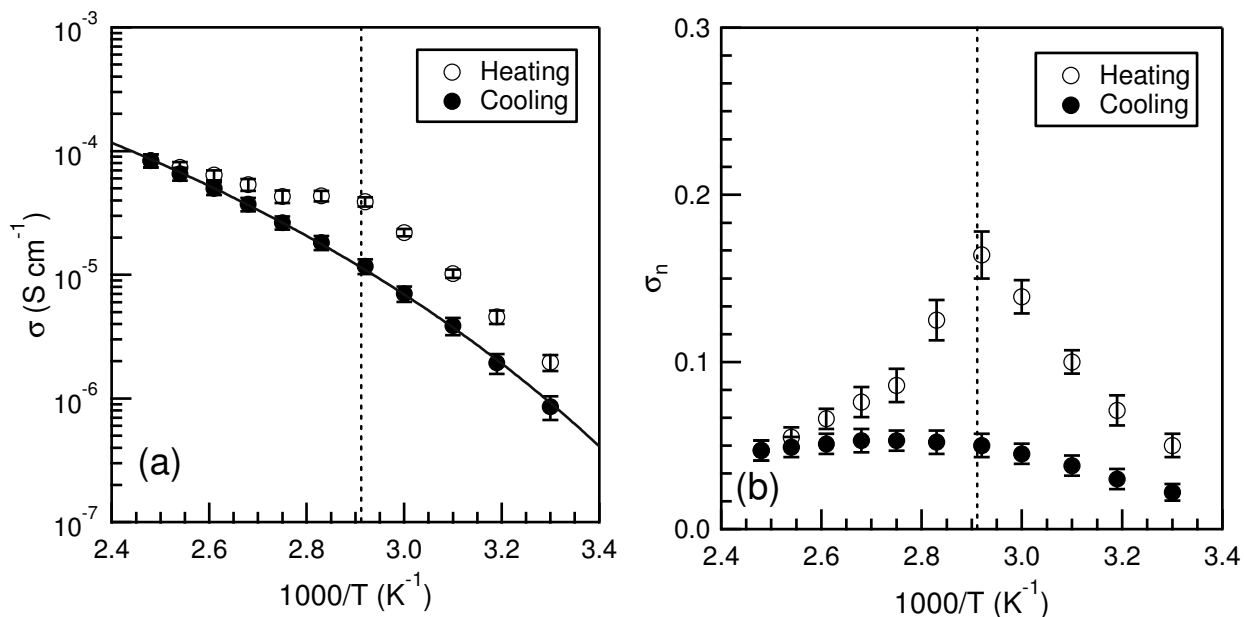


Figure 5-5 Conductivity of SEO(4.9-3.6) at $r = 0.085$.

(a) Conductivity, σ , and (b) normalized conductivity, σ_n , versus inverse temperature for SEO(4.9-3.6) at $r = 0.085$. The solid curve indicates the VTF fitting to the cooling data and the dotted vertical lines denote the glass transition temperature of the PS block, T_g^{PS} .

Figure 5-6a shows the conductivity of SEO(1.5-1.2) with $r = 0.085$ versus inverse temperature during the initial heating and cooling scan. The dotted vertical line indicates the T_g^{PS} of the sample and the solid vertical line indicates the order-disorder temperature, T_{ODT} , of the sample. The solid curve represents a fit of the cooling data to the VTF relation at $T < T_{\text{ODT}}$. As the sample is initially heated, the conductivity increases steadily until it reaches the T_{ODT} , at which point the conductivity exhibits a step change increase while maintaining a similar slope. Upon cooling, the conductivity is superimposed on the heating run at temperatures above the T_{ODT} , at which point there is a smaller step change in conductivity and a smooth decrease parallel to the heating data. This sample shows the opposite trend of that seen in Figure 5-5, since the conductivity during heating is actually lower than the conductivity during cooling, meaning the as-prepared freeze-dried state is less conductive than the annealed state for this molecular weight. Figure 5-6b shows the temperature dependent normalized conductivity, σ_n , of the same sample. We use Equation (5-1) to calculate σ_n as discussed above at $T < T_{\text{ODT}}$, i.e. when the sample is ordered. At $T > T_{\text{ODT}}$, the sample is disordered and we assume that $f = 1$ and σ_{EO} is a function of M_{SEO} and T , as described in ref. 79. Below the T_{ODT} , the slopes of σ_n versus inverse temperature obtained during heating and cooling runs differ substantially. Above the T_{ODT} , the normalized conductivities obtained during heating and cooling converge and σ_n is independent of temperature, consistent with previous work from our group.⁷⁹

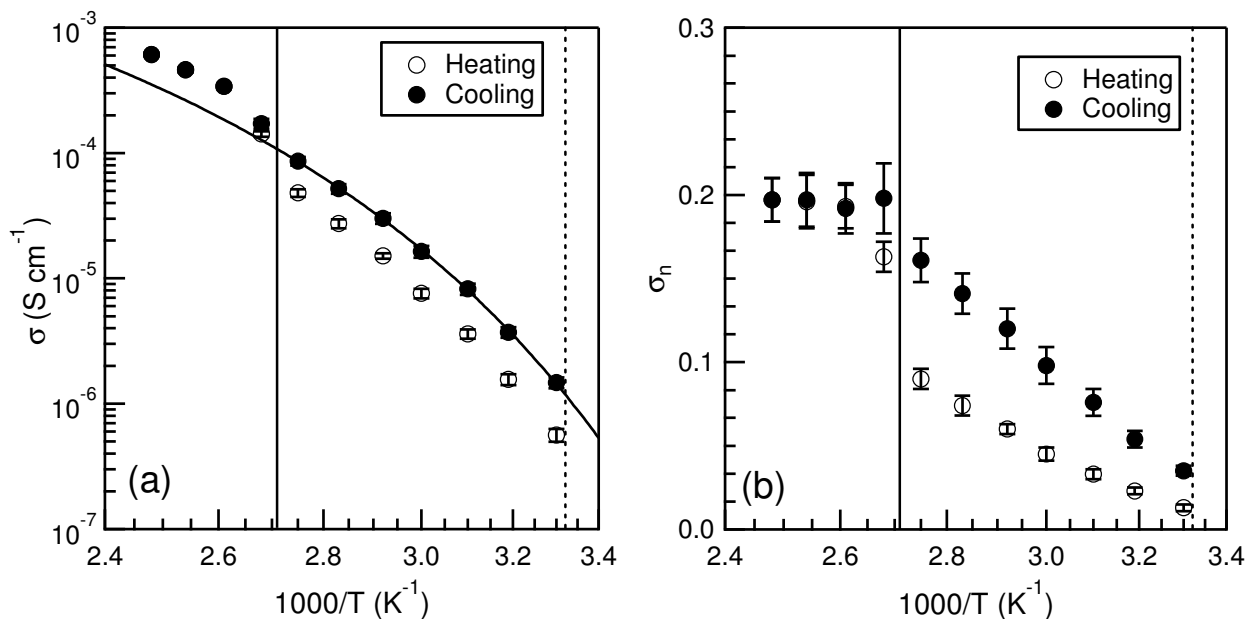


Figure 5-6 Conductivity of SEO(1.5-1.2) at $r = 0.085$.

(a) Conductivity, σ , and (b) normalized conductivity, σ_n , versus inverse temperature for SEO(1.5-1.2) at $r = 0.085$. The solid vertical lines denote the order-to-disorder transition temperature, T_{ODT} , and the dotted vertical lines denote the glass transition temperature of the PS block, T_g^{PS} . The solid curve indicates the VTF fitting to the cooling data

In Figure 5-7 we plot the ratio of the conductivity during cooling to the conductivity during the first heating run, σ_C/σ_H at T_g^{PS} versus M_{SEO} . It is clear that this ratio decreases as a function of M_{SEO} . At the lowest molecular weights, the conductivity increases during annealing, indicated by ratio values greater than unity. As M_{SEO} increases beyond $4\ kg\ mol^{-1}$, σ_C/σ_H drops below unity and continues to decrease, reaching about 0.2 when M_{SEO} is between 8.5 and $13.7\ kg\ mol^{-1}$. In other words, the conductivity of electrolytes in this molecular weight range decreases by 80% upon annealing from the freeze-dried state.

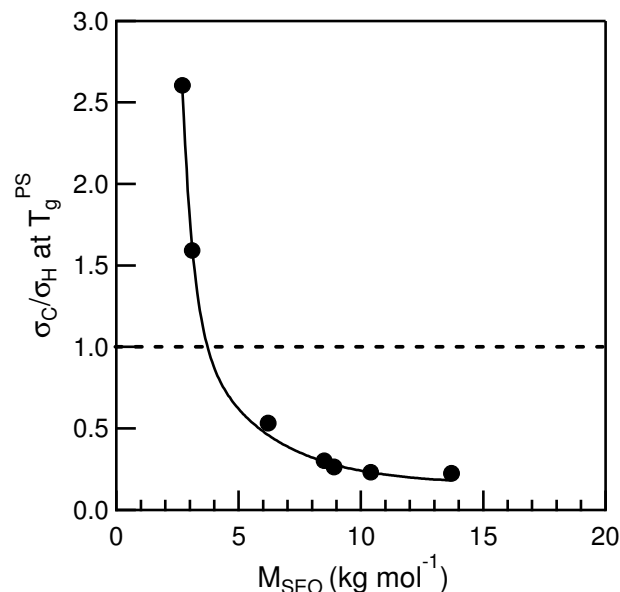


Figure 5-7 Effects of annealing on conductivity as function of molecular weight.

The ratio of the conductivity during cooling to the conductivity during initial heating, σ_C/σ_H , at the glass transition temperature of the PS block, T_g^{PS} , versus the molecular weight of the copolymer, M_{SEO} . The solid curve is meant to guide the eye.

All of the observations in Figure 5-5, Figure 5-6, and Figure 5-7 indicate that samples with poorly ordered domains are more conductive than annealed, highly ordered samples with large grains. This effect is manifested differently in electrolytes with T_g^{PS} above and below room temperature.

For samples with T_g^{PS} greater than room temperature, the chains are frozen in the freeze-dried morphology until they reach the T_g^{PS} , at which point the chains are able to rearrange, resulting in a lamellar structure with long range order. This process can be followed in SAXS experiments. In Figure 5-8a, we show SAXS profiles of SEO(4.9-5.5) with $r = 0.085$, which has a T_g^{PS} of 75 °C, in both freeze-dried and annealed states. The freeze-dried sample at 30 °C exhibits a broad primary scattering peak and hints of higher order scattering peaks at $q/q^* = 2$ and 3. At 130 °C, the sample is fully annealed and well-ordered, as indicated by the sharp primary scattering peak and well-defined higher order peaks at $q/q^* = 2, 3, 4$ and 5. Cooling the sample back to 30 °C does not affect the long range order. This trend can be more clearly followed in Figure 5-8b, where the full width at half maximum of the primary scattering peak is plotted versus inverse temperature for both the initial heating and cooling run. It appears that the irreversible 80% decrease in conductivity seen in Figure 5-7 is due to the irreversible increase in long range order seen in Figure 5-8.

For samples with T_g^{PS} lower than room temperature, the chains are mobile after 'freeze-drying'. SEO(1.5-1.2) and SEO(1.7-1.4) both have a T_g^{PS} value 27.8 °C, and thus the samples have already 'annealed' at room temperature for the lifetime of the sample (on the order of weeks) before the conductivity measurements were started. SAXS measurements on SEO(1.5-1.2) and SEO(1.7-1.4) prior to heating show the presence of a well-ordered lamellar phase (not shown for brevity). We attribute the relatively low values of σ_H for these samples shown in Figure 5-6 and Figure 5-7

to the presence of large, well-ordered grains. When these samples are heated above the T_{ODT} , they become homogeneous and their grain structure disappears, resulting in a collapse of the heating and cooling conductivity data (Figure 5-6). When the samples are cooled below T_{ODT} , the sample reorders and new grains are formed. The new grains formed during the cooling run are likely to be smaller than those present during the heating run. The differences between conductivities measured during the heating and cooling runs in Figure 5-6 is thus attributed to a difference in average grain size. The fact that smaller grains and poorly ordered structures exhibit higher conductivity suggests that either defects formed in well-annealed block copolymers impede ion transport or that ion transport through grain boundaries is more rapid than through the ordered PEO channels.

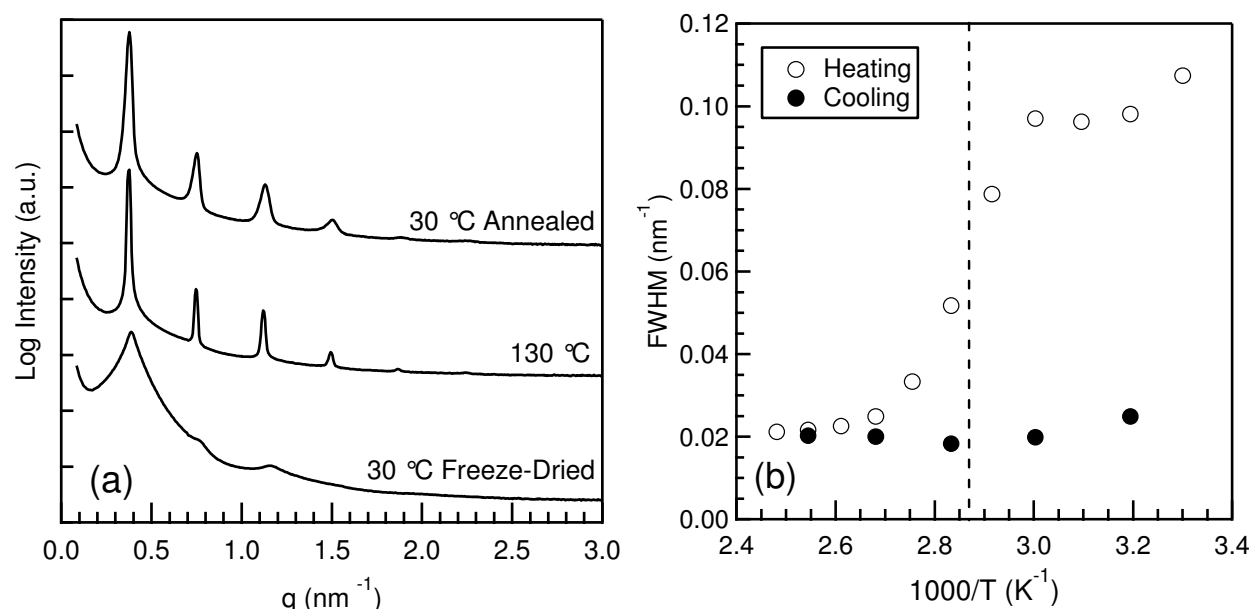


Figure 5-8 Morphological evolution of SEO(4.9-5.5) at $r = 0.085$ during annealing. (a) SAXS intensity versus scattering vector, q , and (b) FWHM of the primary scattering peak versus inverse temperature for SEO(4.9-5.5) at $r = 0.085$. The dotted vertical lines denote the glass transition temperature of the PS block, T_g^{PS} .

5.3.4 VTF Fitting Parameters

The fitting parameters obtained from the VTF relation can provide insight into the difference in conduction mechanisms between samples. One may view the VTF relation (Equation (5-1)) as a description of transport in glassy systems with activation barriers. The pre-factor A is proportional to the 'attempt frequency', i.e. the average number of times the species of interest attempts to cross the barrier, while the parameter E_a is a measure of the barrier energy. The glassy nature of the system is accounted for by T_0 , which in this work is fixed at $T_0 = T_g^{PEO} - 50$ K. In polymer electrolytes, it is often assumed that A is proportional to the concentration of dissociated ions because the attempt frequency must be proportional to this value. However, other parameters such as the intrinsic mobility of the medium can also play a role.

Figure 5-9a shows the VTF fitting parameter, A , as a function of M_{SEO} . The plot shows a cusp with a minimum at 10 kg mol⁻¹. The minimum in σ_h seen in Figure 5-4 occurs at the same value

of M_{SEO} . One might expect the ion concentration to remain constant, since the molar concentration of lithium ions in the PEO block is constant for all samples. However, if the contact between the ions and PS monomers decreases, then one might expect an increase in the concentration of dissociated ions. We attribute the increase in A when M_{SEO} is greater than 10 kg mol^{-1} to this effect. It is obvious from Figure 5-9a that A is influenced by at least one more effect. We propose that the decrease in A seen when M_{SEO} is less than 10 kg mol^{-1} is due to the decreasing mobility of the polymer matrix. This decrease in mobility can be attributed to increasing polymer molecular weight and decreasing concentration of more mobile chain ends. Figure 5-9b shows a plot of the activation energy, E_a , versus T_g^{PS} . To a good approximation, E_a is a linearly decreasing function of T_g^{PS} . The decrease in the activation energy with increasing T_g^{PS} is significant and consistent with the arguments presented above. Low values of T_g^{PS} are obtained in low molecular weight SEO samples where there is more contact between the ions and the polystyrene segments. As M_{SEO} increases, microphase separation leads to increasingly pure PEO phases and this reduces the activation barrier. The data in Figure 5-9a and Figure 5-9b suggest that the non-monotonic trends in σ_n versus M_{SEO} seen in Figure 5-4 arise from changes in attempt frequency, A , and not activation energy, E_a . The discussion in this paragraph is an attempt to explain the non-intuitive variation of A and E_a presented in Figure 5-9. At this point A and E_a are simply fitting parameters and independent experiments are needed to either verify or refute the explanations provided here.

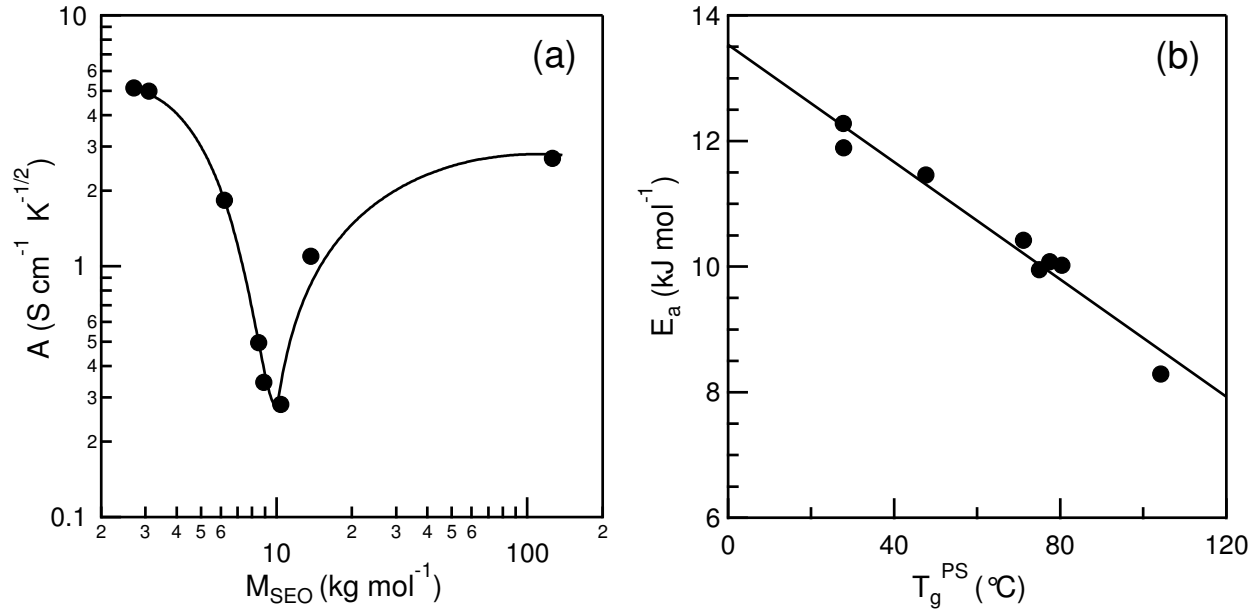


Figure 5-9 VTF fitting parameters of SEO/LiTFSI electrolytes.

(a) 'attempt frequency', A , versus total copolymer molecular weight, M_{SEO} , and (b) the barrier energy, E_a , versus the glass transition temperature of the PS block, T_g^{PS} , in the copolymer electrolyte. The solid curves are meant to guide the eye.

5.4 Conclusion

We have completed a thorough investigation of the effect of molecular weight on the conductivity of symmetric block copolymer electrolytes. In the low molecular weight limit, $M_{\text{SEO}} < 10 \text{ kg mol}^{-1}$, the normalized conductivity is a weakly decreasing linear function of M_{SEO} (Figure

5-4). When M_{SEO} exceeds 10 kg mol^{-1} , σ_h increases sharply and exhibits a sigmoidal dependence on M_{SEO} .^{3, 8} The dependence of σ_h on M_{SEO} appears to be discontinuous at 10 kg mol^{-1} . The non-monotonic dependence of σ_h on M_{SEO} indicates that the ionic conductivity of the nanostructured electrolytes is affected by (at least) two opposing factors: 1) the glass transition temperature of the insulating PS block, T_g^{PS} , and 2) the width of the conducting PEO channel.

In the low molecular weight limit, all ions are in contact with both PEO and PS segments, resulting in a dependence of σ_h on T_g^{PS} . The intermixing between PS and PEO segments is restricted to an interfacial zone of width α . Our experiments suggest that α is about 5 nm. At values of $M_{\text{SEO}} > 10 \text{ kg mol}^{-1}$, the width of the conducting channels exceeds 2α , resulting in the presence of PEO segments in the middle of the channel that are free of PS. Further increase in M_{SEO} results in a greater fraction of 'pure' PEO segments in the conducting channels. In the high molecular weight limit, fraction of ions affected by the interfacial zone is negligible.

The thermal history and T_g^{PS} were found to play an important role in the conductivity of the sample. In general, a poorly ordered morphology and small grains resulted in higher conductivity. At $T > T_g^{\text{PS}}$, the chains in the sample are able to anneal into a better-ordered structure with larger grains, resulting in a drop in normalized conductivity.

Chapter 6 - Conductivity through the Order-Disorder Transition⁴

ABSTRACT

The ionic conductivity of a block copolymer electrolyte was measured in an *in-situ* small angle X-ray scattering experiment as it transitioned from an ordered lamellar structure to a disordered phase. The ionic conductivity increases discontinuously as the electrolyte transitions from order to disorder. A simple framework for quantifying the magnitude of the discontinuity is presented. This study lays the ground work for understanding the effect of more complex phase transitions such as order-order transitions on ion transport.

Polymer electrolytes have the potential to serve as non-flammable alternatives to traditional organic electrolytes in rechargeable lithium batteries.^{10, 12, 69} Nanostructured block copolymer electrolytes with both ionically conducting and hard insulating blocks offer the opportunity of independent control over modulus and ion transport.⁸ At sufficiently high temperatures, the net repulsion between the two blocks driving nanostructure formation is overcome by entropic contributions, resulting in a homogeneous sample. The effect of concentration of diluents such as solvents⁸⁰ and salts²⁶ on the temperature at which this order-to-disorder transition occurs, T_{ODT} , provides fundamental insight into the nature of interactions between chemically distinct polymer chains and the diluents. The purpose of this paper is to report on changes in transport of ions through block copolymer electrolytes at the order-to-disorder transition (ODT). Of particular interest is the fact that we observe a discontinuous change in conductivity at the ODT, in contrast to all previous studies wherein continuous changes in conductivity are reported at the ODT.^{71, 72, 81} The magnitude of the measured discontinuity is consistent with the predictions of a simple model. These results provide insight into continuity of phases in the vicinity of the ODT.

Conductivity changes across the ODT of block copolymers have been reported in refs. 81, 71, and 72. Majewski et al.⁸¹ found a plateau in conductivity in the temperatures surrounding the ODT in a poly(ethylene oxide-*b*-6-(4'-cyanobiphenyl-4-yloxy)hexyl methacrylate) block copolymer with lithium perchlorate (LiClO_4) salt. In contrast, Wanakule et al.⁷¹ and Ruzette et al.⁷² reported no discontinuity in conductivity through the ODT in polystyrene-*b*-poly(ethylene oxide) (SEO)/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and poly(methyl methacrylate)-

⁴Adapted with permission from Teran, Alexander A., Scott A. Mullin, Daniel T. Hallinan Jr., and Nitash P. Balsara. 2012. "Discontinuous Changes in Ionic Conductivity of a Block Copolymer Electrolyte through an Order-Disorder Transition." *ACS Macro Letters*, 1 (2), pp 305–309 doi: 10.1021/mz200183t. Copyright 2012 American Chemical Society

block-poly(oligo oxyethylene methacrylate)/lithium trifluoromethanesulfonate (LiCF₃SO₃) mixtures.

6.1 Lamellar to Disorder Transition

SEO block copolymers and SEO/LiTFSI mixtures were synthesized, purified, prepared, and characterized as described in Chapter 2. This study was conducted on a mixture of SEO(1.7-1.4) and LiTFSI with a salt concentration of $r = 0.085$. Conductivity samples were prepared as described in Chapter 2 and were loaded into a custom heating stage for simultaneous electrochemical and X-ray scattering experiments. Conductivity reported was measured during the second heating run, and the sample was allowed to equilibrate for 10 min at each temperature. A schematic of the *in-situ* small angle X-ray scattering (SAXS) experiment is presented in Figure 6-1.

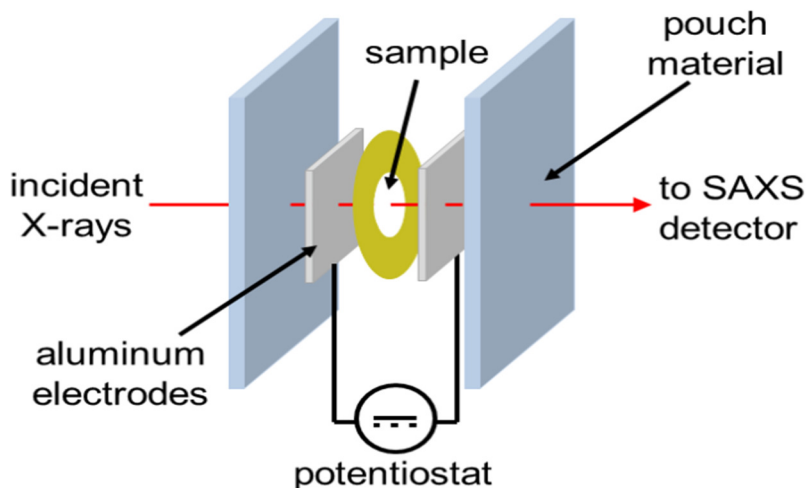


Figure 6-1 Schematic of the *in-situ* SAXS and conductivity experiment.

Symmetric Al/block copolymer electrolyte/Al cells are sealed inside a pouch and connected to an external potentiostat for ac impedance spectroscopy. Incident X-rays pass through the entire cell assembly. Electrode thickness is 17 μm and pouch material (Showa Denko) is aluminum laminated with nylon and polypropylene.

Figure 6-2 shows the results of the simultaneous SAXS and ionic conductivity experiments. Figure 6-2a shows the SAXS profiles of the sample at selected temperatures. At 100 $^{\circ}\text{C}$, the sample exhibits a lamellar morphology with a sharp primary scattering peak at $q^* = 0.825 \text{ nm}^{-1}$. We attribute the lack of higher order peaks in Figure 6-2a to a loss of resolution due to the additional necessary layers of material through which the beam must pass for the *in-situ* experiment. The appearance of an additional broad peak at $q = 0.3 \text{ nm}^{-1}$ is due to scattering from the inert polymer coating on the pouch material. It is clear from Figure 6-2a that the sample undergoes an order-to-disorder transition as temperature is increased, indicated by the sudden broadening of the scattering peak in the vicinity of 118 $^{\circ}\text{C}$. Figure 6-2b shows the full width half maximum (FWHM) of the primary scattering peak as a function of temperature. The abrupt increase in the FWHM indicates the order-disorder temperature (T_{ODT}). The sample is fully ordered at 111 $^{\circ}\text{C}$ and fully disordered at 118 $^{\circ}\text{C}$ (Figure 6-2a). The SAXS profile at 114 $^{\circ}\text{C}$ is a superposition of sharp and broad peaks indicating the coexistence of ordered and disordered phases. This coexistence is required by the Gibbs phase rule. We thus report the T_{ODT} of our

sample to be is 114 ± 4 °C, marked by the gray bar in Figure 6-2b. The domain spacing remains unchanged over the entire temperature range at 7.7 nm. The right axis of Figure 6-2b shows the ionic conductivity of the sample obtained concurrently with the SAXS profiles. Conductivity is a sensitive function of temperature in polymer electrolytes and it is necessary to differentiate expected temperature dependent changes in conductivity from those arising from changes in the morphology of the polymer. The solid black line in Figure 6-2b shows the fit of the conductivity to the Vogel-Tamman-Fulcher (VTF) relation¹² through the conductivity data in the $T < T_{\text{ODT}}$ regime. The VTF relation is an empirical expression often used to describe the temperature-dependence of conductivity data in amorphous solid polymer electrolytes:

$$\sigma_{\text{VTF}}(T) = AT^{-1/2} \exp\left(\frac{-E_a}{R(T - T_0)}\right) \quad (6-1)$$

In this expression, σ_{VTF} is the fitted ionic conductivity, A is the constant proportional to the number of charge carriers, E_a is the apparent activation energy for ion motion, and T_0 is a reference temperature typically associated with the glass transition temperature of the polymer. The curve in Figure 6-2b corresponds to $A = 39.4 \text{ S cm}^{-1} \text{ K}^{-1/2}$, $E_a = 1.99 \times 10^3 \text{ kJ mol}^{-1}$, and $T_0 = 165 \text{ K}$. At $T = T_{\text{ODT}}$, the conductivity exhibits a marked discontinuity, a fundamentally different result from all previous studies of conductivity in the vicinity of the ODT.^{71, 72, 81}

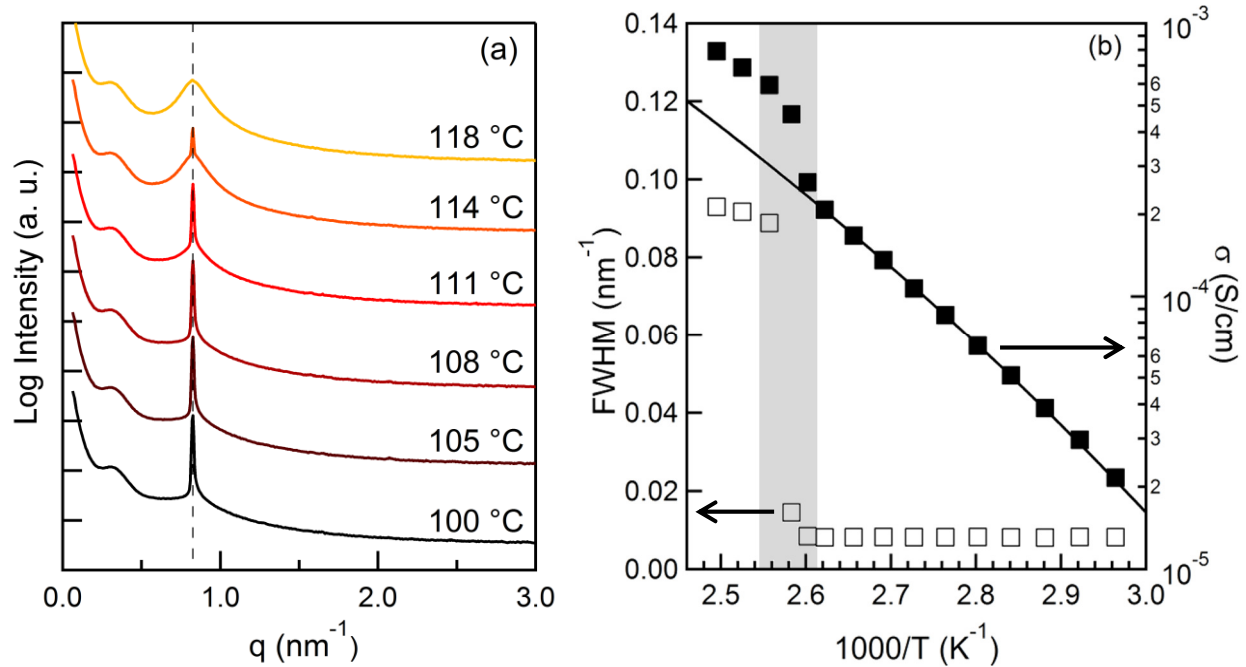


Figure 6-2 In-situ SAXS and conductivity of SEO(1.7-1.4)/LiTFSI at $r = 0.085$.

(a) SAXS intensity versus scattering vector, q , for SEO(1.7-1.4)/LiTFSI at $r = 0.085$ in an *in-situ* pouch cell at select temperatures. The dotted vertical line emphasizes the invariance of the domain spacing with temperature. (b) Left axis (empty squares) shows the full-width half-maximum of the primary scattering peak versus inverse temperature. Right axis (full squares) shows ionic conductivity versus inverse temperature. The gray bar indicates the order-disorder transition temperature, T_{ODT} , and the solid line indicates the VTF fit to conductivity data below the T_{ODT} .

The fitted curve in Figure 6-2b represents the expected increase in conductivity with increasing temperature in the absence of a phase transition. The positive difference between the disordered

phase conductivity data in Figure 6-2b and the fitted curve indicates that the transformation from an ordered lamellar phase to a disordered morphology leads to an *increase* in conductivity. This result may at first seem counterintuitive, since well-defined ion-transporting channels disappear above T_{ODT} . In order to focus on the effect of the ODT on conductivity, the temperature dependence of the measured conductivity normalized by the VTF fit, σ/σ_{VTF} , is plotted in Figure 6-3. The error bars in Figure 6-3 reflect the standard deviation of σ/σ_{VTF} obtained from five independent samples. The normalized conductivity at 114 °C is intermediate between the ordered and disordered values. Thus both the conductivity and SAXS indicate the existence of a region of co-existence (110 – 118 °C) between the ordered and disordered phases.

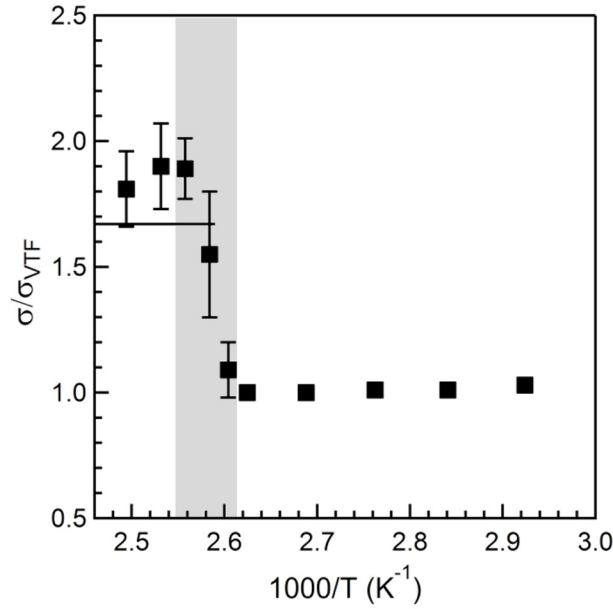


Figure 6-3 VTF-normalized conductivity of SEO(1.7-1.4)/LiTFSI at $r = 0.085$.

Ionic conductivity normalized by VTF fit versus inverse temperature. The gray bar denotes the ODT. The solid horizontal line denotes the expected increase in conductivity from changes in the morphology factor and chain diffusion.

An understanding of the effect of the ODT on conductivity begins with a simple expression for ionic conductivity in composite electrolytes, σ_{comp} :

$$\sigma_{comp}(T) = f \phi_{EO/salt} \sigma_{EO}(T) \quad (6-2)$$

where $\sigma_{EO}(T)$ is the intrinsic conductivity of the conducting phase (the only term that is a strong function of temperature), $\phi_{EO/salt}$ is the volume fraction of the conducting phase, and f is a morphology factor that accounts for constraints imposed by the geometry of the conducting phase. The volume fraction of the PEO/LiTFSI microphase in our sample was calculated to be $\phi_{EO/salt} = 0.50$ using Equation (2-3). In previous work we have argued that f should have a value of $2/3$ for randomly oriented lamellae, and $\sigma_{EO}(T)$ for our system is the conductivity of a mixture of homopolymer PEO and LiTFSI at the same value of salt concentration.⁸ In conventional electrolytes, the motion of ions is coupled to that of the solvation shells that surround the ions. In the case of polymer electrolytes, connectivity of the chains makes this mode of motion ineffective in the high molecular weight limit. It has thus been recognized that transport facilitated by rapid

segmental motion is essential for significant ionic conductivity in the high molecular weight limit.^{60, 82, 83} Shi and Vincent first proposed the following expression for the conductivity of homopolymer electrolytes:

$$\sigma_{EO}(T) = \sigma_0(T) + \frac{K(T)}{M} \quad (6-3)$$

where σ_0 is the ionic conductivity due to segmental motion of the polymer chains (obtained in the limit of infinite polymer molecular weight) and the K/M term accounts for so-called "vehicular" transport, i.e. transport of coupled polymer chains and ions.⁶¹ The temperature dependence of σ_0 and K for PEO/LiTFSI mixtures with $r = 0.085$ are given in ref. 84. We assume that vehicular motion is not possible in the ordered state because the polymer chains form a structure that is assumed to be static on the time scale of interest. Ionic conductivity of the ordered lamellar state is then given by

$$\sigma_{ord}(T) = \frac{2}{3} \phi_{EO/salt} \sigma_0(T) \quad (6-4)$$

The importance of concentration fluctuations in the disordered phase formed by low molecular weight block copolymers was recognized in the pioneering works of Leibler³⁰ and Fredrickson and Helfand.⁶ In ref. 6 it was shown that disordered phases of low molecular weight block copolymer melts are characterized by large amplitude concentration fluctuations. The geometric constraints of a lamellar phase are no longer present in the disordered phase and we thus expect $f = 1$. In addition, SEO molecules are no longer constrained to form a quasi-static ordered phase and thus both segmental motion and vehicular motion are expected to contribute to conductivity of the disordered phase. With these approximations, the conductivity of the disordered phase is given by

$$\sigma_{dis}(T) = \phi_{EO/salt} \left[\sigma_0(T) + \frac{K(T)}{M} \right] \quad (6-5)$$

and the ratio $\sigma_{dis}/\sigma_{ord}$ is given by

$$\frac{\sigma_{dis}}{\sigma_{ord}} = \frac{3}{2} \left[1 + \frac{K(T)}{\sigma_0(T)M} \right] \quad (6-6)$$

Using the total block copolymer molecular weight M of 3.1 kg/mol and values of $K = 1.4 \times 10^{-3} \text{ S kg mol}^{-1} \text{ cm}^{-1}$ and $\sigma_0 = 3.48 \times 10^{-3} \text{ S cm}^{-1}$ reported in ref. 84 at $T = T_{ODT} = 114^\circ \text{C}$, we obtain $\sigma_{dis}/\sigma_{ord} = 1.67$ due to both morphology factor and vehicular transport contributions. The horizontal line in Figure 6-3 in the $T > T_{ODT}$ regime shows this prediction. It is evident that the experimental data are in reasonable agreement with this prediction. If the two contributions were separated, $\sigma_{dis}/\sigma_{ord}$ would equal 1.50 due exclusively to the increase in morphology factor and only 1.11 due to the enabling of vehicular transport. It is thus clear that at this molecular weight, the largest increase is a result of the change in morphology factor.

A more stringent test of the proposed framework is conducted by computing a normalized conductivity, σ_n , defined as

$$\sigma_n(T) = \frac{\sigma(T)}{f\phi_{EO/salt}\sigma_{EO}(T)} \quad (6-7)$$

For $T < T_{ODT}$ we use $f = 2/3$, and $\sigma_c(T) = \sigma_0(T)$ [Equation (6-4)]. For $T > T_{ODT}$ we use $f = 1$, and $\sigma_c(T) = \sigma_0(T) + K(T)/M$ [Equation (6-5)]. Figure 6-4 shows the dependence of σ_n on temperature.

If our framework was exact and the conductive lamellae were equivalent to pure PEO homopolymer, then σ_n would be unity at all temperatures. Instead we find that the normalized conductivity increases monotonically with increasing temperature in the $T < T_{ODT}$ regime and is independent of temperature in the $T > T_{ODT}$ regime. The temperature dependence of σ_n below the ODT indicates that the activation energy for ion conduction in the ordered SEO block copolymer is different from that of PEO homopolymer. The temperature independence of σ_n above the ODT indicates that the activation energy for ion conduction in the disordered SEO block copolymer is identical to that of PEO homopolymer. The fact that σ_n is significantly less than unity in Figure 6-4 can be either due to the fact that the intrinsic conductivity of the PEO-rich microphase is affected by the presence of the PS phase or limitations of the proposed framework. In spite of these limitations, it is clear that the proposed framework provides a starting point for understanding the reason for conductivity changes across the order-disorder transition in block copolymer electrolytes.

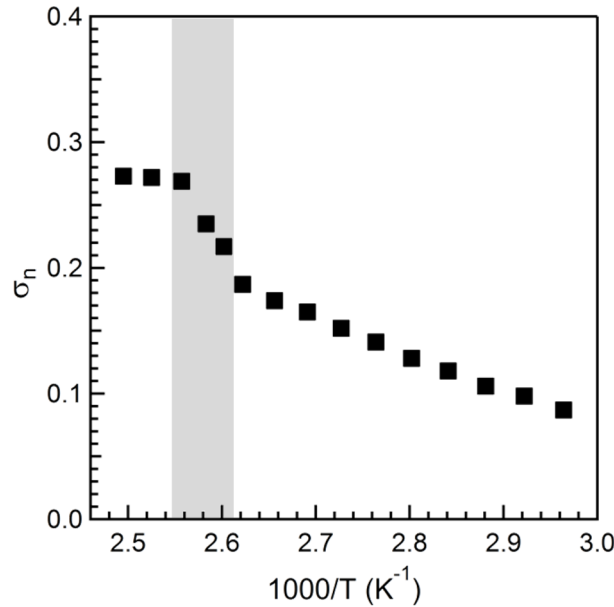


Figure 6-4 Normalized conductivity of SEO(1.7-1.4)/LiTFSI at $r = 0.085$. Normalized conductivity versus inverse temperature. The gray bar denotes the ODT.

6.2 Comparison with Previous Work

Our framework can readily be extended to predict conductivity changes through other transitions (e.g. order-order transitions) in block copolymer electrolytes. Majewski *et al.*⁸¹ observed a plateau in conductivity in the vicinity of the transition from cylinder with minority conducting phase to a disordered phase. Based on the framework presented in this paper, we expected $\sigma/\sigma_{\text{VTF}}$ to be 3 at temperatures above this transition due to an increase of the morphology factor from $\frac{1}{3}$ to unity. In contrast, Majewski *et al.*⁸¹ observed $\sigma/\sigma_{\text{VTF}}$ values less than unity in the disordered phase. This discrepancy may be the result of discontinuous concentration fluctuations due to the small fraction of conducting phase, or the liquid-crystalline nature of insulating block. Wanakule *et al.*⁷¹ report a transition to the disordered phase from both the lamellar phase and majority conducting cylinder phase, as well as an order-order transition (OOT) from the lamellar phase to the gyroid phase. No discontinuity in conductivity is expected for a transition from a majority conducting cylinder phase to a disordered phase if $f = 1$ and M is sufficiently large so that vehicular ion transport is negligible. The lamellar to gyroid transition reported by Wanakule *et al.*⁷¹ occurred over the wide temperature window of 52 -106 °C, which may have obscured the expected increase in conductivity as f changes from $\frac{2}{3}$ to unity. We offer no explanation for the lack of a discontinuity in conductivity for the lamellar to disorder transition reported by Wanakule *et al.*⁷¹ Perhaps improvements in sample preparation and simultaneous morphology characterization and conductivity measurements may have helped elucidate the behavior observed in the present work. Similarly we have no explanation for the lack of discontinuity in conductivity for the order to disorder transition reported by Ruzette *et al.*⁷² Cho *et al.*⁸⁵ reported an order of magnitude increase in conductivity as a PEO-based dendrimer-linear chain diblock copolymer underwent an OOT from minority conducting cylinder phase to a gyroid phase. Based on the framework presented in this paper, an increase by a factor of three would be expected for this transition.

6.3 Conclusions

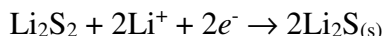
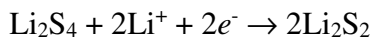
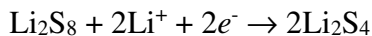
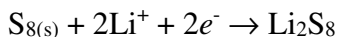
In conclusion, *in-situ* measurements of SAXS and ionic conductivity of a block copolymer electrolyte as it transitioned from an ordered lamellar structure to a disordered phase revealed a discontinuous increase in conductivity at the phase transition by a factor of about 1.8. A simple framework for understanding this result is presented.

Chapter 7 - Effect of Lithium Polysulfides on the Morphology of Block Copolymers⁵

ABSTRACT

Lithium polysulfides (Li_2S_x , $2 \leq x \leq 8$) are produced during the discharge of lithium-sulfur batteries. Lithium-sulfur batteries are of interest due to their high energy density. The morphology of mixtures of polystyrene-*b*-poly(ethylene oxide) (SEO) copolymers and lithium polysulfides were studied using a combination of X-ray diffraction, small-angle X-ray scattering, differential scanning calorimetry, and ultraviolet-visible spectroscopy. This study is motivated by the possibility of using block copolymers as electrolytes in lithium-sulfur cells. The phase behavior of SEO/ Li_2S_x mixtures were found to differ fundamentally from mixtures of SEO and other lithium salts. The morphology of certain SEO/ Li_2S_x mixtures obtained below the melting temperature of the poly(ethylene oxide) block has not been previously observed in block copolymer/salt mixtures.

Lithium-sulfur rechargeable cells are attractive because they offer a theoretical specific energy of 2600 Wh/kg, which is only a factor of five less than that of gasoline.^{86, 87} In contrast to cobalt- and nickel-based intercalation compounds used in the cathodes of conventional lithium-ion batteries, sulfur is inexpensive, non-toxic and abundant. The energy produced during discharge of the lithium-sulfur cell is due to a series of redox reactions involving Li^+ ions that diffuse from the anode to react with sulfur in the cathode. Elemental sulfur (S_8) is reduced through the following series of stepwise redox reactions



⁵Adapted with permission from Teran, Alexander A. and Nitash P. Balsara. 2011. "Effect of Lithium Polysulfides on the Morphology of Block Copolymer Electrolytes" *Macromolecules*, 44 (23), pp 9267-9275 doi: 10.1021/ma202091z. Copyright 2011 American Chemical Society

forming lithium polysulfide intermediates (Li_2S_x , $2 \leq x \leq 8$) with progressively shorter linear sulfur chains until the final reduction product lithium sulfide (Li_2S) is formed. The overall reaction can be represented $\text{S}_8 + 16\text{Li}^+ + 16e^- \rightarrow 8\text{Li}_2\text{S}$.

Despite its obvious advantages, lithium-sulfur chemistry has had limited commercial success due to significant challenges at both electrodes.^{88, 89} At the anode, lithium metal is reactive and prone to dendrite formation upon cycling, resulting in battery failure. Sulfur cathodes suffer from poor utilization of active material and rapid capacity fade upon cycling. The shortcomings of the sulfur electrode arise from the complexity of the species involved in the chemical reactions given above. The reactant and product of the overall reaction are insoluble and electronically insulating. Thus, in principle, the reaction can only be reversibly driven to completion if the reactants and products are confined within nanoscale electronically and ionically conducting channels. Additional complexity arises due to the solubility of the polysulfide intermediates ($2 \leq x \leq 8$) in organic electrolytes. The dissolution of these species into the electrolyte results in irreversible loss of active material from the cathode. To make matters worse, these species can then be reduced at the anode, resulting in either the formation of a parasitic polysulfide shuttle between the electrodes,⁹⁰ or reduction at the cathode surface leading to uncontrolled precipitation.⁹¹ In an important publication, the Nazar group showed that nanostructuring of the active sulfur particles in the electrode dramatically reduces irreversible capacity loss.⁹² A logical question to ask is whether the performance of lithium-sulfur batteries can be improved by using a nanostructured electrolyte.

Previous work in our group has successfully shown that nanostructured block copolymer electrolytes, specifically polystyrene-*b*-poly(ethylene oxide) (SEO) doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), have high ionic conductivity at elevated temperature and sufficiently high modulus to prevent the formation of dendrites.⁸ Additionally, the system has been shown to form a stable interface with lithium metal anodes as well as maintain intimate contact upon cycling.¹³ Having already satisfied concerns pertaining to the lithium metal anode, we have begun a study the viability of this electrolyte against the sulfur cathode. An ideal electrolyte for a sulfur cathode would not allow the dissolution nor diffusion of the polysulfides out of the electrode. It is thus important to study the thermodynamic interactions between the lithium polysulfides and SEO block copolymers.

The present paper on the morphology of mixtures of polysulfides and SEO block copolymers may be considered an extension of previous studies on SEO/salt mixtures.^{23, 26, 71, 93} A major difference is that the polysulfide anions are divalent in contrast to all of the previous studies on SEO/salt mixtures, which are restricted to monovalent counter ions. It is also known that polysulfide species undergo spontaneous reversible reactions such as



The equilibrium constants of the reactions depend on the medium. Thus, when we add a polysulfide to an SEO copolymer, it may transform to give a variety of other polysulfides. For example Li_2S_6 can transform into equal concentrations of Li_2S_4 and Li_2S_8 .

The main purpose of this paper is to describe the phase behavior of SEO/ Li₂S_x mixtures. The results presented here are qualitatively different from all previous studies of block copolymer/salt mixtures

7.1 Sample Preparation

SEO block copolymers were synthesized, purified, and characterized as described in Chapter 2 of this work. SEO/LiTFSI mixtures were also prepared as described in Chapter 2.

Polymer	M _{PS} kg mol ⁻¹	M _{PEO} kg mol ⁻¹	φ _{EO}	PDI
PEO(1.1)	–	1.1	1	1.10
SEO(1.7-1.4)	1.7	1.4	0.44	1.05
SEO(4.9-5.5)	4.9	5.5	0.51	1.04

Table 7-1 Characteristics of polymers used in Chapter 7.

Lithium polysulfides (Li₂S_x) were synthesized by dissolving stoichiometric amounts of elemental sulfur (S₈) and lithium sulfide (Li₂S) in dimethylsulfoxide (DMSO)⁹⁴ and stirred for several days at 90 °C. The sulfur and lithium sulfide were received under argon from Alfa Aesar, opened in the glovebox, and used as received. Our synthesis procedure sets the value of, x_{av} , the molar average length of the polysulfide anion assuming the reactants are completely consumed. Detailed spectroscopic and electrochemical studies of polysulfide/DMSO mixtures indicate that the solutions thus obtained are dominated by a single species.⁹⁵ For example, when $x_{av} = 6$, the solution is predominantly composed of Li₂S₆. Similar studies have not been conducted in SEO copolymers. It is thus conceivable, for example, that the $x_{av} = 6$ mixtures in the SEO copolymers actually contain equal concentrations of Li₂S₄ and Li₂S₈. We synthesized polysulfides with values of $x_{av} = 1, 2, 4, 6$, and 8 . It should be noted that the lithium polysulfide intermediates ($2 \leq x_{av} \leq 8$) cannot be isolated as pure compounds.⁹⁶ For simplicity, we refer to lithium polysulfides as salts.

All polymers were dried at 100 °C under vacuum in a glovebox antechamber for at least 24 h, and then brought immediately into the glovebox. The polysulfide solutions were added to polymers dissolved in DMSO. The polymer/polysulfide solutions were then dried at 90 °C for three days in an air-tight desiccator on a vacuum line under dynamic vacuum. Removal of solvent was confirmed using ¹H NMR and retention of polysulfides in the sample was confirmed using neutron activation analysis (NAA) performed by Elemental Analysis, Inc. (Drying at higher temperatures resulted in significant evaporation of the polysulfide species.) For values of $x_{av} \geq 2$, the dried polymer/salt mixtures have a deep red/orange color while the $x_{av} = 1$ mixtures are brown.

The molar salt concentration in our copolymers is quantified by the molar ratio of lithium atoms to ethylene oxide moieties, r , which ranges from 0.005 to 0.125. The number of EO units in the copolymer is calculated from the molecular weight without correcting for the -OH end groups. Due to the hygroscopic nature of the salts, argon gloveboxes (Vacuum Atmospheres Company) with oxygen and water at sub-ppm levels were used for all sample preparation. Sample

morphologies were determined via SAXS as described in Chapter 2. DSC experiments were performed via methods also described in Chapter 2

7.2 X-Ray Diffraction

We first focus on the X-ray diffraction profiles of the copolymers with the lithium polysulfides. The samples were run in airtight sample holders in transmission mode on a Bruker AXS D8 Discover GADDS XRD diffractometer operating at 40 kV and 20 mA and using Cu-K α radiation. ($\lambda = 1.54178 \text{ \AA}$). Figure 7-1a and Figure 7-1b shows the diffraction profiles for SEO(1.7-1.4)/Li₂S_x and SEO(4.9-5.5)/Li₂S_x respectively at a constant concentration of $r = 0.085$. For reference we also show diffraction profiles of the neat copolymers and pure lithium sulfide (Li₂S) in Figure 7-1. In the 2θ range shown, the Li₂S shows the expected {111}, {200}, {220}, {311} peaks, but the minor {222} peak at $2\theta = 56^\circ$ reported in the literature⁹⁷ was not observed. The XRD profiles of SEO(1.7-1.4)/Li₂S_x at 30 °C are shown in Figure 7-1a. The PEO block of pure SEO(1.7-1.4) does not crystallize, thus the amorphous PEO halo at 20° is the only feature present in the neat copolymer profile. For $x_{av} = 1$ and 2, diffraction peaks corresponding to those for Li₂S are visible, indicating the presence of Li₂S crystals in the mixtures. For $x_{av} = 4, 6$, and 8, there are no diffraction peaks visible, suggesting that the salts present are completely soluble in the polymer. The amorphous halo is significantly depressed for $x_{av} \geq 4$. Polysulfides with $2 \leq x_{av} \leq 8$ have not yet been isolated as pure compounds.⁹⁶ Thus, comparisons between the XRD data obtained from SEO/Li₂S_x mixtures with that of pure Li₂S_x are not possible for $x_{av} \geq 2$. The XRD data rule out the presence of Li₂S or S₈, both of which have well-known powder diffraction patterns. No evidence of S₈ crystals is seen in any of the SEO/Li₂S_x mixtures. The XRD profiles of SEO(4.9-5.5)/Li₂S_x at 80 °C (above the melting point of the PEO block) are shown in Figure 7-1b. The SEO(4.9-5.5)/Li₂S_x mixtures show the {111} peak of Li₂S for the $x_{av} = 1, 2$ and 4 samples. This suggests the presence of crystalline Li₂S at equilibrium with other species for values of $x_{av} = 2$ and 4. The trend of increasing solubility with increasing x_{av} seen in the copolymers is consistent with previous work on organic electrolytes⁹⁴ and homopolymers.^{98, 99}

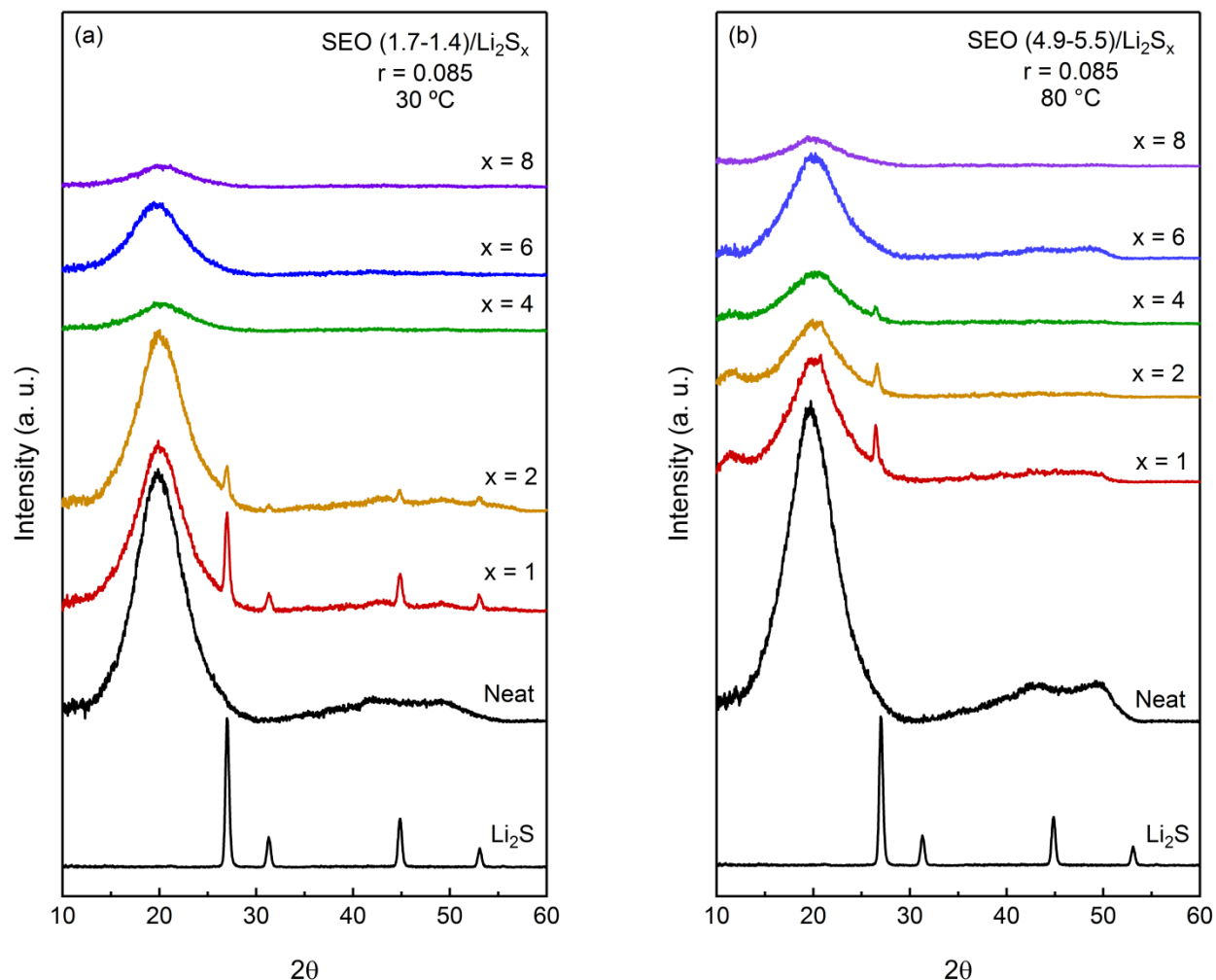


Figure 7-1 XRD of SEO/Li₂S_x mixtures.

Intensity versus scattering angle, 2θ , of (a) SEO(1.7-1.4)/Li₂S_x at 30 °C and (b) SEO(4.9-5.5)/Li₂S_x at 80 °C with at a fixed concentration of $r = 0.085$, with $1 \leq x \leq 8$. Profiles are vertically offset for clarity. WAXS of Li₂S is shown as a reference in both panels.

7.3 Thermal Properties

Next we examine the thermal properties of the SEO copolymers with Li₂S_x. Figure 7-2a shows DSC scans of SEO(4.9-5.5)/Li₂S_x at a constant concentration of $r = 0.085$. The melting temperature, T_m , and the enthalpy of melting, ΔH_m , of the crystalline PEO decrease with increasing polysulfide length. The melting temperature decreases from 52 to 42 °C and ΔH_m decreases from 68.5 to 7.8 J g⁻¹ as x_{av} is increased from 0 to 8. The exothermic peaks at low temperature for $x_{av} = 4, 6$ and 8 are the result of slow re-crystallization of the PEO block. SEO(1.7-1.4)/Li₂S_x thermograms show no features (not shown). Figure 7-2b shows the effect of salt concentration on the crystallinity of the PEO block for each of the lithium polysulfides. For $x_{av} = 1$ and 2, the crystallinity appears to plateau as concentration increases while for $x_{av} = 4, 6$, and 8 crystallinity continues to decrease. For $x_{av} = 6$ and 8 at the highest concentration of $r = 0.125$, crystallinity is completely suppressed. The ether oxygens of the PEO backbone are able to coordinate lithium

ions, causing the salt to preferentially segregate to that block, creating a PEO/Li₂S_x microphase. The coordination of the lithium ions disrupts the ability of the chain to crystallize. It is therefore expected that an increase in lithium ion concentration will result in a decrease in crystallinity. This is not seen for values of $x_{av} = 1$ and 2 indicating the lack of solubility of Li₂S_x in SEO(4.9-5.5). Similar conclusions can be made for SEO(1.7-1.4)/Li₂S_x based on the diffraction data above. It is worth noting that a fixed value of r , crystallinity decreases as polysulfide length increases. The DSC data support the conclusion that the solubility of the polysulfides increases with increasing x_{av} .

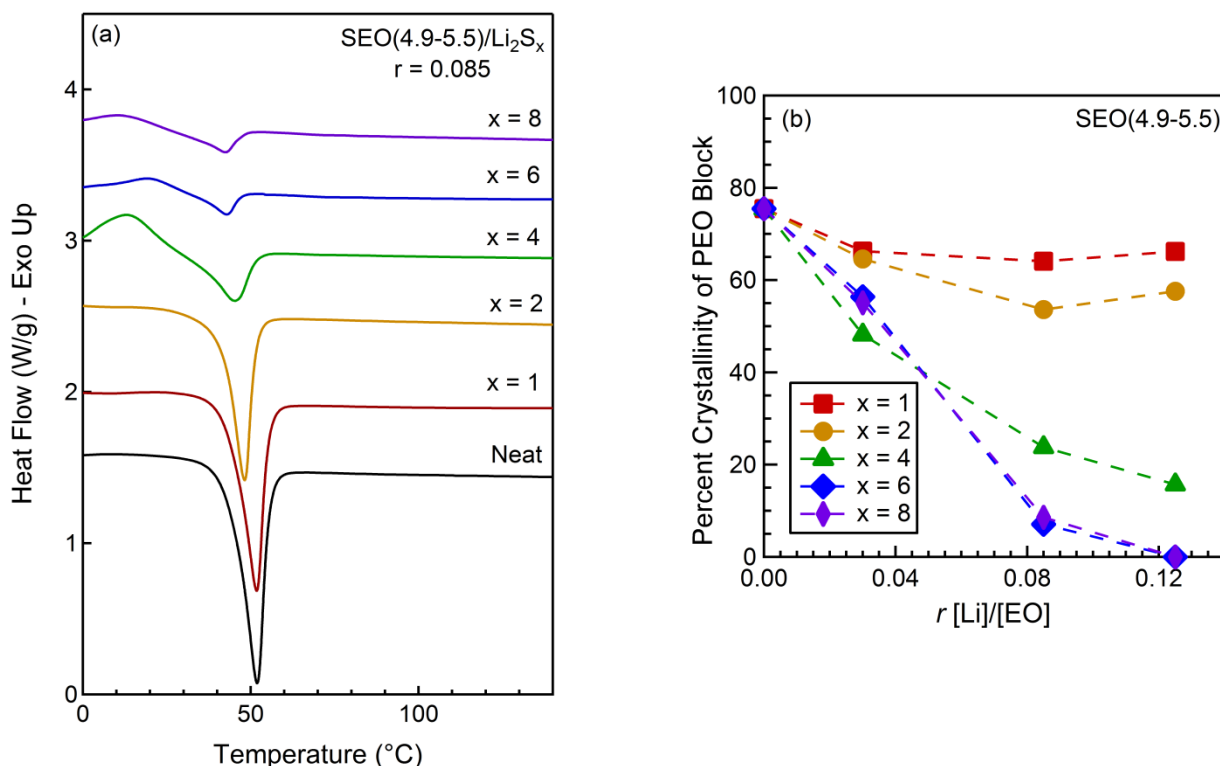


Figure 7-2 Thermal properties of SEO(4.9-5.5)/Li₂S_x mixtures.

(a) DSC traces of SEO(4.9-5.5)/Li₂S_x at $r = 0.085$ and a heating rate of 10 °C/min. The third heating run is shown and profiles are vertically offset for clarity. (b) The effect of polysulfide length and concentration on the crystallinity of the PEO block for SEO(4.9-5.5)/ Li₂S_x samples

7.4 Phase Behavior of SEO/Li₂S_x

The phase behavior of SEO/Li₂S_x as a function of polysulfide length and salt concentration was obtained by SAXS. Figure 7-3a and Figure 7-3b shows 1-D SAXS profiles for SEO(1.7-1.4)/Li₂S_x and SEO(4.9-5.5)/Li₂S_x respectively at a constant concentration of $r = 0.085$ and at a temperature of 80 °C. Although both copolymers are disordered in their neat state at all temperatures, the addition of the polysulfides induces the stabilization of both lamellar (LAM) and gyroid (GYR) morphologies. In Figure 7-3a, SEO(1.7-1.4) in the neat state as well as with the addition of Li₂S shows no scattering peak, indicative of a disordered phase. As the value of x_{av} increases, there is increased segregation in the copolymers. The $x_{av} = 2$ sample shows a broad

disordered peak. The peak appears to be a doublet which is typically not found in pure disordered block copolymers. The $x_{av} = 4$ and 6 samples show a distinct GYR morphology with sharp peaks at $q/q_{\{100\}} = \sqrt{6}$ and $\sqrt{8}$ where $q_{\{100\}}$ corresponds to the magnitude for the scattering vector corresponding to the $\{100\}$ family of reflection planes. As discussed in Chapter 2, $q^* = q_{\{100\}}$ for all ordered morphologies except the gyroid morphology, where $q^* = q_{\{211\}}$. It is possible that the disordered doublet at $x_{av} = 2$ are announcements of the ordered peaks seen at $x_{av} = 4$. The $x_{av} = 8$ sample has a LAM morphology with peaks at $q/q^* = 1$ and 2. In Figure 7-3b, SEO(4.9-5.5) shows a broad disordered peak for both the neat copolymer as well as upon the addition of Li_2S . The $x_{av} = 2$ sample shows a GYR morphology with distinct higher order peaks at $q/q_{\{100\}} = \sqrt{6}, \sqrt{8}, \sqrt{14}, \sqrt{16}, \sqrt{20}, \sqrt{22}, \sqrt{24}$, and $\sqrt{26}$, while the $x_{av} = 4, 6$, and 8 samples show LAM morphology with peaks at $q/q^* = 1, 2, 3$, and 4. In Figure 7-3 the molar concentration of lithium is held constant while the average length of the anion is increased. Increasing segregation with increasing anion radius is consistent with previous studies of SEO copolymers and monovalent salts.^{23, 26, 29}

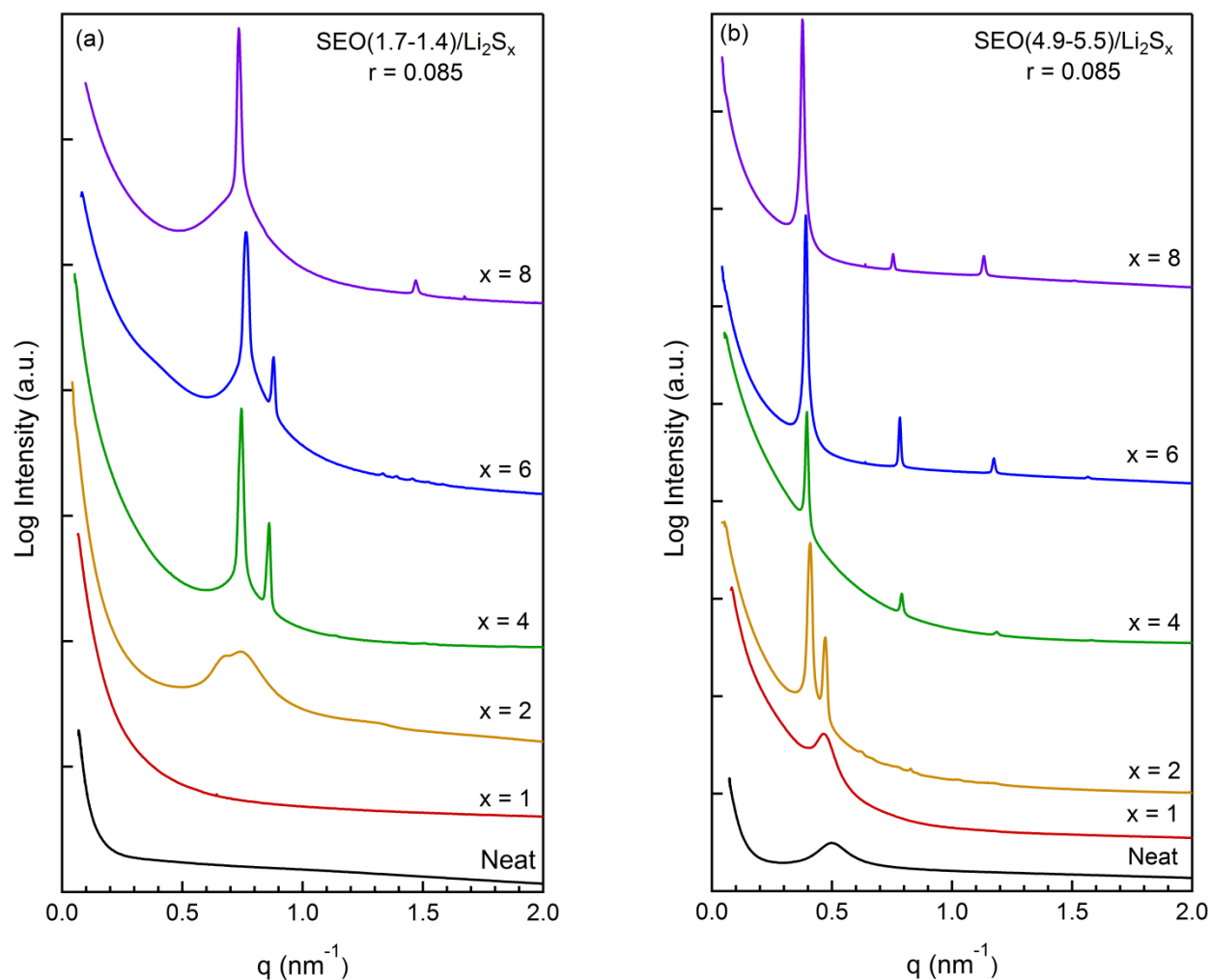


Figure 7-3 SAXS of SEO/ Li_2S_x mixtures.

Intensity versus scattering vector, q , for (a) SEO(1.7-1.4)/ Li_2S_x and (b) SEO(4.9-5.5) Li_2S_x at $r = 0.085$ at 80°C . Profiles are vertically offset for clarity.

Several order-disorder transitions (ODTs) were observed in the SEO/Li₂S_x samples as temperature was increased. Figure 7-4 shows SAXS profiles for SEO(4.9-5.5)/Li₂S₈ at $r = 0.02$ at selected temperatures. The sample exhibits a GYR morphology from 60 to 120 °C. At 140 °C, the profile shows only the $q/q^* = 1$ and $\sqrt{3}$ peaks, indicating a hexagonally packed cylinder (HEX) phase. At 160 °C the sample shows a single broad scattering peak corresponding to a disordered phase. The order-disorder transition temperature (T_{ODT}) of this sample is determined to be 150 ± 10 °C by a sudden increase in the full width at half maximum (FWHM) of the primary SAXS peak from 0.9×10^{-2} to $3.6 \times 10^{-2} \text{ nm}^{-1}$ as shown in the inset of Figure 7-4.

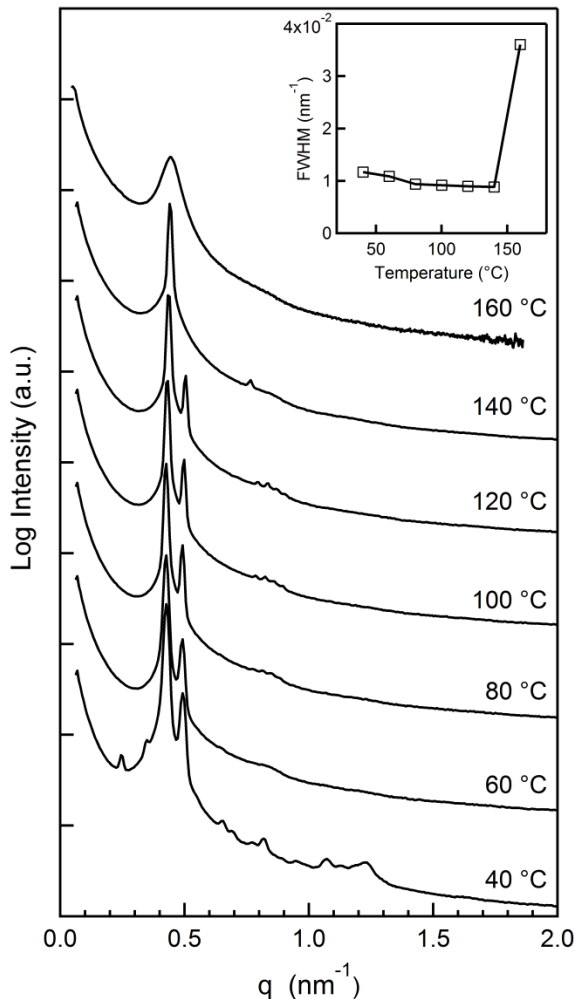


Figure 7-4 Order-disorder transition of SEO(4.9-5.5)/Li₂S₈ at $r = 0.02$. SAXS intensity versus scattering vector, q , for SEO(4.9-5.5)/Li₂S₈ at $r = 0.02$. Profiles are vertically offset for clarity. Inset shows FWHM of Gaussian fit to primary scattering peak as a function of temperature.

The SAXS data of SEO(4.9-5.5)/Li₂S_x samples at low salt concentrations and at temperatures below the melting point of PEO (e.g. 40 °C data in Figure 7-4) present an interesting puzzle. Figure 7-5a shows normalized SAXS profiles (I versus q/q_{max}) for several SEO(4.9-5.5)/Li₂S_x samples at 30 °C. These profiles are remarkable for several reasons. First, they show more than 17 higher order peaks corresponding to the GYR morphology, indicating the presence of considerable long-range order. Typically in semi-crystalline block copolymers, samples below the melting point of

the semi-crystalline block exhibit poor long-range order due to interference of the crystals with microphase separation. This manifests itself in the form of broad peaks and absence of higher order peaks in SAXS profiles.¹⁰⁰ To our knowledge, SEO(4.9-5.5)/Li₂S_x is the only system that exhibits significantly enhanced long-range order when one of the blocks is crystallized (compare 40 and 60 °C data in Figure 7-4).

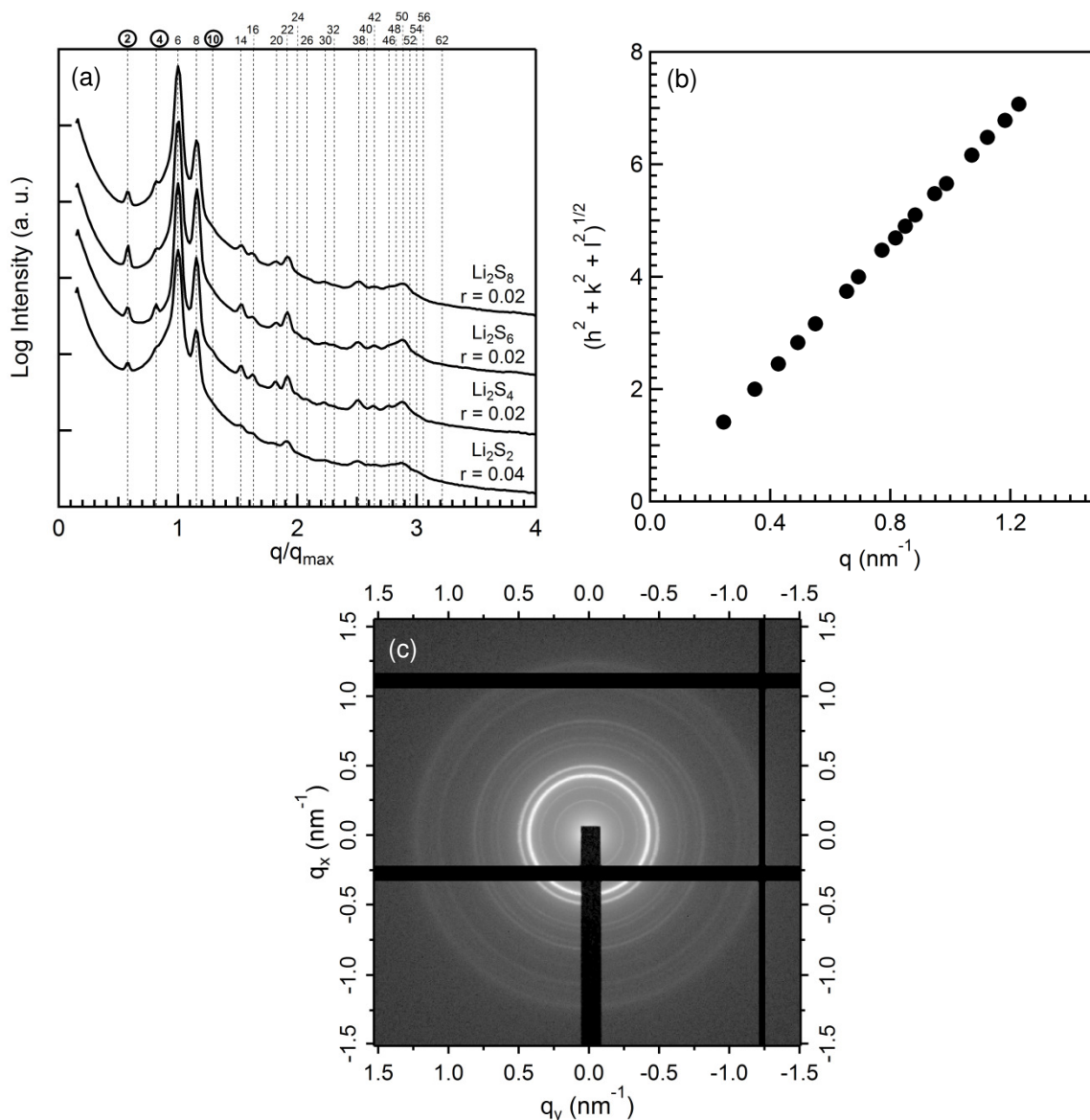


Figure 7-5 SAXS of crystalline SEO(4.9-5.5)/Li₂S_x mixtures.

(a) SAXS intensity versus scattering vector, q , for SEO(4.9-5.5)/Li₂S_x at various values of x_{av} and r . Dotted vertical lines show all the expected Bragg reflections for the GYR morphology, as well as the three unexpected reflections at $h^2 + k^2 + l^2 = 2, 4$, and 10 , shown circled on the top axis. Scattering profiles are vertically offset for clarity. (b) Moduli of the Miller indices of the Bragg peaks versus the peak positions in scattering vector, q , for SEO(4.9-5.5)/Li₂S₄, $r = 0.02$ at 30 °C. The linearity and zero intercept confirm the cubic nature of the morphology and (c) 2-D SAXS image for the same sample.

Figure 7-5b is a plot of the moduli of the Miller indices, $m = (h^2 + k^2 + l^2)^{-1/2}$, versus q corresponding to each of the peaks obtained from SEO(4.9-5.5)/Li₂S₄, $r = 0.02$ at 30 °C with the

first visible peak assigned to the {110} plane. The proportionality between the two quantities plotted in Figure 7-5b confirms the presence of a cubic phase. In Table 7-2 we replicate the analysis of Hadjuk *et al.*,¹⁰¹ showing the expected peaks from the 12 cubic extinction symbols that are consistent with $\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}:\sqrt{20}:\sqrt{22}:\sqrt{24}:\sqrt{26}:\sqrt{30}:\sqrt{32}:\sqrt{38}$ reflections (typical of the gyroid phase). These include all of the cubic space groups with *P* and *I* symmetry. At the bottom of Table 7-2, we summarize the correspondence between expectations of each space group and experiment. At first glance the spacing and relative intensities of the scattering peaks seen in Figure 7-4 and Figure 7-5 appear most closely related to the *Pm3n* space group, seen previously in both block copolymer and surfactant systems.^{85, 102} However several peaks expected from the *Pm3n* space group are not observed, most notably the {210} reflection. All of the cubic space groups with *P* symmetry have many unobserved reflections, whereas nearly all of the peaks expected from the cubic space groups with *I* symmetry are observed. Only the *Ia.d* column has all the expected reflections observed.

Bragg plane	square of modulus (m ²)	Cubic space group extinction symbol												Observed Reflection
		<i>P</i> ...	<i>P4</i> ₂ ..	<i>P4</i> ₁ ..	<i>Pn</i> ..	<i>P</i> .. <i>n</i>	<i>Pn</i> .. <i>n</i>	<i>Pa</i>	<i>I</i> ...	<i>I4</i> ₁ ..	<i>Ia</i> ..	<i>I</i> .. <i>d</i>	<i>Ia.d</i>	
100	1	x												
110	2	X	X	X	X	X	X		X	X				X
111	3	x	x	x	x			x						
200	4	X	X		X	X	X	X	X		X			X
210	5	x	x	x		x		x						
211	6	X	X	X	X	X	X	X	X	X	X	X	X	X
220	8	X	X	X	X	X	X	X	X	X	X	X	X	X
300	9	x	x	x	x			x						
310	10	X	X	X	X	X	X		X	X		X		X
311	11	x	x	x	x			x						
222	12	x	x	x	x	x	x	x	x	x	x			
320	13	x	x	x		x		x						
321	14	X	X	X	X	X	X	X	X	X	X	X	X	X
400	16	X	X	X	X	X	X	X	X	X	X	X	X	X
322/410	17	x	x	x	x	x		x						
411/330	18	x	x	x	x	x	x	x	x	x	x			
331	19	x	x	x	x			x						
420	20	X	X	X	X	X	X	X	X	X	X	X	X	X
421	21	x	x	x	x	x	x	x						
332	22	X	X	X	X	X	X	X	X	X	X	X	X	X
422	24	X	X	X	X	X	X	X	X	X	X	X	X	X
500/430	25	x	x	x		x		x						
431/510	26	X	X	X	X	X	X	X	X	X	X	X	X	X
511/333	27	x	x	x	x	x	x	x						
432/520	29	x	x	x	x	x	x	x						
521	30	X	X	X	X	X	X	X	X	X	X	X	X	X
440	32	X	X	X	X	X	X	X	X	X	X	X	X	X
441/522	33	x	x	x	x			x						
433/530	34	x	x	x	x	x	x	x	x	x	x	x		
531	35	x	x	x	x	x	x	x						
442/600	36	x	x	x	x	x	x	x	x	x	x			
610	37	x	x	x		x		x						
611/532	38	X	X	X	X	X	X	X	X	X	X	X	X	X
observed and expected		14	14	13	14	14	14	12	14	13	12	12	11	
not observed but expected		19	18	18	14	13	7	17	4	4	4	1	0	
observed but not expected		0	0	1	0	0	0	2	0	1	2	2	3	

Table 7-2 Observed vs. expected Bragg reflections.

Listing of allowed Bragg peaks for 12 of the 17 cubic extinction symbols that exhibit reflections consistent with observed scattering. Right-most column lists the observed SAXS peaks of SEO(4.9-5.5)/Li₂S₄, *r* = 0.02 at 40 °C (see Figure 7-5). The Table assumes that the lowest *q* peak is due to the {110} plane. "X" is used to denote expected Bragg peaks that were observed experimentally. "x" is used to denote expected Bragg peaks that are allowed, but not observed experimentally. The *Ia.d* column is the only one with no "x".

In addition to peaks corresponding to the GYR morphology ($Ia3d$ space group), the SAXS profiles in Figure 7-5a contain three additional peaks at $q/q_{\{100\}} = \sqrt{2}$, $\sqrt{4}$, and $\sqrt{10}$. These peaks are normally forbidden for the $Ia3d$ space group, but have been seen before in SAXS data from templated block copolymer nanocomposites.¹⁰³⁻¹⁰⁷ The presence of the forbidden peaks in the block copolymer nanocomposites was first attributed to the presence of the plumber's nightmare morphology ($Im3m$ space group).¹⁰⁷ In a subsequent paper,¹⁰³ some of the coauthors of ref. 107 reanalyzed the data and attributed the presence of the forbidden peaks to a uniaxial deformation of the gyroid structure. The 2-D scattering from such nanocomposite systems show sharp diffraction spots, whereas our samples exhibit isotropic rings such as those shown in Figure 7-5c. Despite this discrepancy, we tentatively conclude that crystalline SEO(4.9-5.5)/Li₂S_x mixtures form a "distorted" gyroid morphology and that the distortions arise due to interactions between Li₂S_x and crystalline PEO.

Our attempts to substantiate our conclusion using transmission electron microscopy were largely unsuccessful. Figure 7-6 shows a TEM micrograph of SEO(4.9-5.5)/Li₂S₄ $r = 0.03$ that was prepared by pressing at 65 °C into an aluminum spacer using a heated press for 24 hr in a glovebox. The sample was then split into two halves: SAXS was performed on one sample to confirm the presence of the 'distorted gyroid' morphology, while the other half was cryo-microtomed and imaged without staining using a transmission electron microscope. Difficulties arose due to the hygroscopic nature of the samples and the lack of instrumentation necessary to section and image samples without exposure to moisture: Despite our best efforts to prevent exposure of the sample to air, our current instrumentation necessitates a brief exposure to ambient conditions as the microtomed sample is inserted into the microscope. The micrograph in Figure 6 shows clearly a lamellar morphology, indicating that even a brief exposure to ambient conditions is sufficient to alter the morphology of these samples.

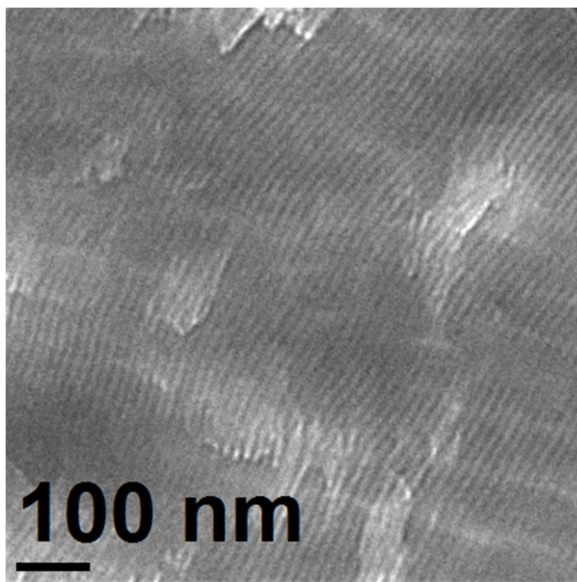


Figure 7-6 TEM micrograph of SEO(4.9-5.5)/Li₂S₄, $r = 0.03$.

The phase behavior observed for the SEO(4.9-5.5)/Li₂S_x samples is summarized in Figure 7-7 with salt concentration on the ordinate and polysulfide length on the abscissa. The diagram covers temperatures from 30 to 160 °C. The phase behavior of SEO(4.9-5.5)/LiTFSI is also shown in Figure 7-7. Each marker in Figure 7-7 represents a sample whose morphology was determined by SAXS. Markers bisected by a phase boundary indicate an ODT was observed. In SEO(4.9-5.5)/Li₂S_x with $x_{av} = 4, 6, \text{ and } 8$ at $r = 0.02$, the GYR-to-DIS transition is interrupted by a HEX phase. This was not observed in SEO(4.9-5.5)/Li₂S₂ at $r = 0.04$. We are not sure if this is due to the finite temperature steps used in this study. The symmetry of the phase diagram indicates that increasing the length of the anion by increasing the value of x_{av} has the same effect on the phase behavior of the copolymer as increasing the anion concentration, r . The disordered phase obtained at low values of x_{av} and r gives way to the GYR morphology at intermediate values of x_{av} and r . Further increase in x_{av} and r results in a GYR-to-LAM transition. An important observation is that the phase diagram of the block copolymer with the polysulfides and that of the block copolymer with LiTFSI are fundamentally different. Not only does SEO(4.9-5.5) transition directly from DIS-to-LAM as salt is added, but the concentration of LiTFSI needed to induce ordering is lower by a factor of 5 on both a molar and weight basis. The phase behavior of SEO(1.7-1.4)/Li₂S_x and SEO(1.7-1.4)/LiTFSI showed a similar trend, though with an expected shift to higher salt concentrations due to molecular weight differences (not shown).

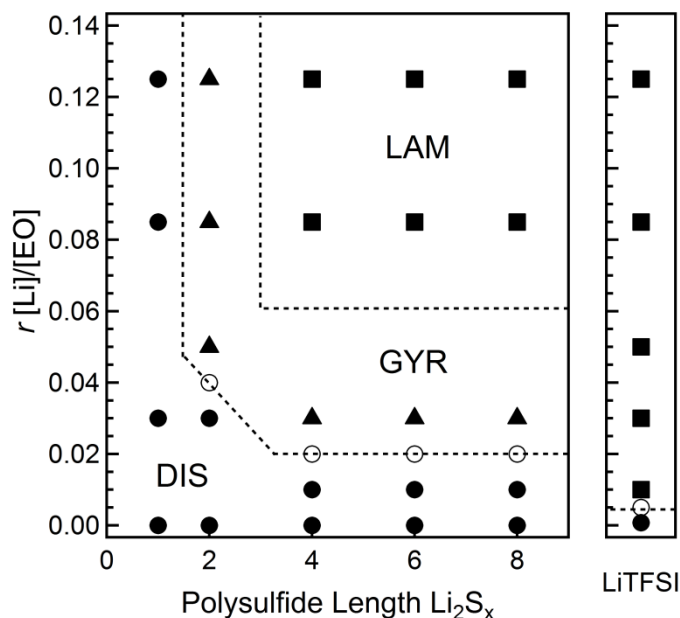


Figure 7-7 Phase diagram of SEO(4.9-5.5)/Li₂S_x and SEO(4.9-5.5)/LiTFSI.

Open points bisected by the dotted phase boundary indicate a phase transition between the two neighboring phases was observed.

Figure 7-8 is a plot of domain spacing, d , versus the weight fraction of salt in the polymer, w , at a fixed temperature of 80 °C. The top axis shows the domain spacing versus the volume fraction of the PEO/Li₂S_x phase, $\phi_{\text{EO/Li}_2\text{S}_x}$. The volume fraction calculations are estimates using the average density of lithium sulfide (1.66 g/cm³) and sulfur (2.07 g/cm³) as the density of the polysulfides and assuming perfect mixing of the salts in the PEO block. The different symbols in Figure 7-8 reflect different morphologies regardless of x_{av} . The collapse of all of the data onto a single curve

and the clustering of similar morphologies in Figure 7-8 indicates that the morphology and domain spacing depends mainly on w , which reflects a particular combination of r and x_{av} .

The question of whether the PEO/Li₂S_x phase forms the network or the matrix of the GYR morphology is an interesting one. In diblock copolymer melts, increasing the volume fraction of the network-forming minority component results in a GYR-to-LAM transition¹⁰⁸. Since increasing $\phi_{\text{EO/Li}_2\text{S}_x}$ results in a GYR-to-LAM transition (Figure 7-8), we conclude that the network must be composed of the PEO/Li₂S_x mixture. The GYR morphology is obtained when $\phi_{\text{EO/Li}_2\text{S}_x}$ is in the 0.51 to 0.53 range (Figure 7-8). In pure block copolymers, the gyroid network is formed by the minority phase at volume fractions of about 0.38. The presence of a salt-containing gyroid network that occupies more than 50% of the sample volume is further evidence of the unique and unprecedented thermodynamic properties that arise when lithium polysulfides are mixed with SEO copolymers. We have not included $x_{av} = 1$ samples in Figure 7-8 as it is clear from the calorimetry and X-ray scattering experiments that Li₂S is nominally immiscible in the SEO copolymers.

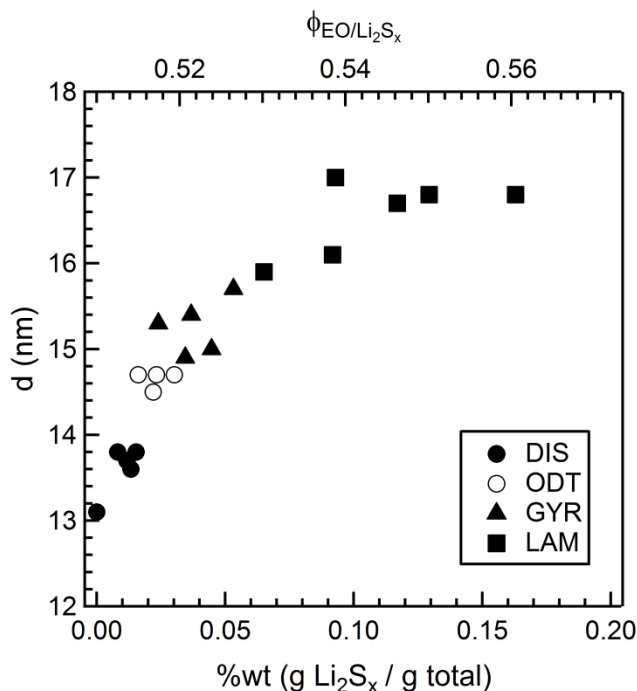


Figure 7-8 Effect of Li₂S_x addition on domain spacing in SEO(4.9-5.5).

Domain spacing versus weight percent salt for SEO(4.9-5.5)/Li₂S_x where $x \geq 2$. Estimated volume fraction of the PEO/Li₂S_x microphase is shown on top axis.

7.5 UV-Vis Spectroscopy

The value x_{av} is the average polysulfide length in the sample and we suspect that at any given value of x_{av} there exists an equilibrium between species with different values of x . Until this point we have provided no insight on the distribution of values of x present in the system. UV-Vis spectroscopy has been used to distinguish the Li₂S_x speciation in organic solvents such as DMSO,^{95, 109-111} DMF,¹¹²⁻¹¹⁶ THF,^{87, 94, 109, 117, 118} dimethylacetamide,¹¹⁹ liquid ammonia,^{120, 121} and acetonitrile.¹²² Detailed spectroelectrochemical experiments are necessary for unambiguous

determination of speciation.^{95, 111, 113, 120} These studies show that the distributions of species present depend crucially on the solvent. We have not yet embarked on such a study and thus we have not determined the species present in SEO block copolymers. Marmorstein, et al.⁹⁸ used UV-Vis spectroscopy to determine speciation in tetraethylene glycol which may be regarded as an oligomeric PEO. However, the speciation model proposed in this study was not backed by the same rigorous analysis used in the studies involving other solvents.

Figure 7-9a shows the UV-Vis spectra of PEO(1.1)/Li₂S_x with $r = 0.005$ at 80 °C. Samples were prepared by placing polymer in a double-sided Scotch[®] tape ‘gasket’, sandwiched between two quartz disks then placed in custom-designed air-free aluminum sample holders. The deep red/orange color of the mixtures necessitated the preparation of samples with extremely low salt concentrations ($r = 0.005$) and thicknesses no more than 100 μm in order to obtain absorbance values between approximately 0.3 and 1 before normalization for path length. Even for very thin samples ($< 100 \mu\text{m}$ thickness), light absorption was too high for the samples with higher values of r . The peaks of PEO(1.1)/Li₂S_x occur in the 400-500 nm region, the same region in which assignments for the species S₄²⁻, S₆²⁻, and S₈²⁻ have been made in DMSO.⁹⁵ We were, however, unable to make definitive assignments of species to specific peaks in the spectra. It should also be noted that our PEO spectra differ substantially from previous work by Marmorstein, et al.⁹⁸ suggesting that factors such as polymer end group concentration may play an important role in speciation of Li₂S_x. Figure 7-9b shows the UV-Vis spectra of SEO(1.7-1.4)/Li₂S_x with $r = 0.005$ at room temperature. The qualitative differences seen in Figure 7-9a and Figure 7-9b make it clear that solvation of Li₂S_x in homopolymer PEO and PEO contained within a block copolymer are very different. It is worth noting that SEO(1.7-1.4) used for the UV-Vis experiment is disordered at $r = 0.005$. Previous studies indicate that even in the disordered state, SEO/salt mixtures are characterized by strong concentration fluctuations and the salt molecules are exclusively located within the PEO-rich fluctuating domains.²⁶ We thus expect the UV-Vis spectra from the SEO(1.7-1.4)/Li₂S_x to reflect interactions between the salt and the PEO block. The qualitative similarity of the spectra of all of the samples in Figure 7-9b suggests that similar species are present in all of the samples. This implies that changing x_{av} as we have done in our experiments may primarily reflect the presence of different concentrations of the same S_x²⁻ anions. The presence of a dominant peak at 480 nm in all samples and the fact that this peak is most prominent in SEO(1.7-1.4)/Li₂S₂, suggests that the S₂²⁻ anion may be present in all samples. It is clear that further work is needed to fully characterize these mixtures. We note, however, that this is a non-trivial task as the experiments conducted on liquid systems are not easily done in the case of a solid electrolyte.

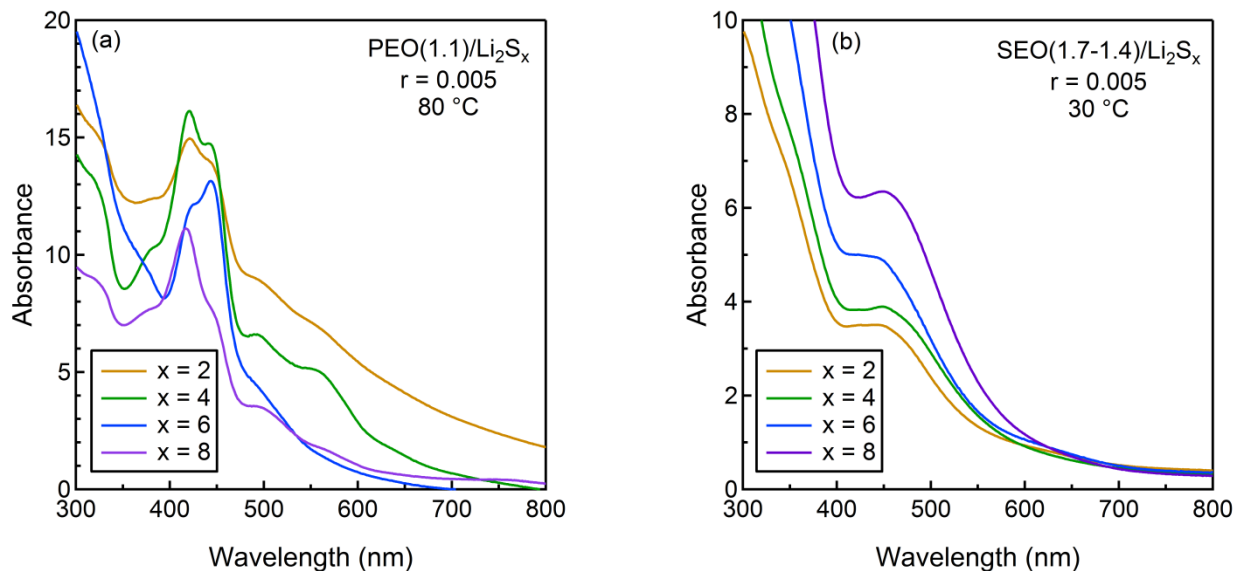


Figure 7-9 UV-Vis spectra of polymer/Li₂S_x mixtures at $r = 0.005$.

a) PEO(1.1) at 80 °C and b) SEO(1.7-1.4) at room temperature. All spectra normalized to 1 mm path length.

7.6 Conclusions

The phase behavior of mixtures of lithium polysulfide salts (Li₂S_x, $1 \leq x_{av} \leq 8$) and SEO diblock copolymers were studied using X-ray diffraction, differential scanning calorimetry, small angle X-ray scattering, and UV-Vis spectroscopy. The SEO copolymers were disordered in the neat state. The addition of the polysulfides resulted in disorder-to-order and order-order phase transitions. Increasing either the molar salt concentration, r , or anion size, x_{av} , resulted in increased segregation between the blocks. However, the morphology is primarily a function of the weight fraction of added salt, w . Increasing w from low to intermediate values results in a disorder-to-gyroid transition. At temperatures where the PEO block was crystalline, the SAXS profiles of the gyroid phase contains peaks that are normally forbidden. The SEO/Li₂S_x phase diagrams show fundamentally different morphologies than exhibited in other SEO/salt systems. Preliminary UV-Vis experiments indicated that the solvation environment of the polysulfides in the SEO block copolymers is very different from that of PEO homopolymers. We have not determined the distribution of anion sizes at a given x_{av} . We hope to address this shortcoming in future publications. In spite of this, we feel that the present paper represents an important first step in understanding how species that are expected to form in a lithium-sulfur cell interact with a block copolymer electrolyte.

Chapter 8 - Solid-State Lithium/Sulfur Cells

ABSTRACT

Nanostructured block copolymer electrolytes were tested in full electrochemical cells with a lithium metal anode and sulfur cathode. Different cathode compositions, electrolyte additives, and cell architectures were tested. Unexpectedly, polysulfides diffused readily out of the cathode and through the block copolymer electrolyte, resulting in a robust polysulfide shuttle. Additionally, the arrival of the polysulfides in the electrolyte changed its mechanical properties, resulting in delamination from the lithium metal anode and ultimately cell failure. Several promising strategies to overcome these problems were investigated and offer exciting avenues for future researchers.

The lithium/sulfur electrochemical pair offers extremely high theoretical energy density, however the unique challenges associated with this chemistry have prevented commercial success. At the negative electrode, lithium metal is highly reactive and susceptible to dendrite formation upon cycling. At the positive electrode, sulfur is prone to rapid capacity fading and poor utilization of the active material due to its insulating nature and the complexities of its reduction mechanism. The reduction of sulfur is discussed in detail in Chapter 7.

A resurgence of interest in the past half-decade has resulted in massive experimentation and yielded impressive improvements in benchtop-level cells, especially regarding the performance and cyclability of the sulfur cathode. Researchers have investigated several approaches to improve the sulfur cathode, the most promising of which focuses on confining the sulfur in the cathode matrix. This is achieved by physical adsorption and absorption via incorporation of the sulfur into a porous carbon structure^{92, 123} or by chemical bonding of the sulfur either onto substrates such as graphene oxide¹²⁴ or into a polymeric material.¹²⁵ There are several excellent reviews that discuss recent progress in lithium/sulfur cells in detail.¹²⁶⁻¹²⁹

Despite improvements in performance, most cells still rely on liquid electrolytes, the most common of which is a mixture of dimethoxyethane (DME) and 1,3-dioxolane (DOL) doped with LiTFSI. These electrolytes are well-known to be thermodynamically unstable against lithium metal and prone to off-gassing and thermal runaway. Additionally, they offer no resistance to the inevitable growth of lithium dendrites upon cycling. For these reasons, many researchers believe that liquid electrolytes will never be compatible with a lithium metal anode, however employing the pure lithium electrode is necessary to realize the full energy density benefits of this electrochemical pair. Solid-state lithium/sulfur cells offer an avenue to safe, high energy density energy storage.

Recently, Nagao and coworkers have published several papers¹³⁰⁻¹³³ on solid-state lithium/sulfur cells using solid $\text{Li}_2\text{S-P}_2\text{S}_5$ glass ceramics as electrolytes. These studies report impressive room temperature cycling results and very good rate capability. Additionally, such cells display a unique voltage profile upon charging/discharging, suggesting that the reduction of

sulfur is occurring via a fundamentally different mechanism than has been previously identified in lithium-sulfur cells. However, these cells rely on high external pressures on the cell stack to maintain contact and the glass ceramics are not stable against pure lithium metal, so a lithium-indium alloy must be used as the negative electrode, reducing the voltage and specific energy of the cell. Finally, they are unable to obtain very high loadings of sulfur in their cells and the processing constraints of their materials may make such cells impractical beyond the laboratory.

Polymer electrolytes offer an alternative approach to achieve solid-state lithium/sulfur cells, however the few previous studies have had similar limitations as traditional liquid cells, including dendrite growth, poor utilization of the active materials, and inability to prevent diffusion of the polysulfides out of the cathode matrix.^{99, 134-136} Previous work from our group has shown that block copolymer electrolytes, specifically polystyrene-*block*-poly(ethylene oxide) (SEO) doped with LiTFSI, have high ionic conductivity at elevated temperature⁹ and sufficiently high modulus to slow the formation of dendrites.¹³ Additionally, the system has been shown to form a stable interface with lithium as well as maintain intimate contact upon cycling. Having satisfied concerns pertaining to the lithium metal anode, and inspired by recent success of sulfur confinement strategies, the purpose of this study was to evaluate the performance of nanostructured block copolymer electrolytes in solid-state lithium/sulfur cells, and determine if they can be used to overcome some of the challenges presented by the sulfur cathode. A schematic of such a cell is shown in Figure 8-1. Several strategies were employed to improve the cell performance, including electrolyte additives, polymer-ceramic hybrid electrolytes, and carbon-sulfur composites as active material. The results of this study improved our understanding of the nanostructured electrolyte and identified failure mechanisms of these cells, clearing the path for future researchers.

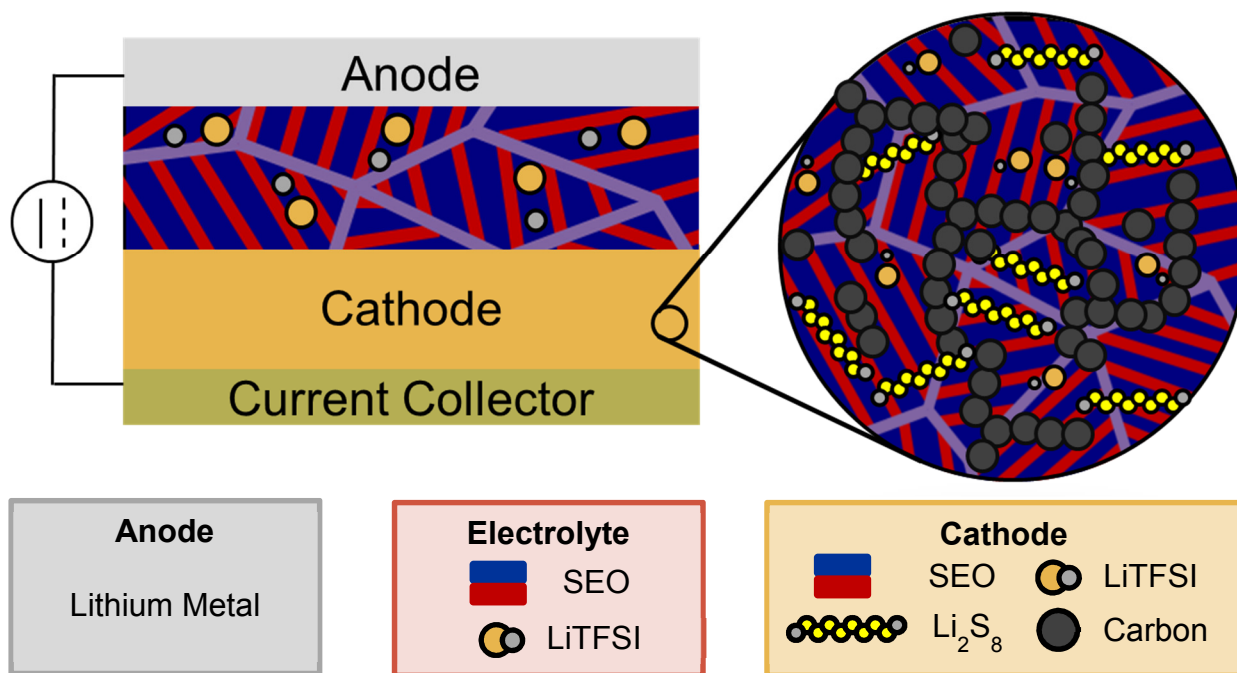


Figure 8-1 Schematic of solid-state lithium/sulfur cell.

8.1 Cell Preparation

8.1.1 Electrolyte Preparation

Electrolytes for this study were prepared exclusively with SEO(240-269) due to its ability to consistently form thin, free-standing membranes. The copolymer and salt (from 0.2 to 1 g total) were dissolved in NMP to achieve roughly 10% solids by weight. The mixture was dissolved with stirring and gentle heating for several hours until the solution was homogeneous. Meanwhile, the solvent caster was prepared by leveling and pre-heating to 60 °C. Nickel foil was cut outside the glovebox, cycled through the large antechamber, placed on the solvent caster, and cleaned with roughly 1 mL of NMP. The doctor blade was leveled and set to the desired height outside the glovebox, cycled through the small antechamber, and placed on the solvent caster. The vacuum pump was switched on immediately prior to casting. Once the solution was dissolved and allowed to cool to roughly room temperature, it was poured on the nickel foil in front of the doctor blade. The doctor blade was pushed across the caster using the motor at low speed. The films were allowed to dry in place overnight, then carefully removed from the nickel foil using a razorblade and tweezers. The freestanding film was then carefully wrapped in the nickel foil and dried overnight in the antechamber under vacuum with heating at 90 °C. For electrolytes that contained lithium polysulfides, the maximum temperature used for casting and drying was 50 °C to avoid sublimation of the sulfur.

The final thickness of the electrolyte depends strongly on several parameters, including the viscosity of the solution, height of the doctor blade, as well as temperature of the solvent caster. In most cases, the doctor blade was set at roughly 22 ticks (550 μm) for SEO/LiTFSI mixtures at 10 wt% solids in NMP cast at 60 °C to obtain a roughly 30 μm thick film. The appropriate values for these parameters were determined empirically, and they typically do not scale linearly. Variations in thickness of 20-30% across a single membrane were common. Occasionally, despite using well-tested conditions, the resulting film would be too thin to peel off the nickel foil.

8.1.2 Cathode Preparation

Solid state cathodes prepared in this study are comprised of three components, each with a distinct role:

Function	Material
Active Material	Li_2S_8
Electron Conductor	Carbon black
Ion Conductor	SEO/LiTFSI
Binder	

Table 8-1 Cathode components and their function.

Cathodes for this study were prepared exclusively with SEO(240-269) as the polymer binder. All cathodes, unless otherwise noted, were prepared with sulfur in the form of dissolved Li_2S_x where $x_{\text{av}} = 8$ by reacting stoichiometric quantities of S_8 and Li_2S in solution. This was done to

ensure homogeneous distribution of the active material throughout the cathode and eliminate the need to pre-process (e.g. ball mill) the active material. A major constraint on cathode formulation was the minimum solution volume (approximately ~3.5 mL) required by the homogenizer. Since a concentration of approximately 15% solids by weight is desired to achieve a sufficiently high viscosity, a minimum of about 0.5 g material was necessary for each cathode.

First, all the dissolvable components (SEO, LiTFSI, S₈ and Li₂S) of the slurry were weighed into a vial containing a stir bar. A quantity of LiTFSI was added such that the molar ratio of lithium ions from LiTFSI to ethylene oxide moieties was equal to 0.085. Sufficient NMP was then added so that the final slurry would contain ~15% solids by weight. The mixture was dissolved with stirring and gentle heating for several hours until the solution was homogeneous. It should be noted that neither S₈ nor Li₂S dissolves in NMP, however they react readily in solution to form soluble lithium polysulfides. Next, the stir bar was removed and carbon black (Denka) was added to the vial. The slurry was then homogenized at 15K RPM on a homogenizer (Polytron) for three intervals of approximately 5 minutes. The high shear forces generated during homogenization cause the temperature of the slurry to increase; this limits the duration of each interval before the slurry must be allowed to cool.

While the slurry is allowed to cool between homogenizations, the solvent caster was prepared by leveling and pre-heating to 50 °C. Electrochemical grade aluminum foil was cut outside the glovebox, cycled through the large antechamber, placed on the solvent caster, and cleaned with roughly 1 mL of NMP. The doctor blade was leveled and set to the desired height outside the glovebox, cycled through the small antechamber, and placed on the solvent caster. The vacuum pump was switched on immediately prior to casting. After the final homogenization, the slurry was immediately poured on the aluminum foil in front of the doctor blade. The doctor blade was pushed across the caster using the motor at low speed. The films were allowed to dry in place overnight, then dried overnight in the antechamber under vacuum with heating at 50 °C. The homogenizer needs to be cleaned immediately after casting to prevent the slurry from drying inside the mixing tip.

No elemental analysis was performed to ensure that sulfur was not lost during the drying process; it is very possible that some sulfur is lost. The amount of sulfur lost will depend on the composition of the cathode, contact with heating surface in antechamber, etc. For the purposes of this study, it did not make a qualitative impact on the results if the specific capacities were underestimated, but as performance improves, this will become more important.

For some experiments, the cathode was ‘calendared’ using the pneumatic hot press in the dry glovebox. In order to do this, a small portion of the cathode was placed in an FEP bag, vacuum sealed in a pouch, and transported to the dry glovebox. The pressure and temperature of the hot press were set as desired, then the cathode was pressed (while remaining sealed in the pouch cell) for a minimum of four one-minute intervals with a 90° rotation between intervals. The sealed cathodes were transported back to the sulfur glovebox. Prior to pressing, the cathodes typically exhibited a matte appearance while after pressing they had a glossy appearance.

8.1.3 Cell Assembly

Electrolytes, cathodes, and lithium foil were punched from larger sheets with 9/16”, 7/16” and 1/2” diameters respectively. The thickness of the cathode and electrolyte were measured with a micrometer, and the weight of the cathode was carefully determined using an analytical balance.

The cathode was centered on the electrolyte, placed inside an FEP bag, and gently handpressed at room temperature until resistance was felt. The assembly was rotated and pressed several more times to ensure even contact. Next the lithium metal was centered on the electrolyte/cathode bilayer and both were placed inside a pouch. Gentle pressure was applied with the thumb on the outside of the pouch to affix the two components. Finally the tabs were affixed to the cell using adhesive Kapton tape, with an aluminum tab on the cathode and nickel tab on the anode. Small pieces of adhesive Kapton tape were necessary to secure the components within the pouch before sealing. Each edge was double sealed using the vacuum sealer and the chamber was allowed to pull vacuum for 90 seconds before the final edge of the cell was sealed. A visual overview of the cell assembly process is shown in Figure 8-2.

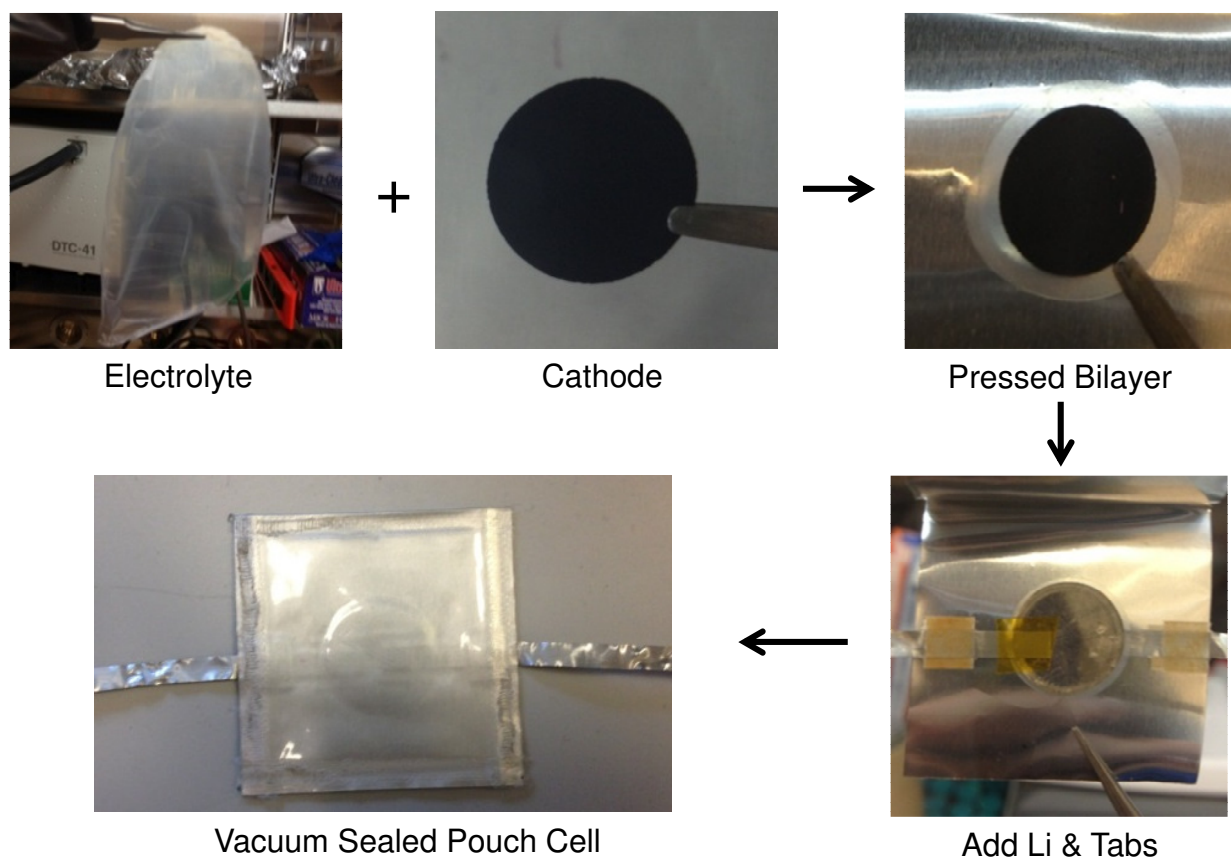


Figure 8-2 Solid-state lithium/sulfur cell assembly process.

8.1.4 Cycling

Cells were annealed for at least six hours at 90 °C before cycling on a 64-channel battery cycler (Maccor). Since cells were assembled with the sulfur in a nearly charged state, the initial step was a discharge at low current density ($10 - 66 \mu\text{A cm}^{-2}$). Subsequent cycling was all done at a higher current density ($40 - 164 \mu\text{A cm}^{-2}$), with one hour rest after each step. Since the area of the cathode was very nearly 1 cm^2 (0.97 cm^2), it is assumed that current passed is the same as current density. Capacity limits were set on both charging and discharging steps so that the program would advance when the theoretical capacity had been reached. The upper voltage limit was always 3.0

V. When the cell contained LiNO_3 , the lower limit was 1.7 V, otherwise the lower limit was 1.5 V.

8.2 Results

8.2.1 Cathode Optimization

Traditional liquid-cell recipes for sulfur cathodes are inappropriate for solid-state cells due to the fact that the polymer electrolyte must act as both binder and ion conductor in the solid-state cathode. Consequently, one of the initial objectives of this study was to explore the composition space and find a suitable recipe for the sulfur cathodes.

Each of the cathode components was varied systematically and a total of eleven compositions were tested, as detailed in Table 8-2. This set of compositions was by no means exhaustive, however was intended to serve as a starting point for the particular system used in this study. The optimized composition for any system depends on many other considerations such as slurry processing and cathode calendaring conditions, as well as active material form.

Carbon: SEO/LiTFSI	Sulfur Loading (as Li_2S_8)				
	10%	25%	40%	60%	70%
2:1	X	Cathode 4 50% Carbon 25% SEO/LiTFSI	Cathode 7 40% Carbon 20% SEO/LiTFSI	X	X
1:1	Cathode 2 45% Carbon 45% SEO/LiTFSI	Cathode 5 38% Carbon 38% SEO/LiTFSI	Cathode 8 30% Carbon 30% SEO/LiTFSI	Cathode 11 20% Carbon 20% SEO/LiTFSI	Cathode 13 15% Carbon 15% SEO/LiTFSI
1:2	X	Cathode 6 25% Carbon 50% SEO/LiTFSI	Cathode 9 20% Carbon 40% SEO/LiTFSI	Cathode 12 13% Carbon 27% SEO/LiTFSI	X
1:3	X	X	X	Cathode 14 10% Carbon 30% SEO/LiTFSI	X

Table 8-2 Cathode compositions for optimization study.

Table 8-3 provides detailed characteristics of each cell tested in the cathode optimization study. The cell names assume the form XX.Y.Z, where XX are the initials of the individual whom assembled the cell, Y corresponds to a specific cathode composition found in Table 8-2, and Z is the number of the cell in the series. For example, cell RY.4.8 is the eighth cell that RY (Rodger Yuan) assembled using cathode composition 4.

Cell	Electrolyte		Cathode				1 st Discharge			Cycling		
	L μm	m mg	m _s mg S	L μm	ρ _c g cm ⁻³	S _{ideal} mAh	i _{D,0} μA cm ⁻²	C/X	S ₀ mAh g ⁻¹ S	i μA cm ⁻²	C/X	Notes
RY.2.3	42	2.9	0.3	45	0.66	0.5	10	45	335	40	11	Cycled well
RY.2.4	38	3.5	0.3	47	0.77	0.6	10	55	196	40	14	
RY.2.5	34	2.2	0.2	38	0.60	0.3	10	35	249	40	9	
RY.4.5	36	4.3	1.0	68	0.65	1.7	10	169	104	40	42	Cycled initially, then infinite charging or cell failure. Strange Discharges.
RY.4.6	33	4.2	1.0	68	0.64	1.7	10	168	89	40	42	
RY.4.7	32	4.5	1.1	68	0.68	1.8	10	177	65	40	44	
RY.4.8	30	4.2	1.0	64	0.68	1.7	10	166	104	40	42	
RY.5.5	28	2.1	0.5	25	0.87	0.8	10	83	381	40	21	Cycled initially, then infinite charging or cell failure
RY.5.6	28	2.0	0.5	25	0.81	0.8	10	78	224	40	19	
RY.5.7	38	2.2	0.5	21	1.08	0.9	10	87	300	40	22	
RY.5.8	39	2.1	0.5	31	0.71	0.8	10	85	268	40	21	
RY.6.1	36	1.3	0.3	16	0.86	0.5	10	53	816	40	13	Mostly infinite charging with one cell cycling.
RY.6.2	36	3.0	0.7	16	1.91	1.2	10	118	1013	40	29	
RY.6.3	36	1.0	0.2	16	0.64	0.4	10	40	792	40	10	
RY.6.4	36	2.5	0.6	16	1.61	1.0	10	99	938	40	25	
RY.7.1	32	4.8	1.8	42	1.18	3.0	10	304	351	40	76	Infinite Charging. Strange Discharge
RY.7.2	44	5.1	1.9	42	1.26	3.3	10	326	311	40	81	
RY.7.4	28	5.2	2.0	42	1.28	3.3	10	330	-	40	82	
RY.8.1	43	4.2	1.6	34	1.27	2.7	10	266	552	40	67	Infinite Charging
AT.8.1	43	4.1	1.6	36	1.17	2.6	10	260	342	40	65	
AT.8.2	55	4.0	1.5	34	1.21	2.5	10	254	220	40	63	
AT.8.3	40	3.1	1.2	35	0.92	2.0	10	199	218	40	50	
RY.9.1	41	3.6	1.4	62	0.59	2.3	10	226	-	40	57	Infinite Charging
RY.9.2	44	3.4	1.3	40	0.88	2.2	10	218	-	40	54	
RY.9.3	36	3.6	1.4	43	0.86	2.3	10	228	485	40	57	
RY.9.4	29	3.5	1.3	36	1.00	2.2	10	222	750	40	55	
RY.11.1	33	3.4	1.9	20	1.8	3.2	10	323	521	40	81	Infinite Charging
RY.11.2	39	3.3	1.9	20	1.7	3.1	10	314	-	40	78	
RY.12.1	39	2.4	1.4	22	1.12	0.6	10	228	-	40	57	Mostly Infinite Charging
RY.12.2	38	2.2	1.3	21	1.10	0.6	10	212	546	40	53	
RY.12.3	32	0.8	0.5	18	0.46	0.6	10	76	509	40	19	
RY.12.4	28	0.5	0.3	11	0.44	0.4	10	44	415	40	11	
RY.12.5	32	3.4	2.0	33	1.07	1.0	10	327	-	40	82	
RY.12.6	28	1.7	1.0	18	0.97	0.6	10	162	523	40	40	
RY.13.1	37	4.8	3.2	44	1.1	5.3	10	533	573	40	133	Infinite Charging
RY.13.2	32	5.8	3.9	48	1.3	6.5	10	647	597	40	162	
RY.14.1	28	0.9	0.5	10	0.9	0.9	10	86	-	40	21	Infinite Charging
RY.14.2	37	2.4	1.4	22	1.1	2.3	10	228	625	40	57	
RY.14.3	31	2.8	1.6	24	1.2	2.7	10	266	598	40	67	

Table 8-3 Cathode optimization cell characteristics.

Electrolyte was SEO(240-269) with $r = 0.085$ LiTFSI. Cathodes pressed at 80 °C with cylinder pressure of 60 psi. Cathode weight and thickness do not include current collector. Cells cycled at 90 °C. Cells without a first discharge capacity listed failed to discharge properly. Samples in bold cycled.

It is important to acknowledge the difficulty in systematically controlling a single variable in the assembly and testing of full electrochemical cells. For example, the current for the initial discharge, $i_{D,0}$, was fixed at 10 μA for the cathode optimization study in order to ensure a constant current density across all the cells. However, due to variations in thickness and sulfur loadings between different cathodes and even thickness variations across the same cathode, the discharge rate varied dramatically between cells in this study. The rates are measured relative to the theoretical capacity of the cell, S_{ideal} , using

$$\frac{C}{X} = \frac{S_{ideal}}{i} \quad (8-1)$$

where

$$S_{ideal} = m_s * 1672 \text{ mAh g}^{-1} \quad (8-2)$$

and X is the number of hours to discharge S_{ideal} at current i , and m_s is the mass of sulfur. For example, an hourly discharge rate of $C/2$ means that theoretical capacity of the cell would be reached after 2 hours of discharge. The fastest initial discharge in Table 8-3 was $C/35$ for RY.2.5 and the slowest was $C/647$ for RY.13.2. The variation in discharge rate between cells influences the cycling performance. Figure 8-3 shows the specific capacity of the first discharge, $S_{D,0}$, versus discharge rate for the Cathode 6 and Cathode 12 cells. The Cathode 6 cells show a strong dependence on discharge rate. The Cathode 12 cells show a weaker dependence and plateaus at sufficiently slow discharge rates. This phenomenon is well understood in electrochemical cells, however complicates the ability to compare performance. If on the other hand, the cathode optimization study had been conducted with a fixed discharge rate, then the current density would have varied wildly between cells.

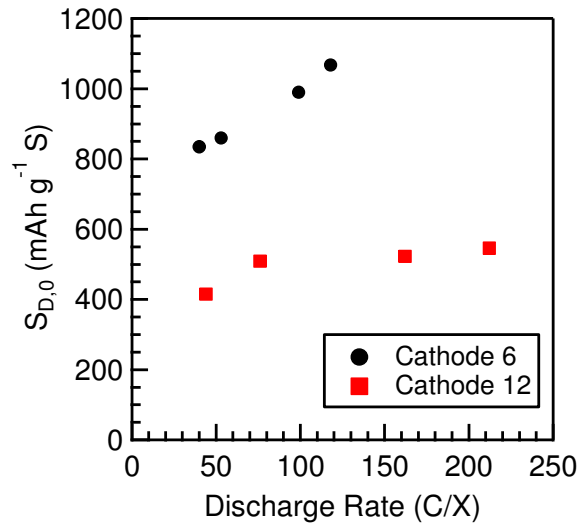


Figure 8-3 Effect of cycling rate on specific capacity. Discharge rate (C/X) versus first discharge capacity, $S_{D,0}$, for Cathode 6 and Cathode 12 cells in Table 8-3.

Figure 8-4 shows the voltage profile during cycling of cell RY.9.3. After an initial discharge, the cell charged until it reached the pre-programmed cut-off capacity equal to S_{ideal} . This behavior is signature of the parasitic polysulfide shuttle.⁹⁰ Since the cell appeared to charge indefinitely, it signifies that the polysulfides were being reduced via the polysulfide shuttle at the same rate as oxidation of the polysulfides was occurring in the cathode. As a result, the Coloumbic efficiency, E_C is below unity where

$$E_c = \frac{S_{D,i}}{S_{C,i}} \quad (8-3)$$

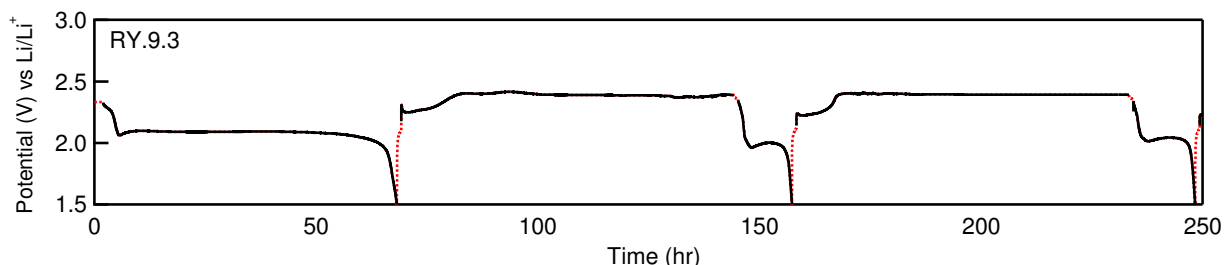


Figure 8-4 Voltage profile for typical cathode optimization cell. Voltage profile for RY9.3. Solid lines show constant current steps and dotted line shows rest step.

In general, compositions with very low sulfur loading did not exhibit a sufficiently robust polysulfide shuttle to cause infinite charging due to a reduced concentration of polysulfides to participate in the shuttle. As sulfur loading increased above 25 wt%, infinite charging was nearly ubiquitous. The only cell with higher sulfur content that was able to cycle for a handful of cycles was RY.12.4, which also had one of the fastest charging rates at C/11. This made it more difficult for the rate of reduction via the polysulfide shuttle to match the rate of oxidation via charging. The overall lack of a significant upper plateau during discharge is further evidence of the self-discharge of the higher-order polysulfides via polysulfide shuttle.

Due to the presence of the polysulfide shuttle, the compositions were evaluated primarily based on the initial discharge of the cells. Of course, this provides no insight into the long-term cycling performance of a given composition. Figure 8-5 presents $S_{D,0}$ from the cathode optimization study normalized by both the active material (Figure 8-5a,b) as well as the total cathode weight (Figure 8-5c,d). The $S_{D,0}$ results are plotted versus sulfur loading (Figure 8-5a,c) as well as versus carbon:SEO/LiTFSI ratio (Figure 8-5b,d). These results show the complex relationship between performance and composition. Cathode 12 (60% Li_2S_8 , 13% C, and 27% SEO/LiTFSI) was selected for further studies.

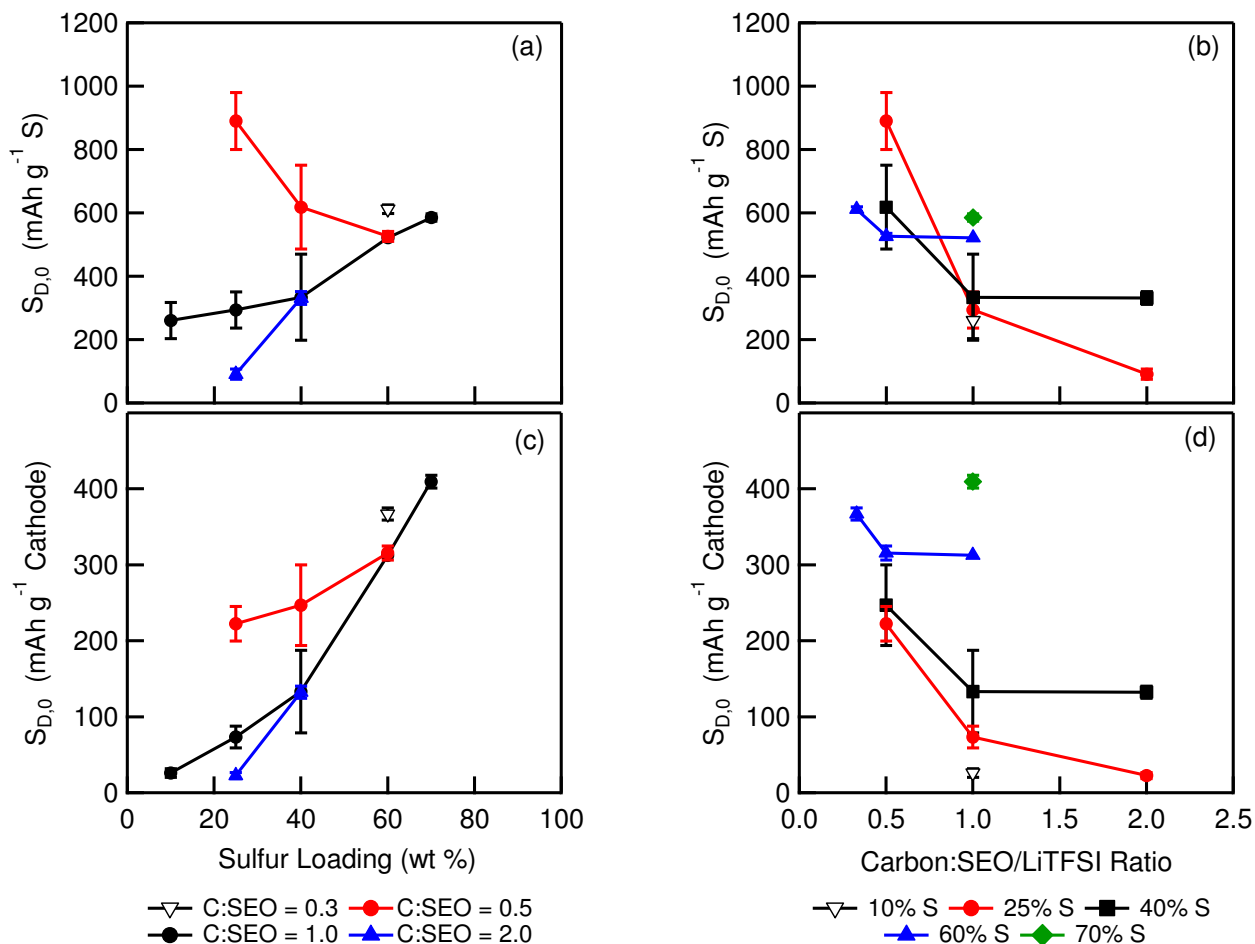


Figure 8-5 Cathode optimization results.

The first discharge capacity, S_0 , normalized by (a), (b) sulfur weight and (c), (d) total cathode weight, is plotted versus (a), (c) sulfur loading and (b), (d) carbon/SEO:LiTFSI ratio.

While cells with $> 25\%$ sulfur were unable to cycle, most of the cells with $\leq 25\%$ sulfur were able to cycle to varying degrees. The cycling results for the best of each of the low-sulfur compositions are presented in Figure 8-6 to give a sense of the cycling performance and voltage profiles of these cells. There are several features in the cycling results related to the mobility of the polysulfides through the electrolyte; these include the low values of E_C and increases in capacity after the initial discharge ($S_{D,1} > S_{D,0}$), despite higher discharge currents. The capacity increases after the initial discharge because there is less time for self-discharge during the 1 hr rest step during cycling than the 6 hr initial annealing step. Additionally, the voltage dip observed at the beginning of the charging step has been observed in liquid cells and is typically attributed to the oxidation and chemical dissolution of the insoluble lithium sulfide into the liquid phase at the beginning of the charge.¹³⁷ Once the formation of the soluble polysulfide intermediate begins, the conductivity increases and the voltage relaxes.

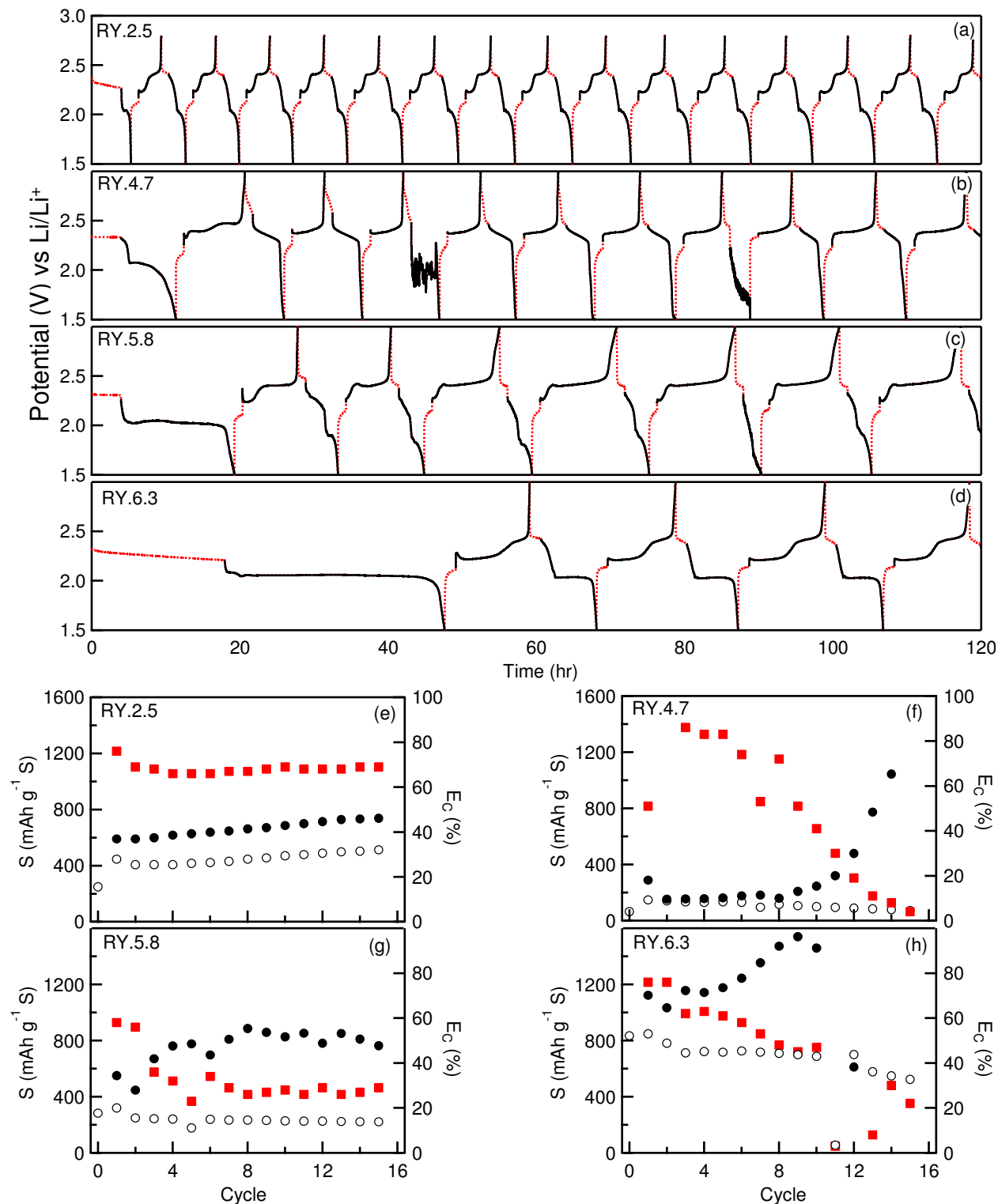


Figure 8-6 Cycling results for cathode optimization cells. Voltage profiles (a) - (d) and cycling performance (e) - (h) of RY.2.5, RY.4.7, RY.5.8, and RY.6.3, respectively. Solid lines show constant current steps and dotted line shows rest step. Left axis shows specific capacity, S , for charge (●) and discharge (○) while right axis shows Coulombic efficiency, E_C (■).

8.2.2 Calendaring Optimization

Calendaring is an important step of cathode processing and allows the tuning of porosity of the final matrix. In typical liquid cells, significant porosity (~20-30%) is desired to allow penetration of the liquid electrolyte into the cathode matrix. This is not necessary in solid cells since the binder and the ion conductor are the same material – in fact there is an argument to eliminate all porosity since voids are insulating and will increase the resistance of the cathode matrix. On the other hand, the sulfur cathode experiences volume expansion during discharge due to incorporation of a large quantity of lithium ions during reduction, resulting in a decrease in density from elemental sulfur (2.07 g cm⁻³) to lithium sulfide (1.66 g cm⁻³). In the cells used in this study, the active material is loaded as Li₂S₈, whose density is unknown but expected to fall at the higher range of those two numbers. Therefore, some porosity might be necessary to accommodate the discharge products.

The hot press has adjustable platen temperatures via temperature controller, and adjustable force via adjustment of the regulator pressure on the gas cylinder. In an attempt to optimize the calendaring procedure, several different temperatures and pressures were used on Cathode 12. Table 8-4 shows the detailed characteristics of the cells used in the calendaring optimization study. In general, un-pressed cathodes had matte appearances while pressed cathodes, regardless of temperature or pressure, appeared glossy.

Cells	Electrolyte		Cathode				Calendaring		1 st Discharge			Cycling	
	L μm	m mg	m _s mg S	L μm	ρ _c g cm ⁻³	S _{ideal} mAh	P psi	T °C	i _{D,0} μA cm ⁻²	C/X	S ₀ mAh g ⁻¹ S	i μA cm ⁻²	C/X
RY.12.S2.0.1	31	2.3	1.3	35	0.68	1.1	0	80	10	219	735	40	55
RY.12.S2.0.2	53	1.7	0.9	37	0.46	0.7	0	80	10	159	653	40	40
RY.12.S2.60.1	21	2.1	1.2	20	1.07	1.0	60	80	10	197	491	40	49
RY.12.S2.60.2	56	2.3	1.3	18	1.30	0.3	60	80	10	216	575	40	54
RY.12.S2.80.1	34	2.0	1.1	26	0.79	0.8	80	80	10	190	651	40	48
RY.12.S2.80.2	24	1.9	1.1	20	0.98	0.8	80	80	10	181	-	40	45
RY.12.S2.100.1	40	2.1	1.2	24	0.92	0.6	100	80	10	203	561	40	51
RY.12.S2.100.2	66	2.0	1.2	21	1.00	0.3	100	80	10	193	643	40	48
AT.12.S2.1	26	2.6	1.5	31	0.88	1.2	0	90	53	47	604	132	19
AT.12.S2.2	26	3.0	1.7	26	1.19	1.0	0	90	60	48	602	150	19
AT.12.S2.3	20	1.7	1.0	19	0.94	1.0	60	90	35	47	618	87	19
AT.12.S2.4	20	2.1	1.2	18	1.22	0.9	60	90	43	47	572	107	19
AT.12.S2.5	31	2.2	1.3	19	1.21	0.6	80	90	45	47	591	112	19
AT.12.S2.6	23	2.4	1.4	22	1.14	1.0	80	90	49	47	-	122	19
AT.12.S2.7	16	2.5	1.4	21	1.21	1.3	100	90	49	48	-	124	19
AT.12.S2.8	19	2.6	1.5	25	1.07	1.3	100	90	52	48	447	130	19

Table 8-4 Calendaring optimization cell characteristics.

Electrolyte was SEO(240-269) with $r = 0.05$ LiTFSI and $r = 0.025$ LiNO₃. Cathode weight and thickness do not include current collector. Cells cycled at 90 °C. Cells without a first discharge capacity listed failed to discharge properly.

Figure 8-7a shows the cathode density, ρ_c , as a function of regulator pressure. The cathode density was calculated by dividing the weight of the cathode material by the measured thickness of the cathode, excluding the current collector in both cases. On average the pressed cathodes exhibited higher density, however the variation was so great that there is essentially no difference in density regardless of calendaring temperature or pressure. Figure 8-7b shows $S_{D,0}$ of cells made with cathodes pressed at different pressures. Again, the difference between the different treatments

was negligible. This surprising result implies that either the cathodes contain no voids or that the calendaring procedure used is not sufficient to change the porosity of the cathode.

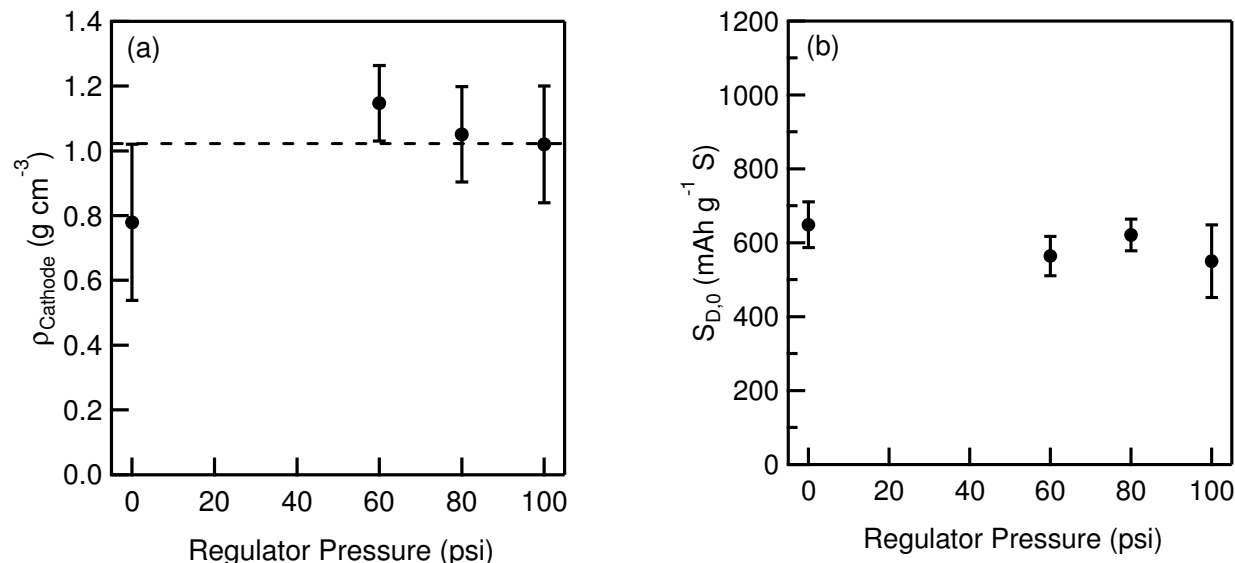


Figure 8-7 Calendaring optimization results. Regulator pressure versus (a) cathode density, ρ_c , and (b) initial discharge capacity, $S_{D,0}$.

Figure 8-8 shows the top-down and cross-sectional X-ray tomography image of a pristine, calendared sample of Cathode 12. Hard X-ray tomography was performed at the Advanced Light Source on beam line 8.3.2 with an energy of 20 keV, a spatial resolution of 1.6 μm , and a beam size of 25 x 5 mm. Despite appearing homogeneous to the eye, the tomography shows 15-20 μm clusters evenly distributed throughout the matrix. These clusters were unexpected and their origin, composition, and persistence upon cycling is unclear and an area for future research.

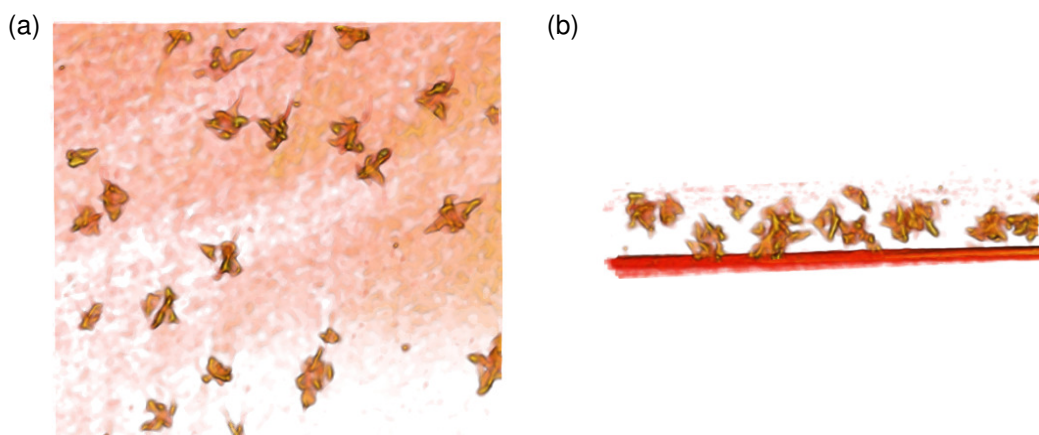


Figure 8-8 X-ray tomography of pressed cathode. Cathode 12 shown from (a) top down and (b) side view with current collector on bottom.

8.2.3 Electrolyte Additives

One strategy to overcome some of the problems associated with the sulfur cathode is to use electrolyte additives. In recent years, it has become commonplace to add small quantities of lithium nitrate (LiNO_3) to the electrolyte. This compound was as an effective way to shut down

the polysulfide shuttle;¹³⁸ the lithium nitrate reacts with the lithium metal to form a passivation layer on the anode surface that is conductive to lithium ions, but does not allow the polysulfide anions to react. More recently some groups have suggested¹³⁹ intentionally seeding the electrolyte with soluble polysulfides (Li_2S_x , $x > 4$) to decrease the concentration gradient between cathode and electrolyte and consequently minimize the diffusion of the polysulfides out of the cathode matrix. Additionally, these polysulfides can serve a dual purpose by replacing traditional charge carriers in the electrolyte, such as LiTFSI.

During the cycling of lithium/sulfur cells, especially those containing additional additives, the electrolyte composition is dynamic and complex. A conductivity study was performed in an attempt to gain a basic understanding of the effects of each of the species on the conductivity of the copolymer. Figure 8-9 shows the conductivity versus total salt concentration for pure LiTFSI, LiNO_3 , and Li_2S_8 , as well as several mixtures. As expected, the highest conductivity is obtained from pure LiTFSI at $r = 0.085$. The conductivity from Li_2S_8 is substantially lower and peaks at $r = 0.06$. The conductivity from LiNO_3 is also lower and a clear maximum was not observed. It is important to keep in mind that once a full cell is assembled, the lithium nitrate is expected to react with the anode and be depleted from the electrolyte. Based on these results, electrolyte compositions were chosen for additional testing in full cells.

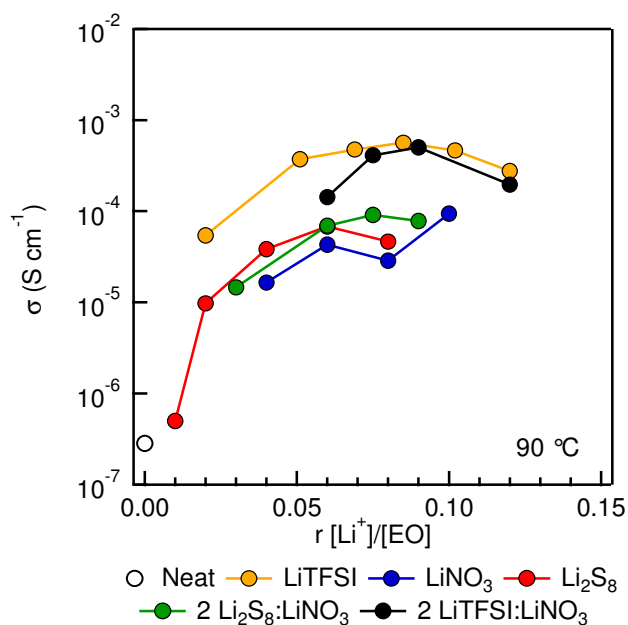


Figure 8-9 Electrolyte additive conductivities.

The ionic conductivity, σ , versus total salt concentration, r , for several pure and mixed salts in SEO(240-269).

8.2.3.1 Lithium Nitrate

In order to study the effect of lithium nitrate on cycling performance of the cells, the traditional SEO/LiTFSI electrolyte was replaced by one containing both LiTFSI and LiNO_3 . Table 8-5 shows the detailed characteristics of the cells used in the lithium nitrate study, where the electrolyte composition was fixed at $r = 0.05$ LiTFSI and $r = 0.025$ LiNO_3 . This concentration was chosen based on the results in Figure 8-9 to provide sufficient LiNO_3 to stop the polysulfide shuttle while maintaining high ionic conductivity in the electrolyte.

Cell	Electrolyte	Cathode					1 st Discharge			Cycling		
	L μm	m mg	m _s mg S	L μm	ρ _c g cm ⁻³	S _{ideal} mAh	i _{D,0} μA cm ⁻²	C/X	S ₀ mAh g ⁻¹ S	i μA cm ⁻²	C/X	Notes
RY.6.S2.1	25	0.7	0.2	11	0.66	0.3	10	28	970	40	7	Cycled well
RY.6.S2.2	23	0.7	0.2	12	0.60	0.3	10	28	858	40	7	
RY.12.S2.3	35	0.6	0.3	38	0.16	0.6	10	57	564	40	14	Most cycled a few times before loss of voltage control and eventual cell failure. Two cycled well
RY.12.S2.4	30	1.9	1.1	19	1.03	1.8	10	181	459	40	45	
RY.12.S2.5	23	1.9	1.1	23	0.85	1.8	10	181	-	40	45	
RY.12.S2.6	26	2.0	1.1	22	0.92	1.9	10	187	518	40	47	
RY.12.S2.7	20	2.0	1.1	22	0.92	1.9	10	187	-	40	47	
AT.12.S2.9	26	2.1	1.2	20	1.08	2.0	42	48	533	105	19	
AT.12.S2.10	25	2.6	1.5	22	1.23	2.5	53	47	623	132	19	
AT.12.S2.11	23	1.8	1.0	26	0.71	1.7	36	48	518	90	19	
AT.12.S2.12	25	2.1	1.2	20	1.10	2.0	43	47	453	107	19	
AT.12.S2.13	30	2.6	1.5	24	1.13	2.5	53	47	-	132	19	
AT.12.S2.14	31	2.7	1.6	23	1.23	2.6	55	47	446	137	19	
AT.12.S2.15	61	2.5	1.4	24	1.07	2.4	50	48	436	125	19	Consistently about 10 cycles before loss of voltage control
AT.12.S2.16	59	2.4	1.3	20	1.22	2.3	47	48	452	119	19	
AT.12.S2.17	44	1.8	1.0	20	0.91	1.7	34	49	555	84	20	
AT.12.S2.18	47	1.4	0.8	25	0.59	1.4	27	50	505	68	20	
AT.12.S2.19	43	2.0	1.1	24	0.86	1.9	38	50	582	95	20	
AT.12.S2.20	49	2.3	1.3	21	1.13	2.2	44	50	591	109	20	
RY.13.S2.1	25	0.3	0.2	15	0.41	0.4	10	37	459	40	9	Mixed results
RY.13.S2.2	29	0.6	0.4	14	0.25	0.7	10	67	581	40	17	
AT.13.S2.1	28	0.7	0.5	14	0.54	0.8	17	48	-	43	19	
AT.13.S2.2	23	0.3	0.2	7	0.39	0.3	6	49	350	16	18	
AT.13.S2.3	92	2.8	1.9	40	0.72	3.1	66	47	130	164	19	
AT.13.S2.4	93	0.5	0.4	14	0.39	0.6	12	49	-	31	19	
AT.13.S2.5	40	0.3	0.2	11	0.28	0.3	7	48	628	17	20	

Table 8-5 LiNO₃ cell characteristics.

Electrolyte was SEO(240-269) with $r = 0.05$ LiTFSI and $r = 0.025$ LiNO₃. Cathode weight and thickness do not include current collector. Cells cycled at 90 °C. Cells without a first discharge capacity listed failed to discharge properly. Samples in bold cycled well.

Figure 8-10a shows the voltage profile for cell AT.12.S2.9. The cell cycled nicely for about four cycles, indicating that the addition of the lithium nitrate was working as expected and suppressing the polysulfide shuttle that had previously resulted in infinite charging. On the 5th charge, the cell loses voltage control and the charging profile become noisy. At this point, the cell charges until it reaches its cutoff capacity and then discharges normally. This continues for several cycles until the cell fails completely and is unable to charge or discharge. This behavior was commonly seen in cells in Table 8-5. The only variable that systematically increased the longevity of these cells was increasing the electrolyte thickness (cells AT.12.S2.15-20). Figure 8-10b shows the voltage profile for AT.12.S2.16 (60 μm electrolyte), which looks very similar to that of AT.12.S2.09 (26 μm electrolyte), except that there are more cycles before the cell begins to fail. AT.12.S2.16 begins to lose voltage control upon charging on the 10th charge and ultimately fails.

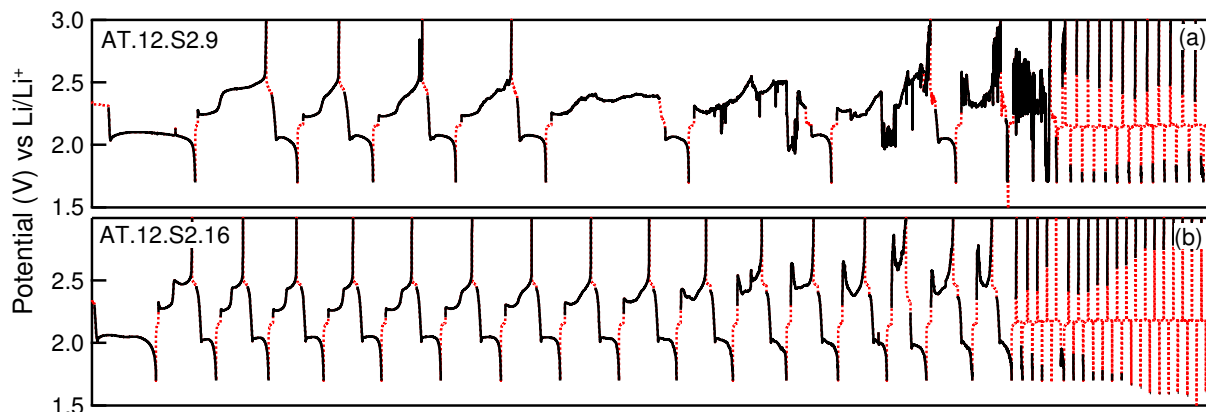


Figure 8-10 Voltage profiles for typical LiNO_3 cells.

Voltage profiles for (a) AT.12.S2.9 and (b) AT.12.S2.16. Solid lines show constant current steps and dotted line shows rest step.

In order to better understand the origins of the cell failure, X-ray tomography was performed on AT.12.S2.16 after failure. Figure 8-11 shows a cross-sectional image of the cell stack. This non-destructive 3D imaging technique shows that the electrolyte/lithium metal interface is riddled with voids. This poor contact explains the loss of voltage control and eventual cell failure. There is no contrast between the cathode matrix and the electrolyte.

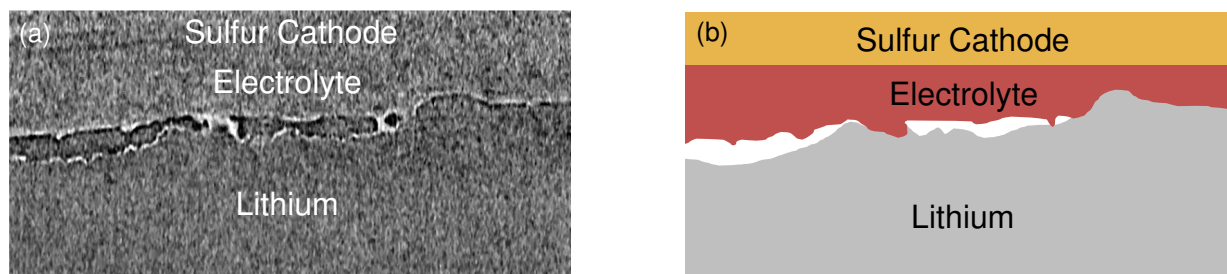


Figure 8-11 Tomography of failed solid-state Li/S cell.

(a) Cross-sectional tomography image and (b) corresponding schematic of AT.12.S2.16 after failure.

While many of the cells suffered the same fate as those in Figure 8-10, there are always exceptional cells. Figure 8-12 shows the cycling performance of the best cell from each of the cathodes in Table 8-5. While the specific capacities vary between cathode compositions, there are several trends that are common between the cells. The Coloumbic efficiency is much higher compared to the cells cycled without LiNO_3 (Figure 8-6), however it is still less than unity. This loss of efficiency suggests the polysulfide shuttle has been suppressed but not been completely eliminated. Additionally, all of the cells exhibit capacity fade, suggesting that active material is diffusing out of the cathode matrix and becoming unavailable for further redox reactions.

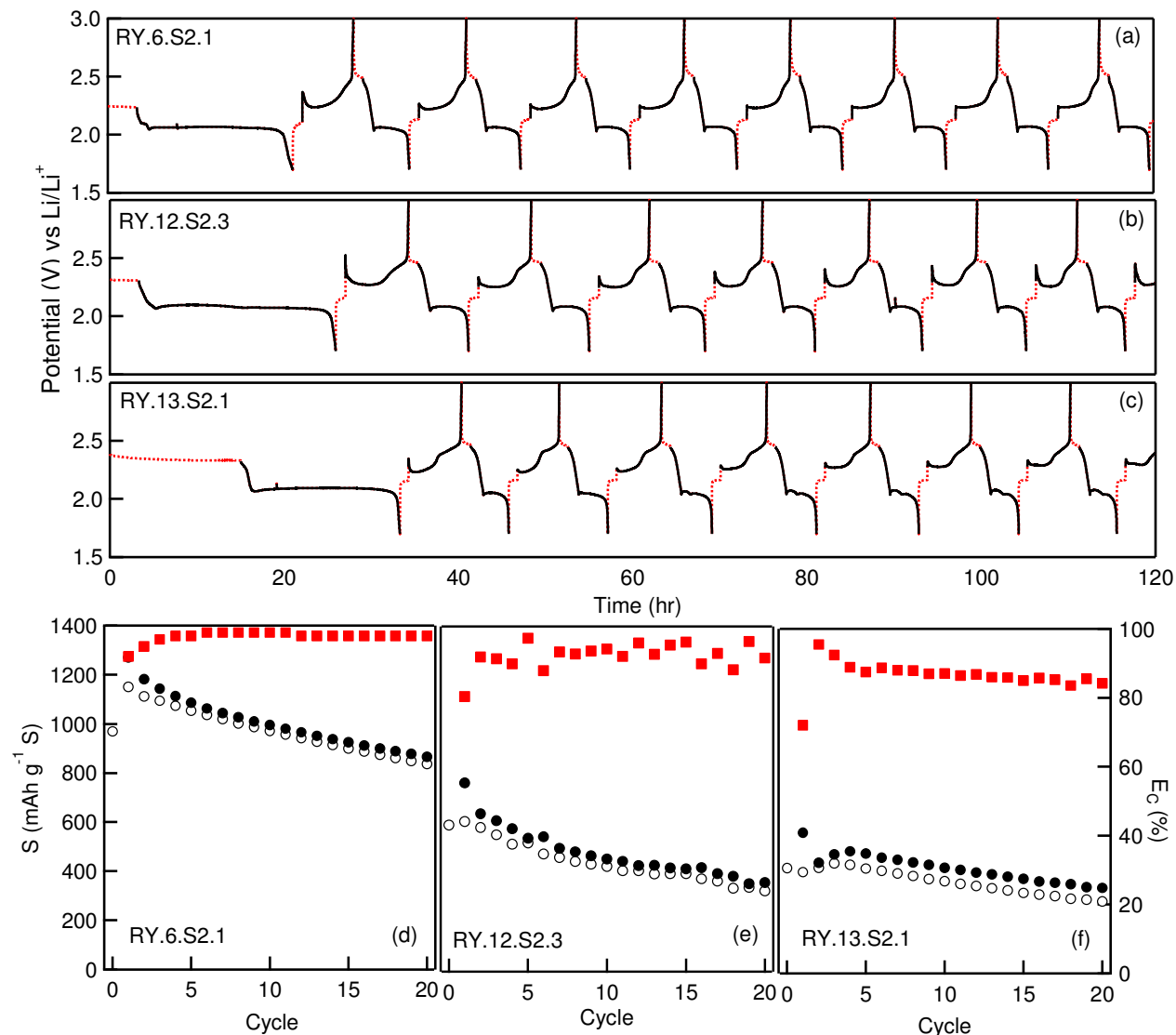


Figure 8-12 Cycling performance for champion LiNO_3 cells. Voltage profiles (a) - (c) and cycling performance (d) - (f) of RY.6.S2.1, RY.12.S2.3, and RY.13.S2.1, respectively. Solid lines show constant current steps and dotted line shows rest step. Left axis shows specific capacity, S , for charge (●) and discharge (○) while right axis shows Coloumbic efficiency, C_E (■).

8.2.3.2 Lithium Polysulfides

One way to prevent the diffusion of active material out of the cathode is to reduce the concentration gradient by seeding the electrolyte with polysulfides. In order to study the effect of seeding the electrolyte with lithium polysulfides on the cycling performance of the cells, the SEO/LiTFSI/LiNO_3 electrolyte was replaced with one containing both Li_2S_8 and LiNO_3 , but no LiTFSI . Table 8-6 shows the detailed characteristics of the cells used in the lithium polysulfide study, where the electrolyte composition was fixed at $r = 0.06 \text{ Li}_2\text{S}_8$ and $r = 0.03 \text{ LiNO}_3$. This concentration was chosen based on the results in Figure 8-9 to provide sufficient LiNO_3 to stop the polysulfide shuttle while maintaining high ionic conductivity in the electrolyte. Based on the

results observed in Figure 8-10, the electrolytes were made intentionally thick in the hopes of getting a large number of cycles before failure.

Cell	Electrolyte			Cathode			1 st Discharge			Cycling		Notes
	L μm	m mg	m_s mg	L μm	ρ_c g cm^{-3}	S_{ideal} mAh	$i_{D,0}$ $\mu\text{A cm}^{-2}$	C/X	S_0 $\text{mAh g}^{-1} \text{S}^{**}$	i_D $\mu\text{A cm}^{-2}$	C/X	
AT.12.S5.1	71	1.5	0.8	26	0.58	1.4	28	50	355	70	20	
AT.12.S5.2	75	2.6	1.5	28	0.95	2.4	49	50	479	122	20	
AT.12.S5.3	59	1.8	1.0	30	0.61	1.7	34	49	424	84	20	
AT.12.S5.4	75	1.6	0.9	15	1.10	1.5	30	51	677	76	20	

Table 8-6 Li_2S_8 cell characteristics.

Electrolyte was SEO(240-269) with $r = 0.06 \text{ Li}_2\text{S}_8$ and $r = 0.025 \text{ LiNO}_3$. Cathode weight and thickness do not include current collector. Cells cycled at 90°C . Cells without a first discharge capacity listed failed to discharge properly. Samples in bold cycled well. ****An honest accounting of active material utilization would include the active material in the electrolyte, however this was ignored for the purposes of this study.**

Figure 8-13 shows the voltage profile for a typical cell from Table 8-6. They typically exhibited a normal initial discharge, but upon the very first charging, would lose voltage control and charge until the capacity cut-off was reached.

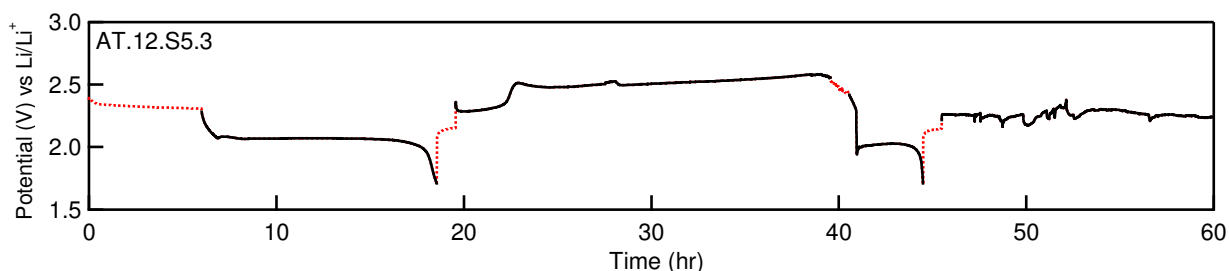


Figure 8-13 Voltage profile for a typical Li_2S_8 cell.

Voltage profile for AT.12.S5.3. Solid lines show constant current steps and dotted line shows rest step.

During the preparation of cells with the polysulfide-containing electrolyte, it was observed that the mechanical properties of the electrolyte films changed substantially. Figure 8-14a shows a picture of the SEO/LiTFSI/ LiNO_3 electrolyte. The film is colorless, translucent, pliable, and sticks to itself and lithium metal when pressure is applied. Figure 8-14b shows an image of the SEO/ Li_2S_8 / LiNO_3 electrolyte. The film has a deep red color, indicative of the presence of the polysulfides. More surprisingly, the film has become much tougher and less able to stick to other materials, including the cathode and lithium metal anode upon cell assembly.

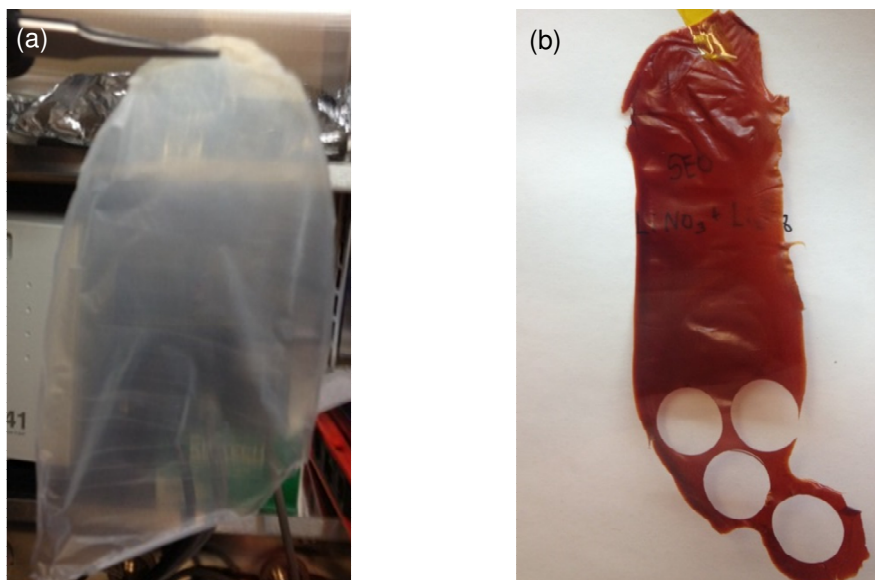


Figure 8-14 Electrolyte membrane comparison.
Picture of (a) SEO/LiTFSI/LiNO₃ and (b) SEO/Li₂S₈/LiNO₃ electrolyte film.

Based on the tomography results and the qualitative differences in the film properties in Figure 8-14, an understanding of the mechanism of cell failure began to emerge. It appears that polysulfides change the material properties of the copolymer, making it stiffer and more rigid. In the full electrochemical cell, polysulfides are able to diffuse into the electrolyte, as evidenced by the polysulfide shuttle, and change its material properties. When this change occurs in the electrolyte near the lithium metal interface, the electrolyte becomes unable to maintain good contact with the lithium metal interface, resulting in delamination. Initially, this delamination occurs locally and manifests as a loss of voltage control upon charging, but eventually the problem becomes widespread resulting in cell failure.

8.2.4 Carbon-Sulfur Composite Active Materials

Since the nanostructured electrolytes proved an ineffective ‘confinement’ strategy in these solid state cells, we attempted to create cells with a carbon-sulfur composite material with a proven ability to confine sulfur. Most of the carbon-sulfur composites reported in the literature are three-dimensional structures that rely on liquid electrolytes to penetrate deep into nanopores to provide ionic conductivity to the active material. Due to the inability of the polymer electrolyte to penetrate into such small pores, we were limited in our selection of carbon-sulfur composites. We obtained samples of a graphene oxide-sulfur (GO-S) composite from Professor Elton Cairns at Lawrence Berkeley National Laboratory. Graphene oxide has a planar, two-dimensional morphology which we hoped would be more suitable with a polymer electrolyte.

The incorporation of the GO-S composite presented several complications regarding the preparation of the cathode. The composite was dried in the antechamber at 50 °C under active vacuum before introduction into the glovebox, as directed by our collaborator. A funnel was placed over the jar containing the composite to protect the jar from the high pressures inlet of argon during refilling of the evacuated antechamber. After drying, crystallized sulfur was found on the interior of the funnel, indicating that some sulfur had sublimed from the composite and recrystallized on the inside of the funnel during drying. The uncontrolled loss of sulfur will obviously call into

question the overall sulfur content of the cathode, and subsequently the cycling rates and specific capacities of the cells created with this material. However, the calculations presented assume no loss of sulfur. The GO-S composite was reported by our collaborators to contain 50% sulfur by weight.

Due to limited quantities of the GO-S composite provided, cathodes containing the GO-S composite were slurry cast from a solution that was only 3-4% solids by weight. This meant the viscosities of the slurries were much lower than those used for other cathodes reported in this dissertation. The slurry casting resulted in cathodes with uneven, inhomogeneous appearance. Most unusually, fairly large GO-S particles appeared intact after homogenization and it appeared these particles poked very small holes in the aluminum current collector as it dried, allowing some of the slurry to leak through the current collector. This happened consistently for each of the several cathodes that were cast with this material. Table 8-7 shows the detailed characteristics of the cells used in the GO-S composite study. The cathode composition was 50% GO-S composite, 25% carbon, and 25% SEO/LiTFSI.

Cell	Electrolyte	Cathode					1 st Discharge			Cycling		
	L μm	m mg	m _s mg	L μm	ρ _c g cm ⁻³	S _{ideal} mAh	i _{D,0} μA cm ⁻²	C/X	S ₀ mAh g ⁻¹ S**	i _D μA cm ⁻²	C/X	Notes
GO.1	32	1.0	0.3	27	0.39	0.4	10	43	333	40	11	Cycled Well
GO.2	40	0.8	0.2	18	0.46	0.3	10	33	465	40	8	
GO.3	27	0.9	0.2	20	0.46	0.4	10	38	471	40	10	

Table 8-7 GO-S cell characteristics.

Electrolyte was SEO(240-269) with $r = 0.085$ LiTFSI. Cathode weight and thickness do not include current collector. Cells cycled at 90 °C.

Figure 8-15 shows the cycling performance for a representative cell from Table 8-7. The results show reasonable cycling with low utilization and high, but not perfect efficiency. Previous work with room temperature liquid cells reported extremely high utilization of the sulfur in this composite¹²⁴ with nearly perfect efficiencies. This suggests that either ionic and electronic conductive pathways were not reaching the active material due to poor connectivity or that the sulfur loss upon drying was substantial. Additionally, based on the efficiencies and post-mortem analysis of the cells, it is clear that some of the polysulfides are not confined in the cathode and are able to diffuse into the electrolyte. It is likely that much better cycling results could have been obtained with this composite after further composition optimization, however due to the difficulty acquiring this material and the processing irregularities, it was not pursued beyond initial testing. There is also some concern that the elevated temperatures necessary for cycling with the polymer electrolyte may break the chemical bonds between the sulfur and the graphene oxide surface, rendering ineffective the ‘confinement’ strategy. In general, carbon-sulfur composite materials remain a promising avenue for future research, however care must be taken to ensure the specific characteristics of the composite are compatible with the constraints imposed by a polymer electrolyte.

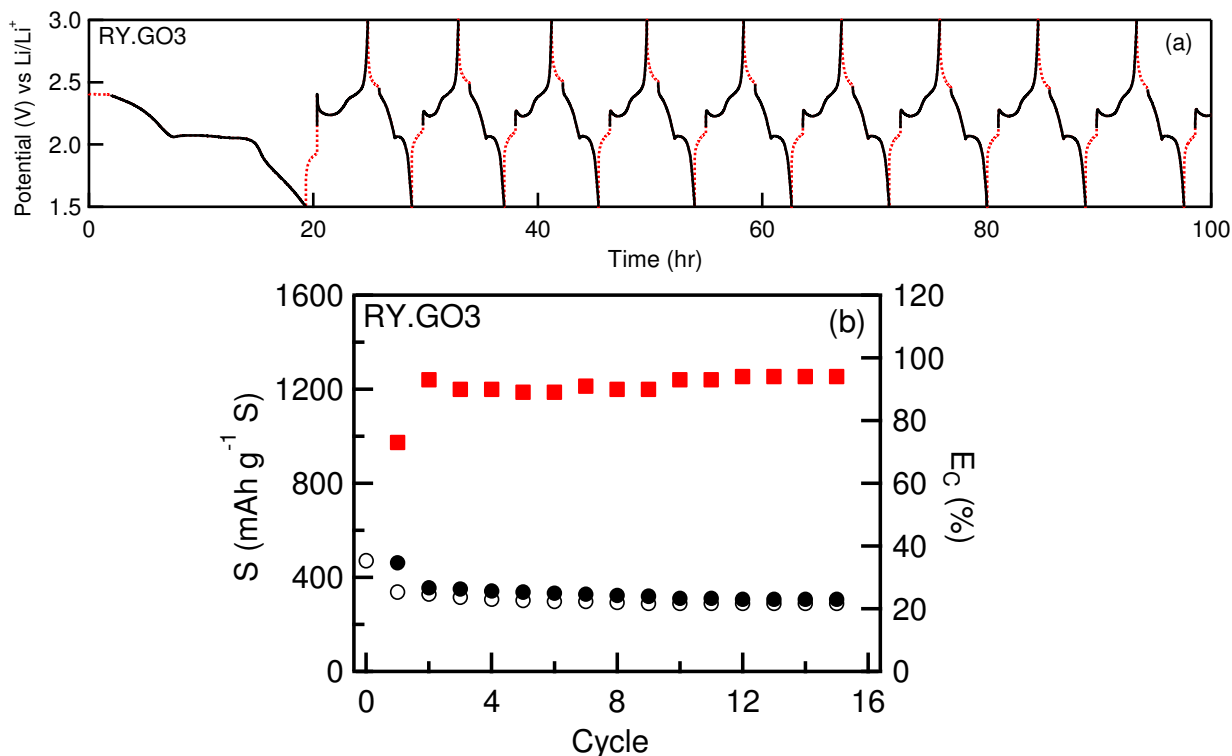


Figure 8-15 Cycling performance of GO-S cells.

Voltage profile (a) and cycling performance (b) of RY.GO.3. Solid lines show constant current steps and dotted line shows rest step. Left axis shows specific capacity, S, for charge ($\bullet$) and discharge ($\circ$) while right axis shows Coulombic efficiency, E_C ($\blacksquare$).

8.2.5 Polymer-Ceramic Hybrid Cells

It became clear that suppressing the polysulfide shuttle was insufficient to enable long-term cycling of the cells. Instead, the polysulfides must be prevented from reaching the electrolyte-anode interface. One strategy is to incorporate an ionically conductive physical barrier, such as a ceramic electrolyte, to block the passage of the polysulfides. Ceramics are the primary alternative to polymers in the field of solid-state electrolytes and offer some significant advantages in some areas such as high modulus and room temperature conductivity as well as a transference number of unity. However, they are often unstable against lithium metal, are brittle and difficult to process, and suffer from poor contact to electrodes. As such, we sought to combine the best properties of each material by creating a cell with a polymer-ceramic hybrid electrolyte, as shown schematically in Figure 8-16. In this configuration, the polymer electrolyte maintains excellent adhesion at the Li metal and ceramic interfaces while the ceramic electrolyte prevents the diffusion of the polysulfides across the cell.

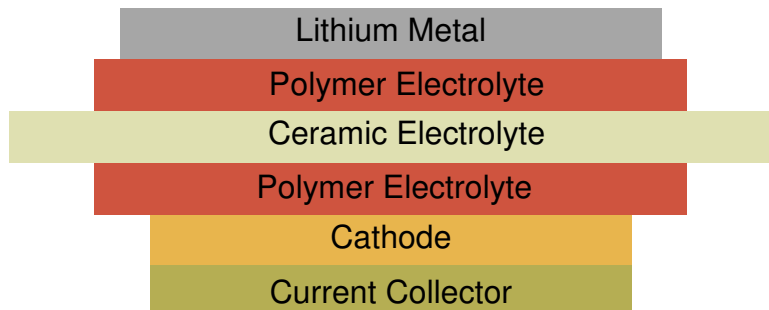


Figure 8-16 Schematic of polymer-ceramic hybrid electrolyte cell.

8.2.5.1 LIC-GC

Initial studies on polymer-ceramic hybrid cells were performed with commercially available Lithium-Ion Conducting Glass-Ceramics (LIC-GC) samples obtained from the Ohara Corporation (150 μm thick, 1" x 1"). The LIC-GC is a Si-doped LATP-type ceramic and has a reported conductivity of $2 \times 10^{-3} \text{ S cm}^{-1}$ at 90 $^{\circ}\text{C}$. Cells were assembled similarly to normal cells, however due to the brittle nature of the ceramic, much less pressure was applied during assembly and the annealing process was primarily responsible for ensuring good contact between layers. Table 8-8 shows the detailed characteristics of the cells assembled with the LIC-GC.

Cell	Electrolyte	Cathode					1 st Discharge			Cycling		Notes
		m mg	m _s mg	L μm	ρ_c g cm^{-3}	S _{ideal} mAh	i _{D,0} $\mu\text{A cm}^{-2}$	C/X	S ₀ mAh g ⁻¹ S	i _D $\mu\text{A cm}^{-2}$	C/X	
RY.GCE.1	SEO LIC-GC SEO	0.7	0.2	-	-	0.3	14	28	972	56	7	
RY.GCE.2	SEO LIC-GC SEO	3.1	0.7	46	1.11	1.2	14	28	98	56	31	

Table 8-8 SEO|LIC-GC|SEO cell characteristics.

Electrolyte was SEO(240-269) with $r = 0.085$ LiTFSI. Cathode 6 was used for all cells. Cathode weight and thickness do not include current collector. Cells cycled at 90 $^{\circ}\text{C}$.

Figure 8-17 shows the cycling performance for both cells in Table 8-8. The voltage profile upon charging for RY.GCE.1 was accidentally not recorded. The extremely high Coloumbic efficiency of these cells (~100%) indicates that the polysulfide shuttle is completely eliminated and the stability after many cycles indicates that excellent adhesion is maintained at all four interfaces in the cell. The active material utilization is very different between the two cells: RY.GCE.1 has very high utilization and exhibits capacity fade while RY.GCE.2 has a slow start but steadily increases utilization over time. The reason for this difference is not clear. These cells verify the proof of concept of the multi-layer polymer-ceramic hybrid electrolyte, however are impractical due to the high cost and fragile nature of the LIC-GC.

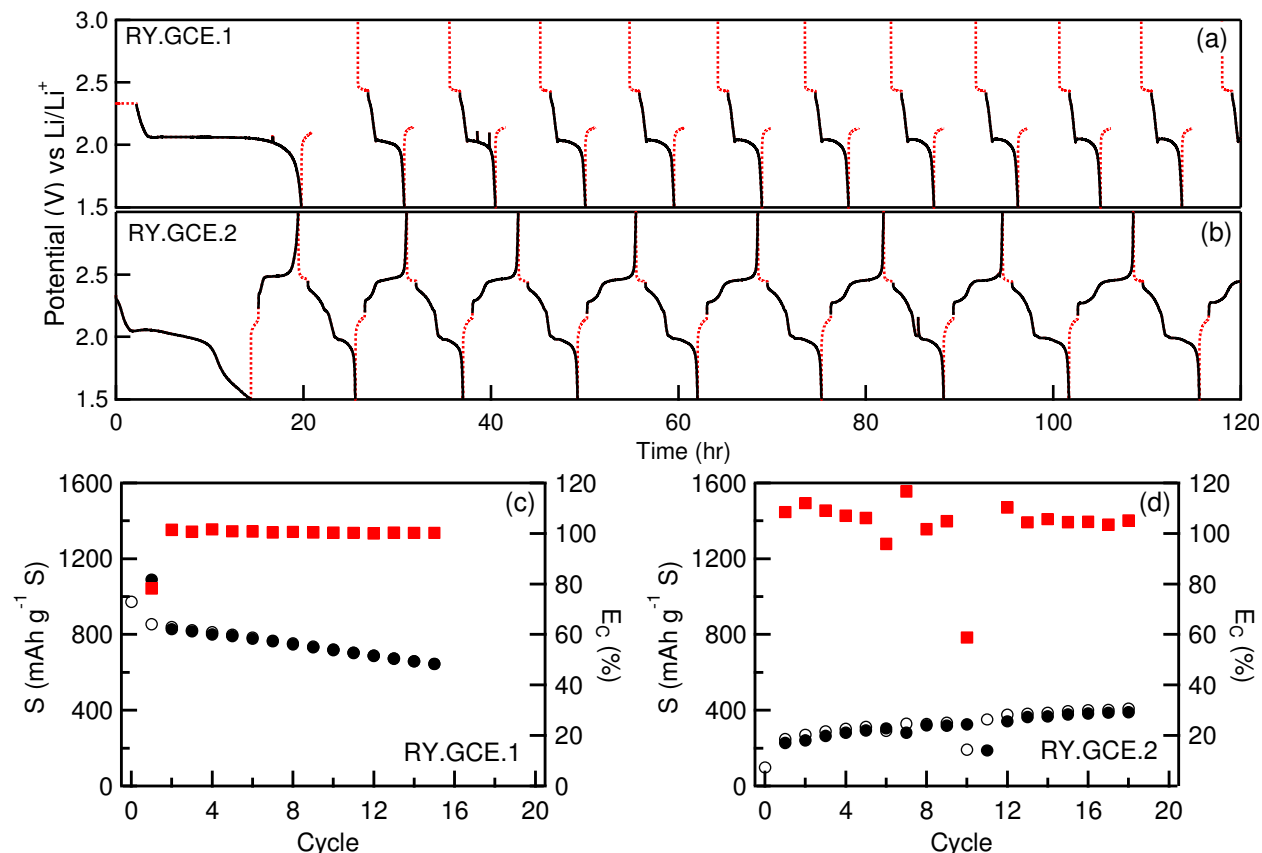


Figure 8-17 Cycling performance for SEOILIC-GC|SEO cells.

Voltage profiles (a), (b) and cycling performance (c), (d) of RY.GCE.1 and RY.GCE.2 respectively. Solid lines show constant current steps and dotted line shows rest step. Left axis shows specific capacity, S , for charge ($\bullet$) and discharge ($\circ$) while right axis shows Coloumbic efficiency, C_E ($\blacksquare$).

8.2.5.2 LiPON

The introduction of the ceramic electrolyte in the polymer-ceramic hybrid electrolyte complicates the cell and adds additional ohmic and charge-transfer resistances. Ideally the polymer-ceramic interfaces would have negligible charge transfer resistance and the ceramic layer would be infinitely thin to minimize ohmic resistances. Producing thin layers of ceramic electrolyte has historically been an elusive goal of the solid state electrolyte community, however recent progress by Dr. Dudney's research group at Oak Ridge National Laboratory^{140, 141} has proven the ability to vacuum deposit thin, uniform layers of LiPON, a lithium conductive glass ceramic, onto a polymeric substrate.

Through a collaboration with Dr. Dudney's group, we fabricated SEO/LITFSI membranes coated with a uniform layer of LiPON on the order of 100 nm thick. Pictures of two such samples are shown in Figure 8-18. An additional layer of SEO/LiTFSI membrane was stacked on top of the LiPON to complete the hybrid electrolyte and a full cell was assembled with the architecture shown schematically in Figure 8-16. The detailed characteristics of the cells created this way can be found in Table 8-9.

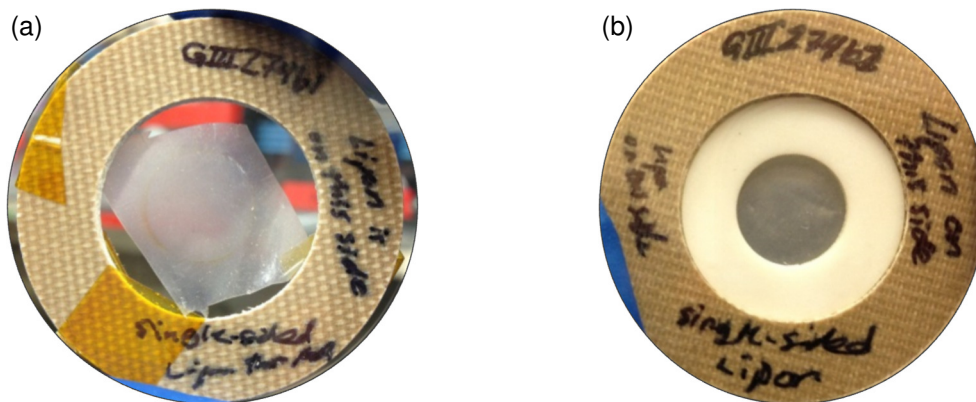


Figure 8-18 Vacuum deposited LiPON on SEO/LiTFSI membrane

Cell	Electrolyte		Cathode				1 st Discharge				Cycling		Notes
			m mg	m _s mg	L μm	ρ _c g cm ⁻³	S _{ideal} mAh	i _{D,0} μA cm ⁻²	C/X	S ₀ mAh g ⁻¹ S**	i _D μA cm ⁻²	C/X	
AT.LiPON.1	SEOILiPONISEO		3.6	2.0	27	1.37	3.4	10	342	-	40	86	Cycled poorly
AT.LiPON.2	SEOILiPONISEO		3.6	2.0	30	1.24	3.4	10	342	518	40	86	

Table 8-9 SEOILiPONISEO cell characteristics.

Electrolyte was SEO(240-269) with $r = 0.085$ LiTFSI. Cathode 12 was used for both cells. Cathode weight and thickness do not include current collector. Cells cycled at 90 °C.

The preliminary cycling results from this study are shown in Figure 8-19. Both cells need several ‘break-in’ cycles before somewhat consistent cycling is observed. The utilization of the active material is quite poor, however the efficiencies are quite high, yet not unity. These results provide a promising first look at a cell architecture that combines the best features of both polymer and ceramic electrolytes in order to enable a fully solid state lithium/sulfur cell.

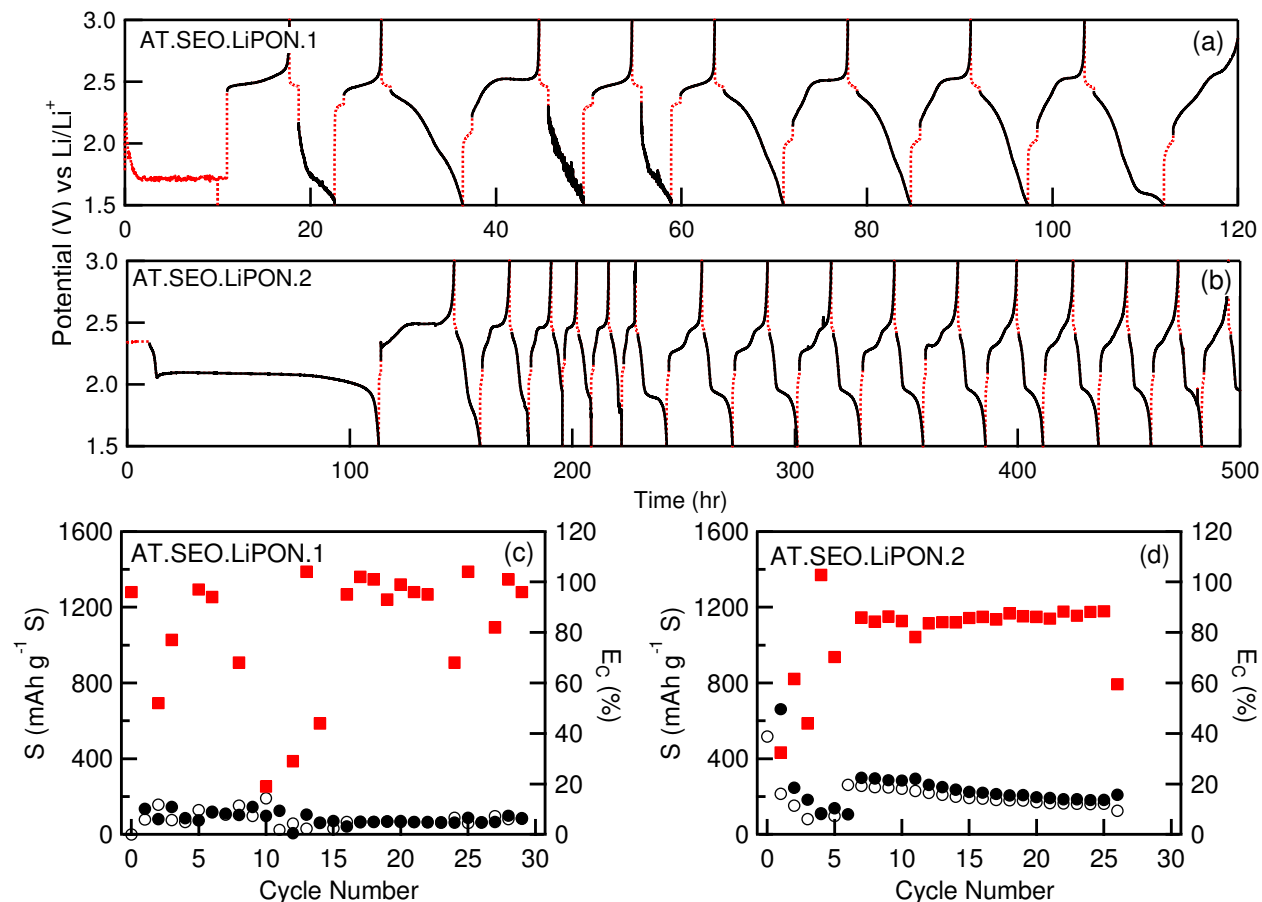


Figure 8-19 Cycling performance of SEO/LiPON/SEO cells. Voltage profile (a), (b) and cycling performance (c), (d) of AT.SEO.LiPON.1 and AT.SEO.LiPON.2, respectively. Solid lines show constant current steps and dotted line shows rest step. Left axis shows specific capacity, S , for charge (●) and discharge (○) while right axis shows Coloumbic efficiency, C_E (■).

8.3 Conclusion

We have evaluated the performance of nanostructured block copolymer electrolytes in solid-state lithium/sulfur cells. This study suggests the lithium polysulfides are able to readily diffuse through the block copolymer electrolyte, resulting in a robust polysulfide shuttle at sulfur concentrations in excess of 25%. Upon the addition of lithium nitrate to suppress the polysulfide shuttle we observed successful cell cycling, however such cells typically failed after no more than a dozen cycles due to loss of contact at the lithium/electrolyte interface. This unanticipated failure mechanism runs contrary to previous work using the SEO/LiTFSI solid-state electrolyte in symmetric lithium metal cells and lithium metal-LiFePO₄ cells.¹⁴

We believe that the presence of soluble lithium polysulfide reaction intermediates in the sulfur cathode are responsible for the surprising delamination at the SEO/Li metal interface, and subsequent cell failure; our results indicate that not only are the lithium polysulfides soluble, but highly mobile in the nanostructured block copolymer, allowing them to readily diffuse out of the cathode matrix and into the electrolyte. At sufficiently high concentration, the polysulfides appear

to change the mechanical properties, making it tougher and less pliable. This in turn, makes the electrolyte unable to conform to the changing lithium metal surface, resulting in loss of contact and loss of voltage control upon charging. As the poor contact becomes widespread, the cell becomes too resistive and unable to charge or discharge. This hypothesis is consistent with the observation that increasing the electrolyte thickness increased cell longevity in the lithium nitrate study; it took longer for the polysulfide concentration to reach the threshold for poor contact due to the increased distance between the SEOLi metal and the cathode matrix. Similarly, the introduction of polysulfides in the electrolyte caused nearly immediate cell failure due to the already-compromised mechanical properties of the electrolyte membrane.

Two promising strategies to overcome this problem were explored: the incorporation of a ceramic as a physical barrier to create a polymer-ceramic hybrid electrolyte, and the confinement of sulfur in the cathode matrix via the incorporation into a carbon-sulfur composite. While further research is needed, it was demonstrated that both of these approaches can eliminate or greatly reduce the polysulfide shuttle in the cell, thus maintaining the integrity of the SEOLi metal interface. Once the polysulfide shuttle is eliminated, attention can be focused on optimizing the cathode architecture and composition to maximize sulfur loading and active material utilization.

Chapter 9 - Summary

Nanostructured block copolymer electrolytes containing an ion-conducting block and a modulus-strengthening block have attracted interest for applications in solid-state lithium metal batteries. The objective of this dissertation is to gain a better fundamental and applied understanding of salt-containing block copolymers, and evaluate their potential for use as solid-state electrolytes, specifically in lithium/sulfur batteries. Polystyrene-*b*-poly(ethylene oxide) (SEO) copolymer doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt was used as a model system. The model system was studied on several levels: from fundamental thermodynamic studies to bulk characterization and finally full electrochemical cell assembly and testing.

In Chapter 2, we discussed synthetic methods for living anionic polymerization of polystyrene-*b*-poly(ethylene oxide) (SEO) copolymers. Characterization techniques were described, and the pertinent characteristics for the polymers used in this study were presented. Importantly, a new purification was developed to remove residual impurities from small molecular weight copolymers.

In Chapter 3, we studied the thermodynamics of neat and salt-containing block copolymers. The Flory-Huggins interaction parameter was determined by fitting small angle X-ray scattering data of disordered systems to predictions based on the random phase approximation. Experiments on neat block copolymers revealed that χ_0 is a strong function of molecular weight. Experiments on salt-containing block copolymers reveal that the relationship between χ_{eff} and salt concentration is highly non-linear, with a sharp initial increase at low salt concentration followed by an apparent saturation, and that the magnitude of the increase in χ_{eff} with concentration depends strongly on the molecular weight of the copolymer. Our results revealed a much more complex relationship between χ_{eff} and salt concentration than the simple linear relationship asserted by all previous studies, indicating the need for improved theories for describing thermodynamic interactions in neat and salt-containing block copolymers.

In Chapter 4, we studied the effect of molecular weight on ion transport in homopolymer electrolytes. Homopolymer electrolytes show an inverse relationship between conductivity and molecular weight, with a plateau in the infinite molecular weight limit. The data are captured by two empirical parameters σ_0 and K that reflect the presence of dual mechanisms of ion conduction in homopolymers; the first mechanism is a result of the segmental motion of the chains surrounding the salt ions while the second mechanism of ion conduction is attributed to diffusion of the entire polymer chain with coordinated ions.

In Chapter 5, we extended the study to investigate the effect of molecular weight on ion transport in block copolymer electrolytes. Equilibrated block copolymer electrolytes exhibit a non-monotonic dependence on molecular weight, decreasing with increasing molecular weight in the small molecular weight limit before increasing when molecular weight exceeds about 10 kg mol⁻¹. Conductivity in annealed electrolytes was shown to be affected by two competing factors: the glass transition temperature of the insulating block and the width of the conducting channel. In the low molecular weight limit, all ions are in contact with segments from both blocks. The intermixing between segments of different blocks is restricted to an interfacial zone of width of about 5 nm. The fraction of ions affected by the interfacial zone decreases as the conducting

channel width increases; in the high molecular weight limit, the fraction of ions affected by the interfacial zone is negligible. Furthermore, the thermal history was found to play an important role in the conductivity of the sample. In general, a poorly ordered morphology and small grains resulted in higher conductivity. At temperatures above the glass transition temperature of the insulating block, the chains are able to anneal into a better-ordered structure with larger grains, resulting in decreases in conductivity of up to 80%.

In Chapter 6, we studied the effect of morphology on ion transport by measuring the ionic conductivity of a block copolymer electrolyte as it transitions from an ordered lamellar structure to a disordered phase. The ionic conductivity increases discontinuously as the electrolyte transitions from order to disorder by a factor of about 1.8. A simple framework for quantifying the magnitude of the discontinuity is presented. This study lays the ground work for understanding the effect of more complex phase transitions such as order-order transitions on ion transport.

In Chapter 7, we examine the interaction of lithium polysulfides with the block copolymers. The lithium polysulfides were found to exhibit similar solubility in the block copolymers as in typical organic electrolytes, however induced unusual and unexpected effects phase behavior of the block copolymers. Increasing either the molar salt concentration or anion size resulted in increased segregation between the blocks, however the morphology is primarily a function of the weight fraction of added salt. Increasing the weight fraction of added salt from low to intermediate values resulted in a disorder-to-gyroid transition. At temperatures where the PEO block was crystalline, the SAXS profiles of the gyroid phase contains peaks that are normally forbidden. The SEO/Li₂S_x phase diagrams show fundamentally different morphologies than exhibited in other SEO/salt systems.

In Chapter 8, we used the nanostructured block copolymer electrolytes in full electrochemical cells with a lithium metal anode and sulfur cathode. Different cathode compositions, electrolyte additives, and cell architectures were tested. Surprisingly, the polysulfides diffused readily out of the cathode and through the block copolymer electrolyte, resulting in a robust polysulfide shuttle. Additionally, the presence of the polysulfides in the electrolyte changed its mechanical properties. The changes in mechanical properties resulted in delamination of the electrolyte from the lithium metal anode and caused cell failure. Several promising strategies to overcome this problem were investigated and offer exciting avenues for improvement for future researchers.

References

1. Matsen, M. W., Effect of Architecture on the Phase Behavior of AB-Type Block Copolymer Melts. *Macromolecules* **2012**, *45* (4), 2161-2165.
2. Claudy, P.; Letoffe, J. M.; Camberlain, Y.; Pascault, J. P., Glass-Transition Of Polystyrene Versus Molecular-Weight. *Polymer Bulletin* **1983**, *9* (4-5).
3. Gomez, E. D.; Panday, A.; Feng, E. H.; Chen, V.; Stone, G. M.; Minor, A. M.; Kisielowski, C.; Downing, K. H.; Borodin, O.; Smith, G. D.; Balsara, N. P., Effect of Ion Distribution on Conductivity of Block Copolymer Electrolytes. *Nano Letters* **2009**, *9* (3), 1212-1216.
4. Faucher, J. A.; Koleske, J. V.; Santee, E. R.; Stratta, J. J.; Wilson, C. W., Glass Transitions Of Ethylene Oxide Polymers. *Journal of Applied Physics* **1966**, *37* (11).
5. Lascaud, S.; Perrier, M.; Vallee, A.; Besner, S.; Prudhomme, J.; Armand, M., Phase-Diagrams and Conductivity Behavior of Poly(Ethylene Oxide) Molten-Salt Rubbery Electrolytes. *Macromolecules* **1994**, *27* (25), 7469-7477.
6. Fredrickson, G. H.; Helfand, E., Fluctuation Effects in the Theory of Microphase Separation in Block Copolymers. *Journal of Chemical Physics* **1987**, *87* (1), 697-705.
7. Monroe, C.; Newman, J., The impact of elastic deformation on deposition kinetics at lithium/polymer interfaces. *Journal of the Electrochemical Society* **2005**, *152* (2), A396-A404.
8. Singh, M.; Odusanya, O.; Wilmes, G. M.; Eitouni, H. B.; Gomez, E. D.; Patel, A. J.; Chen, V. L.; Park, M. J.; Fragouli, P.; Iatrou, H.; Hadjichristidis, N.; Cookson, D.; Balsara, N. P., Effect of molecular weight on the mechanical and electrical properties of block copolymer electrolytes. *Macromolecules* **2007**, *40* (13), 4578-4585.
9. Panday, A.; Mullin, S.; Gomez, E. D.; Wanakule, N.; Chen, V. L.; Hexemer, A.; Pople, J.; Balsara, N. P., Effect of Molecular Weight and Salt Concentration on Conductivity of Block Copolymer Electrolytes. *Macromolecules* **2009**, *42* (13), 4632-4637.
10. Fenton, D. E.; Parker, J. M.; Wright, P. V., Complexes of Alkali-Metal Ions with Poly(ethylene oxide). *Polymer* **1973**, *14* (11), 589-589.
11. Armand, M., *Fast Ion Transport in Solids*. North-Holland: Amsterdam, 1973; p 665 - 673.
12. Gray, F. M., *Solid Polymer Electrolytes. Fundamentals and Technological applications*. VCH: Weinheim, 1991.
13. Stone, G. M.; Mullin, S. A.; Teran, A. A.; Hallinan, D. T.; Minor, A. M.; Hexemer, A.; Balsara, N. P., Resolution of the Modulus versus Adhesion Dilemma in Solid Polymer Electrolytes for Rechargeable Lithium Metal Batteries. *Journal of the Electrochemical Society* **2012**, *159* (3), A2222-A2227.
14. Hallinan, D. T.; Mullin, S. A.; Stone, G. M.; Balsara, N. P., Lithium Metal Stability in Batteries with Block Copolymer Electrolytes. *Journal of the Electrochemical Society* **2013**, *160* (3), A464-A470.

15. Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M., Anionic polymerization: High vacuum techniques. *J Polym Sci Pol Chem* **2000**, *38* (18), 3211-3234.
16. Quirk, R. P.; Kim, J.; Kausch, C.; Chun, M. S., Butyllithium-initiated anionic synthesis of well-defined poly(styrene-block-ethylene oxide) block copolymers with potassium salt additives. *Polym Int* **1996**, *39* (1), 3-10.
17. Eitouni, H. Ambient Temperature Purification of Alkylene Oxides. 2013.
18. Mark, J. E., *Physical Properties of Polymers Handbook*. 2nd ed.; 2007.
19. Ilavsky, J., Nika: software for two-dimensional data reduction. *Journal of Applied Crystallography* **2012**, *45*.
20. Mori, K.; Okawara, A.; Hashimoto, T., Order-disorder transition of polystyrene-block-polyisoprene .1. Thermal concentration fluctuations in single-phase melts and solutions and determination of χ as a function of molecular weight and composition. *Journal of Chemical Physics* **1996**, *104* (19), 7765-7777.
21. Lin, C. C.; Jonnalagadda, S. V.; Kesani, P. K.; Dai, H. J.; Balsara, N. P., Effect of Molecular-Structure on the Thermodynamics of Block-Copolymer Melts. *Macromolecules* **1994**, *27* (26), 7769-7780.
22. Huang, J.; Tong, Z.-Z.; Zhou, B.; Xu, J.-T.; Fan, Z.-Q., Salt-induced microphase separation in poly(epsilon-caprolactone)-b-poly(ethylene oxide) block copolymer. *Polymer* **2013**, *54* (12), 3098-3106.
23. Young, W. S.; Epps, T. H., Salt Doping in PEO-Containing Block Copolymers: Counterion and Concentration Effects. *Macromolecules* **2009**, *42* (7), 2672-2678.
24. Naidu, S.; Ahn, H.; Gong, J.; Kim, B.; Ryu, D. Y., Phase Behavior and Ionic Conductivity of Lithium Perchlorate-Doped Polystyrene-b-poly(2-vinylpyridine) Copolymer. *Macromolecules* **2011**, *44* (15), 6085-6093.
25. Gunkel, I.; Thurn-Albrecht, T., Thermodynamic and Structural Changes in Ion-Containing Symmetric Diblock Copolymers: A Small-Angle X-ray Scattering Study. *Macromolecules* **2012**, *45* (1), 283-291.
26. Wanakule, N. S.; Virgili, J. M.; Teran, A. A.; Wang, Z.-G.; Balsara, N. P., Thermodynamic Properties of Block Copolymer Electrolytes Containing Imidazolium and Lithium Salts. *Macromolecules* **2010**, *43* (19), 8282-8289.
27. Nakamura, I.; Balsara, N. P.; Wang, Z. G., Thermodynamics of Ion-Containing Polymer Blends and Block Copolymers. *Phys. Rev. Lett.* **2011**, *107* (19), 5.
28. Nakamura, I.; Wang, Z.-G., Salt-doped block copolymers: ion distribution, domain spacing and effective χ parameter. *Soft Matter* **2012**, *8* (36), 9356-9367.
29. Wang, J. Y.; Chen, W.; Russell, T. P., Ion-complexation-induced changes in the interaction parameter and the chain conformation of PS-b-PMMA copolymers. *Macromolecules* **2008**, *41* (13), 4904-4907.
30. Leibler, L., Theory of Microphase Separation in Block Co-Polymers. *Macromolecules* **1980**, *13* (6), 1602-1617.

31. Khandpur, A. K.; Forster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K., Polyisoprene-polystyrene diblock copolymer phase diagram near the order-disorder transition. *Macromolecules* **1995**, *28* (26), 8796-8806.
32. Floudas, G.; Vazaiou, B.; Schipper, F.; Ulrich, R.; Wiesner, U.; Iatrou, H.; Hadjichristidis, N., Poly(ethylene oxide-b-isoprene) diblock copolymer phase diagram. *Macromolecules* **2001**, *34* (9), 2947-2957.
33. Wang, Z. G., Effects of Ion Solvation on the Miscibility of Binary Polymer Blends. *Journal of Physical Chemistry B* **2008**, *112* (50), 16205-16213.
34. Wen, S. J.; Richardson, T. J.; Ghantous, D. I.; Striebel, K. A.; Ross, P. N.; Cairns, E. J., FTIR characterization of PEO+LiN(CF₃SO₂)(2) electrolytes. *Journal of Electroanalytical Chemistry* **1996**, *408* (1-2), 113-118.
35. Yuan, R.; Teran, A. A.; Gurevitch, I.; Mullin, S. A.; Wanakule, N. S.; Balsara, N. P., Ionic Conductivity of Low Molecular Weight Block Copolymer Electrolytes. *Macromolecules* **2013**, *46* (3), 914-921.
36. Schweizer, K. S.; Curro, J. G., Integral-Equation Theory of the Structure and Thermodynamics of Polymer Blends. *Journal of Chemical Physics* **1989**, *91* (8), 5059-5081.
37. Schweizer, K. S., Analytic RISM Theory of Polymer Alloys - Molecular Closure Predictions for Structurally Symmetrical Blends. *Macromolecules* **1993**, *26* (22), 6033-6049.
38. Sariban, A.; Binder, K., Critical Properties of the Flory-Huggins Lattice Model of Polymer Mixtures. *Journal of Chemical Physics* **1987**, *86* (10), 5859-5873.
39. Fried, H.; Binder, K., The Microphase Transition in Symmetrical Diblock Copolymer Melts - A Monte Carlo Simulation. *Journal of Chemical Physics* **1991**, *94* (12), 8349-8366.
40. Binder, K.; Fried, H., Asymmetric Block Copolymer Melts near the Microphase Transition - A Monte Carlo Simulation. *Macromolecules* **1993**, *26* (25), 6878-6883.
41. Bates, F. S.; Muthukumar, M.; Wignall, G. D.; Fetters, L. J., Thermodynamics of Isotopic Polymer Mixtures - Significance of Local Structure Symmetry. *Journal of Chemical Physics* **1988**, *89* (1), 535-544.
42. Maranas, J. K.; Mondello, M.; Grest, G. S.; Kumar, S. K.; Debenedetti, P. G.; Graessley, W. W., Liquid structure, thermodynamics, and mixing behavior of saturated hydrocarbon polymers. 1. Cohesive energy density and internal pressure. *Macromolecules* **1998**, *31* (20), 6991-6997.
43. Maranas, J. K.; Kumar, S. K.; Debenedetti, P. G.; Graessley, W. W.; Mondello, M.; Grest, G. S., Liquid structure, thermodynamics, and mixing behavior of saturated hydrocarbon polymers. 2. Pair distribution functions and the regularity of mixing. *Macromolecules* **1998**, *31* (20), 6998-7002.
44. Luettmmer-Strathmann, J.; Lipson, J. E. G., Miscibility of polyolefin blends. *Macromolecules* **1999**, *32* (4), 1093-1102.
45. Muller, M.; Binder, K., Computer Simulation of Asymmetric Polymer Mixtures. *Macromolecules* **1995**, *28* (6), 1825-1834.

46. Wang, Z. G., Concentration fluctuation in binary polymer blends: chi parameter, spinodal and Ginzburg criterion. *Journal of Chemical Physics* **2002**, *117* (1), 481-500.
47. Wittmer, J. P.; Beckrich, P.; Meyer, H.; Cavallo, A.; Johner, A.; Baschnagel, J., Intramolecular long-range correlations in polymer melts: The segmental size distribution and its moments. *Physical Review E* **2007**, *76* (1).
48. Morse, D. C.; Chung, J. K., On the chain length dependence of local correlations in polymer melts and a perturbation theory of symmetric polymer blends. *Journal of Chemical Physics* **2009**, *130* (22).
49. Jian, Q.; Morse, D. C., Renormalized one-loop theory of correlations in polymer blends. *Journal of Chemical Physics* **2009**, *130* (22), 224902 (15 pp.)-224902 (15 pp.).
50. Yethiraj, A.; Schweizer, K. S., Self-Consistent Polymer Integral-Equation Theory - Comparisons with Monte Carlo Simulations and Alternative Closure Approximations. *Journal of Chemical Physics* **1992**, *97* (2), 1455-1464.
51. Scrosati, B.; Vincent, C. A., Polymer electrolytes: The key to lithium polymer batteries. *MRS Bull.* **2000**, *25* (3), 28-30.
52. Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P., Microscopic Investigation of Ionic-Conductivity in Alkali-Metal Salts Poly(Ethylene Oxide) Adducts. *Solid State Ionics* **1983**, *11* (1), 91-95.
53. Druger, S. D.; Nitzan, A.; Ratner, M. A., Dynamic Bond Percolation Theory - A Microscopic Model For Diffusion In Dynamically Disordered-Systems .1. Definition And One-Dimensional Case. *Journal of Chemical Physics* **1983**, *79* (6), 3133-3142.
54. Nitzan, A.; Ratner, M. A., Conduction in Polymers: Dynamic Disorder Transport. *The Journal of Physical Chemistry* **1994**, *98* (7), 1765-1775.
55. De Gennes, P. G., Reptation of a Polymer Chain in Presence of Fixed Obstacles. *Journal of Chemical Physics* **1971**, *55* (2), 572-&.
56. Ferry, J. D., *Viscoelastic Properties of Polymers*. 3 ed.; Wiley: 1980; p 672.
57. Graessley, W. W., *Polymeric Liquids & Networks: Dynamics and Rheology*. Taylor & Francis, Inc.: 2008.
58. Watanabe, H.; Kotaka, T., Viscoelastic Properties And Relaxation Mechanisms Of Binary Blends Of Narrow Molecular-Weight Distribution Polystyrenes. *Macromolecules* **1984**, *17* (11), 2316-2325.
59. Watanabe, H.; Sakamoto, T.; Kotaka, T., Viscoelastic Properties Of Binary Blends Of Narrow Molecular-Weight Distribution Polystyrenes .2. *Macromolecules* **1985**, *18* (5), 1008-1015.
60. Borodin, O.; Smith, G. D., Molecular dynamics simulations of poly(ethylene oxide)/LiI melts. 1. Structural and conformational properties. *Macromolecules* **1998**, *31* (23), 8396-8406.
61. Shi, J.; Vincent, C. A., The Effect of Molecular-Weight on Cation Mobility in Polymer Electrolytes. *Solid State Ionics* **1993**, *60* (1-3), 11-17.

62. Hayamizu, K.; Akiba, E.; Bando, T.; Aihara, Y., H-1, Li-7, and F-19 nuclear magnetic resonance and ionic conductivity studies for liquid electrolytes composed of glymes and polyetheneglycol dimethyl ethers of $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$ ($n=3-50$) doped with $\text{LiN}(\text{SO}_2\text{CF}_3)_2$. *Journal of Chemical Physics* **2002**, *117* (12), 5929-5939.
63. Diddens, D.; Heuer, A.; Borodin, O., Understanding the Lithium Transport within a Rouse-Based Model for a PEO/LiTFSI Polymer Electrolyte. *Macromolecules* **2010**, *43* (4), 2028-2036.
64. Edman, L.; Doeff, M. M.; Ferry, A.; Kerr, J.; De Jonghe, L. C., Transport properties of the solid polymer electrolyte system $\text{P}(\text{EO})_n\text{LiTFSI}$. *Journal of Physical Chemistry B* **2000**, *104* (15), 3476-3480.
65. Volel, M.; Armand, M.; Gorecki, W., Influence of sample history on the morphology and transport properties of PEO-lithium salt complexes. *Macromolecules* **2004**, *37* (22), 8373-8380.
66. Zimm, B. H., Dynamics Of Polymer Molecules In Dilute Solution - Viscoelasticity, Flow Birefringence And Dielectric Loss. *Journal of Chemical Physics* **1956**, *24* (2), 269-278.
67. Doi, M., *Introduction to Polymer Physics*. Clarendon Press: Oxford, 2001.
68. Kim, G. T.; Appetecchi, G. B.; Alessandrini, F.; Passerini, S., Solvent-free, PYR1A TFSI ionic liquid-based ternary polymer electrolyte systems I. Electrochemical characterization. *J. Power Sources* **2007**, *171* (2), 861-869.
69. Tarascon, J. M.; Armand, M., Issues and challenges facing rechargeable lithium batteries. *Nature* **2001**, *414* (6861), 359-367.
70. Ganesan, V.; Pyramitsyn, V.; Bertoni, C.; Shah, M., Mechanisms Underlying Ion Transport in Lamellar Block Copolymer Membranes. *Acs Macro Letters* **2012**, *1* (4).
71. Wanakule, N. S.; Panday, A.; Mullin, S. A.; Gann, E.; Hexemer, A.; Balsara, N. P., Ionic Conductivity of Block Copolymer Electrolytes in the Vicinity of Order-Disorder and Order-Order Transitions. *Macromolecules* **2009**, *42* (15), 5642-5651.
72. Ruzette, A. V. G.; Soo, P. P.; Sadoway, D. R.; Mayes, A. M., Melt-formable block copolymer electrolytes for lithium rechargeable batteries. *Journal of the Electrochemical Society* **2001**, *148* (6), A537-A543.
73. Broseta, D.; Fredrickson, G. H.; Helfand, E.; Leibler, L., Molecular-Weight And Polydispersity Effects At Polymer Polymer Interfaces. *Macromolecules* **1990**, *23* (1), 132-139.
74. Helfand, E.; Tagami, Y., Theory Of Interface Between Immiscible Polymers. *Journal of Polymer Science Part B-Polymer Letters* **1971**, *9* (10).
75. Sun, J.; Stone, G. M.; Balsara, N. P.; Zuckermann, R. N., Structure-Conductivity Relationship for Peptoid-Based PEO-Mimetic Polymer Electrolytes. *Macromolecules* **2012**, *45* (12), 5151-5156.
76. Ye, Y.; Choi, J.-H.; Winey, K. I.; Elabd, Y. A., Polymerized Ionic Liquid Block and Random Copolymers: Effect of Weak Microphase Separation on Ion Transport. *Macromolecules* **2012**, *45* (17).

77. Matsen, M. W.; Bates, F. S., Unifying weak- and strong-segregation block copolymer theories. *Macromolecules* **1996**, *29* (4), 1091-1098.
78. Soo, P. P.; Huang, B. Y.; Jang, Y. I.; Chiang, Y. M.; Sadoway, D. R.; Mayes, A. M., Rubbery block copolymer electrolytes for solid-state rechargeable lithium batteries. *Journal of the Electrochemical Society* **1999**, *146* (1), 32-37.
79. Teran, A. A.; Mullin, S. A.; Hallinan, D. T., Jr.; Balsara, N. P., Discontinuous Changes in Ionic Conductivity of a Block Copolymer Electrolyte through an Order-Disorder Transition. *Acs Macro Letters* **2012**, *1* (2).
80. Lodge, T. P.; Pudil, B.; Hanley, K. J., The full phase behavior for block copolymers in solvents of varying selectivity. *Macromolecules* **2002**, *35* (12), 4707-4717.
81. Majewski, P. W.; Gopinadhan, M.; Jang, W. S.; Lutkenhaus, J. L.; Osuji, C. O., Anisotropic Ionic Conductivity in Block Copolymer Membranes by Magnetic Field Alignment. *Journal of the American Chemical Society* **2010**, *132* (49), 17516-17522.
82. Ratner, M. A.; Shriver, D. F., ION-TRANSPORT IN SOLVENT-FREE POLYMERS. *Chemical Reviews* **1988**, *88* (1), 109-124.
83. Borodin, O.; Smith, G. D., Molecular dynamics simulations of poly(ethylene oxide)/LiI melts. 2. Dynamic properties. *Macromolecules* **2000**, *33* (6), 2273-2283.
84. Teran, A. A.; Tang, M. H.; Mullin, S. A.; Balsara, N. P., Effect of molecular weight on conductivity of polymer electrolytes. *Solid State Ionics* **2011**, *203* (1), 18-21.
85. Cho, B. K.; Jain, A.; Gruner, S. M.; Wiesner, U., Mesophase structure-mechanical and ionic transport correlations in extended amphiphilic dendrons. *Science* **2004**, *305* (5690), 1598-1601.
86. Rauh, R. D.; Abraham, K. M.; Pearson, G. F.; Surprenant, J. K.; Brummer, S. B., Lithium-Dissolved Sulfur Battery With An Organic Electrolyte. *Journal of the Electrochemical Society* **1979**, *126* (4), 523-527.
87. Yamin, H.; Gorenshtein, A.; Penciner, J.; Sternberg, Y.; Peled, E., Lithium Sulfur Battery - Oxidation Reduction-Mechanisms Of Polysulfides In THF Solutions. *Journal of the Electrochemical Society* **1988**, *135* (5), 1045-1048.
88. Kolosnitsyn, V. S.; Karaseva, E. V., Lithium-sulfur batteries: Problems and solutions. *Russian Journal of Electrochemistry* **2008**, *44* (5), 506-509.
89. Akridge, J. R.; Mikhaylik, Y. V.; White, N., Li/S fundamental chemistry and application to high-performance rechargeable batteries. *Solid State Ionics* **2004**, *175* (1-4), 243-245.
90. Mikhaylik, Y. V.; Akridge, J. R., Polysulfide shuttle study in the Li/S battery system. *Journal of the Electrochemical Society* **2004**, *151* (11), A1969-A1976.
91. Cheon, S. E.; Ko, K. S.; Cho, J. H.; Kim, S. W.; Chin, E. Y.; Kim, H. T., Rechargeable lithium sulfur battery - I. Structural change of sulfur cathode during discharge and charge. *Journal of the Electrochemical Society* **2003**, *150* (6), A796-A799.
92. Ji, X. L.; Lee, K. T.; Nazar, L. F., A highly ordered nanostructured carbon-sulphur cathode for lithium-sulphur batteries. *Nat. Mater.* **2009**, *8* (6), 500-506.

93. Young, W. S.; Brigandi, P. J.; Epps, T. H., Crystallization-induced lamellar-to-lamellar thermal transition in salt-containing block copolymer electrolytes. *Macromolecules* **2008**, *41* (17), 6276-6279.
94. Rauh, R. D.; Shuker, F. S.; Marston, J. M.; Brummer, S. B., Formation Of Lithium Polysulfides In Aprotic Media. *Journal of Inorganic & Nuclear Chemistry* **1977**, *39* (10), 1761-1766.
95. Kim, B. S.; Park, S. M., In-situ Spectroelectrochemical Studies On The Reduction Of Sulfur In Dimethyl-Sulfoxide Solutions. *Journal of the Electrochemical Society* **1993**, *140* (1), 115-122.
96. Pickering, T.; Tobolsky, A., *Sulfur in Organic and Inorganic Chemistry*. Marcel Dekker: New York, 1972; Vol. 3.
97. Buehrer, W.; Altorfer, F.; Mesot, J.; Bill, H.; Carron, P.; Smith, H. G., Lattice-Dynamics And The Diffuse Phase-Transition Of Lithium Sulfide Investigated By Coherent Neutron-Scattering. *Journal of Physics-Condensed Matter* **1991**, *3* (9), 1055-1064.
98. Marmorstein, D. Solid State Lithium/Sulfur Batteries for Electric Vehicles : Electrochemical and Spectroelectrochemical Investigations. Ph.D. Thesis, University of California, Berkeley, 2002.
99. Marmorstein, D.; Yu, T. H.; Striebel, K. A.; McLarnon, F. R.; Hou, J.; Cairns, E. J., Electrochemical performance of lithium/sulfur cells with three different polymer electrolytes. *J. Power Sources* **2000**, *89* (2), 219-226.
100. Ryan, A. J.; Hamley, I. W.; Bras, W.; Bates, F. S., Structure Development In Semicrystalline Diblock Copolymers Crystallizing From The Ordered Melt. *Macromolecules* **1995**, *28* (11), 3860-3868.
101. Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J., The Gyroid - a New Equilibrium Morphology in Weakly Segregated Diblock Copolymers. *Macromolecules* **1994**, *27* (15), 4063-4075.
102. de Geyer, A.; Guillermo, A.; Rodriguez, V.; Molle, B., Evidence for spontaneous formation of three-dimensionally periodic cellular structures in a water/oil/surfactant/alcohol system. *Journal of Physical Chemistry B* **2000**, *104* (28), 6610-6617.
103. Toombes, G. E. S.; Finnefrock, A. C.; Tate, M. W.; Ulrich, R.; Wiesner, U.; Gruner, S. M., A re-evaluation of the morphology of a bicontinuous block copolymer-ceramic material. *Macromolecules* **2007**, *40* (25), 8974-8982.
104. Crossland, E. J. W.; Kamperman, M.; Nedelcu, M.; Ducati, C.; Wiesner, U.; Smilgies, D. M.; Toombes, G. E. S.; Hillmyer, M. A.; Ludwigs, S.; Steiner, U.; Snaith, H. J., A Bicontinuous Double Gyroid Hybrid Solar Cell. *Nano Letters* **2009**, *9* (8), 2807-2812.
105. Stefik, M.; Mahajan, S.; Sai, H.; Epps, T. H.; Bates, F. S.; Gruner, S. M.; DiSalvo, F. J.; Wiesner, U., Ordered Three- and Five-ply Nanocomposites from ABC Block Terpolymer Microphase Separation with Niobia and Aluminosilicate Sols. *Chemistry of Materials* **2009**, *21* (22), 5466-5473.
106. Urade, V. N.; Wei, T. C.; Tate, M. P.; Kowalski, J. D.; Hillhouse, H. W., Nanofabrication of double-gyroid thin films. *Chemistry of Materials* **2007**, *19* (4), 768-777.

107. Finnefrock, A. C.; Ulrich, R.; Toombes, G. E. S.; Gruner, S. M.; Wiesner, U., The plumber's nightmare: A new morphology in block copolymer-ceramic nanocomposites and mesoporous aluminosilicates. *Journal of the American Chemical Society* **2003**, *125* (43), 13084-13093.
108. Matsen, M. W.; Bates, F. S., Conformationally asymmetric block copolymers. *Journal of Polymer Science Part B-Polymer Physics* **1997**, *35* (6), 945-952.
109. Brummer, S. B.; Rauh, R. D.; Marston, J. M.; Shuker, F. S., Low Temperature Lithium/Sulfur Secondary Battery. U.S. Energy Research and Development Administration, D. o. E. E. S., Ed. 1976; pp 1-57.
110. Merritt, M. V.; Sawyer, D. T., Electrochemical Reduction Of Elemental Sulfur In Aprotic Solvents . Formation Of A Stable S₈-Species. *Inorganic Chemistry* **1970**, *9* (2), 211-&.
111. Martin, R. P.; Doub, W. H.; Roberts, J. L.; Sawyer, D. T., Further Studies Of Electrochemical Reduction Of Sulfur In Aprotic Solvents. *Inorganic Chemistry* **1973**, *12* (8), 1921-1925.
112. Giggenbach, W., On Nature Of Blue Solutions Of Sulfur. *Journal of Inorganic & Nuclear Chemistry* **1968**, *30* (12), 3189-&.
113. Gaillard, F.; Levillain, E., Visible Time-Resolved Spectroelectrochemistry - Application To Study Of The Reduction Of Sulfur (S₈) In Dimethylformamide. *Journal of Electroanalytical Chemistry* **1995**, *398* (1-2), 77-87.
114. Levillain, E.; Gaillard, F.; Leghie, P.; Demortier, A.; Lelieur, J. P., On the understanding of the reduction of sulfur (S₈) in dimethylformamide (DMF). *Journal of Electroanalytical Chemistry* **1997**, *420* (1-2), 167-177.
115. Levillain, E.; Gaillard, F.; Lelieur, J. P., Polysulfides in dimethylformamide: only the redox couples S-n(-)/S-n(2-) involved. *Journal of Electroanalytical Chemistry* **1997**, *440* (1-2), 243-250.
116. Gaillard, F.; Levillain, E.; Lelieur, J. P., Polysulfides in dimethylformamide: Only the radical anions S-3(-) and S-4(-) are reducible. *Journal of Electroanalytical Chemistry* **1997**, *432* (1-2), 129-138.
117. Yamin, H.; Penciner, J.; Gorenshtain, A.; Elam, M.; Peled, E., The Electrochemical-Behavior Of Polysulfides In Tetrahydrofuran. *J. Power Sources* **1985**, *14* (1-3), 129-134.
118. Tobishima, S. I.; Yamamoto, H.; Matsuda, M., Study on the reduction species of sulfur by alkali metals in nonaqueous solvents. *Electrochimica Acta* **1997**, *42* (6), 1019-1029.
119. Paris, J.; Plichon, V., Electrochemical Reduction Of Sulfur In Dimethylacetamide. *Electrochimica Acta* **1981**, *26* (12), 1823-1829.
120. Levillain, E.; Gaillard, F.; Demortier, A.; Lelieur, J. P., Electrochemical and spectroelectrochemical study of the oxidation of S-4(2-) and S-6(2-) ions in liquid ammonia. *Journal of Electroanalytical Chemistry* **1996**, *405* (1-2), 85-94.
121. Dubois, P.; Lelieur, J. P.; Lepoutre, G., Identification And Characterization Of Lithium Polysulfides In Solution In Liquid-Ammonia. *Inorganic Chemistry* **1988**, *27* (1), 73-80.

122. Fujinaga, T.; Kuwamoto, T.; Okazaki, S.; Hojo, M., Electrochemical Reduction Of Elemental Sulfur In Acetonitrile. *Bulletin of the Chemical Society of Japan* **1980**, 53 (10), 2851-2855.
123. Ji, X.; Evers, S.; Black, R.; Nazar, L. F., Stabilizing lithium-sulphur cathodes using polysulphide reservoirs. *Nature Communications* **2011**, 2.
124. Ji, L.; Rao, M.; Zheng, H.; Zhang, L.; Li, Y.; Duan, W.; Guo, J.; Cairns, E. J.; Zhang, Y., Graphene Oxide as a Sulfur Immobilizer in High Performance Lithium/Sulfur Cells. *J. Am. Chem. Soc.* **2011**, 133, 18522-18525.
125. Chung, S.-H.; Manthiram, A., Nano-cellular carbon current collectors with stable cyclability for Li-S batteries. *Journal of Materials Chemistry A* **2013**, 1 (34), 9590-9596.
126. Ji, X. L.; Nazar, L. F., Advances in Li-S batteries. *Journal of Materials Chemistry* **2010**, 20 (44), 9821-9826.
127. Zhang, S. S., Liquid electrolyte lithium/sulfur battery: Fundamental chemistry, problems, and solutions. *J. Power Sources* **2013**, 231, 153-162.
128. Manthiram, A.; Fu, Y.; Su, Y.-S., Challenges and Prospects of Lithium-Sulfur Batteries. *Accounts of Chemical Research* **2013**, 46 (5), 1125-1134.
129. Yang, Y.; Zheng, G.; Cui, Y., Nanostructured sulfur cathodes. *Chemical Society Reviews* **2013**, 42 (7), 3018-3032.
130. Nagao, M.; Hayashi, A.; Tatsumisago, M., Sulfur-carbon composite electrode for all-solid-state Li/S battery with Li₂S-P₂S₅ solid electrolyte. *Electrochimica Acta* **2011**, 56 (17), 6055-6059.
131. Nagao, M.; Hayashi, A.; Tatsumisago, M., Fabrication of favorable interface between sulfide solid electrolyte and Li metal electrode for bulk-type solid-state Li/S battery. *Electrochemistry Communications* **2012**, 22, 177-180.
132. Nagao, M.; Hayashi, A.; Tatsumisago, M., High-capacity Li₂S-nanocarbon composite electrode for all-solid-state rechargeable lithium batteries. *Journal of Materials Chemistry* **2012**, 22 (19), 10015-10020.
133. Nagao, M.; Hayashi, A.; Tatsumisago, M., Electrochemical Performance of All-Solid-State Li/S Batteries with Sulfur-Based Composite Electrodes Prepared by Mechanical Milling at High Temperature. *Energy Technology* **2013**, 1 (2-3), 186-92.
134. Lecuyer, M.; Gaubicher, J.; Deschamps, M.; Lestriez, B.; Brousse, T.; Guyomard, D., Structural changes of a Li/S rechargeable cell in Lithium Metal Polymer technology. *J. Power Sources* **2013**, 241, 249-254.
135. Zhu, X. J.; Wen, Z. Y.; Gu, Z. H.; Lin, Z. X., Electrochemical characterization and performance improvement of lithium/sulfur polymer batteries. *J. Power Sources* **2005**, 139 (1-2), 269-273.
136. Yu, J.-H.; Park, J.-W.; Wang, Q.; Ryu, H.-S.; Kim, K.-W.; Ahn, J.-H.; Kang, Y.; Wang, G.; Ahn, H.-J., Electrochemical properties of all solid state Li/S battery. *Materials Research Bulletin* **2012**, 47 (10), 2827-2829.

137. Zhang, S. S.; Tran, D. T., A proof-of-concept lithium/sulfur liquid battery with exceptionally high capacity density. *J. Power Sources* **2012**, *211*, 169-172.
138. Skotheim, T. A.; Mikhaylik, Y. V.; Affinito, J. Lithium anodes for electrochemical cells 2007.
139. Rui, X.; Belharouak, I.; Li, J. C. M.; Xiaofeng, Z.; Bloom, I.; Baren, J., Role of polysulfides in self-healing lithium-sulfur batteries. *Advanced Energy Materials* **2013**, *3* (7), 833-8.
140. Tenhaeff, W. E.; Perry, K. A.; Dudney, N. J., Impedance Characterization of Li Ion Transport at the Interface between Laminated Ceramic and Polymeric Electrolytes. *Journal of the Electrochemical Society* **2012**, *159* (12), A2118-A2123.
141. Tenhaeff, W. E.; Yu, X.; Hong, K.; Perry, K. A.; Dudney, N. J., Ionic Transport Across Interfaces of Solid Glass and Polymer Electrolytes for Lithium Ion Batteries. *Journal of the Electrochemical Society* **2011**, *158* (10), A1143-A1149.

Appendix A – Conductivity of Low Molecular Weight SEO

This appendix contains temperature-dependent conductivity for several low molecular SEO copolymers that were not included in Chapter 5 because they were not symmetric or not ordered at the salt concentration of interest. The methods are identical to those described in Chapter 5.

Polymer	M _{PS} kg mol ⁻¹	M _{P_{EO}} kg mol ⁻¹	M _{SEO} kg mol ⁻¹	$\phi_{EO/salt}$	PDI	Morphology
SEO(1.9-0.8)	1.9	0.8	2.7	0.35	1.05	DIS
SEO(1.4-1.6)	1.4	1.6	3.0	0.59	1.03	DIS
SEO(1.4-2.3)	1.4	2.3	3.7	0.68	1.04	HEX→DIS
SEO(2.3-4.2)	2.3	4.2	6.5	0.70	1.04	HEX
SEO(5.7-2.6)	5.7	2.6	8.3	0.42	1.05	LAM

Table A-1 Characteristics of electrolytes at $r = 0.085$ used in Appendix A.

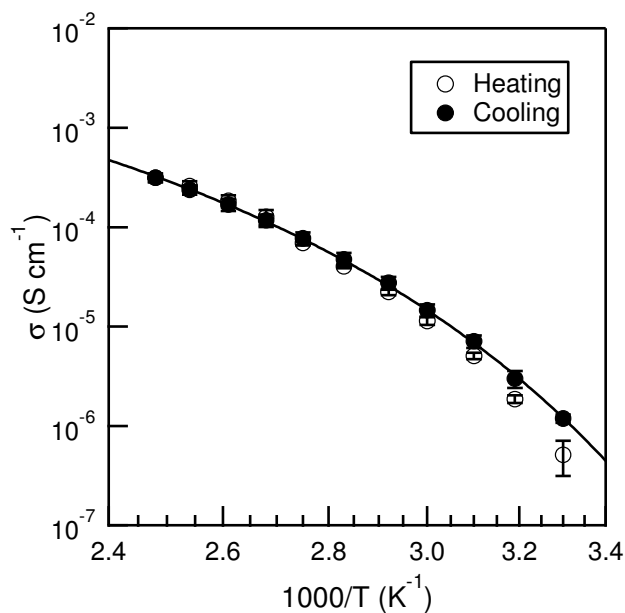


Figure A-1 Conductivity of SEO(1.9-0.8) at $r = 0.085$.

Conductivity, σ , versus inverse temperature for SEO(1.9-0.8) at $r = 0.085$. The solid curve indicates the VTF fitting to the cooling.

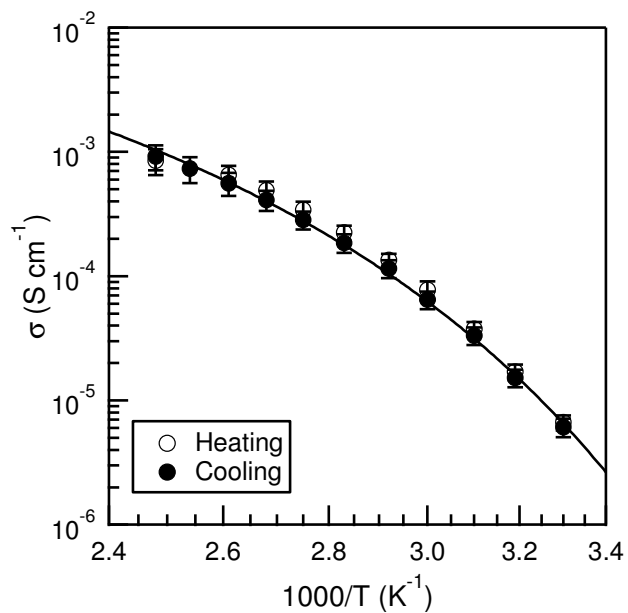


Figure A-2 Conductivity of SEO(1.4-1.6) at $r = 0.085$.

Conductivity, σ , versus inverse temperature for SEO(1.4-1.6) at $r = 0.085$. The solid curve indicates the VTF fitting to the cooling.

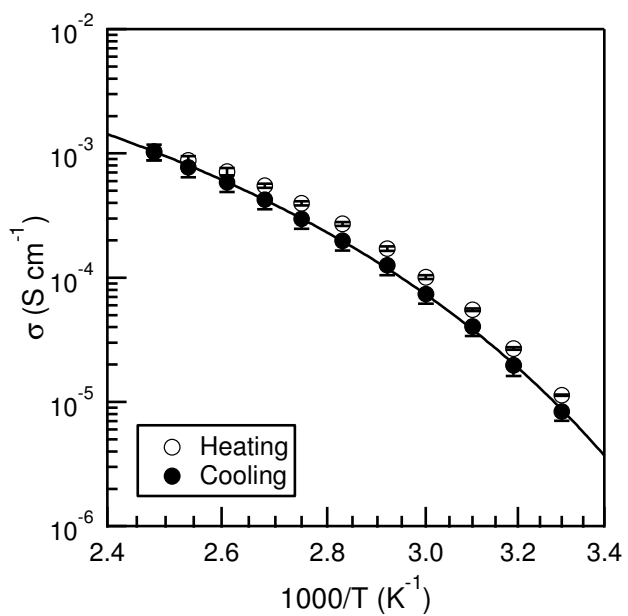


Figure A-3 Conductivity of SEO(1.4-2.3) at $r = 0.085$.

Conductivity, σ , versus inverse temperature for SEO(1.4-2.3) at $r = 0.085$. The solid curve indicates the VTF fitting to the cooling.

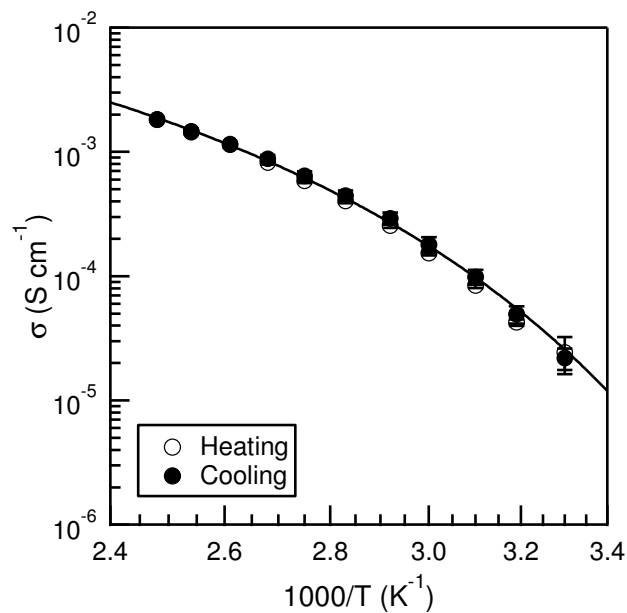


Figure A-4 Conductivity of SEO(2.3-4.2) at $r = 0.085$.

Conductivity, σ , versus inverse temperature for SEO(2.3-4.2) at $r = 0.085$. The solid curve indicates the VTF fitting to the cooling.

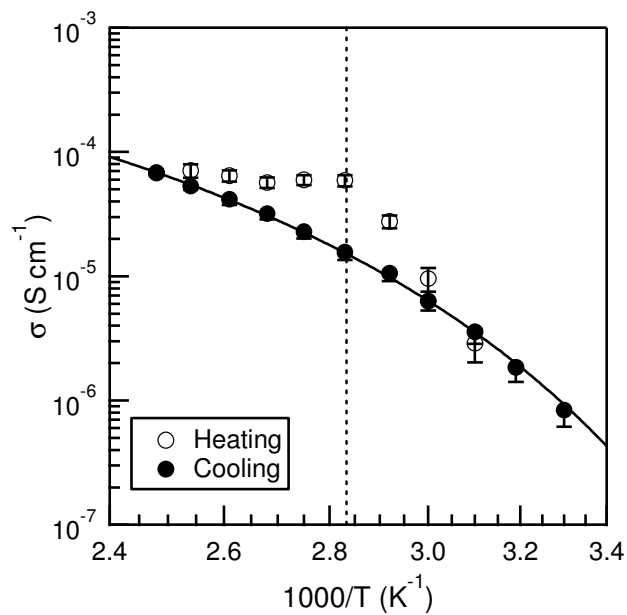


Figure A-5 Conductivity of SEO(5.7-2.6) at $r = 0.085$.

Conductivity, σ , versus inverse temperature for SEO(5.7-2.6) at $r = 0.085$. The solid curve indicates the VTF fitting to the cooling.

Appendix B – Conductivity Through the Order-Disorder Transition

This appendix contains simultaneous in-situ conductivity and x-ray scattering results for several salt-containing low molecular weight SEO copolymers. The methods are identical to those described in Chapter 6.

Lamellar to Disorder Transition

The samples in Figure B-1 both exhibit a lamellar to disorder transition and show qualitatively similar conductivity results to the sample discussed in detail in Chapter 6, where a steep rise in conductivity is observed upon disordering.

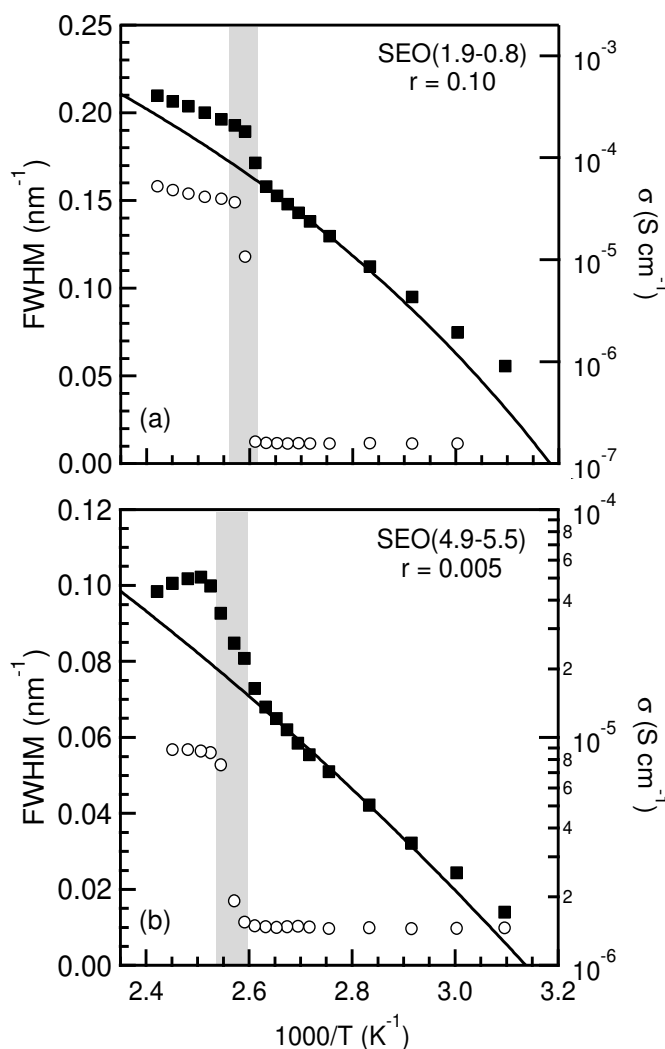


Figure B-1 In-situ SAXS and conductivity of lamellar to disorder transition.

(a) SEO(1.9-0.8)/LiTFSI at $r = 0.10$ and (b) SEO(4.9-5.5)/LiTFSI at $r = 0.005$. Left axis (empty circles) shows the FWHM of the primary scattering peak versus inverse temperature. Right axis (full squares) shows ionic conductivity versus inverse temperature. The gray bar indicates the order-disorder transition temperature, T_{ODT} , and the solid line indicates the VTF fit to conductivity data below the T_{ODT} .

Majority Cylinder to Disorder Transition

The samples in Figure B-2 both exhibit a transition to disorder from a cylindrical morphology with PEO as the matrix. Both samples show qualitatively different conductivity results than the sample discussed in detail in Chapter 6. The conductivity does not deviate significantly from the VTF fitting. While there is no expected change in the morphology factor, f , for these samples, there is an increase in conductivity on the order of 10% expected due to full-chain diffusion contributions upon disordering.

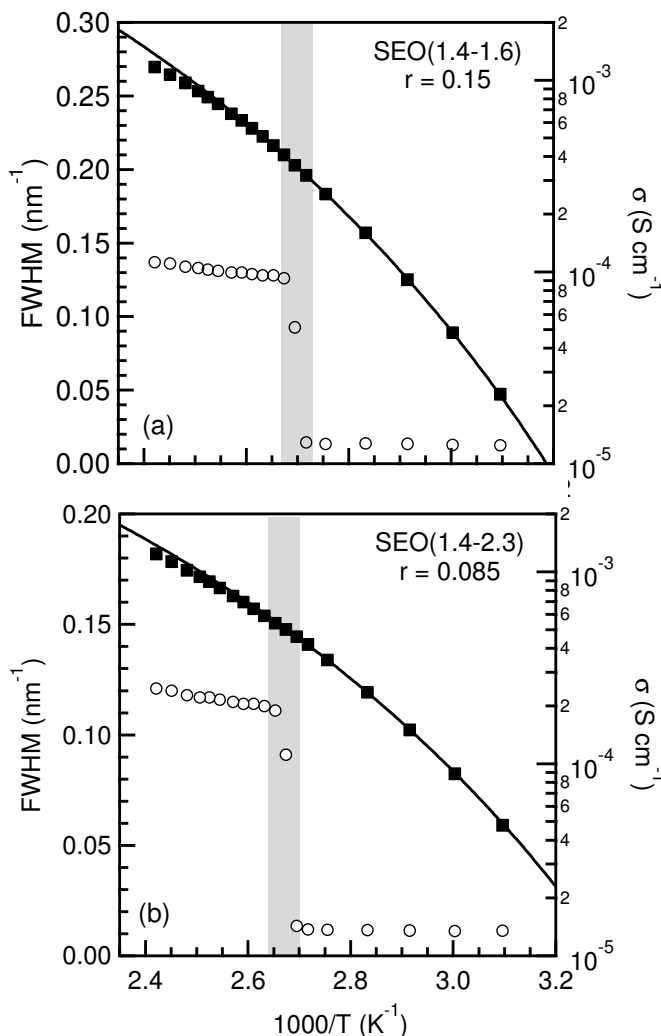


Figure B - 2 In-situ SAXS and Conductivity of a Cylinder to Disorder Transition.

(a) SEO(1.4-1.6)/LiTFSI at $r = 0.15$ and (b) SEO(1.4-2.3)/LiTFSI at $r = 0.085$. Left axis (empty circles) shows the FWHM of the primary scattering peak versus inverse temperature. Right axis (full squares) shows ionic conductivity versus inverse temperature. The gray bar indicates the order-disorder transition temperature, T_{ODT} , and the solid line indicates the VTF fit to conductivity data below the T_{ODT} .