

# Confinement and Interface Effects in Self Assembly of Functional Block Copolymers

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*For Claire, without whom I could never have made it this far.*

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*"It's the questions we can't answer that teach us the most. They teach us how to think. If you give a man an answer, all he gains is a little fact. But give him a question and he'll look for his own answers."*

*- Kvothe, from "The Wise Man's Fear" by Patrick Rothfuss*

# Abstract

Functional block copolymers are of increasing interest for their ability to combine the functional properties of one polymer, such as a polymer electrolyte or semiconductor, with the mechanical properties of another polymer. Balancing properties in this way can be challenging, however, due to the complex relationship between self-assembled morphology and resulting properties. Interface effects in particular, whether due to confinement within a self-assembled domain or at macroscopic boundary, are poorly understood in such functional block copolymers.

This dissertation consists of two main thrusts, each investigating confinement or interfacial effects in a different functional block copolymer system. The first thrust focuses on the relationship between crystallization and self-assembly in diblock block copolymers of poly(3-dodecylthiophene) (P3DDT) and poly(2-vinylpyridine) (P2VP). Through the use of in-situ and time-resolved X-ray scattering, three distinct modes of P3DDT crystallization were observed. These modes were found to depend on both the degree of crystallinity of the P3DDT block as well as the morphology of the block copolymer. Since degree of crystallization in these materials can, in many cases, be tuned without impacting self-assembled morphology (and vice-versa), these findings demonstrate that in this system the parameters that govern classical block copolymer self-assembly are decoupled from those that govern crystallization.

In the second thrust, the impact of interfacial order on the ionic conductivity in block copolymers of polystyrene (PS) and a polymeric ionic liquid (PIL) is investigated. Through a combination of X-ray scattering, impedance spectroscopy,

and island and holes studies on thin films, it was found that the formation of highly-oriented lamellar layers at film interfaces, which results in significant anisotropy in the ionic conductivity of PS-PIL block copolymers. In-plane conductivity was found to be enhanced in these materials by as much as 18x compared to the through-plane conductivity. Interestingly, a similar phenomenon was observed in a random copolymer of styrene and ionic liquid, with in-plane conductivity enhanced by as much as 3x compared to the through plane conductivity. This suggests that interfacial reordering even at very small length scales, which has been observed in amphiphilic random copolymers with large pendant groups, is sufficient to produce significant anisotropy in the ionic conductivity of the film.

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# Chapter 1

## Introduction

Block copolymers are a class of macromolecules characterized by discrete regions (or blocks) of different monomer chemistries. In the simplest case, the sequential polymerization of monomers A and B produces an AB linear diblock copolymer. A wide variety of more complex architectures are possible, however, including additional blocks and monomer chemistries (ABA triblock, ABCBA pentablock, etc.), as well as multiple chains connected at one or more branch points (star or bottlebrush polymers). Block copolymers are used in a wide variety of applications across many fields, ranging from pharmaceuticals to footwear. Despite the wide variety of applications in which block copolymers are used, nearly all leverage the difference in miscibility of the two blocks to serve their given function. In many cases, the self-assembled structure that arises from poor miscibility between the two blocks is the phenomenon that produces the desired properties.

Generally speaking, a polymer of one chemistry tends to be immiscible with a polymer of another chemistry, even if their respective monomers are miscible. This is a result of the inherent low entropy nature of polymers. To understand how the low entropy of polymer systems leads to unfavorable mixing, we can consider the free energy of mixing as

$$\Delta F = \Delta E - T\Delta S \tag{1.1}$$

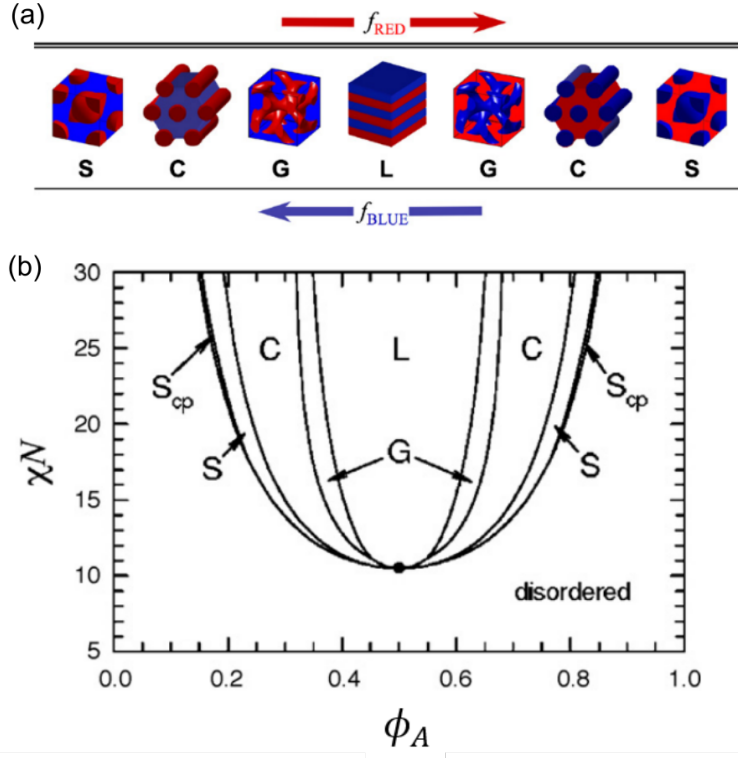
where  $\Delta E$  is the enthalpy of mixing,  $T$  is the absolute temperature, and  $\Delta S$  is the entropy of mixing. From Equation 1.1 it is clear that the favorability of mixing is dependent on both enthalpic and entropic contributions. In the case of small molecules, interactions between two different molecules tends to be less favorable than interaction between two molecules of the same kind, meaning that the enthalpic component generally does not favor mixing. The drastically increased number of available states created by mixing, however, often means that the entropic favorability of mixing dictates that mixing will occur, even if it is enthalpically unfavorable. In a mixture of polymers, however, the long-chain nature of the molecules means that far fewer states are available to the molecules as compared to, for example, a blend of the monomers that comprise them. Because of the significant decrease in entropy of a polymer mixture as compared to small molecules, the enthalpic contribution tends to outweigh the entropic contribution, meaning that the free energy of mixing  $\Delta F$  tends to favor immiscibility. The free energy of such a mixture can be described by Flory-Huggins theory[1], a model of polymer mixing derived from regular solution theory, as

$$\frac{\Delta F}{kT} = \frac{\phi_A \ln \phi_A}{N_A v_A} + \frac{\phi_B \ln \phi_B}{N_B v_B} + \frac{\chi_{AB} \phi_A \phi_B}{v} \quad (1.2)$$

where  $\phi_A$  and  $\phi_B$ ,  $N_A$  and  $N_B$ ,  $v_A$  and  $v_B$  are the volume fractions, degrees of polymerization, and monomer volume of polymers A and B, respectively;  $v$  is a reference volume (typically 0.1 nm<sup>3</sup>),  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\chi_{AB}$  is the Flory-Huggins interaction parameter, which relates to the favorability of interaction between monomers of A and B and is inversely proportional to temperature. In Equation 1.2, the first two terms describe the contribution of the entropy of mixing, while the final term describes the enthalpic contribution. As the degree of polymerization of either polymer increases, the number of possible states decreases, and the free energy of mixing increases. Likewise, as the  $\chi$  parameter increases, the favorability of interactions between the two polymers decreases, and the free energy of mixing increases.

In the case of block copolymers of two or more immiscible polymer chemistries, the covalent bond between the two polymer blocks prevents macro-scale phase separation, resulting in nano-scale phase separation with distinct domains of each block. If the driving force for phase separation between the two blocks, often quantified by the product of the degree of polymerization and Flory-Huggins interaction parameter  $\chi N$ , is large enough, the result is one of several nano-scale morphologies[2]. In diblock copolymers with two flexible, coil-like blocks, the morphology formed depends on the ratio of the two blocks, typically expressed as the volume fraction of one of the blocks, as depicted in Figure 1.1. In this case, roughly equal volume fractions of the blocks result in a sheet-like lamellar structure, where the periodicity of the repeating structure scales as  $d_0 \sim N^{2/3}$ [2]. As the asymmetry of the blocks increases, morphologies with greater degrees of curvature at the domain interface are obtained, such as the gyroid phase, hexagonally close-packed cylinders, and body-centered cubic spheres.

The self-assembled morphology of block copolymers makes it possible to bring together properties from different polymer chemistries in a way that is not possible for other kinds of copolymers. Because of the presence of distinct domains of the different blocks, it is possible to design a material that exhibits the desired properties of each block, rather than some middle-ground between them. One common example is the triblock thermoplastic elastomer known as SEBS, which contains two small end-blocks of polystyrene (PS) and a majority middle-block of rubbery poly(ethylene-butylene). In SEBS self-assembly leads to a continuous matrix of the rubbery middle-block with end-block anchored into PS spheres, creating a material that is both sturdy and flexible, ideal for the soles of shoes. In recent years, there has been interest in extending this class of materials beyond commodity uses and into energy applications such as solid electrolytes with tailored mechanical properties for lithium ion batteries[5–9] or flexible semiconductors for wearable electronics[10, 11]. However, the incorporation of such functional polymers into block copolymer architectures can add new factors that complicate the process of self-assembly, often leading to



**Figure 1.1:** (a) Classical equilibrium morphologies of diblock copolymers: body-centered cubic spheres (S), hexagonally close-packed cylinders (C), gyroid (G), and lamellae (L), reproduced with permission from reference [3]. From left to right, the fraction of blue-block decreases (red-block increase), and the continuous phase switches from blue to red. (b) Phase diagram of diblock copolymer morphologies predicted by self-consistent field theory, reproduced with permission from reference [4].

significant deviations from the simplest case depicted in Figure 1.1[12, 13]. Moreover, combining functionalities from the different polymers is not always straightforward, since factors such as the domain periodicity and the size of grains can have a significant impact on the properties of the resulting material. As a result, while the phase behavior and structure-property relationships of linear, flexible diblocks based on common commodity polymers is very well understood, there is much to learn about the more complex case of functional block copolymers.

For example, conjugated polymers, which are of interest as semiconductors, tend to have very high persistence lengths, making them rod-like as opposed to the more conventional coil-like flexible polymer chains[14, 15]. In addition, they tend to be semi-crystalline. Both of these properties make conjugated homopolymers brittle. To increase their suitability for use as flexible semiconductors, rod-coil block copolymers can be made in which one block is a rod-like conjugated polymer while the other is a coil-like polymer that provides the desired mechanical properties[16, 17]. In a lamellar rod-coil block copolymer, the high persistence length of the conjugated block can lead to significant deviation from the expected domain periodicity scaling of  $d_0 \sim N^{2/3}$  due to liquid crystal-like packing of the rod-like conjugated blocks[2, 13]. In addition, crystallization of the conjugated blocks acts as a force in competition with self-assembly, either distorting the self-assembled domains or disrupting them altogether[17–20]. While competition between self-assembly and crystallization, resulting crystallization "modes" dependent on factors like  $\chi N$  and morphology[21–23], has been studied for block copolymers with crystalline blocks such as polyethylene, the behavior of rod-coil systems is far less understood.

Another example of a poorly understood but potentially impactful functional block copolymer is the case of block copolymer electrolytes, particular those based on ionic liquid monomers[5, 9, 24, 25]. Block copolymers based on polymeric ionic liquids (PILs) are generally designed in order to combine the ionic conductivity of the PIL block with the desired mechanical properties of another block, such as PS. Because only one block is capable of ion transport, the self-assembled morphology has a

significant impact on the resulting material’s conductivity. For example, a material in which PIL domains are isolated from one another will have much poorer conductivity relative to a material with highly connected PIL domains[26–28]. Furthermore, alignment of domains along a particular film axis, either by processing or by a thermodynamically driven interfacial interaction, can lead to increased connectivity in one direction and decreased connectivity in another[29–32]. Once again, while domain connectivity and alignment have been well studied in diblock copolymers based on common commodity polymers, the complex case of polymer electrolytes is less well understood, and will also be considered in this dissertation.

The research detailed in this dissertation consists of two main efforts. Chapter 2 provides an overview of the major experimental techniques used in this dissertation. In the first project, covered in Chapter 3, crystallization modes in linear block copolymers of poly(2-vinylpyridine) and poly(3-dodecylthiophene) are investigated as a function of morphology and degree of crystallinity through the use of *in situ* and time-resolved small- and wide-angle X-ray scattering. In the second project, covered in Chapters 4 and 5, the effect of surfaces on ionic conductivity in lamellar block copolymers of PS and one of two PIL chemistries is studied through a combination of X-rays scattering, impedance spectroscopy, and island and hole studies in thin films. In Chapter 6, the outlook for these efforts and questions to be considered are discussed.

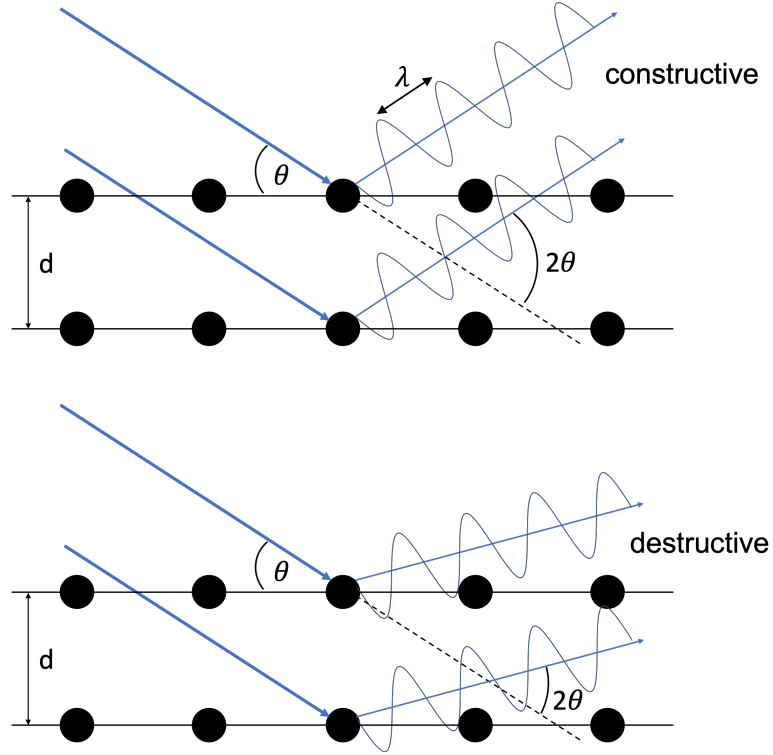
# Chapter 2

## Methods

### 2.1 X-ray Scattering

X-ray scattering is a technique that uses the interference patterns produced by the absorption and re-emission of X-rays to reveal information about the structure of a material[33]. In a typical scattering experiment, a sample is placed between an X-ray source and a photon detector then irradiated by an X-ray beam. The atoms of the sample absorb the X-rays and electrons are excited. When the electrons relax to their original state, X-rays of the same energy as those absorbed (in elastic scattering) are emitted, which interfere with one another either constructively or destructively at certain angles relative to the incoming beam. At angles that produce constructive interference, an increase in intensity is observed. Conversely, a decrease in intensity is observed at angles that produce destructive interference. The resulting interference pattern can be registered by the detector and analyzed for information about the sample's structure (Figure 2.1). Bragg's law expresses the relationship between the scattering angle  $2\theta$  and the characteristic size of the structure  $d$  that leads to scattering as

$$n\lambda = 2d \sin \theta \tag{2.1}$$



**Figure 2.1:** X-rays of wavelength  $\lambda$  scattered by a crystal lattice. At scattering angles  $2\theta$  that produce constructive interference, an increase in intensity is observed, and the relationship between scattering angle and lattice dimension  $d$  is described by Bragg's law (top). At angles where interference is destructive, scattering is not observed (bottom).



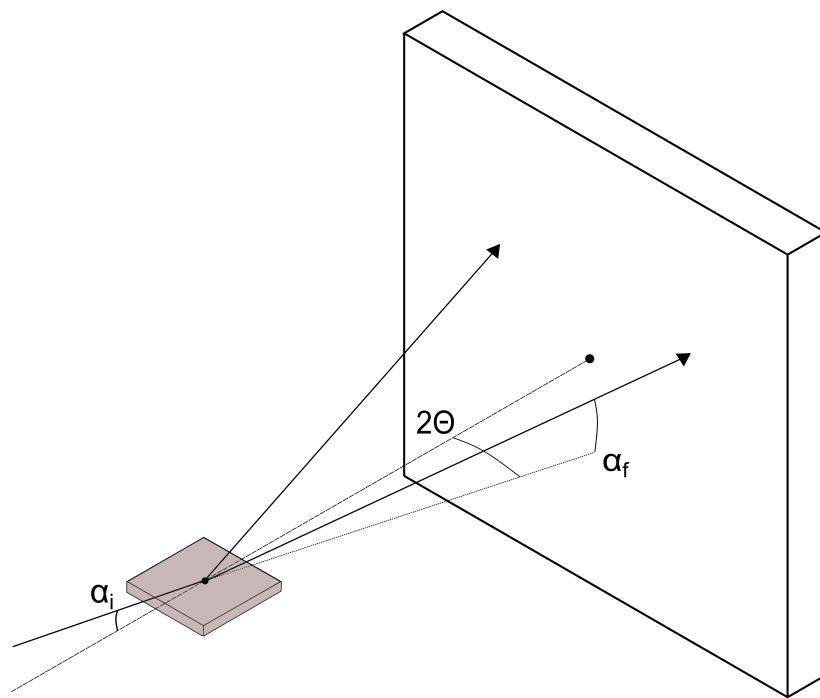
where  $\lambda$  is the wavelength of the X-ray radiation and  $n$  is the diffraction order ( $n = 1$  is first order,  $n = 2$  is second order, etc.). In some X-ray scattering techniques, it is more customary to describe the direction of scattering as the momentum transfer vector  $q$  instead of the scattering angle  $2\theta$ , where

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (2.2)$$

The momentum transfer vector is then related to the characteristic scattering structure size as  $q = 2\pi/d$ .

It is clear from Bragg's law that smaller structures scatter at wider angles (larger  $q$ ), and vice versa. By changing the sample-to-detector distance (SDD), scattering can be captured at wide range of angles and, therefore, a wide range of structure sizes can be probed. Wide-angle X-ray scattering (WAXS) operates at very short SDD (typically on the scale of centimeters) to collect scattering at large angles, and can therefore be used to study atomic or molecular length scales, such as the lattice dimensions of a crystalline material. WAXS is used extensively in Chapter 3 to characterize crystal growth in semicrystalline block copolymers. Small-angle X-ray scattering (SAXS) probes larger structures (1 to 100 nm) by using an SDD on the scale of meters, and is commonly used to characterize the self-assembled morphology of block copolymers, and is used for this purpose in Chapters 3 - 6.

Grazing-incidence small-angle X-ray scattering (GISAXS) is a related technique used for structural characterization of nanostructured thin films, like those formed from block copolymers. In a GISAXS experiment, an X-ray beam strikes a thin film supported on a reflective substrate at an incident angle  $\alpha_i$  (0.05-0.5 °, typically). The beam reflects off the sample or substrate, and X-rays are scattered by the sample onto the detector at in-plane angle  $2\theta$  and out-of-plane angle  $\alpha_f$ , as depicted in Figure 2.2. The depth to which the beam penetrates the sample before reflection is dependent on the value of the incident angle relative to a material-specific critical angle  $\alpha_c$ [34]. If the  $\alpha_i$  is well below  $\alpha_c$ , the beam is totally reflected by the sample, and the penetration



**Figure 2.2:** Geometry of a GISAXS measurement.

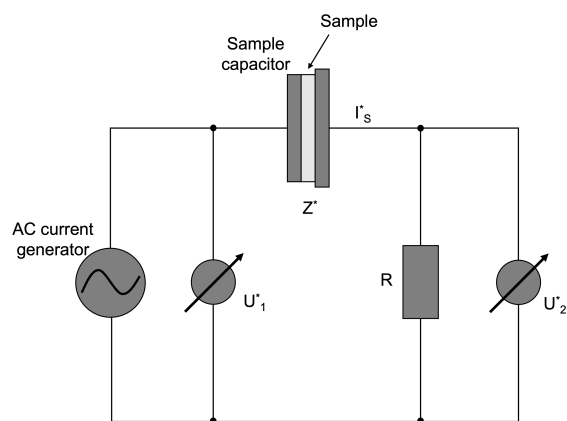
depth is on the order of a few nanometers. Experiments at such low  $\alpha_i$  therefore probe only the vacuum-sample interface. If  $\alpha_i$  is much greater than  $\alpha_c$ , the penetration depth of the beam increases by several orders of magnitude, and scattering occurs throughout this region of the film. If the penetration depth is greater than the film thickness, the beam reflects off the substrate-sample interface. Since scattering can occur from either the incident or reflected beam, multiple scattering features are produced for each “intrinsic” feature[34]. GISAXS is used in Chapters 4 and 5 to characterize the distinct self-assembled structures adopted by block copolymers at interfaces.

## 2.2 Impedance Spectroscopy

Impedance spectroscopy measures the polarization response resulting from the reorientation of dipoles in a material exposed to an alternating electric field. These dipoles can be permanent dipoles (e.g. dipole moments of polar molecules) or induced by relocation or aggregation of charges. At the very highest frequencies ( $10^{15}$  to  $10^{12}$  Hz) the oscillations of electron clouds and vibration of nuclei relative to one another can be observed, but most dipoles of molecular origin—i.e. those of interest in the present work—are observed in the range of  $10^9$  to  $10^{-2}$  Hz[35].

A measurement is made by applying an alternating electric field  $\vec{E} = \vec{E}_0 e^{-i\omega t}$ , where  $\vec{E}_0$  is the field magnitude and  $\omega$  is the frequency. The polarization response results in a current through the sample  $I_S^*$ , calculated using Ohm’s Law by dividing the voltage  $U_2^*$  measured at a voltmeter downstream of the sample by a reference resistor of resistance  $R$ , as depicted in Figure 2.3. From here the complex impedance is  $Z^* = U_S^*/I_S^* = 1/i\omega C^*$ , where  $U_S^*$  is the difference between the voltages  $U_1^*$  and  $U_2^*$ , as depicted in Figure 2.3, and  $C^*$  is the complex capacitance.

The way in which complex impedance is analyzed and what information can be obtain from the spectrum is highly dependent on the sample geometry and impedance



**Figure 2.3:** Schematic representation of the circuit used to measure impedance  $Z^*$  in impedance spectroscopy[35].

technique used. In this work, the two main impedance spectroscopy techniques employed are broadband dielectric spectroscopy (BDS) and electrochemical impedance spectroscopy (EIS). While the two techniques vary in the frequency range accessible (BDS can measure up to  $10^7$  Hz while EIS is limited to  $10^5$  Hz), the manner in which  $Z^*$  is calculated can be considered the same for the purposes of this work. The most important distinction considered here is the difference in electrode configuration that is commonly employed with each technique.

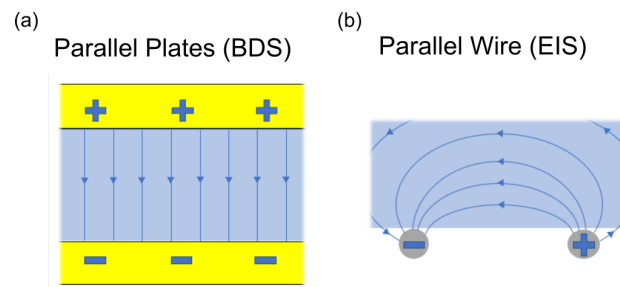
In BDS, a parallel plate electrode geometry is used (Figure 2.4a), and the system can be considered a capacitor[35]. In a capacitor, the complex permittivity is the ratio of complex capacitance to the capacitance of the same geometry in a vacuum,  $\varepsilon^* = C^*/C_0$ . The complex permittivity can be calculated from the complex impedance by the relationship

$$\varepsilon^*(\omega) = \frac{1}{i\omega C_0 Z^*(\omega)} \quad (2.3)$$

where vacuum capacitance can be calculated from the sample geometry such that  $C_0 = \varepsilon_0 A/d$ , where  $\varepsilon_0 = 8.85 \times 10^{-12}$  F/cm is the vacuum permittivity,  $A$  is the electrode area, and  $d$  is the electrode spacing. This relationship for  $C_0$  holds true for parallel plate geometry under the assumption that the electric field lines interacting with the sample are perfectly parallel and that all fringe effects, which arise due to non-uniform field lines bending at the edges of the electrodes, can be neglected.

The complex permittivity  $\varepsilon^*$  is typically used to express the dielectric data for systems in which dipolar relaxation is the primary process of interest. For systems in which conductive processes are of primary concern, such as polymer electrolytes, it is more typical to represent the data using the complex conductivity  $\sigma^*$  and complex electrical modulus  $M^*$ . The complex permittivity relates to the complex conductivity as

$$\sigma^*(\omega) = i\omega\varepsilon_0\varepsilon^*(\omega) \quad (2.4)$$



**Figure 2.4:** Electrode configurations commonly used in impedance spectroscopy and the shape of resulting electric field lines. Parallel plate configuration (a) produces uniform and parallel electric field lines, while field lines produced by parallel wire configuration (b) are neither uniform nor parallel.

where the real and imaginary components of each are related to one another as

$$\sigma'(\omega) = \omega \varepsilon_0 \varepsilon''(\omega) \quad (2.5)$$

$$\sigma''(\omega) = \omega \varepsilon_0 \varepsilon'(\omega) \quad (2.6)$$

The complex permittivity  $M^*$  relates to complex electrical modulus  $M^*$  as

$$M^*(\omega) = 1/\varepsilon^*(\omega) \quad (2.7)$$

where the real and imaginary components of each are related to one another as

$$M'(\omega) = \frac{\varepsilon'(\omega)}{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2} \quad (2.8)$$

$$M''(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2} \quad (2.9)$$

Figure 2.5 depicts typical  $\sigma'$ ,  $\sigma''$ , and  $M''$  spectra for a polymeric ionic liquid and highlights the key information that can be obtained. The characteristic rate at which ions hop from one stable site to the next,  $\omega_c$ , can be estimated from the frequency of the peak in  $M''$ . The hopping of ions at this constant characteristic speed at a given temperature leads to a frequency-independent plateau in  $\sigma'$ , the value of which is considered the DC ionic conductivity,  $\sigma_{DC}$ . At sufficiently low frequency, ions begin to build up at the electrode. This polarization of the electrode causes a decline in  $\sigma'$ . The frequency of the full development of electrode polarization,  $\omega_{EP}$ , can be estimated by the frequency of the low-frequency peak in  $\sigma''$ .

The onset of ion hopping and DC ionic conductivity in the complex conductivity can be modeled by the Jeppe-Dyre model[36], also known as the random barrier model, which describes ion transport across a landscape of random energy barriers to ion hopping and can be stated as

$$\sigma^* = \sigma_0 \frac{i\omega\tau_e}{\ln(1 + i\omega\tau_e)} \quad (2.10)$$

where  $\sigma_0$  is the DC ionic conductivity and  $\tau_e = 1/\omega_c$  is the characteristic ion hopping time. A single Jeppe-Dyre model, however, is insufficient to capture the phenomenon of electrode polarization[36, 37]. Since electrode polarization occurs due to a thin layer of charge building up at the electrode and forming an insulating layer, electrode polarization can be incorporated into the model by treating this thin insulating interfacial layer and the bulk of the film as capacitors in series such that

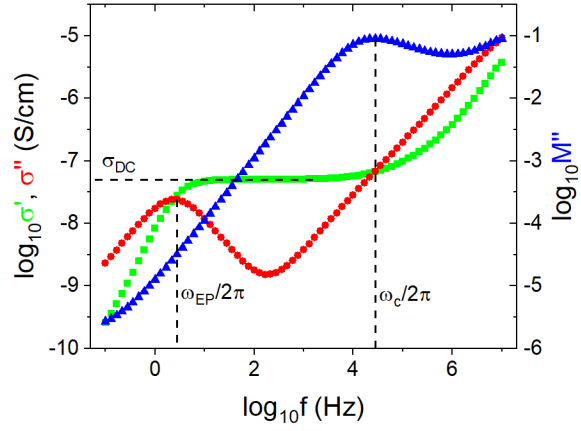
$$\frac{h}{\sigma^*} = \frac{2h_1}{\sigma_1^*} + \frac{h_2}{\sigma_2^*} \quad (2.11)$$

where  $h$  is the thickness of the polymer film,  $h_1$  and  $h_2$  are the thicknesses of the interfacial and bulk regions, respectively, and the complex conductivities of each region ( $\sigma_1^*$  and  $\sigma_2^*$ ) are described by a separate Jeppe-Dyre equations[37]. This model is given a fuller treatment in the context of polymer electrolyte films with interfacial layers of polystyrene in Chapter 5.

In heterogeneous materials, such as block copolymer electrolytes, it is not uncommon to observe additional polarizations due to charge buildup at internal interfaces between materials of different conductivities (e.g. domain interfaces or grain boundaries, in the case of block copolymers). These interfacial polarizations, or Maxwell-Wagner-Sillars (MWS) polarizations[35], generally occur between  $\omega_c$  and  $\omega_{EP}$ , and therefore often obscure the  $\sigma'$  plateau associated with  $\sigma_{DC}$ . In such cases, it is customary to estimate  $\sigma_{DC}$  as the value of  $\sigma'(\omega)$  at  $\omega = \omega_c$ [38, 39].

The complex impedance spectra produced by EIS cannot be analyzed in the same way as the spectra produced by BDS, primarily due to the difference in sample geometry. While EIS is also limited in frequency range compared to BDS, the biggest difference results from the common use of a parallel wire electrode configuration (Figure 2.4b) instead of parallel plates. Recall that in Equation 2.3,  $C_0 = \varepsilon_0 A/d$  is valid under the assumption that electric field lines are perfectly parallel and all fringe





**Figure 2.5:** Representative  $\sigma'$ ,  $\sigma''$ , and  $M''$  spectra as a function of frequency  $f$  for a polymer electrolyte (where  $\omega = 2\pi f$ ). DC ionic conductivity  $\sigma_{DC}$  is determined by the plateau value in  $\sigma'$ . The characteristic ion hopping frequency  $\omega_c$  can be estimate by the peak position in  $M''$ , and the frequency of electrode polarization  $\omega_{EP}$  can be estimated by the position of the peak in  $\sigma''$ .

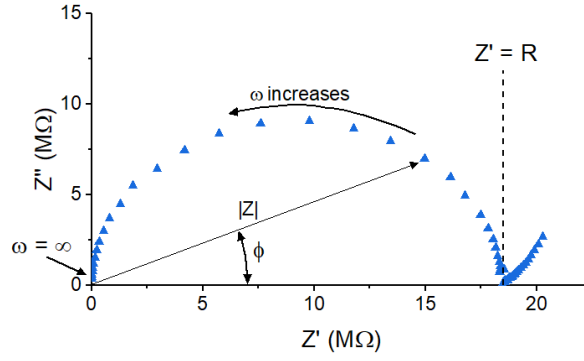
effects can be neglected. This assumption is true for a parallel plate configuration with a sufficiently high diameter-to-thickness ratio. For the parallel wire configuration commonly employed in EIS, however, most of the electric field lines are not parallel to each other—the entire field can be considered, in effect, fringe effects. Because of this, analysis of EIS data must necessarily be limited to the real and imaginary components of the complex impedance,  $Z'(\omega)$  and  $Z''(\omega)$ , respectively, from which  $\sigma_{DC}$  can still be calculated by two methods.

The first method commonly employed is the Nyquist plot, which plots  $Z'$  on the x-axis and  $Z''$  on the y-axis, as depicted in Figure 2.6. The result for a conductive material is a semi-circle. The non-zero x-intercept of the semi-circle is the sample's resistance  $R$ [35]. The DC ionic conductivity can be calculated

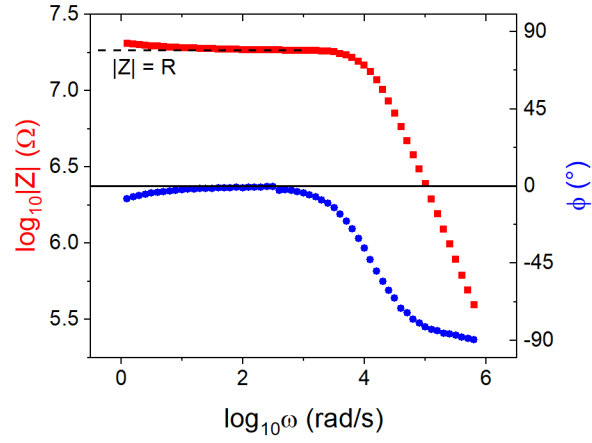
$$\sigma_{DC} = L/(whR) \quad (2.12)$$

where  $L$  is the electrode spacing,  $w$  is the width of the sample, and  $h$  is the sample thickness. A weakness of the Nyquist plot is that, while frequency generally increases counterclockwise around the semi-circle, for any given point the frequency value is not determinable. Therefore, another means of representing EIS data, the Bode plot, is often employed (Figure 2.7). The Bode plot makes use of the fact that in addition to  $Z'$  and  $Z''$ , each point on the Nyquist plot can also be described by the magnitude of the impedance vector  $|Z|$  and the phase angle  $\phi$ . By plotting both  $|Z|$  and  $\phi$  versus  $\omega$  (log scale for  $|Z|$  and  $\omega$ , linear scale for  $\phi$ ), usually on the same plot, the same information as the Nyquist plot can be presented while retaining the frequency dependence of the data. The plateau value of  $|Z|$  in a Bode plot is taken to be resistance  $R$ , from which DC ionic conductivity is calculated using Equation 2.12[35].

The impedance techniques and analysis methods described here are used in Chapters 4, 5, and 6 to characterize the in-plane and through-plane ionic conductivity



**Figure 2.6:** Nyquist plot representation of impedance data for a polymer electrolyte. The greater x-intercept value of  $Z'$  is the resistance  $R$  of the sample.



**Figure 2.7:** Bode plot representation of impedance data for a polymer electrolyte. The plateau value of  $|Z|$  is the resistance  $R$  of the sample.

of block copolymer electrolytes and to elucidate the role of interfacial order in conductive anisotropy in such systems.

## Chapter 3

# Crystallization Modes of Poly(3-dodecylthiophene)-based Block Copolymers

The work described in this chapter was done in collaboration with researchers at the Korea Advanced Institute of Science and Technology (KAIST) and has been published in:

Coote, J. P.<sup>\*</sup>, Kim, J. S.<sup>\*</sup>, Lee, B., Han, J., Kim, B. J., Stein, G. E. "Crystallization Modes of Poly(3-dodecylthiophene)-Based Block Copolymers Depend on Regioregularity and Morphology". *Macromolecules*, 2018, 51(22), 9276–9283.

<sup>\*</sup>equal contributions

J.P. Coote acquired and analyzed all scattering data and wrote the paper. J.S. Kim synthesized and characterized all materials described here and acquired the TEM images.

### 3.1 Introduction

Conjugated polymers have optoelectronic properties that enable their applications in photovoltaics, batteries, light-emitting diodes, and field effect transistors.[6, 10, 11, 40, 41] When conjugated polymers are incorporated in a block copolymer (BCP) architecture, their utility and functions can be enhanced by self-assembly: as examples, the formation of nanoscale functional domains and high interfacial area can tune charge and energy transfer processes[42, 43] or tailor mechanical responses[16, 44]. However, it is well-documented that crystallization of conjugated blocks can disrupt self-assembly, leading to a poorly-ordered fibrillar texture. This behavior has been observed in conjugated-coil BCPs based on highly regioregular poly(3-hexylthiophene) (P3HT)[17–20] and poly(2,5-di(2'-ethylhexyloxy)-1,4-phenylenevinylene)[45].

In BCPs based on polyethylene (PE), it is possible to crystallize PE while maintaining all or some of the self-assembled structure. This is achieved through processes termed “confined” and “templated” crystallization.[21–23] In confined crystallization, confinement is imposed in one of two ways: the amorphous block is glassy at the crystallization temperature, producing a physical boundary that guides crystallization within the self-assembled structure[46–48]; or the amorphous block is rubbery at the crystallization temperature, yet the BCP is so strongly segregated that thermodynamic barriers prevent changes to the self-assembled structure during crystal growth.[21] Templated crystallization is observed when the amorphous block is rubbery and the copolymer is at intermediate segregation strength, so crystal growth can distort the domains, but the overall self-assembled symmetry is preserved.[21, 49] Finally, PE-based BCPs can also undergo a “break out” crystallization process: this is observed when the amorphous block is rubbery and the BCP is more weakly segregated, so crystal growth destroys the melt state symmetry.[21, 50, 51]

Poly(3-alkylthiophenes) (P3ATs) are a popular class of conjugated polymers for fundamental studies of structure-property relations,[40] and show promise for

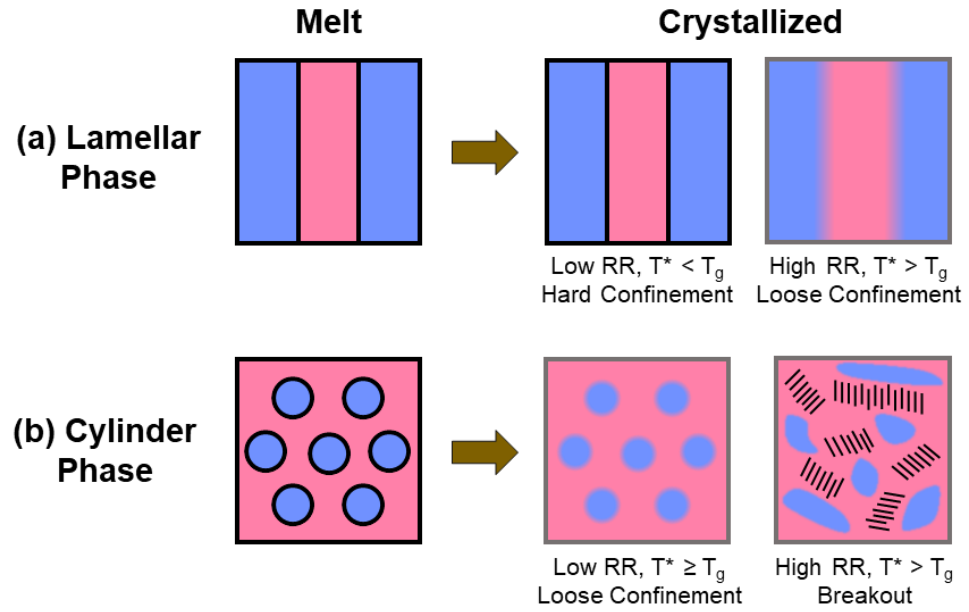
applications in stretchable and wearable electronics.[44, 52–55] P3ATs and PE have distinct chain conformations that lead to different crystallization mechanisms.[56] P3ATs are semiflexible polymers that adopt highly extended chain conformations in a melt state and during crystallization, so crystal growth is largely determined by intermolecular interactions. On the other hand, PE is very flexible and will fold during crystallization, so crystal growth proceeds by both intra- and inter-molecular processes. Despite these differences, it is possible to engineer P3AT-based BCPs that exhibit similar crystallization modes as PE-based BCPs. This is usually accomplished by using bulky alkyl substituents that increase the flexibility of conjugated blocks and reduce the strength of their intermolecular interactions, such that the drive for crystallization and self-assembly is more balanced. Confined crystallization has been demonstrated with lamellar and cylindrical BCPs based on highly regioregular poly(3-(2'-ethyl)hexylthiophene) (P3EHT) and flexible blocks such as poly(lactid acid) (PLA),[57] poly(ethylene oxide) (PEO),[58] poly(methyl acrylate) (PMA),[59, 60] and polystyrene (PS)[59]. Break-out crystallization has also been documented in P3EHT-PEO BCPs when the melt-state morphology is a gyroid, as this symmetry is not compatible with the P3EHT crystal growth.[58] Confined crystallization has also been demonstrated with BCPs based on highly regioregular poly(3-dodecylthiophene) (P3DDT) and poly(methyl methacrylate) when the P3DDT content was low (less than  $\sim 60\%$ ), or the P3DDT block length was very high.[61, 62] Otherwise, break-out of P3DDT crystals destroys the self-assembled morphology.

While systematic changes to alkyl substituents can manipulate chain flexibility and interaction strength in P3ATs,[15] this approach will also change other attributes of the system, including the crystal structure and intrinsic electronic properties.[63] Furthermore, in P3AT-based BCPs, the Flory interaction parameter and conformational asymmetry will vary with the type of alkyl substituent. As an alternative, regioregularity (RR) can tune the chain flexibility and interaction strength of P3ATs,[15] and recent studies have shown that this attribute can be varied systematically in both P3HT and P3DDT.[13, 20, 52] By controlling the RR

of P3AT-based BCPs, one can decouple many of the architectural and thermodynamic parameters that control P3AT crystallization and self-assembly. This approach was first demonstrated with P3HT-*b*-poly(2-vinylpyridine): highly ordered lamellar and cylindrical BCP were observed when RR was less than approximately 80%, but crystal growth disrupted self-assembly when RR was high.[20] However, highly regioregular P3HT has a very high melting temperature ( $> 220^{\circ}\text{C}$ ), so it is difficult to access the melt-state morphology and examine crystallization behavior.

Recently, we reported the synthesis and melt-state structure in a series of P3DDT-*b*-poly(2-vinyl pyridine) (P2VP) materials.[13] These studies are enabled by the low P3DDT melting temperature of approximately  $140^{\circ}\text{C}$  at high RR. When RR is low (70-85%), the P3DDT chains adopt a bilayer conformation that is typical of flexible BCPs. However, when RR is high (94%), the P3DDT chains interdigitate in a liquid crystalline monolayer. These behaviors are observed in both lamellar (ca. 50% P3DDT) and cylindrical (ca. 70% P3DDT) phases. In our present work, we examine the effects of RR on crystallization modes of P3DDT-*b*-P2VP copolymers using time-resolved small angle and wide angle X-ray scattering. All samples are cooled from a melt state to below the crystallization temperature, and then isothermally annealed to examine crystal growth and any changes to the self-assembled structure. We find three different crystallization modes (Figure 3.1) that are similar to the processes in PE-based materials: When lamellar and cylindrical phases are crystallized near or below the glass transition of P2VP, which occurs in systems with low RR, the crystal growth is confined by the block copolymer template. However, when crystallized above the glass transition of P2VP, we observe “loose confinement” in lamellar phases and breakout in cylindrical phases.





**Figure 3.1:** Observed crystallization modes depend on both morphology and  $T^*$  relative to  $T_g$ , where  $T^*$  is defined as the highest temperature at which crystallization is detected in the WAXS spectrum after 2 minutes of isothermal annealing.  $T^*$  is sensitive to RR. Blue domains = P2VP.

## 3.2 Methods

**Materials.** All P3DDT-*b*-P2VP copolymers were prepared by collaborators at Korea Advanced Institute of Science and Technology (KAIST) according to synthetic procedures described in our previous work.[13].

**Sample Preparation.** All P3DDT-*b*-P2VP copolymers were prepared for X-ray scattering by pressing in low mass aluminum DSC pans (10  $\mu$ L). The pans were placed in open glass vials for identification and annealed under high vacuum ( $10^{-7}$  Torr) at 160  $^{\circ}$ C overnight (10-15 h).

**Small Angle/Wide Angle X-ray Scattering (SAXS/WAXS).** Simultaneous small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements were performed at the beamline 12-ID-B at Argonne National Laboratory. The DSC pans holding pre-annealed samples were fit into a Linkam heating stage and illuminated at normal incidence (transmission through the film thickness) under nitrogen at temperatures ranging from 160  $^{\circ}$ C down to 25  $^{\circ}$ C. Feedback to the temperature controller came from a thermocouple embedded in the stage, and a secondary thermocouple measured the temperature at the inserted DSC pan. Temperature stability was considered to be the point at which these two thermocouples recorded the same value. Samples were probed with a 13.3 keV (wavelength  $\lambda = 0.093$  nm) X-ray beam with a sample to detector distance of 2.3 m using a 0.1 sec exposure time. The beam spot size at the sample was approximately 10  $\mu$ m tall by 200  $\mu$ m wide. To avoid beam damage, the position relative to the beam was changed by 11  $\mu$ m along the vertical direction between every exposure. Scattered radiation was collected using a Pilatus 2M detector ( $1475 \times 1679$  pixels, 172  $\mu$ m pixel size). The 2-dimensional (2D) scattering data were reduced to 1-dimensional (1D) scattering curves by azimuthal integration using the SAXSLee software. Scattering data were collected for an empty aluminum DSC pan under nitrogen at ambient conditions, which was used as a background measurement. The scattering data for

samples were corrected by subtracting this background measurement. The magnitude of the scattering vector ( $q$ ) is given by  $q = 4\pi \sin \theta / \lambda$ , where  $2\theta$  is the scattering angle. The  $q$ -range detected was 0.04 to 2.7 nm<sup>-1</sup>. Direct beam transmission intensity was recorded with a photodiode and was then used to calculate the sample thickness at each measurement spot using the equation  $x = -\ln(I_0/I)$ , where  $x$  is the sample thickness at the measurement spot,  $I_0$  is the direct beam intensity prior to transmission, and  $I$  is the direct beam intensity after transmission. The scattered intensity  $I_s$  collected for each spot at the Pilatus detector was then corrected by normalizing with the thickness  $x$ , i.e.,  $I_s/x$ .

**Transmission Electron Microscopy (TEM).** Samples were prepared for TEM by annealing at 200 °C for 2 h then slowly cooling to 160 °C and annealing for 24 h. Samples were then cooled to room temperature over 24 h at a constant cooling rate of 0.09 °C/min. Samples were microtomed to ~50 nm thickness employing an RMC PowerTome-X with a diamond knife and then stained with iodine vapor. All the TEM images were obtained using a JEM-3011 HR electron microscope.

### 3.3 Results and Discussion

The P3DDT-*b*-P2VP materials considered in this work are summarized in Table 3.1. All of the synthetic details and characterization of RR-tuned P3DDT-*b*-P2VP are described elsewhere<sup>[13]</sup> and briefly summarized in Appendix A. For convenience, the copolymers were denoted as RR*X*-VP*Y*, where *X* is the RR of P3DDT block and *Y* is the volume fraction of P2VP block. All copolymers are majority P3DDT and assemble into either lamellar or hexagonally-packed cylindrical morphologies. Within each domain, the chain packing depends on the P3DDT RR.<sup>[13]</sup> When RR is high, the chains interdigitate in a liquid crystalline monolayer (LC). Otherwise, the chains adopt a flexible bilayer conformation (BL).

**Table 3.1:** Summary of materials. RR is regioregularity of P3DDT block, determined by  $^1\text{H}$  NMR; N is degree of polymerization, determined by signal intensities and mass-to-charge ratios from MALDI-ToF for P3DDTs and SEC for P2VPs;  $f_{\text{P2VP}}$  is P2VP volume fraction, calculated from the P2VP mole fraction, determined by  $^1\text{H}$  NMR, and the density of each block;  $\bar{D}$  is the dispersity, determined by SEC.

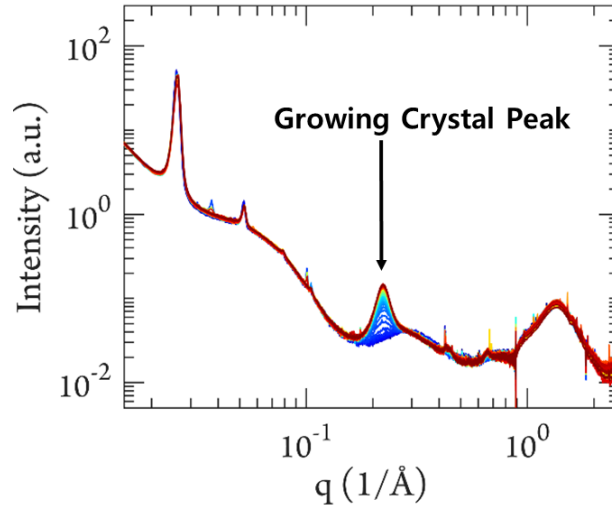
| Sample Name | RR | $N_{\text{P3DDT}}$ | $N_{\text{P2VP}}$ | $f_{\text{P2VP}}$ | $\bar{D}_{\text{P3DDT}}$ | $\bar{D}_{\text{P2VP}}$ |
|-------------|----|--------------------|-------------------|-------------------|--------------------------|-------------------------|
| RR94-VP34   | 95 | 17.6               | 27.6              | 0.34              | 1.09                     | 1.14                    |
| RR79-VP39   | 79 | 19.2               | 30.4              | 0.39              | 1.22                     | 1.16                    |
| RR70-VP37   | 70 | 17.2               | 30.4              | 0.37              | 1.20                     | 1.16                    |
| RR94-VP25   | 94 | 17.6               | 19.0              | 0.25              | 1.09                     | 1.14                    |
| RR79-VP29   | 79 | 19.2               | 19.0              | 0.29              | 1.22                     | 1.14                    |
| RR70-VP29   | 70 | 17.2               | 19.0              | 0.29              | 1.20                     | 1.14                    |

The crystallization temperature for SAXS/WAXS measurements was selected based on the rate of crystallization at a reference temperature  $T^*$ , which is the highest temperature where crystallization is detected after 2 min of isothermal annealing. We defined this reference temperature for convenience: very fast crystallization process cannot be examined under isothermal conditions due to finite cooling rates (maximum of 20 to 30 °C/min), and a very slow crystallization process is impractical due to time limitations at the synchrotron.  $T^*$  was determined by the following procedure: Each sample was first heated to 160 °C for about 8 min to melt any crystals present. The sample was then cooled by a few degrees and a measurement was taken after waiting two min at the new temperature. If there were no crystal peaks visible, then the cooling and waiting process was repeated until the (100) crystal peak for P3DDT was visible, which is the temperature  $T^*$ . Values of  $T^*$  for all samples are reported in Table 3.2. For all cylinder-forming samples,  $T^*$  was greater than or equal to the  $T_g$  of P2VP (95 °C). In the lamellar-forming samples,  $T^*$  was above  $T_g$  of P2VP only for the 94% RR samples. Once  $T^*$  was determined, the sample was heated again to 160°C for at least 8 min. When the crystal peaks were no longer detected in the WAXS spectrum, the sample was cooled to a set point of 5°C above  $T^*$  and held for 1.5 min, which minimizes lag between the set point and actual sample temperature, and then rapidly cooled to a target temperature  $T^e$  below  $T^*$ . SAXS and WAXS data were recorded every few sec until the intensity of the (100) peak reached a plateau.

A representative 1D plot of the scattering data from a single experiment is shown in Figure 3.2. The change in color from one curve to the next indicates the time elapsed since the first measurement was made, with the blues representing the shortest times and the reds the longest times. In the first measurements, when the temperature of the sample is still above the P3DDT melting temperature, the only peaks observed come from the characteristic periodicity of the lamellar or cylindrical self-assembled structure. For example, the short-time data in Figure 3.2 show the primary SAXS peak at  $q = 0.027 \text{ \AA}^{-1}$  and three higher order peaks at integer multiples of this value, indicative of a lamellar structure with periodicity  $d = 233 \text{ \AA}$ . As time progresses

**Table 3.2:** Summary of sample characteristics. Structure is the self-assembled morphology in a melt state (BL = bilayer, LC = liquid crystal), determined by SAXS measurement at 160°C;  $T_c^{\text{DSC}}$  and  $T_m^{\text{DSC}}$  are the P3DDT crystallization and melting temperature, respectively, determined by DSC. In some samples, DSC could not detect the crystallization or melting temperature.

| Sample Name | Structure | $T_c^{\text{DSC}}$ | $T_m^{\text{DSC}}$ | $T^*$ |
|-------------|-----------|--------------------|--------------------|-------|
| RR94-VP34   | LAM, LC   | 106.0              | 138.9              | 140   |
| RR79-VP39   | LAM, BL   | 77.8               | 128.7              | 85    |
| RR70-VP37   | LAM, BL   | -                  | -                  | 80    |
| RR94-VP25   | HPC, LC   | 108.8              | 134.4              | 140   |
| RR79-VP29   | HPC, BL   | -                  | -                  | 105   |
| RR70-VP29   | HPC, BL   | -                  | -                  | 95    |

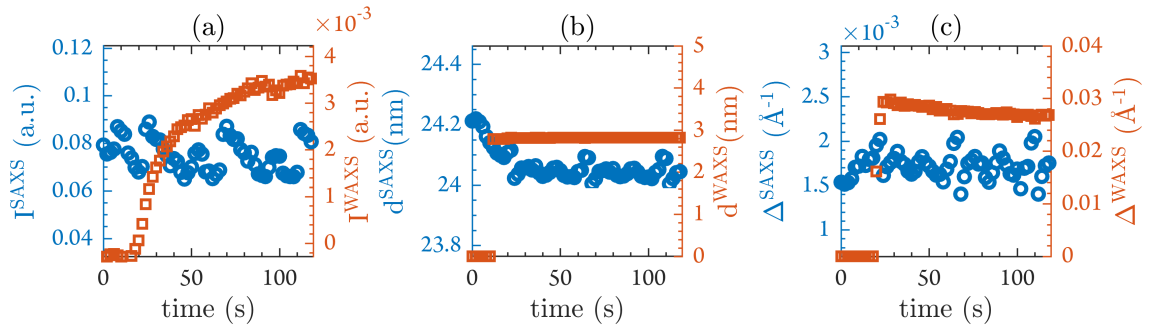


**Figure 3.2:** Scattering data for RR79-VP39. Measurements performed 75 °C (quenched from 160 °C), beginning with blue and ending with red, with 2 s elapsed between measurements.

and the temperature stabilizes below the P3DDT crystallization temperature, the crystalline peaks appear at high  $q$  and grow over time. The most prominent of these is the (100) diffraction peak at  $q = 0.22 \text{ \AA}^{-1}$  that corresponds with the dodecyl side-chain stacking direction.[64–66] The two weaker peaks at  $q = 0.44$  and  $0.66 \text{ \AA}^{-1}$  are higher order multiples of the same direction, i.e., (200) and (300), respectively. In one sample, namely RR79-VP29, a diffraction peak corresponding to the (010) direction for  $\pi$ -stacking of the thiophene rings can be observed at higher  $q$  ( $q \approx 1.6 \text{ \AA}^{-1}$ ). In most cases, however, this peak is not seen, likely due to its position coinciding with the broad amorphous halo from dodecyl side chains.

The effects of P3DDT crystallization on P3DDT-*b*-P2VP self-assembly were examined by tracking the positions, shapes and integrated intensities of each SAXS and WAXS peak as a function of time. Each peak was fit to either a pseudo-Voigt approximation (first SAXS peak) or a Lorentzian function (all other SAXS and WAXS peaks). The trends in each parameter were consistent for both primary and higher-order peaks, so only the primary peak data for SAXS and WAXS are reported here. The center of each primary peak ( $q_1$ ) is used to calculate the corresponding periodicity  $d = 2\pi/q_1$ . The breadth of each peak, which is reflected by the full-width at half max  $\Delta$ , reflects the size and extent of disorder in each block copolymer grain (SAXS) or P3DDT crystallite (WAXS). The integrated intensity  $I$  is proportional to the density of grains or crystallites within the samples. Three distinct crystallization modes are observed, and are controlled by both the self-assembled morphology and proximity of  $T^*$  to the  $T_g$  of P2VP ( $95^\circ\text{C}$ ).

In the first of the crystallization modes, for which  $T^*$  is below the  $T_g$  of P2VP, the P2VP domains are glassy and unable to give way to growing P3DDT crystals. This behavior, referred to here as “confined” crystallization, can be seen in the crystallization of the 79% RR lamellar sample (RR79-VP39,  $T^* = 85^\circ\text{C}$ ) at  $75^\circ\text{C}$  (Figure 3.3). As crystallization proceeds, as indicated by the increased intensity of the primary WAXS peak ( $I^{WAXS}$ ), both the lamellar domain periodicity ( $d^{SAXS}$ ) and the full-width at half max ( $\Delta^{SAXS}$ ) of the primary SAXS peak remain



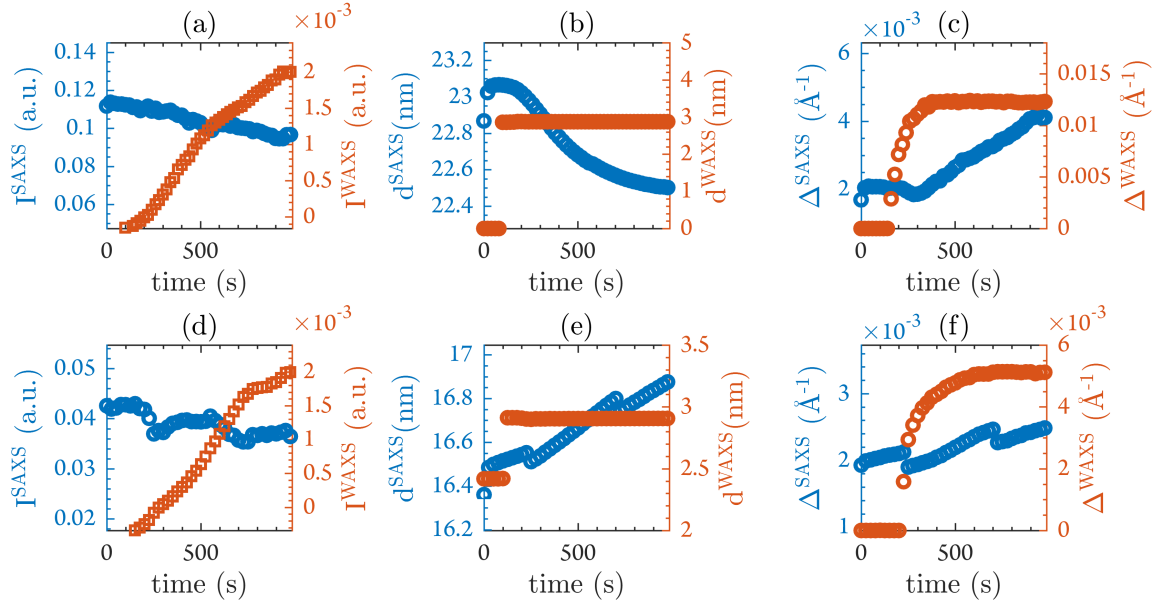
**Figure 3.3:** Change in (a) intensity of primary SAXS and WAXS peaks, (b) domain spacing of SAXS (lamellae) and WAXS (P3DDT crystal) structure, and (c) full-width at half max of SAXS and WAXS peaks for lamellae-forming sample RR79-VP39, with respect to time.



essentially constant. This outcome demonstrates that the hierarchical organization of the lamellae is unchanged through crystallization. Though not shown here, the confined behavior is also observed for crystallization of the 70% RR lamellar sample (RR70-VP37) at 70°C.

The second crystallization mode, referred to here as “loose confinement” behavior, is characterized by an overall retention of the self-assembled symmetry, but with subtle changes in average domain periodicity and grain structure as crystallization progresses. Loosely confined crystallization is observed when  $T^*$  is very near the  $T_g$  of P2VP in the cylindrical samples and when  $T^*$  is near or significantly above the  $T_g$  of P2VP in the lamellar sample. This behavior is shown in Figure 3.4 for the 94% RR lamellar and 79% RR cylinder-forming samples: lamellar RR-94-VP34 at 140°C and cylindrical RR79-VP29 at 105°C. As crystallization proceeds, both samples experience changes in the domain periodicity ( $d^{SAXS}$ ) and an increase in the full-width at half max of the primary SAXS peak ( $\Delta^{SAXS}$ ), but the intensity of the primary SAXS peak ( $I^{SAXS}$ ) remains fairly constant. This indicates that the growing crystals can disrupt the melt morphology, but they do not destroy it altogether. When  $T^*$  is near  $T_g$  of P2VP, it is possible that slow diffusivity inhibits rearrangements in the nanoscale structure. However, when  $T^*$  is much larger  $T_g$  of P2VP in the lamellar RR-94-VP34 sample, the loosely confined behavior does not reflect a diffusion limited process. The characteristics of this process are similar to the templated mode reported in rubbery PE-based block copolymers of intermediate segregation strength.[21]

It is interesting to note that while the domain spacing increases in the 94% RR sample shown in Figure 3.4 (RR94-VP34), the domain spacing decreases in the 79% RR samples. This can be explained by the difference in packing of the P3DDT chains between the 94% and lower RRs. It has been previously shown that BCPs of P2VP and 94% RR P3DDT exhibit a high degree of chain interdigitation, forming a liquid crystalline monolayer.[13, 67] BCPs with low RR, on the other hand, exhibit the bilayer chain packing that is typical of flexible BCP systems. Crystal growth in the tightly-packed liquid crystalline monolayer may promote further chain extension,

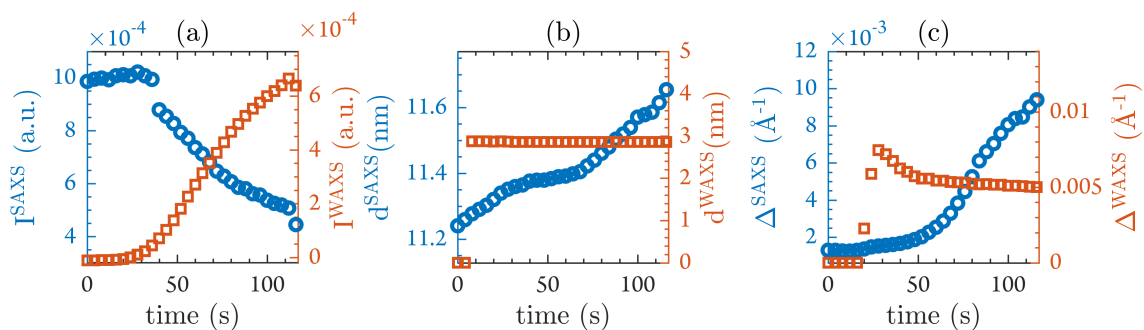


**Figure 3.4:** Change in (a) intensity of primary SAXS and WAXS peaks, (b) domain spacing of SAXS (lamellae) and WAXS (P3DDT crystal) structure, and (c) full-width at half max of SAXS and WAXS peaks for cylinder-forming sample RR79-VP29, with respect to time. The same data are shown for lamellae-forming RR94-VP34 (d, e, f).

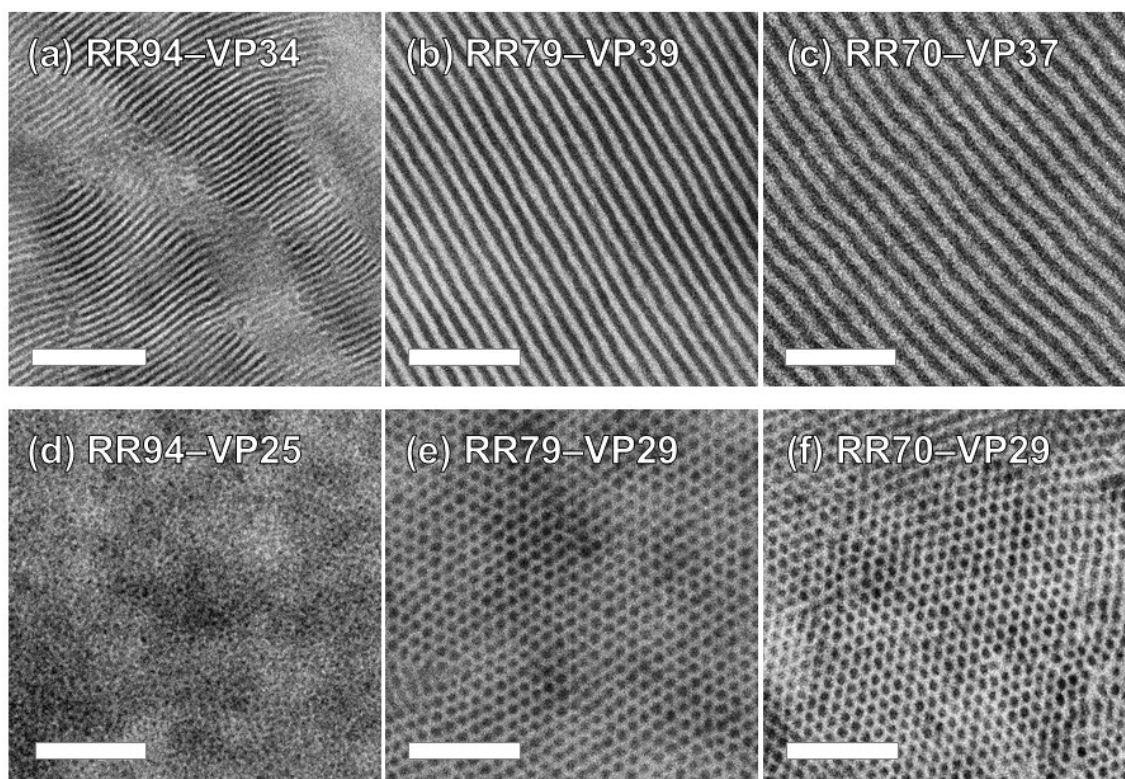
thereby swelling the domain sizes and increasing the periodicity.[67] However, in the bilayer conformation, crystallization will increase the P3DDT density and produce domain contraction.[47]

The third of the observed crystallization modes is breakout, and is seen only in the cylinder-forming sample for which  $T^*$  is significantly higher than the  $T_g$  of P2VP. In this mode, the growing crystals disrupt the self-assembled morphology, as indicated by a decrease in intensity of the primary SAXS peaks coinciding with an increase in the intensity of the primary WAXS peak. Also observed, as might be expected, is a concurrent change in domain spacing and increase in full-width at half max of the primary SAXS peak (Figure 3.5). The presence of the breakout mode is confirmed by TEM measurements. As shown in Figure 3.6, the self assembled structure is preserved in all samples except the 94% RR cylinder-forming sample: instead of the expected cylinders, this micrograph reveals small fibril-like crystal structures.

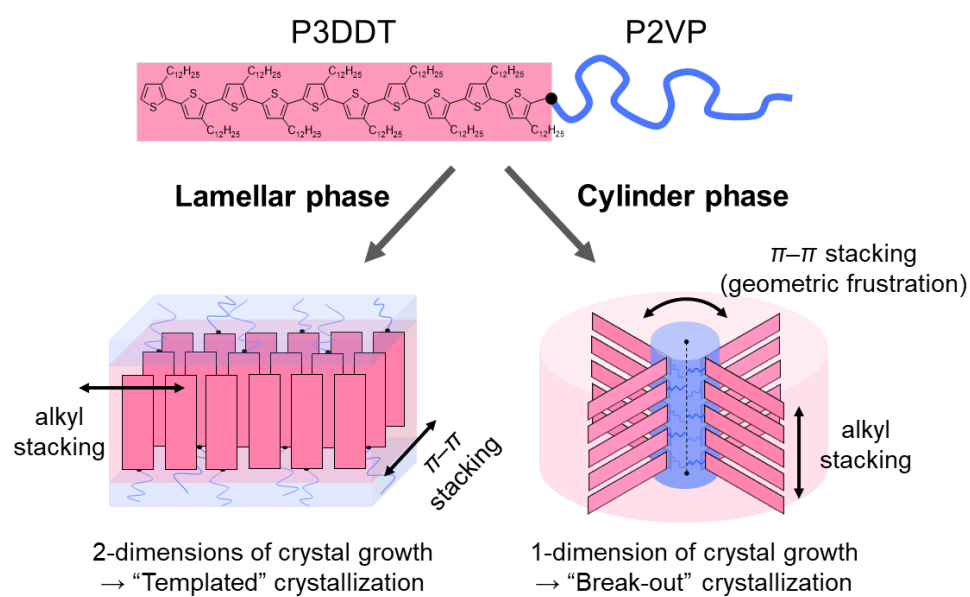
The 94% RR lamellar (RR94-VP34) and cylindrical (RR94-VP25) samples were both examined at crystallization temperatures well above the  $T_g$  of P2VP, but they exhibit different crystallization modes. There are two likely underlying causes for the distinct behaviors. The first explanation relates to geometric frustration, as illustrated in Figure 3.7: In a lamellar structure, the P3DDT chain orientations and crystal symmetry are compatible with the natural dimensions of a lamellar sheet, so crystals can grow along both the (100) alkyl-stacking and (010)  $\pi$ - $\pi$  stacking directions without restriction. In the hexagonal close-packed arrangement of cylindrical domains, the P3DDT chains radiate out from the cylinder center. Crystallization will therefore disrupt curvature at the P3DDT-*b*-P2VP interface, and the only unrestricted direction for crystal growth is along the length of the cylinders. In BCPs of poly(3-(2'-ethyl)hexylthiophene) (P3EHT) and poly(methyl acrylate) in which P3EHT is the minority block, the crystals tend to align with the (100) direction along the cylinder axis.[60] If the same holds true for the P3DDT-based BCPs, then growth along the (010)  $\pi$ - $\pi$  stacking direction competes with the natural hexagonal symmetry, and the maximum crystallite size along this direction that could "fit" in



**Figure 3.5:** Change in (a) intensity of primary SAXS and WAXS peaks, (b) domain spacing of SAXS (cylinders) and WAXS (P3DDT crystal) structure, and (c) full-width at half max of SAXS and WAXS peaks for sample RR94-VP25, with respect to time.



**Figure 3.6:** Cross-sectional TEM images of (a) RR94-VP34; (b) RR79-VP39; (c) RR70-VP37; (d) RR94-VP25; (e) RR79-VP29; (f) RR70-VP29. P2VP domains were selectively stained dark by exposure to iodine vapor. The scale bars are 200 nm.



**Figure 3.7:** An illustration of the possible geometric explanation for the difference in crystallization mode between the 94% RR lamellar and cylinder samples.

the lattice is  $2d$ , where  $d = 11.3$  nm for 94% RR (RR94-VP25). The second possible explanation is that the lamellar sample is more strongly segregated than the cylinder sample. In a typical flexible BCP system, the order-disorder transition for a lamellar-forming polymer occurs at lower values of  $\chi N$  than it does for a cylinder-forming polymer, and the minimum segregation strength for confined crystallization can vary with morphology.[21] Both of these samples have relatively low values of  $N_{P2VP}$ , so it is possible that the state of the cylindrical sample is much closer to the order-disorder transition than the lamellar sample. This is difficult to test experimentally, as no order-disorder transition is detected for a cylindrical specimen (RR79-VP29) after heating to 240°C, so the system is either strongly segregated or the  $\chi$ -parameter is not sensitive to temperature.

Finally, we note that samples with RR below 94% did not crystallize to a measurable extent unless cooled near the  $T_g$  of P2VP. Therefore, these experiments do not offer insight into the role of a liquid crystalline monolayer (RR 94%) versus a flexible bilayer (RR 70 and 79%) on the breakout process. Such packing effects could be interrogated by replacing P2VP with a polymer that has a lower  $T_g$ , which is the subject of ongoing work.

### 3.4 Conclusions

We examine the crystallization modes in P3DDT-*b*-P2VP copolymers as functions of copolymer composition and P3DDT RR. All materials have a majority P3DDT composition and assemble into ordered lamellae or cylinders when annealed above the P3DDT  $T_m$ . As the materials are quenched below the P3DDT  $T_m$ , the crystallization process and self-assembled morphology are monitored with simultaneous SAXS and WAXS. At  $T^*$  below the P2VP glass transition, the crystal growth is confined by the glassy P2VP domains. At  $T^*$  near the P2VP glass transition, the crystal growth perturbs the self-assembled morphology, but there is no large-scale destruction of the lamellae or cylinders. While the characteristics of this process are similar to

the templated growth mode that is observed in other semicrystalline BCP systems, there may be diffusion barriers at these low temperatures that inhibit rearrangements of the nanoscale domains, leading to behavior that is better described as loose confinement. At  $T^*$  well-above the P2VP glass transition, the crystallization mode depends on the BCP morphology. In a lamellar phase, crystal growth and self-assembly can coexist. However, in a cylindrical phase, the crystallites ultimately break-out of the self-assembled structure. As the lamellar and cylindrical materials have very similar molecular weights, we propose that break-out in the cylindrical morphology is associated with mismatch between the natural dimensions of the BCP and P3DDT lattices. It is also possible that the segregation strength of cylinder-forming materials is not high enough for confined crystallization. Significantly, these studies demonstrate that tuning RR of poly(3-alkylthiophenes) can open up multiple crystallization modes with the same monomer chemistries and molecular weights. This approach can decouple the parameters that govern classical BCP self-assembly (segregation strength  $\chi N$ , volume fraction  $f$ ) and interactions between conjugated blocks (Maier-Saupé parameter  $\mu N$ , persistence length  $L_p$ ), providing a model system for fundamental studies of crystallization in conjugated BCPs.

## Chapter 4

# Origins of Anisotropic Ionic Conductivity in Lamellar Block Copolymer Electrolytes

The work described in this chapter has been published in:

Coote, J. P., Kinsey, T., Street, D. P., Kilbey, S. M., Sangoro, J. R., Stein, G. E.  
"Surface-Induced Ordering Depresses Through-Film Ionic Conductivity in Lamellar  
Block Copolymer Electrolytes". ACS Macro Letters, 2020, 9(4), 565–570.

J.P. Coote synthesized and characterized all materials discussed here.

### 4.1 Introduction

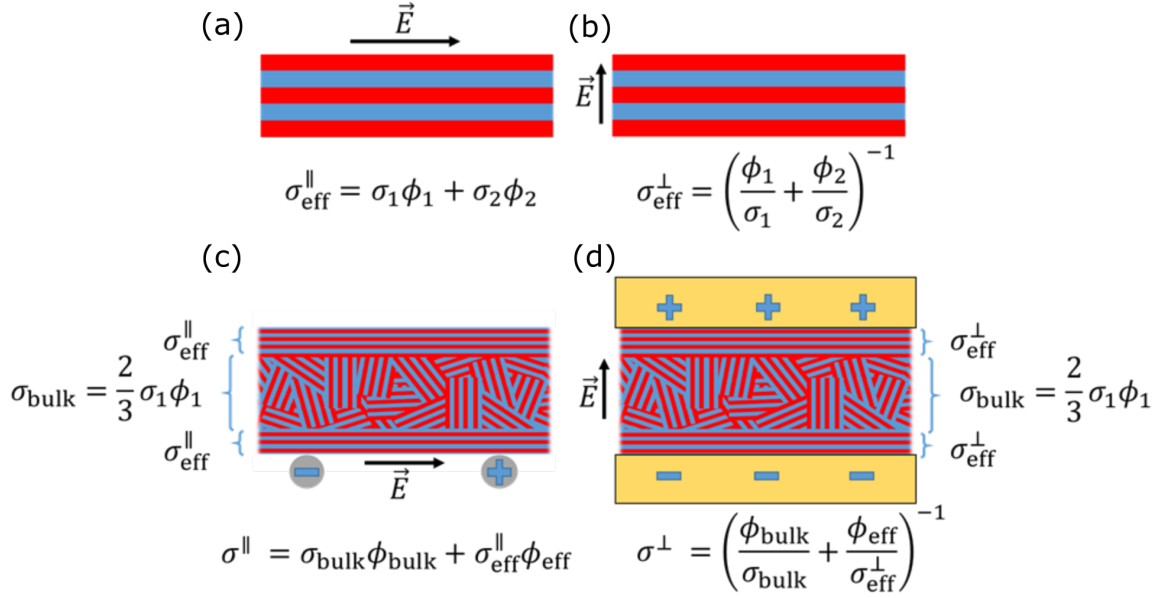
Block copolymers of polymeric ionic liquids (PILs), which consist of a PIL linked to an insulating polymer that provides mechanical stability, are a class of solid polymer electrolytes that show promise in electrochemical energy applications[5, 7–9, 24, 25, 68]. The relationship between self assembled morphology and ionic conductivity in these materials is often quantified by a morphology factor  $f$ , defined as

$$f = \sigma_0 / (\phi_{\text{PIL}} \sigma_{\text{PIL}}) \tag{4.1}$$



where  $\sigma_0$  and  $\sigma_{\text{PIL}}$  are the measured DC ionic conductivity of the block copolymer and PIL homopolymer, respectively, and  $\phi_{\text{PIL}}$  is the volume fraction of the PIL block in the block copolymer[69]. The theoretical or “ideal” morphology factors for cylindrical, lamellar, and gyroid phases are  $f = 1/3$ ,  $2/3$ , and 1, respectively [70]. The interpenetrating network of the gyroid phase is desirable for three-dimensional ion transport, but this morphology is difficult to attain due to its narrow window of stability with respect to composition.[71] The lamellar morphology is often investigated because of its stability across a wide composition range as compared to the gyroid phase. Moreover, if some of the ion-conducting lamellae are continuous across grain boundaries, then randomly-oriented lamellar grains can enable long-range ion transport. Morphology factors have been measured for lamellar block copolymer electrolytes using electrochemical impedance spectroscopy in two- or four-point probe configurations, where the electric field is oriented parallel to the plane of the film, and the values are consistent with  $f = 2/3$  [27, 28, 69, 70]. However, when morphology factors are measured using a parallel plate geometry where the electric field is oriented perpendicular to the plane of the film, the ionic conductivity and corresponding morphology factor are often reduced by orders of magnitude. This reduction is problematic as many devices (*i.e.*, batteries) require through-film ion transport.

Several studies of block copolymer electrolytes have shown that anisotropy in the ionic conductivity (and morphology factor) is correlated with anisotropy in the self-assembled structure.[29–32, 72, 73] Specifically, the ionic conductivity is enhanced or suppressed when the lamellar domains are oriented parallel or perpendicular to the electric field, respectively (Figure 4.1a-b). Many studies have sought to enhance ionic conductivity by controlling the lamellar domains orientations through processing techniques that include electric field alignment,[29] shear alignment,[29] magnetic field alignment,[72, 73] and topographic templates.[32] However, other studies have shown that a small fraction of the lamellar domains will orient parallel to the plane of the film during thermal[29] or solution[29, 31] processing, even though these techniques



**Figure 4.1:** A simple effective medium approximation is used to examine ionic conductivity as a function of lamellar orientation relative to the direction of the applied electric field. For alternating layers of material 1 and material 2, the effective conductivity is described by an arithmetic mean (a) or geometric mean (b) depending on the relative orientation of the electric field. Extending the same method to films that have layering at the interfaces and a polygrain bulk structure (c,d) gives rise to significant anisotropy in the conductivity.

lack a strong structure-directing field. This spontaneous lamellar alignment might be controlled by a thermodynamic process, such as surface-induced ordering that is driven by selective adsorption of one block at a surface.[74] In fact, in a recent study of gyroid-forming block copolymer electrolytes, the authors proposed that preferential adsorption of an insulating block at an electrode surface was responsible for a reduction of through-film ionic conductivity after thermal annealing.[75]

The role of surface interactions on block copolymer ordering is well documented in the literature, although these effects have not been considered in the design of block copolymer electrolytes. In general, one block is preferred over the other at a surface, and this preferential wetting can drive layering of domains through the thickness of a thin film (ca. 100 nm - 1  $\mu$ m).[76–78] If such a phenomenon occurs in lamellar PIL-containing block copolymer electrolytes, then the highly-oriented layers at an electrode would produce an anisotropic ionic conductivity. This point is illustrated using a simple model for ionic conductivity based on an effective medium approximation[26]. The oriented lamellar structure can be approximated as a series of parallel layers of alternating conducting and insulating domains. If the electric field is aligned parallel to the layers (in-plane conductivity,  $\sigma_{\text{eff}}^{\parallel}$ ), then the effective conductivity of the material can be estimated from the arithmetic mean of the conductivities of the two blocks (Figure 4.1a)[79]. However, if the conductivity is measured with the electric field perpendicular to the layers (through-plane conductivity,  $\sigma_{\text{eff}}^{\perp}$ ), then the effective conductivity is best approximated by the geometric mean of the conductivities of the two blocks because the insulating domain will dominate (Figure 4.1b).[79]

Block copolymer electrolytes are usually processed into thick films (ca. 10 to 100  $\mu$ m), and the influence of surface interactions on ordering will decay with distance into the film. For lamellar block copolymers, this means that two distinct structures are anticipated: highly-oriented lamellae at the interfaces and randomly-oriented lamellae in the bulk. The effective conductivity of this morphology can be estimated by the same simple methods described in Figure 4.1a-b, treating the highly-oriented lamellae

at the interface as one distinct component and the randomly-oriented lamellae in the bulk as another. The conductivity of the interfacial regions in the in-plane and through-plane directions is then  $\sigma^{\parallel}_{\text{eff}}$  and  $\sigma^{\perp}_{\text{eff}}$ , respectively, where the bulk conductivity is estimated by assuming a theoretical morphology factor of  $f = 2/3$  for the randomly-oriented lamellae. This simple analysis predicts a highly anisotropic conductivity, with the in-plane value of  $\sigma^{\parallel}$  being orders of magnitude higher than the through-plane value of  $\sigma^{\perp}$  (Figure 4.1c-d).

The objective of this study is to demonstrate that PIL-containing block copolymers will form highly-oriented layers at the interface with the electrode, a consequence of preferential wetting by one block at the electrode surface, leading to significant anisotropy in the ionic conductivity. The materials investigated are two lamellar diblock copolymers of polystyrene (PS) and poly(1-(2-acryloyloxyethyl)-3-butylimidazolium bis(trifluoro-methanesulfonyl)imide) (PIL) having different molecular weights, as well as a PIL homopolymer for comparison (Table 4.1).

## 4.2 Experimental Section

The procedures used for monomer, polymer, and copolymer synthesis in this study are detailed in this section, with additional information appearing in Appendix B. The synthesis of block copolymers was adapted from similar synthetic procedures reported elsewhere.[28] The amounts of reactants and solvents given in the procedures for block copolymer synthesis are all taken from the synthesis of PS4-PIL53.

All materials were synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. Dispersities were determined by gel permeation chromatography (GPC) against polystyrene standards, and were less than 1.3 for all samples. The molecular weights of the PS macro chain transfer agents (PS macroCTA) were determined by GPC and confirmed by  $^1\text{H}$  nuclear magnetic resonance spectroscopy (NMR) using end group analysis. The molecular weights of PIL blocks were determined as described in the Appendix B. The volume fractions of PIL in the

**Table 4.1:** Characteristics of polymers and copolymers. <sup>a</sup>Determined by GPC and NMR; <sup>b</sup>determined by NMR; <sup>c</sup>determined by GPC of the homopolymer or block copolymer prior to quaternization; <sup>d</sup>determined by differential scanning calorimetry (DSC).  $M_{n,PS}$  and  $M_{n,PIL}$  reported in units of g/mol. All temperatures are reported in °C.

| Sample Name | $M_{n,PS}^a$ | $M_{n,PIL}^b$ | $\phi_{PIL}^b$ | $\bar{D}^c$ | $T_{g,PS}^d$ | $T_{g,PIL}^d$ |
|-------------|--------------|---------------|----------------|-------------|--------------|---------------|
| PS          | 10,000       | —             | 0.0            | 1.17        | 91.4         | —             |
| PIL         | —            | 14,900        | 1.0            | 1.27        | —            | -10.4         |
| PS4-PIL53   | 4000         | 6500          | 0.53           | 1.28        | 72.0         | 0.0           |
| PS6-PIL47   | 6000         | 7600          | 0.47           | 1.29        | 84.9         | -3.7          |

PS-PIL block copolymers,  $\phi_{\text{PIL}}$ , were calculated from the molecular weights of each block using a density of 1.04 g/mL for PS and 1.38 g/mL for PIL.[28]

**Materials.** Acryloyl chloride (97%, contains <210 ppm mono-methyl ether hydroquinone (MEHQ) as stabilizer), 2-bromoethanol (95%), sodium chloride, 4-cyano-4-[(dodecylsulfanyl-thiocarbonyl)sulfanyl]pentanoic acid (chain transfer agent (CTA), >97%), benzene (anhydrous), 1-butyrimidazole (98%), and lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI, 97%) were used as received from Sigma Aldrich. Dichloromethane (DCM, 99.9%, HPLC), triethylamine (99%), magnesium sulfate (anhydrous), aluminum oxide (anhydrous), methanol ( $\geq 99.8\%$ , ACS Certified), dioxane (anhydrous, 99%), hexanes ( $\geq 98.5\%$ , ACS Certified), N,N-dimethyl-formamide (DMF, 99%), acetonitrile (anhydrous, 99.9%), deuterated chloroform ( $\text{CDCl}_3$ , 99.8 atom % D), dimethyl-d6 sulfoxide ( $\text{DMSO-d}_6$ , 99.9 atom % D), and tetrahydrofuran (THF,  $\geq 99.9\%$ , Optima for HPLC) were used as received from Fisher Scientific. Azobis(isobutyronitrile) (AIBN, 98%, Sigma-Aldrich) was purified by recrystallization from methanol. Styrene (S, 99%, Fisher Scientific) was purified by passing through a column packed with aluminum oxide.

**Synthesis of 2-bromoethyl acrylate monomer.** The synthesis of 2-bromoethyl acrylate was adapted from similar synthetic procedures reported elsewhere.[80, 81] In a typical reaction, 2-bromoethanol (30.7 g, 0.245 mol) and triethylamine (24.4 g, 0.251 mol) were dissolved in 56 mL of DCM in a 250 mL three-neck round bottom flask containing a magnetic stir bar under nitrogen atmosphere. The flask and its contents were chilled in a methanol/ice bath. Acryloyl chloride (21.9 g, 0.242 mol) dissolved in 24 mL of DCM was added drop-wise to the three-neck flask while stirring. When the addition was complete, the flask was removed from the methanol/ice bath and stirred overnight ( $\geq 18$  h) at room temperature. The solid precipitate (triethylammonium chloride byproduct) was separated from the liquid phase by gravity filtration and washed heavily with DCM until white. The DCM used to wash the precipitate was

collected and combined with the filtrate, which was then washed three times with an NaCl brine (each wash consisting of 15 g NaCl in 150 mL of DI water). After each wash, the DCM phase was collected and the aqueous phase was discarded. The DCM phase was then washed three more times with pure DI water (each wash consisting of 150 mL DI water), collecting the DCM phase each time and discarding the aqueous phase. The solution was dried by stirring with magnesium sulfate, which was then removed by gravity filtration. DCM was removed by rotary evaporation, resulting in a monomer solution that was 15 wt% residual DCM as determined by  $^1\text{H}$  NMR using  $\text{CDCl}_3$  as solvent. Finally, the inhibitor was removed from the product by passing the mixture through a column packed with aluminum oxide.

**Synthesis of PS MacroCTA.** In a typical RAFT polymerization, styrene monomer purified of inhibitor (7.8244 g, 75.13 mmol), CTA (0.2099 g, 0.52 mmol), and AIBN (0.0173 g, 0.1054 mmol) were dissolved in benzene (16.0 mL) in a round-bottom flask containing a magnetic stir bar. The flask was then sealed with a rubber septum, and the reaction mixture was sparged with argon for 20 minutes, after which the flask was placed in an oil bath at 70 °C for 18 h. The polymerization was quenched by removing the flask from the oil bath and immersing it in liquid nitrogen until the contents were frozen solid and then removing the septum. Once the flask contents had thawed, the polymer was precipitated in cold methanol. The polymer was isolated by gravity filtration and then redissolved in a small amount of DCM. The PS macroCTA was again precipitated in cold methanol, collected by gravity filtration and finally dried overnight in a vacuum oven at room temperature (>18 h). Molecular weight and dispersity were determined by gel permeation chromatography (GPC) using THF as the eluent. Molecular weight was confirmed through  $^1\text{H}$  NMR using  $\text{CDCl}_3$  as solvent.

**Synthesis of PS-*b*-PBrEA copolymer.** Polystyrene macroCTA (0.7933 g, 0.1983 mmol), AIBN (0.0319 g, 0.194 mmol), and 2-bromoethylacrylate (BrEA) monomer

with 15 wt% DCM residual from synthesis (0.8851 g solution, 4.203 mmol BrEA) were dissolved in dioxane (16.0 mL) in a round-bottom flask with a magnetic stir bar. The flask was then sealed with a rubber septum and sparged with argon for 20 minutes, after which time the flask was placed in an oil bath at 70 °C for 2 h. The reaction was quenched by removing the flask from the oil bath and placing it in liquid nitrogen until the contents were frozen solid, and then removing the septum. Once the flask contents had thawed, the polymer was precipitated in cold methanol and then recovered by gravity filtration. The polymer, PS-b-PBrEA was isolated by redissolving in a small amount of DCM, precipitating into cold methanol, and finally collected by filtration. It was then dried in a vacuum oven at room temperature overnight (>18 h). Molecular weight and block copolymer composition were determined by  $^1\text{H}$  NMR with  $\text{CDCl}_3$  as solvent, using end group analysis and the ratio of the integrated areas associated with the of peaks assigned to the 5 protons of the PS phenyl group and the 4 protons associated with the two methylene groups of the PBrEA pendant chain. Chain extension and dispersity were confirmed by GPC using THF as the eluent.

**Synthesis of PS-b-PAEBIm-Br copolymer.** PS-b-PBrEA (0.3923 g, 0.0622 mmol polymer, 0.801 mmol BrEA repeat units) and 1-butyylimidazole (0.5353 g, 4.311 mmol) were dissolved in DMF (3.0 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate and stirred at 80 °C for 48 h. After this time, the polymer was precipitated into hexanes three times. The first two times the polymer was precipitated, it was sticky and clung to the sides of the beaker and had to be dissolved in DCM in order to recover. On the third precipitation, the polymer formed flakes that were easily collected by gravity filtration. PS-b-PAEBIm-Br was dried at room temperature under vacuum overnight and characterized by  $^1\text{H}$  NMR analysis using DMSO- $d_6$  as solvent. Elemental analysis (Table [B.1](#)) was used to confirm complete quaternization.



**Synthesis of PS-b-PAEBIm-TFSI copolymer (PS-b-PIL).** PS-b-PAEBIm-Br (0.30 g, 0.038 mmol polymer, 0.488 mmol bromide anion) and LiTFSI (0.4640 g, 1.617 mmol) were dissolved in DMF (3.0 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate and stirred at 50 °C for 24 h, then removed from heat and allowed to cool to room temperature. The polymer was precipitated into DI water twice, collecting by gravity filtration and dissolving in DMF between precipitations. PS-b-PAEBIm-TFSI was collected by filtration and dried in the vacuum oven at 40 °C for 24 h and characterized by  $^1\text{H}$  NMR analysis using DMSO- $d_6$  as solvent. Elemental analysis (Table B.1) was used to confirm the complete anion exchange.

**Synthesis of PBrEA homopolymer.** PBrEA was synthesized using a procedure similar to that reported by Perrier et al[81]. CTA (0.0819 g, 0.203 mmol), AIBN (0.0032 g, 0.019 mmol), and 2-bromoethylacrylate (BrEA) monomer with 15 wt% residual DCM from synthesis (1.0897 g solution, 6.088 mmol BrEA) were dissolved in dioxanes (19.25 mL) in a round-bottom flask with a magnetic stir bar. The flask was then sealed with a rubber septum and sparged with argon for 20 minutes, after which the flask was placed in an oil bath at 70 °C for 2 h. The reaction was quenched by removing the flask from the oil bath and placing it in liquid nitrogen until the contents were frozen solid and then removing the septum. Once the flask contents had thawed, the polymer was precipitated in cold methanol with 10 vol% DI water. The methanol/water was decanted and the polymer that was left behind was redissolved in a small amount of DCM. The polymer was precipitated again in cold methanol with 10 vol% DI water and the methanol/water was decanted, leaving the polymer behind. PBrEA was collected by redissolving in a small amount of DCM, transferred to a 20 mL glass vial and concentrated via rotary evaporation. The polymer was then dried under vacuum at room temperature overnight (>18 h). Molecular weight was determined by  $^1\text{H}$  NMR end group analysis using  $\text{CDCl}_3$  as solvent. Dispersity was determined by GPC using THF as the eluent.

**Synthesis of PAEBIm-Br homopolymer.** PBrEA (0.36 g, 0.068 mmol polymer, 2.011 mmol BrEA repeat units) and 1-butyylimidazole (1.2622 g, 10.16 mmol) were dissolved in DMF (3.0 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate to stir at 80 °C for 48 h, then removed from heat and allowed to cool to room temperature. The polymer was precipitated into hexanes three times, decanting the hexanes and redissolving the polymer left behind in a small amount of DCM between precipitations. PAEBIm-Br was collected after the last precipitation by redissolving the polymer (left behind after the hexanes were decanted) in a small amount of DCM. Then, the solution was transferred to a 20 mL glass vial and concentrated via rotary evaporation. The polymer was then dried under vacuum at room temperature overnight (>18 h) and characterized by <sup>1</sup>H NMR using DMSO-d<sub>6</sub> as solvent. Elemental analysis (Table B.1) was used to confirm complete quaternization.

**Synthesis of PAEBIm-TFSI homopolymer (PIL).** PAEBIm-Br (0.6627 g, 0.0741 mmol polymer, 2.187 mmol bromide anion) and LiTFSI (2.1 g, 7.32 mmol) were dissolved in DMF (4.0 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate and stirred at 50 °C for 24 h, then removed from heat and allowed to cool to room temperature. The polymer was precipitated into DI water twice, decanting the DI water and dissolving the polymer left behind in a small amount of acetonitrile between precipitations. PAEBIm-TFSI was collected by decanting the DI water after the last precipitation and redissolving the polymer left behind in a small amount of acetonitrile, transferring the solution to a 20 mL glass vial, and concentrating via rotary evaporation. The polymer was then dried under vacuum at 40 °C for 24 h and characterized by <sup>1</sup>H NMR using DMSO-d<sub>6</sub> as solvent. Elemental analysis (Table B.1) was used to confirm the complete anion exchange.

**Small-Angle X-Ray Scattering (SAXS).** SAXS was performed using a SAXSLAB Ganesha instrument equipped with a Cu K $\alpha$  Xenocs GeniX3D microfocus

source ( $\lambda = 0.154\text{nm}$ ) and a  $172\text{ }\mu\text{m}$  pixel size, single photon counting Dectris Pilatus 300k detector. Samples were prepared by casting onto Kapton from a solution of 10 wt% polymer in THF. In a typical preparation, the solution was dripped onto the Kapton with a pipette and allowed to evaporate over the course of 1 h in the fume hood. The samples, consisting of the dried film on Kapton, were annealed on a hot plate at  $120\text{ }^{\circ}\text{C}$  in a glovebox under inert nitrogen atmosphere and low humidity for 24 h. Scattering measurements were performed under vacuum at room temperature with 20-minute exposure times. The 2-dimensional (2D) scattering data were reduced to 1-dimensional (1D) scattering curves by azimuthal integration using the SAXSGUI software.

**Grazing Incidence Small Angle X-Ray Scattering (GISAXS).** GISAXS was performed using a Xenocs Xeuss 3.0 instrument equipped with a Cu  $K\alpha$  Xenocs GeniX3D HFVL microfocus source ( $\lambda = 0.154\text{nm}$ ) and a single photon counting Dectris Pilatus3 R 300k detector with a  $172\text{ }\mu\text{m}$  pixel size. Films were prepared by flow coating onto a silicon wafer from either THF or acetonitrile and annealing at  $120\text{ }^{\circ}\text{C}$  on a hotplate for 24 h. Samples were illuminated at an incidence angle of  $\alpha_i \approx 0.18^{\circ}$ . The thick drop-cast films are very rough, so it is difficult to estimate the X-ray penetration depth into the film (as the angle of incidence is poorly defined). However, the intensity along the Debye-Scherrer rings is clearly anisotropic: as indicated by the arrows, there is a population of lamellar stacks normal to the surface in addition to randomly-oriented lamellar grains.

**Impedance Spectroscopy.** Impedance measurements were performed using two distinct electrode configurations in order to probe ionic conductivity in the in-plane and through-plane directions. Through-plane measurements were performed with a parallel-plate electrode configuration using a Novocontrol High Resolution Alpha Dielectric Analyzer equipped with a Quatro Cryosystem for temperature control. Samples were prepared by casting films approximately  $100\text{ }\mu\text{m}$  thick from a solution

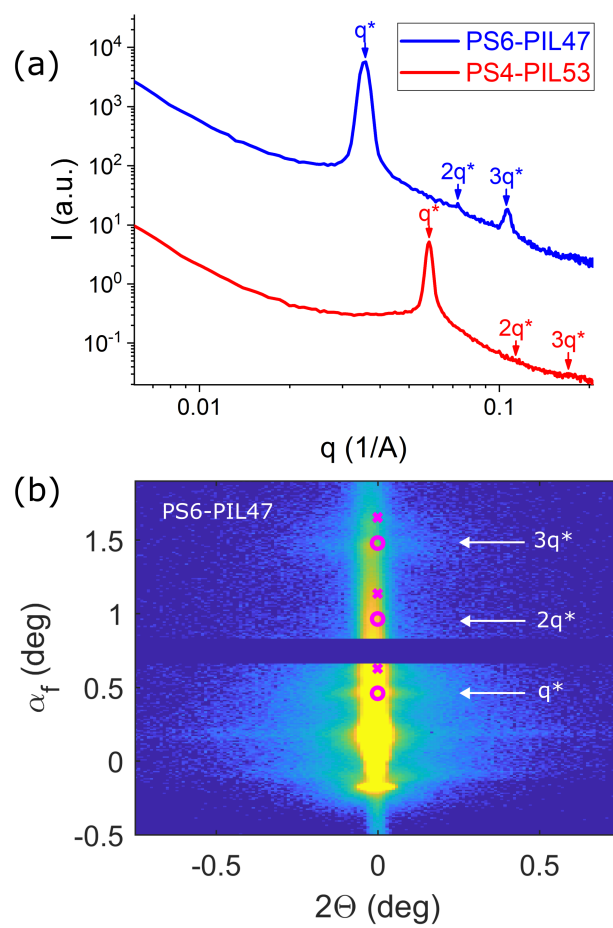
of 10 wt% polymer in THF onto an electrode of either brass or highly-doped silicon with diameter of 10 mm. Sample thickness was measured using a digital micrometer. In a typical preparation, the solution was dripped onto the electrode with a pipette, and the solvent was allowed to evaporate over the course of 1 h in the fume hood. To control the thickness of the film, two 100  $\mu\text{m}$  silica spacers were pressed into the film before the solvent had fully evaporated. A second electrode of the same material with diameter of 20 mm was then pressed on top in a parallel plate arrangement. The sample, consisting of the top and bottom electrodes, film, and spacers was annealed, small electrode up, on a hot plate at 120  $^{\circ}\text{C}$  in a glovebox under inert nitrogen atmosphere and low humidity for 24 h. The sample was then placed in the spectrometer and annealed again at 120  $^{\circ}\text{C}$  for approximately 1 h while making measurements to ensure that the spectra obtained did not change over time. Measurements were then conducted at a range of temperatures, equilibrating for 10 minutes at each temperature before beginning a measurement. Liquid nitrogen was used by the temperature control system alongside a heating element to control the sample temperature to within 0.1 K of the set point while preventing the introduction of additional moisture into the system. DC ionic conductivity was taken to be the value of the real conductivity function  $\sigma'(\omega)$  at the frequency at which a maximum occurs in the imaginary modulus function  $M''(\omega)$ . In-plane measurements were performed using a GAMRY Reference 600 Potentiostat/Galvanostat/ZRA in a two point probe configuration using electrodes of platinum wire. Samples were prepared by casting a film approximately 50  $\mu\text{m}$  thick, 10 mm wide, and greater than 1 cm long from a solution of 10 wt% polymer in THF onto a glass slide. In a typical preparation, the solution was dripped onto the slide with a pipette and allowed to evaporate over the course of 1 h in the fume hood. Once most of the solvent had evaporated, the film was annealed on a hot plate at 120  $^{\circ}\text{C}$  in a glovebox under inert nitrogen atmosphere and low humidity for 24 h. The sample was then placed in the spectrometer and measured at 20  $^{\circ}\text{C}$ . The resistance  $R$  was determined from the non-zero x-intercept of a semicircular regression of the data represented in the form

of a Nyquist plot. Conductivity  $\sigma$  was calculated using the resistance and sample geometry by the equation  $\sigma = L/(wxR)$ , where  $w$  is the width of the film,  $x$  is the thickness measured as described above, and  $L$  is the distance between electrodes (1 cm).

### 4.3 Results and Discussion

The bulk self-assembled structure of the block copolymer samples was examined using transmission small-angle X-ray scattering (SAXS). Samples were annealed at 120 °C for 24 h. The azimuthally-integrated intensity for both block copolymer samples are shown in Figure 4.2a. Sample PS6-PIL47 shows peaks at a  $q^*:2q^*:3q^*$  ratio, where  $q^* = 0.036 \text{ \AA}^{-1}$ , indicative of lamellae with a domain periodicity of  $d_0=17.5 \text{ nm}$ . The intensity of the  $2q^*$  peak is reduced relative to the  $q^*$  and  $3q^*$  peaks, which is expected as this position coincides with a minimum in the form factor of equal-volume lamellae. PS4-PIL53 shows a single sharp peak at  $q^*$ , which indicates a high degree of order, but the higher-order peaks are not observed. It can be reasonably inferred from the PIL volume fraction that the sample organizes into a lamellar structure with a domain periodicity of  $d_0 = 10.8 \text{ nm}$ ; the absence of the  $2q^*$  peak is attributable to a minimum in the form factor, while the absence of the  $3q^*$  peak is attributable to interface attenuation resulting from a weaker segregation strength due to lower molecular weight.[82, 83] The 2D scattering data (see Figures S9-S10 in Appendix B) for both copolymer films show no indication of anisotropy, demonstrating that the bulk structure adopted by both samples is randomly-oriented lamellae. The full-width at half max (fwhm) of the  $q^*$  peak is  $0.0029 \text{ \AA}^{-1}$  and  $0.0027 \text{ \AA}^{-1}$  for PS6-PIL47 and PS4-PIL53, respectively. Using the Scherrer equation,[33] the bulk grain size ( $\approx 2\pi/\text{fwhm}$ ) is approximately  $0.2 \text{ }\mu\text{m}$  in both materials.

The effect of surfaces on lamellar self-assembly was probed through grazing-incidence small-angle X-ray scattering (GISAXS), microscopy and contact angle goniometry from thin films annealed at 120 °C for 24 h. Representative GISAXS data

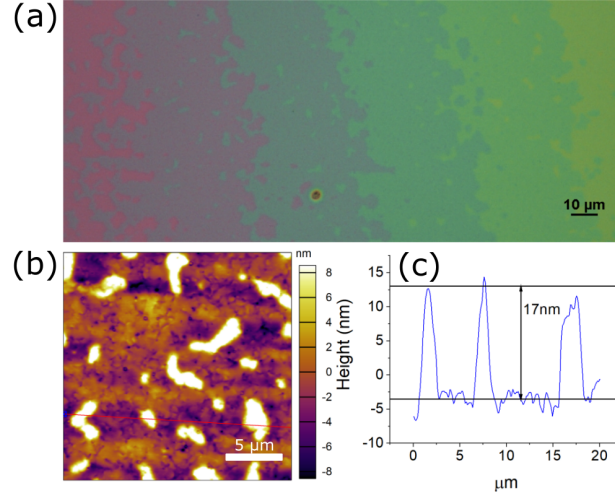


**Figure 4.2:** (a) Azimuthally-integrated SAXS data of bulk block copolymer samples. (b) GISAXS data of PS6-PIL47 thin film (300 nm) flow coated on silicon, measured at an incidence angle of  $0.18^\circ$ .

for a 300 nm film of PS6-PIL47 on silicon are shown in Figure 4.2b as a function of in-plane ( $2\theta$ ) and out-of-plane ( $\alpha_f$ ) scattering angles. The scattering was concentrated into Bragg peaks along the out-of-plane direction, which is a signature of lamellar layers through the film thickness. The positions of the two Bragg peaks for each order of reflection ( $q^*$ ,  $2q^*$ ,  $3q^*$ ) were predicted for a lamellar periodicity of 17 nm and incidence angle of  $0.18^\circ$ , following procedures described elsewhere,[34] and are marked by the “x” and “o” symbols in Figure 4.2b. The predicted Bragg peak positions for  $q^*$  and  $3q^*$  agree with the experimental data. As with the SAXS data, the peaks associated with the even reflection ( $2q^*$ ) are not observed.

Another signature of surface-induced layering of lamellar domains in thin films is island and hole formation, which arises when the thickness of the as-cast film is incommensurate with the thickness of each lamellar domain.[78] When both the air surface and substrate are preferential to one block, the height of islands (and depth of holes) is equal to  $d_0$ . Films of PS4-PIL53 and PS6-PIL47 having thickness gradients were prepared by flow coating from either THF or acetonitrile. The as-cast films showed a continuous transition in thickness along the flow coating direction. However, after thermal annealing, the films separated into regions of discrete thicknesses that were separated by islands and holes. Optical microscopy data for PS6-PIL47 in Figure 4.3a shows the islands and holes between these regions of discrete thicknesses. Atomic force microscopy images for the same sample in Figures 4.3b-c demonstrates that the height of islands is equal to approximately 17 nm, consistent with measurements of  $d_0$  obtained from bulk SAXS and thin film GISAXS measurements.

To identify the block that is present at the air surface, water contact angles were recorded from thin films of each block copolymer, as well as from PS and PIL homopolymers. These data are reported in Table 4.2. The average water contact angle for both block copolymer films and for the PIL homopolymer was in the range of  $74^\circ$  to  $77^\circ$ , while the average water contact angle on PS homopolymer was  $91^\circ$ . While no direct measurement could be made of the wetting behavior at the silicon substrate, the more polar PIL block is likely preferred over PS on the thin native oxide



**Figure 4.3:** Island and hole formation observed in thin film of PS6-PIL47 is observed by optical microscopy (a) and AFM (b). The film was annealed at 120 °C for 24 h. The AFM tapping mode height image is  $20 \times 20 \mu\text{m}^2$ . Cross-section of the AFM height image (c) shows island height is approximately equal to  $d_0 = 17 \text{ nm}$ .

**Table 4.2:** Static water contact angles on thin films flow-coated on silicon. The average water contact angle is calculated from three measurements per sample, and the uncertainty is reported as  $\pm 1$  standard deviation.

| Sample Name | $\theta$ (°)   |
|-------------|----------------|
| PS          | $91.1 \pm 0.4$ |
| PIL         | $74.0 \pm 1.3$ |
| PS4-PIL53   | $74.8 \pm 1.8$ |
| PS6-PIL47   | $76.8 \pm 1.5$ |



at this boundary. The interfacial structure that results from preferential wetting at an air surface and silicon substrate is relevant to measurements of the in-plane (Figure 4.1c) and through-plane (Figure 4.1d) ionic conductivity, respectively.

The SAXS measurements of bulk PS-PIL samples reveal randomly-oriented lamellae, while thin film experiments reveal layers of lamellae between the air surface and silicon substrate. It is reasonable to expect that a thick film of PS-PIL will have randomly-oriented lamellae throughout most of the thickness, with highly-oriented lamellar layers at each surface. This statement is supported by GISAXS measurements of a thick film on a silicon substrate (ca. 100  $\mu\text{m}$ ), which show a mixture of highly-oriented and randomly-oriented lamellar domains (see Appendix B Figure B.11). However, the films are thick and the free surfaces are rough due to the solution-casting process. As a result, GISAXS cannot quantify the depth-dependent distribution of domain orientations.

The ionic conductivity of these materials was measured using impedance spectroscopy with two different electrode configurations. The in-plane ionic conductivity of both PS-PIL block copolymer and PIL homopolymer samples was measured using a two-point probe configuration, as illustrated in Figure 4.1c. The through-plane conductivity was measured using a parallel plate configuration, which means the films are sandwiched between two electrodes. Two types of electrodes were used for through-plane measurements, highly-doped silicon and brass, and both yielded the same result. All films were 40-100  $\mu\text{m}$  thick and annealed at 120  $^{\circ}\text{C}$  for 24 h prior to impedance spectroscopy measurements at room temperature (20  $^{\circ}\text{C}$ ). Procedures for sample preparation and measurement using the two-point and parallel plate configurations are detailed in Appendix B. The results of the impedance measurements of both electrode geometries are summarized in Table 4.3. The measured ionic conductivity of the PIL homopolymer was similar along the in-plane and through-plane directions. For both block copolymer samples, however, the in-plane ionic conductivity was approximately 20 times greater than the through-plane ionic conductivity.

**Table 4.3:** Summary of conductivity data (S/cm) at 20 °C. <sup>a</sup>In-plane DC conductivity, determined by impedance spectroscopy in two-point electrode configuration; <sup>b</sup>through-plane DC conductivity, determined by impedance spectroscopy in parallel plate electrode configuration; <sup>c</sup>morphology factors calculated via Equation 4.1; <sup>d</sup>ratio of  $\sigma_{\text{dc}}^{\parallel}$  to  $\sigma_{\text{dc}}^{\perp}$ .

| Sample Name | $\sigma_{\text{dc}}^{\parallel a}$ (S/cm) | $\sigma_{\text{dc}}^{\perp b}$ (S/cm) | $f^{\parallel c}$ | $f^{\perp c}$ | $a^d$ |
|-------------|-------------------------------------------|---------------------------------------|-------------------|---------------|-------|
| PIL         | $1.0 \times 10^{-6}$                      | $7.7 \times 10^{-7}$                  | —                 | —             | 1.3   |
| PS4-PIL53   | $1.8 \times 10^{-7}$                      | $8.1 \times 10^{-9}$                  | 0.32              | 0.033         | 22    |
| PS6-PIL47   | $3.0 \times 10^{-7}$                      | $1.2 \times 10^{-8}$                  | 0.62              | 0.024         | 26    |

The morphology factors calculated from the in-plane ionic conductivities are consistent with those reported for similar materials that were also characterized by in-plane impedance spectroscopy measurements. [27, 28]. PS6-PIL47 exhibited a morphology factor of 0.62. Sample PS4-PIL53 exhibited a lower morphology factor of 0.3, possibly resulting from broader interfacial regions between domains due to reduced segregation strength. In contrast, the morphology factors calculated from the through-plane data are lower by more than an order of magnitude compared to their in-plane counterparts. This discrepancy between in-plane and through-plane conductivity is consistent with highly-oriented lamellar layers at the film-electrode interfaces. Both in-plane and through-plane measurements of ionic conductivity are probing two distinct structures within the film: an interfacial region of highly-oriented lamellae and a bulk region of randomly-oriented lamellae.

## 4.4 Conclusions

These studies demonstrate that preferential interactions at an electrode or air surface will drive alignment of lamellar PS-PIL domains parallel to the plane of a film. As a result, the structure of PS-PIL thick films is comprised of randomly-oriented lamellae in the bulk and highly-oriented lamellae at surfaces. A consequence of the two distinct structures is a corresponding anisotropy in the DC ionic conductivity, with in-plane ionic conductivity exhibiting a more than twenty-fold increase over the through-plane ionic conductivity. Anisotropy in the DC ionic conductivity has significant implications with respect to applications such as lithium ion batteries, as ion transport is generally required in the through-plane direction. It is important to note that surface-induced ordering is likely encountered with other types of block copolymer electrolytes, as there are few examples of chemically-distinct polymers that are equally attracted to the same boundary.[74] However, one could suppress preferential interactions at a surface using methods that are already established

for block copolymer lithography, including surface-active additives or thin “neutral” coatings on the electrodes.[84, 85]

# Chapter 5

## Interfacial Effects in Block Copolymer Electrolytes

The work described in this chapter has not yet been submitted for publication.

### 5.1 Introduction

Block copolymer electrolytes are a class of materials of interest for a number of electrochemical applications, ranging from lithium ion batteries to fuel cells to carbon capture[5, 7–9, 24, 25, 68, 80]. Typically, these materials consist of a polymer electrolyte block linked to an insulating block that provides mechanical stability. Provided that  $\chi N$  is sufficiently high, where  $\chi$  is the Flory-Huggins interaction parameter between the two blocks and  $N$  is the overall degree of polymerization, the material self-assembles into classical block copolymer mesophases[2]. The impact of self-assembled morphology on ionic conductivity is often captured by the morphology factor  $f$ , defined as

$$f = \sigma_0 / \sigma_c \phi_c \tag{5.1}$$

where  $\sigma_0$  is the ionic conductivity of the block copolymer material,  $\sigma_c$  is the ionic conductivity of the electrolyte homopolymer, and  $\phi_c$  is the volume fraction of the

electrolyte block in the block copolymer[69]. Theoretical values of  $f$  for cylinder, lamellar, and gyroid morphologies are  $f = 1/3$ ,  $2/3$ , and 1, respectively, based on an idealized geometry of each morphology[26, 86]. The interpenetrating network that produces high theoretical morphology factor of the gyroid phase makes it attractive for three dimensional ion transport; however, the gyroid is only stable under a narrow range of composition and temperature.[71]. Randomly oriented lamellae, by contrast, are stable over a wide composition window and can potentially deliver long-range ion transport, provided there is sufficient connectivity of the PIL domain across grain boundaries.

Several studies of lamellar block copolymer electrolytes have found morphology factors roughly consistent with the  $2/3$  theoretical value when ionic conductivity is measured in the in-plane direction, i.e., conductivity along the plane of the film[27, 28, 69, 86]. In contrast, through-plane ionic conductivity (i.e., conductivity across the film thickness) has been shown to be significantly reduced in several block copolymer electrolyte systems, producing morphology factors which are far below  $f = 2/3$ , by factors ranging from roughly 2 to more than an order of magnitude[29, 38, 87, 88]. This anisotropy in the ionic conductivity has been correlated with structural anisotropy, some of which can be caused by certain processing conditions (melt pressing, electric or magnetic field alignment, shear alignment)[29–32, 72, 73, 87].

A persistent source of structural anisotropy, however, is thermodynamic in origin, whereby preferential interactions between one block and a surface lead to wetting layers that drive layering of domains[76]. In a recent paper, we showed that lamellar block copolymers of polystyrene (PS) and poly(1-(2-acryloyloxyethyl)-3-butylimidazolium bis(trifluoromethanesulfonyl)imide) will form highly aligned layers at an air or electrode surface[87]. Layering of lamellae at this interface produces alternating continuous regions of PS and polymer electrolyte, in which the PS regions act as a barrier to through-plane ion transport and the polymer electrolyte regions act as low-tortuosity pathways favorable to in-plane ion transport. We measured significant anisotropy in the ionic conductivity: the in-plane morphology factors were

similar to the expected  $f = 2/3$ , as noted by others for the same block copolymer chemistry[27, 28], while the through-plane morphology factors were an order of magnitude lower. We concluded that the surface-induced ordering of lamellar domains was depressing the through-film conductivity. A similar conclusion was reached by another study that examined a gyroid-forming lithium salt-doped poly(isoprene-*b*-styrene-*b*-ethylene oxide), where the PEO block is the conducting phase, and ionic conductivity improved by a factor of 7 when the electrodes were coated with a PEO brush to suppress the formation of a PS wetting layer.

In this study, we revisit our prior conclusion and consider whether surface effects merely enhance the in-plane conductivity rather than depressing the through-film conductivity. If so, then in-plane morphology factors that match the expected value of  $f = 2/3$  are coincidental, and the true conductivity of PIL-based block copolymers is actually much lower. This possibility was interrogated using a series of PS and poly(4-vinylbenzyl-butylimidazolium bis(trifluoromethanesulfonyl)imide) copolymers (PS-PIL) and a PIL homopolymer. First, we construct a model trilayer system consisting of PIL films sandwiched between thin layers of polystyrene (PS). This allows us to examine whether bulk conductivity measurements using through-film impedance techniques are sensitive to insulating layers at the electrode. Second, we compare through-film conductivity of PS-PIL on smooth and rough electrodes, where the latter is used to disrupt the formation of highly aligned layers. Finally, we perform in-plane conductivity measurements (top-contact) and calculate the anisotropy factors. Collectively, these studies indicate that the in-plane conductivities are enhanced by rearrangements near the surface.

## 5.2 Experimental Section

The procedures used for the synthesis and characterization of PS, PIL, and copolymers thereof are detailed in this section, with additional information appearing in Appendix C. The synthetic protocols of block copolymers and PIL homopolymer was adapted

from those reported elsewhere.[27, 89] Block copolymers are named PX-PILY such that X is the  $M_n$  of the PS block in kg/mol and Y and is the PIL composition in vol% PIL. The amounts of reactants and solvents given in the procedures for block copolymer synthesis are all taken from the synthesis of PS5-PIL53.

**Materials.** 4-cyano-4-[(dodecylsulfanyl-thiocarbonyl)sulfanyl]pentanoic acid (chain transfer agent (CTA), >97%), benzene (anhydrous), 1-butylimidazole (98%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 97%) were used as received from Sigma Aldrich. Dichloromethane (DCM, 99.9%, HPLC), 4-vinylbenzyl chloride (VBC, 90%), diethyl ether anhydrous (BHT Stabilized/Certified ACS), aluminum oxide (anhydrous), methanol ( $\geq 99.8\%$ , ACS Certified), N,N-dimethyl- formamide (DMF, 99%), acetonitrile (anhydrous, 99.9%), deuterated chloroform ( $\text{CDCl}_3$ , 99.8 atom % D), dimethyl-d6 sulfoxide ( $\text{DMSO-d}_6$ , 99.9 atom % D), and tetrahydrofuran (THF,  $\geq 99.9\%$ , Optima for HPLC) were used as received from Fisher Scientific. Azobis(isobutyronitrile) (AIBN, 98%, Sigma-Aldrich) was purified by recrystallization from methanol. Styrene (S, 99%, Fisher Scientific) was dehbitted by passing through a column packed with aluminum oxide.

**Synthesis of PS MacroCTA.** In a typical RAFT polymerization, styrene monomer purified of inhibitor (7.84 g, 75.3 mmol), CTA (0.14 g, 0.35 mmol), and AIBN (0.0053 g, 0.032 mmol) were dissolved in benzene (6.4 mL) in a round-bottom flask containing a magnetic stir bar. The flask was then sealed with a rubber septum, and the reaction mixture was sparged with argon for 10 minutes, after which the flask was placed in an oil bath at 70 °C for 18 h. The polymerization was quenched by removing the flask from the oil bath and immersing it in liquid nitrogen until the contents were frozen solid and then removing the septum. Once the contents had thawed, the polymer was precipitated in cold methanol. The polymer was isolated by gravity filtration and then redissolved in a small amount of DCM. The PS macroCTA was again precipitated in cold methanol, collected by gravity filtration and finally



dried overnight under vacuum at room temperature (>18 h). Molecular weight and dispersity were determined by gel permeation chromatography (GPC) using THF as the eluent. Purity of product was confirmed through  $^1\text{H}$  NMR using  $\text{CDCl}_3$  as the solvent.

**Synthesis of PS-b-PVBC copolymer.** Polystyrene macroCTA (1.40 g, 0.275 mmol), AIBN (0.0047 g, 0.029 mmol), and vinylbenzyl chloride (VBC) (4.92 g, 32.2 mmol) were dissolved in benzene (8.25 mL) in a round-bottom flask with a magnetic stir bar. The flask was then sealed with a rubber septum and sparged with argon for 10 minutes, after which time the flask was placed in an oil bath at 70 °C for 24 h. The reaction was quenched by removing the flask from the oil bath and placing it in liquid nitrogen until the contents were frozen solid, and then removing the septum. Once the contents had thawed, the copolymer was precipitated in cold methanol and then recovered by gravity filtration. The copolymer, PS-b-PVBC was isolated by redissolving in a small amount of DCM, precipitating into cold methanol, and finally collected by gravity filtration. It was then dried under vacuum at room temperature overnight (>18 h). Block copolymer composition was determined by  $^1\text{H}$  NMR with  $\text{CDCl}_3$  as the solvent, using the ratio of the integrated areas of the peaks associated with the ortho protons of PS and PVBC phenyl rings and the 2 protons associated with the methylene group of the PVBC pendant chain. Molecular weight, dispersity, and chain extension were confirmed by GPC using THF as the eluent.

**Synthesis of PS-b-PVBBuIm-Cl copolymer.** PS-b-PVBC (1.55 g, 0.204 mmol copolymer, 3.25 mmol VBC repeat units) and 1-butyylimidazole (1.31 g, 10.5 mmol) were dissolved in DMF (5.0 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate and stirred at 80 °C for 24 h. After this time, DMF was removed by rotary evaporation and 15 mL of DI water added to the vial and contents stirred until copolymer precipitated. Vial contents added to 150 mL of DI water and stirred to wash. PS-b-PVBBuIm-Cl was collected by gravity filtration, dried at room

temperature under vacuum overnight and characterized by  $^1\text{H}$  NMR analysis using DMSO- $d_6$  as the solvent.

**Synthesis of PS-*b*-PVBBuIm-TFSI copolymer.** PS-*b*-PVBBuIm-Cl (1.59 g, 0.118 mmol copolymer, 3.56 mmol chloride anion) and LiTFSI (1.90 g, 6.62 mmol) were dissolved in DMF (5.0 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate and stirred at 50 °C for 24 h, then removed from heat and allowed to cool to room temperature. The copolymer was precipitated into 50 vol% DI water and methanol, collecting by gravity filtration, washed with an additional 100 mL of DI water, and dried in under vacuum at 40 °C for 24 h. The copolymer was then characterized by  $^1\text{H}$  NMR analysis using DMSO- $d_6$  as the solvent.

**Synthesis of P(S-*r*-VBC) copolymer.** Styrene (2.7507 g, 26.4 mmol), VBC (4.0201 g, 26.3 mmol), and AIBN (0.0324 g, 0.197 mmol) were mixed in a round-bottom flask with a magnetic stir bar. The flask was then sealed with a rubber septum and sparged with argon for 10 minutes, after which the flask was placed in an oil bath at 70 °C for 45 min. The reaction was quenched by removing the flask from the oil bath and placing it in liquid nitrogen until the contents were frozen solid and then removing the septum. Once the contents had thawed, the copolymer was precipitated in cold methanol. The copolymer was isolated by gravity filtration and then redissolved in a small amount of DCM. The PVBC was again precipitated in cold methanol, collected by gravity filtration and finally dried overnight under vacuum at room temperature (>18 h). Molecular weight and dispersity were determined by gel permeation chromatography (GPC) using THF as the eluent. The copolymer composition was determined by  $^1\text{H}$  NMR with  $\text{CDCl}_3$  as the solvent, using the ratio of the integrated areas associated with the of peaks assigned to the ortho protons of the PS and PVBC phenyl rings and the 2 protons associated with the methylene group of the PVBC pendant chain.

**Synthesis of P(S-r-VBBuIm-Cl) copolymer.** P(S-r-VBC) (0.4871 g, 0.0138 mmol copolymer, 2.08 mmol VBC repeat units) and 1-butyylimidazole (0.7812 g, 6.29 mmol) were dissolved in DMF (4.0 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate to stir at 80 °C for 24 h, then removed from heat and allowed to cool to room temperature. The copolymer was precipitated by add 15 mL diethyl ether to the vial and stirring rapid. The copolymer was isolated by gravity filtration and then redissolved in a small amount of DMF. The copolymer was precipitated again in diethyl ether, collected by gravity filtration, dried overnight under vacuum at room temperature (>18 h), and characterized by <sup>1</sup>H NMR using DMSO-d<sub>6</sub> as the solvent.

**Synthesis of P(S-r-VBBuIm-TFSI) copolymer (P(S-r-IL).** P(S-r-VBBuIm-Cl) (0.3103 g, 0.00576 mmol copolymer, 0.864 mmol chloride anion) and LiTFSI (1.2726 g, 4.43 mmol) were dissolved in DMF (4.8 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate and stirred at 50 °C for 24 h, then removed from heat and allowed to cool to room temperature. The copolymer was precipitated into DI water three times, decanting the DI water and dissolving the copolymer left behind in a small amount of DMF between precipitations. The copolymer was collected by decanting the DI water after the last precipitation, transferring the copolymer to a 20 mL glass vial, and drying overnight under vacuum at room temperature (>18 h). The copolymer was characterized by <sup>1</sup>H NMR using DMSO-d<sub>6</sub> as the solvent.

**Synthesis of PVBC homopolymer.** CTA (0.039 g, 0.097 mmol), AIBN (0.0017 g, 0.10 mmol), and VBC (5.73 g, 37.5 mmol) were mixed in a round-bottom flask with a magnetic stir bar. The flask was then sealed with a rubber septum and sparged with argon for 10 minutes, after which the flask was placed in an oil bath at 70 °C for 24 h. The reaction was quenched by removing the flask from the oil bath and placing it in liquid nitrogen until the contents were frozen solid and then removing the septum.

Once the contents had thawed, the polymer was precipitated in cold methanol. The polymer was isolated by gravity filtration and then redissolved in a small amount of DCM. The PVBC was again precipitated in cold methanol, collected by gravity filtration and finally dried overnight under vacuum at room temperature (>18 h). Molecular weight and dispersity were determined by gel permeation chromatography (GPC) using THF as the eluent. Purity of product was confirmed through  $^1\text{H}$  NMR using  $\text{CDCl}_3$  as the solvent.

**Synthesis of PVBBuIm-Cl homopolymer.** PVBC (1.11 g, 0.0822 mmol polymer, 7.28 mmol VBC repeat units) and 1-butyylimidazole (2.64 g, 21.3 mmol) were dissolved in DMF (5.5 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate to stir at 80 °C for 24 h, then removed from heat and allowed to cool to room temperature. The polymer had precipitated overnight. Supernatant solution was decanted and PVBBuIm-Cl dissolved in methanol, the precipitated in diethyl ether 5 times, redissolving in methanol between precipitations. Polymer then transferred to 20 mL vial, dried under vacuum at room temperature overnight (>18 h) and characterized by  $^1\text{H}$  NMR using DMSO- $d_6$  as the solvent.

**Synthesis of PVBBuIm-TFSI homopolymer (PIL).** PVBBuIm-Cl (0.71 g, 0.029 mmol polymer, 2.56 mmol chloride anion) and LiTFSI (3.48 g, 12.1 mmol) were dissolved in DMF (7.1 mL) in a 20 mL glass vial with a stir bar. The vial was placed on a hot plate and stirred at 50 °C for 24 h, then removed from heat and allowed to cool to room temperature. The polymer was precipitated into DI water three times, decanting the DI water and dissolving the polymer left behind in a small amount of methanol between precipitations. PVBBuIm-Cl was collected by decanting the DI water after the last precipitation and redissolving the polymer left behind in a small amount of methanol, transferring the solution to a 20 mL glass vial, and concentrating via rotary evaporation. The polymer was then dried under vacuum at 40 °C for 24 h and characterized by  $^1\text{H}$  NMR using DMSO- $d_6$  as the solvent.

**Grazing Incidence Small Angle X-Ray Scattering (GISAXS).** GISAXS was performed using a Xenocs Xeuss 3.0 instrument equipped with a Cu K $\alpha$  Xenocs GeniX3D HFVL microfocus source ( $\lambda = 0.154\text{nm}$ ) and a single photon counting Dectris Pilatus3 R 300k detector with a  $172\text{ }\mu\text{m}$  pixel size. Thin films were prepared by spin coating from acetonitrile solution at 4000 rpm for 60 s. Thick films were prepared by method described for in-plane impedance spectroscopy measurements. Samples were illuminated at an incidence angle of  $\alpha_i \approx 0.20^\circ$  for thin films and at  $0.10^\circ$  for thick films.

**Impedance Spectroscopy.** Impedance measurements were performed using two distinct electrode configurations in order to probe ionic conductivity in the in-plane and through-plane directions. Through-plane measurements were performed via broadband dielectric spectroscopy (BDS) with a parallel-plate electrode configuration using a Novocontrol High Resolution Alpha Dielectric Analyzer equipped with a Quatro Cryosystem for temperature control. Samples were prepared by casting films approximately  $100\text{ }\mu\text{m}$  thick from a solution of 10 wt% polymer in THF onto an electrode of either stainless steel or highly-doped silicon with diameter of 10 mm. Sample thickness was measured using a digital micrometer. In a typical preparation, the solution was dripped onto the electrode with a pipette, and the solvent was allowed to evaporate over the course of 1 h in the fume hood. To control the thickness of the film, two  $100\text{ }\mu\text{m}$  silica spacers were pressed into the film before the solvent had fully evaporated. A second electrode of the same material with diameter of 20 mm was then pressed on top in a parallel plate arrangement. The sample, consisting of the top and bottom electrodes, film, and spacers was annealed (small electrode up) under vacuum at  $120\text{ }^\circ\text{C}$  for 24 h. The sample was then placed in the spectrometer and annealed again at  $120\text{ }^\circ\text{C}$  for approximately 1 h while taking measurements to ensure that the spectra obtained did not change over time. Measurements were then conducted across a range of temperatures, equilibrating for 10 minutes at each temperature before beginning a measurement. Liquid nitrogen was used by the temperature

control system along with a heating element, which enabled control of the sample temperature to within 0.1 K of the set point while preventing the introduction of additional moisture into the system. DC ionic conductivity was taken to be the value of the real conductivity function  $\sigma'(\omega)$  at the frequency at which a maximum occurs in the imaginary modulus function  $M''(\omega)$ .

In-plane measurements were performed via electrochemical impedance spectroscopy (EIS) with a GAMRY Reference 600 Potentiostat/Galvanostat/ZRA in a two point probe configuration using electrodes of platinum wire and a Fumatech MK3 Measuring Cell. Samples were prepared by casting a film between 18 and 41  $\mu\text{m}$  thick, 20 mm wide, and greater than 1 cm long from a solution of 10 wt% polymer in THF onto a glass slide. In a typical preparation, the solution was drop cast onto the slide and allowed to evaporate over the course of 1 h in the fume hood. Once most of the solvent had evaporated, the film was annealed on under vacuum at 120 °C for 24 h. The sample was then placed in the spectrometer and annealed again at 120 °C for approximately 1 h. Measurements were made at a range of temperatures, equilibrating for 1 h at each temperature before beginning a measurement, which was found to be sufficiently long for proper thermal equilibration, judged by reproducibility of data at a given temperature during thermal cycling. The resistance  $R$  was determined from the plateau value of the impedance data represented in the form of a Bode plot. Conductivity  $\sigma$  was calculated using the resistance and sample geometry by the equation  $\sigma = L/(whR)$ , where  $w$  is the width of the film,  $h$  is the thickness measured as described above, and  $L$  is the distance between electrodes (1 cm).

### 5.3 Results and Discussion

Table 5.1 summarizes the characteristics of all polymers used in this study. Several PS-PIL block copolymers, a PIL homopolymer, and a low-molecular weight PS homopolymer (PS-low) were synthesized using reversible addition-fragmentation

**Table 5.1:** Characteristics of polymers. <sup>a</sup>Determined by GPC and NMR; <sup>b</sup>determined by NMR; <sup>c</sup>calculated from  $M_{n,PS}$ ,  $M_{n,PIL}$ , and densities of PS (1.04 g/mL) and PIL (1.50 g/mol); <sup>d</sup>determined by GPC of the homopolymer or block copolymer prior to quaternization; <sup>e</sup>determined by transmission SAXS.

| Sample Name | $M_n^a$ | mol% PIL <sup>b</sup> | vol% PIL <sup>c</sup> | $\bar{D}^d$ | morphology <sup>e</sup> | $d_0^e$ (nm) |
|-------------|---------|-----------------------|-----------------------|-------------|-------------------------|--------------|
| PS5-PIL53   | 13400   | 26.0                  | 53.3                  | 1.08        | lamellar                | 11.1         |
| PS8-PIL42   | 15900   | 18.3                  | 42.0                  | 1.10        | lamellar                | 13.8         |
| PS12-PIL36  | 22700   | 14.9                  | 36.2                  | 1.09        | lamellar                | 19.9         |
| P(S-r-IL)   | 90600   | 56.0                  | —                     | 1.7         | amorphous               | —            |
| PIL         | 46000   | 100.0                 | 100.0                 | 1.11        | amorphous               | —            |
| PS-low      | 5700    | 0.0                   | 0.0                   | 1.01        | amorphous               | —            |
| PS-high     | 177800  | 0.0                   | 0.0                   | 1.03        | amorphous               | —            |

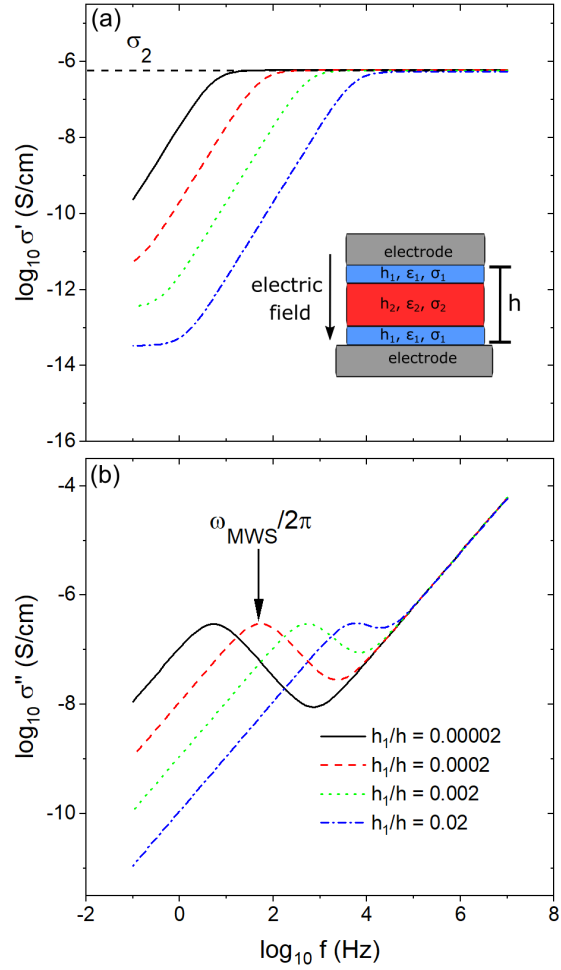
chain transfer (RAFT) polymerization. In addition, PS-PIL random copolymer was synthesized by free radical polymerization. The PIL homopolymer and PS-PIL random copolymer were used as controls to see whether anisotropic conductivity was unique to block copolymers. A high molecular weight and low dispersity PS (PS-high) was also purchased from Scientific Polymer and used as received. A bulk lamellar structure was determined for all block copolymers through transmission SAXS measurements of 50  $\mu\text{m}$  films that had been annealed for 24 h at 130  $^{\circ}\text{C}$ . The volume fractions of PIL in the block copolymers were calculated from the molecular weights of each block using a density of 1.04 g/mL for PS and 1.50 g/mL for PIL. The density of the PIL was calculated at room temperature from the mass and volume of a pendant PIL droplet, where the latter was measured using a DataPhysics OCA 15EC.

Understanding the impact of insulating interfacial layers on the bulk ionic conductivity, as measured by through-plane impedance spectroscopy methods such as BDS, necessarily begins with a discussion of the origins of interfacial polarization in dielectric media. The phenomenon of interfacial polarization, frequently referred to as Maxwell-Wagner-Sillars (MWS) polarization, occurs at the interface of two media with different conductivities, which causes a build-up of charge at that interface. The simplest case, proposed by Whitehead and elaborated by van Beek, consists of a bilayer of two materials with different frequency-independent dielectric constants and conductivities[90, 91]. Since our aim is to understand interfacial polarization caused by insulating layers at electrode interfaces, we can extend this bilayer to a trilayer system, in which a conducting layer of thickness is sandwiched between two thinner insulating layers, as depicted in Figure 5.1. When these layers are treated as capacitors in series, a frequency-dependent polarization arises which can be described by the Debye equations,

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_S - \epsilon_{\infty}}{1 + \omega^2\tau^2} \quad (5.2)$$

$$\epsilon'' = \frac{\sigma}{\epsilon_0\omega} + \frac{(\epsilon_S - \epsilon_{\infty})\omega\tau}{1 + \omega^2\tau^2} \quad (5.3)$$





**Figure 5.1:** (a) Real and (b) imaginary contributions to the complex conductivity of a system comprised of two phases of different conductivities and permittivities, calculated using Equations 5.2 - 5.7. For all cases,  $h = 100 \mu\text{m}$ ,  $\sigma_1 = 6.7 \times 10^{-16}$  S/cm,  $\sigma_2 = 6.0 \times 10^{-7}$  S/cm,  $\epsilon_1 = 4$ , and  $\epsilon_2 = 11$ .

where  $\omega$  is the angular frequency of the electric field,  $\varepsilon'$  and  $\varepsilon''$  are the real and imaginary components of the complex permittivity, respectively, and  $\varepsilon_0$  is the permittivity of free space;  $\tau$  is the characteristic time of the MWS polarization,  $\sigma$  is the conductivity of the bilayer system as a whole, and  $\varepsilon_S$  and  $\varepsilon_\infty$  are the high and low frequency values of the relative permittivity associated with the MWS polarization, respectively. These parameters can be expressed in terms of the thickness, dielectric constant, and conductivity of each layer such that

$$\varepsilon_S = \frac{h(2\varepsilon_1 h_1 \sigma_2^2 + \varepsilon_2 h_2 \sigma_1^2)}{(\sigma_1 h_2 + 2\sigma_2 h_1)^2} \quad (5.4)$$

$$\varepsilon_\infty = \frac{h\varepsilon_1\varepsilon_2}{\varepsilon_1 h_2 + 2\varepsilon_2 h_1} \quad (5.5)$$

$$\tau = \frac{\varepsilon_0(\varepsilon_1 h_2 + 2\varepsilon_2 h_1)}{\sigma_1 h_2 + 2\sigma_2 h_1} \quad (5.6)$$

$$\sigma = \frac{h\sigma_1\sigma_2}{\sigma_1 h_2 + 2\sigma_2 h_1} \quad (5.7)$$

where  $\sigma_1$  and  $\sigma_2$ ,  $\varepsilon_1$  and  $\varepsilon_2$  are the conductivity and dielectric constant of components 1 (insulator) and 2 (conductor), respectively,  $h$  is the thickness of the trilayer system as a whole,  $h_2$  is the thickness of the conducting layer, and  $h_1$  is the thickness of a single insulating layer, with a combine thickness of  $2h_1$ .

Figure 5.1 depicts the real and imaginary parts of the complex conductivity  $\sigma^*$ , which is related to the complex permittivity as  $\sigma^* = i\omega\varepsilon_0\varepsilon^*$ , calculated from Equations 5.2 and 5.3. It is evident that as the fraction of component 1 increases, the value of the  $\sigma'$  plateau, corresponding to  $\sigma_2$ , remains constant. At the same time, the characteristic frequency of MWS polarization  $\omega_{MWS}$ , easily identified as a low frequency peak in  $\sigma''$ , increases as the fraction of component 1 increases. This simple model, however, neglects the frequency dependence of the dielectric function  $\varepsilon^*$  of each layer.

A more complex model of MWS polarization in a trilayer is there therefore necessary to fully capture the polarization response of a real polymer system. A

model developed by Serghei et al. to describe the process of electrode polarization can be adapted to this purpose[37]. By again treating the two layers as capacitors in series, the complex dielectric function in a bilayer of a conducting and insulating layers can be expressed as

$$\frac{h}{\varepsilon^*} = \frac{2h_1}{\varepsilon_1^*} + \frac{h_2}{\varepsilon_2^*} \quad (5.8)$$

where  $\varepsilon_1^*$  and  $\varepsilon_2^*$  are the complex permittivity of the insulating and conducting layers, respectively,  $h_1$  and  $h_2$  are the thicknesses of those layers, respectively, and  $\varepsilon^*$  and  $h$  are the complex permittivity and thickness of the bilayer system as a whole. Separating Equation 5.8 into real and imaginary components yields

$$\varepsilon' = \frac{(\varepsilon_1'\varepsilon_2' - \varepsilon_1''\varepsilon_2'')(y\varepsilon_1' + x\varepsilon_2') + (\varepsilon_1''\varepsilon_2' + \varepsilon_1'\varepsilon_2'')(y\varepsilon_1'' + x\varepsilon_2'')}{(y\varepsilon_1' + x\varepsilon_2')^2 + (y\varepsilon_1'' + x\varepsilon_2'')^2} \quad (5.9)$$

$$\varepsilon'' = \frac{(\varepsilon_1''\varepsilon_2' + \varepsilon_1'\varepsilon_2'')(y\varepsilon_1' + x\varepsilon_2') - (\varepsilon_1'\varepsilon_2' - \varepsilon_1''\varepsilon_2'')(y\varepsilon_1'' + x\varepsilon_2'')}{(y\varepsilon_1' + x\varepsilon_2')^2 + (y\varepsilon_1'' + x\varepsilon_2'')^2} \quad (5.10)$$

where  $x = h_1/h$  and  $y = 1 - x$ . The complex dielectric function of each layer can be described using the Jeppe Dyre model[36], also known as the random barrier model, which considers the hopping of ions in a random energy barrier landscape, expressed as

$$\sigma_1^* = i\omega\varepsilon_0\varepsilon_1^* = \varepsilon_\infty + \sigma_{0,1} \frac{i\omega\tau_{e,1}}{\ln(1 + i\omega\tau_{e,1})} \quad (5.11)$$

$$\sigma_2^* = i\omega\varepsilon_0\varepsilon_2^* = \sigma_{0,2} \frac{i\omega\tau_{e,2}}{\ln(1 + i\omega\tau_{e,2})} \quad (5.12)$$

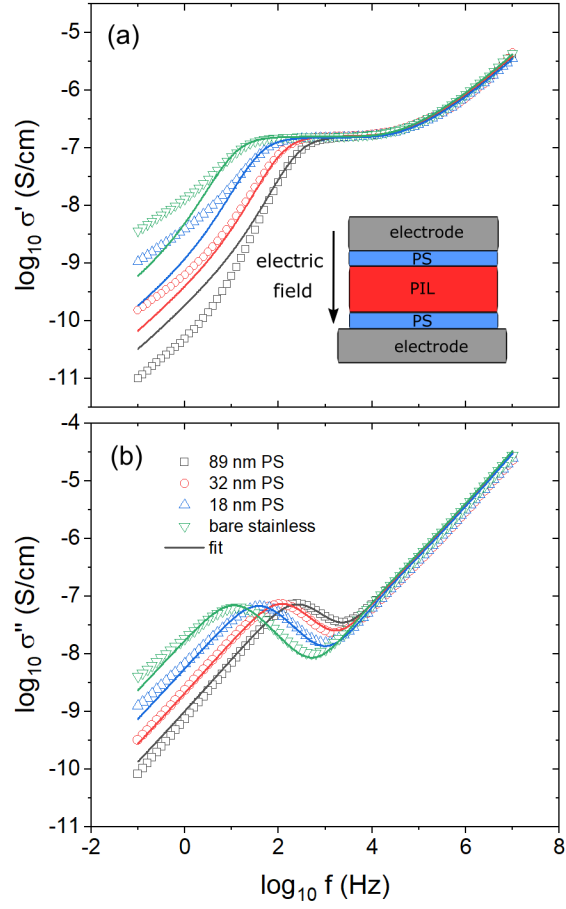
where  $\sigma_0$  is the plateau value of  $\sigma'$  (DC ionic conductivity) and  $\tau_e$  is the characteristic ionic hopping time.

In order to compare this model to the polarization response of a real polymer electrolyte trilayer system, PIL films with a thickness 100  $\mu\text{m}$  were prepared between stainless steel electrodes which had been coated with a thin film of PS-high. The PS films with thicknesses of 18, 32, and 89 nm were used. Through-plane impedance measurement were performed on these trilayer samples using BDS at temperatures

ranging from 353 to 243 K. The temperature range was selected in order to remain below the glass transition temperature of PS but include temperatures above and below the glass transition temperature of PIL (282 K)[27].

Figure 5.2 shows the real and imaginary components of the complex conductivity,  $\sigma'$  and  $\sigma''$  respectively, for each of these films. The experimental data were fit using Equations 5.8-5.12, and the optimized curves are shown as solid lines in Figure 5.2. The values of  $x$  and  $\tau_{e,2}$  were optimized for each sample and at each temperature as a means of validating the model. Optimized values were compared to known values acquired by other means (thickness of the PS layer was measured by ellipsometry and used to calculate  $x$ , and the frequency of the peak in  $M''$  was used to estimate  $\tau_{e,2}$ ). Variation of the optimized value of  $\tau_{e,2}$  at a given temperature across all three samples was found to be less than 5%, and the temperature dependence was consistent with that of the values estimated from  $M''$ . No appreciable temperature dependence was observed for optimized values of  $x$ . The value of  $\sigma_{0,1}$  was optimized at each temperature for one sample only (electrodes with 89 nm PS coating), then fixed at those optimized values for other samples. Optimized values of  $\sigma_{0,1}$  fell within the range reported in the literature. The values of  $\sigma_{0,2}$ ,  $\tau_{e,1}$ , and  $\varepsilon_\infty$  were held fixed for all samples at all temperatures:  $\sigma_{0,2}$  was taken to be the  $\sigma'$  plateau value of PIL films measured on unmodified stainless steel electrodes;  $\tau_{e,1}$  was estimated using the fit value of  $\sigma_{0,1}$  and the Barton-Nakajima-Namikawa relation, which states that  $\sigma_0 \sim \omega_c$ , where  $\omega_c$  is the critical ion hopping frequency and  $\tau_e = 1/\omega_c$ [92, 93];  $\varepsilon_\infty$  was taken to be the high frequency value of  $\varepsilon'$ . Optimized parameter values are provided as a function of temperature in Appendix C (Figures C.20 and C.21).

The model was able to quantitatively capture the data across a wide range of frequencies and temperatures, and the thickness of the PS layers calculated from the fit values of  $x$  on the basis of a 100  $\mu\text{m}$  trilayer sample agree with those measured using ellipsometry to within 1-2 nm for all samples. Importantly, while the experiment and model both demonstrate that  $\omega_{MWS}$  shifts to higher frequency as  $h_1$  increases, the plateau value of  $\sigma'$  (corresponding to  $\sigma_{DC}$ ) remains constant. This outcome shows



**Figure 5.2:** Measured and calculated (Equations 5.8 - 5.12) (a) real and (b) imaginary contributions to the complex conductivity of a  $100 \mu\text{m}$  PIL film between stainless steel electrodes coated in films of PS of various thicknesses.

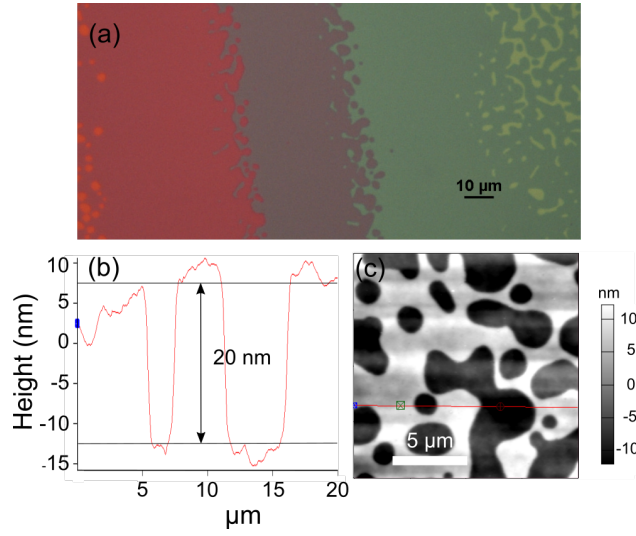
that the ionic conductivity measured by impedance spectroscopy is not depressed by insulating interfacial layers. Neither these experiments nor the model, however, can be expected to fully represent the case of lamellar block copolymers with interfacial regions of parallel aligned lamellae. In the PS/PIL/PIL trilayer, the boundaries between PS interfacial layers and PIL bulk are clearly delineated and the thicknesses of each layer are known. In a block copolymer, there are several additional factors that cannot be accurately capture by the simple model and trilayer experiment, such as the ill-defined boundary between interfacial and bulk regions, differences in domain connectivity within these regions, and additional MWS polarizations that can arise at domain interfaces and grain boundaries.

To examine how alignment of lamellar domains at an electrode might contribute to measurements of ionic conductivity, films of all PS-*b*-PIL block copolymers were annealed between either smooth silicon (Si) electrodes or rough stainless steel (SS) electrodes. When polymers have very different surface energies, such as PS (42 mN/m)[94] and PIL (29 mN/m, measured from a pendant PIL droplet using a DataPhysics OCA 15EC.), wetting layers will form at both the free surface and the substrate. This tends to drive layering of domains parallel to the surfaces, and that layering can propagate all the way through a thin film. However, if the substrate is very rough, then wetting layers can be disrupted. As the SS electrodes are extremely rough, as shown in Figure C.22, it is doubtful that PS-PIL lamellae could adopt the parallel orientation across the entire surface.

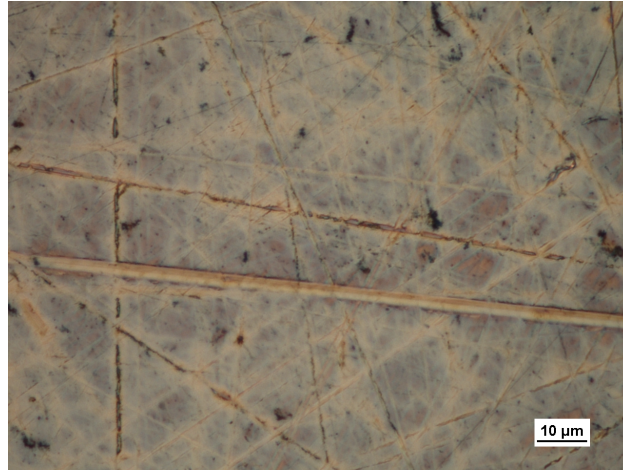
To confirm that electrode topography can influence lamellar alignment, thin films (100-750 nm) of each PS-*b*-PIL material were cast on both Si and SS followed by annealing under vacuum at 120 °C for 18 h. Films were first inspected for islands and holes using optical microscopy and atomic force microscopy (AFM) for the presence of islands and holes. In a lamellar block copolymer, islands and holes are observed when domains are aligned parallel to the surfaces and the thickness of the as-cast film is incommensurate with the domain periodicity.[78]. The height of islands (or depth of holes) is equal to the domain periodicity  $d_0$  when both the air and the substrate

interfaces are preferential to one of the blocks. As-cast block copolymer films on silicon substrates were smooth, but islands or holes were observed after annealing, as shown in Figure 5.3, which depicts representative microscopy data for PS12-PIL36 on silicon. Optical microscopy data in Figure 5.3a shows the presence of islands and holes in the annealed film, and AFM data in Figure 5.3b and 5.3c demonstrates that the height of the islands is approximately 20 nm, consistent with the domain periodicity  $d_0$  obtained from bulk transmission SAXS and thin film GISAXS. In contrast to the silicon results, no islands or holes were observed in any films on stainless steel (Figure 5.4).

Contact angles of water and diiodomethane were recorded for each block copolymer film that exhibited islands and holes (i.e. those on silicon substrates) as well as PIL and PS homopolymers to identify the block that is present at the air interface. PS-low was used for the PS film, as a low molecular weight PS synthesized through RAFT was expected to provide a good analogue to the PS block in the block copolymers. The recorded contact angles are reported in Table 5.2. The water contact angle for all block copolymers and for the PIL homopolymer was between 78 and 81°, while the water contact angle for the PS homopolymer was 90°. Similarly, the diiodomethane contact angle for all block copolymers and for the PIL homopolymer was between 60 and 66°. The diiodomethane contact angle of the PS homopolymer could not be measured as diiodomethane was found to dissolve PS at such a low molecular weight, but was measured for a higher molecular weight PS at 36°, consistent with values reported elsewhere[94]. These data demonstrate the PIL block is preferred over the PS block at the air interface.



**Figure 5.3:** Island and hole formation observed in thin film of PS12-PIL36 on silicon by (a) optical microscopy and (b,c) AFM. The film was annealed at 120 °C for 18 h. The AFM tapping mode height image is 20 x 20  $\mu\text{m}^2$ . Horizontal line cut of the AFM height image (b) shows island height is approximately equal to  $d_0 = 20$  nm.



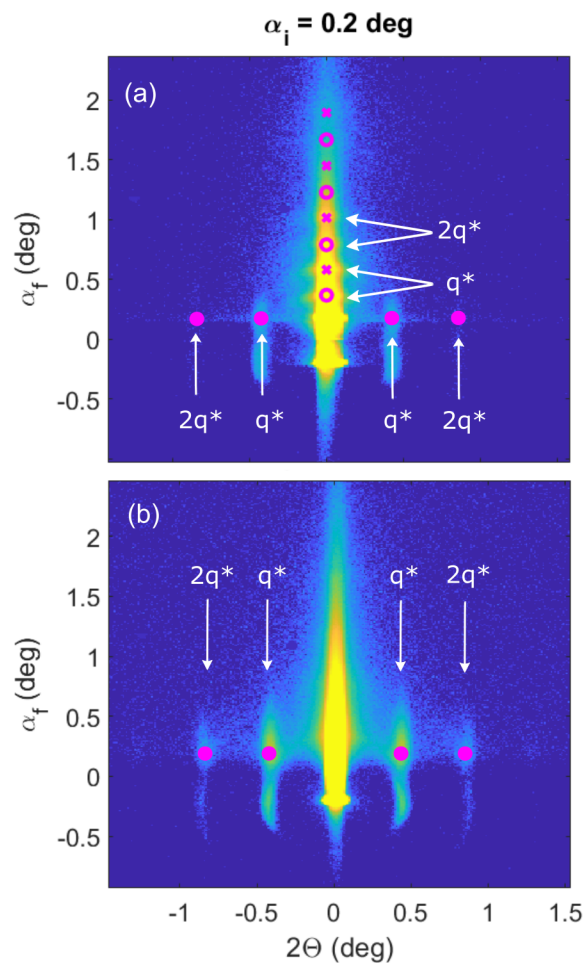
**Figure 5.4:** Image of PS12-PIL36 thin film on stainless steel obtained by optical microscopy. The film was annealed at 120 °C for 18 h. No evidence of island and hole formation observed, but it is clear that the surface is rough.



**Table 5.2:** Static contact angles of water and diiodomethane on thin films. Average contact angle is calculated from three measurements per sample.

| Sample Name | $\theta_{water}$ ( $^{\circ}$ ) | $\theta_{diiodomethane}$ ( $^{\circ}$ ) |
|-------------|---------------------------------|-----------------------------------------|
| PS          | 90.4 $\pm$ 0.7                  | —                                       |
| PIL         | 80.4 $\pm$ 1.5                  | 60.5 $\pm$ 0.6                          |
| PS5-PIL53   | 78.6 $\pm$ 0.2                  | 65.7 $\pm$ 1.4                          |
| PS8-PIL42   | 78.3 $\pm$ 0.4                  | 64.0 $\pm$ 0.6                          |
| PS12-PIL36  | 78.4 $\pm$ 0.3                  | 62.8 $\pm$ 0.3                          |

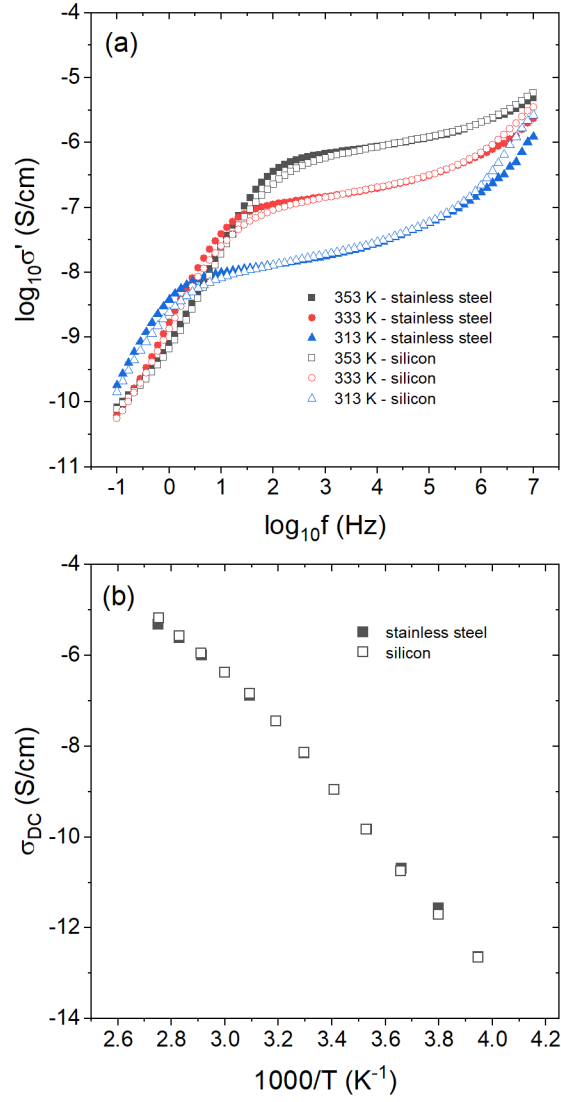
GISAXS experiments were also performed on all block copolymer thin films. Representative GISAXS data for films of PS12-PIL36 on silicon and stainless steel substrates are shown in Figure 5.5a and 5.5b, respectively, as a function of in-plane ( $2\theta$ ) and out-of-plane ( $\alpha_f$ ) scattering angles. In the case of the film on silicon, there are signatures of order along both the out-of-plane ( $\alpha_f$ ) and in-plane ( $2\theta$ ) axes. The out-of-plane scattering arises from layering of lamellar domains through the film thickness. The in-plane scattering, which is weaker than the out-of-plane scattering, is consistent with domains that are oriented perpendicular to the surfaces. However, it is important to recognize that the in-plane scattering intensity is enhanced by standing waves (the Yoneda effect), and the form factor for perpendicular lamellae is not observed, so this scattering may arise from a small fraction of misoriented grains in the interior of the film. In the case of the film on stainless steel, the scattering includes a weak Debye-Scherrer ring from randomly-oriented lamellar grains along with relatively strong in-plane scattering that arises from the perpendicular orientation of lamellar domains. In both cases, the positions of one or two Bragg peaks for several order of reflection ( $q^*$ ,  $2q^*$ ,  $3q^*$ , etc.) were predicted in either the out-of-plane or in-plane directions for a lamellar periodicity of 19.9 nm (value determined from transmission SAXS, Figure C.17) and incident angle of  $0.2^\circ$ , following procedures described elsewhere[34]. Out-of-plane predictions are marked by the "x" and "o" symbols, and in-plane predictions are marked with "•" symbols. The predicted Bragg peak positions for  $q^*$  and  $2q^*$  agree with the experimental data in both the silicon and stainless steel supported films. Using contact angle data, evidence of island/hole formation in microscopy, and GISAXS, we can infer that films on silicon form well-defined layers through the film thickness. For stainless steel, we know that the PIL block forms a wetting layer at the surface, but absence of islands/holes and parallel peaks in GISAXS suggests that interfacial order does not propagate very far. The strong in-plane scattering consistent with perpendicular peaks is therefore a consequence of roughness at the substrate, which disrupts the parallel alignment.



**Figure 5.5:** GISAXS data of (a) a 280 nm film of PS12-PIL36 on silicon and (b) a 748 nm film of the same block copolymer on stainless steel. The films were annealed at  $120 \text{ }^\circ\text{C}$  for 18 h. Both samples measured at an incident angle of  $0.2^\circ$

With evidence that PS-PIL lamellae adopt different orientations on Si and SS electrodes, the next step was to check if the BDS spectra ( $\sigma_{DC}$ ) were appreciably different in each case. The through-plane ionic conductivity of each block copolymer and the PIL homopolymer was measured with BDS using both silicon and stainless steel electrodes in a parallel plate configuration. In Figure 5.6, representative spectra of the real component of the complex conductivity  $\sigma'$  are shown for PS8-PIL42 at three temperatures using either Si or SS electrodes. For all polymers measured, neither the  $\sigma'$  spectra nor  $\sigma_{DC}$  were appreciably changed by the choice of electrode material. These data confirm the key outcome of the trilayer experiment, that interfacial structures do not impact the value of  $\sigma_{DC}$  measured by through-plane impedance spectroscopy methods, contrary to suggestions in prior studies[87]. These results also imply that if anisotropic ionic conductivity in block copolymer electrolytes is a consequence of domain alignment near surfaces, then it is due to enhancement in the in-plane direction rather than depression in the through-plane direction.

Having shown that through-film conductivity is not impacted by differences in the interfacial structure, the final objective was to test whether the in-plane ionic conductivity is enhanced relative to the through film value for this PS-PIL material. The PIL homopolymer and a P(S-r-IL) random copolymer were used as controls. The in-plane ionic conductivity of each block copolymer, the PIL homopolymer, and the P(S-r-IL) random copolymer was measured using electrochemical impedance spectroscopy (EIS) in a two-point probe configuration. The results were compared to those of the through-plane measurements (stainless steel electrodes) and are summarized in Figure 5.7. Ionic conductivity of the PIL homopolymer was similar along the in-plane and through-plane directions. However, for all block copolymers the in-plane conductivity was significantly greater than the through plane conductivity, ranging from roughly 2 times greater in PS12-PIL36 to as much as 19 times greater in PS12-PIL36 at the lowest temperature measured (30 °C). Interestingly, the random

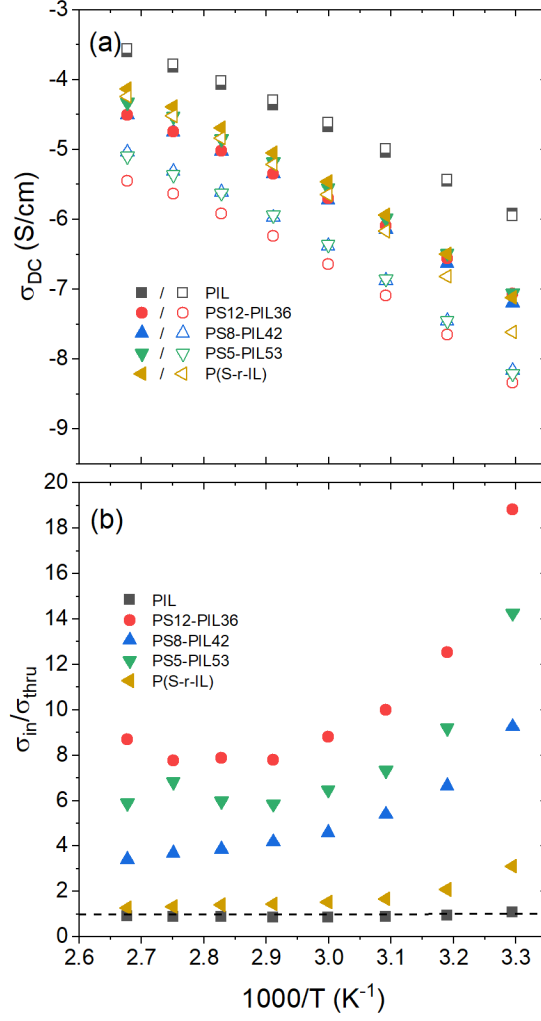


**Figure 5.6:** (a) Real component of the complex conductivity as a function of frequency and (b) DC ionic conductivity as a function of inverse temperature for 100  $\mu\text{m}$  thick PS8-PIL42 films between silicon (open symbols) or stainless steel (solid symbols) electrodes.

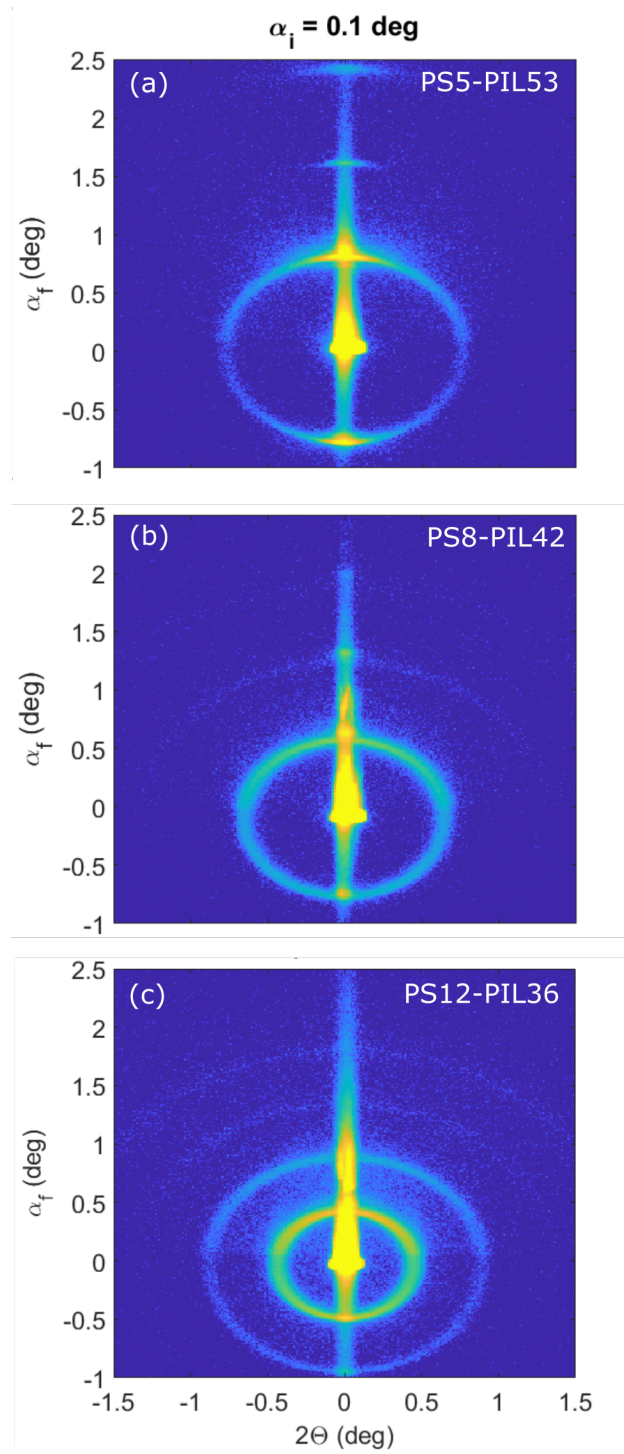
copolymer P(S-r-IL) also exhibited anisotropy in the ionic conductivity, where the in-plane conductivity was 3 times greater than the through-plane conductivity at 30 °C.

GISAXS measurements were performed on the block copolymer films used in EIS measurements to probe the lamellar domain orientations at the free surface, which was the surface in contact with the electrodes during impedance measurements. A low incident angle of  $0.1^\circ$  was used to limit the X-ray penetration depth to the top 10-100 nm of the film [34], thereby probing the surface structure. The results are summarized in Figure 5.8. A clear difference in degree of ordering at the air interface can be seen between the three block copolymers. In PS5-PIL53 (Figure 5.8a) scattering is concentrated in Bragg peaks along the out-of-plane direction, consistent with parallel alignment of lamellar domains at the surface, along with a weaker Debye-Scherrer ring that arises from randomly-oriented grains. The same features are observed in PS8-PIL42, but the out-of-plane Bragg peaks are weaker and the Debye-Scherrer ring is stronger. PS12-PIL36 appears nearly isotropic.

There does not appear to be a correlation between extent of surface ordering and enhanced in-plane conductivity. PS12-PIL36 exhibits the greatest enhancement in in-plane conductivity, despite appearing to be nearly isotropic at the air interface. These data suggest that a wetting layer of PIL at a surface is sufficient to enhance in-plane conductivity significantly. It is notable that the random copolymer also shows an enhancement. This raises the question of whether the random copolymer, which is amorphous in bulk (determined by transmission SAXS, Figure C.18), can restructure at the surface. Certain amphiphilic random copolymers with relatively long pendant chain have been shown to self-assemble in solution and in bulk by rotation of pendant groups along the backbone[95], and to layer at interfaces due to preferential interactions between a surface and one of the repeat unit pendant groups[96]. It is possible that the PIL pendant chain preferentially wets the air interface in PS-PIL random copolymers, resulting in a very thin surface layer with higher ionic content than that of the bulk of the film.



**Figure 5.7:** (a) DC ionic conductivity determined by either through-plane (open symbols) or in-plane (closed symbols) impedance techniques as a function of temperature, and (b) the ratio of in-plane to through-plane DC ionic conductivity as a function of temperature. The dotted line corresponds to the value  $\sigma_{in}/\sigma_{thru} = 1$  (isotropic).



**Figure 5.8:** GISAXS data of films of (a) PS5-PIL53, (b) PS8-PIL42, and (c) PS12-PIL36 ranging in thickness from 25 to 41  $\mu\text{m}$ , measured at an incident angle of  $0.1^\circ$ .



Although the precise mechanism of in-plane conductivity enhancement remains unclear, these data demonstrate that even very small interfacial rearrangements can lead to anisotropy in the conductivity. In light of this finding, and given that interfacial rearrangement in block copolymers is a near-ubiquitous phenomenon, it is highly likely that values of in-plane ionic conductivity in block copolymer electrolytes reported elsewhere in the literature are similarly enhanced compared to the true bulk ionic conductivity of the block copolymer material studied. Indeed, in-plane conductivities of the block copolymers in this study (as well as the morphology factors, provided in Appendix C) were comparable to values for similar blocks copolymers based on polymeric ionic liquids reported for which conductivities were similarly determined through EIS with an in-plane, top-contact electrode configuration[27, 28]. The morphology factors in particular often are, misleadingly, roughly in line with the expected theoretical value of  $2/3$  for randomly oriented lamellae. These results are often interpreted as representative of bulk ion transport in the material. The results of this work, however, have shown that the values of in-plane conductivity should not necessarily be considered representative of the bulk. Rather, through-plane measurements, due to their insensitivity to interfacial interactions, are a far more reliable in capturing the bulk ionic conductivity.

## 5.4 Conclusions

In this work, the impact of interfacial interactions in block copolymer electrolytes on the ionic conductivity measured either in the in-plane or through-plane directions was investigated. It was demonstrated insulating interfacial layers do not impact the ionic conductivity measured by through-plane impedance methods. This holds for both simple PS and PIL trilayer systems as well as for block copolymers with parallel-aligned lamellae at the electrode interfaces. Ionic conductivity measured by in-plane impedance methods, in contrast, was shown to be highly sensitive to even very slight interfacial enrichment of PIL groups, with in-plane conductivities

elevated as much as 14x compared to the through-plane values. Due to the ubiquitous nature of interfacial rearrangement in block copolymers and the sensitivity of in-plane measurements to such interfacial interactions, in-plane impedance methods should not be relied upon for the measurement bulk ionic conductivity in block copolymer electrolytes without thorough characterization of interfacial structure and wetting behavior. Rather, through-plane impedance methods, due to their insensitivity to interfacial layers, are far more reliable in these cases.

Even through-plane impedance techniques, however, have limitations; while their insensitivity to interfacial layers allows for accurate measurement of bulk ionic conductivity, through-plane impedance measurements still do not capture ion transport across the entire film. For most applications, through-film transport from one interface of the film to the other is critical. As has been discussed in a previous work, a simple effective medium approximation can be used to demonstrate that even a small region of parallel-oriented lamellae at the interface of a film can lead to a decrease in conductivity by several orders of magnitude. As such, while bulk ionic conductivity can be accurately measured using through-plane impedance methods despite the presence of interfacial order, such oriented interfacial region can be detrimental to device performance in applications such as lithium ion batteries. The avoidance of interfacial alignment should be a primary concern when block copolymer electrolytes designed for such applications. Methods to suppress preferential interactions at a surface, such as the addition of a thin "neutral" coating, are already established in block copolymer lithography and could be applied to this case as well[84, 85].

# Chapter 6

## Outlook

While the results in Chapters 4 and 5 clearly demonstrate that anisotropy in the ionic conductivity of PIL-based block copolymer electrolytes results from interfacial order, the precise origin of the in-plane enhancement is still something of an open question. A significant degree of anisotropy is exhibited by all block copolymers studied, even when little-to-no evidence of lamellar layering at the air interface is observed. In addition, contact angle measurements indicate enrichment of the PIL block at the air interface of all block copolymers studied. These data suggest that a single PIL block wetting layer is sufficient to yield an increase in in-plane conductivity as high as 18x over the through-plane value. Similarly, the increase in in-plane conductivity in the random copolymer P(S-r-IL) suggests that orientation on the length scale of repeat units, rather than the block, might be sufficient to enhance in-plane conductivity.

The exact reason why small degrees of interfacial order produce such disproportional anisotropy in the conductivity is not well understood, but may be due to the uneven electric field lines in a parallel wire electrode configuration weighting the near-electrode interface more than the rest of the film. Because all PS-PIL block copolymers studied in Chapters 4 and 5 had PIL volume fractions of around equal volume or less, it was hypothesized that the high degree of in-plane enhancement may be caused by interfacial order creating a region of high PIL connectivity in

a material that otherwise has very poor PIL connectivity. Indeed, the through-plane conductivity of all PS-PIL block copolymers studied is significantly lower than expected relative to the homopolymer, with morphology factors no higher than  $f = 0.15$  and as low as  $f = 0.01$  (ideal lamellar morphology factor is  $f = 2/3$ ). This seemingly supported the idea that the PS-PIL block copolymers studied had poor PIL domain connectivity.

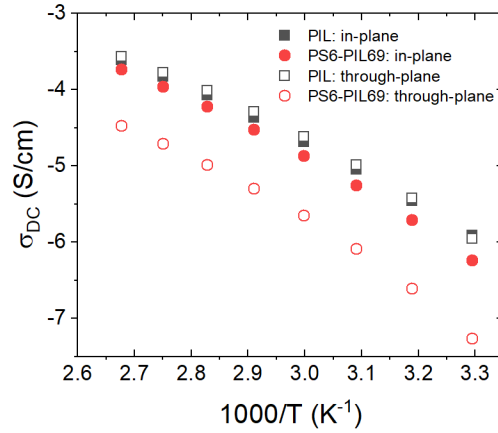
To test this hypothesis, a block copolymer of PS and poly(4-vinylbenzyl-butylimidazolium bis(trifluoromethanesulfonyl)imide) (PIL) with high PIL content was synthesized using RAFT, described in Table 5.1. A PIL content of greater than 60 vol% was targeted so that the resulting material would have a continuous PIL phase. The expectation was that conductive anisotropy would be low, since interfacial alignment does not offer any enhanced PIL connectivity at the interface for a material with a bulk continuous PIL phase. In addition, through-plane conductivity was expected to be significantly higher compared to the other block copolymers studied, with a morphology factor approaching  $f = 1$ .

The material was found to self-assemble strongly, but the morphology, which was interrogated using transmission SAXS following the procedures described in Appendix C, was ambiguous due to lack of higher-order peaks. Water and diiodomethane contact angles on thin films of PS6-PIL69 which were annealed under vacuum for 24 h at 120 °C were 79.1 and 59.0°, respectively, indicating that a PIL wetting layer forms at the air interface.

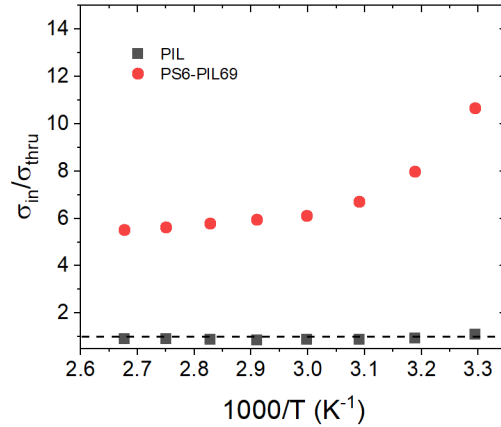
The in-plane and through-plane conductivities, as well as the anisotropy in conductivity, were determined using the procedures detailed in Chapter 5, and the results are shown in Figures 6.1 and 6.2 alongside those of homopolymer PIL (described in Table 5.1). PS6-PIL69 exhibited a large degree of in-plane enhancement, similar in degree to the other block copolymers studied. GISAXS was performed on the film that was used for EIS at an incident angle of 0.1°, revealing no indication of lamellar layering at the air interface. This unexpected result demonstrates that a large number of well-defined layers parallel to the surface is not necessary for enhancement

**Table 6.1:** PS-PIL block copolymer with high PIL content. <sup>a</sup>Determined by GPC and NMR; <sup>b</sup>determined by NMR; <sup>c</sup>calculated from  $M_{n,PS}$ ,  $M_{n,PIL}$ , and densities of PS (1.04 g/mL) and PIL (1.50 g/mol); <sup>d</sup>determined by GPC of the homopolymer or block copolymer prior to quaternization.

| Sample Name | $M_n^a$ | mol% PIL <sup>b</sup> | vol% PIL <sup>c</sup> | $\bar{D}^d$ |
|-------------|---------|-----------------------|-----------------------|-------------|
| PS6-PIL69   | 24800   | 40.7                  | 68.9                  | 1.21        |



**Figure 6.1:** DC ionic conductivity of PIL and PS6-PIL69 determined by in-plane (solid symbols) and through-plane (open symbols) impedance techniques.

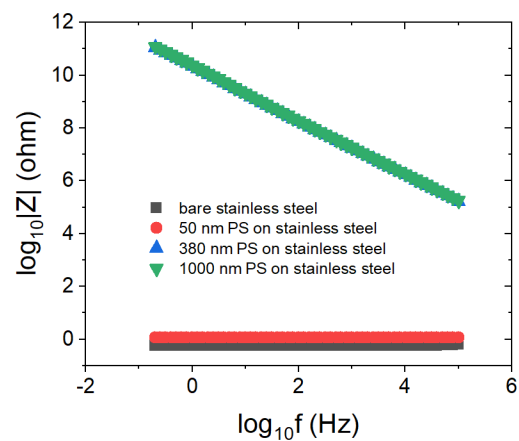


**Figure 6.2:** Ratio of the in-plane to through-plane DC ionic conductivity of PIL and PS6-PIL69 as a function of temperature. The dotted line corresponds to the value  $\sigma_{in}/\sigma_{thru} = 1$  (isotropic).

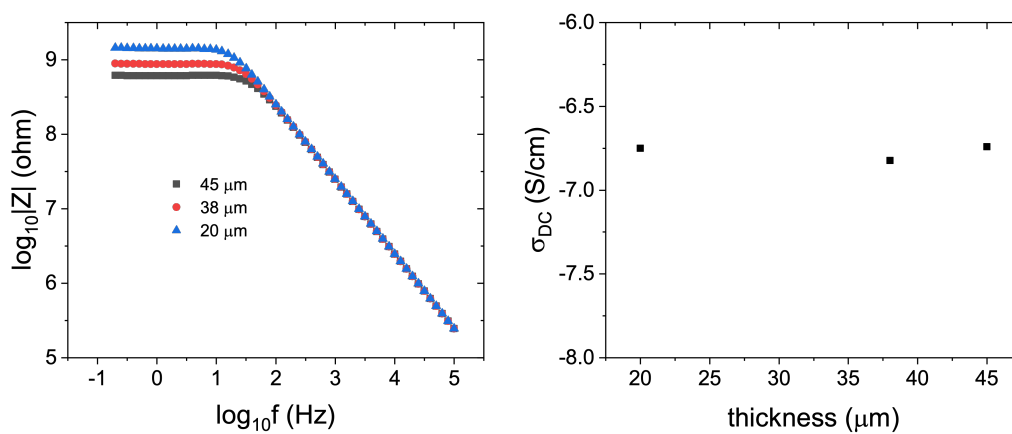
along the in-plane direction. It is possible that the molecular weight of the PIL block plays a role in the degree of enhancement—larger PIL blocks create thicker PIL wetting layers—but additional experiments are needed to more fully understand this phenomenon.

The possibility was considered that low skin depth in EIS measurements was the source of in-plane enhancement—i.e., the electric field in EIS measurements only penetrates a short distance into the film, making the oriented interface a larger fraction of the probed volume and producing an apparently enhanced in-plane conductivity. As a first estimate of skin depth in an insulating polymer film, a series of films of PS-high (described in Table 5.1) were coated on stainless steel (SS) discs (using the procedure described in Chapter 5. EIS measurements were performed at ambient conditions on the PS-coated discs with the PS film in contact with the electrodes, and the results are shown in Figure 6.3. Bare SS exhibited a very low and frequency-independence  $|Z|$  value of around 1 ohm (essentially a short between the electrodes). Likewise, the SS disc coated with a 50 nm PS film, while showing a slight increase in impedance relative to the bare SS, exhibited a similarly low, frequency-independent impedance, suggesting that the electric field was probing the conductive SS substrate through the PS film. Measurements of SS discs coated with 380 nm and 1000 nm PS films, however, do not exhibit conductive behavior at all, suggesting that the skin depth is lower than the PS film thickness, and the substrate is not probed.

EIS measurements performed on thick films of PS6-PIL69 on glass (45, 38, and 20  $\mu\text{m}$ ), however, indicated that the skin depth of the block copolymer is much larger than the thickness of films measured in these experiments or in Chapters 4 or 5, and the electric field does in fact probe the entire film. EIS measurements were performed at ambient conditions using the procedures described in 5, and the impedance and conductivity results are shown in Figure 6.4. It is clear from the Bode plot data that impedance decreases with film thickness, as expected if the entire film were probed. If only a portion of the film was probed by the electric field, impedance would not change with thickness so long as the thickness of the film was greater than the skin



**Figure 6.3:** EIS results for PS thin films of varied thickness supported on stainless steel substrates.



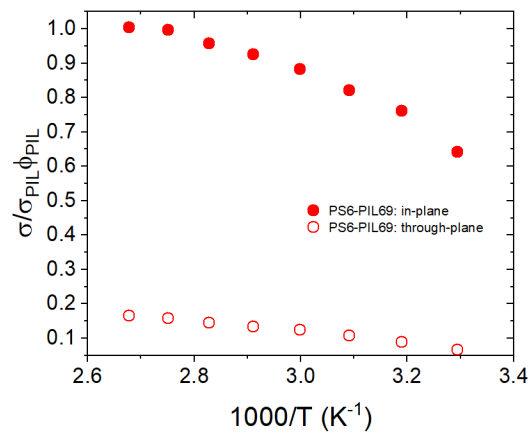
**Figure 6.4:** EIS results for PS6-PIL69 films of varied thickness supported on glass substrates.

depth. Additionally, the value of  $\sigma_{DC}$  calculated using Equation 2.12 is consistent for each film thickness. Moreover, if the electric field were probing a smaller thickness of film than the value used in the  $\sigma_{DC}$  calculation, a decrease in the calculated  $\sigma_{DC}$  would result, not an increase. These factors together make it clear that low skin depth is not the source in-plane enhancement in these block copolymers.

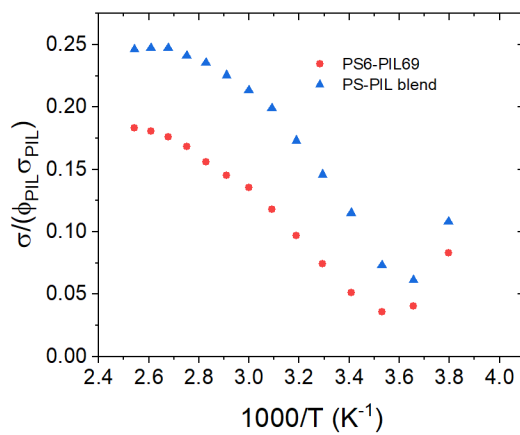
Interestingly, the through-plane conductivity of PS6-PIL69 (Figure 6.1) was still surprisingly low compared to the PIL homopolymer, despite the high PIL content. The through-plane morphology factor (Figure 6.5) ranged from  $f = 0.16$  to as low as  $f = 0.07$ , significantly lower than the expected  $f = 1$ , demonstrating that low conductivity in the block copolymers studied in Chapters 4 and 5 is not a result of poor domain connectivity, but may rather be intrinsic to this block copolymer system.

In order to investigate whether low conductivity stemmed specifically from the self-assembled morphology, a blend of PIL and PS-low (both described in Table 5.1) with a PIL content of 65 vol% was prepared, and its through-plane ionic conductivity was measured by BDS following the procedures described in Chapter 5. The through-plane morphology factor of the PS-PIL blend is compared to that of block copolymer PS6-PIL69 in Figure 6.6. The morphology factor exhibited by the PS-PIL blend, while slightly higher than that of the block copolymer, is nowhere near the value of  $f = 1$  expected for a macro-phase separated blend with such high PIL content. It is clear from these results that the low conductivity exhibited by the block copolymers studied does not stem solely from the self-assembled morphology. It is possible that because the PIL has a styrenic backbone, there is some degree of miscibility between the two polymers. In the block copolymers this may manifest itself as a diffuse domain interface, where ions of the PIL block may have a high concentration of styrenic neighbors, effectively trapping the mobile anions. In the PS-PIL blend, it may be that there is some PS dissolved in the PIL matrix, reducing conductivity. Probing the glass transition temperature of both the block copolymer and the blend should offer some insight into the extent of mixing, and such studies are currently underway.





**Figure 6.5:** In-plane (solid symbols) and through-plane (open symbols) morphology factors of PS6-PIL69 as a function of temperature.



**Figure 6.6:** Through-plane morphology factors of block copolymer PS6-PIL69 and a blend of PS and PIL (65 vol% PIL).

Further experiments are required to fully understand the cause of the low conductivity in this system. Future experiments should include synthesis of highly asymmetric PS-PIL block copolymers to target hexagonally close-packed cylinders or body-centered cubic spheres of polystyrene within a continuous PIL matrix. Measuring the ionic conductivity of such materials may help provide insight into the origins of low conductivity observed in these block copolymers. Specifically, these studies can eliminate the influence of domain connectivity on ion transport, thereby providing a simpler platform to examine the role of block copolymer interfaces and molecular weight on ionic conductivity.

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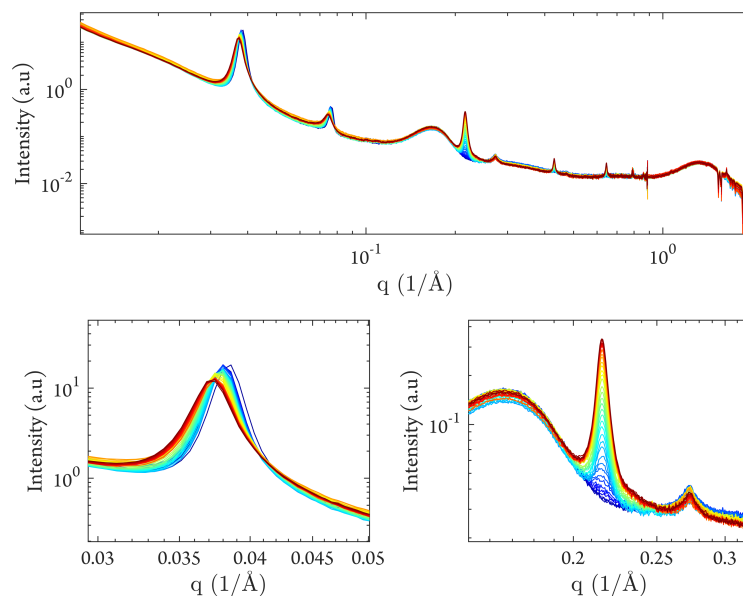
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# Appendix

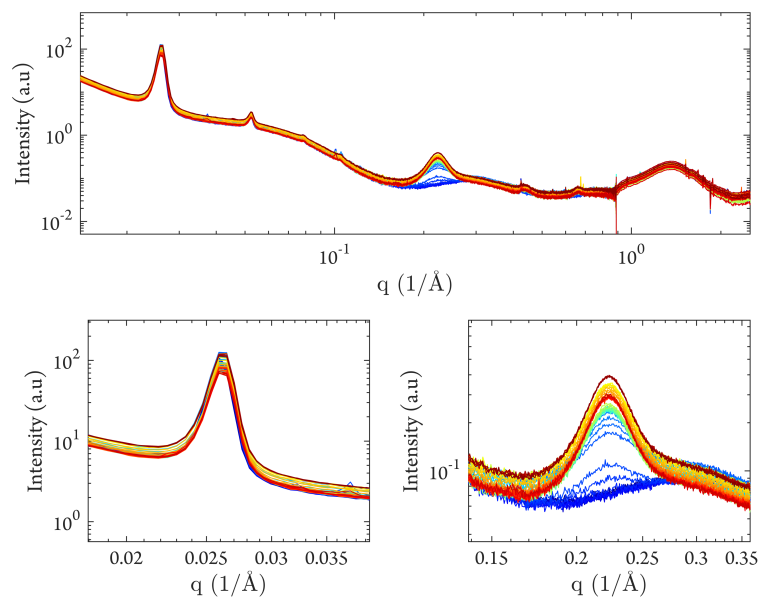
# Appendix A

## Supporting Information for: Crystallization Modes of Poly(3-dodecyl-thiophene)-based Block Copolymers

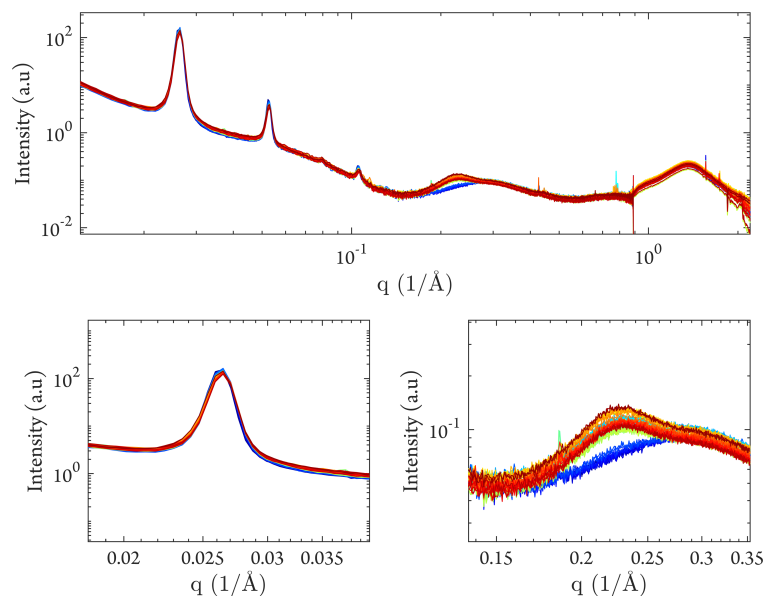
The following figures show the SAXS and WAXS profiles as a function of time for each sample. Increasing time from blue to red.



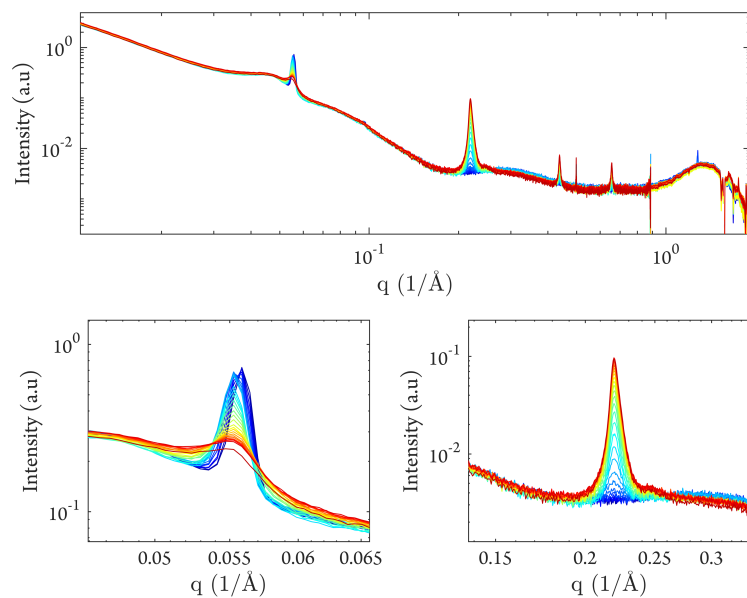
**Figure A.1:** Top: simultaneous SAXS and WAXS spectra for sample RR94-VP34 at 140°C; bottom left: close up of primary SAXS peak; bottom right: close up of (100) WAXS peak.



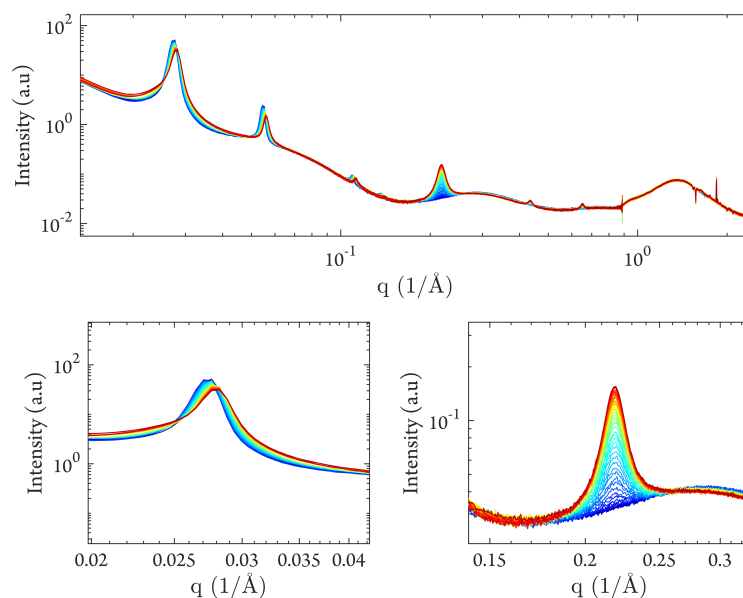
**Figure A.2:** Top: simultaneous SAXS and WAXS spectra for sample RR79-VP39 at 75°C; bottom left: close up of primary SAXS peak; bottom right: close up of (100) WAXS peak.



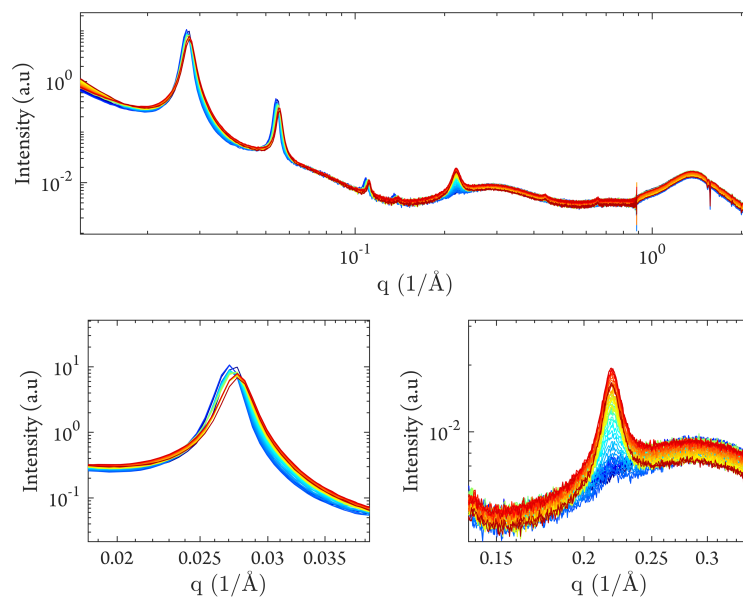
**Figure A.3:** Top: simultaneous SAXS and WAXS spectra for sample RR70-VP37 at 70°C; bottom left: close up of primary SAXS peak; bottom right: close up of (100) WAXS peak.



**Figure A.4:** Top: simultaneous SAXS and WAXS spectra for sample RR94-VP25 at 125°C; bottom left: close up of primary SAXS peak; bottom right: close up of (100) WAXS peak.



**Figure A.5:** Top: simultaneous SAXS and WAXS spectra for sample RR79-VP29 at 105°C; bottom left: close up of primary SAXS peak; bottom right: close up of (100) WAXS peak.



**Figure A.6:** Top: simultaneous SAXS and WAXS spectra for sample RR70-VP29 at 95°C; bottom left: close up of primary SAXS peak; bottom right: close up of (100) WAXS peak.

# Appendix B

## Supporting Information for: Origins of Anisotropic Ionic Conductivity in Lamellar Block Copolymers Electrolytes

### B.1 Synthesis and Characterization

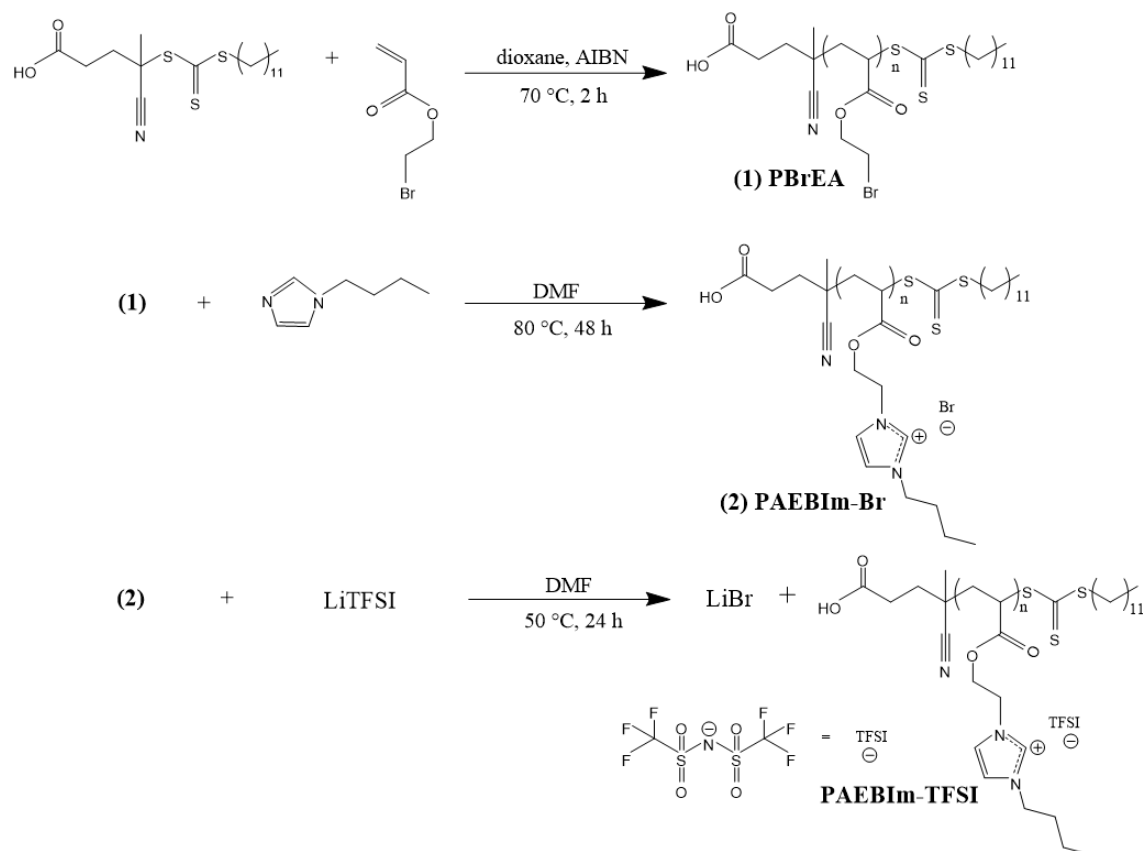
**Elemental Analysis.** Atomic composition of polymer samples was determined by elemental analysis performed by Atlantic Microlab, Inc. Outcomes are summarized in Table B.1. Expected percentage of each element is in parentheses beside the measured percentage. The absence of bromine in all samples confirms both complete quaternization with 1-butyylimidazole and complete anion exchange to TFSI<sup>-</sup>.

[p]

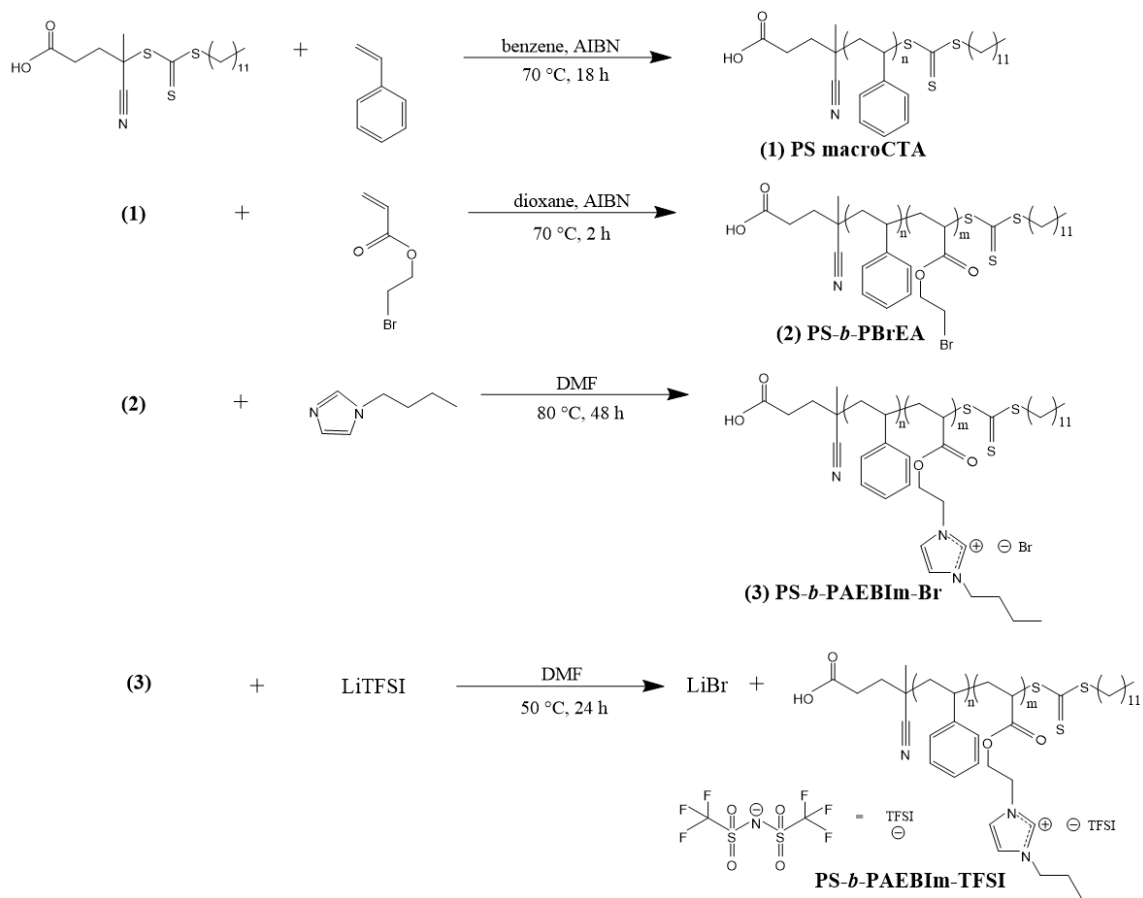
**Table B.1:** Measured and expected elemental composition of polymers.

| Samples   | %C            | %H          | %N          | %S            | %F            | %Br         |
|-----------|---------------|-------------|-------------|---------------|---------------|-------------|
| PIL       | 35.17 (33.40) | 4.09 (3.80) | 7.89 (8.30) | 12.26 (12.70) | 21.50 (22.70) | 0.00 (0.00) |
| PS4-PIL53 | 56.37 (56.00) | 5.29 (5.30) | 5.03 (5.10) | 7.51 (7.80)   | 12.50 (14.00) | 0.00 (0.00) |
| PS6-PIL47 | 60.24 (60.00) | 5.55 (5.50) | 4.48 (4.60) | 6.48 (7.00)   | 11.64 (12.40) | 0.00 (0.00) |





**Figure B.1:** Synthesis of PAEBIm-TFSI by RAFT polymerization.

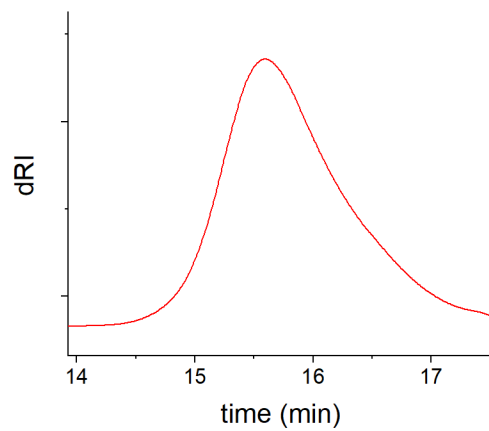


**Figure B.2:** Synthesis of PS-*b*-PAEBIm-TFSI copolymer by RAFT polymerization.

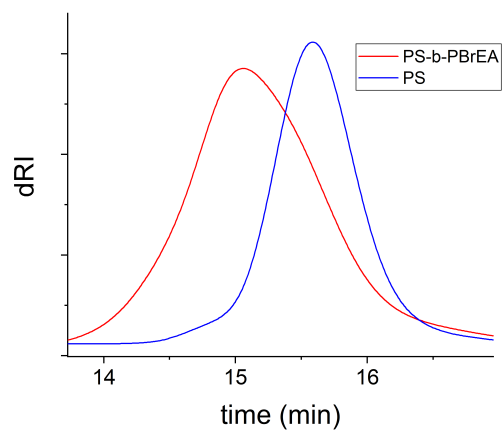
**Gel Permeation Chromatography (GPC).** Molecular weights and dispersities of PS macroCTA and dispersities of PBrEA and PS-b-PBrEA polymers were assessed using a system consisting of an Agilent 1260 Infinity II isocratic pump with two Agilent ( $7.5 \times 300$  mm) mixed-D type columns in sequence, a Wyatt Dawn Helios 8 Multi-Angle Light Scattering Detector, a ViscoStar III viscometer, and an Optilab T-rEX RI detector. THF was used as the mobile phase with a flow rate of 1 mL/min at 40 °C. Molecular weights and dispersities for PS macroCTAs and dispersities for PBrEA and PS-b-PBrEA were calculated relative to PS standards.

**Nuclear Magnetic Resonance (NMR) Spectroscopy.**  $^1\text{H}$  NMR spectra of all polymer products along the synthesis route were acquired in either  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  at 25°C using a Varian VNMRS 500MHz spectrometer.

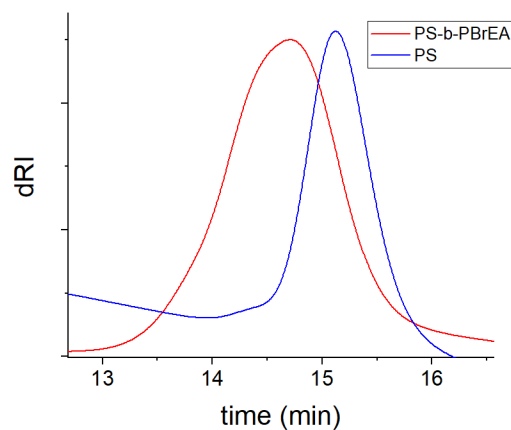
**Calculation of PIL Molecular Weight and Volume Fraction.** Molecular weights of the PIL block were determined through a combination of GPC for the PS macroCTA and NMR for the PS-b-PBrEA precursor as follows: First, the number-average degree of polymerization for each PS macroCTA,  $N_{\text{PS}}$ , was calculated from the number-average molecular weight ( $M_{\text{n,PS}}$ ) determined by GPC. The value of  $N_{\text{PS}}$  determined by GPC was found to be consistent with that determined by NMR spectroscopy (Figures S7a and S8a), which used the integrated areas from the 5 protons of the styrene phenyl rings (a, b, c) and the 2 protons from the end group (★). Second, the average number of styrene monomers relative to BrEA monomers was determined from NMR data (Figures S7b and S8b) using the integrated areas from the 5 protons of the styrene phenyl rings (a, b, c) and the 4 protons associated with the methylene groups on the BrEA pendant groups (e, d). Third, the average degree of polymerization for the PIL is equal to that of the PBrEA precursor, and is  $N_{\text{PIL}} = N_{\text{PS}} \times (A_{\text{BrEA}}/4)/(A_{\text{S}}/5)$ , where  $A_{\text{BrEA}}$  and  $A_{\text{S}}$  are the integrated areas for BrEA and styrene, respectively, from the preceding step. Finally, the number-average molecular weight for PIL is  $M_{\text{n,PIL}} = N_{\text{PIL}}m_{\text{IL}}$ , where  $m_{\text{IL}} = 506$  g/mol is



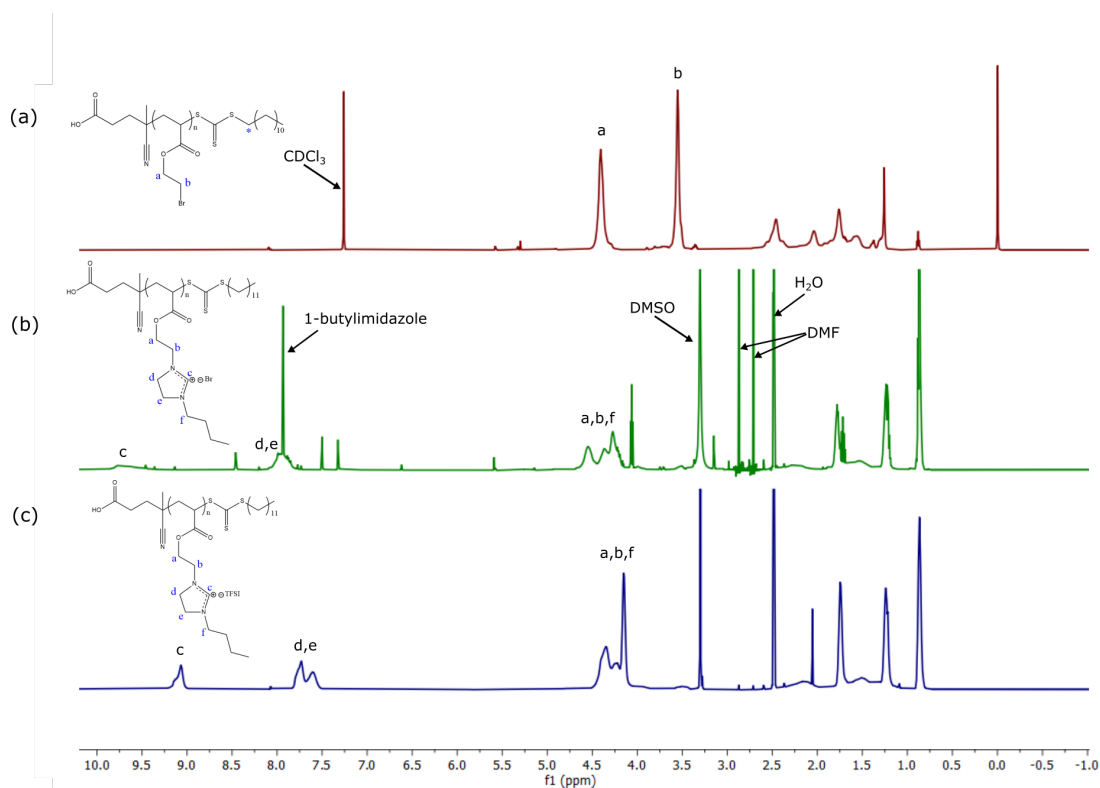
**Figure B.3:** GPC trace of PBrEA, which is the precursor of PIL.



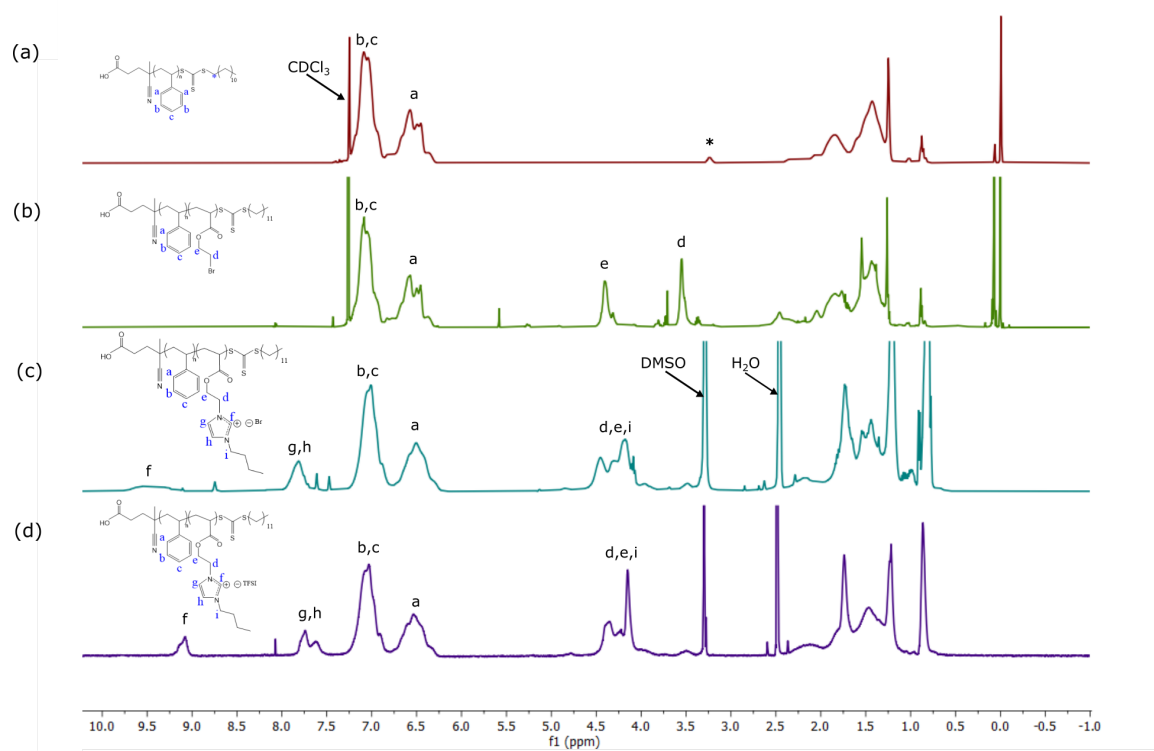
**Figure B.4:** GPC traces of PS macroCTA and PS-b-PBrEA, which are precursors of PS4-PIL53, demonstrate chain extension of PS macroCTA with PBrEA.



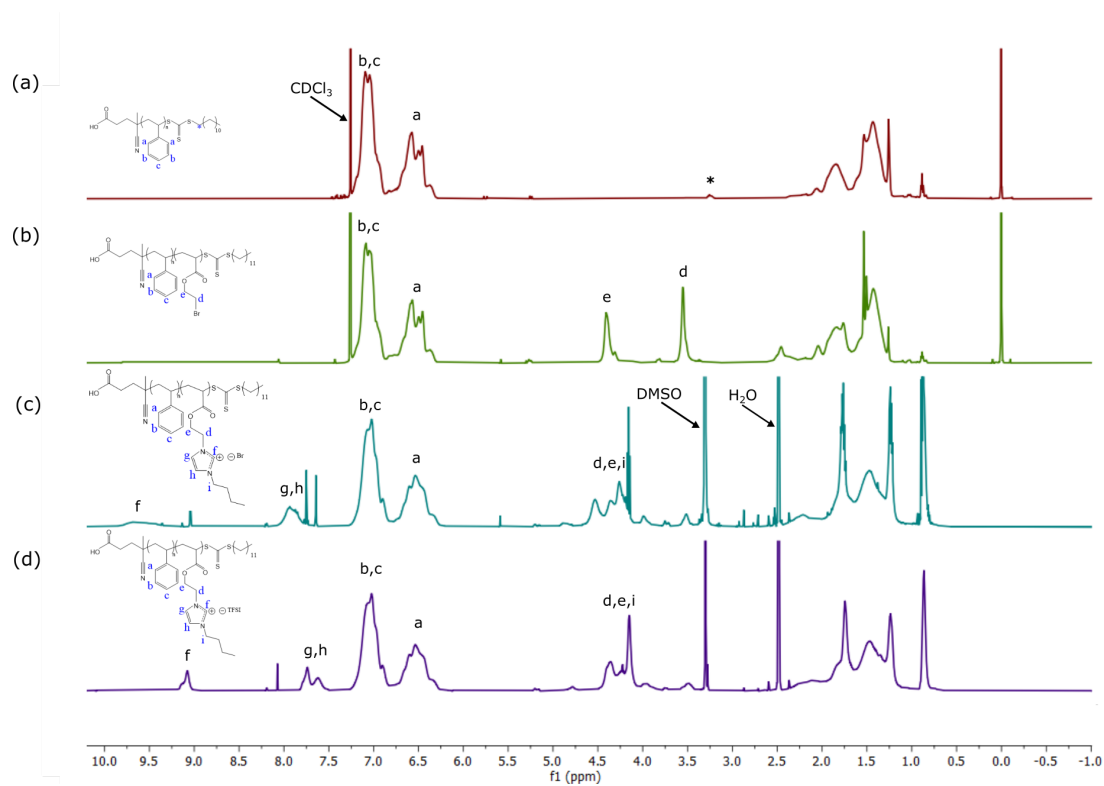
**Figure B.5:** GPC traces of PS macroCTA and PS-b-PBrEA, which are precursors of PS6-PIL47, demonstrate chain extension of PS macroCTA with PBrEA.



**Figure B.6:**  $^1\text{H}$  NMR spectra for (a) PBrEA, (b) PAEBIm-Br, and (c) PAEBIm-TFSI in the synthesis of sample PIL.



**Figure B.7:**  $^1\text{H}$  NMR spectra for (a) PS macroCTA, (b) PS-b-PBrEA, (c) PS-b-PAEBIm-Br, and (d) PS-b-PAEBIm-TFSI in the synthesis of sample PS4-PIL53.



**Figure B.8:**  $^1\text{H}$  NMR spectra for (a) PS macroCTA, (b) PS-b-PBrEA, (c) PS-b-PAEBIm-Br, and (d) PS-b-PAEBIm-TFSI in the synthesis of sample PS6-PIL47.

the molecular weight of the IL monomer. The volume fraction of PIL in the PS-PIL block copolymers,  $\phi_{PIL}$ , is calculated from the molecular weights and mass densities of each block:

$$\phi_{PIL} = \frac{M_{n,PIL}/\rho_{PIL}}{M_{n,PIL}/\rho_{PIL} + M_{n,PS}/\rho_{PS}} \quad (\text{B.1})$$

using a density of  $\rho_{PS} = 1.04$  g/mL for PS and  $\rho_{PIL} = 1.38$  g/mL for PIL.[28]

**Differential Scanning Calorimetry (DSC).** The calorimetric glass transition temperature of each sample was measured using a TA DSC Q2000. Sample were sealed in Tzero low-mass aluminum pans with hermetic lids. Measurements were made using an empty pan as a reference, beginning by annealing at 120 °C for 10 minutes, then cycling three times at a rate of 10 °C/min between 120 and -50 °C. Within each cycle and before commencing a temperature ramp, isothermal conditions were maintained for 5 minutes. The glass transition temperatures,  $T_g$ , obtained from these measurements are given in Table 4.1.

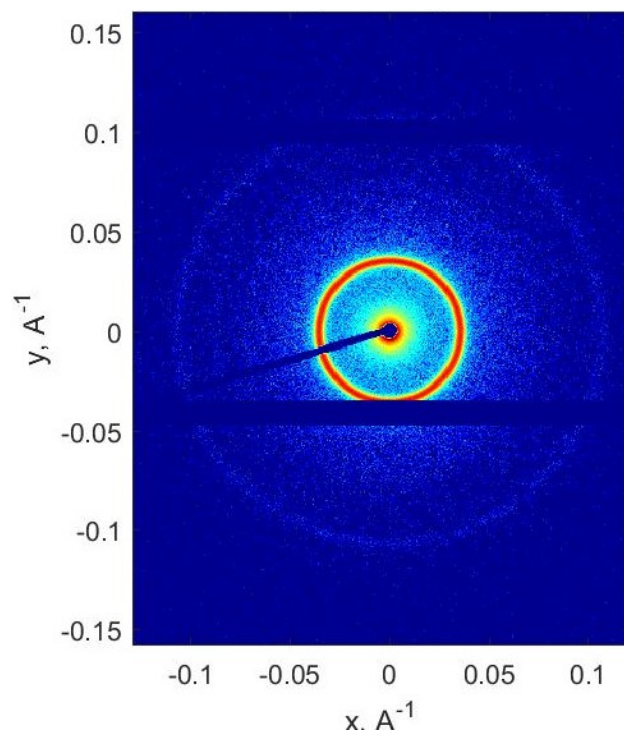
## B.2 Sample Preparation and Characterization

**Atomic Force Microscopy (AFM).** Films were prepared by flow coating onto silicon wafer from either THF or acetonitrile and annealing at 120 °C on a hotplate for 24 h. AFM was performed using an Asylum MFP-3D Atomic Force Microscope. The topography and phase contrast were measured by scanning in tapping mode. The probes were silicon with a spring constant of approximately 9 N/m and a resonance frequency of 115 kHz. The parameters used for image acquisition were 0.8 Hz scan frequency, 20  $\mu\text{m}$  x 20  $\mu\text{m}$  scan size, and 256 x 256 image resolution. Raw AFM data were processed using the software provided by Asylum Instruments. First-order flattening was used to process both height and phase images. This eliminates any Z offsets formed between scan lines by subtracting each point in the scan line with an average Z value ( $Z = \text{phase or height}$ ).

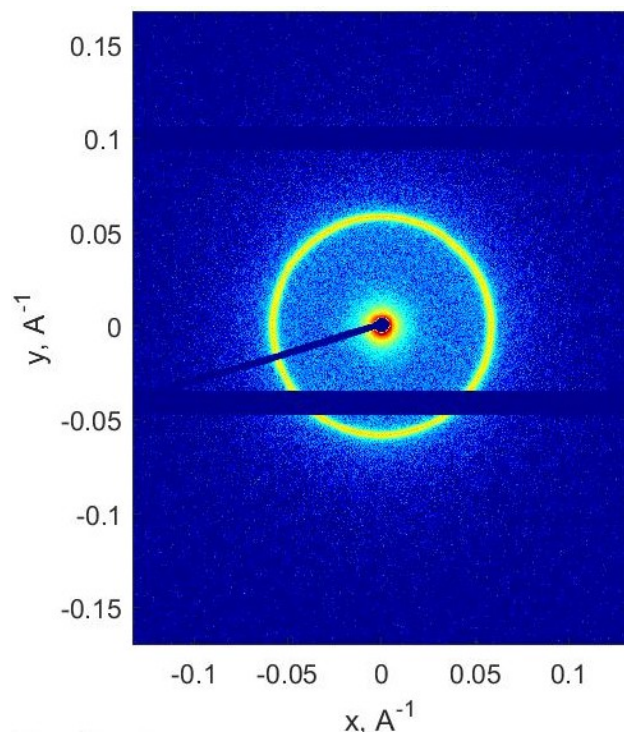


**Optical Microscopy.** Films were prepared by flow coating onto a silicon wafer from either THF or acetonitrile and annealing at 120 °C on a hotplate for 24 h. Optical microscopy images were taken using a Nikon LV100 reflected light microscope at 50x magnification, both before and after annealing.

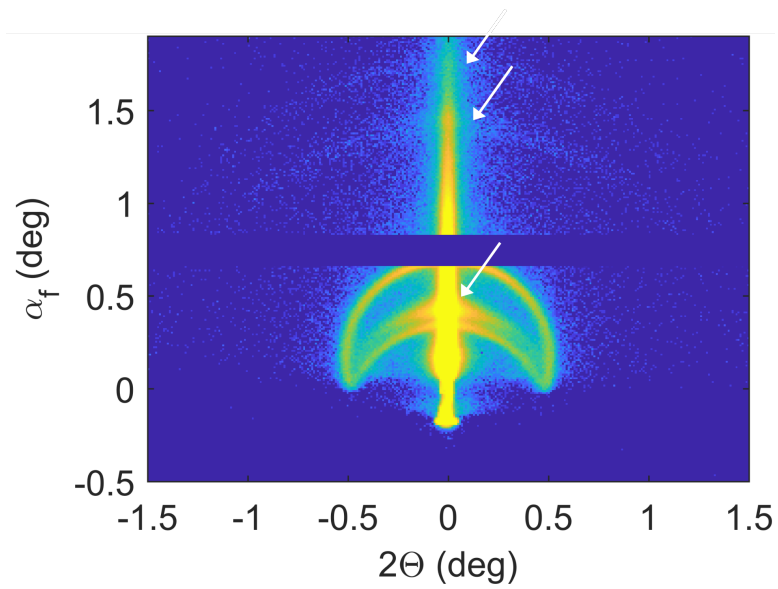
**Contact Angle.** Films were prepared by flow coating onto a silicon wafer from either THF or acetonitrile and annealing at 120 °C on a hotplate for 24 h. Static contact angle measurements were made using a DataPhysics OCA 15EC at ambient conditions with DI water used as the probe liquid. Contact angles were measured 30 s after contact with film. The contact angle values reported are averages (with standard deviation) derived from three separate measurements from different regions of each film. Measurements were performed both before and after annealing, and results were the same within the reported uncertainty.



**Figure B.9:** Transmission SAXS data for sample PS6-PIL47 shows no sign of anisotropy, suggesting a bulk structure of randomly oriented lamellae.



**Figure B.10:** Transmission SAXS data for sample PS4-PIL53 shows no sign of anisotropy, suggesting a bulk structure of randomly oriented lamellae. The absence of higher order rings is attributable to interface attenuation resulting from a weaker segregation strength due to lower molecular weight.



**Figure B.11:** GISAXS data from a thick PS6-PIL47 film prepared on a glass slide for in-plane impedance spectroscopy. Arrows indicate contribution of oriented lamellae at the interfaces, while the presence of rings confirms presence of isotropic lamellar grains in the bulk.

# Appendix C

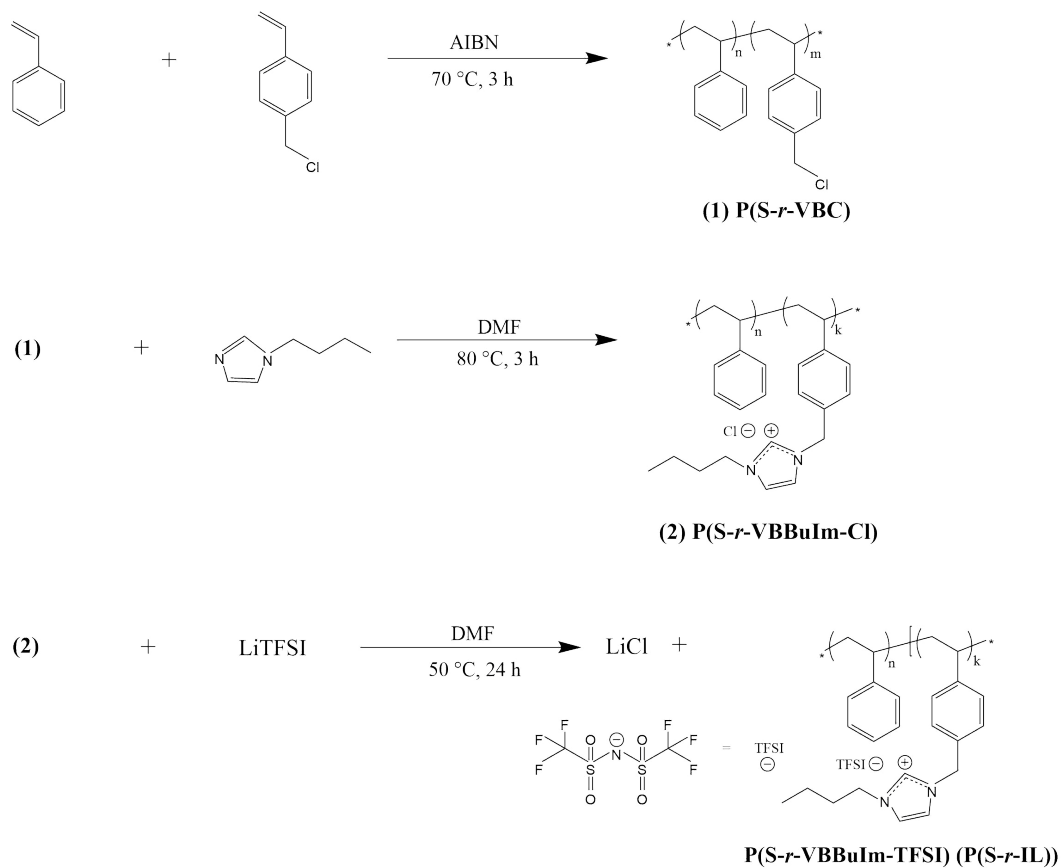
## Supporting Information for: Interfacial Effects in Block Copolymer Electrolytes

### C.1 Synthesis and Characterization

#### Calculation of Reactivity Ratios for Styrene and Vinylbenzyl Chloride.

Four random copolymers of styrene and VBC were synthesized following the procedure described in Chapter 5 and depicted in Figure C.1, varying the molar ratio of styrene and VBC in the starting solution. The mole fraction of VBC in the resulting copolymer  $F_{VBC}$ , determined by  $^1\text{H}$  NMR as described in Chapter 5, was plotted as a function of mole fraction of VBC in the comonomer feed  $f_{VBC}$  (Figure C.2). The relationship between these two quantities and the reactivity ratios of styrene and VBC for this copolymerization,  $r_S$  and  $r_{VBC}$ , respectively, can be expressed by the equation

$$F_{VBC} = \frac{r_{VBC}f_{VBC}^2 + f_{VBC}f_S}{r_{VBC}f_{VBC}^2 + 2f_{VBC}f_S + r_Sf_S^2} \quad (\text{C.1})$$



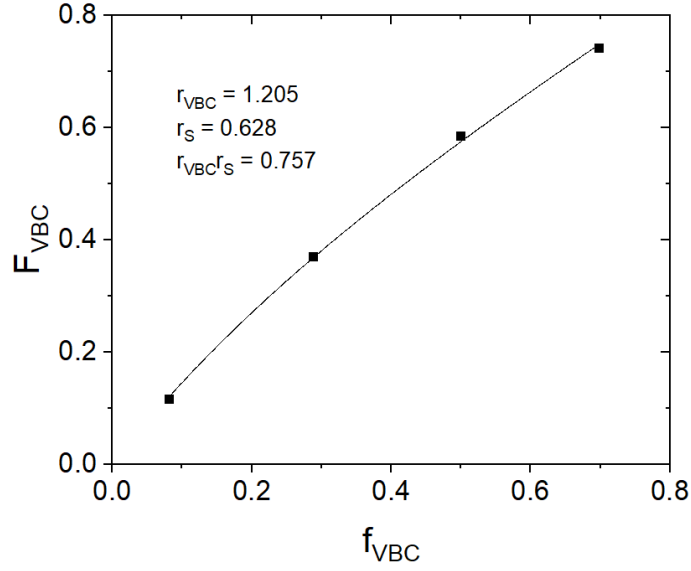
**Figure C.1:** Synthesis of P(S-*r*-VBBuIm-TFSI)(P(S-*r*-IL)) by free radical polymerization, followed by reactive modification.

The data in Figure C.2 were fit with Equation C.1. Reactivity ratio were determined to be  $r_S = 0.628$  and  $r_{VBC} = 1.205$  ( $r_{VBC}r_S = 0.757$ ), indicating that incorporation of the two monomers into a copolymer is roughly statistical with a slight tendency toward alternation.

**Gel Permeation Chromatography (GPC).** Molecular weights and dispersities of PS macroCTA and dispersities of PBrEA and PS-b-PBrEA polymers were assessed using a system consisting of an Agilent 1260 Infinity II isocratic pump with two Agilent ( $7.5 \times 300$  mm) mixed-D type columns in sequence, a Wyatt Dawn Helios 8 Multi-Angle Light Scattering Detector, a ViscoStar III viscometer, and an Optilab T-rEX RI detector. THF was used as the mobile phase with a flow rate of 1 mL/min at 40 °C. Molecular weights and dispersities for PS macroCTAs and dispersities for PVBC and PS-b-PVBC were calculated relative to PS standards.

**Nuclear Magnetic Resonance (NMR) Spectroscopy.**  $^1\text{H}$  NMR spectra of all polymer products along the synthesis route were acquired in either  $\text{CDCl}_3$  or  $\text{DMSO-d}_6$  at 25°C using a Varian VNMRs 500MHz spectrometer.

**Differential Scanning Calorimetry (DSC).** The calorimetric glass transition temperature of each sample was measured using a TA DSC Q2000. Sample were sealed in Tzero low-mass aluminum pans with hermetic lids. Measurements were made using an empty pan as a reference, beginning by annealing at 120 °C for 5 minutes, then cycling twice times at a rate of 10 °C/min between 120 and -20 °C. Within each cycle and before commencing a temperature ramp, isothermal conditions were maintained for 5 minutes. The glass transition temperatures,  $T_g$ , obtained from these measurements are given in Table C.1.

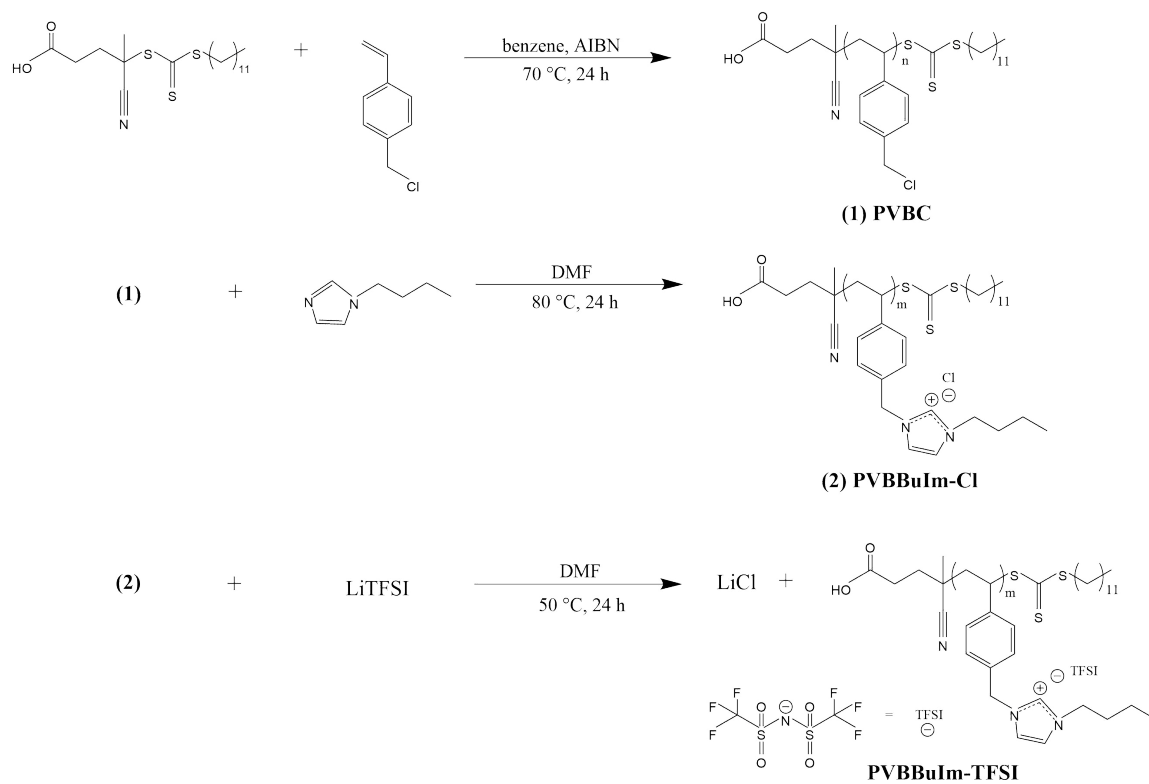


**Figure C.2:** Mole fraction of VBC in comonomer feed,  $f_{VBC}$ , versus mole fraction of VBC in copolymer,  $F_{VBC}$ . Data were fit with Equation C.1 to determine reactivity ratios of styrene and VBC,  $r_S$  and  $r_{VBC}$ , respectively.

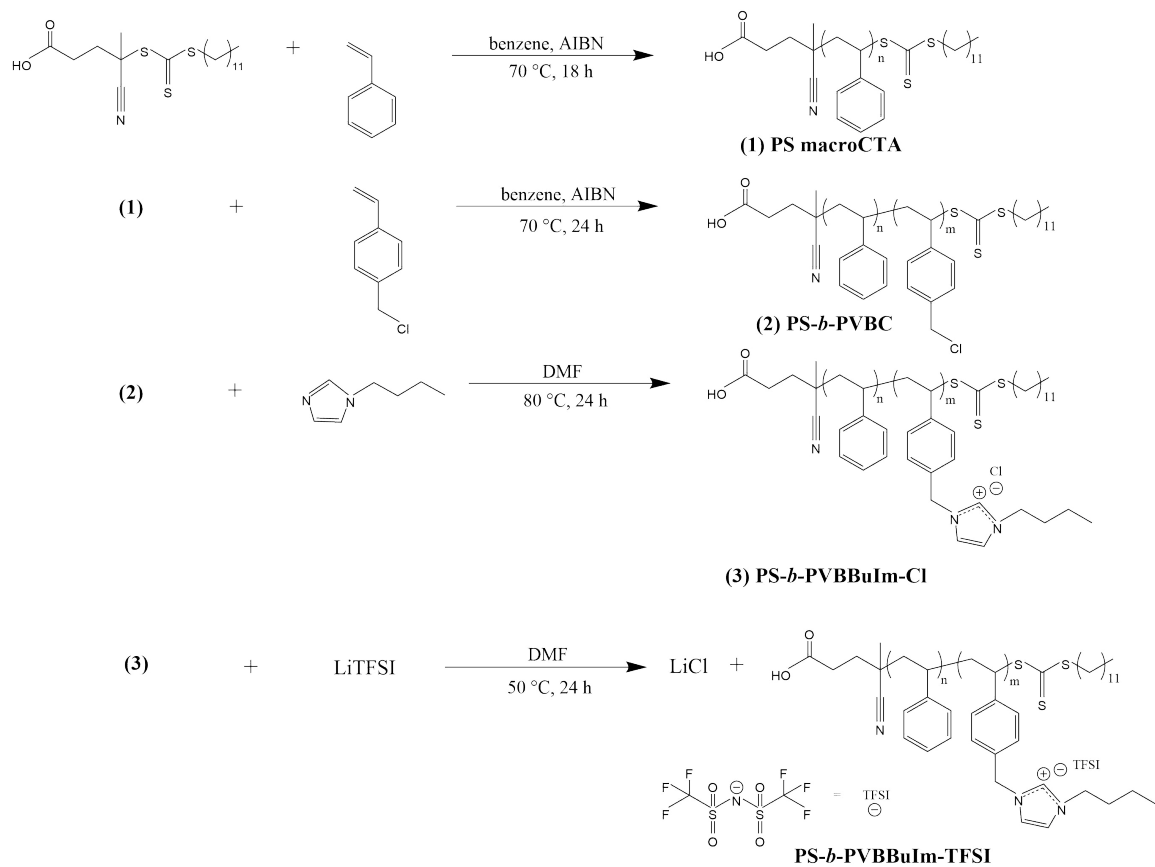
**Table C.1:** Glass transition temperatures of polymers and copolymers. All temperatures are reported in °C.

| Sample Name | $T_{g,1}$ | $T_{g,2}$ |
|-------------|-----------|-----------|
| PIL         | -0.5      | –         |
| P(S-r-IL)   | 26.0      | –         |
| PS5-PIL53   | 25.5      | 80.1      |
| PS8-PIL42   | 25.8      | 89.3      |
| PS12-PIL36  | 19.1      | 98.1      |
| PS6-PIL69   | 10.2      | 73.0      |

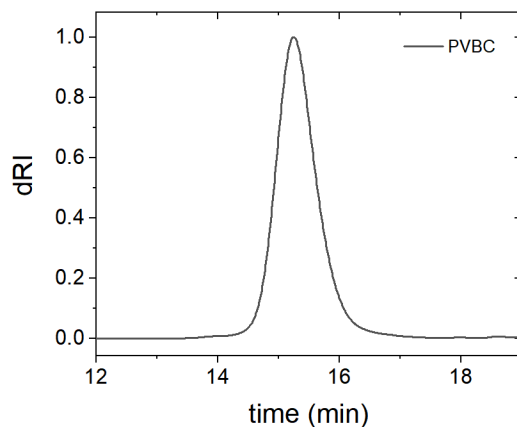




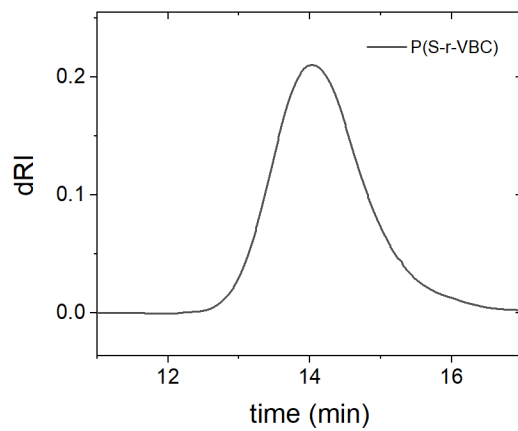
**Figure C.3:** Synthesis of PVBBuIm-TFSI by RAFT polymerization, followed by reactive modification.



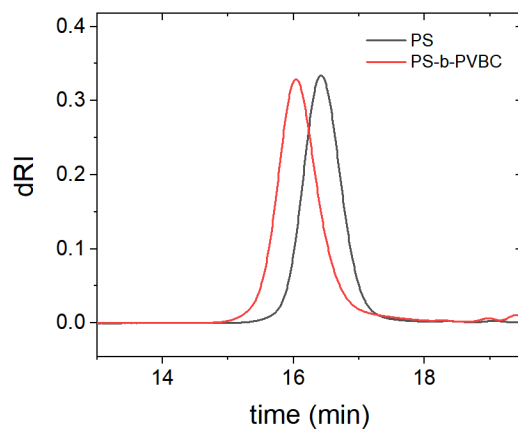
**Figure C.4:** Synthesis of PS-*b*-PVBBuIm-TFSI copolymer by RAFT polymerization, followed by reactive modification.



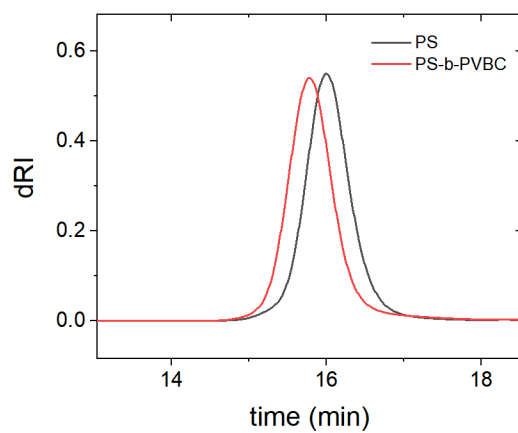
**Figure C.5:** GPC trace of PVBC, which is the precursor of PIL.



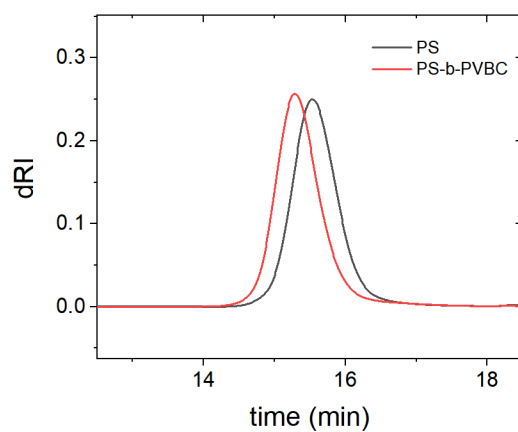
**Figure C.6:** GPC trace of P(S-r-VBC), which is the precursor of P(S-r-IL).



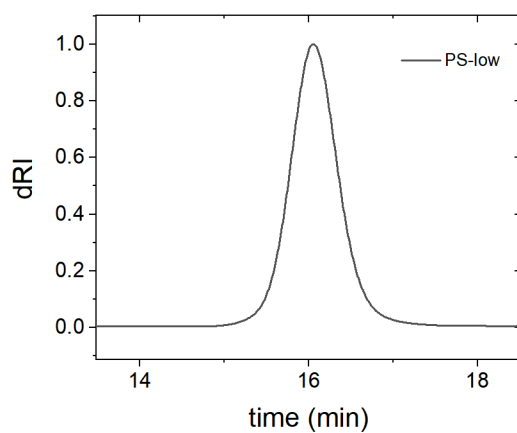
**Figure C.7:** GPC traces of PS macroCTA and PS-b-PVBC, which are precursors of PS5-PIL53, demonstrate chain extension of PS macroCTA with PVBC.



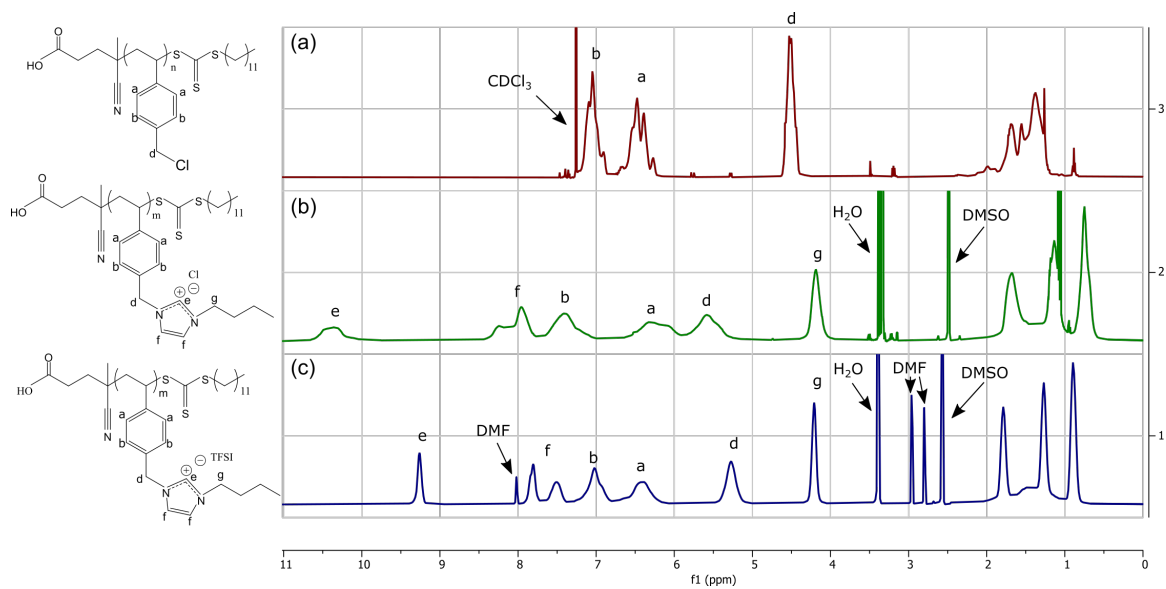
**Figure C.8:** GPC traces of PS macroCTA and PS-b-PVBC, which are precursors of PS8-PIL42, demonstrate chain extension of PS macroCTA with PVBC.



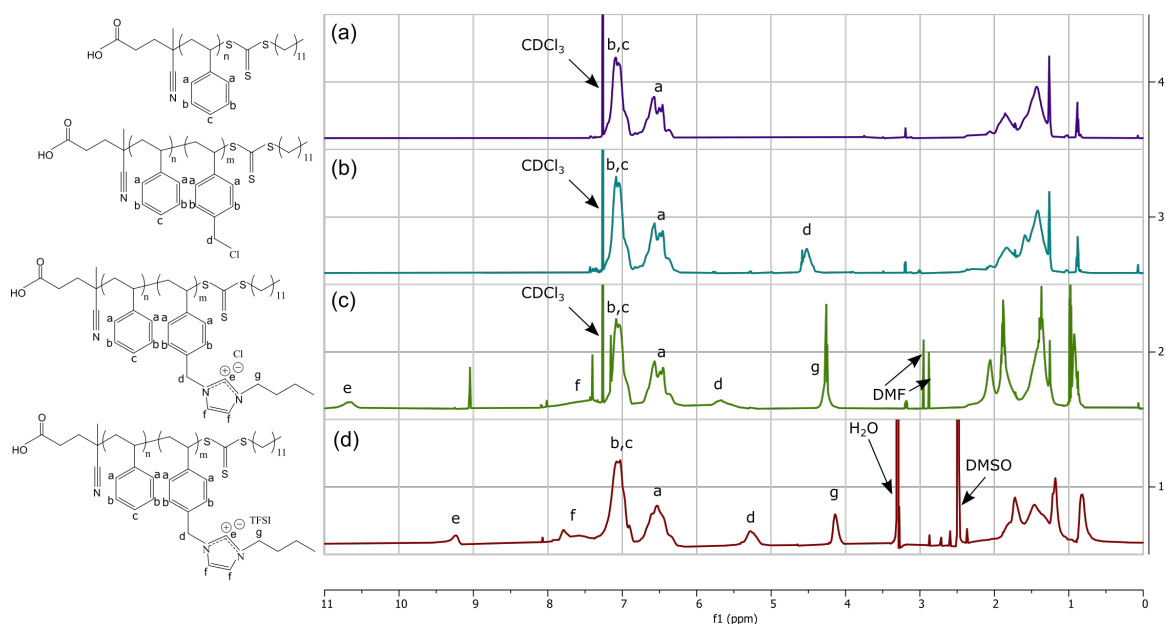
**Figure C.9:** GPC traces of PS macroCTA and PS-b-PVBC, which are precursors of PS12-PIL36, demonstrate chain extension of PS macroCTA with PVBC.



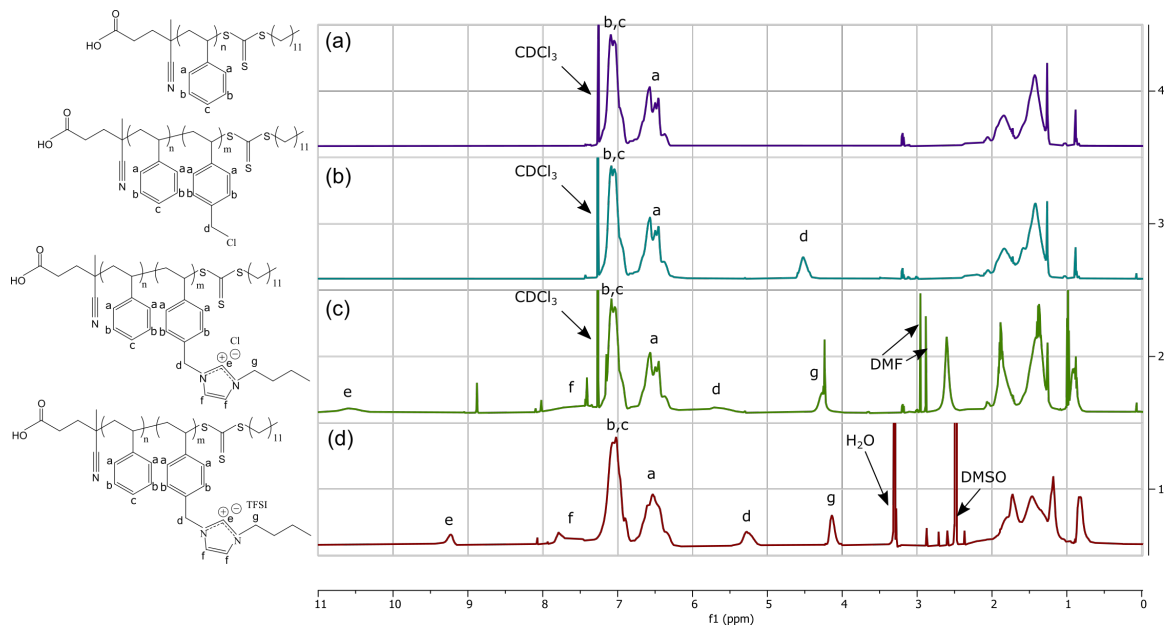
**Figure C.10:** GPC trace of PS-low.



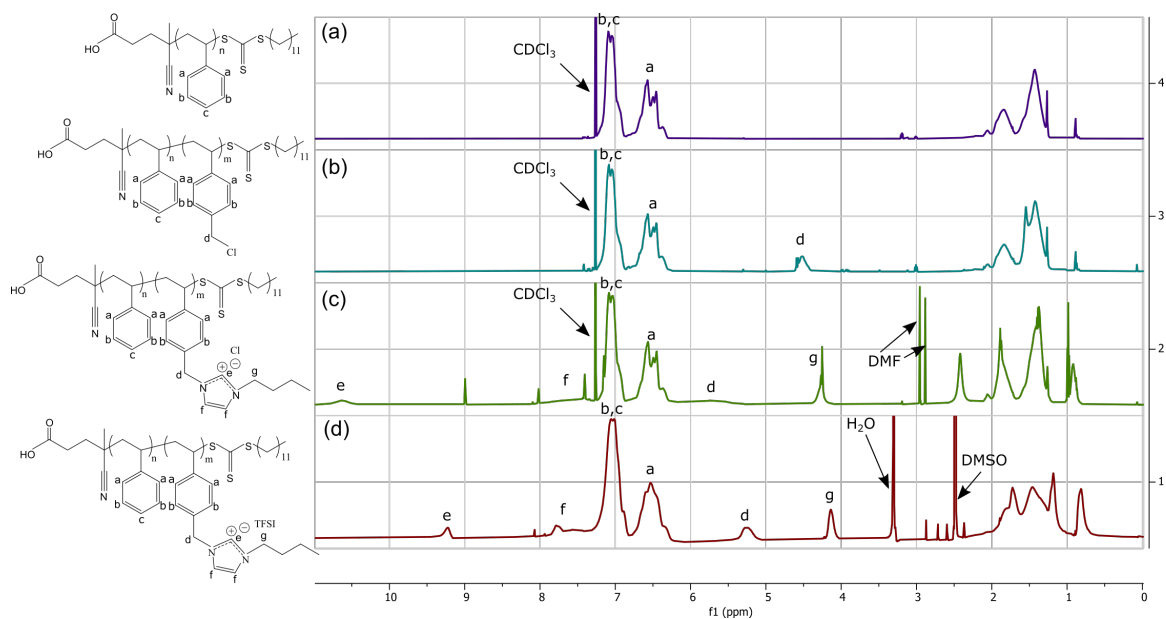
**Figure C.11:**  $^1\text{H}$  NMR spectra for (a) PVBC, (b) PVBBuIm-Cl, and (c) PVBBuIm-TFSI in the synthesis of sample PIL.



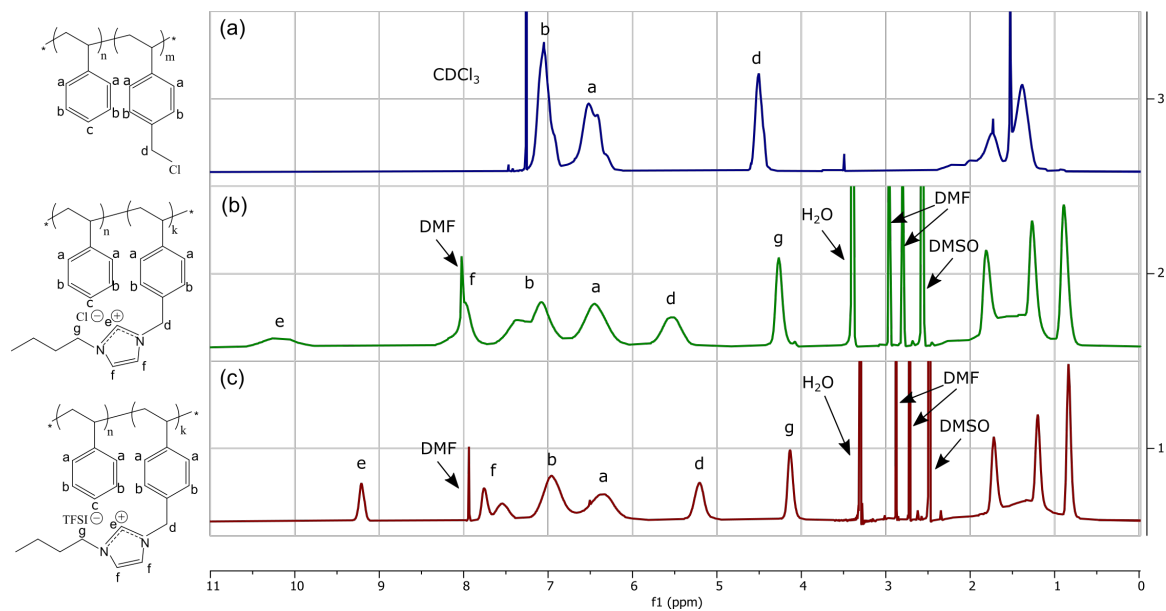
**Figure C.12:**  $^1\text{H}$  NMR spectra for (a) PS macroCTA, (b) PS-b-PVBC, (c) PS-b-PVBBuIm-Cl, and (d) PS-b-PVBBuIm-TFSI in the synthesis of sample PS5-PIL53.



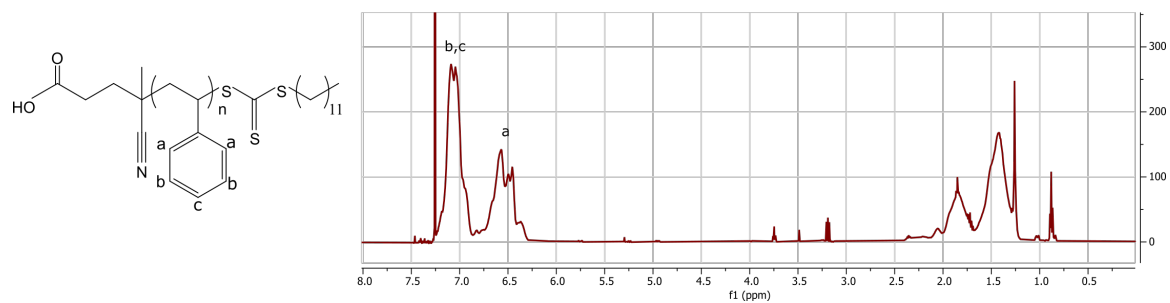
**Figure C.13:**  $^1\text{H}$  NMR spectra for (a) PS macroCTA, (b) PS-b-PVBC, (c) PS-b-PVBBuIm-Cl, and (d) PS-b-PVBBuIm-TFSI in the synthesis of sample PS8-PIL42.



**Figure C.14:**  $^1\text{H}$  NMR spectra for (a) PS macroCTA, (b) PS-b-PVBC, (c) PS-b-PVBBuIm-Cl, and (d) PS-b-PVBBuIm-TFSI in the synthesis of sample PS12-PIL36.



**Figure C.15:**  $^1\text{H}$  NMR spectra for (a) P(S-r-VBC), (b) P(S-r-VBBuIm-Cl), and (c) P(S-r-VBBuIm-TFSI) in the synthesis of sample P(S-r-IL).



**Figure C.16:**  $^1\text{H}$  NMR spectra for PS-low.



## C.2 Sample Preparation and Characterization

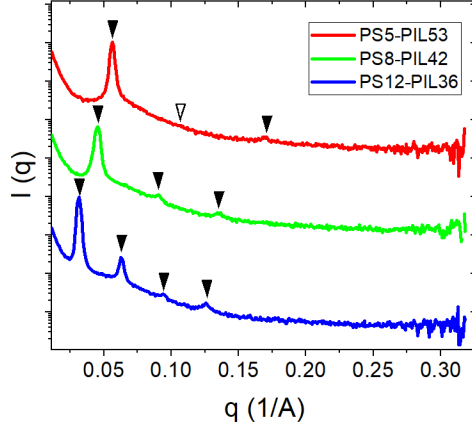
**Atomic Force Microscopy (AFM).** Films were prepared by spin-coating onto either a silicon or stainless steel substrate from acetonitrile and annealing at 120 °C under vacuum for 18 h. AFM was performed using an Asylum MFP-3D Atomic Force Microscope. The topography and phase contrast were measured by scanning in tapping mode. The probes were silicon with a spring constant of approximately 9 N/m and a resonance frequency of 115 kHz. The parameters used for image acquisition were 0.8 Hz scan frequency, 20  $\mu\text{m}$  x 20  $\mu\text{m}$  scan size, and 256 x 256 image resolution. Raw AFM data were processed using the software provided by Asylum Instruments. First-order flattening was used to process both height and phase images. This eliminates any Z offsets formed between scan lines by subtracting each point in the scan line with an average Z value (Z = phase or height).

**Optical Microscopy.** Films were prepared by spin-coating onto either a silicon or stainless steel substrate from acetonitrile and annealing at 120 °C under vacuum for 18 h. Optical microscopy images were taken using a Nikon LV100 reflected light microscope at 50x magnification, both before and after annealing.

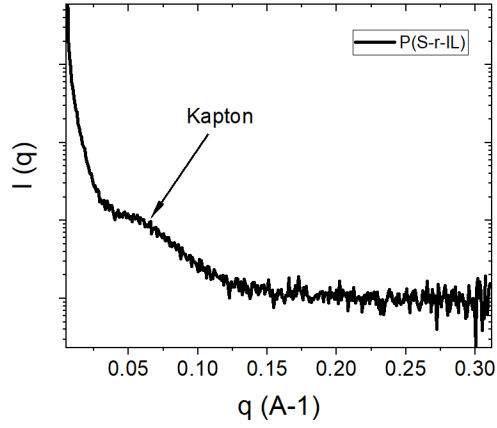
**Contact Angle.** Films were prepared by spin-coating onto either a silicon or stainless steel substrate from acetonitrile and annealing at 120 °C under vacuum for 18 h. Static contact angle measurements were made using a DataPhysics OCA 15EC at ambient conditions with DI water and diiodomethane used as the probe liquid. Contact angles were measured 30 s after contact with film. The contact angle values reported are averages (with standard error) derived from three separate measurements from different regions of each film.

**Small-Angle X-Ray Scattering (SAXS).** SAXS was performed using a Xenocs Xeuss 3.0 instrument equipped with a Cu K $\alpha$  Xenocs GeniX3D HFVL microfocus source ( $\lambda = 0.154\text{nm}$ ) and a single photon counting Dectris Pilatus3 R 300k detector

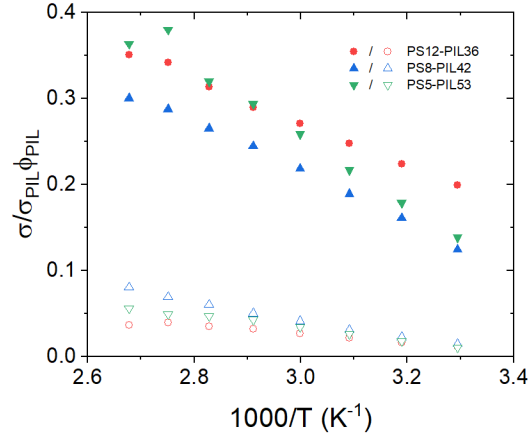
with a 172  $\mu\text{m}$  pixel size. Samples were prepared by casting onto Kapton from a solution of 10 wt% polymer in THF. In a typical preparation, the solution was dripped onto the Kapton with a pipette and allowed to evaporate over the course of 1 h in the fume hood. The samples, consisting of the dried film on Kapton, were annealed for 24 h under vacuum at 130 °C. Scattering measurements were performed under vacuum at room temperature with 20-minute exposure times. The 2-dimensional (2D) scattering data were reduced to 1-dimensional (1D) scattering curves by azimuthal integration using the XSACT software.



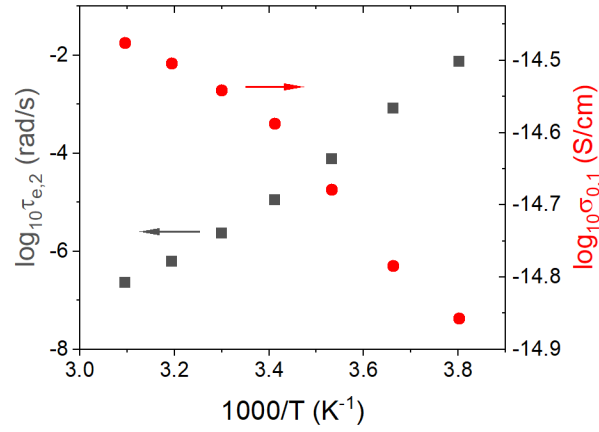
**Figure C.17:** Azimuthal integration of transmission SAXS data for all block copolymers.



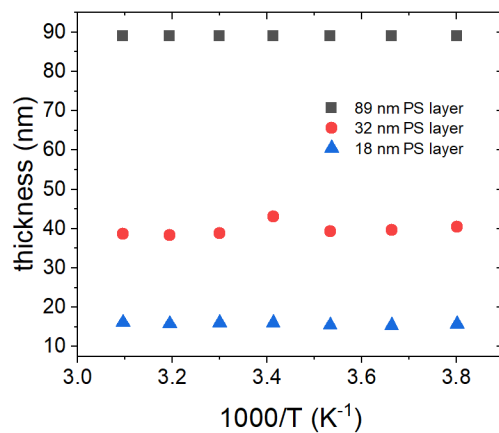
**Figure C.18:** Azimuthal integration of transmission SAXS data for P(S-r-IL).



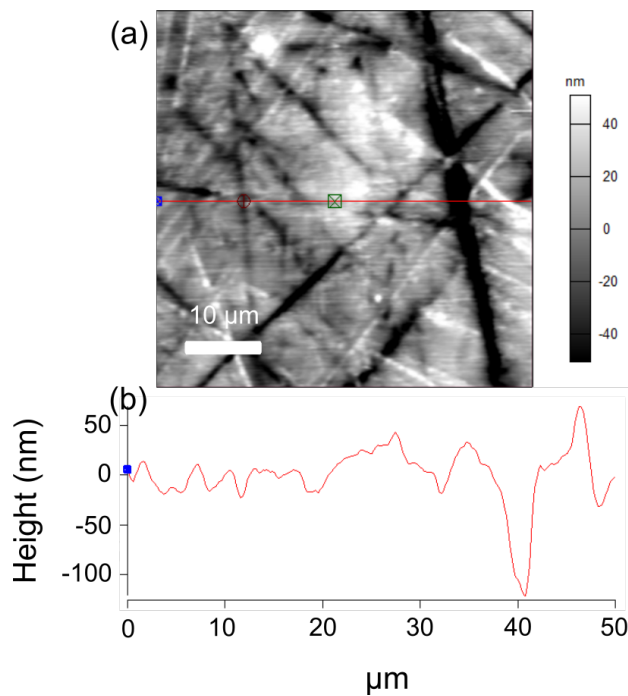
**Figure C.19:** In-plane (solid symbols) and through-plane (open symbols) morphology factors of all block copolymers.



**Figure C.20:** Temperature dependence PS-PIL-PS trilayer model parameters  $\tau_{e,2}$  and  $\sigma_{0,1}$ .  $\tau_{e,2}$  values are averages of optimized values obtained from samples with 89, 32, and 18 nm PS layers; error bars are smaller than symbol size.  $\sigma_{0,1}$  values were optimized for the 89 nm PS layer sample only, then held constant for the others.



**Figure C.21:** Temperature dependence of PS layer thickness calculated from PS-PIL-PS trilayer model parameter  $x$ . Parameter was optimized for all fits. Thickness values given in the legend were measured directly by ellipsometry.



**Figure C.22:** Image (a) and horizontal line cut (b) of bare stainless steel electrode obtain by AFM.

# Products

## Publications

1. **Coote, J. P.**, Kinsey, T., Street, D. P., Kilbey, S. M., Sangoro, J. R., Stein, G. E. "Surface-Induced Ordering Depresses Through-Film Ionic Conductivity in Lamellar Block Copolymer Electrolytes". ACS Macro Letters, 2020, 9(4), 565–570.
2. Truong, P. V., Black, R. L., **Coote, J. P.**, Lee, B., Ardebili, H., Stein, G. E. "Systematic Approaches to Tailor the Morphologies and Transport Properties of Solution-Cast Sulfonated Pentablock Copolymers". ACS Applied Polymer Materials, 2019, 1(1), 8–17.
3. Kim, J. S., Lee, Y. J., **Coote, J. P.**, Stein, G. E., Kim, B. J. "Confined, Templated, and Break-Through Crystallization Modes in Poly(3-dodecylthiophene)-block-poly(ethyl methacrylate) Block Copolymers". Macromolecules, 2019, 52(12), 4475-4482.
4. **Coote, J. P.\***, Kim, J. S.\* , Lee, B., Han, J., Kim, B. J., Stein, G. E. "Crystallization Modes of Poly(3-dodecylthiophene)-Based Block Copolymers Depend on Regioregularity and Morphology". Macromolecules, 2018, 51(22), 9276–9283.
5. Harris, M. A., Heres, M. F., **Coote, J.**, Wenda, A., Strehmel, V., Stein, G. E., Sangoro, J. "Ion Transport and Interfacial Dynamics in Disordered Block

- Copolymers of Ammonium-Based Polymerized Ionic Liquids". *Macromolecules*, 2018, 51(9), 3477–3486.
6. Kim, J. S., Han, J., Kim, Y., Park, H., **Coote, J. P.**, Stein, G. E., Kim, B. J. "Domain Structures of Poly(3-dodecylthiophene)-Based Block Copolymers Depend on Regioregularity". *Macromolecules*, 2018, 51(11), 4077–4084.
  7. Ransom, R., **Coote, J.**, Moulton, R., Gao, F., Shantz, D. F. "Synthesis and Growth Kinetics of Zeolite SSZ-39". *Industrial and Engineering Chemistry Research*, 2017, 56(15), 4350–4356.

\*Equal Contribution

## Presentations

1. **Coote, J. P.**, Kinsey, T., Street, D. P., Kilbey, S. M., Sangoro, J. R., Stein, G. E. 2022. "Interface-induced Order in Block Copolymer Electrolytes". American Physical Society March Meeting, N00.00102: DPOLY Poster
2. **Coote, J. P.**, Kinsey, T., Street, D. P., Kilbey, S. M., Sangoro, J. R., Stein, G. E. 2021. "Impact of Surface-Induced Order on Ion Conductivity in Block Copolymer Electrolytes". American Institute of Chemical Engineers Annual Meeting: Oral.
3. **Coote, J. P.**, Sangoro, J.R., Stein, G.E. 2021. "Confinement Effects in Self Assembly of Functional Block Copolymers". American Institute of Chemical Engineers Annual Meeting: Poster
4. **Coote, J. P.**, Kinsey, T., Street, D. P., Kilbey, S. M., Sangoro, J. R., Stein, G. E. 2021. "Impact of Interfacial Order on Ion Transport in Block Copolymer Electrolytes". Virtual Polymer Physics Symposium: Oral.
5. **Coote, J. P.**, Kinsey, T., Street, D. P., Kilbey, S. M., Sangoro, J. R., Stein, G. E. 2021. "Impact of Interfacial Order on Ion Transport in Block Copolymer

Electrolytes". Virginia Polytechnic Institute and State University. National Graduate Research Polymer Conference: Oral.

6. **Coote, J. P.**, Kinsey, T., Street, D. P., Kilbey, S. M., Sangoro, J. R., Stein, G. E. 2021. "Surface-Induced Ordering Depresses Through-Film Ionic Conductivity in Lamellar Block Copolymer Electrolytes". American Physical Society March Meeting, S02.00009: DPOLY Oral.
7. **Coote, J. P.**, Kinsey, T., Street, D. P., Kilbey, S. M., Sangoro, J. R., Stein, G. E. 2020. "Surface-Induced Ordering Depresses Through-Film Ionic Conductivity in Lamellar Block Copolymer Electrolytes". Applied Polymer Technology Extension Consortium 8th Annual Research Symposium: Oral.
8. **Coote, J. P.**, Kim, J. S., Lee, B., Han, J., Kim, B. J., Stein, G. E. 2019. "Crystallization Modes in Conjugated-Coil Block Copolymers". Southeastern Polymer Forum, Oak Ridge, TN: Poster.



# Vita

Jonathan grew up in New Orleans, Louisiana, where he earned his Bachelor of Science and Engineering in Chemical Engineering from Tulane University. After two years working as a consulting engineer for EDG, Inc., he decided to pursue a career in research. He returned to Tulane University for a year, where he worked as a research assistant under Dr. Dan Shantz studying zeolite synthesis kinetics, before moving to Knoxville, where he began his PhD work at the University of Tennessee under Dr. Gila Stein and Dr. Joshua Sangoro. In 2018 he married his wonderful wife Claire, and in 2022 their daughter Rosario was born. After graduation, Jonathan will continue his research career as a postdoc at the University of Minnesota under the supervision of Dr. Chris Ellison and Dr. Frank Bates, where he hopes to apply and expand his expertise into the field of sustainable polymers.