Studies of Block Copolymer Thin Films and Mixtures with an Ionic Liquid

by

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Abstract

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Block copolymers are capable of self-assembling into structures on the 10-100 nm length scale. Structures of this size are attractive for applications such as nanopatterning and electrochemical membrane materials. However, block copolymer self-assembly in these examples is complicated by the presence of surfaces in the case of thin films and the presence of an additive, such as an ionic liquid, in the case of electrochemical membrane materials. Improved understanding of the structure and thermodynamics of such systems is necessary for the development of structure-property relationships in applications for block copolymers, such as nanopatterning and electrochemical devices.

To address the challenge of block copolymer thin film characterization over large areas, resonant soft X-ray scattering (RSoXS) has been applied to characterize order formation in copolymer thin films. Using theory and experiment, the dramatic chemical sensitivity of RSoXS to subtle differences in the bonding energies of different blocks of a copolymer is demonstrated. The unambiguous identification of structure and domain size in block copolymer thin films using RSoXS enables a quantitative comparison of the bulk block copolymer structure and domain size, leading to improved understanding of the impact of surfaces on block copolymer self-assembly.

The self-assembly of block copolymer/ionic liquid mixtures has been characterized as a function of block copolymer composition and molecular weight, mixture composition, and temperature using small-angle X-ray scattering (SAXS), optical transmission characterization, wide-angle X-ray scattering (WAXS), and differential scanning calorimetry (DSC). The resulting phase behavior is reminiscent to that of block copolymer mixtures with a selective molecular solvent and lamellar, cylindrical, ordered spherical micelles, and disordered phases are observed. Analysis of order-disorder transitions and molecular weight scaling analysis qualitatively indicates that the segregation strength between block copolymer phases increases with ionic liquid loading. DSC characterization of the thermal properties of the block copolymer/ionic liquid mixtures reveals two composition dependent regimes. At high block copolymer concentrations, a “salt-like” regime corresponding to an increase in the block copolymer glass transition temperature is observed, while at intermediate block copolymer concentrations, a “solvent-like” regime corresponding to a decrease in the block copolymer glass transition temperature is observed.
The distribution of ionic liquid within microphase-separated domains of a block copolymer has been characterized using contrast matched small-angle neutron scattering (SANS) and DSC. The ionic liquid is shown to partition selectively into domains formed by one block of a block copolymer in agreement with studies of the phase behavior of ionic liquid/block copolymer mixtures. Unexpected differences in ionic liquid partitioning are observed in mixtures containing a deuterated versus hydrogenated ionic liquid.
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Chapter 1. Introduction

Block copolymer self-assembly offers a novel route for nanostructuring materials for a wide variety of applications, including lithographic patterning and electrochemical devices. In the first example, a block copolymer thin film serves no direct functional purpose; instead, the material provides a template for patterning a metal or magnetic material onto an underlying substrate, and after patterning deposition the copolymer film is removed. In the second example, judicious selection of copolymer chemistry enables the incorporation of disparate properties, such as mechanical stability and ion transport in an energy conversion device in the form of a bulk block copolymer membrane. Small molecule additives, such as salts or solvents, however, are often necessary to realize functional materials and optimize their performance. Such small molecule additives are known to dramatically influence the self-assembly of block copolymer nanostructures. In this work, the effect of the addition of an ionic liquid on the structure and thermodynamics of block copolymers is studied with application towards electrochemical devices. In addition, a novel technique for the large-area characterization of nanostructure in block copolymer thin films is developed with application towards improved understanding of block copolymer thin film self-assembly over technologically-relevant length scales.

1.1. Block Copolymer Self-Assembly

The self-assembly of block copolymers has been studied extensively. In the simplest case of an AB diblock copolymer, two polymer segments with disparate segments are linked covalently to form a single polymer chain. The self-assembly of the block copolymer results from the free energy minimization of enthalpic interactions between the chemically dissimilar copolymer segments and the entropic chain stretching penalty that results from the joined copolymer segments. The resulting block copolymer self-assembly, or microphase separation, is parameterized by the copolymer composition, \( f_A \), or the volume fraction of the A block and \( \chi_{AB} N \), the product of the Flory-Huggins interaction parameter, \( \chi_{AB} \), and the degree of polymerization, \( N \). Variation of copolymer composition and segregation strength (\( \chi_{AB} N \)) has been shown both experimentally and theoretically to lead to the formation of a variety of ordered, microphase-separated structures including spheres on a body-centered cubic (BCC) lattice, cylinders with a hexagonally close-packed (HCP) arrangement, a bicontinuous gyroid structure, and lamellae. Experimentally, modification of \( \chi_{AB} N \), or the segregation strength between copolymer segments, can be achieved by variation of \( N \) or temperature, as the \( \chi_{AB} \) parameter is inversely related to temperature for many olefin-based polymer systems. As \( \chi_{AB} N \) is decreased, a transition from an ordered, microphase separated phase to a homogeneous, disordered phase has been observed in a wide variety of block copolymer chemistries and is designated an order-disorder transition (ODT). For samples in the ordered phase with values of \( f_A \) and \( \chi_{AB} N \) that lie close to the boundary between differing microphase separated structures, such as the HCP cylinder and the gyroid phases, temperature variation of \( \chi_{AB} N \) has been shown to induce transitions between ordered phases and is designated an order-order transition (OOT).

1.2. Block Copolymer Self-Assembly in the Presence of an Ionic Liquid

1.2.1. Physical Properties of Ionic Liquids and their Applications

Ionic liquids are a novel class of organic materials comprised of a cation and anion, which are non-volatile and have melting temperatures less than 100 °C. The low melting
temperature compared to ionic salts results from charge delocalization in the cation and anion that ensures that inter-ionic interactions are relatively weak. In the case of the cation, typical chemistries include imidazolium, pyrrolidinium, and quaternary ammonium salts, in which alkyl substitution of an amine or incorporation of an amine or imine into a ring structure leads to charge delocalization. In the case of the anion, typical chemistries include bis(trifluoromethanesulphonyl)imide ([TFSI]), bis(fluorosulphonyl)imide, tetrafluoroborate ([BF₄]), and hexafluorophosphate ([PF₆]), in which the presence of strong electron withdrawing groups leads to charge delocalization. The ionic nature and wide electrochemical stability window of ionic liquids, along with tunable solvation properties has led to the application of ionic liquids in a variety of applications including environmentally benign reaction media, solvation of cellulose-based natural materials, dye-sensitized solar cells, and electrochemical devices.

The choice of cation and anion chemistries is known to dramatically influence the physical properties of ionic liquids. Of particular interest to the present work are developments in the understanding of the solubilization of polymers using ionic liquids. Solvatochromic methods, in which the effects of an ionic liquid solvent on the absorption of light by a solvatochromic dye, have been utilized to empirically determine the degree of polarity of various ionic liquids. In addition, the dielectric constant of ionic liquids, which is a measure of solvent polarity and a reasonable estimate of the electrostatic energy associated with solute-solvent interactions, has been determined using microwave dielectric spectroscopy. Utilizing a series of 1-alkyl-3-methylimidazolium ionic liquids, Wakai et al. observed an increase in the dielectric constant as the chain length of the alkyl substituent was increased, as well as a strong dependence of the dielectric constant on anion chemistry. While solvatochromic and dielectric methods reveal information about the polarity of ionic liquids, the Abraham solvation model allows for a more nuanced characterization of ionic liquid solvation behavior. The Abraham solvation model quantifies the interaction of the ionic liquid with π- and n-electrons of the solute, along with the polarizability, hydrogen bond acidity/basicity, and dispersion interactions with a solute. Anderson et al. used ionic liquids as gas-liquid stationary phases in gas phase chromatography to determine the Abraham solvation parameters for a variety of imidazolium- and tributylammonium-based ionic liquids. It was found that the choice of anion strongly affects the degree of hydrogen bond basicity and polarizability, while the choice of cation had a negligible effect on these solubility parameters. Dispersion interactions were not observed to vary significantly amongst the two classes of ionic liquids studied, while π interactions were strongly influenced by alkyl substitution in the imidazolium cation, which add electron density to the imidazolium cation. The Hildebrand solubility parameter, δₕ, is included among the Abraham solvation parameters and is related to the energy required to produce a mole of cavities in a solvent of a size and shape sufficient to solubilize solute molecules. Close agreement has been found between values of δₕ estimated from reaction rates of 1,4-dimethylnaphthalene and intrinsic viscosity measurements of various imidazolium-based ionic liquids. As with solvatochromic and dielectric characterizations, measurements of δₕ revealed a strong dependence on anion choice and length of alkyl group substituent in 1-alkyl-3-methylimidazolium-based ionic liquids.

Despite extensive studies of polymer/molecular solvent interaction parameters, to date there have been no reports of the application of Flory-Huggins theory to polymer/ionic liquid solutions. Early work on binary ionic liquid mixtures has focused on imidazolium-based ionic liquids mixtures with carbon dioxide or with water and identified anion chemistry as critical...
towards understanding solute behavior in both cases. Lopes et al. have estimated the Flory interaction parameters of pairs of 1-alkyl-3-methylimidazolium cations with a common anion and the interaction parameter of pairs of [TFSI], [BF4], or [PF6] anions with a 1-butyl-3-methylimidazolium cation from measurements of excess molar volume in ionic liquid binary mixtures.16 Crosthwaite et al. have studied alcohol/1-alkyl-3methylimidazolium-based ionic liquid mixtures and demonstrated that the upper critical solution temperature (UCST) is highly dependent on anion choice, alkyl substituent chain length on the imidazolium cation, and alcohol chain length and degree of branching.17 Lachwa et al. have studied binary mixtures of 1-alkyl-3-methylimidazolium [TFSI] ionic liquids with chloroform and observed a high temperature lower critical solution temperature (LCST) with a low temperature closed-loop and found the high temperature LCST to increase with alkyl chain length.18 Recent theoretical progress has been made towards improved understanding of ion-ion interactions in mixtures of two ionic liquids and mixtures of ionic liquids and a molecular solvent. Aerov et al. have applied Flory-Huggins theory to a mixture of an ionic liquid and a molecular solvent and predicted an enlargement of the homogenous region of a two component mixture in comparison to a mixture of two molecular solvents due to short-range repulsive interactions between anions and cations.19

Of particular interest to the present study, is the application of ionic liquids in electrochemical devices, such as fuel cells and lithium ion batteries. In the case of fuel cells, a cation, in which one or more of the amine or imine groups present coordinates with a proton, provides a proton carrier and a novel approach to proton exchange membrane fuel cells with operating temperatures greater than 100 °C. Noda et al. have demonstrated the use of an imidazolium [TFSI] ([Im][TFSI]) ionic liquid as both a novel proton carrier and as a proton donor and acceptor for O2 reduction and H2 oxidation, respectively.6 In this example, the highest conductivities were observed in asymmetric mixtures of [Im][TFSI] with an imidazole excess. In the case of lithium ion batteries, a combination of low viscosity to facilitate rapid ion transport and stability towards cathodic electrochemical reactions have been identified as critical to the selection of ionic liquids and has led to the interest in a N-alkyl-N-methylpyrrolidinium [TFSI] ionic liquid as a battery electrolyte.20

1.2.2. Self-Assembly of Mixtures of Block Copolymers and Molecular Solvents

The addition of low molecular weight plasticizers, “tackifying” agents, or molecular solvents is important for many commercial applications of block copolymers, and thus fundamental understanding of the structure and thermodynamics of mixtures of low molecular weight additives with block copolymers is critical for understanding structure property relationships in these mixtures. In the case of mixtures of block copolymers with molecular solvents, such as cyclohexane or toluene, the solvent selectivity is related to the solubility of a copolymer block in the molecular solvent. Mixtures in which the solvent is poor for all of the copolymer blocks present leads to macrophase-separation and is not of interest for many applications. When the copolymer blocks have equal solubility in the molecular solvent the solvent is described as neutral, while if one of the copolymer blocks has greater solubility in the molecular solvent the solvent is described as selective. In both the neutral and selective solvents, a rich variety of lyotropic and thermotropic phase transitions in mixtures with block copolymers have been observed. Parameterization of the self-assembly of an AB diblock copolymer/molecular solvent mixture requires three variables in addition to those described previously for the self-assembly of a neat AB diblock copolymer. The enthalpic interactions of A and B monomer units with solvent molecules (χAS and χBS) are described by two additional
Flory-Huggins interaction parameters, while the composition of the mixture is given by $\phi_P$, or the volume fraction of copolymer. The scaling behavior with respect to the thermodynamics and structure of these mixtures has been studied extensively experimentally and theoretically.

Helfand and Tagami proposed the “dilution approximation” to predict the segregation strength between AB copolymer blocks in the presence of a neutral solvent. The addition of a neutral solvent to a block copolymer leads to an effective reduction in the segregation strength between the A and B blocks of the copolymer, which is given by the product $(\chi_{AB} N \phi_P)$. Thus, the value of $\chi_{AB}$ at which an ODT is observed is increased (decreasing the temperature) in mixtures of a block copolymer in a neutral molecular solvent. Noolandi and Hong developed self-consistent mean-field (SCFT) theory for such mixtures to predict the domain size scaling behavior and polymer/solvent density profiles in mixtures of symmetric AB diblock copolymers with a neutral solvent. Fredrickson and Leibler subsequently predicted that the free energy gain due to screening of unfavorable enthalpic interactions between the A and B copolymer blocks leads to a slight excess accumulation of neutral solvent molecules at the interface of the A and B copolymer blocks, and this prediction was later experimentally verified by Lodge and coworkers. Based on the dilution approximation, the ODT temperature of the block copolymer/neutral solvent mixture is predicted to scale as $(\chi_{AB} N \phi_P)_{ODT} = F(f_A)$, where the value of $F(f_A)$ is compositionally dependent ($f_A$) and is determined using the random phase approximation. This anticipated scaling, however, has been shown both theoretically and experimentally to be invalid as the dilution approximation is unable to capture chain swelling effects in semi-dilute mixtures. Chain swelling of a copolymer block occurs in the presence of a good solvent in which the polymer chain assumes a coil dimension greater than the random walk distribution characteristic of a $\theta$ solvent. Incorporation of such chain swelling effects by Fredrickson and Leibler and de la Cruz has led to the scaling prediction of $\chi_{AB}^{1.59} N \phi_P^{1.59} = (\chi_{AB} N \phi_P)_{ODT} = F(f_A)$, where ‘$a$’ is the length of a monomer repeat unit. Thus in a AB block copolymer, the addition of a neutral solvent leads to a decrease the characteristic domain spacing due to the screening of enthalpic interactions between A and B blocks.

The addition of a selective solvent to a block copolymer leads to rich lyotropic and thermotropic phase behavior due to the three independently varying $\chi$ parameters present in this two component system. Birshstein and Zhulina developed a scaling analysis for strongly segregated block copolymers in the presence of a selective solvent and showed that preferential swelling of one copolymer block is able to induce a lyotropic phase transition. Banaszak and Whitmore applied SCFT to the mixtures of a weakly segregated AB block copolymer with a slightly selective solvent and found that the addition of solvent destabilizes the microphase-separated ordered phase leading to a decrease in the ODT temperature. Subsequent work by Huang and Lodge applied SCFT to related mixtures over a wide range of copolymer block compositions ($f_A$) and degree of solvent selectivity ($\chi_{AS}$ vs. $\chi_{BS}$) and found that the effect of solvent addition on the ODT temperature varies dramatically with solvent selectivity. For a solvent that is not extremely selective for either copolymer block (as in the case of Reference 32), the microphase-separated region of the phase diagram is diminished, while for a very selective solvent, the microphase-separated region of the phase diagram is broadened. In other words, for block copolymer mixtures in weakly selective solvents the ODT temperature is
decreased, whereas for mixtures in strongly selective solvents the ODT temperature is increased. Hanley et al. demonstrated using experiment and SCFT that the domain scaling relationship in block copolymer/selective solvent mixtures follows the relationship $d \sim \phi^{-\alpha}$, where $\alpha$ is related to the solvent selectivity and is a sensitive function of $\chi_{AS}$ and $\chi_{BS}$. The concentration dependence of the domain spacing scaling was found to be consistent with a crossover from behavior governed by block interactions at high $\phi_P$ to solvent-polymer interactions at low $\phi_P$. Lai et al. further investigated the dependencies of $\alpha$ and showed that this parameter is composed of both geometric (lamellae, HCP cylinders, gyroid, BCC sphere) and solvent selectivity contributions.

In addition to solvent selectivity, studies of block copolymer/molecular solvent mixtures can be categorized by the copolymer concentration range. Many of the aforementioned studies have focused on concentrated mixtures ($\phi_P \geq 0.20$) using olefin-based block copolymer/organic solvent chemistries. Above the critical micelle concentration, dilute copolymer mixtures in a selective solvent form a diverse set of micelles that lack long range order, the morphology of which is dependent on $f_A$, $N$, and copolymer architecture. Jain et al. observed the formation of micelles consisting of bilayered vesicles, three-dimensional random network, cylinders, or spheres in poly(butadiene-block-ethylene oxide) (PB-PEO) copolymer/water mixtures depending on the relative length of the water-soluble PEO block compared to the water-insoluble PB block and $N$. In particular, formation of the random network phase was found to be $N$-dependent, leading to the speculation that conformation freedom associated with relatively long PB blocks is critically necessary for the formation of this morphology. Alexandridis et al. studied the critical micelle concentration and temperature of Pluronic (PEO-block-poly(propylene oxide)-block-PEO copolymer (PEO-PPO-PEO))/water mixtures with varying compositions of water-soluble (PEO) and water–insoluble (PPO) blocks in order to study the energetics of micelle formation. The process was determined to be entropy-driven in close analogy to micelle formation in aqueous surfactant mixtures. Both PEO and PPO block length ($N$), copolymer block sequence (PPO-PEO-PPO copolymers were found to be insoluble in water), and strong water/polymer hydrogen bonding interactions were identified as critical to understanding the self-assembly of Pluronic/water mixtures.

### 1.2.3. Self-Assembly of Mixtures of Block Copolymers and Ionic Salts

The addition of ionic salts to block copolymers is of technological interest for applications including solid-polymer electrolyte battery materials and light-emitting electrochemical cells in which microphase-separated block copolymers enable the optimization of disparate properties such as mechanical stability and light emission or ion transport. Block copolymers containing a PEO block or side-chain, a poly(methyl methacrylate) (PMMA) block, or a poly(2-vinyl pyridine) (P2VP) block have been frequently utilized in such studies due to the ability of the ether, acrylate, and pyridine chemistries to solvate a wide variety of ions. The addition of an ionic salt to a homopolymer, such as PEO, is well-known to increase the glass transition temperature ($T_g$) of the polymer chains via physical cross-linking. Robitaille and Prud’homme studied the mechanical properties of PEO-block-polyisoprene-block-PEO (PEO-PI-PEO) copolymers mixed with sodium thiocyanate and demonstrated that complexation of PEO chains with solvated ions increases the tensile strength of the mixtures relative to the neat PEO-PI-PEO copolymer. The authors speculated that the improved mechanical properties stemmed from increased crystallization within ion-complexed PEO domains. Khan et al. studied mixtures of lithium salts with ABA copolymers, in which the A block is composed of PMMA...
with oligomeric ethylene oxide side chains and the B block is composed of polystyrene (PS). The insertion of the “hard” PS block was observed to improve the mechanical properties of the homopolymer of PMMA with oligomeric ethylene oxide side chains while reducing the ionic conductivity of these samples. As in studies of homopolymer/salt mixtures, it was demonstrated that the \( T_g \) of block comprised of ion-containing PMMA with oligomeric ethylene oxide side chains increases monotonically with the addition of salt.

Fundamental understanding of the structure and thermodynamics of block copolymer/salt mixtures is critical for developing structure property relationships in applications such as solid-polymer electrolytes. Addition of an ionic salt to a block copolymer containing an ion-solvating block leads to changes in the effective \( \chi \) parameter and statistical segment length. Ruzette et al. observed a monotonic increase in the ODT temperature of ordered PMMA-b-poly(oligo oxyethylene methacrylate) copolymer (PMMA-POEM)/lithium trifluoromethane sulfonate mixtures with salt concentration revealing an increase in the effective \( \chi \) parameter with salt loading. The statistical segment length of the PMMA-POEM copolymer was also observed to dramatically increase in the disordered state presumably due to ion-induced changes in the coil conformations of PMMA and POEM. Wang et al. witnessed a similar increase in the effective \( \chi \) parameter and statistical segment length with salt loading in PS-PMMA/lithium chloride mixtures and observed that the effective \( \chi \) parameter becomes less temperature dependent at high salt concentrations, suggesting that ion entropy dominates in highly salt-doped mixtures. Lee et al. studied mixtures of PS-P2VP or PS-block-poly(4-vinyl pyridine) (PS-P4VP) copolymers with cadmium chloride and observed intra polymer chain interactions in PS-P2VP/CdCl\(_2\) mixtures versus inter polymer chain interactions in PS-P4VP/CdCl\(_2\) mixtures. In the case of the PS-P2VP/CdCl\(_2\) mixtures, salt concentration-dependent changes in block copolymer domain sizes were attributed to a salt-induced increase in the statistical segment length of P2VP. The complexity of ion/block copolymer interactions and challenges in experimentally isolating ion effects on polymer chain statistics and interaction parameters has led to interest in theoretical studies of these systems.

Wang has developed a mean field analytical theory describing the effects of ion solvation on the miscibility of binary polymer blends that captures the competition between the entropic tendency for uniform ion distribution and enthalpic considerations that drive the ion to the higher dielectric polymer in the blend. In the limit of blends of polymers with low dielectric constants (\( \varepsilon_{\text{PEO}} = 8.0 \)) and low salt concentration, the theory predicts that the effective \( \chi \) parameter will increase monotonically with salt concentration. Wanakule et al. have corroborated this finding experimentally in PS-PEO diblock copolymer mixtures with a lithium salt demonstrating the applicability of Wang’s theory to block copolymer/ionic salt mixtures despite the fact that the entropic loss due to block copolymer microphase separation has yet to be incorporated into this mean field theory.

1.2.4. Mixtures of Polymers and Ionic Liquids

The earliest study of a polymer/ionic liquid mixture dates back to the 1930’s with the observation that triethylammonium nitrate was able to solubilize plant-derived cellulose. While interest in the use of ionic liquids for processing cellulose for biofuels has gained renewed attention, fundamental studies of synthetic polymer/ionic liquid mixtures have also enjoyed recent attention. Early synthetic polymer/ionic liquid mixtures consisted of polymer networks formed via in situ polymerization in an ionic liquid and were limited by both monomer solubility and initiation of the radical polymerization. Sneddon et al. conducted the first
systematic study of polymer solubility in ionic liquids comprised of three 1,3-dialkylimidazolium cation chemistries with varying alkyl chain length and [TFSI], [PF6], and [BF4] anions and found co-dissolution with a volatile molecular solvent and subsequent solvent evaporation necessary to solubilize the majority of the 17 polymers studied. The authors determined empirically that [1-octyl-3-methylimidazolium][TFSI], which had the longest alkyl chain length of the cations considered, was most effective at dissolving both hydrophobic and hydrophilic polymers; however, this finding was not universal for all polymer chemistries considered and underscores the limited understanding of these systems. Subsequent polymer solubility studies in a [1-ethyl-3-methylimidazolium][TFSI] ([emIm][TFSI]) ionic liquid found polyacrylates and polymethacrylates to be readily soluble in [emIm][TFSI], while polystyrene and polymers with strong hydrogen bonding groups, such as polyvinylalcohol, poly(methacrylic acid), and poly(2-hydroxyethyl methacrylate), were insoluble.

A number of novel thermo-sensitive polymer/ionic liquid pairs have been identified for use in switching or sensing materials that draw parallels to polymer/solvent mixtures. Poly(N-isopropylacrylamide) (PNIPAm)/[emIm][TFSI] mixtures have been shown to exhibit UCST behavior, in contrast to the well known LCST behavior observed in PNIPAm/water mixtures. Ueki et al. identified LCST behavior in poly(benzyl methacrylate) (PBnMA)/[emIm][TFSI] mixtures and speculated that a negative $\Delta S_{\text{mix}}$ resulted from strong cation/$\pi$-interactions. In addition, the LCST of a series of 1,3-dialkylimidazolium [TFSI] ionic liquids with varying alkyl chain length (methyl to hexyl) in PBzMA was found to increase monotonically with alkyl chain length. A subsequent study examined the effect of anion chemistry in PBzMA mixtures and found 1,3-dialkylimidazolium [BF$_4$] ionic liquids of varying alkyl chain length unable to solubilize PBzMA, while mixtures containing [emIm][PF$_6$] exhibited an LCST below that of [emIm][TFSI]. Triolo et al. demonstrated that deuterated PEO chains assume a Gaussian conformation in dilute mixtures with an [1-butyl-3-methylimidazolium][BF$_4$] ionic liquid using small-angle neutron scattering. In subsequent studies of mixtures of the PEO derivative poly(ethyl glycidyl ether) (PEGE) with [emIm][TFSI], Tsuda et al. observed LCST behavior and utilized $^1$H NMR to study the hydrogen bonding behavior of [emIm][TFSI] with oxygen atoms in PEGE chains. While a priori understanding of the behavior of these mixtures is still elusive, these studies highlight the diversity of polymer/ionic liquid interactions and point to the importance of alkyl chain length in 1,3-dialkylimidazolium cations, anion chemistry, and hydrogen bonding strength of polymers in predicting the phase behavior of polymer/ionic liquid mixtures.

### 1.3. Challenges in the Characterization of Block Copolymer Thin Films

Large area block copolymer thin films are of technological interest for nanopatterning of microelectronic components, such as magnetic media and silicon capacitors, in which the copolymer film provides a template for patterning a functional material onto an underlying substrate, and after pattern deposition the copolymer film is removed. In addition, nanostructured block copolymer thin films, in which the blocks are comprised of p and n type conducting polymers, are candidate materials for large area photovoltaics and light emitting diodes. Improved understanding and control of copolymer/inorganic interfaces comprised of a platinum catalyst or lithium metal-oxide electrode is critical for the development of high efficiency energy conversion devices containing a block copolymer electrolyte, such as fuel cells and batteries.
The confinement of a block copolymer to thin film form leads to the formation of copolymer domains with a high degree of orientation compared to the randomly-oriented domains typically observed in bulk block copolymers. The interplay between minimization of interfacial energy between copolymer domains and minimization of the surface energy between copolymer domains and substrate or air interfaces, combined with dimensional confinement in thin film form creates added complexity towards understanding the self-assembly of block copolymer thin films. Conceptually, the simplest example is that of a compositionally symmetric AB diblock copolymer ($f_A=0.50$) thin film with one interface at a hard substrate and the second a free interface with air. The wetting behavior of the film is described as “symmetric” in the case that the A block prefers both air and substrate interfaces, while the wetting behavior of the film is described as “asymmetric” in the case that the A block prefers the air interface and the B block the substrate interface. The natural periodicity of the block copolymer ($L_0$) and the copolymer film thickness ($t$) lead to smooth films in the case of symmetric wetting if $t = nL_0$ (n=1, 2, 3…) and in the case of asymmetric wetting if $t = (n + \frac{1}{2})L_0$. Taking symmetric wetting as an example and assuming $t > L_0$, deviations in film thickness from $t = nL_0$ lead to island and hole formation in which copolymer chains reorient to produced terraced structures with $t = nL_0$ and $(n-1)L_0$. The vast majority of block copolymer films have been observed to form lamellar domains with an orientation parallel to the hard substrate due to the aforementioned minimization of interfacial and surface energies. However, block copolymer domains with a high degree of lateral order and perpendicular orientation to a hard underlying surface are desired for many of the aforementioned applications.

A variety of techniques have been developed for control over orientation of self assembled block copolymer thin films, including film thickness control, substrate wetting properties, heteroepitaxy and graphoepitaxy, and the application of external fields. Knoll et al. characterized the morphology and orientation of cylinder-forming PS-PB-PS triblock copolymers and observed a disordered structure in films thinner than the periodicity of the copolymer and a thickness-dependent orientation of the cylinders for films thicker than the periodicity of the copolymer. Mansky et al. controlled the wetting behavior of PS-PMMA thin films by varying the composition of PS-random-PMMA copolymer brushes that were pre-deposited on the hard substrate. Yang et al. lithographically patterned self assembled monolayers with a periodicity commensurate with that of a symmetric PS-PMMA copolymer to create well ordered lamellae with an orientation orthogonal to the hard substrate, using a process more generally known as heteroepitaxy. Segalman et al. lithographically patterned a hard substrate to create raised topographical regions that induce lateral ordering of copolymer domains, utilizing a process more generally known as graphoepitaxy. Morkved et al. used an external electric field to align PMMA cylindrical domains of a PS-PMMA copolymer parallel to a substrate surface. Albalak et al. utilized roll casting to vertically-align cylindrical domains of block copolymer films using shear alignment. The thicknesses of these films were on the order of several millimeters and subsequently Angelescu et al. developed a shear alignment technique using a polydimethylsiloxane stamp applicable to copolymer films with thicknesses less than 100 nm.

The development of the aforementioned methods for controlling the self-assembly of block copolymer thin films has been aided by the development of a large number of real and reciprocal space techniques capable of characterizing the in-plane and out-of-plane order of block copolymer thin films. Much of the effort surrounding the development of these techniques has been directed at enhancing their resolution and chemical specificity.
profiling techniques include forward recoil spectroscopy, nuclear reaction analysis, and dynamic secondary ion mass spectrometry (DSIMS). Of these techniques, DSIMS possesses depth resolution on the order of 5-10 nm; however, the technique is destructive, requiring ion beam etching of a sample, and is limited with respect to chemical sensitivity in that an abundant heteroatom or deuterium labeling is needed for unambiguous depth profiling. Cross sectional transmission electron microscopy (TEM) is a versatile characterization tool for the out-of-plane order of block copolymer thin films with resolution less than 5 nm; however, difficult sample preparation and a limited set of staining chemistries (OsO₄, RuO₄, and I₂) necessary for enhancing imaging contrast limit the range of materials easily studied using this technique. Neutron and X-ray reflectivity are nondestructive, reciprocal space depth profiling techniques that are limited by deuterium labeling, interfacial smoothness, and a priori knowledge of internal film structure to which an appropriate data fitting model can be applied.

Scanning probe (SPM) and scanning electron (SEM) microscopies, along with TEM have been applied for real space characterization of in-plane order in block copolymer thin films. SPM and SEM techniques possess spatial resolution less than 5 nm, but often rely on height or modulus differences within a thin film sample for identification of microphase-separated copolymer domains and characterization is limited to the surface of the copolymer film. While TEM shares the outstanding spatial resolution of these techniques, chemical specificity is often limited by available staining chemistries necessary for contrast enhancement and sample thicknesses less than 100 nm. For large area applications, such as nanolithography, in which ordered domains on the order of square millimeters are desired, all three microscopies are further limited by the sample area that can be readily characterized on reasonable time scales. More recently, reciprocal space techniques such as grazing incidence small-angle neutron and X-ray scattering (GISANS and GISAXS, respectively), and resonant soft X-ray scattering (RSoXS) have emerged as promising non-destructive techniques for characterization of lateral order in block copolymer thin films. GISANS and GISAXS are capable of selectively probing near-surface structure in copolymer thin film and are further capable of characterizing in-plane and out-of-plane structure simultaneously with a high degree of resolution (less than 5 nm). These techniques are limited by the complex modeling necessary to account for scattering from specular and transmitted X-rays or neutrons. Beyond the deuterium labeling necessary for GISANS measurements, both methods are limited in their ability to resolve scattering from multi-component systems, such as ABC triblock copolymers. Recently, Virgili et al. exploited the chemical specificity of soft X-rays using RSoXS for large area characterization of lateral order in block copolymer thin films. While RSoXS has shown promise in characterization of in-plane order in copolymer films, the strong interactions of soft X-rays with polymeric materials limits the application of this technique to film thicknesses on the order of hundreds of nanometers.

1.4. Motivation and Thesis Outline
Nanostructured block copolymers are a compelling class of materials for emerging applications in energy conversion devices and nanopatterning based on the opportunity to self assemble regularly ordered domains of two or more materials with disparate properties. In the case of block copolymer thin film applications, such as nanopatterning and photovoltaics, new thin film characterization techniques that combine high spatial resolution and chemical specificity, such as RSoXS, are critical for improved understanding of block copolymer thin film self-assembly over technologically-relevant length scales. In the case of energy conversion devices such as fuel
cells and batteries, the addition of an ionic liquid to a block copolymer is an attractive means of facilitating ion transport within one block of the copolymer, while the properties of the second copolymer block can be optimized for dimensional stability and as a barrier to gas diffusion. The fundamental study of the phase behavior of block copolymer/ionic liquid mixtures is an important first step in enabling rational design of membrane materials for energy conversion devices.

In Chapter 2, the ability of RSoXS to characterize in-plane order over large areas in diblock copolymer thin films is demonstrated. In Chapter 3, a study of the phase behavior of mixtures of a symmetric S2VP copolymer with an [Im][TFSI] ionic liquid using small angle X-ray scattering and optical transmission characterization is described. This study is expanded in Chapter 4 to explore the effects of block copolymer composition and molecular weight on the phase behavior of S2VP copolymer/[Im][TFSI] mixtures. In Chapter 5, the distribution of the [Im][TFSI] ionic liquid within S2VP copolymer domains is characterized using small angle neutron scattering and differential scanning calorimetry and the effects of mixture composition and deuterium labeling on the partitioning of ionic liquid are explored.

1.5. References
50. Graenacher, C. Cellulose Solution. 1,943,176, 1934.

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The lateral order of poly(styrene-block-isoprene) copolymer (PS-b-PI) thin films is characterized by the emerging technique of resonant soft X-ray scattering (RSoXS) at the carbon $\pi^*$ resonance and compared to ordering in bulk samples of the same materials measured using conventional small-angle X-ray scattering. We show using theory and experiment that the loss of scattering intensity expected with a decrease in sample volume in the case of thin films can be overcome by tuning X-rays to the $\pi^*$ resonance of PS or PI. Using RSoXS, we study the microphase ordering of cylinder- and sphere-forming PS-b-PI thin films and compare these results to position space data obtained by atomic force microscopy. Our ability to examine large sample areas (~9000 $\mu$m$^2$) by RSoXS enables unambiguous identification of the lateral lattice structure in the thin films. In the case of the sphere-forming copolymer thin film, where the spheres are hexagonally arranged, the average sphere-to-sphere spacing is between the bulk (body-centered cubic) nearest neighbor and bulk unit cell spacings. In the case of the cylinder-forming copolymer thin film, the cylinder-to-cylinder spacing is within experimental error of that obtained in the bulk.

2.1. Introduction

Ordered block copolymer thin films are the subject of intense interest for nanolithographic applications ranging from magnetic data storage to transistors and capacitors. These applications require not only regularly sized, regularly spaced structures, but also control over in-plane order. As a result, a number of efforts have been made to control in-plane order and orientation. Techniques to analyze long-range order in block copolymer thin films, however, are significantly lacking. Dynamic secondary ion mass spectrometry destructively detects periodic order in the direction perpendicular to the surface while neutron and X-ray reflectivity are nondestructive reciprocal space techniques capable of providing similar information. Ordering in the plane of the film is generally studied via transmission electron, scanning electron, and scanning force microscopies. Transmission electron microscopy techniques generally require staining of an organic domain to create contrast, while scanning force microscopies require careful choice of block copolymer components to create height, modulus, or other surface contrast which may be exploited by the probe tip. In fact, many block copolymer thin films contain a glassy surface brush layer that prevents imaging of the underlying pattern via scanning force techniques without a prior etching step. Although undersampled imaging using scanning force microscopy expands the analysis area slightly, these techniques are only capable of studying areas of a few square microns at a time, yielding limited statistical information. Reciprocal space techniques have the inherent advantage of providing statistical averages over significantly larger sample sizes. The purpose of this paper is to demonstrate the utility of resonant soft X-ray scattering (RSoXS) for characterizing the in-plane order in 50 nm thick block copolymer films. We demonstrate that RSoXS provides an important complement to existing reciprocal space methods for studying lateral order in block
copolymer thin films such as grazing incidence small-angle X-ray scattering (GISAXS) and guided wave depolarized light scattering (GWDLS). GISAXS shows promise in allowing one to probe surface and thin film structure.\textsuperscript{16, 17} However, quantitative analysis of grazing incidence scattering experiments is difficult due to the complexity in modeling GISAXS scattering data. For example, determining the in-plane structure of block copolymer thin films can be quantitative but only after scattering from both the refracted and reflected waves have been accounted for.\textsuperscript{16} GWDLS results reported thus far are qualitative in nature and restricted to films that are 1 \( \mu \text{m} \) thick.\textsuperscript{18}

In classical scattering of light, X-rays, or neutrons the relationship between the transmitted and incident beam fluxes \( J_x \) and \( J_0 \) is given by Beer's law

\[
T = \frac{J_x}{J_0} = e^{-\mu t}
\]

(2.1)

where \( T \) is the transmission coefficient, \( \mu \) is the absorption coefficient, and \( t \) is the sample thickness. The optimal value of \( \mu t \) for X-ray and neutron scattering experiments is unity; i.e. \( t=1/\mu \). Samples with smaller thickness are suboptimal due to insufficient encounters between the incident beam and scattering centers in the sample, while the incident and/or scattered beams from samples with larger thicknesses are heavily attenuated before they reach the detector. For hard X-ray (~ 10000 eV) and neutron beams, \( 1/\mu \approx 1 \text{ mm} \) in polymers. For soft X-rays, \( 1/\mu \) is 5 orders of magnitude smaller, i.e., \( 1/\mu \approx 100 \text{ nm} \). Resonant soft X-ray scattering allows us to exploit this property and study the structure of thin films.

Studies closely related to RSoXS fall under three categories: differential anomalous small-angle X-ray scattering (DAS), anomalous small-angle X-ray scattering (ASAXS), and resonant hard X-ray scattering. DAS was initially applied toward structure determination in amorphous binary alloys\textsuperscript{20, 21} and later in polymer electrolytes.\textsuperscript{22} ASAXS has been used to study the morphology of Ni neutralized ionomers\textsuperscript{23, 24} and the distribution of counterions in polyelectrolyte solutions.\textsuperscript{25} Resonant hard X-ray scattering has been used to study interlayer structures in smectic liquid crystals.\textsuperscript{26} In each of these studies, X-rays were tuned to absorption edges of high atomic number (\( \geq 16 \)) atoms that fall in the hard X-ray regime. While similar changes in the complex scattering amplitude of selected elements is achieved in both hard and soft X-ray resonant scattering, in the hard X-ray range the intrinsic energy resolution (determined by the lifetime of the core hole in the resonant scattering process) of several electronvolts is very large. The only relevant core level (1s) for organic constituents C, N, and O occurs in the soft X-ray range (280–550 eV), where much sharper intrinsic energy resolution of ~ 0.2 eV provides direct sensitivity to the bonds formed by these constituents.

Soft X-rays in the energy range near the carbon absorption edge (280–320 eV) have been used to investigate structure in polymer systems via near edge X-ray absorption fine structure (NEXArafS) for contrast in conjunction with scanning transmission microscopy.\textsuperscript{27} NEXArafS microscopy is routinely used to study near surface molecular orientation and structure but has limited resolution (40 nm) when studying phase separation. Soft X-ray reflectivity at the carbon absorption edge has been used to characterize the polymer-polymer and polymer-air interfaces of a polystyrene-poly(methyl methacrylate) bilayer.\textsuperscript{28} RSoXS has been used to characterize porous polymer films,\textsuperscript{29} latex spheres,\textsuperscript{29} and structured latexes.\textsuperscript{30} To our knowledge, there is only one abstract in the literature in which RSoXS has been used to study block copolymer thin films.\textsuperscript{31} While this study clearly showed that in-plane periodicity in block copolymer thin films can be
detected by RSoXS, the nature of the periodic structure could not be determined due to the lack of higher order scattering peaks. The purpose of the present paper is to determine the nature of lateral order in block copolymer thin films using higher order RSoXS peaks in a manner that is analogous to the use of hard X-rays and neutrons for the study of bulk block copolymer samples. Here, we demonstrate RSoXS to be a unique tool in block copolymer structure analysis by providing radial information with the scattering vector q confined strictly to the plane of the film. Further, we anticipate that since the X-ray wavelength can be tuned, much more complicated block copolymers may be studied. For instance, the ordering of an ABC triblock copolymer is difficult to fully understand using hard X-rays alone, but RSoXS may be used to exploit contrasts between each of the three components of the block copolymer by tuning to one or more resonance peaks of a polymer containing oxygen, nitrogen, or other heteroatoms.

2.2. Experimental Section

Poly(styrene-block-isoprene) copolymers (PS-b-PI) were synthesized anionically using standard methods described in ref 32. All polymers had polydispersities less than 1.05. Polymers were stabilized with 0.7 wt% 2,6-di-tert-butyl-4-methylphenol (BHT). The polymers studied are designated SI(7-79) and SI(4-35) where the numbers in parentheses refer to the number-averaged molecular weights in kg/mol of the polystyrene and polyisoprene blocks, respectively. The relevant polymer characteristics are summarized in Table 2.1.

Bulk self-assembly was characterized with small-angle (hard) X-ray scattering (SAXS) performed on beamline 1-4 of the Stanford Synchrotron Radiation Laboratory (SSRL). The beamline was configured with an X-ray wavelength of 1.488 Å and focused to a 0.5 mm diameter spot. Samples were prepared by annealing polymers at 180 °C (above the order-disorder transition) under vacuum for 1 h and then 20 h at 110 °C to form samples of thicknesses 1.3 mm (SI(7-79)) and 2.2 mm (SI(4-35)). Samples were held in aluminum sample cells and sealed with Kapton windows. A single quadrant of two-dimensional scattering patterns was collected on a CCD detector with a 100 mm diameter. The scattering patterns were radially averaged and corrected for detector null signal, dark current, and empty cell scattering. The scattering intensities were converted into absolute intensities using a polyethylene standard.

PS-b-PI block copolymers with rubbery polyisoprene as the major component were chosen for this study because the modulus contrast between the microphases allowed position space imaging in tapping mode on a Digital Instruments Multimode atomic force microscope (AFM). Fifty nanometer thick films were made by spin-casting 1 wt% toluene solutions of the block copolymers onto Si₃N₄ windows for scattering experiments (SPI Supplies) and silicon substrates for AFM (University Wafer). The films were heated under vacuum for 9 h at 120 °C, followed by annealing at 95 °C for 16 h, and finally quenched to room temperature. From earlier studies of PS-b-PI films it is known that PI wets the substrate and air interfaces and minor PS phases segregate away from the interfaces. This morphology is consistent with the films studied here. Films cast on Si wafers were initially 50 nm thick as confirmed by ellipsometry. Optical microscopy and AFM reveal that the surface is covered with a complete monolayer of spheres or cylinders and additional material is contained in an incomplete second layer of domains (islands) on the top surface of the film. For SI(7-79), 6% of the surface is covered by a bilayer (as opposed to a monolayer) of spheres while for SI(4-35), 36% of the area is covered by a second layer of cylinders. RSoXS samples were spun-coat on Si₃N₄ windows under identical conditions to those cast on Si wafers and should nominally be of the same thickness. Ellipsometry and AFM, however, are not possible on these small, delicate windows so the actual
Table 2.1. Block Copolymer Characteristics and Center-to-Center Domain Spacing

<table>
<thead>
<tr>
<th>polymer</th>
<th>mol wt (g/mol)</th>
<th>volume fraction PS</th>
<th>domain morphology</th>
<th>SAXS q* position (nm(^{-1}))</th>
<th>SAXS bulk spacing (nm)</th>
<th>RSoXS q* position (nm(^{-1}))</th>
<th>RSoXS thin film spacing (nm)</th>
<th>AFM thin film spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI(4-35)</td>
<td>39,200</td>
<td>0.21</td>
<td>cylinders</td>
<td>0.309</td>
<td>23.5 ± 0.5</td>
<td>0.261</td>
<td>24.1 ± 0.2</td>
<td>24.8 ± 2.5</td>
</tr>
<tr>
<td>SI(7-79)</td>
<td>85,900</td>
<td>0.10</td>
<td>spheres</td>
<td>0.223</td>
<td>39.9 ± 3.1(^{+})</td>
<td>0.200</td>
<td>36.3 ± 0.2</td>
<td>34.9 ± 3.5</td>
</tr>
</tbody>
</table>

\(^{+}\) 39.9 ± 3.1 nm is the bulk lattice spacing (a\(_{\text{bulk}}\)), while the bulk nearest neighbor spacing (\(\sqrt{3/2}\)a\(_{\text{bulk}}\)) is 34.5 ± 2.7 nm
fractional coverage of islands is unknown. Since these substrates are substantially smaller than
the Si wafer pieces (a few millimeters on a side as opposed to 1 cm), films for RSoXS may be
slightly thicker than 50 nm. It is important to note that, unlike GISAXS, RSoXS is not limited to
smooth films and the presence of surface structures is not detrimental to this technique.

RSoXS experiments were conducted at beamline 6.3.2 at the Advanced Light Source
(ALS), Lawrence Berkeley National Laboratory (LBNL). The PS-b-PI thin films were placed on
a standard two-axis diffractometer equipped with a channel electron multiplier detector that
recorded the scattering intensity in photon counting mode. The beam spot size was
approximately 300 µm by 30 µm. The energy of the incident beam was tuned using a varied line
spacing grating monochromator with an exit slit providing resolving power (E/ΔE) of ~ 2000.
Incident X-ray energies (hν) of 265-325 eV, corresponding to a wavelength (λ) range of 4.68-
3.82 nm were used, and the scattering angle, θ, varied from 1° to 25°. We report the scattering
intensity I(q) in arbitrary units after correcting for background scattering recorded from a blank
Si3N4 window (q=4πsin(θ/2)/λ is the magnitude of the scattering vector). The scattering angle
was changed by simultaneously rotating the substrate by an angle θ/2 (relative to the incident
beam) and the detector by an angle θ. This ensures that the scattering vector always lies in the
plane of the film, parallel to the substrate. Transmission-absorption spectra were collected with
the X-ray beam normal to the film.

2.3. Results and Discussion

2.3.1. Factors governing resonant scattering contrast and signal

We begin with a discussion of the origin of X-ray scattering contrast in a binary film
composed of polystyrene and polyisoprene. Our treatment includes the hard X-ray spectral range
where X-ray absorption is negligible as well as the soft X-ray range where absorption is
significant. The amplitude of the scattered field from each phase scales with its complex
refractive index

\[ n(\lambda) = 1 - \delta(\lambda) - i\beta(\lambda) \quad (2.2) \]

where δ and β are the dispersive and absorptive contributions, respectively. Alternatively, the
index can be defined as

\[ n(\lambda) = 1 - \frac{r_e^2}{2\pi} \sum_i \rho_i f_i(\lambda) \quad (2.3) \]

where \( r_e \) is the electron radius, \( \rho_i \) is the number density of atoms of type i (in PS and PI there are
only two types of atoms: C and H), and \( f_i(\lambda) \) are the atomic scattering factors of the atoms

\[ f_i(\lambda) = f_{i,1}(\lambda) + if_{i,2}(\lambda) \quad (2.4) \]

where \( f_{i,1} \) and \( f_{i,2} \) are the real and imaginary contributions, respectively. Here we assume that all
carbon atoms in each phase can be described by a single scattering factor for that phase (\( f_{c,PI} \) and
\( f_{c,PS} \)). This simplifying assumption may not always hold in practice since different carbon bonds
generally yield different spectral features, and significant anisotropy exists in systems such as oriented planar molecules. These refinements will provide interesting opportunities in future studies. For now we note that \( f_{c,\text{PI}} \) and \( f_{c,\text{PS}} \) are assumed to represent spherically averaged values in both the phase-separated films and the neat samples whose NEXAFS spectra were used to obtain them.

The X-ray absorption length in equation 2.1 is given by

\[
1/\mu = \lambda / 4\pi\beta. \quad (2.5)
\]

The scattering contrast between the PS and PI phases is proportional to \( \Delta n\Delta n^*/\lambda^4 \), where \( \Delta n = n_{\text{PS}} - n_{\text{PI}} \) and \( \Delta n^* \) is the complex conjugate of \( \Delta n \). For a transmission geometry scattering sample with illuminated area, \( A \), thickness, \( t \), and transmission, \( T \), the scattering intensity in the single scattering limit is

\[
I \propto \left( \frac{\Delta n\Delta n^*}{\lambda^4} \right) (At)T = \left( \frac{(\beta_{\text{PS}} - \beta_{\text{PI}})^2 + (\delta_{\text{PS}} - \delta_{\text{PI}})^2}{\lambda^4} \right) (At)T. \quad (2.6)
\]

It is instructive to separate the contributions of the two bracketed terms in eq 6; the first gives the inherent spectral contrast that shows enhancement at the carbon K edge, and the second represents the sample volume. Evaluation of the first term begins with analysis of the carbon K edge region of the NEXAFS spectra of PS and PI.\(^{34}\) Standard methods are used to convert NEXAFS spectra to \( f_2(\lambda) \).\(^{21}\) \( f_1(\lambda) \) is obtained using the Kramers-Kronig dispersion relation. Tabulated \( f(\lambda) \) values for nonresonant species are available in refs 35 and 36. Substituting the atomic scattering factors into equation 2.3 gives \( n(\lambda) \) (or equivalently \( \beta(\lambda) \) and \( \delta(\lambda) \)) of PS and PI. The \( \beta(\lambda) \) and \( \delta(\lambda) \) values near the carbon K edge for PS and PI thus obtained are shown in Figure 2.1. In both phases we find sharp resonant absorption lines at 285 eV in \( \beta \) that result from dipole transitions from 1s to empty \( \pi^* \) states (this energy is characteristic of C = C double bonds). In contrast, the broad absorption peaks at energies above 288 eV are predominantly from 1s to \( \sigma^* \) transitions. In our RSoXS experiment we exploit the presence of the sharp absorption lines at the \( \pi^* \) resonance. Note that the scattering contrast (equation 2.6) arises from the difference \( n_{\text{PS}} - n_{\text{PI}} \). The \( \pi^* \) resonances in PS and PI have slightly different shapes and intensities due to differences in the carbon-carbon double bond orbital energies in aromatic PS and aliphatic PI. This difference between two sharply peaked functions can be significant even if they are of comparable magnitude and located at similar abscissa values, provided they are sharp enough. The \( \pi^* \) resonances in Figure 2.1 satisfy this criterion. In contrast, the \( \sigma^* \) peaks are much broader and thus are not useful for RSoXS. In this case, the C \( \pi^* \) resonance was used to obtain scattering contrast, but if only one of the component phases contained a light element such as N or O, then the presence and absence of resonant scattering at certain energies (400 eV for N and 530 eV for O) can be the source of the scattering contrast.

In Figure 2.2 we show \( \beta(\lambda)/\lambda^2 \) and \( \delta(\lambda)/\lambda^2 \) of PS and PI over a wide range of energy (100-30000 eV) in which values obtained from measured NEXAFS are spliced into tabulated values away from the carbon K edge.\(^{35}\) It is clear that both \( \beta \) and \( \delta \) contributions are comparable near the carbon K edge. In the hard X-ray range (10000 eV), \( \beta \) is negligible compared to \( \delta \).
Figure 2.1. Real and Imaginary Parts of the Refractive Index $n=1-\delta-i\beta$ for PS and PI Near the Carbon K Edge. Sharp lines near 285 eV correspond to resonant transitions of C = C bonds from 1s to $\pi^*$ states. Features at higher energies result predominantly from transitions to $\sigma^*$ states. Data were evaluated using absorption spectra from ref 34 as described in the text.
Figure 2.2. Imaginary and Real Contributions to the Scattering Amplitude. Imaginary (top) and real (bottom) parts of the scattering amplitude for PS and PI are plotted from below the carbon K edge (~285 eV) into the hard X-ray spectral region (~10,000 eV).
contrast term in equation 2.6, $\Delta n\Delta n^*/\lambda^4$, is the sum of the square of the difference between the $\beta(\lambda)/\lambda^2$ and $\delta(\lambda)/\lambda^2$ curves for PS and PI in Figure 2.2. We plot $\Delta n\Delta n^*/\lambda^4$ vs energy for PS and PI phases in the region near the carbon K edge (Figure 2.3a) and over a wide energy range (Figure 2.3d). At energies above the edge (above ~300 eV), the value of $\Delta n\Delta n^*/\lambda^4$ is remarkably constant. Near the carbon K edge, however, we see an increase in $\Delta n\Delta n^*/\lambda^4$ by about two orders of magnitude. In Figure 2.3b,e we show the energy dependence of the X-ray absorption length, $1/\mu=\lambda/4\pi<\beta>$, where $<\beta>$ is the average value of $\beta$ of PS and PI. In this calculation we use the arithmetic mean of the $\beta$ values of PS and PI. For specific samples, the actual composition of the sample should be used; however, the quantitative features discussed are insensitive to the differences in $<\beta>$. In the hard X-ray range $1/\mu$ approaches the 1-10 cm range, while near the carbon K edge $1/\mu$ is about 100 nm. In Figure 2.3c,f, we plot the scattering intensity obtained by multiplying the contributions in Figure 2.3a,d ($\Delta n\Delta n^*/\lambda^4$) with the contributions in Figure 2.3b,e ($1/\mu$), respectively, assuming that the optimal sample thickness $t_0=1/\mu$ is used to obtain the scattering. The scattering intensity at the resonance from a 100 nm film is only approximately a factor of 100 lower than that obtained in a standard SAXS experiment using hard X-rays and a 1 mm thick film in spite of the decrease in the sample volume by 4 orders of magnitude. It should be clear from Figure 2.3 that the RSoXS signal from PS-b-PI block copolymer thin films is facilitated by both large contrast enhancement and small penetration depth.

In Figure 2.4 we plot the theoretically predicted scattering intensity (line) as a function of energy for a 50 nm thick PS-b-PI film accounting for all of the three terms in equation 2.6 and the finite energy resolution of our instrument. The latter was taken to be a Gaussian function with a full width at half-maximum (fwhm) of 0.2 eV. The symbols in Figure 2.4 show data obtained from SI(7-79) at the lowest order structural peak observed by RSoXS labeled $q^*$ in Figure 2.7a. The two data sets are offset vertically for comparison, and the intensity scale is logarithmic. It is evident that the main features of the experimentally determined $I(h\nu)$ spectrum (location and height of main peak) are in general agreement with this theoretical model. Weaker features away from the predominant $\pi^*$ line at 284.6 eV are in less agreement. This is probably due to differences in spectral features between pure PS and PI used in the model calculations and microphase-separated samples due to the presence of interfaces in the latter case. Additional differences are expected due to structural interference effects that have not been included in the model. In spite of these differences, the level of agreement seen in Figure 2.4 is sufficient to demonstrate the general validity of our theoretical description.

### 2.3.2. Structural analysis of block copolymer thin films

In Figure 2.5 we show a series of scattering intensity versus energy scans obtained at selected angles, using a three-dimensional $I(q, h\nu)$ plot from a 50 nm SI(7-79) thin film. The $q$ value varies slightly along each scan because of the relationship $q=4\pi\sin(\theta/2)/\lambda$. The $\pi^*$ resonance dominates the $I(q, h\nu)$ plots at all scattering angles; indeed the structural peak is not observed above and below the $\pi^*$ resonance energy, emphasizing the essential value of the resonant enhancement in these studies. The thick solid curve in Figure 2.5 shows the scattering profile at $h\nu=284.5$ eV and is analogous to the $I(q)$ scattering profiles observed in typical SAXS experiments in the hard X-ray regime. The primary peak at $q^*=0.2$ nm$^{-1}$ indicates the presence of an in-plane periodic structure.

We first discuss results obtained from a bulk SI(7-79) sample which forms spheres packed on a body-centered cubic (bcc) lattice. The bulk structure was confirmed with SAXS.
Figure 2.3. Origin of the Predicted Scattering Intensity in PS-b-PI Thin Films. (a, d) Square of the scattering contrast between PS and PI vs energy (hv). (b, e) Inverse absorption length, or optimal transmission sample thickness, for a phase-separated PS-b-PI sample vs energy. (c, f) Predicted spectral variation of the scattered intensity given by the products (a) times (b) and (d) times (e) vs energy. The left-hand figures are enlargements of the right-hand figures in the energy range near the carbon K edge.
Figure 2.4. Predicted and Measured Scattering Intensity of PS-b-PI Thin Films. Predicted scattering intensity spectra from a phase-separated PS-b-PI film (line) compares well with a measured spectrum from a 50 nm SI(7-79) thin film (symbols) at $\theta = 3.96^\circ$. The model spectrum is convoluted with a Gaussian of 0.2 eV fwhm to simulate the energy resolution in the measurement, and the curves are offset vertically for clarity.
Figure 2.5. **RSoXS Intensity from a SI(7-79) Thin Film.** RSoXS intensity (in arbitrary units) plotted as a function of energy, $h\nu$, and scattering vector, $q$, near the primary scattering peak of a 50 nm thick SI(7-79) film. At constant scattering angle, maximum scattering intensity is observed at 284.77 eV. A guide to the eye (bold line) shows scattering at constant energy (284.5 eV) in which the primary scattering peak of the block copolymer thin film is at $q \approx 0.2 \text{ nm}^{-1}$. 
using hard X-rays which revealed a primary peak at $q^*=0.223 \text{ nm}^{-1}$ and higher order peaks at 0.271 and 0.312 \text{ nm}^{-1} (Figure 2.6a). The bulk sphere-to-sphere spacing along the unit cell edge ($a_{\text{bulk}}$) was determined to be 39.9 nm from the SAXS analysis. Note that the shortest sphere-to-sphere spacing in a bcc lattice is along the body diagonal and is $\sqrt{3}/2 \cdot a_{\text{bulk}}=34.6$ nm. A broad peak was observed at 0.567 nm$^{-1}$ corresponding to a maximum in the spherical form factor ($R_{\text{micelle}}$). Following the analysis of bcc block copolymer spheres of Thomas, et al.,$^{37}$ we determine the radius of the PS spheres to be 9.2 nm. Our structural characterization results are summarized in Table 2.1.

Microscopy studies of block copolymer thin films indicate that spheres in sphere-forming block copolymers organize on a hexagonal (hex) lattice, although the difference between a hexagonal lattice and the distorted hexagonal lattice of the (110) plane in the bcc lattice is subtle.$^{37, 38}$ In Figure 2.7a we show an AFM micrograph of SI(7-79). The use of AFM to quantify lateral domain spacing is complicated by the fact that the instrument alternately compresses and stretches images in the slow scan direction of successive scans due to drifting of the piezo.$^{39}$ Small amounts of drift are associated not only with previous changes in scan location and scan size but also with the presence of drafts and gradients in ambient temperature and are generally unavoidable. This effect can best be seen by examining the asymmetry of two-dimensional Fourier transforms of the position space data along the slow and fast scan directions. This asymmetry was corrected, in this work, by compressing or expanding the data along the slow scan axis to achieve images with symmetric 2D Fourier transforms. Both the position space image and the 2D Fourier transform shown in Figure 2.7a were obtained after these corrections were made. The presence of numerous spots in the Fourier transform indicates the presence of numerous grains in the scanned portion of the sample with concomitant defects. The difference between the (110) closest packed plane of a bcc structure and the close-packed hexagonal lattice is only a very subtle stretching along the 100 direction of the bcc lattice. Resolving between these structures with position space images is thus not easy when the sample contains many defects and the raw images exhibit likely distortions. It is thus difficult to establish the symmetry of the lattice formed by SI(7-79) based on the position space data in Figure 2.7a.

In Figure 2.7b we show RSOXS $I(q, \nu h=284.5 \text{ eV})$ of SI(7-79) in a log-linear format. The sharp primary scattering peak at $q^*=0.200 \text{ nm}^{-1}$ and higher order peaks at $\sqrt{3}q^*$ and $2q^*$ are clear signatures of the presence of layers of hexagonally packed spheres. The missing $\sqrt{2}q^*$ peak, which is a signature of scattering from a bcc lattice, demonstrates the difference between the bulk and thin film structure. The sphere-to-sphere spacing of 36.3 nm determined by RSoXS ($a_{\text{film}}$) is within experimental error of the sphere spacing as measured by AFM (34.9 nm) (Table 2.1).

Experiments were also conducted with SI(4-35), which forms hexagonally packed cylinders in the bulk. The bulk structure was confirmed with SAXS with a primary peak observed at $q^*=0.309 \text{ nm}^{-1}$ and higher order peaks at 0.529, 0.806, and 0.908 nm$^{-1}$ (Figure 2.6b). The bulk cylinder-to-cylinder spacing ($c_{\text{bulk}}$) was determined to be 23.5 nm by SAXS.

In Figure 2.8a we show an AFM micrograph of a 50 nm film of SI(4-35). The PS cylinders are observed to orient with their long axis parallel to the SiO$_2$ surface based on the lower surface energy between PI and both the SiO$_2$ and free surfaces present in the thin film. This observation is consistent with previous observation of PI wetting layers at both the free and SiO$_2$ surfaces in block copolymer thin films of PS spheres in a PI matrix.$^{33}$ The AFM image has been corrected for piezo drift by the previously described method to produce symmetric 2D
Figure 2.6. Bulk SAXS of SI(7-79) and SI(4-35) Copolymers. (a) SAXS of SI(7-79) shows a primary peak at $q^* = 0.223 \text{ nm}^{-1}$ and higher order peaks at 0.295 \text{ nm}^{-1} and 0.381 \text{ nm}^{-1}$ corresponding to body-centered cubic spheres. The broad peak at $q = 0.567 \text{ nm}^{-1}$ corresponds to a maximum in the scattering form factor. Our definition of the bulk lattice spacing, $a_{\text{bulk}}$, is shown on the bcc lattice (inset). (b) SAXS of SI(4-35) shows a primary peak at $q^* = 0.309 \text{ nm}^{-1}$ and higher order peaks at 0.529, 0.806, and 0.908 \text{ nm}^{-1}$ corresponding to cylinders on a hexagonal lattice. Our definition of the bulk cylinder-to-cylinder spacing, $c_{\text{bulk}}$, is shown on the hex lattice (inset).
Figure 2.7. AFM and RSoXS of a SI(7-79) Thin Film. (a) AFM phase image of a 50 nm thick sphere-forming SI(7-79) film. Fourier transform of the phase image (inset) demonstrates a high degree of local order, but overall polycrystallinity in the sample. (b) RSoXS at the carbon edge (284.5 eV) of a 50 nm thick SI(7-79) film. A primary peak at 0.200 nm$^{-1}$ is observed along with higher order reflections corresponding to $\sqrt{3}q^*$ and $2q^*$ confirming hexagonal arrangement of PS spheres in the PI matrix.
Figure 2.8. **AFM and RSoXS of a SI(4-35) Thin Film.** (a) AFM phase image of a 50 nm thick cylinder-forming SI(4-35) film. The cylinders lie parallel to the surface. A preferred orientation of PS cylinders is demonstrated by the Fourier transform of the phase image (inset). (b) RSoXS at the carbon edge (284.5 eV) of a 50 nm thick SI(4-35) film. A primary peak at 0.261 nm$^{-1}$ is observed along with 2$q^*$ and 3$q^*$ higher order reflections, confirming that the cylinders are parallel to the surface.
Fourier transforms. The two regions of high intensity in the 2D Fourier transform (inset, Figure 2.8a) show a preferred orientation of many PS cylinders in the 1.5 x 1.5 µm AFM scan, indicating the presence of a large grain within the scan.

In Figure 2.8b we show RSoXS I(q, hv=284.5 eV) of the SI(4-35) thin film in a log-linear format. A sharp primary scattering peak is seen at q* = 0.261 nm⁻¹. The second-order peak at 2q* is much stronger than the third-order peak at 3q*. As discussed earlier, the films used in this study were not smooth and in fact contained a fractional coverage of a second layer of cylinders. This is one major advantage of the RSoXS technique: the presence of surface structures is not detrimental, and in fact RSoXS may be used to understand the relationship of structure in these layers. We expect the second layer to register with and orient parallel to the first layer but with second layer cylinders located in the gaps between first layer cylinders.40 Because the scattering vector is oriented strictly in the film plane for these data, the RSoXS peaks reflect the projected in-plane spacing of the one- or two-layer thick regions. The relevant periodicity in the monolayer regions is simply the nearest-neighbor spacing, while that in the bilayer regions is precisely half of this value. With this understanding we note that the sharp primary peak at q* = 0.261 nm⁻¹ corresponds to a cylinder-to-cylinder spacing (c_film) of 24.1 nm, which is quite close to the bulk spacing obtained by SAXS (Table 2.1). This q* peak is forbidden in the bilayer regions leading to the conclusion that only the monolayer regions contribute to the q* peak. For the bilayer regions the fundamental peak occurs at 2q*. Furthermore, the 2q* peak from the bilayer regions results from the same spacing as the \( \sqrt{3}q^* \) peak in the bulk sample. Possible higher harmonics of q* from monolayer regions are allowed at nq* for n=2, 3, 4, …, and for the bilayer regions at twice these values. Thus, the 2q* peak can have contributions from both mono- and bilayer regions, while the just visible feature at 3q* results from monolayer regions only.

For SI(4-35), the nearest-neighbor spacing between PS cylindrical domains is measured to be 3 ± 4% larger in the thin film compared to the bulk (c_bulk/c_film). For SI(7-79), the nearest-neighbor spacing observed in the plane of the thin film is between the two relevant distances in the bcc lattice: spacings between the 100 planes (a_bulk/a_film=1.10 ± 0.04) and the nearest neighbor spacing (\( \sqrt{3}/2^{*}a_{bulk}/a_{film}=0.95 ± 0.04 \)). This finding appears consistent with the expected rearrangement of spheres from 2D hexagonal planes in thin films to bcc lattices in the bulk,37,41 a more in-depth understanding of surface reconstruction and the effect of film thickness on nanostructure is the subject of ongoing work.

2.4. Conclusions

The ability to characterize the lateral order over large areas of block copolymer thin films has been demonstrated using RSoXS. We have shown theoretically that the combination of small differences in the strong \( \pi^{*} \) resonance of PS and PI and the polymers’ small absorption length in the soft X-ray regime can be exploited to obtain sufficient scattering intensity to overcome the roughly 4 orders of magnitude decrease in sample volume in a thin film sample vs a typical SAXS sample. The energy-dependent scattering intensity measured from PS-b-PI films compares qualitatively with theoretically predicted scattering profiles. RSoXS characterization of block copolymer thin films should be extendable to any block copolymer system in which a resonant transition is sharply defined with respect to energy. The resonant transition should be sufficiently spaced vis-à-vis other resonant transitions and with respect to the energy resolution limit of the monochromator. The lateral order of sphere- and cylinder-forming PS-b-PI thin films was characterized with AFM and RSoXS. Two-dimensional Fourier transforms of the real
space AFM images demonstrated localized order; however, definitive assignment of the lattice type is complicated due to drift of the AFM piezo. In contrast, RSoXS scattering profiles revealed higher order peaks, enabling the unambiguous assignment of lattice type as well as characterization over surface areas ~1000 times larger than single AFM scans. The sphere-to-sphere spacing in thin films was found to be between the bulk nearest-neighbor spacing ($\sqrt{3/2}a_{\text{bulk}}$) and the bulk lattice spacing ($a_{\text{bulk}}$), while the cylinder-to-cylinder spacing was found to be conserved between the bulk and thin film form within experimental error.

2.5. Acknowledgements

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2.6. References


Chapter 3. Phase Behavior of Polystyrene-block-Poly(2-vinyl pyridine) Copolymers in a Selective Ionic Liquid Solvent

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The phase behavior of poly(styrene-block-2-vinyl pyridine) copolymer solutions in an imidazolium bis(trifluoromethane)sulfonamide ([Im][TFSI]) ionic liquid has been studied using small angle X-ray scattering (SAXS) and optical transmission characterization. Through scaling analysis of SAXS data, we demonstrate that the [Im][TFSI] ionic liquid behaves as a selective solvent toward one of the blocks. We observe lyotropic and thermotropic phase transitions that correspond qualitatively to the phase behavior observed in block copolymer melts and block copolymer solutions in molecular solvents. In addition, we have studied the thermal properties of block copolymer solutions in the ionic liquid using differential scanning calorimetry and wide angle X-ray scattering. We observe distinct composition regimes corresponding to the change in the block copolymer’s glass transition temperature, \( T_g \), with respect to the concentration of polymer in ionic liquid. At high block copolymer concentrations, a “salt-like” regime corresponding to an increase in the block copolymer \( T_g \) is observed, while at intermediate block copolymer concentrations, a “solvent-like” regime, corresponding to a decrease in the block copolymer \( T_g \) is observed. An unusual thermal transition consisting of crystallization and subsequent melting of the ionic liquid is observed at the lowest block copolymer concentration characterized.

3.1. Introduction

Ionic liquids are a novel class of solvents composed entirely of ions which exhibit exceptional physiochemical properties, such as nonflammability, negligible vapor pressure, high ionic conductivity, and electrochemical stability.\(^1\) The outstanding electrochemical properties of ionic liquids have led to studies involving their use in lithium battery electrolytes,\(^2,3\) fuel cells,\(^4-8\) and dye-sensitized solar cells.\(^9-12\) While the need for introducing ionic liquids into a solid supporting matrix for these applications has been recognized,\(^13\) the combination of block copolymers and ionic liquids results in a new class of functional materials with intricate structure on the nanometer scale.\(^14\) The structure is created by block copolymer self-assembly, while the functionality is obtained by exploiting the properties of ionic liquids. Block copolymer/ionic liquid systems enable the design of materials whose ion-conducting and mechanical properties can be separately optimized.

Effects resulting from the addition of both selective and non-selective molecular solvents to block copolymers on both the self-assembled nanostructure and the thermodynamic driving forces affecting self-assembly have been extensively investigated using both experiments\(^15-17\) and theory.\(^18-20\) At fixed temperature, the addition of solvents to diblock copolymers results in a rich variety of lyotropic phase transitions.\(^15,16\) The temperature dependence of interactions between the two blocks, and interactions between the blocks and the solvent, lead to an additional set of thermotropic phase transitions. Lai et al. observed temperature dependent scaling behavior of the characteristic domain spacing in polystyrene-block-poly(isoprene) (SI) copolymer solutions in selective solvents.\(^21\) This observation was attributed to the temperature dependence of the
solvent/block copolymer segment interaction parameter, leading to changes in solvent partitioning between the polystyrene and polyisoprene microphases as temperature was varied. Hanley et al. have shown that thermotropic properties of mixtures of SI copolymers and diethyl phthalate arise from the temperature dependence of solvent selectivity. \(^{18}\) Alexandridis et al. have conducted a thorough investigation of the phase behavior of PEO-block-poly(propylene oxide)-block-PEO copolymers (Pluronic) in water, a solvent that is selective toward the PEO block. \(^{22}\) One of the observations of Alexandridis et al. was the strong temperature dependence of micelle formation in dilute Pluronic/water mixtures. \(^{23}\) The temperature dependence of block copolymer/solvent interactions, however, is not universal across all systems. For example, Hadjuk et al. observed weak temperature dependence of solvent/polymer interactions in concentrated solutions of an asymmetric PEO-block-poly(ethylene) copolymer in water, \(^{24}\) despite strongly thermotropic interactions between PEO and water. \(^{25}\) These findings suggest that block copolymer composition and the local structure of water molecules surrounding the PEO segments play an important role in determining the phase behavior of copolymer solutions containing PEO blocks.

Water-containing polyelectrolyte membranes are of interest for fuel cell applications \(^{26, 27}\) and the incorporation of nanostructure has recently been shown to significantly improve water uptake, while maintaining mechanical stability. \(^{28, 29}\) Incorporation of ionic liquids into polymer membranes is also of interest due to their high conductivities and potential use at elevated temperatures. \(^{5, 30, 31}\) Several approaches towards achieving solid, nanostructured ionic-liquid-containing polymer films have been demonstrated. Ohno et al. synthesized ion conducting polymers with ionic liquid groups tethered to flexible side chains of vinyl-based monomers. \(^{32}\) Susan et al. prepared ionic gels through in situ polymerization of poly(methyl methacrylate) (PMMA) in a (1-ethyl-3-methylimidazolium bis(trifluoromethane)sulfonamide ([EMI][TFSI]) ionic liquid. \(^{13}\) Matsuoka et al. synthesized a polybase with a coupled phenylene/oxadiazole repeat unit and doped HTFSI into this solid matrix. \(^{5}\) Yoshio et al. incorporated an ionic liquid moiety into liquid crystalline molecules that were self-assembled and then photopolymerized into well-defined nanostructures. \(^{33}\) He et al. produced ABA triblock copolymer gels by co-dissolving small amounts of block copolymer and ionic liquid with a co-solvent and subsequent removal of the solvent. \(^{34}\) These ionic gels exhibit conductivities comparable to the neat ionic liquid and possess significant mechanical strength. In work closely related to the present study, Simone and Lodge studied the lyotropic phase behavior of poly(butadiene)-block-poly(butylene-1,4-oxide)-block-PEO (PB-block-PEO) copolymer solutions in two imidazolium ionic liquids ([EMI][TFSI] and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMI][PF\(_6\)]), and demonstrated that the ionic liquids behave essentially as a selective solvent. \(^{14}\)

The addition of charged species affects the thermal properties of both homopolymers and block copolymers. The addition of salt to PEO increases the glass transition temperature (\(T_g\)) of the polymer due to physical crosslinking of the polymer chains. \(^{35}\) This effect has also been observed in samples comprised of a block copolymer and salt. \(^{36}\) In PMMA ionic gels containing an [EMI][TFSI] ionic liquid, Susan et al. observed a monotonic decrease in the \(T_g\) of PMMA as the concentration of ionic liquid was increased, suggesting a solvent-like plasticizing effect of the ionic liquid. \(^{13}\) In PEO ionic gels containing a related imidazolium ionic liquid, Klingshirn et al. observed values of the \(T_g\) and the crystallization and melting temperatures (\(T_c\) and \(T_m\), respectively) of the ionic liquid within the gel that were identical to that of the pure ionic liquid, leading to the conclusion that the bulk ionic liquid existed in a free, unbound environment within the PEO gel. \(^{37}\) These reports suggest that the specific chemistries of the polymer/ionic liquid,
along with the ionic gel structure play a critical role in affecting the thermal properties of the composite material.

In this study, we report on the thermotropic and lyotropic phase behavior of a poly(styrene-block-2-vinyl pyridine) (S2VP) copolymer in an imidazolium bis(trifluoromethane)sulfonamide ([Im][TFSI]) ionic liquid (Figure 3.1). We expect the ionic liquid to associate preferentially with the poly(2-vinyl pyridine) block. This system was chosen because the imidazolium cation can complex with H\(^+\) in the absence of water to provide a non-hydrated proton-conducting medium. The S2VP copolymer in [Im][TFSI] ionic liquid thus serves as a model system for a non-hydrated proton exchange fuel cell membrane.

3.2. Experimental Section

Polymer Synthesis and Characterization. A poly(styrene-block-2-vinyl pyridine) copolymer and poly(2-vinyl pyridine) (P2VP) homopolymer were synthesized via anionic polymerization using standard methods.\(^{38}\) The molecular weight of the polystyrene (PS) homopolymer was determined using gel permeation chromatography (GPC) and the total molecular weight of the block copolymer determined via \(^1\)H NMR (Bruker AVB-300). The molecular weight of the P2VP homopolymer was determined using \(^1\)H NMR end-group analysis. The polydispersity of each polymer was assessed using GPC. The poly(styrene-block-2-vinyl pyridine) copolymer is designated S2VP(13-15), where the numbers in parentheses refer to the number averaged molecular weights in kg/mole of the PS and P2VP blocks, respectively. The P2VP homopolymer is designated P2VP(20), where the number in parentheses refers to the number averaged molecular weight in kg/mole. The measured polydispersity of S2VP(13-15) was 1.10, while the that of P2VP(20) was 1.12.

Ionic Liquid Purification. Imidazole (≥95%) and bis(trifluoromethane)sulfonamide (HTFSI, ≥95%) were purchased from Sigma Aldrich and purified by sublimation under vacuum. Differential scanning calorimetry (DSC) and \(^1\)H NMR were used to assess the purity of the two starting materials. Purified imidazole and HTFSI were combined in equimolar quantities in a glove box, sealed, and heated in an oven outside the glove box to 100 °C for 2-3 hours to prepare the ionic liquid [Im][TFSI]. The composition of the ionic liquid was confirmed by comparing the measured melting point of the compound, using DSC, with literature.\(^4\)

X-ray Scattering Sample Preparation and Methods. Dichloromethane was degassed using three freeze, pump, thaw cycles, stirred over CaH\(_2\) overnight, then distilled into a collection flask, brought into a glove box, and stored on molecular sieves. Predetermined quantities of [Im][TFSI] and S2VP(13-15) were weighed into glass vials, and ca. 5 wt% solutions were prepared using dichloromethane in the glove box. Solutions were stirred overnight. Samples were cast into sample cells with an aluminum spacer sealed onto a Kapton window on one side in the glove box. The polymer/ionic liquid solution was put into the sample cell one drop at a time. Solvent was allowed to evaporate before addition of the next drop until a ca. 1 mm solid sample was obtained in the sample cell. Samples were heated to 60 °C (above the boiling point of dichloromethane) in the glove box for ca. 18 hours to remove remaining solvent. A second Kapton window was glued to seal the samples which were stored with desiccant when outside the glove box to reduce the chance of water contamination. Samples are designated by the value of the estimated polymer volume fraction (for both S2VP and P2VP solutions), \(\phi_P\), assuming ideal mixing. The density of [Im][TFSI] was estimated to be 1.67 g/cm\(^3\) from scattering length density fits of small-angle neutron scattering (SANS) intensity profiles\(^{39}\) and the densities of PS and P2VP were taken to be 1.15 and 1.05 g/cm\(^3\), respectively.
Figure 3.1. Chemical Structure of [Im][TFSI] and S2VP Copolymer. Imidazolium bis(trifluoromethane)sulfonamide ([Im][TFSI]) ionic liquid and the poly(styrene-block-2-vinyl pyridine) (S2VP) copolymer chemical structures.
Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) were performed on beamline 7.3.3 of the Advanced Light Source (ALS), and SAXS was performed on beamline 1-4 of the Stanford Synchrotron Radiation Laboratory (SSRL). At the ALS, the beamline was configured with an X-ray wavelength of 1.240 Å and focused to a 50 by 300 µm spot. Full two-dimensional scattering patterns were collected on an ADSC CCD detector with an active area of 188 by 188 mm. The scattering patterns were radially averaged and the scattering intensity corrected with the post-ion chamber intensity using Nika version 1.18. At SSRL, the beamline was configured with an X-ray wavelength $\lambda = 1.488$ Å and focused to a 0.5 mm diameter spot. A single quadrant of a two-dimensional scattering pattern was collected on a CCD detector with an active area of 25.4 by 25.4 mm. The scattering patterns were radially averaged and corrected for detector null signal, dark current, and empty cell scattering.

**Optical Transmission Sample Preparation and Methods.** Samples were prepared between two quartz windows with a 0.5 mm Teflon spacer. Samples were solvent cast from dichloromethane solutions in a manner similar to X-ray scattering sample preparation. All samples were prepared and sealed within a glove box to minimize water exposure. Optical transmission measurements were performed on a home-built instrument as previously described. Samples were heated to 145 °C, annealed for 1 hour, and then cooled to room temperature. This process was repeated twice for each sample. We report values of the transmitted intensity of a HeNe laser beam ($\lambda = 632.8$ nm) normalized by that of the incident beam.

**Differential Scanning Calorimetry Sample Preparation and Methods.** Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2920. Samples were solution cast in a glove box into aluminum DSC pans from the same solutions used to prepare X-ray scattering samples. The samples were heated to 60 °C in the glove box for ca. 18 hours to remove remaining solvent. The samples were then crimped within the glove box using hermetically sealed pans and placed inside a container with desiccant for transfer to the DSC. Indium and dodecane were used as calibration standards for the DSC. Samples underwent three heating and cooling cycles and glass, crystallization, or melting transitions were recorded upon the second heating.

**Thermal Gravimetric Analysis Sample Preparation and Methods.** Thermal gravimetric analysis (TGA) was performed on a TA Instruments TGA 2950. Samples were solution cast under the same conditions used for DSC sample preparation into open platinum pans, and dichloromethane was removed in a similar manner. Samples were heated at 5 °C/min from 30 °C to 450 °C under a nitrogen atmosphere.

### 3.3. Results and Discussion

Representative SAXS profiles from varying concentrations of S2VP(13-15) in the [Im][TFSI] ionic liquid are shown in Figure 3.2. All of the scattering profiles were recorded at 145 °C, well above the glass transition temperature of the neat copolymer. The neat copolymer exhibits a lamellar morphology with peaks at $q=q^*, 2q^*$ and $3q^*$, where $q=(4\pi/\lambda)\sin(\theta/2)$, $\theta$ is the scattering angle, and $q^*$ is the value of $q$ at the primary scattering peak. The center-to-center distance between adjacent PS lamellae, $d=2\pi/q^*$, is 19.9 nm, in the case of the neat copolymer. A qualitatively similar lamellar phase with $d=23.6$ nm is obtained in the $\phi_P=0.93$ sample. The large change in the domain spacing upon addition of a small amount of ionic liquid is noteworthy. This expansion is also seen in the $\phi_P=0.86$ sample, which exhibits a lamellar morphology. There are, however, significant differences when one compares the neat block
Figure 3.2. SAXS Intensity Profiles of S2VP/[Im][TFSI] Mixtures. $\phi_P=0.28$ to $\phi_P=1.0$ S2VP(13-15) copolymer in [Im][TFSI] (offset for clarity). In all cases, the peak labels correspond to the $q/q^*$ for scattering peaks of a particular composition.
copolymer (and the \( \phi_P=0.93 \) sample) to the \( \phi_P=0.86 \) sample. The \( \phi_P=0.86 \) sample shows peaks that are significantly broader compared to the neat S2VP(13-15) copolymer. The peak at \( q=2q^* \) is distinctly bimodal. These facts suggest the existence of two populations of lamellae with \( d=26.2 \) and 27.5 nm. Roughly 55% of the higher order peak at \( 2q^* \) and 86% at \( 3q^* \) can be attributed to lamellae with \( d=26.2 \) nm. We propose that this indicates the presence of two coexisting phases with unequal amounts of ionic liquid.

As the concentration of S2VP copolymer is decreased to \( \phi_P=0.78 \), the primary scattering peak becomes bimodal. The locations of the higher order peaks indicate the coexistence of lamellar and hexagonally-packed cylindrical microstructures with \( d=26.9 \) and 28.7 nm, respectively. For the cylindrical phase, \( d \) represents the spacing between adjacent 110 scattering planes. The presence of higher order scattering peaks at \( \sqrt{7}q^* \) and \( \sqrt{12}q^* \) indicate regions of hexagonally-packed cylinders within the sample, while the breadth of the \( 2q^* \) and \( 3q^* \) peaks is attributed to the distinct characteristic length scales of lamellae and cylinders. The absence of a peak at \( \sqrt{3}q^* \) is due to a minimum in the form factor of scattering from cylinders with a 10.5 nm radius.\(^{41}\) The radius was determined using the composition of the sample and assuming that the ionic liquid resides exclusively in the P2VP microphase. It appears that the larger lamellae seen in the \( \phi_P=0.86 \) sample give rise to the hexagonal phase at \( \phi_P=0.78 \). The coexistence of microstructures persists after a long (24 hour) preanneal at 145 °C prior to SAXS characterization and also after annealing the sample at 145 °C for 30 minutes on the SAXS beamline. In general, we find the microphase-separated structures observed in S2VP(13-15) copolymer/[Im][TFSI] solutions to be stable over long periods of time. Samples stored 1-2 months at room temperature in the glove box exhibit the same microphase-separated structure and thermodynamic transitions as samples prepared immediately prior to SAXS experiments. As the concentration of the S2VP(13-15) copolymer is further reduced to \( \phi_P=0.70 \), the SAXS profile reveals a single hexagonally-packed cylinder phase (Figure 3.2). The scattering intensity of the \( \sqrt{7}q^* \) and \( \sqrt{12}q^* \) peaks is observed to increase dramatically compared to the \( \phi_P=0.78 \) sample, while the scattering intensity of the \( 3q^* \) and \( 4q^* \) scattering peaks decreases.

The data obtained from the \( \phi_P=1.0 \) to \( \phi_P=0.70 \) samples in Figure 3.2 establishes a lamellae-to-hexagonally packed cylinder lyotropic phase transition upon the addition of ionic liquid. It is important to note that the Gibbs phase rule requires a coexistence window between two single phase regions in any binary mixture. This coexistence is clearly seen in data from the \( \phi_P=0.86 \) and \( \phi_P=0.78 \) samples in Figure 3.2. Since the coexistence window must contain the two single phases that lie on either side of the window,\(^{42}\) we conclude that the \( \phi_P=0.78 \) sample is at equilibrium while the \( \phi_P=0.86 \) sample is not. We propose that equilibration at \( \phi_P=0.86 \) is not possible within our experimental window due to small quench depth. Hexagonally-perforated lamellae have been determined to be non-equilibrium phases in bulk diblock copolymer systems,\(^{43}\) as well as studies of block copolymers in selective molecular solvents,\(^{44}\) and do not appear in the present system.

At a composition of \( \phi_P=0.50 \), we observe the emergence of the \( \sqrt{3}q^* \) scattering peak, along with the presence of \( \sqrt{7}q^* \), \( 3q^* \), and \( 4q^* \) higher order scattering peaks (Figure 3.2). The \( 2q^* \) scattering peak is not observed, due to a minimum in the form factor of scattering from cylinders with a 10.2 nm radius. Further reduction of the block copolymer concentration to \( \phi_P=0.40 \) results in increased broadening of the primary scattering peak and a decrease in the scattering intensity. A further decrease in scattering intensity and broadening of the main peak is seen in the \( \phi_P=0.28 \) sample (Figure 3.2). The scattering profile from these two samples is similar to those found from micellar phases without long-range order.\(^{14, 18, 45}\) A plot of the full-width at
half-maximum (fwhm) of the primary scattering peak at 145 °C as a function of block copolymer concentration (Figure 3.3) shows three regimes. The smallest values of fwhm are obtained in the lamellar samples, intermediate values are obtained in the coexistence window and the cylindrical samples, and large values are obtained in the micellar samples. The optical transmission coefficient of the S2VP(13-15) copolymer in [Im][TFSI] solutions at 145 °C shows a dramatic decrease as the concentration of block copolymer is reduced from $\phi_P=0.50$ to $\phi_P=0.40$, and continues to decrease for the $\phi_P=0.28$ sample (Figure 3.3). Single–phase, anisotropic block copolymers (lamellar and cylindrical phases) are generally transparent and birefringent. The optical characteristics of the $\phi_P=0.50$ sample were consistent with this expectation, while those of $\phi_P=0.28$ and $\phi_P=0.40$ were not. Based on the optical and SAXS experiments, we conclude that samples with $\phi_P=0.28$ and $\phi_P=0.40$ are a micellar phase with liquid-like local structure. In the case of cylinder phases, it has been shown that small grain sizes may prevent the observation of birefringence; however in the $\phi_P=0.28$ and $\phi_P=0.40$ samples we do not know the origin of the low optical transmission coefficient in the micellar samples. The transition from ordered microstructures to disordered micelles occurs at $\phi_P=0.45 \pm 0.05$.

In related studies of block copolymer/ionic liquid mixtures, Simone and Lodge discovered the presence of disordered networked cylinders between lamellar and hexagonally-packed cylinder regions of the phase diagram. The optical properties of the disordered network phase were not presented in ref. 14. Further work is needed to determine if the disordered phase observed in our system has a similar morphology, or if it more closely related to spherical micelles with liquid-like local structure observed in diblock copolymer melts.

Both experimental and theoretical studies have previously shown that the addition of non-selective solvents leads to a decrease in $d$ due to screening of unfavorable interactions between the two block copolymer segments. In the case of selective solvents, Banaszak and Whitmore used self-consistent mean-field theory (SCFT) to show that addition of a selective solvent results in an increase in $d$ due to changes in the configuration of the polymer chains as they minimize unfavorable thermodynamic interactions between the selective solvent and block copolymer segment with poor solubility in the solvent. The domain spacing of a block copolymer swollen with a selective solvent has been shown experimentally and theoretically to follow the power law:

$$d \sim \phi_P^\alpha$$  \hspace{1cm} (3.1)

where $\alpha$ depends on solvent-polymer interactions and interfacial curvature. In Figure 3.4, we plot the SAXS domain spacing from the primary 100 scattering peak of lamellar S2VP(13-15)/[Im][TFSI] mixtures, versus $\phi_P$ ($0.93 \leq \phi_P \leq 1.0$). We observe $\alpha$ values of -2.31 and -3.16 at temperatures of 145 °C and 225°C, respectively. The negative values of $\alpha$ are not surprising as it demonstrates selectivity of the [Im][TFSI] ionic liquid solvent towards one segment of the S2VP(13-15) copolymer, which we believe to be the P2VP block. Our finding is in qualitative agreement with the selective solvent domain scaling behavior observed by Simone and Lodge using a PB-block-PEO copolymer in imidazolium ionic liquids. Previous studies on the effect of temperature on solvent selectivity for molecular solvents such as water and high boiling point organics have obtained $\alpha$ values that are sensitive functions of temperature due to the temperature dependencies of the underlying thermodynamic factors. This appears to also be true for the S2VP(13-15)/[Im][TFSI] system. Based on the temperature dependence of $\alpha$, SCFT of mixtures of block copolymers and selective molecular solvents, and this limited data set, we are led to the conclusion that the selectivity of [Im][TFSI] toward the P2VP block increases with increasing temperature.
Figure 3.3. SAXS fwhm and Optical Characterization of S2VP/[Im][TFSI] Mixtures. fwhm from the SAXS primary scattering peak (left axis, ○) and optical transmission coefficient (right axis, ▲) plotted as a function of block copolymer volume fraction, $\phi_P$, at 145 ± 5°C.
Figure 3.4. Ionic Liquid Selectivity in S2VP/[Im][TFSI] Mixtures. Domain spacing, $d$, versus block copolymer volume fraction, $\phi_P$, determined from SAXS data at 145 °C (□) and 225 °C (▲). These plots are used to assess the ionic liquid’s solvent selectivity for the S2VP(13-15) copolymer, using a power law fit, $d \sim \phi_P^\alpha$ to obtain $\alpha$. At 145 °C, $\alpha = -2.31$, and at 225 °C, $\alpha = -3.16$. 
Figure 3.5. Temperature and Composition Dependence of Domain Size in S2VP/[Im][TFSI] Mixtures. Primary SAXS peak position of S2VP/[Im][TFSI] mixtures, $q^*$, plotted as a function of temperature for (a) $\phi_P=1.0$ (□), neat copolymer, $\phi_P=0.99$ (▲), $\phi_P=0.97$ (○), and $\phi_P=0.86$ (■), and (b) $\phi_P=0.78$ (▲), $\phi_P=0.70$ (■), $\phi_P=0.50$ (Δ), $\phi_P=0.40$ (□), and $\phi_P=0.28$ (○).
The temperature dependence of q* for S2VP(13-15)/[Im][TFSI] mixtures over a wide concentration range is shown in Figure 3.5. At high S2VP(13-15) concentrations (φP ≥ 0.97), q* increases with increasing temperature (Figure 3.5a). In this regime of low ionic liquid concentration, we expect the interactions between the PS and P2VP segments to dominate. This would lead to an increase in q* with increasing temperature due to a decrease of the Flory-Huggins interaction parameter between PS and P2VP, \( \chi_{PS/P2VP} \). The data in Figure 3.5a are consistent with this expectation. While we believe that the \( \chi_{PS/P2VP} \) interaction parameter dominates in this composition range, it is instructive to examine the temperature dependence of domain size in block copolymer/salt mixtures. In systems based on LiClO\(_4\) salts in triblock copolymers containing a PEO segment, small decreases in domain spacing upon heating were attributed to the physical crosslinking behavior of the salt,\(^{51}\) in agreement with results from the S2VP(13-15)/[Im][TFSI] system. At intermediate block copolymer concentrations (0.40 ≤ φP ≤ 0.86), the domain spacing is nearly independent of temperature at low temperatures, while q* decreases rapidly at high temperatures as the samples approach the order-disorder transition (ODT) temperature (Figures 3.5a and b). For φP = 0.28, the domain spacing is nearly independent of temperature. In contrast, both experiments and SFCT indicate that q* of block copolymers in selective molecular solvents increases with increasing temperature, regardless of polymer concentration.\(^{44, 50}\)

While we have not yet modeled interactions between ionic liquids and block copolymers, there is little doubt that substantial extension of the standard SCFT will be needed to describe the self-assembly of these systems.

In Figure 3.6a we show the temperature dependence of the SAXS profile of the φP = 0.99 sample. At 145 °C, the sample exhibits a lamellar morphology, as seen by the 2q* and 3q* higher order scattering peaks. When the sample is heated to 235 ± 10 °C, the higher order peaks disappear. This is one of the signatures of an order-disorder transition.\(^{52, 53}\) Figure 3.6b shows the dependence of the value of I(q*) and the fwhm of the primary SAXS peak versus temperature. The discontinuity in the value of I(q*) at 235 ± 10°C is a standard signature of an ODT and we conclude that the φP = 0.99 sample undergoes an ODT at 235 ± 10°C. An abrupt broadening of the primary scattering peak when the ordered phase gives way to the disordered phase is a typical signature of the ODT in neat block copolymers and block copolymers dissolved in molecular solvents. However, in the φP = 0.99 sample, there is no abrupt change in fwhm at the ODT as seen in Figure 3.6b.

In Figure 3.7a, we plot the SAXS intensity versus q from the φP = 0.70 sample at selected temperatures above the \( T_g \) of the neat block copolymer (94 °C). At 145 °C, the sample exhibits a hexagonally-packed cylinder morphology, as evidenced by the \( \sqrt{3}q^* \), \( 2q^* \), \( \sqrt{7}q^* \), and 3q* higher order scattering peaks. Samples annealed for 24 hours at 145 °C exhibit the same hexagonally-packed cylinder morphology, indicating that this morphology is not dependent on processing history. This morphology persists upon heating until 225 ± 10°C when an order-order transition (OOT) to a lamellar microstructure is observed, as evidenced by the disappearance of higher order scattering peaks corresponding to hexagonal symmetry and the persistence of the 2q*, 3q*, and 4q* higher order scattering peaks. Upon heating to 235 ± 10°C, all higher order scattering peaks disappear and the primary peak broadens considerably. In Figure 3.7b, we show the temperature dependence of both the value of I(q*) and fwhm for the φP = 0.70 sample. The SAXS signatures of this sample are consistent with those obtained in neat block copolymers and their mixtures with molecular solvents at the ODT, i.e. the higher order peaks disappear and the fwhm of the primary peak increases abruptly as the ODT is crossed.\(^{52, 54, 55}\) In contrast, crossing the cylinder-to-lamellae transition results in an increase in I(q*) and a decrease in fwhm. Sequential
Figure 3.6. ODT in a $\phi_p=0.99$ S2VP/[Im][TFSI] Mixture. (a) SAXS intensity profiles (offset for clarity) of $\phi_p=0.99$ S2VP(13-15) in [Im][TFSI] at varying temperatures. In all cases, the peak labels correspond to the $q/q^*$ for scattering peaks. (b) Plot of $I(q^*)$ (denoted ■) and fwhm (denoted Δ) versus temperature (°C). The ODT is identified as the point at 235 ± 10 °C (vertical arrow).
Figure 3.7. ODT in a $\phi_P=0.70$ S2VP/[Im][TFSI] Mixture. (a) SAXS intensity profiles (offset for clarity) of $\phi_P=0.70$ S2VP(13-15) in [Im][TFSI] at varying temperatures. In all cases, the peak labels correspond to the $q/q^*$ for scattering peaks. (b) Plot of $I(q^*)$ (denoted ■) and fwhm (denoted △) versus temperature ($^\circ$C). The OOT and ODT are identified at 225 ± 10 $^\circ$C and 235 ± 10 $^\circ$C, respectively (vertical arrows).
cylinder-to-lamellae-to-disorder transitions have been seen previously in mixtures of block copolymers and selective molecular solvents wherein the selectivity of the solvent decreases with increasing temperature. However, the data in Figure 3.4 suggest that in the S2VP(13-15)/[Im][TFSI] system, the selectivity of [Im][TFSI] toward the P2VP block increases with increasing temperature.

For values of $\phi_p \geq 0.93$, the ODT is reversible, i.e. cooling the sample below the ODT temperature after disordering results in the reformation of the ordered phase and the data from this composition range are not shown. In the $\phi_p = 1.00$ and $\phi_p = 0.93$ samples, the ODT is characterized by the disappearance of higher order scattering peaks, a discontinuity in the value of $I(q^*)$, and an abrupt increase in the fwhm of the primary peak revealing phase mixing in the disordered state, consistent with ODT behavior in block copolymer melts and solutions in molecular solvents. In the $\phi_p = 0.99$ sample and $\phi_p = 0.97$ sample (data not shown), the disappearance of higher order scattering peaks and a discontinuity in the value of $I(q^*)$ is interpreted to be an ODT (Figure 3.7). While the disordered state in the range of $0.99 \geq \phi_p \geq 0.97$ lacks long range orientational order, the narrow width of the $I(q^*)$ peaks leads to speculation that the presence of small amounts of ionic liquid enforces local phase separation of PS and P2VP domains.

In contrast to the $\phi_p \geq 0.93$ samples, none of the samples with $\phi_p \leq 0.86$ exhibit reversible ODTs. Cooling the sample below the ODT temperature after disordering does not result in the reformation of the ordered phase in spite of annealing the samples in the ordered state for 1 hour at 145 °C. In Figure 3.8 we compare SAXS profiles obtained above and below the ODT for these samples. The SAXS profiles obtained from the disordered state at $\phi_p = 0.86$ and $\phi_p = 0.78$ contain broad shoulders in addition to the primary peak suggesting the presence of a micellar phase with liquid-like local structure rather than a fluctuating disordered phase. It is conceivable that the formation of complex ordered phases from such micellar phases requires annealing times that are much longer than those used in this study. The presence of significant low angle scattering ($q < 0.03 \text{ Å}^{-1}$) in the disordered phase for samples with $\phi_p \leq 0.70$ indicates the formation of non-periodic, large length scale structures. These structures do not reform ordered structures on experimental time scales after the samples are cooled below the ODT temperature. The fact that we were able to observe reversible phase transitions at low ionic liquid concentrations ($\phi_p \geq 0.93$) in the same temperature window suggests that thermal degradation does not play a role in these unusual transitions. In addition, we find that the molecular weight distribution as characterized by GPC of the neat block copolymer sample does not change after heating to 250 °C for 24 hrs under vacuum. We were unable to make related GPC measurements of the block copolymer/ionic liquid mixtures after heating to 250 °C, as HTFSI is a super-acid and would cause irreparable damage the GPC columns. We also conducted TGA experiments on S2VP(13-15)/[Im][TFSI] mixtures and found that the temperatures at which a weight loss of 10% was observed was well above 300 °C (Table 1).

In Figure 3.9, we present the phase diagram of S2VP(13-15)/[Im][TFSI] mixtures. The measured ODTs andOOTs are indicated with markers, while lines are drawn to indicate interpolated phase boundaries. We limit our attention to temperatures above the glass transition temperature of the neat block copolymer (94 °C). At high S2VP(13-15) copolymer concentrations ($\phi_p \geq 0.93$), lamellae are observed at temperatures well above $T_g$. Upon heating above 235 ± 10 °C, samples in the high copolymer concentration range ($\phi_p \geq 0.93$) undergo a reversible ODT. As the concentration of block copolymer is decreased to $\phi_p = 0.86$ and $\phi_p = 0.78$, coexisting phases are obtained. These systems exhibit an irreversible ODT at 235 ± 10 °C to a
disordered micelle morphology with liquid-like order. We note that the \( \phi_p = 0.86 \) sample exhibits a coexisting lamellar phase, which we believe is a non-equilibrium phase due to small quench depth. Thus, the width with respect to \( \phi_p \) of this coexisting region may in fact be narrower at infinite equilibration times. The \( \phi_p = 0.70 \) and \( \phi_p = 0.50 \) samples form hexagonally-packed cylinders at low temperatures, and exhibit an OOT from hexagonally-packed cylinders to lamellae at 225 \( \pm \) 10°C. This transition was not reversible upon cooling to 215 °C for 30 minutes, and indicates that longer annealing times may be required to reform hexagonally-packed cylinders. Upon heating the \( \phi_p = 0.70 \) and \( \phi_p = 0.50 \) samples to 235 \( \pm \) 10°C an irreversible ODT is observed. As the concentration of block copolymer is further reduced to \( \phi_p = 0.40 \), a lyotropic phase transition to a micellar morphology with liquid-like order is observed. This morphology persists at a block copolymer concentration of \( \phi_p = 0.28 \). Upon heating the \( \phi_p = 0.28 \) sample to 245 \( \pm \) 20°C, an irreversible phase transition to a non-periodic disordered phase is obtained.

The thermal properties of S2VP(13-15)/[Im][TFSI] mixtures were obtained from DSC heating scans at 10 °C/min and the results are given in Figure 10 and the observed thermal transitions are summarized in Table 3.1. Both PS and P2VP homopolymers are known to undergo a glass transition in the vicinity of 100-105 °C in the high molecular weight limit. It is thus not surprising that S2VP(13-15) exhibits a single glass transition temperature of 94 °C. On the other hand, pure [Im][TFSI] exhibits a melting transition at 74 °C (Figure 3.10). It would be reasonable to expect the block copolymer/ionic liquid mixtures to exhibit a combination of the phase transitions seen in the pure components. It is thus not surprising that mixtures with \( \phi_p \geq 0.97 \) exhibit a single glass transition with \( T_g \) values in the vicinity of 100 °C. It is interesting to note that the \( T_g \) values obtained from S2VP(13-15)/[Im][TFSI] mixtures are slightly higher than that of the neat S2VP(13-15) copolymer (Table 3.1). Salt ions are known to induce physical crosslinks in polymer matrices, which in turn, lead to an increase in \( T_g \), e.g. LiClO\(_4\)/PEO electrolytes. The \( \phi_p = 0.93 \) sample exhibits two \( T_g \)'s at 95 and 120 °C. The phase with the high \( T_g \) is likely the P2VP-rich microphase, in which most of the [Im][TFSI] is expected to reside. The \( \phi_p = 0.78 \) sample exhibits two well-separated \( T_g \)'s at 58 and 95 °C. It appears that at this relatively high [Im][TFSI] concentration, the plasticization effect due to the presence of the low molecular weight ionic liquid overwhelms the increase in \( T_g \) due to the presence of the physical crosslinks. The \( \phi_p = 0.70 \) sample exhibits a glass transition at 40 °C corresponding to a plasticized P2VP microphase and a melting transition at 69 °C. This suggests the existence of pools of nearly pure [Im][TFSI] that probably reside within the P2VP phase. The \( \phi_p = 0.50 \) sample exhibits a sharp \( T_g \) at -4 °C, and a broad \( T_g \) between 47 and 95 °C, corresponding to plasticization of the P2VP and PS microphases, respectively. The \( \phi_p = 0.40 \) mixture exhibits interesting behavior that is not seen in either of the pure components. Heating the \( \phi_p = 0.40 \) sample first results in a prominent crystallization peak (\( T_c = 24 \) °C) followed by a melting peak (\( T_m = 51 \) °C). This sequence of phase transitions is typically seen in non-stoichiometric [Im][TFSI] systems (salt in ionic liquid), in which a homogenous liquid is formed, while phase-separation occurs in the solid state. However, we have added stoichiometric amounts of imidazole and HTFSI to the block copolymer.

We propose that specific P2VP/ionic liquid interactions lead to this unusual sequence of phase transitions. In Figure 3.11a we show DSC thermograms from the \( \phi_p = 0.40 \) in S2VP copolymer and a \( \phi_p = 0.28 \) sample in P2VP(20) homopolymer at a 10 °C/min scan rate. Both samples exhibit a qualitatively similar crystallization transition followed by melting transition.
Figure 3.8. SAXS from Ordered versus Disordered State. Comparison of ordered and disordered state SAXS scattering profiles (offset for clarity) for S2VP(13-15)/[Im][TFSI] mixtures at varying concentrations of block copolymer, $\phi_P$. In all cases, the peak labels correspond to the $q/q^*$ for scattering peaks. For ordered state samples, $L_1/L_2$ corresponds to coexisting lamellae, $\text{L/C}$ corresponds to coexisting hexagonally-packed cylinders and lamellae, $\text{C}$ corresponds to cylinders, and $\text{DM}$ corresponds to micelles with liquid-like local structure. In all cases, the ordered state SAXS profiles were obtained at 145 °C and the disordered (DM) or non-periodic disordered (NP) SAXS profiles were obtained at 245 °C.
Figure 3.9. Phase Diagram of S2VP(13-15)/[Im][TFSI] Mixtures. Filled symbols (■) indicate order-disorder transition temperatures, while open symbols (Δ) indicate order-order transitions observed using SAXS with indicated error bars. The solid line indicates the boundary between ordered and disordered (DS), disordered micelle with liquid-like local structure (DM), or non-periodic disordered (NP) phases. The dashed lines indicate boundaries between lamellae (L) and hexagonally-packed cylinders (C) ordered phases, and DS, DM, and NP disordered phases. A region of coexistence (coexist) is observed between L and C regions.
Figure 3.10. Composition Dependence of Thermal Properties. DSC thermograms (offset for clarity) of varying concentrations of S2VP(13-15) copolymer in [Im][TFSI]. The heating rate is 10 °C/min.
Table 3.1. Thermal Properties of S2VP(13-15)/[Im][TFSI] Mixtures

<table>
<thead>
<tr>
<th>$\phi_P$</th>
<th>$T_g$ (°C)$^a$</th>
<th>$T_c$ (°C)$^a$</th>
<th>$T_m$ (°C)$^a$</th>
<th>$T_d$ (°C)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>94</td>
<td>--</td>
<td>--</td>
<td>378</td>
</tr>
<tr>
<td>0.99</td>
<td>101</td>
<td>--</td>
<td>--</td>
<td>370</td>
</tr>
<tr>
<td>0.97</td>
<td>99</td>
<td>--</td>
<td>--</td>
<td>332</td>
</tr>
<tr>
<td>0.93</td>
<td>95, 120</td>
<td>--</td>
<td>--</td>
<td>not measured</td>
</tr>
<tr>
<td>0.78</td>
<td>58, 95</td>
<td>--</td>
<td>--</td>
<td>not measured</td>
</tr>
<tr>
<td>0.70</td>
<td>40</td>
<td>--</td>
<td>69</td>
<td>not measured</td>
</tr>
<tr>
<td>0.50</td>
<td>-4, 47-95</td>
<td>--</td>
<td>--</td>
<td>327</td>
</tr>
<tr>
<td>0.40</td>
<td>--</td>
<td>24</td>
<td>51</td>
<td>not measured</td>
</tr>
<tr>
<td>0.0</td>
<td>--</td>
<td>--</td>
<td>74</td>
<td>not measured</td>
</tr>
</tbody>
</table>

$^a$ Onset temperatures of heat capacity change (glass transition temperature, $T_g$), an exotherm peak (crystallization temperature, $T_c$), and an endotherm peak (melting temperature, $T_m$) during heating scan using differential scanning calorimetry. $^b$ Temperature of 10% weight loss heating scan from room temperature using thermal gravimetric analysis.
Figure 3.11. Unusual Thermal Transition in a $\phi_P=0.40$ S2VP/[Im][TFSI] Mixture. (a) DSC thermograms (offset for clarity) of $\phi_P=0.40$ in S2VP(13-15) copolymer and $\phi_P=0.28$ in P2VP(20) at a 10 °C/min scan rate. (b) WAXS intensity profiles (offset for clarity) of $\phi_P=0.40$ in S2VP(13-15) copolymer at varying temperatures and empty Kapton cell. The features at $q=0.85 \text{ Å}^{-1}$ are an artifact of the empty cell subtraction. (c) WAXS intensity profiles (offset for clarity) of $\phi_P=0.40$ in S2VP(13-15) copolymer, neat [Im][TFSI], neat imidazole, and neat HTFSI at room temperature.
demonstrating that crystallization induced by microphase separation of the block copolymer does not play a role in this unusual transition. The enthalpy associated with these thermal transitions was found to be independent of scan rate. Vinyl pyridine/imidazole interactions or intermolecular imidazole interactions induced by the P2VP environment appear to enable this transition. The $T_m$ in the $\phi_P=0.40$ S2VP copolymer sample was confirmed with wide angle X-ray scattering (WAXS) and is shown in Figure 3.11b. In addition, the structure of the [Im][TFSI] ionic liquid, neat imidazole, and neat HTFSI were characterized with WAXS and are shown in Figure 3.11c. The diffraction peak at $q=1.95 \text{ Å}^{-1}$ present in the $\phi_P=0.40$ S2VP copolymer and neat imidazole sample coincides with intermolecular interactions present in crystalline imidazole.\textsuperscript{57} While this suggests the presence of imidazole-rich phases within the $\phi_P=0.40$ S2VP copolymer sample, additional vinyl pyridine/imidazole or vinyl pyridine/ionic liquid interactions appear to give rise to the complex scattering profile observed in the $\phi_P=0.40$ S2VP/[Im][TFSI] mixture and we have not determined the nature of the crystals therein.

### 3.4 Conclusions

We have examined the lyotropic and thermotropic phase behavior of a S2VP copolymer in [Im][TFSI] using SAXS and optical transmission characterization. We established that the ionic liquid selectively solvates one of the block copolymer segments, which we believe to be the P2VP domain. The SAXS data indicated the existence of lamellar, cylindrical, and disordered phases. Some of the signatures of order-order and order-disorder transitions in S2VP/[Im][TFSI] mixtures differ from those found in mixtures of block copolymers and molecular solvents. The thermal properties of the system provide interesting insight into the nature of the self-assembled microdomains. At high block copolymer concentrations ($\phi_P \geq 0.93$), the ionic liquid behaves as a salt, causing a slight increase in the $T_g$ of P2VP domains, while at intermediate block copolymer concentrations (0.50$\leq \phi_P \leq 0.78$) the ionic liquid behaves as a plasticizer, causing a decrease in the $T_g$ of P2VP domains. At $\phi_P=0.40$ an unusual thermal transition consisting of crystallization and subsequent melting is observed and is attributed to specific P2VP/[Im][TFSI] interactions.

### 3.5 Acknowledgments

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### 3.6 References

Chapter 4. Effect of an Ionic Liquid Solvent on the Phase Behavior of Block Copolymers


The phase behavior of two series of poly(styrene-block-2-vinyl pyridine) (S2VP) copolymers in mixtures with an imidazolium bis(trifluoromethane)sulfonamide ([Im][TFSI]) ionic liquid have been studied using small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), and differential scanning calorimetry (DSC) to explore the effects of copolymer molecular weight and composition on the self-assembly of the mixtures. The glass transition temperature of the [Im][TFSI]-swollen poly(2-vinyl pyridine) (P2VP) phase is characterized using DSC and found not to follow the concentration dependence predicted by the Gordon-Taylor or Fox equations. The lyotropic phase behavior of the two copolymer series, the first in which total molecular weight is held constant and the second in which the molecular weight of the P2VP block (N_{P2VP}) is held constant, is studied using SAXS and SANS and is found to be reminiscent of the lyotropic phase behavior of block copolymer/molecular solvent mixtures. The interfacial area occupied by each S2VP chain, however, is found to decrease upon the addition of [Im][TFSI], in contrast to observations of block copolymer/molecular solvent mixtures. Scaling analysis of the SAXS-determined structural length scales shows that S2VP/[Im][TFSI] mixtures follow strong segregation limit scaling, \( d \sim N_{P2VP}^{2/3} \) over a broad range of ionic liquid loadings, with the prefactor dependent on the molar ratio of [Im][TFSI] to N_{P2VP}. Qualitative observations of an increased order-disorder transition temperature in the mixtures are made using SAXS.

4.1 Introduction

Ionic liquids are an exciting class of materials due to unique properties including high thermal and electrochemical stability, negligible volatility, and high ionic conductivity. This exceptional combination of properties makes them candidates for a variety of applications such as fuel cells, transistors, and battery electrolytes for which it would be desirable to integrate the ionic liquid into a solid polymeric matrix. Such a material can be realized by selectively incorporating the ionic liquid into a continuous block copolymer phase, forming a membrane in which the second phase provides mechanical stability. Both “solvent-like” and “salt-like” properties of the ionic liquid have been observed in such mixtures. Therefore, fundamental understanding of block copolymer/ionic liquid interactions and the resulting self-assembly is essential for predictable structure and property control.

Addition of a molecular solvent to block copolymer typically results in lyotropic phase transitions, changes in characteristic domain spacing (d), and changes in the order-disorder transition temperature (T_{ODT}). In the case of block copolymer/salt mixtures, changes in the phase behavior relative to the neat copolymer have been interpreted as changes in the effective segregation strength, chain statistics, or intermolecular coordination. Recently, Wang has developed an analytical expression for an effective interaction parameter, \( \chi_{eff} \), for homopolymer blend/salt mixtures that incorporates ion solvation and entropic effects. Previous experimental studies of the self-assembly of dilute and concentrated poly(1,2-butadiene-block-ethylene oxide)/ionic liquid mixtures, have highlighted the similarity of the phase behavior of the
mixtures to that of block copolymer/molecular solvent mixtures. However, studies of the thermal properties of poly(styrene-block-2-vinylpyridine) (S2VP) copolymer/ionic liquid mixtures have shown an increased glass transition temperature ($T_g$) of the poly(2-vinylpyridine) (P2VP) phase at low ionic liquid concentrations due to a salt-like physical cross linking, while at high ionic liquid concentrations the $T_g$ of the P2VP block was depressed as it would be by the presence of a molecular solvent.\textsuperscript{15}

In this work the effect of block copolymer volume fraction, $f_{PS}$, and degree of polymerization, $N_T$, on the phase behavior of concentrated S2VP copolymer mixtures with an imidazolium bis(trifluoromethane sulfone)imide ionic liquid ([Im][TFSI]) (Figure 4.1) is explored in order to more fully understand the thermodynamics of self-assembly in this complex system. [Im][TFSI] is shown to have a unique effect on S2VP phase behavior, which can be classified as neither completely solvent-like or salt-like. In particular, thermal characterization of the S2VP copolymer/[Im][TFSI] mixtures reveals an unusual composition dependence of $T_g$ not predicted by either the Gordon-Taylor or Fox equations for polymer/molecular solvent mixtures. The lyotropic phase behavior of the mixtures is studied using small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) and compared to that of mixtures of block copolymers in selective molecular solvents. Lastly, the composition dependence of the domain spacing and the $T_{ODT}$ are shown to be consistent with predictions for block copolymers at high segregation strengths.

4.2 Experimental Section

**Polymer Synthesis and Characterization.** S2VP copolymers and P2VP homopolymer were synthesized via anionic polymerization using standard methods.\textsuperscript{29} The molecular weight of the polystyrene (PS) homopolymer was determined using gel permeation chromatography (GPC) and the total molecular weight of the block copolymer was determined via $^1$H NMR (Bruker AVB-300). The molecular weight of the P2VP homopolymer was determined using $^1$H NMR end-group analysis. The polydispersity of each polymer was assessed using GPC. The S2VP copolymers are designated S2VP(xx-yy) and the P2VP homopolymer is designated P2VP(yy), where ‘xx’ and ‘yy’ refer to the number averaged molecular weights in kg/mol of the PS and P2VP blocks, respectively. The total molecular weight, volume fraction of polystyrene, $f_{PS}$, and polydispersity index (PDI) of the polymers are given in Table 4.1. One of the ten polymers, dS2VP(7.1-6.8), was synthesized with d8-styrene monomer obtained from Polymer Source.

**Ionic Liquid Purification.** Imidazole (≥95%) and bis(trifluoromethane)sulfonamide (HTFSI, ≥95%) were purchased from Sigma Aldrich and purified by sublimation under vacuum. Differential scanning calorimetry (DSC) and $^1$H NMR were used to assess the purity of the two starting materials. Purified imidazole and HTFSI were combined in equimolar quantities in a glove box, sealed, and heated in an oven outside the glove box to 100 °C for 2-3 hours to prepare the ionic liquid [Im][TFSI]. The composition of the ionic liquid was confirmed by comparing the measured melting point of the compound, using DSC, with literature.\textsuperscript{30} Care was taken to limit air and water exposure of the hydroscopic ionic liquid by handling in air-free glove box and sealed environments.

**Scattering Sample Preparation and Methods.** Dichloromethane was degassed using three freeze, pump, thaw cycles, stirred over CaH$_2$ overnight, then distilled into a collection flask, brought into a glove box, and stored on molecular sieves. All further sample preparation was performed within a glove-box environment. Predetermined quantities of [Im][TFSI] and S2VP were weighed into glass vials, and ca. 5 wt% solutions were prepared using
Figure 4.1. Chemical Structure of [Im][TFSI] and S2VP Copolymer. Imidazolium bis(trifluoromethane)sulfonamide ([Im][TFSI]) ionic liquid and the poly(styrene-block-2-vinyl pyridine) (S2VP) copolymer chemical structures.
dichloromethane and stirred overnight. Samples were cast one drop at a time into sample cells formed by an aluminum spacer sealed onto a Kapton window on one side until a ca. 1 mm solid sample was obtained. Samples were heated to 60 °C (above the boiling point of dichloromethane) for ca. 18 hours to remove remaining solvent. A second Kapton window was glued to seal the samples. When storage and/or transportation of the sealed samples was necessary, samples were sealed in jars under in the presence of dessicant in inert environments. Samples are designated by the value of the polymer volume fraction (for both S2VP and P2VP solutions), \( \phi_p \), assuming ideal mixing. The density of [Im][TFSI] was estimated to be 1.67 g/cm\(^3\) from scattering length density fits of SANS intensity profiles\(^{31} \) and the densities of PS and P2VP were taken to be 1.15 and 1.05 g/cm\(^3\), respectively.

SAXS was performed on beamline 7.3.3 of the Advanced Light Source (ALS) and beamline 1-4 of the Stanford Synchrotron Radiation Lightsource (SSRL). At the ALS, the beamline was configured with an X-ray wavelength of \( \lambda = 1.240 \) Å and focused to a 50 by 300 \( \mu \)m spot. Full two-dimensional scattering patterns were collected on an ADSC CCD detector with an active area of 188 by 188 mm. The scattering patterns were radially averaged and the scattering intensity corrected with the post-ion chamber intensity using Nika version 1.18. At the SSRL, the beamline was configured with an X-ray wavelength \( \lambda = 1.488 \) Å and focused to a 0.5 mm diameter spot. A single quadrant of a two-dimensional scattering pattern was collected on a CCD detector with an active area of 25.4 by 25.4 mm. The scattering patterns were radially averaged and corrected for detector null signal, dark current, and empty cell scattering.

SANS measurements were performed at Oak Ridge National Laboratory on the SANS-I instrument. Neutrons with a \( \lambda = 6 \) Å wavelength and a sample to detector distance of 4 and 10 m were utilized. Data from room temperature samples was collected and the intensity corrected for instrumental background, empty cell scattering, sample transmission, and incoherent background and placed on an absolute intensity scale by use of a porous carbon standard (Al4).\(^{32} \) In some samples, a small positive scattering intensity, typically on the order of 0.1 cm\(^{-1}\), remained after this data reduction procedure, likely due to incoherent scattering.\(^{33} \) In these cases, the residual intensity was removed by subtracting the average intensity over the range 0.085<q<0.100 Å\(^{-1}\).

**Differential Scanning Calorimetry Sample Preparation and Methods.** Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2920. Samples were solution cast in a glove box into aluminum DSC pans from the same solutions used to prepare X-ray scattering samples. The samples were heated to 60 °C for ca. 18 hours to remove remaining solvent. The samples were then crimped within the glove box using hermetically sealed pans and placed inside a container with desiccant for transfer to the DSC. Indium and dodecane were used as calibration standards for the DSC. Samples underwent three heating and cooling cycles and glass transitions were recorded upon the second heating.

### 4.3 Results and Discussion

#### 4.3.1. Thermal Properties of S2VP/[Im][TFSI] System

The thermal properties of S2VP/[Im][TFSI] mixtures highlight the complex effect of ionic liquid on block copolymers. For neat S2VP copolymers, a single \( T_g \) is observed in the vicinity of 100 °C, due to the similarity of the \( T_g \) of the PS and P2VP homopolymers. The presence of a sufficient amount of ionic liquid (>4 wt%) leads to a decrease in the \( T_g \) of the P2VP-rich phase due to the selectivity of [Im][TFSI] for this phase.\(^{31} \) In Figure 4.2, the low temperature \( T_g \) is plotted as a function of weight fraction of ionic liquid in the P2VP-rich phase,
### Table 4.1. Characteristics of Block Copolymers Studied.

<table>
<thead>
<tr>
<th>Constant N_T</th>
<th>Sample</th>
<th>Total MW (g/mole)</th>
<th>f_PS</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S2VP(4.4-10.8)</td>
<td>15,200</td>
<td>0.29</td>
<td>1.07</td>
</tr>
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<td></td>
<td>S2VP(4.9-6.6)</td>
<td>11,500</td>
<td>0.43</td>
<td>1.13</td>
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<tr>
<td></td>
<td>dS2VP(7.1-6.8)</td>
<td>13,900</td>
<td>0.50</td>
<td>1.10</td>
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<tr>
<td></td>
<td>S2VP(11.6-7.8)</td>
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<td>0.60</td>
<td>1.18</td>
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</table>

<table>
<thead>
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<th>Constant N_P2VP</th>
<th>Sample</th>
<th>Total MW (g/mole)</th>
<th>f_PS</th>
<th>PDI</th>
</tr>
</thead>
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<tr>
<td></td>
<td>S2VP(4.4-10.8)</td>
<td>15,200</td>
<td>0.29</td>
<td>1.07</td>
</tr>
<tr>
<td></td>
<td>S2VP(8.7-12.0)</td>
<td>20,800</td>
<td>0.42</td>
<td>1.02</td>
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<td></td>
<td>S2VP(12.0-12.4)</td>
<td>24,300</td>
<td>0.49</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>S2VP(18.4-11.4)</td>
<td>29,800</td>
<td>0.62</td>
<td>1.10</td>
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<tr>
<td></td>
<td>S2VP(28.5-10.7)</td>
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<td>0.73</td>
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</tr>
<tr>
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<td>P2VP(13.1)</td>
<td>13,100</td>
<td>0.00</td>
<td>1.06</td>
</tr>
</tbody>
</table>
w_{IL} (where w_{IL} and w_{P2VP} sum to one). The ratio of [Im][TFSI] to P2VP is found to be predictive of the P2VP/[Im][TFSI] $T_g$, regardless of $f_{PS}$ and $N_T$ of the S2VP copolymers, as indicated by the collapse of the data onto a single curve. The Gordon-Taylor\textsuperscript{34} and Fox\textsuperscript{35} equations have been routinely used to describe the $T_g$ of polymer/molecular solvent mixtures and polymer ion gels,\textsuperscript{36}:

\[ T_g = v_{IL} * T_{g,IL} + v_{P2VP} * T_{g,P2VP} \] (4.1)

\[ \frac{1}{T_g} = \frac{w_{IL}}{T_{g,IL}} + \frac{w_{P2VP}}{T_{g,P2VP}} \] (4.2)

where $v_{P2VP}$ and $v_{IL}$ are the volume fractions of P2VP and [Im][TFSI] in the P2VP/[Im][TFSI] phase. The $T_g$ of [Im][TFSI] is below the range of our DSC (-40 to 725 °C) and also not available from the literature. Thus, [Im][TFSI] $T_g$ was used as a fitting parameter to compare equations 4.1 and 4.2 to the P2VP/[Im][TFSI] $T_g$ data. Neither the Gordon-Taylor nor the Fox equations capture the composition dependence of the $T_g$ data. Both equations predict a monotonically decreasing relationship between the $T_g$ of a polymer and the solvent weight or volume fraction with a concave-up curve shape. In contrast, an unusual concave-down curve shape is observed in Figure 4.2. It is conceivable that specific interactions between [Im][TFSI] and P2VP that are not captured by the Gordon-Taylor or the Fox equations lead to the unique composition dependence of the $T_g$ of the P2VP phase observed in Figure 4.2.

4.3.2. Lyotropic Phase Behavior

The phase behavior of two series of S2VP copolymers in ionic liquid, one with constant $N_T$ and one with constant $N_{P2VP}$ (Table 4.1), demonstrate the similarity between mixtures of block copolymers with a selective molecular solvent and with an ionic liquid. Representative SAXS profiles are shown in Figure 4.3 from S2VP copolymers of both series in solution with [Im][TFSI] to highlight specific lyotropic phase transitions. Additional scattering data is available in the Supporting Information, Figures S1 and S2. In Figure 4.3a, the neat S2VP(4.4-10.8) copolymer with $f_{PS}=0.29$ exhibits a hexagonally-close packed (HCP) cylinder morphology with a domain spacing ($d$) of 14.9 nm (110 scattering plane). As expected, the addition of ionic liquid ($\phi_P=0.94-0.48$) increases $d$ indicating that [Im][TFSI] acts as a selective solvent in the S2VP copolymer.\textsuperscript{15} At a composition of $\phi_P=0.42$, the higher order scattering peaks reveal a lyotropic transition to spheres packed on a body-centered cubic (BCC) lattice. The presence of the $\sqrt{7}q^*$ scattering peak, as well as the higher scattering intensity of the $\sqrt{3}q^*$ peak compared to the $\sqrt{2}q^*$ peak differentiates the observed SAXS profile from that of spherical micelles oriented on a simple cubic (SC) lattice.\textsuperscript{37} It appears that the coexistence window required by Gibb’s phase rule between the two phases is small ($\lesssim \phi_P=0.06$).\textsuperscript{38} As $\phi_P$ is decreased to $\phi_P=0.37$ and $\phi_P=0.33$, distinct shoulders are observed on the primary scattering peak. At $\phi_P=0.23$ the $q^*$ peak narrows and the higher order scattering peaks corresponding to BCC-packed spheres persist, indicating that the $\phi_P=0.33$ and $\phi_P=0.37$ mixtures consist of coexisting BCC-packed spheres with slightly incommensurate unit cells. This finding suggests that long equilibration times are necessary for the formation of stable, ordered micellar structures in block copolymer/ionic liquid mixtures,\textsuperscript{28} consistent with experimental observations of the formation of ordered micelles in block copolymer/molecular solvent mixtures.\textsuperscript{39}
Figure 4.2. **Glass Transition Temperature of P2VP/[Im][TFSI] Phase.** $T_g$ of P2VP/[Im][TFSI] phase as a function of weight fraction ionic liquid $w_{IL}$ added to the P2VP block determined using DSC. The curves for both constant $N_T$ and $N_{PVP}$ copolymers collapse.
Figure 4.3. SAXS Profiles of S2VP/[Im][TFSI] Mixtures. SAXS profiles of varying $\phi_P$ with block copolymers at 145 °C of (a) S2VP(4.4-10.8), (b) S2VP(4.9-6.6), and (c) S2VP(28.5-10.7). In all cases, the peak labels correspond to the $q/q^*$ for scattering peaks.
In a more nearly symmetric S2VP(4.9-6.6) copolymer with \( f_{PS} = 0.43 \) the neat lamellar structure swells to form a HCP cylinder phase when \( 0.61 < \phi_p < 0.86 \) (Figure 4.3b). At \( \phi_p = 0.51 \), a distinctive broadening of the \( q^* \), \( \sqrt{3}q^* \), \( \sqrt{7}q^* \) and \( 3q^* \) scattering peaks suggests a lyotropic transition; however, the likelihood of coexistence makes phase identification impossible. Upon further decreasing \( \phi_p \) to \( \phi_p = 0.28 \), reflections at \( \sqrt{3}q^* \), \( \sqrt{4}q^* \), \( \sqrt{8}q^* \), and \( \sqrt{20}q^* \) are observed corresponding to a lyotropic transition to FCC-packed spheres.

Figure 4.3c illustrates the qualitative differences in the lyotropic phase behavior of copolymers with a PS-majority phase. The HCP PS cylinders observed in the neat \( f_{PS} = 0.73 \) S2VP(28.5-10.7) copolymer undergo a lyotropic phase transition to a lamellar microstructure at \( \phi_p = 0.95 \). At \( \phi_p = 0.70 \), a dramatic broadening of the \( q^* \) peak is observed along with weak, undulating higher order scattering peaks revealing micelles with liquid-like order which persist as \( \phi_p \) is further reduced to \( \phi_p = 0.28 \). The asymmetry of the PS and P2VP blocks in the \( f_{PS} = 0.73 \) S2VP(28.5-10.7) copolymer likely leads to packing frustration in the PS phase upon addition of ionic liquid, which disrupts the formation of long-range order (\( \phi_p \leq 0.70 \)). These findings demonstrate the rich variety of microstructures attainable in S2VP copolymer/[Im][TFSI] mixtures through modification of \( f_{PS} \) and \( N \). Further, from the sequence of lyotropic phase transitions observed in the \( f_{PS} = 0.29, 0.43, \) and 0.73 copolymers it is evident that the [Im][TFSI] ionic liquid selectively solvates the P2VP block.

Lyotropic phase diagrams of solutions of the S2VP/[Im][TFSI] mixtures for the series of S2VP copolymers with constant \( N_T \) and \( N_{P2VP} \) demonstrate similarities to the lyotropic phase behavior of block copolymer/selective molecular solvent mixtures (Figure 4.4). For example, spheres on a BCC lattice are both predicted and experimentally observed in selective solvent/block copolymer systems in which the corona layer is large relative to the core, and are also observed in S2VP(4.4-10.8) (\( f_{PS} = 0.29 \)) at low \( \phi_p \). Similarly for "inverted spheres," in which the corona is small relative to the core, FCC- and BCC-packing has been predicted and observed. Block copolymers with thin corona layers in the most highly-selective solvents for the corona tend to form FCC-packed spheres, which is consistent with the behavior of mixtures containing the compositionally symmetric S2VP(4.9-6.6) and S2VP(8.7-12.0) copolymers. For \( f_{PS} \geq 0.42 \), micelles with liquid-like order (DM) are observed in mixtures with the lowest values of \( \phi_p \) characterized. The concentration range for the DM structures increases with \( f_{PS} \), similar to observations in molecular solvent systems.

The lyotropic phase behavior of the constant \( N_T \) series (Figure 4.4a) and \( N_{P2VP} \) series (Figure 4.4b) are qualitatively similar with the notable exception that mixtures of the PS-majority copolymers have a narrower \( \phi_p \) window between lamellar and micellar phases in the \( N_{P2VP} \) series. The entropic penalty associated with packing the relatively long PS blocks into HCP-ordered structures is substantial in the \( f_{PS} = 0.62 \) and \( f_{PS} = 0.73 \) samples and may lead to the narrowing (\( f_{PS} = 0.62 \)) and complete disappearance (\( f_{PS} = 0.73 \)) of the HCP PS cylinder (CPS) region observed in this phase diagram. Further, in Figure 4.4b, the unexpected narrowing of the lamellar window in mixtures with the \( f_{PS} = 0.73 \) copolymer compared to the less PS-rich copolymers also points to the role that packing frustration of PS chains may play in the rich lyotropic phase behavior of these materials. In block copolymer/selective molecular solvent mixtures, inversion of cylindrical phases has been widely reported. Inversion of cylindrical phases has been recently observed in PB-block-PEO copolymer/ionic liquid mixtures, although the ionic liquids studied in these mixtures exhibit less selectivity compared to the S2VP/[Im][TFSI] system. It is anticipated that packing frustration in the \( f_{PS} = 0.73 \) copolymer mixtures in combination with the strong selectivity of the ionic liquid for the P2VP block
Figure 4.4. Lyotropic Phase Diagrams of S2VP Copolymers in [Im][TFSI]. (a) Fixed $N_T$ and (b) fixed $N_{P2VP}$ at $T=145$ °C. Markers indicate phases identified using small-angle scattering and dashed lines are drawn to indicate interpolated phase boundaries. Regions of co-existence are indicated with diagonal shading. Phases are labeled as follows: Lamellae (L), HCP-packed PS cylinders ($C_{PS}$), HCP-packed P2VP cylinders ($C_{P2VP}$), FCC- and BCC-oriented PS spheres ($S_{PS, FCC}$ and $S_{PS, BCC}$, respectively), and micelles with liquid-like order (DM).
preclude formation of inverted cylindrical phases on experimental time scales and instead lead to the formation of micelles with liquid-like order.

From Figures 4a and 4b it is observed that the $\phi_p$ at which the lamellae to C$_{PS}$ lyotropic phase transition occurs, $\phi_{P,C-L}$, decreases monotonically as $f_{PS}$ increases. The lamellar/C$_{PS}$ phase boundary for a neat S2VP copolymer is determined by $f_{PS}$ and the segregation strength, $\chi_N$. Self-consistent mean-field theory predicts a lamellar/C$_{PS}$ phase boundary between $0.32 \leq f_{PS} \leq 0.33$ for strongly segregated S2VP copolymers, and predicts the $f_{PS}$ of this transition to decrease with increasing $\chi_N$ for $24.6 \leq \chi_N \leq 35.6$. $f_{PS,eff}$ is defined as the effective PS volume fraction at the $\phi_{P,L}$ phase transition and was calculated by assuming complete partitioning of the ionic liquid into the P2VP phase. The values of $\chi_N$ for the neat S2VP copolymers with constant N$_{P2VP}$ and $\phi_{P,L}$ and $f_{PS,eff}$ for the mixtures are shown in Table 4.2. It is evident in Table 4.2 that $f_{PS,eff}$ is larger than the $f_{PS}$ of the lamellar/C$_{PS}$ phase boundary predicted for strongly segregated copolymers, and that $f_{PS,eff}$ increases with increasing $\chi_N$. It is possible that the addition of ionic liquid alters the statistical segment lengths of the two copolymer blocks, as has been observed in block copolymer/salt mixtures, leading to this set of observations.

4.3.3. Domain Spacing

Theoretical and experimental studies have shown that the addition of a selective molecular solvent to a block copolymer increases $d$ following the power law:

$$d \sim \phi_p^\alpha \quad (4.3)$$

where $\alpha$ is a measure of the solvent selectivity. Previously, the domain spacing of a symmetric S2VP block copolymer swollen with [Im][TFSI] was shown to increase according to equation (4.3) ($\alpha<0$), indicating that the ionic liquid selectively solvates one block of the S2VP copolymer. In Figure 4.5, $d$ versus $\phi_p$ for lamellar mixtures of the constant N$_{P2VP}$ copolymer series at 145 ºC are plotted to examine the effect of $f_{PS}$ on $\alpha$. The “affine dilution” limit describes the scenario in which the insoluble block is large compared to the solvated block. In this limit $\alpha=-1$ and the interfacial area per chain ($A$) remains constant upon the addition of solvent. For a lamellar phase, $A$ is given by:

$$A = \frac{V}{d\phi_p} \quad (4.4)$$

where $V$ is the volume of the insoluble phase. For mixtures containing the highly asymmetric f$_{PS}$=0.72 S2VP(28.5-10.7) copolymer in [Im][TFSI], $\alpha=-1.1 \pm 0.1$. As $f_{PS}$ decreases, the value of $\alpha$ becomes more negative, in stark contrast to observations of mixtures with molecular solvents. Based on equations 4.3 and 4.4 and values of $\alpha<1$, $A$ must decrease with decreasing $\phi_p$, revealing that interfacial chain stretching perpendicular to the interface dominates over chain swelling parallel to the interface.

In Figure 4.6, the domain spacing of the neat S2VP copolymers with constant N$_{P2VP}$ is shown to vary with $N_T$ as $d \sim \gamma^\delta N_T^{\delta}$, where $\delta=2/3$ within error, in agreement with strong segregation limit (SSL) scaling and experimental observations of the intermediate segregation regime ($18 \leq \chi_N \leq 47$ for the neat copolymers at 145 ºC, as calculated from the Flory-Huggins temperature dependence suggested by Schulz et al.). The pre-factor, $\gamma$, is known to depend on morphology, $f_{PS}$, the ratio of the two statistical segment lengths ($a_{PS}/a_{P2VP}$), and $\chi$. Since the SSL scaling behavior of $d \sim N_T^{2/3}$ is observed for varying values of IL:2VP (IL:2VP is molar ratio of [Im][TFSI] to P2VP monomers), $\gamma$ is a function of IL:2VP. In Table 4.3, $\gamma$ is tabulated as a
Table 4.2. Values of $f_{\text{PS,eff}}$ for S2VP Copolymers with the Same N$_{\text{P2VP}}$.

<table>
<thead>
<tr>
<th>$f_{\text{PS}}$ of neat copolymer</th>
<th>$\chi^N$</th>
<th>$\phi_{\text{P,C-L}}$†</th>
<th>$f_{\text{PS,eff}}$†</th>
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</thead>
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<tr>
<td>0.42</td>
<td>24.6</td>
<td>0.84 ± 0.02</td>
<td>0.35 ± 0.01</td>
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<tr>
<td>0.49</td>
<td>28.9</td>
<td>0.78 ± 0.08</td>
<td>0.38 ± 0.04</td>
</tr>
<tr>
<td>0.62</td>
<td>35.6</td>
<td>0.67 ± 0.03</td>
<td>0.42 ± 0.02</td>
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</tbody>
</table>

* $\chi^N$ (T=145 °C) was determined from ref. 50.
† Error in $\phi_{\text{P,C-L}}$ and $f_{\text{PS,eff}}$ is related to the range of $\phi_P$ separating lamellar and C$_{\text{PS}}$ samples in Figure 4.4b.
Table 4.3. Values of $\gamma$ as a Function of IL:2VP.

<table>
<thead>
<tr>
<th>IL:2VP</th>
<th>$\gamma$‡</th>
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</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.48 ± 0.07</td>
</tr>
<tr>
<td>0.28</td>
<td>0.59 ± 0.12</td>
</tr>
<tr>
<td>0.74</td>
<td>0.68 ± 0.35</td>
</tr>
</tbody>
</table>

‡ Error in $\gamma$ is one standard deviation of the fit.
Figure 4.5. Scaling Analysis of S2VP/[Im]TFSI Mixtures. Lamellar domain spacing, d, versus $\phi_P$ determined from SAXS data at 145 °C. A power law, $d \sim \phi_P^\alpha$, is used to obtain $\alpha$ and the errors represent one standard deviation of the fit.
Figure 4.6. Evidence of Strong Segregation Limit Scaling in S2VP/[Im][TFSI] Mixtures. Lamellar domain spacing, $d$, versus $N_T$ determined by SAXS data at 145 °C for S2VP copolymers with fixed $N_{P2VP}$ for the neat copolymer (▲), IL:2VP=0.74 (■), and IL:2VP=0.28 (♦). A power law fit, $d = \gamma N_T^\delta$, is used to obtain $\delta$ (reported errors are one standard deviation of the fit).
Figure 4.7. Temperature Dependent SAXS Profiles of S2VP/[Im][TFSI] Mixtures. (a) SAXS profiles (offset for clarity) of $\phi_P=1.00$, S2VP(4.9-6.6) at varying temperatures, (b) Plot of $I(q^*)$ (□) and fwhm (△) versus temperature (°C) of $\phi_P=1.00$, S2VP(4.9-6.6). The ODT is defined as the point at 185 ± 20 °C and duplicate data points at a given temperature were recorded upon heating and cooling. (c) SAXS profiles (offset for clarity) of S2VP(4.9-6.6) copolymer/[Im][TFSI] mixtures at varying $\phi_P$ at 225 °C.
function of IL:2VP, where $\gamma$ was calculated from power law fits to the data in Figure 4.6 with both $\gamma$ and the $N_T$ power law dependence as fitting parameters. $\gamma$ was found to increase monotonically with IL:2VP. While the effective $\chi$ is expected to increase with IL:2VP based on the highly negative values of $\alpha$ observed, further studies of chain statistical dimensions are necessary to quantitatively estimate the effective $\chi$ from the domain spacing data.

4.3.4. Thermotropic Phase Behavior

It is anticipated that addition of [Im][TFSI] will increase the $T_{ODT}$ of neat S2VP copolymers due to increased segregation strength of the system. In Figure 4.7a, SAXS profiles are shown for the neat, lamellar S2VP(4.9-6.6) copolymer sample with $f_{PS}$=0.43 at varying temperatures. An ODT is evident at 185 ± 20 °C based on the discontinuous change in the full width at half maximum (fwhm) and intensity of the $q^*$ peak shown in Figure 4.7b. The ODT is fully reversible upon cooling, and in close agreement with the predicted ODT temperature (197 °C) of a $f_{PS}$=0.50, $N_T$=110 copolymer (as calculated from the Flory-Huggins temperature dependence suggested by Schulz et al.50). In Figure 4.7c, SAXS profiles for S2VP(4.9-6.6) copolymer/[Im][TFSI] mixtures for varying $\phi_P$ at 225 °C are shown. The profiles are remarkably similar to those observed at 145 °C (Figure 4.3b), and indicate that across a wide-range of $\phi_P$, the ordered block copolymer phase is stabilized with respect to temperature by the presence of ionic liquid. While the origin of the increased $T_{ODT}$ in the S2VP/[Im][TFSI] system cannot be definitively established from the current, limited data set, such behavior could result from one of the following possibilities: (1) the PS and P2VP interaction parameters with [Im][TFSI] are strongly temperature-dependent, or (2) the presence of ions in the high dielectric P2VP phase decreases PS/P2VP miscibility due to the higher enthalpic free energy gain from ion solvation in the P2VP phase compared to the entropic penalty to confining the ions to a single phase.26 The latter justification is corroborated by the increased segregation strength observed from domain scaling analysis.

4.4. Conclusions

The phase behavior of S2VP/[Im][TFSI] mixtures has been studied using SAXS, SANS, and DSC. The observed dependence of the P2VP/[Im][TFSI] phase $T_g$ on IL:2VP was found to be independent of $f_{PS}$ and $N_T$ of the copolymer and cannot be predicted by standard polymer/molecular solvent theories. SAXS and SANS characterization revealed the existence of lamellar, cylindrical, ordered micellar, and disordered micellar phases, in agreement with studies of block copolymer/selective molecular solvent mixtures. Scaling analysis of the S2VP/[Im][TFSI] mixtures revealed an increase in segregation strength upon the addition of ionic liquid, and $d$ of the mixtures was found to follow the scaling predicted by SSL theory across a broad range of IL:2VP ratios. An increase in the $T_{ODT}$ of the S2VP/[Im][TFSI] mixtures compared to the neat copolymer was in qualitative agreement with the scaling analysis.

4.5. Acknowledgements

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Laboratory's (ORNL) High Flux Isotope Reactor. All three are national user facilities supported by the Department of Energy, Office of Basic Energy Sciences. We gratefully acknowledge Dr. Alexander Hexemer, Dr. Cheng Wang, and Dr. Eric Schaible for experimental assistance at the ALS, Dr. John Pople for experimental assistance at the SSRL, and Dr. Yuri Melnichenko and Dr. Gang Cheng for experimental assistance at ORNL.

4.6. Appendix: Supporting SAXS and SANS Data
Figure 4.A1. Small-angle Scattering Profiles of Varying $\phi_p$ with Block Copolymers of Fixed $N_T$. (a) dS2VP(7.1-6.8) and (b) S2VP(11.6-7.8) at 145 °C. In all cases, the peak labels correspond to the $q/q^*$ for scattering peaks.
Figure 4.A2. SAXS Profiles of Varying $\phi_P$ with Block Copolymers of Fixed N_{PVP}. (a) S2VP(8.7-12.0), (b) S2VP(12.0-12.4), and (c) S2VP(18.4-11.4). In all cases, the peak labels correspond to the $q/q^*$ for scattering peaks.
4.7. References


Chapter 5. Ionic Liquid Distribution in Ordered Block Copolymer Solutions


The distribution of an ionic liquid within microphase-separated domains of a block copolymer in mixtures of the two components is studied using contrast-matched small-angle neutron scattering (SANS) and differential scanning calorimetry (DSC). In concentrated mixtures of a poly(styrene-block-2-vinyl pyridine) (S2VP) copolymer in an imidazolium bis(trifluoromethane)sulfonamide ([Im][TFSI]) ionic liquid (ionic liquid volume fraction ranging from 0.50 to 0.86), the ionic liquid preferentially pervades the poly(2-vinyl pyridine) (P2VP) blocks. Unexpected differences in the degree of partitioning into P2VP-rich and polystyrene-rich (PS) microphases are observed in mixtures with hydrogenated versus deuterated [Im][TFSI]. In the case of mixtures with hydrogenated [Im][TFSI], the microphase partition coefficient, defined as the ratio of the ionic liquid volume fraction in the PS-rich microphase relative to that in the P2VP-rich microphase, ranges from 0.0 to 0.1. In contrast, the microphase partition coefficient in mixtures with deuterated [Im][TFSI] range from 0.2 to 0.5.

5.1. Introduction

Block copolymers are an extensively studied class of materials that self-assemble on the 10 nm length scale. Additives such as molecular solvents, salts, and nanoparticles, have been combined with block copolymers in order to provide functionality, and the resulting multiphase systems are themselves topics of vibrant research. Polymer/ionic liquid mixtures have been the subject of an increasing number of publications due to the opportunities created by the combination of a solid polymer support and the attractive physiochemical properties of ionic liquids, such as nonflammability, negligible vapor pressure, high ionic conductivity, and wide electrochemical stability window, for applications including battery electrolytes, fuel cells, and field-effect transistors. Block copolymer-based electrolytes show promise in decoupling mechanical and ion-conducting properties critical for such applications.

To date, studies of block copolymer/ionic liquid mixtures have largely explored the self-assembly of these systems from the perspective of polymer/solvent interactions over a broad range of compositions and these prior studies are comprehensively reviewed in ref. 11. In most cases, the block copolymers contain a polar block that is miscible with the ionic liquid, and a non-polar block that is immiscible with the ionic liquid. The miscible block forms the functional ion-transporting channel while the immiscible block provides mechanical stability. To our knowledge there are no prior studies of the distribution of ionic liquids in block copolymer microphases. This knowledge is crucial for enabling applications, as high concentrations of the ionic liquid in the non-polar microphases may decrease the efficiency of ion transport and plasticize the microphases that are intended to provide mechanical stability.

Small-angle neutron scattering (SANS), resonant soft X-ray scattering (RSoXS), and energy filtered transmission electron microscopy (EFTEM) are techniques that can, in principle, be used to determine the distribution of a component of interest in complex, multicomponent systems. In this study, we report on the use of contrast-matched SANS to characterize the distribution of an imidazolium bis(trifluoromethane)sulfonamide ([Im][TFSI]) ionic liquid within poly(styrene-block-2-vinyl pyridine) (S2VP) copolymer domains (Figure...
A simple model is presented for determining the distribution of [Im][TFSI] in PS- and P2VP-rich microphases at varying block copolymer concentrations. Together with thermal characterization of the S2VP/[Im][TFSI] mixtures using differential scanning calorimetry, we find an unexpected dependence of the partitioning of [Im][TFSI] within block copolymer domains on deuterium labeling of the ionic liquid.

5.2. Experimental Section

**Polymer Synthesis and Characterization.** Three poly(styrene-block-2-vinyl pyridine) (S2VP) copolymers were synthesized via anionic polymerization using standard methods. The number-averaged molecular weight ($M_N$) of the polystyrene (PS) homopolymers and polydispersity (PDI) of each block copolymer were determined using gel permeation chromatography (GPC) and the total number-averaged molecular weights of the block copolymers were determined via $^1$H NMR (Bruker AVB-300). The S2VP copolymers are designated hS2VP(xx-yy) or dS2VP(xx-yy), where xx and yy refer to the number averaged molecular weights in kg/mol of the PS and P2VP blocks, respectively, and the prefix h or d indicates a hydrogenated or deuterated PS block. For dS2VP, d8-styrene monomer (Polymer Source) was utilized. In Table 5.1, the $M_N$, PS volume fraction ($f_{PS}$), and polydispersities of all copolymers are given.

**Ionic Liquid Purification.** Imidazole ($\geq 95\%$) and bis(trifluoromethane)sulfonamide (HTFSI, $\geq 95\%$) were purchased from Sigma Aldrich and d-imidazole (d4, $\geq 98\%$ deuteration, $\geq 98\%$ purity) was purchased from Cambridge Isotopes. Each compound was purified by sublimation under vacuum. Differential scanning calorimetry (DSC) was used to assess the purity of the starting materials. Purified imidazole and HTFSI were combined in equimolar quantities in a glove box, sealed, and heated in an oven outside the glove box to 100 $^\circ$C for 2-3 hours to prepare the ionic liquid [Im][TFSI]. The composition of both [hIm][TFSI] and [dIm][TFSI], where the prefix h or d indicates a hydrogenated or deuterated imidazolium cation, respectively, was confirmed by comparing the melting point (72-74 $^\circ$C) with literature.

**Differential Scanning Calorimetry Sample Preparation and Methods.** Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC 2920. Samples were solution cast in a glove box into aluminum DSC pans from the same solutions used to prepare scattering samples. The samples were heated to 60 $^\circ$C (above the boiling point of dichloromethane) in the glove box for ca. 18 hours to remove remaining solvent and then annealed 2-3 hours at 145 $^\circ$C inside the glove box. The samples were then crimped within the glove box using hermetically sealed pans and placed inside a container with desiccant for transfer to the DSC. Indium and dodecane were used as calibration standards for the DSC. Samples underwent three heating and cooling cycles to ensure reproducibility.

**Small-Angle Neutron Scattering Sample Preparation and Methods.** Dichloromethane was degassed using three freeze, pump, thaw cycles, stirred over CaH$_2$ overnight, then distilled into a collection flask, brought into a glove box, and stored on molecular sieves. Predetermined quantities of [hIm][TFSI], [dIm][TFSI], hS2VP(7-7), hS2VP(12-12), and dS2VP(7-7) were weighed into glass vials, and ca. 5 wt% solutions were prepared using dichloromethane in the glove box. Solutions were stirred overnight. Samples were cast into sample cells with an aluminum spacer sealed onto a quartz window on one side in the glove box. The polymer/ionic liquid solution was put into the sample cell one drop at a time. Solvent was allowed to evaporate before addition of the next drop until a ca. 1 mm solid sample was obtained.
Figure 5.1. Chemical Structure of [Im][TFSI] and S2VP Copolymer. Imidazolium bis(trifluoromethane)sulfonamide ([Im][TFSI]) ionic liquid and the poly(styrene-block-2-vinyl pyridine) (S2VP) copolymer chemical structures.
Table 5.1. Characteristics of Copolymers Used in this Study

<table>
<thead>
<tr>
<th>Block Copolymer</th>
<th>$M_N$ PS (g/mol)</th>
<th>$M_N$ P2VP (g/mol)</th>
<th>$f_{PS}$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>dS2VP(7-7)</td>
<td>7,100</td>
<td>6,800</td>
<td>0.50</td>
<td>1.10</td>
</tr>
<tr>
<td>hS2VP(7-7)</td>
<td>7,400</td>
<td>7,000</td>
<td>0.48</td>
<td>1.13</td>
</tr>
<tr>
<td>hS2VP(12-12)</td>
<td>12,000</td>
<td>12,400</td>
<td>0.49</td>
<td>1.19</td>
</tr>
</tbody>
</table>
in the sample cell. Samples were heated to 60 °C in the glove box for ca. 18 hours to remove remaining solvent and then annealed 2-3 hours at 145 °C inside the glove box. A second quartz window was glued to seal the samples in the glove box, which were stored with desiccant when outside the glove box to reduce the chance of water contamination. Samples are designated by the value of the estimated polymer volume fraction, $\phi_p$, assuming ideal mixing. The densities of [hIm][TFSI] and [dIm][TFSI] were estimated to be 1.67 g/cm$^3$ and 1.69 g/cm$^3$, respectively, from scattering length density fits of small-angle neutron scattering (SANS) intensity profiles presented in this paper. The densities of hPS, dPS, and P2VP were taken to be 1.13, 1.15 and 1.05 g/cm$^3$, respectively.

Small-angle neutron scattering (SANS) measurements were performed at the National Institute of Standards and Technology (NIST) on the NG7 SANS instrument. Neutrons with a 6 Å wavelength and a sample to detector distance of 13, 4.5 and 1 m were utilized at NIST. Data from room temperature samples was collected and the intensity corrected for instrumental background, empty cell scattering, sample transmission, and incoherent background with user-facility developed software. This gives the coherent scattering intensity, $I$, as a function of the magnitude of the scattering vector, $q$, $q=(4\pi/\lambda)\sin(\theta/2)$, where $\lambda$ is the neutron wavelength and $\theta$ is the scattering angle. In some samples, a small positive scattering intensity in the range of 0.1 cm$^{-1}$, remained after this data reduction procedure, probably due to the fact that our procedures for correcting for incoherent scattering are approximate. In these cases, the residual intensity was removed by subtracting the average intensity over the range 0.40<$q<$0.59 Å$^{-1}$.

5.3. Results and Discussion

Experimental Observations. Representative SANS profiles from mixtures with a fixed polymer concentration $\phi_p$=0.86 are shown in Figure 5.2. All scattering profiles were recorded at 30 °C. The parameter $f_d$, defined as the volume fraction of dS2VP(7-7) in the mixture without ionic liquid, indicates the composition of the deuterated polymer in each mixture. S2VP/[hIm][TFSI] data are shown in Figure 5.2a. The mixture with $f_d$=1.00 exhibits a lamellar morphology with peaks at $q$=$q^*$, $2q^*$ and $3q^*$ (where $q^*$ is the magnitude of the scattering vector at the primary peak). The introduction of hS2VP(7-7), i.e. decreasing $f_d$, results in a decrease in the intensity of the primary peak and a loss of higher order peaks due to a decrease in the neutron scattering contrast between the PS-rich and the P2VP-rich lamellae. At $f_d$=0.20, the primary peak is absent, indicating a perfect match in the contrasts of the PS-rich and the P2VP-rich lamellae. Further reduction of $f_d$ leads to an increase in scattering intensity of the primary peak intensity. At $f_d$=0.10, higher order peaks corresponding to the lamellar phase reappear. Qualitatively similar results are obtained from S2VP/[dIm][TFSI] mixtures with the contrast matching condition occurring at $f_d$=0.25, as shown in Figure 5.2b. The center-to-center distance between adjacent PS lamellae, $d=2\pi/q^*$, is 19.8 ± 0.2 nm in the $f_d$=1.00 samples in both [hIm][TFSI] and [dIm][TFSI] ionic liquids, indicating that deuteration of imidazole does not influence the observed morphology. The small change in $d$ observed in both [hIm][TFSI] and [dIm][TFSI] mixtures with S2VP copolymer as $f_d$ is varied is probably caused by a slight mismatch of molecular weight in the hS2VP(7-7) and dS2VP(7-7) copolymers. Additional contrast matching experiments were performed on $\phi_p$=0.69 and $\phi_p$=0.50 S2VP copolymer mixtures in both [hIm][TFSI] and [dIm][TFSI]. The SANS profiles of these samples are shown in the Appendix, Figures 5.A1 and 5.A4.
Figure 5.2. SANS Intensity Profiles of $\phi_p=0.86$ Solutions. (a) [hIm][TFSI] and (b) [dIm][TFSI] with varying $f_d$ of the hS2VP(7-7)/dS2VP(7-7) copolymers at 30 °C (offset for clarity). In all cases, the individual intensity profiles are labeled with the volume fraction of dS2VP.
SANS Contrast Matching. The scattering intensity from a given sample wherein only $f_d$ is varied is given by ref. 19:

$$I(q^*) = \left( b_{PS,eff} - b_{P2VP,eff} \right)^2 \quad (5.1)$$

where $I(q^*)$ is the primary peak scattering intensity and $b_{i,eff}$ is the effective scattering length density of microphase $i$ (PS-rich or P2VP-rich). Assuming a homogeneous distribution of [Im][TFSI] within PS-rich and P2VP-rich microphases, we can write $b_{i,eff}$ as:

$$b_{i,eff} = \sum_j \phi_{i,j} b_j \quad (5.2)$$

where $\phi_{i,j}$ is the mean intra-block volume fraction of component $j$ within microphase $i$ and $b_j$ the scattering length density of component $j$, given in Table 5.2. Thus, for example, the intra-block volume fraction of ionic liquid within the PS-rich microphase is given by $\phi_{PS,IL}$. The intra-block volume fractions, $\phi_{i,j}$, of each microphase $i$ is constrained by

$$\sum_j \phi_{i,j} = 1 \quad (5.3)$$

We introduce a variable, $f_{phase,PS}$, the volume fraction of the PS-rich microphase swollen with ionic liquid. By definition, $f_{phase,P2VP}$, the volume fraction of the P2VP microphase swollen with ionic liquid, is given by:

$$f_{phase,P2VP} = 1 - f_{phase,PS} \quad (5.4)$$

The intra-block volume fraction of ionic liquid within the microphases, $\phi_{PS,IL}$ and $\phi_{P2VP,IL}$, are related by:

$$\phi_{P2VP,IL} = \left( \frac{1 - \phi_P}{f_{phase,P2VP} \times \phi_{PS,IL}} \right) \quad (5.5)$$

The degree of mixing between the PS/P2VP blocks, quantified by $\phi_{PS,P2VP}$ and $\phi_{P2VP,PS}$, are related by:

$$\phi_{P2VP,PS} = \left( \frac{f_{PS} \times \phi_P - f_{phase,PS} \times \phi_{PS,PS}}{f_{phase,P2VP}} \right) \quad (5.6)$$

where $f_{PS}$ is the known volume fraction of PS in the copolymer and $\phi_P$ is the known overall volume fraction of polymer in the mixtures. Equations 5.2-6 contain eight unknown variables and thus there are three independent variables that we determine from the SANS data: $\phi_{PS,IL}$, $\phi_{PS,P2VP}$, and $f_{phase,PS}$. Previous studies that examine the effect of deuterium labeling on polymer thermodynamics suggest that the effect of deuterium labeling of PS chains on thermodynamics should be negligible. We thus assume that changes in $f_d$ do not affect the distribution of the components.

Primary peak intensities, $I(q^*)$, were extracted from the SANS data assuming a power law background in the vicinity of the peak. We focus on $I(q^*)/I_0(q^*)$, which is the peak intensity normalized by the peak intensity of the $f_d=0.00$ sample. Initial values of $f_{phase,PS}$ and $f_{phase,P2VP}$ for calculating $I(q^*)/I_0(q^*)$ were determined by assuming all of the ionic liquid pervades the
Table 5.2. Scattering Length Densities of Polymers and Ionic Liquids.

<table>
<thead>
<tr>
<th>Component</th>
<th>Neutron, b/v * 10^b (Å^-2)</th>
<th>Volume (Å^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hPS</td>
<td>1.41</td>
<td>179</td>
</tr>
<tr>
<td>dPS</td>
<td>5.95</td>
<td>179</td>
</tr>
<tr>
<td>P2VP</td>
<td>1.96</td>
<td>179</td>
</tr>
<tr>
<td>[hIm][TFSI]</td>
<td>3.06</td>
<td>347</td>
</tr>
<tr>
<td>[dIm][TFSI]</td>
<td>5.04</td>
<td>347</td>
</tr>
</tbody>
</table>
P2VP phase (φ_{PS, IL}=0.00) using equation 5.7. An iterative procedure, based on equation 5.7 was used to re-calculate the values of \( f_{\text{phase, PS}} \) and \( f_{\text{phase, P2VP}} \) as the partitioning of ionic liquid and mixing between PS/P2VP blocks was varied,

\[
f_{\text{phase, P2VP}} = f_{\text{P2VP}} \phi_p + (1 - \phi_p) \left( \frac{f_{\text{phase, P2VP}}^* \phi_{\text{P2VP, IL}}^*}{f_{\text{phase, P2VP}}^* \phi_{\text{P2VP, IL}}^* + f_{\text{phase, PS}} \phi_{\text{PS, IL}}^*} \right) \tag{5.7}
\]

where an \('*'\) superscript denotes the corresponding composition values for the prior iteration. The iterations were repeated until the calculated and measured dependence of \( I(q^*)/I_h(q^*) \) on \( f_d \) were in agreement.

From our previous work, we have found that S2VP/[Im][TFSI] mixtures with similar molecular weights as the copolymers used in this study exhibit Strong Segregation Limit molecular-weight-dependent scaling behavior over a broad range of \( \phi_p \). Helfand and Tagami have shown using self-consistent field theory (SCFT) that the interfacial width, \( w \), between block copolymer domains scales as \( w \sim \chi^{-1/2} \) for small values of \( \chi \), where \( \chi \) is the Flory-Huggins interaction parameter. Subsequently, Shull determined the dependence of \( w \) on \( \chi N \) for finite values of \( \chi N \) in block copolymers where \( N \) is defined as the degree of polymerization. In the case of block copolymers dissolved in a selective molecular solvent, Huang et al. determined using SCFT that the chain inter-mixing increases with dilution. Based on ref. 27, we estimate that the width of the interface increases by about a factor of two or less relative to the dry state, when \( \phi_p = 0.5 \) (the lower limit of our experimental window). Using the argument that \( \phi_{\text{P2VP, PS}} \) and \( \phi_{\text{PS, P2VP}} \) are of order \( w/d \), we obtain the restriction that \( 0 \leq \phi_{\text{PS, P2VP}} \leq 0.15 \) and \( 0 \leq \phi_{\text{PS, P2VP}} \leq 0.15 \). We use this restriction to evaluate the partitioning of the ionic liquid between the PS-rich and the P2VP-rich phases.

In Figure 5.3a we compare the experimentally observed \( I(q^*)/I_h(q^*) \) values (symbols) from \( \phi_p = 0.86 \) S2VP/[Im][TFSI] with calculations (curves) based on equations 5.1-7. The two curves in Figure 5.3a correspond to two different compositions that are labeled p1-p2. The volume fractions of the components within the PS- and PVP-rich microphases, corresponding to profiles p1-p2 are given in Figure 5.3b. Profile p1 assumes complete partitioning of [Im][TFSI] into P2VP blocks with moderate mixing of PS and P2VP phases (\( \phi_{\text{PS, P2VP}} = 0.15, \phi_{\text{P2VP, PS}} = 0.12 \)). The predicted dependence of \( I(q^*)/I_h(q^*) \) on \( f_d \) based on p1 exhibits a contrast match at \( f_d = 0.20 \) in agreement with experiments. In addition, the measured increase of \( I(q^*)/I_h(q^*) \) as \( f_d \) deviates from the matching point is in agreement with the predictions based on p1. Profile p2 results from the same degree of PS and P2VP mixing as p1, but some of the [Im][TFSI] is allowed to pervade the PS phase (\( \phi_{\text{PS, IL}} = 0.06 \) and \( \phi_{\text{P2VP, IL}} = 0.20 \)). The predicted dependence of \( I(q^*)/I_h(q^*) \) on \( f_d \) based on p2 exhibits a contrast match at \( f_d = 0.17 \) which is well-removed from the experimental observation. In addition, profile p2 substantially overpredicts \( I(q^*)/I_h(q^*) \) at high values of \( f_d \).

We define a microphase partition coefficient of the ionic liquid, \( \gamma_{IL} \), as:

\[
\gamma_{IL} = \frac{\phi_{IL, PS}}{\phi_{IL, P2VP}} \tag{5.8}
\]
Figure 5.3. Model Fits and Composition Profiles for $\phi_p=0.86$ Solutions. (a) Comparison of experimentally measured and modeled $I(q^*)/I_{h}(q^*)$ for $\phi_p=0.86$ solutions in [hIm][TFSI] as a function of $f_d$ at 30 °C. Inset shows detail near contrast match composition. (b) Composition of PS and P2VP phases in $\phi_p=0.86$ S2VP copolymer/[hIm][TFSI] mixtures for profiles p1-p2 corresponding to $I(q^*)/I_{h}(q^*)$ profiles in (a).
Figure 5.4. Model Fits for $\phi_P=0.86$ Solutions in [dIm][TFSI]. Comparison of experimentally measured and modeled $I(q^*)/I_{h}(q^*)$ for $\phi_P=0.86$ solutions in [dIm][TFSI] as a function of $f_d$ at 30 °C. Inset shows detail near contrast match composition. See Figure 5.3b for the composition of PS and P2VP phases in $\phi_P=0.86$ S2VP copolymer/[dIm][TFSI] mixtures of profiles p1-p2.
The values of $\gamma_{IL}$ were determined from the best fit of the dependence of $I(q^*)/I_h(q^*)$ on $f_d$. Error bars for $\gamma_{IL}$ are determined from the 95% confidence interval of the best fit determined from analysis of the residuals and represent a range of $\gamma_{IL}$ values that satisfy the residuals constraint, and not a standard deviation. Using this approach we obtain $\gamma_{IL}$ for [hIm][TFSI] in S2VP at $\phi_P=0.86$ to be 0.00 ± 0.01.

In Figure 5.4 we compare the experimentally observed $I(q^*)/I_h(q^*)$ values (symbols) from $\phi_P=0.86$ S2VP/[hIm][TFSI] with calculations (curves) based on equations 5.1-7. The two curves in Figure 5.4 correspond to compositions p1-p2 defined in Figure 5.3b. In this case, profile p1, predicts a minimum at $f_d=0.33$ which is well-removed from the experimentally observed contrast matching point. In addition, the calculations severely under-predict the value of $I(q^*)/I_h(q^*)$ at large values of $f_d$. In contrast, both the location of the minimum in $I(q^*)/I_h(q^*)$, and the increase in $I(q^*)/I_h(q^*)$ as the composition departs from the contrast matching point is captured by predictions based on profile p2. It is evident that there is a relatively large concentration of [dIm][TFSI] in the PS-rich phase. Based on the method described above, we determine $\gamma_{IL}$ for [dIm][TFSI] in S2VP at $\phi_P=0.86$ to be 0.17 ± 0.10.

We repeated the analysis described above for varying $\phi_P$ values. Results obtained at $\phi_P=0.69$ and $\phi_P=0.50$ S2VP/[hIm][TFSI] and S2VP/[dIm][TFSI] mixtures are given in the Appendix. The results of this analysis are summarized in Figure 5.5, where we plot $\gamma_{IL}$ versus $\phi_P$ for the S2VP/[hIm][TFSI] and S2VP/[dIm][TFSI] mixtures. Included in Figure 5.5 are data obtained from mixtures of hS2VP(12-12) and dS2VP(7-7) copolymers (our discussion thus far has been focused on mixtures of hS2VP(7-7) and dS2VP(7-7) copolymers). The analysis indicates that $\gamma_{IL}$ for [dIm][TFSI] ranges from 0.09 to 0.58 while that of [hIm][TFSI] is in the vicinity of 0 to 0.09. In spite of the large error bars, it is evident that $\gamma_{IL}$ increases with increasing ionic liquid concentration in the case of [dIm][TFSI]. The observed [dIm][TFSI] partitioning is not significantly affected by morphological changes; both the $\phi_P=0.86$ and $\phi_P=0.69$ mixtures exhibit a lamellar morphology, while the $\phi_P=0.50$ mixture exhibits a hexagonally close-packed cylinder morphology.

The striking difference in partitioning of the deuterated and protonated ionic liquid in the PS- and P2VP-rich phases, seen in Figures 3-5, is unexpected. The error bars in Figure 5.5 mainly reflect our inability to ascertain the extent of inter-mixing of the PS and P2VP chains and the fact that the calculations are constrained by $0\leq\phi_{PS,P2VP}\leq0.15$ and $0\leq\phi_{P2VP,PS}\leq0.15$. Figure 5.6 is a plot of $\gamma_{IL}$ as a function of $\phi_{PS,P2VP}$ for $\phi_P=0.69$ S2VP mixtures in [hIm][TFSI] and [dIm][TFSI] where there are no constraints on $\phi_{PS,P2VP}$ and $\phi_{P2VP,PS}$. For the $\phi_P=0.69$ S2VP/[hIm][TFSI] mixtures, a minimum degree of PS/P2VP mixing ($\phi_{PS,P2VP}=0.11$) is necessary to achieve an acceptable fit to the contrast match SANS data. As $\phi_{PS,P2VP}$ is increased above this value, a range of $\gamma_{IL}$ values are consistent with the SANS data as indicated in Figure 5.6. In the case of the S2VP/[dIm][TFSI] mixtures a satisfactory fit can be achieved with no PS/P2VP mixing ($\phi_{PS,P2VP}=0.00$). We thus show $\gamma_{IL}$ obtained over the entire range $0\leq\phi_{PS,P2VP}\leq0.35$. At $\phi_{PS,P2VP}$ values above 0.35, the predictions and measured dependencies of $I(q^*)/I_h(q^*)$ on $f_d$ are not in agreement, and the absolute upper bound for $\phi_{PS,P2VP}$ is thus 0.35. In Figure 5.6 we see that $\gamma_{IL}$ from [dIm][TFSI] samples is significantly larger than that of [hIm][TFSI] for all values of $\phi_{PS,P2VP}$. The larger value of $\gamma_{IL}$ of [dIm][TFSI] samples is expected to lead to more inter-mixing, i.e. a larger value of $\phi_{PS,P2VP}$. This will only increase the disparity between $\gamma_{IL}$ from the [dIm][TFSI] mixture relative to the [hIm][TFSI] mixture. Our conclusion that $\gamma_{IL}$ is greater in the case of the deuterated ionic liquid is thus robust.
In the case of the $\phi_P=0.50$ S2VP/[hIm][TFSI] mixtures, we were unable to achieve a satisfactory fit to the contrast match SANS data with the PS/P2VP mixing constraint $\phi_{PS,P2VP}\leq 0.15$. Relaxing the PS/P2VP mixing constraint to $\phi_{PS,P2VP}\leq 0.25$, a satisfactory fit to SANS data is achieved with $\gamma_{IL}=0.02 \pm 0.02$, a value that is similar to that found at other values of $\phi_P$ for the [hIm][TFSI] mixtures. We have not included this data point in Figure 5.5 as it was obtained using a different constraint on $\phi_{PS,P2VP}$.

Another constraint on the value of $\phi_{PS,P2VP}$ is obtained when we examine the temperature-dependence of the SANS results. In Figure 5.7, we plot the temperature dependence of $I(q^*)/I(q^*, T=30^\circ C)$ for the $\phi_P=0.86$ hS2VP(12-12)/[hIm][TFSI] and dS2VP(7-7)/[hIm][TFSI] mixtures (left-hand y-axis). $I(q^*)/I(q^*, T=30^\circ C)$ is defined as the ratio of the SANS-determined (or calculated) $I(q^*)$ to the $I(q^*)$ of the same sample (or calculation) obtained at 30°C. The corresponding SANS profiles are given in the Appendix, Figure 5.A10. We anticipate that as the temperature of the mixture increases, the selectivity of [Im][TFSI] for the P2VP phase will decrease along with an increase in the degree of mixing between PS and P2VP blocks. Based on the scattering length densities of the components (Table 5.2) and equations 5.1-7, this expectation would lead to a monotonic decrease in the value of $I(q^*)/I(q^*, T=30^\circ C)$ for both hS2VP(12-12)/[hIm][TFSI] and dS2VP(7-7)/[hIm][TFSI] mixtures with increasing temperature. Instead, we observe that $I(q^*)/I(q^*, T=30^\circ C)$ of hS2VP(12-12)/[hIm][TFSI] increases with temperature. This trend can only be explained by a decrease of the partitioning of [Im][TFSI] into the PS phase accompanied by an increase in PS/P2VP mixing. The contrast matching results from the $\phi_P=0.86$ S2VP/[hIm][TFSI] mixtures at 30°C indicated that $\gamma_{IL}=0.035 \pm 0.035$ (Figure 5.5). Predictions of $I(q^*)/I(q^*, T=30^\circ C)$ based on equations 5.1-7 are represented by the curves in Figure 5.7, and the right-hand y-axis in Figure 5.7 shows the temperature dependence of $\gamma_{IL}$ that were used in the predictions. The value of $\gamma_{IL}$ at 30°C used in these predictions is 0.07 which is at the upper end of the range of $\gamma_{IL}$. The temperature dependence of intermixing of the PS and P2VP blocks obtained from this analysis is given in the Appendix, Figure 5.A11. Using $\gamma_{IL}$ values less than 0.045 at 30°C lead predictions that are inconsistent with experimental data. The temperature-dependent data shown in Figure 5.7 provide valuable additional constraints on determination of the ionic liquid distribution within the PS and P2VP microphases.

DSC thermograms for varying $\phi_P$ of S2VP/[Im][TFSI] mixtures in which either PS or [Im][TFSI] is deuterated are presented in Figure 5.8a. For the neat copolymer samples, the $T_g$ of hS2VP(12-12) and of dS2VP(7-7) are 95 and 98°C, respectively, due to the similarities of the $T_g$'s of the PS and P2VP homopolymers. Samples with [Im][TFSI] exhibit two $T_g$'s, the low temperature $T_g$ representing the P2VP-rich microphase plasticized by [Im][TFSI], and the high temperature $T_g$ representing the PS-rich microphase ($T_g,PS$) that contains a much lower concentration of [Im][TFSI]. In Figure 5.8b, we plot $T_g,PS$ as a function of [Im][TFSI] partitioning in the PS-rich microphase determined by SANS. Error bars in Figure 5.8b correspond to the range of $\gamma_{IL}$ values shown in Figure 5.5. For the hS2VP/[hIm][TFSI] mixtures, the $T_g,PS$ is in the vicinity 100°C, due to the near-complete partitioning of [Im][TFSI] in the P2VP-rich microphase. In contrast, mixtures containing [dIm][TFSI] exhibit a lower $T_g,PS$. This finding is consistent with the SANS data that reveal a significant concentration of [dIm][TFSI] in the PS-rich microphase.
Figure 5.5. Composition Dependence of Ionic Liquid Partitioning. Effect of $\phi_P$ on the partitioning of ionic liquid between P2VP and PS blocks for the S2VP/[hIm][TFSI] and S2VP/[dIm][TFSI] mixtures at 30 $^\circ$C. For $\phi_P=0.86$ mixtures only, “HMW” denotes the use of hS2VP(12-12) in place of hS2VP(7-7). Error bars for $\gamma_L$ are determined from the 95% confidence interval of the best fit determined from analysis of the residuals and represent a range of $\gamma_L$ values that satisfy the residuals constraint.
Figure 5.6. Ionic liquid Partitioning as a Function of PS/P2VP Mixing. Ionic liquid partitioning into PS blocks ($\gamma_{IL}$) for $\phi_P = 0.69$ S2VP/[hIm][TFSI] and S2VP/[dIm][TFSI] mixtures as a function of PS/P2VP mixing ($\phi_{PS, P2VP}$) at 30 °C. Error bars for $\gamma_{IL}$ are determined from the 95% confidence interval of the best fit determined from analysis of the residuals and represent a range of $\gamma_{IL}$ values that satisfy the residuals constraint.
Figure 5.7. Temperature Dependence of SANS Intensity and Ionic Liquid Partitioning. SANS-determined values of $I(q^*)/I(q^*, T=30 \, ^\circ\text{C})$ of $\phi_p=0.86$ samples with [hIm][TFSI] in hS2VP(12-12) ($\triangle$) and dS2VP(7-7) ($\square$) copolymers along with predicted temperature-dependent values of $I(q^*)/I(q^*, T=30 \, ^\circ\text{C})$ (lines, left-hand axis) and $\gamma_{IL}$ (●, right-hand axis).
Figure 5.8. Thermal Properties of S2VP/[Im][TFSI] Mixtures. (a) DSC thermograms (offset for clarity) and (b) $T_{g,PS}$ versus $\gamma_{IL}$, for varying S2VP/[Im][TFSI] mixture compositions and deuterium labelings. In (a), $\phi_P$, high (↓) and low (▼) temperature $T_g$'s are specified and the heating rate is 10 °C/min. In (a-b), h and d correspond to hS2VP(12-12) and dS2VP(7-7), respectively, while [hIm] and [dIm] correspond to [hIm][TFSI] and [dIm][TFSI], respectively. In (b), error bars for $\gamma_{IL}$ are determined from the 95% confidence interval of the best fit determined from analysis of the residuals and represent a range of $\gamma_{IL}$ values that satisfy the residuals constraint.
Our DSC measurements on [hIm][TFSI] and [dIm][TFSI] indicate that the melting temperature of the salts were within experimental error (72-74 °C), but the heat of fusion of [hIm][TFSI] ($\Delta H_{\text{fus}} = 18.2 \pm 2.8 \text{ kJ/mol}$) was slightly less than that of [dIm][TFSI] ($\Delta H_{\text{fus}} = 21.1 \pm 1.4 \text{ kJ/mol}$). Simple theories based on ideal solution thermodynamics would indicate that [hIm][TFSI] would be expected to exhibit higher solubility in a non-polar polymer such as PS. The fact that we observe the opposite effect indicates the need for more sophisticated theories for understanding the interplay between molecular structure and solubility of ionic liquids in polymers.

Based on $\chi$ measurements of hydrogenated versus deuterated polymers, such as PS and poly(methyl methacrylate), we anticipate variations of order 0.001 for $\chi_{\text{PS/P2VP}}$ caused by deuterium labeling. It is thus not surprising that deuteration of the copolymers has little effect on thermodynamics. Much less is known about the effect of deuteration on ionic interactions and hydrogen bonding. These effects are likely to play an important role in determining ionic liquid partitioning of S2VP/[Im][TFSI] mixtures. Tsuda et al. have demonstrated a monotonic increase in the strength of hydrogen bonding interactions with $\phi_p$ in mixtures of a poly(ethylene oxide)-based homopolymer and 1-ethyl-3-methylimidazolium [TFSI] mixtures related to the properties of disassociated ions and their interactions with polymer chains. Similar effects might underlie our observations in S2VP/[Im][TFSI] mixtures.

5.4. Conclusion

We have examined the distribution of an [Im][TFSI] ionic liquid within microphase-separated S2VP copolymer domains in concentrated mixtures of the two components. Using SANS contrast matching and differential scanning calorimetry we established that the ionic liquid selectively partitions into P2VP domains for mixtures in the composition range $0.50 \leq \phi_p \leq 0.86$. Much more precise measurements of the distribution of ionic liquid would be possible if the extent of intermixing of the PS and P2VP blocks in the presence of ionic liquid was known from independent experiments. In spite of this limitation, we show conclusively that deuterated [Im][TFSI] is present in both PS-rich and P2VP-rich microphases while hydrogenated [Im][TFSI] is mainly present in the P2VP-rich microphase. Further work is needed to determine the underpinnings of this unexpected deuterium labeling effect.

5.5. Acknowledgements

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5.6. Appendix: Supporting SANS profiles, ionic liquid distribution model intensity fits and compositions, and temperature-dependence of PS/P2VP mixing.
Figure 5.A1. SANS Intensity Profiles of φ_p=0.69 Solutions. (a) [hIm][TFSI] and (b) [dIm][TFSI] with varying f_d of the hS2VP(7-7)/dS2VP(7-7) copolymers at 30 °C (offset for clarity). In all cases, the individual intensity profiles are labeled with the volume fraction of dS2VP.
Figure 5.A2. Model Fits and Composition Profiles for $\phi_p=0.69$ Solutions. (a) Comparison of experimentally measured and modeled $I(q^*)/I_h(q^*)$ for $\phi_p=0.69$ solutions in [hIm][TFSI] as a function of $f_d$. Inset shows detail near contrast match composition. (b) Composition of PS and P2VP phases in $\phi_p=0.69$ S2VP copolymer/[hIm][TFSI] mixtures for profiles p1-2 corresponding to $I(q^*)/I_h(q^*)$ profiles in (a).
Figure 5.A3. Model Fits for $\phi_P=0.69$ Solutions. Comparison of experimentally measured and modeled $I(q^*)/I_h(q^*)$ for $\phi_P=0.69$ solutions in [dIm][TFSI] as a function of $f_d$. Inset shows detail near contrast match composition. See Figure 5.A2b for the composition of PS and P2VP phases in $\phi_P=0.69$ S2VP copolymer/[dIm][TFSI] mixtures of profiles p1-2.
Figure 5.A4. SANS Intensity Profiles of $\phi_f=0.50$ Solutions. (a) [hIm][TFSI] and (b) [dIm][TFSI] with varying $f_d$ of the S2VP copolymer at 30 °C (offset for clarity). In all cases, the individual intensity profiles are labeled with the volume fraction of dS2VP.
**Figure 5.A5. Model Fits and Composition Profiles for $\phi_P=0.50$ Solutions.** (a) Comparison of experimentally measured and modeled $I(q^*)/I_h(q^*)$ for $\phi_P=0.50$ solutions in [hIm][TFSI] as a function of $f_d$. Inset shows detail near contrast match composition. (b) Composition of PS and P2VP phases in $\phi_P=0.50$ S2VP copolymer/[hIm][TFSI] mixtures for profiles p1-2 corresponding to $I(q^*)/I_h(q^*)$ profiles in (a).
Figure 5.A6. Model Fits for $\phi_p=0.50$ Solutions. Comparison of experimentally measured and modeled $I(q^*)/I_h(q^*)$ for $\phi_p=0.50$ solutions in [dIm][TFSI] as a function of $f_d$. Inset shows detail near contrast match composition. See Figure 5.A5b for the composition of PS and P2VP phases in $\phi_p=0.50$ S2VP copolymer/[dIm][TFSI] mixtures of profiles p1-2.
Figure 5.A7. SANS Intensity Profiles of $\phi_p=0.86$ Solutions. (a) [hIm][TFSI] and (b) [dIm][TFSI] with varying $f_d$ of the S2VP copolymer at 30 °C (offset for clarity). In all cases, the individual intensity profiles are labeled with the volume fraction of dS2VP and hS2VP(12-12) is utilized in place of hS2VP(7-7).
Figure 5.A8. Model fits and Composition Profiles for $\phi_P=0.86$ Solutions. (a) Comparison of experimentally measured and modeled $I(q^*)/I_h(q^*)$ for $\phi_P=0.86$ solutions in [hIm][TFSI] as a function of $f_d$. hS2VP(12-12) is utilized in place of hS2VP(7-7). Inset shows detail near contrast match composition. (b) Composition of PS and P2VP phases in $\phi_P=0.86$ S2VP copolymer/[hIm][TFSI] mixtures for profiles p1-2 corresponding to $I(q^*)/I_h(q^*)$ profiles in (a).
Figure 5.A9. Model Fits for $\phi_p=0.86$ Solutions. (a) Comparison of experimentally measured and modeled $I(q^*)/I_0(q^*)$ for $\phi_p=0.86$ solutions in [dIm][TFSI] as a function of $f_d$. hS2VP(12-12) is utilized in place of hS2VP(7-7). Inset shows detail near contrast match composition. See Figure 5.A8b for the composition of PS and P2VP phases in $\phi_p=0.86$ S2VP copolymer/[dIm][TFSI] mixtures of profiles p1-2.
Figure 5.A10. Temperature Dependence of SANS Intensity Profiles of $\phi_p=0.86$ Mixtures with [hIm][TFSI]. (a) hS2VP(12-12) and (b) dS2VP(7-7) copolymers at varying temperatures.
Figure 5.A11. Temperature Dependence of PS/P2VP Mixing. Degree of PS/P2VP mixing in $\phi_p=0.86$ mixtures with [hIm][TFSI] at varying temperatures.
5.7. References