MORPHOLOGY AND TRANSPORT PROPERTIES OF ION-CONTAINING TRIBLOCK COPOLYMERS

A Thesis in
Materials Science and Engineering
by
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ABSTRACT

Ion-containing polymers are an interesting subset of polymeric materials with applications in structural materials, water treatment, energy storage, and energy conversion. Within this class of polymers, ion-containing block copolymers hold promise in advancing our understanding of the structure-property relationships of water-absorbing, ion-containing membranes through their unique ability to form tunable ionic domain morphologies.

Non-ionic block copolymers have been studied extensively and the theory of how their nanophase structure is formed and the experimental methods for probing their phase behavior are well-documented in the literature. However, the addition of ions to these systems may change the traditional descriptors of phase formation in block copolymers by introducing strong electrostatic or hydrogen bonding interactions into one of the blocks. Therefore, much attention has recently been given to the study of how the chemical composition and ion content of ion-containing block polymers affect their morphology. These studies of phase formation, combined with work on how the microphase separated morphology affects transport properties, e.g. ion conductivity, will help to advance the design of next-generation, ion-containing block copolymer membranes for ion and water transport applications.

The focus of this thesis is to elucidate the phase behavior and ion transport properties of sulfonated and quaternary ammonium-containing triblock copolymers. The polymers studied in this work are sulfonated poly(hexyl methacrylate)-b-poly(styrene)-b-poly(hexyl methacrylate) [PHMA-SPS-PHMA], sulfonated poly(perfluorooctyl methacrylate)-b-poly(styrene)-b-poly(perfluorooctyl methacrylate) [PFMA-SPS-PFMA], and quaternary ammonium functionalized poly(styrene)-b-poly(ethylene/butylene)-b-poly(styrene) [QA-SEBS]. In particular, the work presented here describes the investigation of the effect of functionalizing the
midblock of the sulfonated triblock copolymers with the idea that the hydrophobic endblocks will help to increase mechanical stability of the film when the polymer is introduced to humidity. This study also investigated how the morphology of end-block functionalized quaternary-ammonium containing triblock copolymers change when introduced to varying levels of humidity. Small angle x-ray scattering and transmission electron micrography were used to quantitatively probe the morphology of the samples. Water uptake and impedance spectroscopy provided information on the transport properties of these samples. Comparisons are drawn between samples with different levels of functionalization and some comments are made on the basic mechanisms of phase formation in sulfonated and quaternary-ammonium containing block copolymers.

In the study of midblock functionalization, two different endblocks, poly(hexyl methacrylate) and poly(perfluorooctyl methacrylate), were chosen to observe how the hydrophobic portion of the polymer affected the morphology and conductivity of the membranes. Fluorinated PFMA endblocks produced materials with less order that materials with PHMA triblocks in unannealed solvent cast films, likely due to solubility and kinetic trapping issues, and these less-ordered samples showed lower proton conductivity. Better ordering of the non-fluorous PHMA-containing block copolymers was due to their low T\textsubscript{g} and good solubility during membrane casting. Poly(hexyl methacrylate)-\textit{b}-sulfonated poly(styrene)-\textit{b}-poly(hexyl methacrylate) transitioned from lamellar to disordered to hexagonally packed cylindrical morphologies with increasing functionalization while poly(perfluorooctyl methacrylate)-\textit{b}-sulfonated poly(styrene)-\textit{b}-poly(perfluorooctyl methacrylate) remained disordered throughout all tested levels of functionalization.
Quaternary ammonium functionalized SEBS block copolymers showed no change in morphological order with increased functionalization or increased humidity. The ionic domains swelled during water uptake, and the change in interdomain spacing with relative humidity depended on the percent functionalization of the styrene domain. High conductivity with low water uptake was obtained for a QA-SEBS sample with high unfunctionalized styrene content which had very low swelling upon humidification.

These results demonstrate that different trends may be observed for sulfonated and quaternary ammonium triblock copolymers as dictated by the ion clustering in each system and the chemical details of the backbone.
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Chapter 1

Introduction

Material innovation is one of the cornerstones of technological advancement. So much so that material development has come to define eras in human existence. Eras such as the Iron Age, the Bronze Age, and most currently, what could be considered the Polymer Age.\(^1\)

Polymers are long chain molecules made up of covalently bonded repeat units that can have a range of properties from brittle to ductile and everything in-between including viscoelastic behavior. It is this wide range of properties that has made polymers a driver of current high-tech devices. Like other materials, enhanced properties can be developed through mixing of chemically distinct polymers or blending of polymers with other materials to create polymer blends or polymer composites. However, unlike other materials, polymers tend to be immiscible with each other in the absence of strong interactions, which has prompted the study of block copolymers.

Homopolymers, like poly(styrene), are composed of chemically identical repeat units whose sequence persists for the entire length of the chain. Simple diblock copolymers consist of two chemically differentiated homopolymers covalently bonded together at one junction so that while the blocks are typically immiscible, they are chemically tied together usually by a covalent bond. This special situation introduces the possibility of phase separation of the distinct components into predictable morphologies. Because the ionic phase size and connectivity can be tuned by controlling the properties of the block copolymer, these polymers have found great potential in the field of ion-containing polymers.\(^2\)
Ion-containing block copolymers have shown promise as proton exchange membranes (PEMs). It is thought that by harnessing the ability of block copolymers to concentrate ions in a specific domain and leaving a structural, non-ionic domain, next-generation PEMs with improved conductivity and mechanical properties can be designed. However, the fundamental relationships between chemical structure, morphology, and membrane properties must first be understood before predictive design can be accomplished.

Therefore, it is the purpose of this study to deepen the knowledge base of the structure-property relationships of ion-containing block copolymers. This work examines the morphology, ionic conductivity, and water uptake of three different ion-containing triblock copolymers. While most research to date has focused on sulfonation of diblock and endblock functionalized triblock copolymers, this study intends to broaden understanding of these systems by investigating midblock sulfonated triblock copolymers. By functionalizing the midblock, it is hypothesized that the hydrophobic endblocks will help to provide mechanical stability under increasing water uptake with the increase in relative humidity these materials can expect to see when in use. Additionally, a series of quaternary-ammonium containing triblock copolymers was investigated and compared to the sulfonated systems in terms of how different ions may affect the morphology of ion-containing block copolymers.
Chapter 2

Literature Review

2.1. Block Copolymers

Copolymers are polymers in which sequences of two or more immiscible chains of repeat units are covalently bonded together. This arrangement results in phase separation of the different chemical constituents to form nanometer sized, tunable morphologies. Block copolymers come in a range of topologies including diblocks, triblocks, graft, star, and random copolymers among others. This study focuses heavily on block copolymers, which have attracted much attention in recent years as proton exchange membranes (PEMs). Block copolymers consist of alternating sequences of monomers in which the repeat unit is usually AB, ABA, or ABC. This study focuses on ABA triblock copolymers.

2.1. Block Copolymer Phase Separation

Phase separation of block copolymers into unique morphologies has been extensively studied. The fundamental thermodynamics underlying phase separation in polymers was first described by Paul Flory and Maurice Huggins. Flory and Huggins developed what is known as Flory-Huggins theory, which applied ideas of free energy of mixing to block copolymers. The theory incorporates the enthalpic contribution of mixing into an interaction parameter, $\chi$. This interaction parameter, when multiplied by the degree of polymerization, $N$, is used to determine the morphologies visualized in Figure 2-1 for a theoretical diblock copolymer. As can be seen in this figure, below a certain $\chi N$ value, as well as below a certain volume fraction of monomer, the polymer is in a disordered state. However, above the Order-Disorder Transition (ODT), the polymer phase separates into defined, predictable morphologies.
Figure 2-1. Theoretical phase diagram for an AB diblock copolymer. The phases shown are close packed spherical (CPS), spherical (S), hexagonally packed cylindrical (C), gyroid (G), and lamellar (L).²

In this theoretical example, the different attainable morphologies as read from 0 vol % monomer A to 50 vol % monomer A are: disordered, close packed spherical, spherical (typically in a body centered cubic (BCC) arrangement), hexagonally packed cylindrical, gyroid, and lamellar. As the volume fraction of monomer A exceeds 50 vol %, the series repeats itself in inverse with monomer A being the majority phase and monomer B the minority. An illustration depicting these phases is shown in Figure 2-2.
Figure 2-2. Illustrative depiction of phases from Figure 2-1. Phases read with increasing $f_A$ are close packed spherical (CPS), spherical (S), hexagonally packed cylindrical (C), gyroidal (G), and lamellar (L) up to 0.5 $f_A$ and then in inverse up to 1 $f_A$. Red corresponds to monomer A while blue corresponds to monomer B.2

2.2. Flory-Huggins Theory

There are several complementary theories as to why block copolymers form these morphologies with changes in their chemical composition. The principal treatment of block copolymer phase separation is Flory-Huggins theory, which is rooted in the free energy of mixing of the different polymer segments. The free energy of mixing can be described by

$$
\Delta G = \Delta H - T\Delta S
$$

(2-1),

where $G$ is the free energy of mixing, $H$ is enthalpy, $T$ is absolute temperature, and $S$ is entropy. If the free energy of mixing is negative, then it is favorable for the system to mix. However, if the free energy of mixing is positive, then mixing is unfavorable and phase separation occurs. Several factors come into play when applying this equation to block copolymers. The enthalpic portion of the equation incorporates the interaction between monomers while the entropic portion of the equation encompasses possible polymer configurations as well as the covalent bond tying monomers together. Because monomers are typically immiscible, the enthalpic portion of the equation will usually be negative and any change from the free, unbonded, pure monomer to a polymerized mixed state results in a negative entropy change. Therefore it is the relative
magnitudes of these two negative quantities that determine whether or not a block copolymer will microphase separate. In block copolymers, the enthalpic change is typically small and therefore the free energy of mixing is positive. If the molecular weight of the blocks are reduced, there is an increase in entropy and the free energy decreases towards zero and may become negative, thus the blocks will mix. This change in molecular weight affects the entropic portion of the mixing because with smaller block lengths there is less restraint on configurations of the chains.

This application of the free energy of mixing to polymers was realized by Flory and Huggins separately, although nearly simultaneously. A brief review of their derivation follows. The entropic contribution to the free energy of mixing equation is modified so that instead of mole fractions of components, volume fractions are used. This change is a result of the relatively large volume of a polymer molecule as compared to that of solvent. The volume fraction of a polymer as is defined as,

$\Phi_A = \frac{n_A M_A}{n_A M_A + n_B M_B}$

(2-2)

where $n$ is the number of molecules of each respective component and $M$ is the number of segments in each polymer chain. It should be clarified that $M$ is not the degree of polymerization but rather the volume of solution occupied by the particular polymer chain divided by the reference volume. In the case of block copolymers, this reference volume is typically taken as the molar volume of one of the chemical repeat units. This definition of volume fraction allows the entropic contribution to the free energy of mixing to be written as,

$\frac{-\Delta S}{R} = n_A \ln \Phi_A + n_B \ln \Phi_B$

(2-3).
The enthalpic contribution to the free energy of mixing employs the interaction parameter, \( \chi \), and describes the interaction between two different polymer segments. The energy change associated with this interaction can be mathematically described as,

\[
\Delta \omega_{AB} = \omega_{AB} - \frac{1}{2} (\omega_{AA} + \omega_{BB})
\]

where \( \omega_{xx} \) describes the interaction between the polymer segments of composition A and B. Assuming that the number of contacts between segments is approximately \( z n_A \Phi_B \), where \( z \) is the coordination number of the lattice, the change in enthalpy can be written as,

\[
\Delta H = z \Delta \omega_{AB} n_A \Phi_B
\]

If the interaction parameter is now defined as,

\[
\chi = \frac{z \Delta \omega_{AB}}{kT}
\]

where \( k \) is the Boltzmann’s Constant, the change in enthalpy can now be rewritten as follows,

\[
\Delta H = kT \chi n_A \Phi_B
\]

Finally, substituting equations (2-3) and (2-7) into equation (2-1) and rearranging, the Flory-Huggins equation is obtained,

\[
\frac{\Delta G}{RT} = n_A \ln \Phi_A + n_B \ln \Phi_B + n_A \Phi_B \chi
\]
It should be noted that the interaction parameter can also be estimated through a relationship to the solubility parameters of the constituent polymers. This definition of the interaction parameter is as follows,

$$\chi = \frac{V_r}{RT} (\delta_A - \delta_B)^2$$  \hspace{1cm} (2-9)

where $V_r$ is the reference volume as defined above and $\delta_x$ is the respective solubility parameter of the constituent repeat unit.$^6$

2.3. Conformational Asymmetry

While the Flory-Huggins theory of microphase separation describes the chemical, compositional, and temperature variables that lead to block copolymer phase separation, the conformational asymmetry of the blocks can explain the distortions of the above shown theoretical phase diagram.$^7$-$^{12}$ Conformational asymmetry results from a difference in either monomer volume or a difference in Kuhn length between the two blocks. Vavasour and colleagues suggest that conformational asymmetry is such a strong factor in determining the copolymer equilibrium phase diagram that instead of the above mentioned $\chi N$ vs $f_x$, phase diagrams should be shown as $\chi r_c$ vs $f_x$. They claim that these two values along with conformational asymmetry, $\varepsilon$, are the contributing factors to phase equilibrium. In the case of $\chi_{\text{eff}} r_c$, $r_c$ is defined as,

$$r_c = \rho_0 \left[ \frac{N_A}{\rho_{0A}} + \frac{N_B}{\rho_{0B}} \right]$$  \hspace{1cm} (2-10)

where $\rho_0$ is the reference density used in defining the Flory-Huggins interaction parameter, and $\rho_{0x}$ designates the respective densities for each monomer. In the case where $\rho_{0A} = \rho_{0B}$, the
densities cancel and \( r_c = N_A + N_B = N \) and the \( \chi_r \) becomes the aforementioned \( \chi N \). The conformational symmetry parameter, \( \varepsilon \), is defined by the ratios of volume fraction and unperturbed radii of gyration of the polymers. The ratio of monomer volume fractions for a diblock copolymer is,

\[
\frac{f_A}{f_B} = \frac{N_A \rho_{0B}}{N_B \rho_{0A}}
\]  

(2-11)

and the ratio of polymer unperturbed radii of gyration,

\[
\frac{R_{A,g}^2}{R_{B,g}^2} = \frac{N_A b_A^2}{N_B b_B^2}
\]  

(2-12)

where \( N \) is the degree of polymerization and \( b \) is the Kuhn length. Finally, the conformational symmetry parameter is defined as,

\[
\varepsilon = \frac{f_A}{f_B} \frac{R_{A,g}^2}{R_{B,g}^2} = \frac{\rho_{0B} b_B^2}{\rho_{0A} b_A^2}
\]  

(2-13)

From this definition of the conformational symmetry parameter it is easy to see how a difference in monomer densities or Kuhn lengths could result in a value that does not equal unity. When \( \varepsilon \) is greater or less than one, the order-order transition (OOT) boundaries of the phase diagram shift to higher volume fractions of the block with a higher density, smaller Kuhn length, or both. Figure 2-3 illustrates this point through a comparison of a diblock copolymer with \( \varepsilon = 1 \) and a diblock copolymer with \( \varepsilon = 0.6 \). The symmetric diblock copolymer phase diagram is shown on the left and closely resembles that of Figure 2-1. When conformational
asymmetry is introduced as in the phase diagram on the right, the OOT boundaries are skewed to higher $f_A$ values. This shift can be understood when the density and unperturbed radii of gyration of the two polymers, A and B, are considered. If monomer A has a higher density, smaller unperturbed radius of gyration, or both, the lamellar layers would be of different thicknesses for polymers with equal number of A and B repeat units. For the layers to be more symmetric in thickness, the copolymer would need to consist of a higher volume fraction of monomer A thus shifting the OOT boundaries to larger values of $f_A$. The shift in the volume fraction of A is because of a tighter packing of the A layer as visualized in Figure 2-4. Figure 2-4 allows for a more illustrative description of the difference in compositional and conformational asymmetry. With a symmetric conformation and composition, a diblock copolymer will reside in the lamellar phase so long as it is above the order-disorder transition (ODT). If the copolymer has conformation symmetry but compositional asymmetry, there will be a change in the interfacial curvature in which the interfacial curvature becomes concave around the block with a lower volume fraction. There will also be a spontaneous interfacial curvature change in the case of compositional symmetry and conformational asymmetry in which the curvature will become concave around the more tightly packed block. It should also be noted that while the OOT boundaries shift, the ODT boundaries remain the same.
Figure 2-3. Comparison of a theoretical diblock phase diagram with $\varepsilon = 1$ (left) and $\varepsilon = 0.6$ (right). In these diagrams $Z$ is used to denote degree of polymerization.$^{9,10}$

Figure 2-4. Illustrative description of compositional vs conformational symmetry.$^{12}$

2.4. Defects, Kinetic Trapping, and Annealing

An important field of study within block copolymer morphology is that of topological defect structures (henceforth denoted defect structures). Defect structures can be divided into two major categories, intra- and intergranular defects.$^{13}$ Intragrannular defects are typically thought of
as the classical defect structures as seen in Figure 2-5, while intergranular defects are those associated with the grain boundaries of the block copolymer as seen in Figure 2-6. Defect structures within block copolymers are mesomorphic phases that are a result of kinetic trapping within the morphology. Kinetic trapping results from the dependency of the polymer’s post-processing morphological state on the procedures used to form a solid film from solution or from the melt. The term kinetic trapping is used because the polymer’s morphology is essentially trapped in a non-equilibrium state while the system is still moving towards the state of lowest free energy. Methods of promoting the polymer to approach an equilibrium morphology are discussed below.

Defect structures are characterized by a central energy region, the location of the defect, as well as a far field region which slowly relaxes in space. Therefore, defect structures can come into contact with each other either directly or through their far field regions. When these defect structures are in close proximity, it has been shown that annealing the polymer will cause these defects to annihilate and disperse the remaining defects throughout the material so as to reduce the overall defect structure density. An example of this defect reduction is shown in Figure 2-7. According to Amundson et al., intragranular defect structures prefer to cluster. Since defect structures prefer to cluster, most of the defects will be within a range to allow annealing to annihilate and disperse them.

Some polymers, including the later mentioned ion-containing polymers, cannot be thermally annealed because of very high glass transition temperatures, \( T_g \). Therefore other methods of obtaining equilibrium morphologies such as slow solvent evaporation when casting the material and solvent annealing must be used. Slow solvent casting (over the period of days or weeks) is the process of controlling the rate of solvent evaporation from the polymer during the casting
process to a rate that allows for more time for the phase formation to approach an equilibrium morphology. Solvent annealing can be completed either alone or in combination with thermal annealing. The logic behind this process involves placing the cast polymer in the presence of a solvent (that is selective for one or both blocks) so that the polymer will solvate to an extent that allows for segmental motion and thus the polymer phases can evolve towards the equilibrium morphology. In essence, this process lowers the polymer’s glass transition temperature below room temperature, which allows for movement in the same manner that would have occurred with thermal annealing. When combined with thermal annealing, a solvent can be used to lower the glass transition temperature and simultaneously the entire solvent-polymer system can be raised above this lowered glass transition temperature so as to allow for segmental motion. This latter form of solvent annealing is especially useful in the case that lowering the effective $T_g$ below room temperature is difficult.

![Figure 2-5. Classical defect structures in block copolymers: (a) edge dislocation, (b) + ½ disclination, (c) – ½ disclination, and (d) paired ± ½ disclination.](image)

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Figure 2-6. Schematic examples of intergranular defect structures: Chevron (A), T-junction (B), and Ω (C). W corresponds to the boundary width, R to the curvature radius, θ to the tilt angle, L to the lamellar long period, and h* to the equilibrium flat layer thickness. The lamellar long period increases to $L/\cos(\theta/2)$ at the boundary in the Chevron defect.\textsuperscript{16}

Figure 2-7. Atomic force microscopy (AFM) images showing the annihilation of a disclination quadrupole (+ $\frac{1}{2}$ disclinations are blue, - $\frac{1}{2}$ disclinations are red) during annealing. Insets diagram what is happening in the AFM image for better visualization. Annealing time increases from A to D.\textsuperscript{17}
2.5. Ion-Containing Polymers

Ion-containing polymers have found important roles in several fields including fuel cell membranes,\textsuperscript{18,19} water treatment systems,\textsuperscript{20-22} and solid-state Li-ion battery electrolytes.\textsuperscript{23} These polymers are useful as structural materials as well as ion conducting materials. This work focuses on their ion-conducting properties.

Ion-containing polymers conduct ions by two distinct mechanisms: segmental motion and water dynamics. Polymers without entrained water such as those used in Li-ion batteries conduct ions through polymer segmental motion while hydrated proton exchange membranes (PEMs) rely on thermally activated water dynamics for ionic conduction. Figure 2-8 illustrates the difference in the temperature-dependent conductivity for materials that rely on water dynamics to move ions and those that rely on polymer segmental motion for ion diffusion. From this plot, it is evident that the temperature dependent conductivity of the Li-ion solid-state electrolyte follows a Vogel-Tamman-Fulcher (VFT) dependence indicative of the ion conductivity being controlled by long-range polymer segmental motion, while the PEM follows an Arrhenius dependence indicative of proton hopping and conductivity through water.
PEMs rely on both solid-state organization of acid groups, or an ionic nanophase, and water dynamics to achieve high conductivities. Poly(perfluorosulfonic acid) membranes (PFSA) are the most common polymers used in fuel cells. These polymers show ionic conduction around 80 °C when fully hydrated. While it is desirable to operate fuel cell systems at higher temperatures to increase the catalytic efficiency, PFSA membranes tend to lose conductivity at high temperatures because of the difficulties of keeping water in the membrane at high temperatures and due to the morphological disordering that occurs as the temperature is raised.

Ion-containing, water-absorbing polymers to be used as fuel cell electrolytes must maintain high ion conductivity across a range of hydration levels, low fuel crossover, and proper mechanical stability in the face of operating conditions including thermal and relative humidity (RH) cycling. While the PFSA polymers mentioned above do perform well under most conditions, there are several issues pushing new research in fuel cell membranes. The basic
flaws of PFSAs include high fuel crossover in direct methanol fuel cells (DMFC), high cost of manufacture, environmental concerns, low conductivity at low hydration, and poor mechanical properties at high temperature. Research programs in this field are focused on creating practical materials that can replace PFSAs in devices and fundamental research is being conducted, all with the aim of creating next-generation electrolytes.

Both short-range and long-range water motions are thought to promote high conductivity. Measurements of short-range water motions can be accomplished by NMR relaxation and vibrational spectroscopy.\textsuperscript{24, 25} It has been shown that the T1 D\textsubscript{2}O relaxation time increases as the polymers become more hydrated and polymers with higher proton conductivity tend to have longer T1 relaxation times indicating that the water is more mobile in these materials.\textsuperscript{26} Water self-diffusion has been measured using pulse-field gradient nuclear magnetic resonance (PFGNMR) and shows that faster diffusing water tends to lead to high proton conductivity in random and block copolymer PEMs.\textsuperscript{27}

Water exists in these polymer membranes as either free or bound water. At low temperatures (i.e., sub-freezing), most of the water is bound and therefore diffusion and ion conductivity is limited. As the temperature is increased, more water is free to diffuse through the system and ionic conductivity is increased. This phenomenon can be visualized through the change in slope at 273 K shown in Figure 2-8.

2.6. Ion-Containing Block Copolymers

There has been much effort in finding suitable alternative polymer backbones to PFSAs and exploring different polymer architectures to achieve the desired properties.\textsuperscript{28-32} However, it has been difficult to create new proton exchange membranes that have the key property of high conductivity at low relative humidity. One promising approach for achieving high conductivity
in non-PFSA polymers is to employ block copolymers to create concentrated, interconnected ionic phases. Previous work has found that block copolymers provide for higher conductivities than their random analogs.\textsuperscript{33, 34} The chemically distinct phases in ion-containing block copolymers allow for independent modifications on distinct locations of the polymer chain to optimize the conductivity of the hydrophilic ionic phase, and adjust the mechanical support or other features of the hydrophobic phase.\textsuperscript{2} It is thought that this ability to produce tunable morphologies with concentrated ionic domains can be used to design the ideal hydrophilic, ionic phase which results in the high conductivities (even at low relative humidities) found in PFSAs (Figure 2-9). Moreover, block copolymers provide the ability to adjust the hydrophobic block that can be used to improve the mechanical properties of the membrane while retaining high ionic conductivity of the optimized ionic phase.
Up to a certain point, the addition of ionic groups to an ion-containing polymer will increase its ionic conductivity. However, with this addition of tethered ions to the polymer backbone, comes excessive water uptake and the loss of mechanical integrity in the presence of water. Most work to date on ion-containing block copolymers consists of studies of diblock and end-block sulfonated triblock copolymers.\textsuperscript{36-38} Several of these polymers have displayed higher conductivities than PFSA membranes.\textsuperscript{28, 33, 34, 39-41} These high conductivity block systems typically incorporate high degrees of functionality to attain their high ionic conductivities and therefore have the tradeoff of lower mechanical stability due to increased water uptake. One notable example is a study by Elabd and coworkers in which they report on poly(styrene-b-isobutylene-b-styrene) triblock copolymers at high ion-exchange capacities.\textsuperscript{39} In this study, the
authors report a conductivity that is three times higher than that of Nafion 117 at an IEC of 2.0 meq/g. However, the high conductivity comes at a cost of ~ 14 times greater water uptake. As will be discussed later, and as has been reported in the literature, there have been studies conducted on mid-block sulfonated triblock copolymers which allow for high functionalization with the reliance on hydrophobic end-blocks for mechanical stability in the presence of water.

2.7. Phase Separation in Block Copolymers with Tethered Ions

The addition of ionic groups to block copolymers can result in modifications to the theoretical descriptions discussed above to explain the morphologies observed in block copolymers. Specifically, the strong electrostatic or hydrogen bonding interactions in these systems may lead to large conformational asymmetry beyond what has been observed for block copolymers that do not contain ions. When ions are added to a block copolymer and the polymer is then dissolved in a low dielectric constant solvent, the polymer will tend to show a coil to globular transition due to strong ion pairing interactions. This attraction can follow into the cast polymer and become kinetically trapped into a morphology that is influenced by significant conformational asymmetry and therefore a shift in the phase diagram.

The addition of ions to block copolymers at high degrees of functionalization has also shown to disrupt the long range order. This disruption of order in ion-functionalized block copolymers can be attributed to both ion pairing interactions as well as the inclusion of mass to the polymer system. However, Balsara and coworkers have been able to show block copolymer systems with high degrees of sulfonation, on the order of 53 mol %, that have well-ordered phases. In addition, solubility issues including finding suitable solvents for all constituents of a given system can lead to difficulties in obtaining equilibrium structures.
Functionalization of block copolymers with tethered ionic moieties also increases the interaction parameter to levels in the strong segregation limit. A simple example of this can be seen through Equation 2-9. Using the solubility parameters for styrene and sulfonated styrene as determined by Lu and Weiss of $18.6 \text{ (J cm}^{-3}\text{)}^{1/2}$ and $34 \text{ (J cm}^{-3}\text{)}^{1/2}$ respectively \textsuperscript{44}, the interaction parameter for poly(styrene-co-sulfonated styrene) can be estimated at $\sim11$. Therefore, for typical degrees of polymerization, the $\chi_N$ value for poly(styrene-co-sulfonated styrene) will be extremely high.

In addition to modifications of the typical phase separation descriptors in block copolymers through the inclusion of ions, the incorporation of ions to the block copolymer allows for changes in morphology in the presence of water. An example of this phenomenon was reported by Park and colleagues through their study of poly(styrenesulfonate)-b-poly(methylbutylene)\textsuperscript{45}. As can be visualized in Figure 2-10, as the humidity is increased while degree of functionalization and temperature are held constant, a second scattering peak was observed to appear at around $70 \%$ RH. The authors showed how for this polymer system, variations in temperature, degree of sulfonation, and relative humidity contribute to the morphological state of the block copolymer.
Figure 2-10. In-situ SANS profiles of poly(styrenesulfonate-b-methylbutylene) with IEC = 1.513 as a function of RH at 25 °C. Inset shows a discontinuous change in the full width at half max (FWHM) of the primary scattering peak at RH = 70%.45

Given the complexities of ionic interactions and water absorption in sulfonated polymers, it is easy to see how the introduction of ions to block copolymers has opened up a whole new line of research in polymer science. However, in order to advance the application of these polymers, we need to deepen our fundamental understanding of these systems. Comprehensive studies of the morphological, transport, and structural properties of these block copolymers are needed and this work is intended to help advance the fundamental knowledge of the structure-property relationships of these systems.
Chapter 3
Experimental Procedures

3.1. Introduction

This chapter details the materials used in this study as well as sample preparation and experimental procedures. The first section of this chapter will detail the materials used and provide a brief overview of synthetic procedures. Next, a description of film casting procedures will be presented. Finally, each experimental procedure will be explained in individual sections.

In this study, four characterization methods were employed to study the structure-property relationships of the block copolymers. These methods include: small angle x-ray scattering (SAXS), transmission electron micrography (TEM), impedance analysis, and water uptake measurements.

3.2. Materials

Several different base block copolymer structures were studied in this work: poly(hexyl methacrylate)-b-poly(styrene)-b-poly(hexyl methacrylate) [PHMA-PS-PHMA],

poly(perfluorooctyl methacrylate)-b-poly(styrene)-b-poly(perfluorooctyl methacrylate) [PFMA-PS-PFMA], and poly(styrene)-b-poly(ethylene/butylene)-b-poly(styrene) [SEBS].

The SEBS samples were provided by Tokuyama Corporation and were generally about 70,000 g/mol in total molecular weight with 30 wt % styrene content. The styrene domains were functionalized with quaternary ammonium groups. The midblock sulfonated triblock copolymers were synthesized using atom transfer radical polymerization (ATRP) from difunctional initiators to afford symmetric ABA triblock architectures with poly(styrene) center blocks and poly(methacrylate) endblocks. Poly(hexyl methacrylate)-b-poly(styrene)-b-
poly(hexyl methacrylate) and poly(perfluoroctyl methacrylate)-b-poly(styrene)-b-poly(perfluoroctyl methacrylate) had molecular weights of 58.6-b-69.1-b-58.6 kg mol\(^{-1}\) and 33.1-b-69.1-b-33.1 kg mol\(^{-1}\), respectively, by \(^1\)H NMR. The PDIs were 1.27 for the PS macroinitiator and 1.17 for the PHMA-PS-PHMA triblock copolymer and 1.25 for the PFMA-PS-PFMA triblock copolymer. The poly(styrene) block was selectively sulfonated using acetyl sulfate to varying degrees of sulfonation (DS) without side reactions. The chemical structures of the resulting polymers are shown in Figure 3-1.

![Figure 3-1. Chemical structure for (a) PHMA-sPS-PHMA and (b) PFMA-sPS-PFMA.](image)

### 3.3. Membrane Casting

The films were solution cast in PTFE molds with a glass cover for a period of 2 - 3 d to 1 week using the solvents described in Table 3-1. After the sample was dried under ambient conditions, it was placed in a vacuum oven at 40 °C overnight to ensure complete evaporation of solvent. The resulting dry film thicknesses were approximately 80 μm.
Table 3-1. Polymer casting solvents

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Degree of Functionalization</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHMA-sPS-PHMA</td>
<td>0 – 45 %</td>
<td>Dioxane</td>
</tr>
<tr>
<td></td>
<td>45 – 100 %</td>
<td>Dimethylformamide (DMF)</td>
</tr>
<tr>
<td>PFMA-sPS-PFMA</td>
<td>0 %</td>
<td>Trifluorotoluene:Toluene 8:2</td>
</tr>
<tr>
<td></td>
<td>29 %</td>
<td>DMF:Trifluorotoluene 8.5:1.5</td>
</tr>
<tr>
<td></td>
<td>45 %</td>
<td>DMF:MeOH:Trifluorotoluene 7:2:1</td>
</tr>
<tr>
<td></td>
<td>61 %</td>
<td>DMF:MeOH:Trifluorotoluene 7:2:1</td>
</tr>
<tr>
<td></td>
<td>73 %</td>
<td>DMF:MeOH:Trifluorotoluene 5:4:1</td>
</tr>
<tr>
<td></td>
<td>100 %</td>
<td>DMF:MeOH 2:8</td>
</tr>
</tbody>
</table>

3.4. Small Angle X-Ray Scattering (SAXS)

SAXS measurements were performed on a Rigaku (formerly Molecular Metrology) instrument equipped with a pinhole camera with Os Mic microfocus source and parallel beam optic. The instrument is equipped with a Cu target (\(\lambda = 1.542 \text{ Å}\)) and a multiwire area detector. Two types of measurements were made using the SAXS. The first was a dry measurement in which measurements were taken under vacuum at ambient temperature on dried samples. The dried samples were dried under vacuum at 40 °C for a minimum of 3 h prior to measurement.

Samples equilibrated at varying levels of relative humidity were also measured for their x-ray scattering. To prepare samples for this measurement, cast membranes were placed in an enclosed environment with a LiCl solution prepared so as to obtain the desired humidity (or
water activity)\(^{47}\) and allowed to equilibrate for a minimum of 2 d. Once equilibrated, the samples were placed in a vacuum tight SAXS liquid cell. This allowed for scattering from the sample at a predetermined relative humidity through Kapton windows. Relative humidities were varied from 20 \(\%\) to 90 \(\%\). The volume of the sealed liquid cell was small to maintain hydration of the polymer.

Typical measurement times varied from 10 – 30 min dependent upon the sample. Scattering intensities were normalized for background scattering and beam transmission using,

\[
I_{\text{Corrected}} = (I_{\text{Sample}} - I_{\text{Dark}}) - T(I_{\text{Open}} - I_{\text{Dark}})
\]  

(3-1)

where,

\[
T = \frac{V_{\text{Sample}} - V_{\text{Dark}}}{V_{\text{Open}} - V_{\text{Dark}}}
\]

(3-2).

In equation (3-1) and (3-2), \(I_{\text{Sample}}\) refers to the scattering intensity of the sample, \(I_{\text{Dark}}\) to the scattering intensity measured with no beam present, \(I_{\text{Open}}\) to the scattering intensity measured through an empty cell (whether that be air or Kapton), \(T\) to the transmitted beam, and \(V_{X}\) refers to the photodiode reading of each condition.
3.5. Transmission Electron Micrography (TEM)

Cast membrane samples were sectioned at -120 °C using a Leica Ultracut UC6 ultramicrotome with EMFC6 cryo attachment. The 100 nm thick sections were collected on 400hex Carbon/Formvar coated grids. Imaging was performed on a JEOL EM-2010 microscope equipped with a LaB6 emitter operating at 200 kV. Images were recorded on a Gatan interline transfer CCD camera using Digital Micrograph software. All images were taken of unstained samples.

3.6. Impedance Spectroscopy

Impedance spectroscopy was used to measure proton conductivity of the ion-containing block copolymers. Measurements were taken on a Solartron SI 1260A Impedance/Gain-Phase Analyzer. The conductivity of free-standing films was measured using a two-point, in-plane geometry at frequencies between 1 MHz and 100 Hz.48 Humidity and temperature were controlled using an Espec SH-241 humidity chamber. Temperature was held at 30 °C while relative humidity was varied from 20 % to 90 %. The impedance data was reflective of an ideal resistor or parallel capacitor-resistor from which the membrane resistance was computed from the intersection of the impedance plot with the real axis. Proton conductivity (σ) was calculated using,

\[
\sigma = \frac{1}{RA}
\]

(3-3)

where l is the length between electrodes, R is the resistance of the membrane, and A is the cross-sectional area of the membrane available for ionic current.
3.7. Water Uptake

Water uptake was determined by measuring the sample’s mass on a Mettler-Toledo AB304-S/FACT scale at 30 °C over a range of relative humidity from 20 % to 90 %. Humidity and temperature were controlled using an Espec SH-241 humidity chamber. Water uptake per sulfonate group or hydration number (λ) was calculated using,

\[
\lambda = \left( \frac{M - M_o}{18.01} \right) \left( \frac{1000}{M_o \cdot \text{IEC}} \right)
\]

(3-4)

where M is the sample mass at a given RH, M_o is the dry mass, and IEC is the ion exchange capacity.\(^49\)
Chapter 4

Morphology and Transport of Midblock-Sulfonated Triblock Copolymers


4.1. Introduction

The morphology of PEMs plays a role in their proton conductivity. When using block copolymers for proton exchange membranes, it is necessary to account for their chemical composition, solid-state morphology (including long-range order and defect structures), and transport properties. This chapter discusses a study on the morphology of two series of mid-block sulfonated triblock copolymers and contrasts the effect of order in each system. It was found that the addition of fluorine did not have the anticipated effect of increased order. Instead, it is theorized that the more flexible, non-fluorous polymer was more capable of attaining order in the as-cast state. This theory is further evidenced by the increase in ionic conductivity in the fluorous polymer when subjected to thermal annealing.

As discussed in Chapter 1, most research to date has been on diblock and end-block sulfonated triblock copolymers. The work presented here explored the morphology and transport properties of mid-block sulfonated triblock copolymers with different hydrophobic endblock composition. It is thought that the hydrophobic endblocks will provide for mechanical stability with increasing sulfonation of the center block.

4.2. Morphology

The first polymer series, poly(hexyl methacrylate)-b-sulfonated poly(styrene)-b-poly(hexyl methacrylate) (PHMA-b-sPS-b-PHMA), had flexible, less hydrophobic endblocks
with a glass transition temperature ($T_g$) of the PHMA being about -6 – 0 °C, while the poly(perfluorooctyl methacrylate)-b-sulfonated poly(styrene)-b-poly(perfluorooctyl methacrylate) (PFMA-b-sPS-b-PFMA) polymers, had more rigid, hydrophobic PFMA endblocks with a $T_g$ of c.a. 28 – 36 °C. These two polymers were sulfonated to varying degrees and films for analysis were solution cast. Their respective chemical structures are shown schematically in Figure 4-1.

![Chemical structures](image)

Figure 4-1. Chemical structures of (a) poly(hexyl methacrylate)-b-sulfonated poly(styrene)-b-poly(hexyl methacrylate), and (b) poly(perfluorooctyl methacrylate)-b-sulfonated poly(styrene)-b-poly(perfluorooctyl methacrylate) triblock copolymers. Chemical structures shown for 100 mol % DS.

At 0 mol % degree of sulfonation (DS), PHMA-b-PS-b-PHMA did not have enough electron density contrast between the two block phases to show domain structure in either SAXS or TEM. The same was true of 4 mol % sulfonated PHMA-b-sPS-b-PHMA. SEM (after etching for 10 s in oxygen plasma) was performed on a cast thin film of the 0 % sulfonated polymer (Figure 4-2) which showed disordered structure. It is not possible to determine whether the morphology was cylinders or lamella from this micrograph, but the composition of the unfunctionalized triblock copolymer was 25 vol % PS and 75 vol % PHMA, which would likely lead to a cylindrical phase.
At 20 mol % sulfonation, PHMA-\textit{b}-sPS-\textit{b}-PHMA exhibited a morphology showing two distinguishable peaks in the scattering profile as shown in Figure 4-3.

Figure 4-3. SAXS profiles for the PHMA-\textit{b}-sPS-\textit{b}-PHMA polymer series with sulfonation levels (mol \%) shown adjacent to each curve.
The maxima of the two peaks from the 20 mol % sulfonated PHMA-\textit{b}-sPS-\textit{b}-PHMA scattering data occurred in a ratio of q\textsuperscript{*}:2q\textsuperscript{*} (Gaussian peaks simultaneously fit to scattering profile), which indicated a lamellar morphology as could be anticipated from the volume fractions of the initial PHMA-\textit{b}-PS-\textit{b}-PHMA copolymer.\textsuperscript{50} Lack of higher order peaks signified that the sample had poor long-range order. The lack of long-range order was confirmed by TEM, which showed disordered lamellar structures, Figure 4-4.

![Figure 4-4](image)

Figure 4-4. Unstained transmission electron micrographs of (a) 20 mol % and (b) 29 mol % sulfonated PHMA-\textit{b}-sPS-\textit{b}-PHMA samples.

The small-angle x-ray scattering of 29 mol % sulfonated PHMA-\textit{b}-sPS-\textit{b}-PHMA indicated a lamellar morphology as well, which was confirmed by TEM (Figure 4-4). The 29 mol % sulfonation level, like the 20 mol % sulfonated sample, did not have higher order peaks or long-range order as observed by microscopy. It is difficult to derive interdomain size or spacing information from the micrographs presented in Figure 4-4, since only local pictures of the morphology are possible with microscopy. Therefore, in this study, we have relied on SAXS as a bulk average technique for quantitative measurements of the interdomain spacing.
At intermediate sulfonation levels of 58 and 81 mol %, the PHMA-b-sPS-b-PHMA samples showed several changes in both SAXS and TEM. In the SAXS profiles, single, broad peaks were observed at intermediate sulfonation, which suggested a decrease in order compared to the lower sulfonation levels. As shown in the transmission electron micrograph in Figure 4-5, there was no longer a lamellar morphology in the 58 mol % sample and a similar observation was made in TEM for the 81 mol % sample.

![Figure 4-5. Unstained transmission electron micrograph of 58 mol % sulfonated PHMA-b-sPS-b-PHMA.](image)

The disappearance of lamellar order at c.a. 50 - 80 mol % sulfonation could have been due to the sulfonated and unsulfonated styrene monomers comprising similar volume fractions in the midblock. This situation, where there was significant unsulfonated styrene, sulfonated styrene, and hexylmethacrylate coexisting on the same polymer chain might have disrupted the self-assembly behavior of the triblock copolymers. The solubility parameters of the three phases are 18.6, 34.0, and 17.6 (J cm$^{-3}$)$^{-1/2}$,$^{51,52}$ respectively, which suggests that all three phases have a tendency to phase separate from one another if appreciable sequence lengths exist. Certainly, the sulfonated styrene will have a propensity to form its own phase within the styrene block due to
its high solubility parameter and tendency to form ionic clusters as has been demonstrated in sulfonated poly(styrene) with low degrees of sulfonation.\textsuperscript{53, 54} The solution processing and film formation of these polymers could also present challenges in obtaining equilibrium morphologies giving poor ordering at intermediate levels of functionalization. The 58 and 81 mol % sulfonated samples were cast from DMF, while the lower mol % sulfonated samples were cast from 1,4-dioxane. While all polymer solutions were clear to the eye before casting, there could be aggregation of the polymer chains in solution, which may influence the ordering properties of the cast, unannealed films.

At 100 mol % sulfonation, the SAXS data could be fit with two Gaussian peaks with peak maxima in a ratio of $q^*:\sqrt{3}q^*$, indicative of hexagonally packed cylindrical morphology, however, TEM evidence did not clearly reflect this finding as evidenced in Figure 4-6. The difficulty in interpreting the TEM data was most likely a product of poor ordering in the cast, unannealed film, which caused difficulty in accurately visualizing the morphology in unstained samples. Additionally, the mechanical properties of the 100 mol % DS sample were poor, resulting in lower quality microtomed samples, which presented challenges for obtaining unambiguous micrographs. Fitting the 100 mol % DS sample SAXS profile with peak maxima occurring at a ratio of $q^*:2q^*$ did not give as good a fit as the $q^*:\sqrt{3}q^*$ fit, therefore, the SAXS evidence suggests a OOT between low DS and high DS samples.
Figure 4-6. TEM image of 100% sulfonated PHMA-sPS-PHMA.

A closer examination of the interdomain spacing of the PHMA-\(b\)-sPS-\(b\)-PHMA scattering peaks, as given in Table 4-1, shows that with increasing sulfonation, the primary scattering peaks shift to high scattering vectors, which is indicative of decreased interdomain spacing as the number of sulfonate groups is added to the center block. Also given in Table 4-1, are theoretical interdomain spacings for the lamellar morphology in these samples which was calculated using,

\[
D = 0.80\chi^{1/6}bN^{2/3}
\]  \hspace{1cm} (4-1)

where \(D\) is the theoretical interdomain spacing, \(\chi\) is the interaction parameter, \(b\) is the Kuhn length (6 Å in this case), and \(N\) is the degree of polymerization.\(^{55}\)

Equation 2-9 was used to calculate \(\chi\) and is reprinted below for reference.

\[
\chi = \frac{V}{RT} (\delta_A - \delta_B)^2
\]  \hspace{1cm} (4-2)
Solubility parameters for polystyrene, sulfonated polystyrene, and poly(hexyl methacrylate) were taken from the literature. The solubility parameter for the mixed PS-sPS midblock was calculated using,

\[
d_{PS-sPS} = \frac{\text{%DS}}{100} \frac{V_{m_{PS-sPS}}}{100} + 1 \frac{\text{%DS}}{100} \frac{V_{m_{PS}}}{100} - \frac{\text{%DS}}{100} \frac{V_{m_{PS}}}{100}
\]

where %DS is the degree of sulfonation expressed as a percentage and Vm is the molar volume of styrene (100 cm³ mol⁻¹) or sulfonated styrene (130 cm³ mol⁻¹).

The theoretical interdomain spacing correlates fairly well for the lamellar morphologies (20 and 29 mol % DS) but continues to increase with increasing sulfonation while the experimental interdomain spacings decrease. This is difference in experimental and theoretical interdomain spacing calculations is attributed to the approximation of the theoretical interdomain spacing equation or the possibility that the sulfonated polymers are not well-described by the traditional considerations of \( \chi_N \), as discussed in the next paragraph. Equation 4-2 is only valid for lamellar morphologies and the SAXS shows that the morphology of these samples is not lamellar beyond 29 % DS.

Table 4-1. Primary and secondary peak positions for the PHMA-b-sPS-b-PHMA samples as a function of sulfonation.

<table>
<thead>
<tr>
<th>DS (mol %)</th>
<th>1° peak (Å⁻¹)</th>
<th>2° peak (Å⁻¹)</th>
<th>Experimental Interdomain Spacing ( a ) (nm)</th>
<th>Theoretical Interdomain Spacing ( b ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0086</td>
<td>0.0166</td>
<td>73</td>
<td>65</td>
</tr>
<tr>
<td>29</td>
<td>0.0094</td>
<td>0.0179</td>
<td>67</td>
<td>71</td>
</tr>
<tr>
<td>58</td>
<td>0.0094</td>
<td>-</td>
<td>67</td>
<td>84</td>
</tr>
<tr>
<td>81</td>
<td>0.0106</td>
<td>-</td>
<td>59</td>
<td>91</td>
</tr>
<tr>
<td>100</td>
<td>0.0154</td>
<td>0.0264</td>
<td>41</td>
<td>95</td>
</tr>
</tbody>
</table>

\( a \) calculated from the primary peak position using \( d = 2\pi/q \)

\( b \) only valid for lamellar morphologies
The decrease in interdomain spacing with an increase in the sulfonation level runs counter to the predicted increase in interdomain spacing due to a change in $\chi$ and in molar volume of the center block upon sulfonation. As sulfonate groups are attached to the styrene residues, the molar volume of the repeat unit of the center block increases from 100 cm$^3$ mol$^{-1}$ for styrene to 130 cm$^3$ mol$^{-1}$ for sulfonated styrene. Thus, one might expect the center phase to swell, or the peak position to shift to smaller scattering vectors, with sulfonation. However, that is clearly not the case in the presented data on the PHMA triblock systems. Strong dipolar or electrostatic interactions exist in sulfonated polymers as evidenced by the increase in $T_g$ and presence of ionic clusters, even at low degrees of sulfonation.$^{57}$ Thus, we hypothesize that the decrease in the interdomain spacing of the triblock copolymers with an increase in sulfonation level was due to ion condensation within the midblock which changed the conformational asymmetry parameter of the system. A compression of the sulfonated phase would cause a corresponding decrease in the interdomain spacing of the block copolymer as depicted in Figure 4-7. As the number of sulfonate groups was increased, the ion pairing interactions became stronger as evidenced by the SAXS primary peak shift to larger scattering vectors with sulfonation. As the sulfonated phase compressed and densified, there was also a tendency to increase the mean curvature towards the sulfonated phase. The densification and mean curvature increase of the styrene block resulted in a transition from a lamellar phase at 20 and 29 mol % sulfonation to a cylindrical morphology for the 100 mol % sulfonated sample, as evidenced by the position of the SAXS peaks.
Figure 4-7. Cartoon depicting compression of the sulfonated phase (red) with increasing sulfonation. The unsulfonated phase is shown in blue and does not change.

An alternative hypothesis to the sulfonate groups changing the intrinsic interdomain spacing of the block copolymers through ion condensation and attractive chain collapse, is that the presence of sulfonate groups may have changed the aggregation of the polymer chains in solution. As the materials reported in this study were solvent cast and not annealed, ordering in solution could have had an influence on the solid-state structures observed. If the solution-state structure of the block copolymers influenced the solid-state morphology, one would have expected the solvent composition and kinetic rearrangement of the chains during the casting process to have an influence on the observed membrane structure.

The solution cast PFMA-\textit{b}-sPS-\textit{b}-PFMA polymer series did not display long-range order as given by the SAXS profiles, Figure 4-8, and as observed in TEM studies. The lack of order for polymers with poly(perfluorooctyl methacrylate) endblocks could have been the result of two different properties of the endblocks. First, the PFMA endblock is stiffer than the PHMA endblock as given by its higher T\textsubscript{g}, and therefore could have hindered the self-assembly of the
phases during the solvent casting process. Second, the solubility of the PFMA-based triblock copolymers in the casting solvent was more limited than the PHMA-based materials. A single polar solvent, namely 1,4-dioxane or DMF, produced homogeneous solutions for the PHMA-based samples for all sulfonation levels. In the case of PFMA-based polymers, mixtures of DMF, methanol, and trifluorotoluene were required to solubilize the polymers sufficiently for membrane casting (Table 3-1). The poor solubility of the PFMA-based samples during the casting process could have contributed to their lack of order in the solid state. As it is difficult to anneal sulfonated polymers due to the high T_g of sulfonated poly(styrene), the solution state of the polymers during casting must be considered. A previous study by Gromadzki, et al. revealed that polymers cast from solution, such as those in our study, retain the ionic aggregation and structure that is present in the solution. They found lamellar morphologies at low degrees of sulfonation, which became increasingly disordered with the introduction of more ions. The effects of solvent casting these types of films and the possibility of kinetically trapped nonequilibrium phases are currently being explored in our lab by subjecting the samples to thermal and solvent annealing.
Figure 4-8. SAXS profiles for the PFMA-b-sPS-b-PFMA polymer series with sulfonation levels (mol %) shown next to each curve.

Shown in Figure 4-9 are SAXS and conductivity data for a solvent cast and hot pressed 61 mol % sulfonated PFMA sample. The hot pressed sample showed higher conductivity than the sample that was solution cast. There was not a large difference in the SAXS profiles, however, the total scattered intensity was greater for the hot pressed sample. Increased phase separation brought about by hot pressing (a method of partial annealing) could have contributed to the increased conductivity by concentrating the ionic groups in a random percolated network, even in the absence of ordered phases.
4.3. Water Uptake and Conductivity

The water content and conductivity of the PHMA and PFMA triblock copolymers were investigated to determine whether the morphological differences between the two series of materials, as discussed above, impacted the proton transport properties. The mass % water uptake and hydration numbers (square) for the 29 mol % and 100 mol % sulfonated samples are shown in Figure 4-10.
The IECs of the PFMA samples were ~ 25% higher than the PHMA samples at equivalent DS, due to the lower molecular weight endblocks of PFMA as compared to PHMA. However, the water uptakes were similar at 29 mol % sulfonation, leading the PHMA membranes to have greater hydration numbers for a given relative humidity. At 100 mol % sulfonation, the PHMA sample sorbed more water than the PFMA sample, likely due to the soft PHMA endblocks. The hydrophobic component of the membrane plays a key role in constraining the swelling of the sulfonated domains. At low degrees of sulfonation, there was some reinforcement of the structure by the unsulfonated styrene, which has a high, c.a. 100 °C, $T_g$, rendering similar water sorption for the two series of materials. When sulfonated to 100 mol %, the sulfonated styrene phase was completely hydrated and the hydrophobic blocks provide the membranes’ only mechanical support. Therefore, the higher $T_g$ phase, PFMA, limited the water uptake at 100 mol % sulfonation, while the more flexible PHMA phase yielded a material with higher water sorption. The influence of increased order in the PHMA materials, as evidenced by SAXS, on the water uptake is difficult to decouple from the effect of softer blocks. In future studies, we will determine if more ordered materials, of the same composition, show the same water uptake, or if there is a morphological component to water swelling as has been shown in other studies of dissimilar materials.\textsuperscript{58}

The conductivity of the PHMA-based samples was higher for both 29 mol % and 100 mol % sulfonated samples as shown in Figure 4-11.
The greater conductivity of the PHMA-based samples can be attributed to the higher degree of water uptake and self-assembly in these materials. In many cases, the addition of fluorine increases the extent of phase separation of sulfonated polymers, which can increase the conductivity of membranes.\(^4^9\) In these block copolymers, the higher \(T_g\) and poor solubility of the PFMA blocks prevented assembly of well-ordered phases. The poorer self-organization and the lower water uptake thus decreased the conductivity of the membranes. The conductivity of the 100 % sulfonated PHMA sample exceeded that of Nafion above 65 % RH. While there is still improvement needed in these materials to surpass the conductivity of Nafion over all hydration conditions, there is much room to optimize these triblock copolymers based on modular manipulation of the properties of the separate hydrophilic and hydrophobic blocks.

**4.4 Conclusions**

In this chapter, the self-assembly of mid-block sulfonated triblock copolymers was correlated to the polymer chemical structure and the membrane ion conductive properties. The membranes showed distinctly different phase ordering in the solid state when the hydrophobic
outer A blocks of the ABA triblock copolymers were varied. Both SAXS and TEM revealed short-range lamellar order in triblock copolymers with flexible, soluble poly(hexylmethacrylate) endblocks at low degrees of sulfonation. Additionally, there was SAXS evidence of a hexagonally ordered cylindrical phase in the 100 mol % sulfonated PHMA-b-sPS-b-PHMA sample. At intermediate levels of sulfonation, 50 - 80 mol %, no self-assembly was observed in solvent-cast films. Interestingly, the principal peak in the scattering profiles shifted to higher scattering vectors with an increase in sulfonation indicating that the interdomain spacing decreased with increased electrostatic interactions in the center block.

In PFMA-based triblock copolymers, SAXS and TEM revealed no long-range self-assembled order in cast films. The unordered PFMA samples showed lower conductivity than the ordered PHMA-based materials. The self-assembly of the sulfonated phase and the water uptake of each system were determined to be the main factors for the conductivity increase in the PHMA samples.
Chapter 5

Effects of Relative Humidity on the Morphology of Triblock Copolymer Anion Exchange Membranes

5.1. Introduction

It is well known that with increasing water content, proton conductivity increases in proton exchange membranes. Most reports of PEM characterization are accompanied by proton conductivity data as a function of relative humidity. However, some groups have explored how the morphology of block copolymers change with relative humidity.\textsuperscript{45, 59} Of particular interest is the study by Park et al. which details the humidity-induced phase changes of sulfonated poly(styrene-\textit{b}-methylbutylene).\textsuperscript{45} A graphical representation of their results is given in Figure 5-1. From this figure, it is clear that as with temperature and IEC, relative humidity can have an effect on the morphology of the block copolymer. This is of particular interest in PEMs because of their typical use under varying relative humidities. It is important to understand how these polymers can change over the course of their intended use so that they may be properly designed for a given task. This chapter will discuss water uptake, SAXS, and RH influenced SAXS measurements on a poly(styrene-\textit{b}-ethylene/butylene-\textit{b}-styrene) (SEBS) triblock copolymer functionalized with quaternary ammonium groups. The chemical structure of this polymer is given in Figure 5-2.
Figure 5-1. A 3-dimensional phase cube of sulfonated poly(styrene-b-methylbutylene) as a function of temperature, relative humidity, and ion content.\textsuperscript{45}

Figure 5-2. Chemical structure of poly(styrene-b-ethylene/butylene-b-styrene) functionalized with quaternary ammonium.

5.2. Morphology

Four different QA-SEBS resins were analyzed in the dry state with SAXS. Their respective properties are listed in Table 5-1. The results of the SAXS characterization are graphically illustrated in Figure 5-3 and tabulated in Table 5-2. In Table 5-2, theoretical interdomain spacings for a lamellar morphology are given which correlate very well with those interdomain spacings obtained experimentally.\textsuperscript{60} Theoretical interdomain spacings were calculated using Semenov’s equation\textsuperscript{60}
\[ D = 1.1 \chi^{\frac{1}{6}} b N^{\frac{2}{3}} \]  

(5-1)

where \( b \) is estimated at 3.9 Å (1/3 of the molar volume), and \( \chi \) is as calculated in Equation (2-9). This equation employs a coefficient of 1.1 as opposed to the 0.8 coefficient in Equation (4-1). A coefficient of 0.8 allowed for a closer fit to the sulfonate ions while 1.1 was a better fit for the quaternary ammonium ions. This indicates that the sulfonate ions have a stronger interionic interaction than that of the quaternary ammonium ions.

Given the correlation between the theoretical calculations for a lamellar morphology and the experimental data, as well as SAXS primary and secondary peak ratios of approximately \( q^*:2q^* \), it can be concluded that the most probable morphology for these polymers is lamellar. As can be visualized in Figure 5-3 and Table 5-2, the interdomain spacing trends with the molecular weight of the ethylbutylene block. In other words, the larger the EB block, the larger the interdomain spacing.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>IEC (mmol g(^{-1}))</th>
<th>Mol % Quaternary Functionalization</th>
<th>Molecular Weight (kg mol(^{-1}))</th>
<th>Styrene Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 1</td>
<td>1.45</td>
<td>50</td>
<td>54</td>
<td>30</td>
</tr>
<tr>
<td>Resin 2</td>
<td>1.55</td>
<td>58</td>
<td>73</td>
<td>29</td>
</tr>
<tr>
<td>Resin 3</td>
<td>1.18</td>
<td>68</td>
<td>102</td>
<td>18</td>
</tr>
<tr>
<td>Resin 4</td>
<td>1.68</td>
<td>26</td>
<td>52</td>
<td>67</td>
</tr>
</tbody>
</table>
Figure 5-3. SAXS of poly(styrene-b-ethylene/butylene-b-styrene) triblock copolymer; Resin 3 (Blue), Resin 2 (Black), Resin 1 (Green), and Resin 4 (Red).

Table 5-2. Interdomain spacing for dry SAXS of poly(styrene-b-ethylene/butylene-b-styrene) triblock copolymer.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Theoretical Interdomain Spacing (nm)</th>
<th>Experimental Interdomain Spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resin 4</td>
<td>20</td>
<td>21</td>
</tr>
<tr>
<td>Resin 1</td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>Resin 2</td>
<td>33</td>
<td>32</td>
</tr>
<tr>
<td>Resin 3</td>
<td>46</td>
<td>42</td>
</tr>
</tbody>
</table>

5.3. Effect of Relative Humidity on Morphology

While the poly(styrene-b-ethylene/butylene-b-styrene) triblock copolymer did not change morphology with an increase in RH, there was a change in interdomain spacing. As would be expected with an increase in relative humidity, the interdomain spacing increased due to water sorption into the hydrophilic domains. In this work, the molecular weights of the block
copolymers were much higher than that of Park, et al. where an OOT was observed with changes in RH. In our case, the high molecular weight increased the $\chi$ and likely kinetically trapped the as-cast morphology of the dry sample.

A plot showing interdomain spacing as a function of relative humidity for the four different resins is given in Figure 5-4. It is interesting to note that the interdomain spacing of Resin 4 remained nearly constant up to 90 % RH. This small change in interdomain spacing with hydration could be attributed to the high content of unfunctionalized styrene providing for mechanical reinforcement of the ionic phase. In a comparison of the conductivity of these QA-SEBS samples with randomly functionalized poly(sulfone) AEMs containing quaternary ammonium groups, the conductivity of Resin 4 was the only block copolymer AEM which exceeded the conductivity of the random copolymers for a given water uptake (Figure 5-5). This high conductivity with low water uptake was attributed to the large fraction of unfunctionalized styrene in Resin 4, which prevented overswelling of the block structure.

![Figure 5-4. Interdomain spacing change of poly(styrene-b-ethylene/butylene-b-styrene) triblock copolymer as a function of RH. Resin 4 (■), Resin 1 (♦), Resin 2 (▲), Resin 3 (▼)
To further examine the effect of relative humidity on the morphology of the polymer, Resin 1 was functionalized to varying degrees and SAXS profiles were recorded under the influence of changes in RH. A comparison of the primary scattering peak for this resin at two different IECs and three different levels of humidity is shown in Figure 5-6. The principal peak position of Resin 1 with an IEC of 0.9 does not change much with an increase in humidity. However, at an IEC of 1.9, there is an obvious shift in the primary scattering peak position to smaller scattering vectors (larger interdomain spacings) with increasing humidity. This data shows the expected result that highly functionalized polymers sorb more water and in turn swell to a greater extent which is reflected in the change in the interdomain spacing of the polymer.
Figure 5-6. Effect of humidity on SAXS data for 0.9 IEC (A) and 1.9 IEC (B) for Resin 1. Dry (Black), 35 % RH (Red), 90 % RH (Green)

The interdomain spacing as a function of degree of functionality for both PHMA-SPS-PHMA and QA-SEBS is shown in Figure 5-8. Interestingly, the interdomain spacing of the QA-SEBS series of polymers increases only slightly with increasing functionalization even though the quaternary ammonium unit is 42 % larger than styrene (141 cm$^3$ mol$^{-1}$ and 99 cm$^3$ mol$^{-1}$ respectively). In the case of the sulfonated polymers discussed above, the interdomain spacing changed 8 nm for a 52 % change in the degree of sulfonation. However, for a 41 % increase in functionalization of the quaternary ammonium polymers, the d-spacing changed only 2 nm. The larger change in interdomain spacing in the sulfonated triblocks in comparison with the quaternary ammonium functionalized ions indicates a stronger interionic interaction with the sulfonate ions. This is in agreement with the theoretical domain comparison discussed above in which a coefficient of 0.8 [Equation (4-1)] was used for the sulfonated triblocks while a coefficient of 1.1 [Equation (5-1)] was used for the quaternary ammonium functionalized triblocks.
Figure 5-7. Interdomain spacing of PHMA-SPS-PHMA (▲) and quaternary ammonium functionalized SEBS (■).

5.4. Water Uptake

The gravimetric water uptake (mass %) vs RH alongside the interdomain spacing vs RH for the varying IEC’s of Resin 1 is shown in Figure 5-8. From this figure, it is discovered that interdomain spacing changes with RH are much less than the water uptake change with RH. Gravimetric uptake is a measure of the volume % water sorption in these systems, while the interdomain spacing change only gives an average change in the characteristic length scale of the phase separated morphology. Further work is ongoing to compare volumetric and expansion and morphological expansion of these polymers.
Figure 5-8. Gravimetric water uptake (left) and interdomain spacing change (right) as a function of relative humidity for Resin 1 at varying IECs. The percent change in interdomain spacing from 0 to 90 % RH is given. 0.9 IEC (■), 1.2 IEC (●), 1.5 IEC (▲), 1.7 IEC (▼), 1.9 IEC (♦)

5.5. Conclusions

In this chapter, poly(styrene-b-ethylene/butylene-b-styrene) functionalized with quaternary ammonium groups was studied both in the dry state and as a function of RH in order to determine the effect of relative humidity on the morphology of the polymer. SAXS on dry films indicated that interdomain spacing is strongly dependent on the length of the EB block. Conductivity studies revealed that only Resin 4 had a conductivity higher than the triblock copolymer’s random counterpart due to its low swelling as a result of a high fraction of unfunctionalized styrene in the ionic block.

RH dependent SAXS on Resin 1 with varying IEC’s revealed that the interdomain spacing change was highly dependent on the ion content of the functionalized block. However, the interdomain spacing was not a strong function of the IEC for dry samples. This behavior is different than in the sulfonated polymer studied where the characteristic morphological length scale was a function of the degree of ionic functionalization.
Chapter 6

Conclusions and Future Directions

The intention of this study was to enhance the fundamental understanding of the structure-property relationships of ion-containing block copolymers, specifically the effects that the addition of tethered sulfonate and quaternary ammonium groups have on block copolymer morphology. This goal was accomplished through the investigation of morphology, ionic conductivity, and water uptake of poly(hexyl methacrylate)-b-sulfonated poly(styrene)-b-poly(hexyl methacrylate), poly(perfluorooctyl methacrylate)-b-sulfonated poly(styrene)-b-poly(perfluorooctyl methacrylate), and poly(styrene)-b-poly(ethylene/butylene)-b-poly(styrene). The two mid-block functionalized triblock copolymers were directly compared in Chapter 4 so as to investigate the affect of endblock composition.

Through this study, it was found that the more flexible and soluble, poly(hexylmethacrylate) endblock provided for a more ordered structure as well as higher conductivity. This observation ran contrary to the thought that the addition of fluorine would cause greater phase separation and therefore higher conductivity.

In Chapter 5, the effect of relative humidity on the morphology of an endblock quaternary ammonium functionalized triblock copolymer was studied. This work detailed the expansion of the hydrophilic phase with increasing humidity. While the morphology did not undergo an OOT with humidity changes, likely due to the high molecular weight and triblock topology, there was an obvious increase in interdomain size changes with increasing humidity. It was also revealed in Chapter 5 that the interdomain spacing of QA-SEBS did not change greatly.
with the degree of functionalization, which is different than what was observed in the sulfonated systems.

Finally, this work pointed towards some new directions in the study of these materials. In Chapter 4, data was presented on a midblock sulfonated triblock copolymer which was hot pressed. This sample, while showing little to no change in SAXS, showed an increase in conductivity. This increase in conductivity was attributed to thermal annealing and preferentially parallel morphologies to the surface that are obtained with hot pressing. This additional annealing and alignment increased the in-plane conductivity of the sample. This observation leads to the hypothesis that higher conductivities and higher ordered morphologies should be obtainable through annealing. While improved order through annealing is realized in many other systems, highly sulfonated systems are difficult to thermally anneal due to their very high glass transition temperatures. Therefore, future work will include, along with the study of other types of attached ions and block copolymer chemistries and topologies, studies of the effects of the membrane properties on solvent and solvent/thermal annealing. Solvent annealing will allow for the reduction of the glass transition temperature to a level that will allow annealing either at ambient temperature or at a temperature below that of degradation.
References


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EDUCATION

**M.S. Materials Science and Engineering**, May 2011
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