THE EFFECT OF IONOMER ARCHITECTURE ON THE MORPHOLOGY IN GEL STATE FUNCTIONALIZED SULFONATED SYNDIOTACTIC POLYSTYRENE

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Abstract

This dissertation presents a discussion of blocky and randomly functionalized sulfonated syndiotactic polystyrene copolymers. These copolymers have been prepared over a range of functionalization (from 2% to 10%) in order to assess the effect of the incorporation of these polar side groups on both the thermal behavior and morphology of these polymer systems. The two different architectures are achieved by conducting the reaction in both the heterogeneous gel-state to obtain blocky copolymers and in the homogeneous solution state to obtain randomly functionalized copolymers. In order to compare both the thermal properties and morphology of these two systems several sets of samples were prepared at comparable levels of sulfonation. Thermal analysis of these two systems proved that the blocky functionalized copolymers provided superior properties with regard to the speed and total amount of the crystalline component of sulfonated syndiotactic polystyrene. Above 3% functionalization the randomly functionalized copolymer was no longer able to crystallize, whereas, the blocky functionalized copolymer is able to crystallize even at a functionalization level of 10.5% sulfonate groups. When considering the morphology of these systems even at low percentages of sulfonation it is clear that the distribution of these groups is different based on the amplitude of the signal measured by small angle x-ray scattering. Additionally, methods were developed to describe both the distribution of ionic multiplets, which varies between blocky and randomly functionalized systems, but also the distribution of crystals. At a larger scale ultra-small angle x-ray scattering
was employed to attempt to understand the clustering of ionic multiplets in these systems. Randomly functionalized polymers should a peak that is attributed to ion clusters, whereas blocky polymers show no such peak. Additional studies have also been done to look at the analysis of crystallite sizes in these systems when there are multiplet polymorphs present, it was observed the polymorphic composition is drastically different. All of these studies support that these systems bear vastly different thermal behavior and possess significantly different morphologies. This supports the hypothesis that this gel-state heterogeneous functionalization procedure produces a much different chain architecture compared to homogeneous functionalization in the solution-state.
Polymers are a class of chemicals that are defined by having a very large set of molecules that are chemically linked together where each unit (monomer) is repeated within the chemical structure. In particular, this dissertation focuses on the construction what are termed as “blocky” copolymers, which are defined by having two chemically different monomers that are incorporated in the polymer chain. The “blocky” characteristic of these polymers means that these two different monomers are physically segregated from each other on the polymer chain, where long portions of the chain that are of one type, followed by another section of the polymer that has the other type of monomer. The goal of creating this type of structure is to try to take advantage of the properties of both types of monomers, which can create materials with superior synergistic properties. In this case a hydrophobic (water hating) monomer is combined with a hydrophilic (water loving) chain. This hydrophobic component in the polymer is able to crystallize, which provides mechanical and thermal stability in the material by acting as a physical tether to hold neighboring chains together. With the other set of hydrophilic monomers, which in this case have an ionic component incorporated, we can now take advantage of this chemical components ability to aide in the transportation of ions. Transportation of ions is useful in a variety of commercially relevant applications, two of the most important applications of these ionic materials is in membranes that can be used to purify water or membrane materials in fuel cell technologies, specifically for proton exchange membranes. The focus of this research in
particular was to create a simple synthesis technique that can create these blocky polymer chain architectures, which is done by performing the reaction while the polymer is made into a gel. The key to this is that the crystals within the gel act as a barrier to chemical reactions, creating conditions where we have substantial portions of the material that are able to be functionalized and the crystals within the material that are protected from being functionalized. By looking at the thermal characteristics, such as melting temperatures and amount of crystals within these systems we have seen that functionalizing these polymers in the heterogeneous gel state gives substantially better properties than functionalizing these materials randomly. Much like oil and water, incompatible polymer chains will phase separate from each other. In this case the hydrophobic and ionic components will phase separate from each other. The shape and distribution of these phase separated structure will dictate many of the material properties, which can be described by modeling the data collected from x-ray scattering experiments. All of this information will tell us based on the initial conditions that these polymers were created in, what properties should be expected based on the morphology and thermal behavior. This gives a better understanding of how to fine tune these properties based on the structure of the gel and chemical reaction conditions.
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<th>Description</th>
</tr>
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<tbody>
<tr>
<td>%X&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Percent crystallinity (volume or weight)</td>
</tr>
<tr>
<td>aPS</td>
<td>Atactic polystyrene</td>
</tr>
<tr>
<td>sPS</td>
<td>Syndiotactic polystyrene</td>
</tr>
<tr>
<td>Random</td>
<td>Solution state functionalization</td>
</tr>
<tr>
<td>Blocky</td>
<td>Gel-state functionalization</td>
</tr>
<tr>
<td>SsPS</td>
<td>Sulfonated syndiotactic polystyrene</td>
</tr>
<tr>
<td>APS</td>
<td>Advanced Photon Source</td>
</tr>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
</tr>
<tr>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Inverse centimeters</td>
</tr>
<tr>
<td>q</td>
<td>Momentum transfer vector</td>
</tr>
<tr>
<td>I(q)</td>
<td>Intensity as a function of momentum transfer vector</td>
</tr>
<tr>
<td>2θ</td>
<td>Twice the scattering angle</td>
</tr>
<tr>
<td>λ</td>
<td>Wavelength of light</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half max of a normal distribution</td>
</tr>
<tr>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>Weight average molecular weight</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>WAXD</td>
<td>Wide-angle x-ray diffraction</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small-angle x-ray scattering</td>
</tr>
<tr>
<td>USAXS</td>
<td>Ultra small-angle x-ray scattering</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Melting temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
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</tr>
<tr>
<td>w/v %</td>
<td>Weight per volume percent</td>
</tr>
<tr>
<td>Å</td>
<td>Angstroms</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;f&lt;/sub&gt;</td>
<td>Heat of fusion</td>
</tr>
<tr>
<td>ΔH&lt;sub&gt;f°&lt;/sub&gt;</td>
<td>Heat of fusion at 100% crystallinity</td>
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Chapter I: 
Introduction to Ionomer Morphology and Research Objectives

Introduction

Ionomers are polymers that generally contain less than 15 mol% of ionic functionality incorporated into or as side-group to a hydrophobic polymer backbone through copolymerization or post-polymerization modification of a homopolymer. Ionomers are a class of materials that have sparked a great deal of academic and commercial interest due to the morphological arrangements they can possess and the properties that these ionic moieties can impart with both the ionic characteristics, as well as, the properties already possessed by the parent homopolymer’s hydrophobic backbone. Ionomers can be utilized in a variety of applications such as the compatibilization of two polymers, where there is a large difference in polarity of two components, acting as interface between the two incompatible phases. Ionomers can also be used to help improve adhesion in incompatible polymer systems by lowering the interaction energy between neighboring phases. Ionomers can also be important in processes for purification of water, including desalination and removal of any ionic components that can affect water quality. Additionally, ionomers have been found to be important in creating membranes for fuel cell membranes by aiding in the transport of both water and ions from the anode and cathode.

Ionomers can be used in a wide variety of applications that require advanced materials. This necessitates the need to describe the relationship between the emergent properties and the
morphological arrangement of phases in these systems. These studies are fundamental to developing methods to improve the desired properties in ionomers and can aid in methods for designing the architecture and processing protocols for use in a variety of applications that can help improve advanced materials. The incorporation of these ionic component can give rise to properties that are much different than the non-ionic counterparts by providing both hydrophobic and hydrophilic characteristics to these systems, both in solution\(^{44-59}\) and in the solid-state\(^{60-74}\), allowing for synergistic properties in these materials. Many of these properties that differ from their non-ionic counterparts can be attributed to the phase separated morphology that forms in ionomer systems where there is a nonpolar backbone with polar functional groups. A discussion of the morphological models describing this behavior is presented in the following section.

**Morphological Models for Ionomers**

A variety of morphological models have been employed to describe the arrangement of phases within ionomers in order to capture how the hydrophilic ionic phase can phase separate from the hydrophobic polymer backbone. There are many interactions that can drive the type of phase separation that occurs in polymers, including but not limited to, the type of functional group used, the choice of counter-ion, in respect to, counter-ion size and charge density, the polymer glass transition temperature, polymer dielectric constant, the rigidity of the polymer backbone, length and rigidity of the attached functional group, plasticization, and processing conditions.
There are many competing models that can accurately describe several aspects of these systems, but no single model seems to be able to accurately predict a generalized description of the behavior of these systems. First, several qualitative models had been proposed to describe the morphology of these ionomers, most notably the models proposed by Bonotto and Bonner in 1968, as well as, the model proposed by Longworth and Vaughan, also in 1968. The Longworth and Vaughan proposed that the ionic peak that arose in small-angle x-ray scattering data from poly(ethylene-co-methacrylic acid) and its corresponding salt forms, at a Bragg spacing of 5.0 nm, is due to ordering of hydrocarbon chains between aggregates rather than the aggregates themselves. However, this model does not properly reflect the fact that a more intense peak is observed for the lithium salt of these ionomers compared to the cesium salts. Additionally, it does not properly reflect the relatively similar melting point and degree of crystallinity between the salts and the acid form of these ionomers.

Several other qualitative models have been proposed that attempt to account for the “ionic” peak observed in SAXS data. One of the first models that was proposed to describe the scattering peak observed in ionomers was proposed by Eisenberg in 1970. This theoretical model proposes that when the concentration of ions reaches a critical number the electrostatic forces will favor the formation of spherical, “droplet-like”, aggregates that contain no hydrocarbon chains within these aggregates. These aggregates that contain only ions and their associated functional group were termed multiplets. It was additionally proposed that electrostatic interactions between these multiplets could potentially cause these multiplet structures to agglomerate into a phase separated domain, termed clusters. The formation of these clusters is favorable due to electrostatic interactions, but are energetically unfavorable due
to the elastic forces from the nonpolar matrix phase. This model proposes that the balance of electrostatic forces and elastic forces is energetically favorable for the formation of clusters in random ionomers with a low dielectric constant and at some critical ion concentration. However, this model did not attempt in any detailed way to analyze the features of small angle x-ray scattering data.

More in depth theoretical approaches were also proposed by Forsman, Dreyfus, Dreyfus, and Datye and Taylor, based on a similar idea of electrostatic and elastic forces. These studies arrived at similar conclusions to the theoretical model proposed by Eisenberg, but provided additional insight. Based on experiments that were performed by Earnest and coworkers, Forsman suggested that the aggregation of these ions may cause the polymer coil to expand upon aggregation. However, Squires and coworkers suggested that this expansion of these polymer coil is unnecessary to describe the ionic aggregation in random ionomers.82

Marx and coworkers proposed that the SAXS peak arises from the electron density difference between the cations in the ionic aggregate and the hydrocarbon backbone of the polymer. The size of these aggregates are proposed to be very small and are treated as points on a paracrystalline lattice. While this model can qualitatively describe the SAXS data, it does not satisfactorily account for the presence of two glass transition temperatures observed in dynamic mechanical analysis. Binsbergen and Kroon in 1973 proposed a similar model which assumes the scattering centers and points at the center of spheres, which have random packing. This model is fundamentally similar to the model proposed by Marx, and also fails to account for the two-phase behavior seen in the dynamic mechanical behavior of these systems.
Yarusso and Cooper proposed a hard-sphere model that proposes that these ionic aggregates possess and liquid-like ordering with a specific minimum distance that ionic aggregates can be away from each other.\textsuperscript{85} This model can successfully model the x-ray scattering curves observed and is in excellent agreement with the SAXS “ionic” peak for syndiotactic polystyrene ionomers. This model again makes no attempt to reconcile the observed phase separation observed in DMA.

A very successful model proposed by Ding and coworkers\textsuperscript{86} has been proposed to describe anomalous SAXS data that is able to accurately describe the entire SAXS profile. This model, similar to the Yarusso and Cooper model treats these ionic aggregates as hard spheres, but includes an additional contribution to the scattering profile from lone pairs of ions that exist in the matrix material. This model successfully accounts for the “ionomer peak” and the characteristic small angle upturn that is observed in ionomer systems. However, this model does not make an attempt to describe the mechanical data observed in DMA.

MacKnight proposed an additional model in 1974 that that attempted to model the x-ray scattering peak in poly(ethylene-co-cesium methacrylate) ionomers using another type of core-shell model.\textsuperscript{87} MacKnight proposed that the ions would exist as a cluster with a radius $0.8 – 1.0$ nm containing approximately 50 ion pairs. Surrounding this ion cluster is the shell, which is composed of hydrocarbon chains from the polymer backbone. MacKnight proposed that an electrostatic potential between the cluster and matrix ions controls the size of this shell. This distance between the cluster ions and the matrix ions is estimated to be approximately 2.0 nm. This model considers the “ionic” peak to be due to scattering from intraparticle distances, rather than interparticle distances. This model may be able to provide a plausible explanation for the
existence of the high temperature “cluster” glass transition temperature, which can be accounted for by the relatively large size of the core-shell particle.

Roche proposed a similar model to that of MacKnight. However, a key difference between these models is in the proposed geometry of the cluster in the core-shell model. In the case of Roche’s model, he has proposed that the central ionic core is actually a lamellar geometry instead of a spherical geometry, and the shell consists of a depleted region of ions on either side of the lamellar core. Similarly, to McKnight’s model, the spacing between the core and shell accounts for the SAXS peak and the size of the core-shell aggregate could provide a possible explanation for the observation of multiple phases in ionomers.

The model developed by Eisenberg, Hird, and Moore (EHM) has been widely accepted as the model that can provide the most accurate description of both the morphological observations from small angle x-ray scattering (SAXS) and the observation of multiple distinct mechanical phases from dynamic mechanical analysis (DMA). The EHM model has many advantages compared to these other models, the most obvious advantage is that it bears no apparent inconsistencies with both SAXS and DMA observations. If we consider the observations from SAXS data EHM, the model assumes that most of the scattering occurring at 1.5 nm$^{-1}$ (c.a. 4.2 nm) arises from intermultiplet scattering. This intermultiplet scattering arises primarily from within an individual cluster (intracluster), although there would be some contribution from scattering between clusters (intercluster) scattering. This behavior will be described later in this dissertation where mathematical descriptions of these peaks are considered using the “liquid-like hard-sphere model”. It is additionally important to note that this model does not require any electrostatic potential between multiplets, in fact these clusters form due to a local proximity
rather than a condensation into clusters. This model predicts that the average behavior can be entirely described by the shape and size of aggregates, and the intracluster distribution of aggregates.

**Figure I-1**: Eisenberg Hird Moore morphological model. Adapted with permission from Macromolecules. Copyright 1990 American Chemical Society.⁸⁹

DMA has shown that these polystyrene ionomer systems in fact show two loss tangent peaks exist, corresponding to the presence of two glass transition temperatures ($T_g$). This indicated to Eisenberg, Hird, and Moore, that there were in fact two mechanically distinct phases even at ion contents as low at 2 mol% in poly(styrene-co-sodium methacylate) ionomers.⁸⁹ However, SAXS analysis has shown that there are not two phases that are continuous in respect to changes in electron density. The EHM model accounts for this behavior by assuming that the multiplet structures have a shell of polymer surrounding multiplets that are restricted in mobility. These restricted shells can form a continuous, mechanically distinct phase when there are enough multiplets in the matrix that these restricted polymer chains from neighboring multiplets
begin to overlap with each other. This feature of the model accounts for the observation of two distinct \( T_g \)'s in these ionomer systems. These researchers also observed changes in the relative magnitude of the two \( T_g \)'s when the concentration is changed, this indicates that there are changes in the relative volume fraction of clustered and unclustered material. Figure I-1 shows a pictorial representation of this model.

**Ionomer Architecture**

The architecture of ionomers has a large impact on the material properties that can be obtained in these systems. Architecture in this case refers to the placement and sequence of ionic groups along the polymer backbone. The greatest effect is seen on the morphological assembly of the attached ionic moieties into the previously described multiplets and clusters. Highlighted below in Figure I-2 are four examples of the types of architectures that can be considered: random, block, linear telechelic, and branched telechelic arrangements (although more complex architectures certainly exist). The EHM model attributes different morphological attributes in respect to multiplet formation specifically for random ionomers and linear telechelics. It is proposed in this model that random ionomers would create smaller multiplet structures compared to those observed using telechelics. This can plausibly be explained by considering steric effects, where, in the case of random ionomers there is significant steric hindrance to forming large multiplets due to the ionic functional group being attached most often in the center of chains, thus the multiplet must allow for more room between adjacent ionic attached due to the fact that two chains must protrude from the multiplet with each ionic attachment. In the case
of telechelic ionomers only one chain end will be protruding from the multiplet surface, allowing for a higher density of chains to be packed into an individual multiplet. This eludes to that there must be some limiting size for a multiplet with a given polymer backbone that fundamentally depends on the stiffness of a polymer and the architecture of the polymer.

In this dissertation our focus is in comparing block ionomers versus random ionomers. In this case it is expected that on a local size scale (on the order of multiplet sizes) that ionomers of comparable ionic incorporation that block copolymers should form a multiplet morphology similar to that of random ionomers. Both of these architectures will require that ionic groups have two attachment ends, since on average ionic functional groups will be found in the middle of a chain rather than at the ends. However, fundamental differences in the density of ionic groups does exist between these two architectures on small size scales. Block ionomers of
comparable ionic content will have a much higher density of polar moieties in regions of the chain where ions are found compared to their random counterparts, which would possess a more diffuse distribution of ionic groups along the backbone on average. This effectively creates regions of high ion density, which according to the EHM model, may create either multiplets of similar size that are closer together, multiplets that are larger, or some combination of these two effects. However, it should be noted again that multiplet size is fundamentally limited by steric factors that will limit the ability of chains to pack, which would be controlled by the effective volume of a chain and the stiffness of these chains.

Effect of Counterions

The choice of counterion can have a significant effect on the electrostatic network formed in these ionomer systems. A great deal of experimental evidence is present in the literature that has demonstrated differences in ionomers synthesized used counterions of differing sizes, valency, and overall charge densities. The differences in the size and valency of these counterions can have a profound impact on the strength of electrostatic interaction within multiplets. The strength of this electrostatic network can control both how well ions are able to be transported throughout the system and the ability of polymer chains to diffuse throughout the amorphous regions. This can impact the ability of polymers to crystallize with high thermal input or to effectively transport water or other types of charged ions through a matrix in the case of materials being used for PEMFC's.
Research Objectives

The main goals of this research are to explore the relationship between ionic interactions and the morphological development of these semi-crystalline ionomers. Specifically, a comparison between the morphology of randomly functionalized sulfonated syndiotactic polystyrene (R-SsPS) and blocky functionalized sulfonated syndiotactic polystyrene (B-SsPS). It was already noted in past research that using a blocky architecture leads to significantly improved crystallization properties such as, higher crystallization rate, higher total crystallinity, and increased melting temperature.\textsuperscript{106,107} However, very little is understood about the morphological differences that exist when creating these two different chain architectures, thus it is prudent to develop a quantitative method to characterize the fundamental differences in phase arrangements that exist between these two functionalization methods. In particular, this dissertation hopes to provides a methodology to explore the size, shape, and distribution of phases within these materials, as well as, an approximation to explain the sequencing of sulfonate groups along the backbone in the case of these “blocky” structures. Additionally, the hierarchical structure of the ionic morphology is explored in order to provide a relationship between the small ionic aggregates and the clustering of these aggregates. In particular, this dissertation will explore blocky architectures that have been produced using a novel gel-state synthesis that will be described further in the proceeding chapters.
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Chapter II:
Research Background Semi-Crystalline Ionomers

Introduction

Although sulfonated atactic polystyrene (SaPS), an amorphous ionomer, has been studied in great detail, many of the industrially important ionomers such as Nafion® and Surlyn® are semi-crystalline in nature and the morphologies of semi-crystalline ionomers are complex three-phase systems made up of an ion rich phase, crystalline domains, and an amorphous matrix. Given the complex interactions that can exist in these materials, it has been shown that the process of ionic aggregation significantly influences the crystallization process of semi-crystalline ionomers as one polymer chain may traverse all three phases of the semi-crystalline ionomer.¹ As a model semi-crystalline ionomer, Orler and coworkers developed a method to produce sulfonated syndiotactic polystyrene (SsPS)¹⁻⁴ using a mild post-polymerization sulfonation procedure similar to that used by Makowski to sulfonate atactic polystyrene.⁵ Although SsPS may be considered as a model semi-crystalline ionomer, it was found that incorporation of as little as 2 mol% of sulfonate groups onto sPS significantly decreased the ability of SsPS to crystallize in the ionized form.²

Morphology of Semi Crystalline Ionomers

Semi-crystalline ionomers can provide a framework for creating polymer networks with synergistic properties. It has been explained in the previous section that the incorporation of
ionic groups can drastically change the material properties even when adding only small amounts of the ionic functionality. However, the introduction of a crystallizable backbone in ionomer systems can be utilized in a variety of applications such as food packaging, membranes for filtration, chemical and electrical sensors, biodegradable materials, proton exchange membranes, and many other potential commercially important uses. Compared to their amorphous counterparts these semicrystalline ionomers bear a three-phase morphology consisting of amorphous matrix, ionic aggregates, and crystalline segments. Each of these components can impart unique properties to the polymeric material as a whole.

Several important representations have been presented to describe the arrangement of these phases. Specifically, the work of Longworth and Vaughn presents an excellent representation of what can be referred to as the “random phase morphology”. Figure II-1 shows a morphology where the crystalline assemblies and the ionic aggregates are arranged randomly with respect to each other, since there is no clear driving force for a highly ordered segregation of these morphological features. The morphology of both the ionic aggregates and the crystallites depends greatly on both the physical characteristics of the hydrophobic backbone (backbone rigidity, stiffness, crystallizability, matrix diffusion rate, etc.) and the ionic functionality (electrostatic attraction, matrix diffusion, attached counter ion, etc.). These two morphological structures are also intermittently linked due to the fact that a single chain may be involved in all three phases, since a chain may possess long runs of unfunctionalized crystallizable homopolymer and polymer with ionic moieties attached.
Figure II-1: Representation of the Longworth and Vaughn model for semicrystalline ionomer morphology. Adapted with permission of Nature. Copyright 1968 Nature.

Of particular interest in the scientific community are Nafion® and Suryln® have been studied in great detail. Nafion® and Suryln® are two ionomers that have a distinctly different backbone and ionic functionality. Nafion® is a perfluorosulfonate ionomer with a poly(tetrafluoroethylene) backbone, whereas Suryln® is an ethylene methacrylic acid ionomer. However, due to the fact that many of the commercially available semicrystalline ionomers are produced via copolymerization it is very difficult to control the molecular weight of these systems. This makes them difficult to use as model systems to understand the link between the ionic aggregation and the crystallization behavior in these systems. Additionally, the morphology of Nafion®, while extensively studied, is poorly understood and there are still a variety of models that are used to describe the morphology of the ionic aggregates and the crystallite morphology. These models in include the cluster-network model from Gierke and co-workers, the lamellar model by Litt and coworkers, the fringed micelle model by Kim and coworkers, a core-shell
model by Fujimura and coworkers,\textsuperscript{29, 30} the sandwich-like model proposed by Haubold and coworkers,\textsuperscript{31} the fibrillar nanostructure model by Rubatat and coworkers,\textsuperscript{32-34} the worm-like model by Kim and coworkers,\textsuperscript{35} the Parallel water channel model developed by Schmidt-Rohr and Chen,\textsuperscript{36} a simulated bicontinuous network model by Elliot and coworkers,\textsuperscript{37} and the SAXS and SANS studies performed by Gebel that demonstrated a morphological transformation of dry Nafion membranes that exist as inverse micelles to a rod-like structure in the solution state,\textsuperscript{38} which was evident in other studies performed by Loppinet as well.\textsuperscript{39, 40} Clearly, using Nafion\textsuperscript{®} as a model system to study the link between ionic aggregation and crystallization presents a system that is both difficult to control in precise manner and is a poorly understood system.

In light of this complex morphology a model semicrystalline ionomer system can be used, thus Orler and coworkers utilized sulfonated syndiotactic polystyrene to study these systems.\textsuperscript{1-4} Sulfonated syndiotactic polystyrene is a good candidate for studying the link between ionic aggregation and crystallization for a variety of reasons including the simplicity of the backbone structure, the fast crystallization rate, the high thermal stability of this polymer, the hydrophobicity of the backbone, the extensive information on the morphology of both the crystalline and ionic aggregate structure in these polymers, and the high stability of the polymers when sulfonating syndiotactic polystyrene (sPS).

**Ionic Influence on Crystallization**

Ionic groups profoundly impact the ability for the homopolymer to crystallize. Orler and coworkers in fact have shown that in randomly functionalized copolymers that there is little
evidence for crystallization for sPS functionalized with greater than 3.4 mol% of the sulfonate salt attached. The proposed rationale for the lack of crystallization in these random copolymers is that the ionic functionalities act as defects during the formation of crystallites, thus you cannot form crystallities containing sulfonated sPS. This has been observed by Orler and coworkers resulting in a profound reduction in the crystallization rate, the melting point of these polymers, and total crystallinity when a sufficient number of sulfonate groups are incorporated. Additionally, the strength of the electrostatic network was also found to have a profound effect on the ability of these polymers to crystallize. Orler and coworkers that if the ionic aggregates contain stronger electrostatic interactions in the case of Na+ functionalized sulfonated sPS ionomers that these semicrystalline ionomers crystallize at both a slower rate and are not able to crystallize to as high of a total crystallinity when compared to Cs+ functionalized sulfonated sPS ionomers. This indicates that the ability to crystallize quickly and to obtain a high volume fraction of crystallites depends strongly on the charge density of the salt used in these ionomers, where larger counter ions will have a lower electrostatic interaction within these aggregates and will provide enough mobility for neighboring chains to assemble into crystallographic registry.

Orler in particular studied the influence of the K+ and the Cs+ salt forms of sulfonated sPS and found profound effects on the thermal behavior. First they noted that under melt-quench scans in differential scanning calorimetry (DSC) of 2.0 mol% SsPS that the K+ form fails to crystallize during the time frame of the experiment, while the Cs+ salt tends to crystallize similarly to the acid form of these polymers. A DSC thermogram shown in Figure II-2, shows that while the acid and the Cs+ forms both show a clear crystallization exotherm and melting endotherm, while no crystallization or melting are observed in the K+ salt. It also important to note that in
these DSC scans, a higher crystallization temperature was observed in the Cs\(^+\) form was observed compared to the acid form, indicating a higher thermal input is required when considering systems that are subject to ionic interactions that will lower the chain mobility of these polymers.

![DSC scans showing different heat flows and temperatures for various counterions](image)

**Figure II-2**: Effect of counterion type on the thermal properties of melt-quenched SsPS ionomers containing 2.0 mol\% sulfonation. Reprinted with permission of the American Chemical Society. Copyright 1994 American Chemical Society.\(^2\)

Orler and coworkers in this paper also noted that the rate of crystallization when considering these two salt forms have a large difference in the rate of crystallization.\(^3\) Orler performed Avrami analysis on the crystallization data (Figure II-3) ionomers using the following relationship:

\[
\ln[-\ln(1 - X_t)] = \frac{1}{2.3} \ln K + n \ln t
\]  

(1)
where $X_t$ is the fractional crystallinity, $K$ is the kinetic growth rate constant, $n$ is the Avrami exponent, and $t$ is the time of crystallization. Using this analysis Orler found that the time it takes to reach half of the maximum crystallinity ($t_{1/2}$) is twice the amount of time in the case of the K$^+$-form compared to the Cs$^+$-form. In addition to the increased rate and total crystallinity when considering the Cs$^+$-form compared to the K$^+$-form, Orler found that the equilibrium melting temperature changes be a small amount from 264°C to 262°C for the Cs$^+$-form and K$^+$-form respectively.

Figure II-3: Fractional crystallization versus time profiles for sPS and SsPS-2.0 ionomers isothermally crystallized at a supercooling of 40°C. Reprinted with permission of the American Chemical Society. Copyright 1994 American Chemical Society.

Further studies on the effect of counter-ions on the crystallization kinetics were performed by Orler using DSC, which studied a wider variety of counter ions (Figure II-4). Orler and coworkers found that when neutralizing sulfonated sPS ionomers with a monovalent salt
that the thermal input required to crystallize these polymers increases dramatically, these results have also been partially confirmed later in this dissertation when the thermal properties of random and blocky ionomers are studied further. It should be noted that the crystallization peak becomes broader when compared to the acid-form in SsPS.

Figure II-4: Effect of alkali metal counterion type on the thermal behavior of melt-quenched SsPS ionomers containing ion contents of 1.4 mol %. All thermograms are normalized with respect to sample mass and were acquired during a heating scan of 20 °C/min. Reprinted with permission of the American Chemical Society. Copyright 1996 American Chemical Society.¹

The melting temperatures are also seen to decrease due to neutralization, these temperatures have been extrapolated to the $T_c = T_m$ line in order to approximate an “equilibrium melting temperature”, although it is noted in Orlé’s work that there is no “true” equilibrium melting temperature for copolymers as they can never form crystals of infinite extent. The results show that even for ionomers functionalized at 1.4 mol% sulfonate groups that there is a
depression in the observed equilibrium melting temperature from 275°C to 268°C for the homopolymer and neutralized ionomers, respectively.

Figure II-5: Effect of alkali metal counterion type on the isothermal crystallization of SsPS containing ion contents of 1.4 mol % at T_c) 210 °C. Reprinted with permission of the American Chemical Society. Copyright 1996 American Chemical Society.1

A much more profound effect is observed due to neutralization on the crystallization kinetics was observed by Orler. Figure II-5 shows the fractional crystallinity, X_c(t), versus time shows that all neutralized salts crystallize slower than the acid form of SsPS. However, this trend also shows that the ionomers tend crystallize much slower with smaller counter ions (Na⁺) and much faster with larger counter ions (Cs⁺). This provides evidence that the crystallization kinetics fundamentally depend on the charge density of these counter ions, where a higher charge density slows down crystallization due to less chain mobility in these systems.
Using dynamic mechanical analysis, shown in Figure II-6, Orler additionally observed significant effects on the mechanical behavior of ionomers functionalized with 2.1 mol% ionic functional groups. Orler notes in his analysis that when the mechanical behavior is analyzed below 180°C that the storage modulus versus temperature is independent of counter ion type. However, as is evident in the data presented in Figure II-6 the storage modulus begins to significantly deviate when considering the rubbery plateau that exists between 180°C and 300°C. It can be seen in decreasing counter ion size the rubbery plateau extends to higher temperature and the temperature at which flow is observed coincides with this extended plateau to higher temperature. Hara and coworkers have observed very similar results for sulfonated atactic polystyrene ionomers with an ion content of 4.1 mol%. This further supports the notion that
Orler describes throughout his work, which indicates that the counter ion size has a significant effect on the mobility of chains in these systems, driven by the strength of ionic interactions.

Figure II-7: Effect of isothermal crystallization temperature on the half-time of crystallization for 1.4 mol % SsPS ionomers neutralized with various counter ions. Reprinted with permission from the American Chemical Society. Copyright 1996 American Chemical Society.

Orler also studied the dependence of the shape on the crystallization temperature versus crystallization half time \( t_{1/2} \) curve on the type of counter ion (Figure II-7). A maximum crystallization rate appears between the \( T_g \) (where polymer chains gain enough mobility to crystallize) and the \( T_m \) (where chains possess too much thermal energy to crystallize) of this polymer as is expected for any semicrystalline polymer system. Of interest for this discussion about the effect of counter ions there is again a significant effect on the speed of crystallization for a given temperature with changing counter ion size. It should be noted that the crystallization rates are relatively similar in the nucleation and growth regime (temperatures lower than the
maximum crystallization rate), but begin to deviate significantly when the rates depend on the diffusion in these systems. This again supports the claim that larger ions allow for more mobility in these systems, where the crystallization rate decreases with decreasing size when considering temperature that are diffusion controlled, effected primarily by the strength of the electrostatic network in these ionomers.

![Correlation of crystallization half-time with the ionic radii of the alkali metal counter ions at various isothermal crystallization temperatures.](image)

**Figure II-8:** Correlation of crystallization half-time with the ionic radii of the alkali metal counter ions at various isothermal crystallization temperatures. Reprinted with permission of the American Chemical Society. Copyright 1996 American Chemical Society.¹

Similar to the previous discussion when considering the crystallization temperature versus $t_{1/2}$ (**Figure II-8**), the $t_{1/2}$ is effected by the size of the counter ion. Interestingly, it is observed in this paper that the $t_{1/2}$ has a linear dependence on the ionic radius. While this behavior is interesting, it is not well understood why there is such a simple relationship between the crystallization temperatures, crystallization rate, and the ionic radius. However, the general
trend further supports that the dynamics of crystallization are controlled by the charge density of the ions within the ionic aggregates in these systems.

Hsu and coworkers observed similar results on similar systems that were researched by the Moore research group.\textsuperscript{42} However, Hsu looked at the effect of sulfonation percentage on the thermal behavior of the acid form of SsPS. In particular Hsu observed that with increasing sulfonation percentage that both the melting point and the total crystallinity was reduced. This is consistent with results that are presented in both this dissertation, but as well as Orlr’s work and several other researchers. An example of the changing thermal properties with changing sulfonate content can be seen in Figure II-9 below.

![Figure II-9: DSC scans of amorphous sulfonated sPS: (A) 6.3 mol %; (B) 4.4 mol %, (C) 3.4 mol %; (D) 1.4 mol %; (E) 0 mol %. Reprinted with permission of Society of Chemical Industry. Copyright 2001 Society of Chemical Industry.](image)

Lin and coworkers also studied the effect of the choice of counter ion on the crystallization behavior.\textsuperscript{43} In this case another observation was seen that has been consistent throughout the
body of research that surrounds sPS ionomers. It was seen in this research that with the incorporation of sulfonate groups that the crystallization rate is slowed dramatically, and when a counter ion is used the crystallization rate becomes even slower than when compared to the acidic form of the copolymer. **Figure II-10** shows crystallization rate data which clearly shows the effect of both the incorporation of sulfonate groups and the addition of counter ions.

![Crystallization Rate Data](image)

**Figure II-10**: Fractional crystallization versus time profiles for (a) sPS and (b) SsPS-H-1.7, (c) SsPS-H-1.7, (d) SsPS-Na-1.7, (d) SsPS-Zn-1.7 ionomers non-isothermally crystallized at a cooling rate of 20°C/min. Reprinted with permission of Society of Chemical Industry. Copyright 2001 Society of Chemical Industry.

Additional studies were performed by He and Yu on maleic anhydride grafted to polypropylene ionomers (mPP). In their studies a profound influence of the type of counter-ion used and the degree of neutralization was also found to have a profound effect on the crystallization kinetics. **Figure II-11** shows three different data sets that reflect the changes in the crystallization rate. **Figure II-11 (a)** shows a simple comparison of the base polypropylene homopolymer, where the crystallization rate of the acid form of the functionalized maleic...
copolymers actually crystallizes faster than the base homopolymer. The authors propose that this can be attributed to the functional group acting as nucleation sites for crystalline growth.

In Figure II-11 (b) a comparison of different counter-ions are shown. When comparing the rate of crystallization the figure shows the following trend in respect to crystallization rate: \( \text{Na}^+ > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{H}^+ \). The main point for this particular research is that it appears as if monovalent counter-ions will crystallize faster than divalent ions, and that in this case the acidic form crystallizes the slowest. This may be acting via a different mechanism than is seen for SsPS copolymers, because the trend suggested by the studies mPP suggests a different mechanism than that seen by Orler where increasing the ionic radius will decrease the crystallization time (at a set crystallization temperature). The differences could be that the valency is changing in the study done by He and Yu, and the type of highest occupied orbital is also different in the case of comparing \( \text{Mn}^{2+} \) and \( \text{Ca}^{2+} \). This does however show that exchanging the type of counter-ion has a dramatic impact on the crystallization properties.
Figure II-11: (a) Plots of $t_{1/2}^{-1}$ versus crystallization temperature of PP and H$^+$-form mPP. (b) Plots of $t_{1/2}^{-1}$ versus crystallization temperature of various ionomers. (c) Plots of $t_{1/2}^{-1}$ versus...
crystallization temperature of Na\textsuperscript{+}-form mPP with different neutralization. Reprinted with permission of Elsevier. Copyright 1999 Elsevier.

Finally, in this study the effect of percent neutralization was investigated. It was found that a higher degree of neutralization with the Na\textsuperscript{+} counter-ion causes the crystallization rate to increase. Within the context of this study this is consistent with the data from Figure II-9 (c) that shows the Na\textsuperscript{+} form crystallizes faster than the H\textsuperscript{+} form. Thus, if more of the copolymer exists in the Na\textsuperscript{+} form one should expect that this will promote faster crystallization.

![Graph](image)

**Figure II-12:** Plots of ln[-ln(1-X\textsubscript{c})] versus ln t for Na\textsuperscript{+}-form mPP. Reprinted with permission of Elsevier. Copyright 1999 Elsevier.

The authors in this study also investigated the impact of cooling rate on the rate of crystallization. The authors found that increasing the cooling rate actually decreases the crystallization half time (t\textsubscript{1/2}). This is consistent with the theory of crystallization that the chain mobility must slow down enough to be able to crystallize, thus, a faster cooling rate will allow the samples to reach the optimal crystallization temperature more quickly. This trend is shown in Figure II-12.
Influence of Chain Architecture on Crystallization

Significant differences are observed in the crystallization behavior when comparing different ionomer architectures, of particular interest for this dissertation are the comparisons between a blocky architecture and the random architecture in ionomers. The primary motivation for creating blocky architectures is to improve the ability of these polymers to crystallize, which can improve the thermo-mechanical stability of these ionomers. As noted in the previous section, the development of crystallinity is significantly inhibited when ionic groups are incorporated in a random fashion, where the crystallinity is almost entirely inhibited when including more than 3.4 mol% of ionic groups. Preliminary work on these systems were performed by Dr. Sonya Benson and myself that show significantly improved crystallization rate, total crystallinity, and higher melting temperature when a blocky architecture is used. These observations will be elaborated upon further in the discussion of our current research of these systems of blocky systems created through functionalization in the gel-state.

Conclusion

Semicrystalline ionomers can create unique morphologies that contain both ionic aggregates and crystallizable components. A very simple model of these morphologies has been provided by Longworth and Vaughn showing a possible description for randomly functionalized semicrystalline ionomers using a random network. However, depending on the choice of counter-ion used in these systems many of the thermal properties can be significantly influenced, which appears to fundamentally depend on the charge density of the ionic functionalities. The strength
of these ionic interactions can fundamentally dictate many of the crystallization properties, including the melting temperature, crystallization temperature, ability to crystallize, crystallization kinetics, and the mechanical behavior at high temperatures. However, in the case of randomly functionalized ionomers the ability to grow a crystalline component is significantly limited due to the fact that randomly distributed defects will prevent crystallization in these polymers. In order to retain the synergistic properties of having both an ionic component that can transport ions and a mechanically and thermally stable crystalline phase a different sequence of ions can be must be created, such as blocky sequencing of ionic components. In this dissertation a blocky functionalization method is being studied that allows for the creation of semicrystalline ionomers with a high ion content that may be more useful in advanced materials applications where both high ion content and crystallizability will be desirable. In order to be able to finely tune these properties a new morphological model to describe the distribution of the ionic components and crystallized components could be of great use for designing the architecture and processing conditions.
References


Chapter III:
Introduction the Small Angle X-ray Scattering as a Probe of Ionomer Morphology

Introduction

Small angle x-ray scattering (SAXS) is a technique commonly used to find structural information concerning phase separated materials in the range of 1 nm to several micrometers. This technique is performed by measuring the scattering angle of x-rays from a material using a collimated x-ray source and then measuring the signal from these scattered x-rays using some form of x-ray sensitive detector. SAXS has been found to be especially useful in the field of polymer science due to the frequent occurrence of incompatible chemical components when dealing with blended polymer systems, block copolymers, and semi-crystalline polymers, all of which may phase separate, where each phase often will have a significant difference in the electron density, which is necessary to resolve phase separation with SAXS. The size of objects that can be measured using x-ray scattering is only limited by the diffraction limit for a given wavelength when considering very large angles and the size of the detector pixels (small dimensions < 0.01 nm) and the ability to resolve extremely small angles (very large size scales up to several micrometers). This allows one to probe dimensions small enough to see crystallographic information corresponding to the ordering of crystalline objects, as well as long range information that can correspond to microscopic phase separation or collections of phase separated material, such as ionic aggregates and the clustering of these aggregates. In order to completely understand how scattered x-rays can be used to describe the distances of nanoscale
objects the theory of x-ray scattering can be used, and will be described in the proceeding sections. The next section will describe the theory behind the observed diffraction patterns from light and the dependence on the geometry of the scattering centers that are being probed.

Scattering Vectors in Small Angle X-ray Scattering: Bragg’s Law

First the scattering from two identical scattering centers \( \mathbf{O} \) and \( \mathbf{M} \) is considered, such as in Figure III-1.\textsuperscript{2, 3} These scattered x-rays will be measured at a plane tangent to the vector \( \mathbf{S}_0 \), which corresponds to the incident beam direction. The vectors of emitted waves from \( \mathbf{O} \) and \( \mathbf{M} \) are used to compute a phase difference between these two vectors, which will depend on the distance between the centers \( \mathbf{O} \) and \( \mathbf{M} \). A phase difference between the two wave vectors is calculated as follows:

\[
\varphi = \frac{2\pi \delta}{\lambda}
\]  

(1)

where, \( \delta \) defines a path length difference between the two scattered x-rays. This path length difference can be calculated as follows:

\[
\delta = mM + Mn = -\mathbf{S} \cdot \mathbf{r} + \mathbf{S}_0 \cdot \mathbf{r} = -\left(\mathbf{S} - \mathbf{S}_0\right) \cdot \mathbf{r}
\]  

(2)

Here \( m \) and \( n \) are defined as the projections of \( \mathbf{O} \) onto the rays passing through \( \mathbf{M} \). \( \mathbf{S} \) and \( \mathbf{S}_0 \) define the unit vectors in the direction of the scattered and incident x-rays respectively and \( \mathbf{r} \) is a vector that describes the path between scattering center \( \mathbf{O} \) and scattering center \( \mathbf{M} \). Using these relationships between the vectors, the phase difference is defined in terms of the unit vectors \( \mathbf{S} \) and \( \mathbf{S}_0 \), as well as the vector \( \mathbf{r} \) joining the two scattering centers.
\[ \varphi = 2\pi s \cdot r \]  

(3)

where \( s \) is just a substitute variable defined by

\[ s = \frac{\delta}{\lambda} = \frac{-(S - S_0)}{\lambda} \]  

(4)

The scattering angle \( 2\theta \) can be related to the magnitude of the scattering vector \( s \) as follows:

\[ |s| = \frac{2}{\lambda} \sin \theta \]  

(5)

The value of \( s \) can be substituted for the more commonly used momentum transfer vector, \( q \), to obtain a more familiar version of the Bragg equation, where \( q = 2\pi s \), which gives the following:

\[ q = \frac{4\pi}{\lambda} \sin \theta \]  

(6)

Finally, this equation is related to the repeat spacing in domains, “the real space distance”, \( d \), between the two scattering centers by considering that \( s = 1/d \). Substituting this relationship in for the equation (5), another form of the Bragg equation is obtained in terms of the distance between two scattering centers.

\[ 2d \sin \theta = \lambda n \]  

(7)

Where, \( n \) is the diffraction order. If we consider the periodic system that can has multiple interference maxima like would be expected for Young-Thomas double slit diffraction. In Figure III-2 an example of double-slit diffraction is shown, which includes contributions from both scattering from the width of the slit (the single slit envelope scattering) and the distance between two adjacent slits. This diagram shows how interference forms from plane waves and then will form diffraction patterns from constructive interference between these two slits. In fact, this diagram shows an example of what would appear from a lamellar type scattering where two
adjacent planes are arranged in parallel to each other, where the pattern will have both a component from the shape of the slit and the average distance between slits.

**Figure III-1**: Diagram of scattering vectors from interference between two scattering centers O and M.

**Figure III-2**: Example of double slit diffraction pattern (equivalent to lamellar scattering).
Scattering from a Free Electron

In order to calculate the amplitude from a set of scattering particles, it is prudent to derive the scattering from the simplest unit of scattering, the scattering length from a free electron. First a reference frame for the scattering of a free electron is considered, in this case an electron at the origin is used, O, and a plane polarized (polarized in the XZ plane in Figure III-3) x-ray passes through the electron. The electron will accelerate when subjected to the oscillating electric field $E_0$, where the amplitude of this electric field is $\gamma = E_0 e/m$, where $e$ is the electron charge and $m$ is the mass of the electron. The electron will emit and electric field in the Z direction at point P that can be calculated as:

$$E_Z = E_{0,Z} \frac{e^2}{m c^2} \times \frac{1}{r} \quad (8)$$

where, $r$ is the magnitude of the vector $OP$, $m = 9.116 \times 10^{-31}$ Kg, $e = 1.6 \times 10^{-19}$ coulombs, and $c$ is the speed of light.

Next a beam polarized along the Y-axis is considered. Since the polarization direction is no longer perpendicular to the direction of the oscillating electron, the resulting electric field vector magnitude must now be computed by using the following cross product:

$$E_Y = E_{0,Y} \frac{e^2}{m c^2} \times \frac{\cos 2\theta}{r} \quad (9)$$

By computing a beam polarized in both the Z-axis and the Y-axis, this allows computation of the scattering from a beam of arbitrary polarization. The magnitude of the electric field vector,
$E_0$, can be computed by considering the $Y$ and $Z$ components and using the Pythagorean theorem to compute the magnitude of this vector.

$E_0^2 = E_{0,Y}^2 + E_{0,Z}^2$  \hspace{1cm} (10)

For an unpolarized beam this equation can be transformed in terms of the expectation values of $E_{0,Y}$ and $E_{0,Z}$, which will obey the following relationships:

$E_0^2 = \langle E_{0,Y}^2 \rangle + \langle E_{0,Z}^2 \rangle$  \hspace{1cm} (11)

$\langle E_{0,Y}^2 \rangle = \langle E_{0,Z}^2 \rangle = \frac{1}{2} E_0^2$  \hspace{1cm} (12)

From these relationships we can compute the flux per unit area, which will allow for computation of the differential scattering cross section. The flux is proportional to $E^2 = E_Y^2 + E_Z^2$ and can thus be defined as follows:

$I_0 \left( \frac{e^2}{m c^2} \right)^2 \frac{1}{r^2} \frac{1 + \cos^2 2\theta}{2}$  \hspace{1cm} (13)

where, $I_0 = E_0^2$. The unit area disc at the point $P$ subtends a solid angle of $\frac{1}{r^2}$ at point $O$, therefore the energy scattering in the direction $OP$ per unit solid angle per second of scattered x-rays is computed as:

$I_e = I_0 \left( \frac{e^2}{m c^2} \right)^2 \frac{1 + \cos^2 2\theta}{2}$  \hspace{1cm} (14)

where, $\left( \frac{e^2}{m c^2} \right)$ is the classical electron radius, $r_e$. The term $I_e$ can be renamed in a form familiar form termed the differential scattering cross section as follows:
\[
\left( \frac{d\sigma}{d\Omega} \right)_e = b_e^2 = r_e^2 \frac{1 + \cos^2 2\theta}{2}
\]

Thus, the scattering length density is trivially calculated as:

\[
b_e = r_e \left( \frac{1 + \cos^2 2\theta}{2} \right)^{1/2}
\]

This scattering length density \((b_e)\) is fundamentally related to the description of the scattering intensity. These individual particle-particle scattering intensities can be extended to include collections of particles if a summation over all states is included. This summation can either be computed explicitly, in the case of simulated systems, or through a continuous approximation. Throughout the rest of this dissertation the continuous approximation will be the primary focus, as this will provide a base equation to develop models that describe the approximate size, shape, and distribution of electron density in a variety of phase separated systems. The next section will focus on the extension of this description of single electron scattering intensity to continuous electron distributions.
Figure III-3: Vector Diagram for scattering of a free electron with a plane XZ polarized x-ray parallel to the X-axis.

Scattering from Multiple Centers

For an ensemble of scattering centers, the scattering amplitude is defined as a function of the momentum transfer vector, \( \mathbf{q} \), by computing a sum over all scattering interactions.\(^2\) First this summation is defined as follows:

\[
A(q) = b_e \sum_{k=1}^{n} \exp(-i q r_k)
\]  \( (17) \)

In this case \( A(q) \) is the normalized amplitude of scattering and \( r_k \) is the position of the \( k^{th} \) scattering center. A continuous approximation of equation 17 is used in order to truncate this equation into a simpler form, rather than computing an extremely prohibitive explicit sum over
the ensemble of functional groups present. This approach of using discrete positions can be redefined in terms of a continuous number density distribution $n(r)$ as follows by replacing this summation with the integrand of the number density distribution function.

$$A(q) = \int b_e n(r) \exp(-i q r) \, dr$$

(18)

Then a term called the scattering length density distribution can be defined using the following relationship:

$$\rho(r) = \sum b_e n(r)$$

(19)

Substituting the scattering length density distribution into the amplitude equation the final result for computing the amplitude function in equation is obtained.

$$A(q) = \int \rho(r) \exp(-i q r) \, dr$$

(20)

In order to compute the intensity of this function the magnitude of this equation is calculated. For complex functions the magnitude must be computed as the product of $A(q)$ and $A^*(q)$, where $A^*(q)$ is the complex conjugate of $A(q)$. Thus we arrive at the scattering intensity for an ensemble of scattering centers:

$$I(q) = A(q) A^*(q) = \left| \int \rho(r) \exp(-i q r) \, dr \right|^2$$

(21)

This equation can be used to define different distributions of particles in terms of both collections of particles within a given phase (intraparticle scattering) and the scattering between phases (interparticle scattering). In the following sections methods for computing these approximations.
will be described in order to develop the models that will be used to describe the scattering data from the semi-crystalline ionomer systems studied in this dissertation.

**Scattering from Dilute Particles**

The scattering for a dilute system of particles can be defined fairly simply by considering the scattering to be the product of the number of scattering centers and the scattered intensity arising from a single particle with a given density distribution \( p(r) \). We can define this in terms of the relationship derived by Guinier and Fournet:

\[
I(q) = K N F(q)
\]

(22)

where \( K \) is a constant that scales the intensity in terms of the source used and the sample characteristics, \( N \) is the number of scattering particles, and \( F(q) \) is called the form factor. The form factor, \( F(q) \), defines the single particle intensity function.

The form factor for a sphere is derived here for two reasons, it provides a simple demonstration of the derivation of form factors, and it is an equation that is fundamental to many of the total scattering equations used throughout this dissertation. First a spherical collection of scattering centers with a homogeneous density is considered. The scattering length density distribution is described mathematically as follows:

\[
p(r) = \begin{cases} 
\rho_0 & r \leq R \\
0 & r > R 
\end{cases}
\]

(23)

where \( r \) is defined as the distance from the center of the sphere and \( R \) is the radius of the sphere. Additionally, \( F(q) \) can be defined as follows:
\[ F(q) = v_0^2 \Phi^2(qR) \]  

(24)

where \( v_0 \) is the sphere volume and \( \Phi(qR) \) is the integrated spherical form factor defined as:

\[ \Phi(qR) = \frac{3}{(qR)^3} (\sin qR - qR \cos qR) \]  

(25)

Equations (22, 24, and 25) can be combined to the scattering intensity function for \( N \) spherical particles scattering.

\[ I(q) = K N v_0^2 \Phi^2(qR) \]  

(26)

This general form can be expanded upon to include the interferences between neighboring particles, as will be described in the next section. Many other form factors can be used alternatively to describe these types of dilute systems, shown below in Table III-1 is an example of the most commonly used shapes that have high symmetry for dilute systems.\(^4\)
Table III-1: Table of common form factors for SAXS. Note: $j_1$ is defined as the spherical Bessel function of the first kind.

<table>
<thead>
<tr>
<th>Form Factor Shape</th>
<th>Form Factor, $F(q)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>$F(q) = \frac{3}{(q R)^3} (\sin q R - q R \cos q R)$</td>
</tr>
</tbody>
</table>
| Ellipsoid         | $F(q) = \int_0^1 \frac{3 j_1(v)}{v} d\mu$  
$v = q[A^2 \mu^2 + B^2 (1 - \mu^2)]^{1/2}$ |
| Cylinder          | $F(q) = \int_0^{\pi/2} \left[ 2.3 j_1(q R \sin \alpha) \frac{\sin(q L \cos(\frac{\alpha}{2}))}{q R \sin \alpha} \frac{\sin(q L \cos(\frac{\alpha}{2}))}{q L \cos(\frac{\alpha}{2})} \right]^2 \sin \alpha \ d\alpha$ |
| Lamellae          | $F(q) = \frac{2}{q^2} \left[ 1 - \cos(q \delta) \right] \left[ 1 - \frac{q^2 \sigma^2}{2} \right]$ |

**Polydispersity in Dilute Particle Systems**

In order to include the effects of multiple sizes of particles a distribution function that will give some probability to having a set of a particles of a given size is included into the intensity function. This will become important when considering the size of clusters of ionic aggregates, in particular when obtaining quantitative information about the distribution of collections of ionic multiplets. In order to consider this, the intensity function that arises from intraparticle scattering (i.e. the form factor) is modified by integrating over all possible particle volumes. As an example the equation derived previously for the scattering intensity function derived for spheres is modified as follows:\(^5\)
\[ I(q) = |\Delta \rho|^2 \int_0^\infty |F(q)|^2 V^2(r) N P(r) dr \]  

(27)

Where, \( \Delta \rho \) is the electron contrast between phases, \( F(q) \) is the form factor described previously, \( V(r) \) is the distribution of density in the particle volume, \( N \) is the number of particles, and \( P(r) \) is the probability of a scattering center of radii \( r \). In order to increase the stability and speed of computation used for a fitting procedure we can compute this equation explicitly by using several finite bins of the particle radii, \( r \).

\[ I(q) = |\Delta \rho|^2 \sum_{r_{\text{min}}}^{r_{\text{max}}} |F(q)|^2 V^2(r) N P(r) \Delta r \]  

(28)

The two distributions that have been employed in this dissertation will include both a Gaussian distribution and the Log-normal distribution. The Gaussian distribution is used to treat systems with high symmetry in the distribution of sizes, whereas the log-normal distribution is used to treat systems that have some minimum size cutoff, yet can also have shapes that possess a large radius in the distribution. The two functions are defined below of as \( G(r) \) and \( LN(r) \).

\[ G(r) = \frac{1}{\sigma \sqrt{2 \pi}} \exp \left[ -\frac{1}{2} \left( \frac{x - \mu}{\sigma} \right)^2 \right] \]  

(29)

\[ LN(r) = \frac{\exp[-(\ln(x - x_{\text{min}}) - \mu)^2/(2\sigma^2)]}{(x - x_{\text{min}})\sigma \sqrt{2 \pi}} \]  

(30)

**Scattering from Concentrated Particles**

In order to include both the scattering due to the shape and size of particles, as well as, the distribution of particles another contribution to the scattering must be included termed the
“structure factor” of these particles, \( S(q) \). Zernlike and Prins derived the following relationship for monodisperse scattering particles:

\[
I(q) = KNF(q)S(q)
\]  
(31)

Where, \( S(q) \) is a term to describe the interparticle x-ray interference intensity, given by:

\[
S(q) = 1 + 4\pi n \int_{0}^{\infty} (g(r) - 1) \frac{\sin q r}{q r} r^2 \, dr
\]  
(32)

In this equation \( n \) is the number density of particles and \( g(r) \) is the radial distribution function of particles. This equation must be solved under specific conditions to provide either closed form solutions, as will be seen for the liquid-like hard sphere structure factor, or numerically if more complex solutions to \( g(r) \) are used.

Many different approximations exist for describing the structure factor of most notable importance is the decoupling approximation\(^8,9\) and the local monodisperse approximation.\(^10\) The fundamental differences between these two approximations that the decoupling approximation assumes that the scattering from the size and shape of particles is completely independent of the positions and distribution of these particles. The local monodisperse approximation assumes the opposite, the size, shape, and position of these particles are highly correlated on small size scales. The derivation shown in the proceeding section utilizes the local monodisperse approximation, since there will be a spherical shell included on the outside of particles, which will inherently dictate the relative positions of these particles. In fact, all such “hard-particle” models utilize a correlated position and shape in their derivation, which will allow us to distribute particles in space with no overlapping positions.


**Liquid-like Hard Sphere Structure Factor**

In order to compute a distribution that essentially defines the distribution of particles in a “liquid-like” arrangement we must solve the equation for the interparticle interference function (equation 32). Using a liquid-like ordering will allow us to describe an arrangement of particles that are separated by some minimum distance that will be termed the “radius of closest approach” ($R_{ca}$), and are separated by an average volume occupied per particle ($V_p$). The first consideration that must be made to mathematically provide a solution to the structure factor is to consider the form of the radial distribution function, $g(r)$. First, $g(r)$ is cast into the two body correlation function, $h(r_{12})$ as follows:  

$$h(r_{12}) = g(r_{12}) - 1$$  \hspace{1cm} (33)

Ornstein and Zernike proposed a solution to $h(r_{12})$, which breaks the problem up into two components. The first component is to describe the direct correlation between particle 1 and its nearest neighbor particle 2 and then a second component is included to extend this interaction to all other particles. Ornstein and Zernike proposed a simple solution to this problem:  

$$h(r_{12}) = c(r_{12}) + n \int c(r_{13}) h(r_{32}) dr_3$$  \hspace{1cm} (34)

The first component of the equation, the direct correlation function $c(r_{12})$ is a term that describes the short range ordering of particles (nearest neighbor interactions), which will quickly
decay to zero with increasing separation distance. Percus and Yevick have derived a useful approximation for this direct correlation function using the following expression:\(^{13}\)

\[
c(r) \approx \left( \exp \left[ -\frac{\phi(r)}{kT} - 1 \right] \right) \exp \left[ -\frac{\phi(r)}{kT} \right] g(r) \tag{35}
\]

Wertheim\(^{14}\) and Thiele\(^{15}\) independently derived the direct correlation function with an analytical closed-form expression for a hard-sphere fluid. They solved this equation under the following conditions; when \(r > R\) (where, \(R\) is the sphere radius) both \(\phi(r)\) and \(c(r)\) will be zero. Kinning and Thomas\(^{16}\) derived the following set of relationships, where we consider \(r < 2R\), \(c(r)\) can be cast using the following polynomial solution to the Percus-Yeckick in order to approximate the correlation function:

\[
c(r) = -(\alpha + \beta s + \gamma s^3) \tag{36}
\]

where the polynomial coefficients are defined as follows:

\[
\alpha = (1 + 2\eta)^2/(1 - \eta)^4 \tag{37}
\]

\[
\beta = -6\eta(1 + \eta/2)^2/(1 - \eta)^4 \tag{38}
\]

\[
\gamma = -\eta/2 (1 + 2\eta)^2/(1 - \eta)^4 \tag{39}
\]

\[
s = \frac{r}{2R} \tag{40}
\]

\[
\eta = \frac{4}{3} \pi \frac{R_{CA}^3}{V_p} \tag{41}
\]

In this derivation, \(\eta\), is the hard-sphere volume fraction. The Fourier transform of the Ornstein-Zernike equation can be combined with interference equation to obtain:

\[
S(q) = \frac{1}{1 + n C(q)} \tag{42}
\]
where, \( C(q) \) is derived by computing the Fourier transform of the direct correlation function from equation 34 as follows:

\[
C(q) = -4\pi \int_0^\infty (\alpha + \beta s + \gamma s^3) \frac{\sin q r}{q r} r^2 dr
\]

(43)

This integrand has been evaluated by to give the following closed form solution to the structure factor.

\[
S(q) = \frac{1}{1 + 24\eta (G(A)/A)}
\]

(44)

,where \( A = 2q R_{CA} \) and

\[
G(A) = \frac{\alpha}{A^2} (\sin A - A \cos A) + \frac{\beta}{A^3} (2A \sin A + (2 - A^2) \cos A - 2) + \frac{\gamma}{A^5} (-A^4 \cos A
\]

\[
+ 4((3A^2 - 6) \cos A + (A^2 - 6A) \sin A + 6)
\]

(45)

The normalized structure factor can be given by computing \( S(0) \) (the structure factor at zero-angle), which gives \( 1/\alpha \), thus the normalized structure factor is simply \( \frac{S(q)}{S(0)} = \alpha S(q) \).

**Liquid-like Hard-Ellipsoid Scattering Intensity**

In order to treat crystallite systems a different set up models must be employed to properly account for the asymmetry in particle dimensions that occur due to the existence of a lamellar fold surface versus the lateral surface. There are several ways to account for anisotropic dimensions in this case, including the use a lamellar form factor, cylindrical form factor, or in this case an ellipsoidal form factor. It may prove to be artificial to distinguish between these three cases, however, using the ellipsoidal model allows for the use of liquid-like ordering for the
structure, which in turn allows us to incorporate something that mimics the inclusion of a rigid amorphous fraction.

The total scattering intensity for the scattering of liquid-like ellipsoids can be treated similarly to the derivation seen in the previous section for liquid-like hard spheres. First to start we consider a scattering intensity in the familiar Zernike and Prins scattering intensity:

\[ I(q) = K N F(q) S(q) \]  

(46)

where, again we have scaling constants to define the amplitude \( K \) and \( N \), the liquid-like structure factor \( S(q) \), and finally the ellipsoidal form factor.

To define the ellipsoid shape a major and minor axes are defined as \( A \) and \( B \) respectively. In order to create a form factor that is free of any orientation effects the form factor must be averaged over all orientations, this can be done be averaging the spherical Bessel function of the first kind \( j_1(\pi) \) used for computing the anisotropic spheroid as follows:

\[ F(q) = \int_0^1 3 j_1(\pi) \left( \frac{v}{\sqrt{3}} \right)^2 d\mu \]  

(46)

where,

\[ v = q\left[A^2\mu^2 + B^2(1 - \mu^2)\right]^{1/2} \]  

(47)

and

\[ j_1(\pi) = \frac{\sin \pi}{\pi} - \frac{\cos \pi}{\pi} \]  

(48)

**The Fractal-like nature of Polymer Interfaces**
The last component that is critical to treat is the scattering that arises from the matrix phase. The scattering from this component can be treated as a generalized Porod’s law type scattering. Scattering from fractal like objects can be approximated as follows:\textsuperscript{19}

\[ I_{Matrix}(q) = \frac{K}{q^{6-d}} \]  

(49)

, where K is defined as the Porod constant, which in this case is treated an amplitude variable, and d represents the fractal dimension, which can be used to either describe surface fractals or mass fractals. If \( d = 2-3 \) this would be considered scattering arising from heterogeneity of interfaces within the system. A fractal dimension of \( d = 3-4 \) could be linked to the power-law like scattering that arises from scattering of Gaussian chains. However, no real significant morphological parameters are needed from this particular fit at the moment and can be thought of as part of treating the background scattering of the system since no significant geometric parameters are used from this component for describing the distribution of phases in these ionomer materials, although they could potentially be used in a future analysis.

**Total Scattering Intensity from Three Phase Systems**

Using the intensity defined for each component the total scattering intensity can now be considered from the linear combination of scattering intensities:

\[ I_{total}(q) = \sum_i I_i(q) = I_{Ionic} + I_{Xtal} + I_{Matrix} + I_{Bg} \]  

(50)
, where $I_{\text{ Ionic}}$ is the liquid-like hard sphere scattering from multiplets, $I_{\text{Xtal}}$ is the liquid-like hard ellipsoid scattering arising from crystallites, $I_{\text{Matrix}}$ is the Porod scattering from the matrix components, and $I_{\text{Bg}}$ represents the background intensity and can be generally regarded as constant throughout the range. One note of caution for this method of describing the total scattering intensity is that this assumes that these scattering entities are entirely independent of each other. This assumption is used to reduce the complexity of modeling these systems.

Fitting this function requires a particularly robust fitting algorithm to avoid divergent solutions and often require good initial guesses for the parameters. In order to fit these components each component must be transformed into an algebraic form so the residuals can properly be compared. In order to perform these fits two different methods were used. For fits that contained a crystalline component the Levenberg-Marquardt\textsuperscript{20}, a variant of the Gauss-Newton method\textsuperscript{21} was used. For the interpretation of data that was taken at Argonne National Labs using their ultra-small-angle x-ray scattering system the standard fitting method used in IgorPro has been used, which using a least squared fitting method utilizing maximum entropy regularization.\textsuperscript{5, 22}

**Contrast Variation**

An alternative representation of the scattering intensity can be used that casts the equation in terms of three primary components; the intraparticle scattering (the form), the interparticle scattering (the structure), and the contrast between phases.\textsuperscript{2, 3}
\[ I(q) \propto \Delta \rho^2 F(q) S(q) \]  

(51)

where \( \Delta \rho \) is the contrast difference between two phases in a phase separated system. If the electron density from two phases, \( \rho_1 \) and \( \rho_2 \) are considered, this contrast term can be expanded as follows:

\[
\Delta \rho^2 = (\rho_2 - \rho_1)^2 = (\rho_1 - \rho_2)^2 = \rho_1^2 - \rho_1 \rho_2 + \rho_2^2
\]  

(52)

The expansion shown above shows a basic justification for the Babinet principle, which states that the intensity of a given component contributing to the SAXS intensity depends on the difference between the scattering length density of each phase. However, the phase which is lower in scattering length density cannot be distinguished without apriori knowledge. In this case the contrast between phases can be used to represent the relative differences between the amorphous ion-rich phase and the crystalline ion-free phase.

**Conclusion**

A theory for the treatment of small angle x-ray scattering data has been described here. This derivation and description builds upon the fundamental physics of scattering single particle systems and extends these calculations to collections of particles. This treatment allows one to compute critical geometric parameters that can describe many important aspects in phase separated systems including the size, shape, and polydispersity of individual particles, as well as, the distribution of these particles relative to each other. These treatments are important for studying phase separated systems in order to connect the morphological description of materials
to their thermal and mechanical properties. Ultimately, providing an accurate picture of these materials will provide a wealth of information for understanding how phase separated materials can be altered and fine-tuned in order to optimize the properties of high-performance materials that may be valuable in both scientific research and commercial products. In this research it has proven to be extremely useful in quantitatively describing the fundamental morphological differences in both the ionic and crystalline components when comparing the syndiotactic polystyrene homopolymer, randomly functionalized sulfonated syndiotactic polystyrene, and the recently described “blocky” gel-state functionalized sulfonated syndiotactic polystyrene.
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Chapter IV:  
Synthesis and Thermal Characterization of Random and Blocky  
Sulfonated Syndiotactic Polystyrene Ionomers

Abstract

Blocky sulfonated syndiotactic polystyrene (SsPS) copolymers were produced using a recently developed postpolymerization functionalization procedure conducted in the gel state. The thermal properties and crystallization behavior of a matched set of blocky and random SsPS copolymers containing 3 and 10 mol % sulfonate groups were compared using differential scanning calorimetry (DSC), which shows that the blocky functionalization architecture displays a much faster rate of crystallization even at low sulfonate contents and a higher crystallizability at high sulfonate contents. The glass transition temperature for gelstate-functionalized copolymers was found to be independent of sulfonic acid content above 4% sulfonation, consistent with behavior observed in previous studies of sodium styrenesulfonate block copolymers.

Introduction

Earlier it has been described in the Chapter II that Orler and coworkers have shown through extensive study that randomly functionalized semicrystalline ionomers will significantly inhibit the ability for these systems to crystallize at high ion contents.\textsuperscript{1-4} Such a pronounced decrease in the ability of a polymer to crystallize at low ion contents may be a challenge in utilizing SsPS in applications where high ion content and a high degree of crystallinity are
desirable (e.g., in membrane applications). For example, a proton exchange membrane for fuel cell applications requires high ion content for the transport of water and ions through the membrane.\textsuperscript{5-8} A proton exchange membrane must also possess mechanical stability to withstand harsh fuel cell operation conditions and low solvent swelling behavior as well.\textsuperscript{9} The mechanical integrity necessary for operation in harsh environments such as elevated temperature with low swelling may be derived from a membrane containing a reasonable crystalline component.\textsuperscript{10} Consequently, it would be desirable to produce a semi-crystalline ionomer with a degree of sulfonation that is appropriate for proton conduction and a high degree of crystallinity.\textsuperscript{11} Crystallinity has been linked to improved barrier properties and decreased membrane swelling in the presence of solvents.\textsuperscript{12} Additionally, crystalline domains have been proposed to act as physical crosslinks that enhance mechanical properties.\textsuperscript{13} In order to produce systems with both a high ion content and high crystallinity, blocky ionomer architectures are being investigated.

McGrath and coworkers have shown that block ionomers possess unique and advantageous morphologies that enhance proton conductivity and hydrolytic stability against swelling over random or statistical copolymers.\textsuperscript{14} For multi-block polyarylethersulfone (PAES) copolymer systems, the hydrophilic, sulfonated PAES segments provide the ionic character, which is necessary for proton conduction, while the hydrophobic poly(arylene ether) segments lends hydrolytic stability.\textsuperscript{14} Moreover, the creation of multiblock copolymers with long runs of hydrophilic and hydrophobic segments facilitates the formation of microphase-separated microstructures, which have been shown to enhance proton conduction. The increased proton conductivity of the multi-block system, relative to the random analog BPSH-35 copolymer membrane, was attributed to enhanced connectivity of the hydrophilic regions within the
hydrophobic matrix, and directly related to the ionic content and the hydrophilic/hydrophobic block lengths. Furthermore, in a similar study, block copolymers were found to exhibit greater proton conductivity than their random copolymer analogs when studied in the partially hydrated state. In order to take advantage of these superior morphology-property relationships, there is great interest in finding experimentally simple and economically desirable methods to produce these block ionomer architectures.

The Moore research group has developed a post-polymerization method to sulfonate syndiotactic polystyrene to yield a blocky distribution of the sulfonate groups along the polymer backbone. This method is based upon conducting the sulfonation process while sPS is in the solvent-swollen, semi-crystalline gel-state. sPS gels can be formed from a variety of solvents, which forms a physical network consisting of both crystalline and solvent swollen amorphous domains. During the course of the reaction, the sulfonating reagent is sterically excluded from the crystalline domains, and thus is only capable of reacting with the solvent-swollen amorphous chain segments in the semi-crystalline gel network. Our working hypothesis is that this gel-state reaction creates a blocky architecture, which inherently preserves long sequences of unsulfonated (and thus crystallizable) sPS homopolymer segments separating runs of sulfonated SsPS units along the polymer chains.

It is important to note that other groups have reported heterogeneous functionalization reaction schemes for semi-crystalline polymers. Polyethylene powders have been suspended in chlorinating reagents, in an unswollen state, to achieve a blocky functionalization. Borriello and coworkers, employed a heterogeneous reaction scheme in the sulfonation of cast or compression-molded sPS films to create materials suitable for absorbing volatile organic
compounds from water. In this work, the authors proposed that during this solid-state reaction, a uniform sulfonation of the amorphous phase is obtained, while the crystalline phase remains unfunctionalized. However, since this solid state or “bulk” functionalization method involves an interplay of diffusion and reaction processes, it was shown for compression-molded films, that this procedure created a gradient of sulfonation from the interior to the exterior, similar to that observed earlier for aPS films. For cast films, a more uniform sulfonation across the film thickness was observed, along with a noticeable decrease in crystallinity with increasing sulfonation. More recently, Borriello and coworkers created sulfonated aerogels of sPS by exposing bulk gel specimens to chlorosulfonic acid. This procedure is similar to that described in this report; however, sulfonation through-out the bulk specimen (6 mm by 35 mm) could be non-uniform compared to small (sub-millimeter) gel particles. While this study clearly demonstrated preferential sulfonation of the amorphous component in the semi-crystalline gels, no evidence was presented to indicate the formation of a blocky architecture that could preserve crystallizability in subsequent processing. Our current study is focused on exploiting the gel-state morphology to template the functionalization chemistry as a means to create a blocky architecture along the polymer backbone that preserves crystallizability.

**Experimental**

**Materials**

Syndiotactic polystyrene (Questra 102) having a weight average molecular weight ($M_W$) of 310,000 g/mol was obtained from the Dow Chemical Company. Reagent grade 1,2,4-trichlorobenze (TCB), methanol, sulfuric acid, and potassium monopthalate were obtained from
Fisher Scientific. Hexanoic anhydride, benzyltrimethylammonium hydroxide, and benzoic acid were received from Sigma Aldrich.

**Preparation of Sulfonation Reagent**

A mild sulfonation reagent (hexanoyl sulfate) was prepared according to previously published procedures using TCB as the solvent. TCB was added to a volumetric flask containing 0.03 moles of hexanoic anhydride per mL of sulfuric acid. The TCB/hexanoic anhydride solution was cooled in an ice bath for 1 hour, and then 1-10 mL (depending on the target degree of sulfonation) of concentrated sulfuric acid was added to the chilled solution and shaken vigorously to allow for complex formation. Additional TCB was then added to the fill the remaining space in the volumetric flask.

**Random Sulfonation of Syndiotactic Polystyrene**

sPS was dissolved in TCB under reflux for 1.5 h to yield a 10% w/v solution. After 1.5 h, the solution was cooled to 70 °C and then additional TCB was added to yield a 1% w/v sPS solution. The sPS solution was allowed to equilibrate at 70 °C under a nitrogen purge for 1.5 hr. After equilibration, the appropriate amount of sulfonating reagent was added, and the reaction was allowed to proceed for 1 hour at 70 °C under a nitrogen purge. After 1 h, 10 mL methanol was added to the solution to terminate the reaction. The solution was poured into a large excess of methanol (~ 2L) to precipitate the copolymer, followed by filtration and washing with deionized water. For the random copolymers containing higher than 5 mol% sulfonation, ethyl ether was used to precipitate the polymer instead, and water was used for the entire washing process in order to avoid dissolution of the polymer into methanol. The random SsPS precipitates were filtered and washed with deionized water repeatedly until all remaining traces of TCB,
sulfonating reagent, and methanol were removed. The resulting polymer was dried under vacuum at 100 °C for 12 h.

**Blocky Sulfonation of Syndiotactic Polystyrene**

Syndiotactic polystyrene was dissolved in TCB under reflux for 1.5 h to yield a 10% w/v solution. After 1.5 h, the solution was cooled to room temperature. Upon cooling, the 10% w/v sPS solution was allowed to remain at room temperature for 24 hours. During this cooling process, the sPS solution crystallizes and forms a physical gel. The solid gel was manually broken in small, submillimeter-scale particles using a spatula. The sPS gel particles were diluted in additional TCB to yield a 1% w/v sPS suspension. The sPS gel-particle dispersion was allowed to equilibrate at 70 °C under a nitrogen purge for 1.5 hr. After equilibration, the appropriate amount of sulfonating reagent was added and the reaction was allowed to proceed for 1 hour at 70 °C under a nitrogen purge. No visible change in the solvent-suspended gel particles was observed during the course of the reaction. After 1 h, 10 mL methanol was added to the dispersion to terminate the reaction. The dispersion was poured into a large excess of methanol in order to precipitate the polymer. The SsPS particles were filtered and washed with deionized water repeatedly until all remaining traces of TCB, sulfonating reagent, and methanol were removed. The resulting polymer was dried under vacuum at 100 °C for 12 h.

**Determination of Degree of Sulfonation**

The randomly and blocky sulfonated SsPS copolymers were redissolved in 95/5 v/v TCB/methanol for 1.5 h to yield 0.5% w/v solution. These 0.5% w/v solutions were used to determine the degree of sulfonation via non-aqueous titration with methanolic benzyltrimethylammonium hydroxide. The benzyltrimethylammonium hydroxide was
standardized using benzoic acid. SsPS ionomers of low sulfonic acid content and high ion content were prepared. Low sulfonic acid content SsPS containing 3.2 to 3.5 mol% sulfonate groups are identified as SsPS3.5H⁺Random and SsPS3.2H⁺Blocky, where the H⁺ denotes the copolymers are in the acid-form. The Random and Blocky nomenclature denotes homogeneous functionalization of SsPS in solution and functionalization of SsPS in the gel-state, respectively. High sulfonic acid content SsPS random and blocky copolymers were also prepared for this study containing 9.2 and 10.5 mol% sulfonate groups, respectively. These copolymers are identified as SsPS9.2H⁺Random and SsPS10.5H⁺Blocky.

**Differential Scanning Calorimetry**

Thermal behavior and crystallization kinetics of the SsPS copolymers were studied using differential scanning calorimetry (DSC). A TA Instruments Q2000 DSC was used to probe the thermal behavior of SsPS. Dried powders of the sulfonated copolymers and thin film samples with controlled thermal history were analyzed. Thin film samples were prepared for these experiments by thermally pressing each sample between Kapton sheets at 200 °C and 3000 psi for 3 min using a Carver laboratory press. The SsPS films were allowed to cool to room temperature under ambient conditions after removal from the press. Samples from the thermally pressed films were die cut and placed within aluminum DSC pans. The weight for each sample was maintained between 6 – 8 mg.

DSC analysis was performed under a continuous nitrogen flow to minimize sample degradation. The glass transition, crystallization temperature, and melting temperatures of the SsPS3.5H⁺Random and SsPS3.2H⁺Blocky copolymers were determined from the second DSC scan, after erasing the thermal history, using the TA Instruments Universal Analysis Software.
Isothermal crystallization was carried out for the low sulfonic acid content SsPS copolymers. TA Instruments Universal Analysis software was used to analyze the resulting DSC traces. The crystallization half-time, \( t_{1/2} \), the time at which the material reaches 50% of its maximum crystallinity, was obtained from isothermal scans at various temperatures, and was used as a measure of the crystallization rates of the random and blocky sulfonated SsPS copolymers. The thermal transitions of the high ion content ionomers were evaluated from the DSC heating scan, post isothermal crystallization.

Results and Discussion

The strategy for producing a blocky SsPS ionomer architecture is depicted in Figure IV-1. A homogenous solution of sPS will crystallize upon cooling the solution from elevated temperature to room temperature. Over time, the number and size of the crystalline domains increase until a physical gel is formed from the initial homogenous solution. The physical network within these gels consists of the crystallites (acting as multi-functional physical crosslinks) that are linked together by solvent-swollen amorphous chain segments (acting as ties chains). The presence of crystalline domains, that establish the gel structure, provide a means by which to preserve sequences of unsulfonated material when the sulfonation process is conducted within the gel-state. During this gel-state sulfonation process, the sulfonation reagent (represented by the red circles in Figure IV-1) is not able to penetrate within the crystalline regions. Thus, the sulfonation reagent is only able to react with the amorphous chain segments spanning the solvent-swollen domains between the physical crosslinks. Consequently, we hypothesize that “blocks” of partially sulfonated sPS chains are created, leaving long sequences of unsulfonated
sPS homopolymer isolated within the crystallites. In contrast, it can be seen in Figure IV-1 that conducting the sulfonation process while sPS is a homogenous solution leads to a “statistical” or random placement of sulfonate groups along the polymer backbone with comparatively shorter sequences of unsulfonated material. The aforementioned method of sulfonating sPS while in the gel-state may provide a very simple post-polymerization modification approach to create a blocky placement of sulfonate groups along the polymer backbone. The thermal properties, crystallization behavior, and morphologies of these materials are investigated to elucidate the effect of these distinct sulfonation methods on ionomer architecture and properties.

Figure IV-1: Diagram of solution state and gel-state sulfonation post-polymerization methods.

Thermal Analysis

DSC thermograms of the low sulfonic acid content SsPS copolymers SsPS3.5H*Random, SsPS3.2H*Blocky, and the sPS homopolymer are shown in Figure IV-2. The thermogram for the sPS homopolymer (Figure IV-2) contains three thermal transitions: a broad endothermic event near 175 °C, followed by a small exothermic event at 190 °C, and then prominent melting
endotherm at 270 °C. In the vicinity of 190 °C, solvent-treated sPS is known to undergo a transformation from a helical γ-form crystal structure to an all-trans α or β crystal form that melts near 270 °C. Since the sPS homopolymer sample in this analysis was precipitated from TCB (consistent with the process used to isolate the SsPS copolymers), the observed thermal events below 200 °C are thus attributed to the helical to all-trans crystal transformation. Similar to the behavior of solvent treated sPS, the lightly sulfonated copolymers also show thermal transitions near 190 °C (Figure IV-2), attributed to the helical to all-trans crystal transformation, and the melting of the α and/or β crystal polymorphs near 270 °C. It is interesting to note, however, that the exothermic event near 190 °C for the SsPS3.5H+Random sample is much more distinct than that observed for both the SsPS3.2H+Blocky and sPS homopolymer samples. During the time-frame of this heating scan, we suspect that the reorganization event that establishes the all-trans crystal forms is delayed in the random copolymer (yielding a more pronounced separation of the overlapping endothermic and exothermic events) due to the close proximity of the interacting defects (i.e., the sulfonated styrene units) to the crystalline stems.
Figure IV-2: Relative heat flow versus temperature of sPS homopolymer (H), SsPS3.5H*Random (R), and SsPS3.2H*Blocky (B) copolymers. Samples were precipitated from TCB, annealed at 150 °C for 2 hours, then quenched to room temperature prior to scanning at 20 °C/min. (b) Samples were isothermally crystallized from the melt at 200 °C for 2 hours prior to scanning at 20 °C/min. All thermograms have been vertically offset to facilitate comparison.
Figure IV-3: Relative heat flow versus temperature of sPS homopolymer (H), SsPS3.5H*Random (R), and SsPS3.2H*Blocky (B) copolymers. Samples were isothermally crystallized from the melt at 200 °C for 2 hours prior to scanning at 20 °C/min. All thermograms have been vertically offset to facilitate comparison.

Given the consequence of the sulfonate groups acting as structural defects along the sPS chains, it is not surprising that the melting point for both of the sulfonated copolymers during the heating scans (as shown in Figure IV-2) is observed to be depressed from 270 °C (for the sPS homopolymer) to 260 °C and 266 °C for the SsPS3.5H*Random and SsPS3.2H*Blocky copolymers, respectively. Following isothermal crystallization at 200 °C for two hours (Figure IV-3), the melting point of the SsPS3.5H*Random copolymer is further depressed to 257 °C, while the melting point for the SsPS3.2H*Blocky copolymer remains at 266 °C (nearer to that of the sPS homopolymer at 272 °C). The higher melting point for the blocky copolymer suggests the presence of thicker crystalline lamellae relative to the random analog. This behavior may be attributed to the gel-state functionalization, which is expected to inherently preserve longer runs...
of crystallizable sPS units between the functional defects, and thus allow for the formation of thicker crystals during this isothermal crystallization process.

**Figure IV-4**: Relative heat flow versus temperature of sPS homopolymer (H), SsPS10.5H*Blocky (B), and SsPSsdsd9.2H*Random (R) copolymers. All samples were isothermally crystallized at 200°C for 2 hours prior to scanning at 10 °C/min. All traces have been vertically offset to facilitate comparison.

The area under the melting endotherms of the data in Figure IV-3 was used to determine the overall degree of crystallinity $X_c$, for these samples using the following relationship:

$$X_c = \frac{\Delta H_f}{\Delta H_f^0}$$

The value of $\Delta H_f^0$ for sPS is 82.6 J/g.\textsuperscript{29} The degree of crystallinity for the SsPS3.2H*Blocky copolymer ($X_c = 35\%$) is nearly identical to that of the sPS homopolymer ($X_c = 36\%$). In contrast, the degree of crystallinity of the SsPS3.5H*Random copolymer is significantly reduced ($X_c = 26\%$).
Although the thermal properties of the random and blocky copolymers are only moderately different at low degrees of sulfonation, our previous work has demonstrated that the crystallizability of random SsPS at ion contents above 3 mol% is severely limited. However, based on our working hypothesis that the gel-state functionalization can preserve crystallizability and effectively decouple the functional group aggregation phenomenon from the crystallization process, it is of interest to explore the impact of this prospective route to create blocky architectures at significantly higher degrees of sulfonation. Figure IV-4 compares the DSC thermograms of the sPS homopolymer to that of the highly sulfonated SsPS9.2H\textsuperscript{+}Random and SsPS10.5H\textsuperscript{+}Blocky copolymers, following isothermal crystallization. It is clear from these data that even after thermal annealing, the SsPS9.2H\textsuperscript{+}Random copolymer is not able to crystallize and remains completely amorphous. In contrast, a large melting endotherm is observed at 244 °C for the SsPS10.5H\textsuperscript{+}Blocky copolymer, indicative of the development of a high degree of crystallinity during the annealing period. This behavior demonstrates that the gel-state sulfonation process indeed preserves the crystallizability of the SsPS copolymer at a high degree of sulfonation, and lends strong evidence (albeit indirect) supporting our hypothesis that the heterogeneous gel-state functionalization reaction yields a blocky architecture that conserves long runs of pure sPS units between functional units. In contrast, the homogeneous solution state functionalization yields a random architecture, with statistically shorter runs of pure sPS units between sulfonated units, which completely inhibits crystallization. Moreover, after isothermal crystallization at 200 °C for 2 hours, the degree of crystallinity for the SsPS10.5H\textsuperscript{+}Blocky copolymer is measured to be $X_c = 23\%$. Surprisingly, this high degree of crystallinity for the blocky SsPS copolymer containing 10.5 mol% sulfonate groups is 66\% of that for the pure sPS sample ($X_c = 35\%$)
crystallized under the same conditions. Again, this remarkably enhanced crystallizability of the SsPS10.5H*Blocky strong evidence for the blocky architecture stemming from the gel-state functionalization process, which preserves a significant quantity of long runs of crystallizable sPS units along the functionalized chains.

Differential scanning calorimetry has revealed key differences in the role of functionalization in gel-state on the architecture. The relative peak heights of each crystallization exotherm, which is indicative of the relative $\alpha$ and $\beta$ crystallite populations in the sample. Additionally, it is important to note the increase melting temperature in blocky functionalized systems when compared to the randomly functionalized analogue even at low ion contents, which is indicative of the increased thermal stability of blocky functionalized materials. It is evident from this data that there may be multiple populations of crystals both in size and in polymorphic composition. However, some of the lower temperature peaks may be artifacts of the experiment during the heat or are the melting and recrystallization of smaller crystallites.
Figure IV-5: DSC thermograms for sample preparation procedure used in scattering experiments. Heat flow versus temperature of sPS (H), SsPS3.5H*B (B), and SsPS3.2H*R (R) post-isothermal crystallization at 220°C, 225°C, 230°C, and 235°C for 1 hour using a heating rate of 10°C/min.

Crystallization Kinetics
The effect of ionomer architecture (random versus blocky) on the crystallization behavior of the SsPS materials was evaluated using DSC isothermal crystallization experiments. The development of crystallinity within a matched set of SsPS3.2H*Random and SsPS3.2H*Blocky copolymers was monitored by applying the following relationship:

\[
F_c(t) = \frac{\int_0^t \frac{dH}{dT} dt}{\int_0^\infty \frac{dH}{dT} dt} \tag{2}
\]

The expression given in equation 2 represents the bulk fractional crystallinity of the functionalized copolymer systems, \( F_c(t) \) and is equal to the heat evolved during isothermal crystallization at a specific time \( t \) divided by the total exothermic heat generated during the entire crystallization process. Figure IV-6 displays plots of \( F_c(t) \) versus ln time for isothermal crystallization temperatures of 220, 225, 230, and 235 °C for the SsPS3.2H*Random and SsPS3.2H*Blocky copolymers. Comparing the isotherms of the SsPS3.2H*Random and SsPS3.2H*Blocky copolymers, it is evident that both copolymers are crystallizing on a comparable time scale for the lower crystallization temperatures. For higher crystallization temperatures, however, the two systems diverge where the SsPS3.2H*Blocky copolymer is observed to crystallize significantly faster than the random analog.
Figure IV-6: $F_c(t)$ versus ln time at 220, 225, 230, and 235 °C for (R) SsPS3.2H+R and (B) SsPS3.2H+B copolymers. Polarized light micrographs for (R) SsPS3.2H+R and (B) SsPS3.2H+B copolymers captured at 30 min during isothermal crystallization at 235 °C.

Polarized light microscopy of spherulites growing at an isothermal crystallization temperature of 235 °C show (in **Figure IV-6**) that the SPS3.2H+Blocky copolymer yields a lower nucleation density relative to the SsPS3.2H+Random copolymer. This behavior may also be attributed to the blocky vs random architecture. The long runs of crystallizable sPS segments in the SPS3.2H+Blocky copolymer, that are well removed from the sulfonated units, are expected to have a relatively high mobility. In this nucleation controlled regime, high segment mobility
reduces the rate of primary nucleation. For the SsPS3.2H*Random copolymer, however, the shorter runs of crystallizable sPS segments, that are in close proximity to the interacting sulfonated units, are relatively restricted in their mobility. Consequently, the rate of primary nucleation is enhanced in the SsPS3.2H*Random copolymer.

**Figure IV-7:** Crystallization half-time versus crystallization temperature for SsPS3.2H*Random and SsPS3.2H*Blocky copolymers.

To quantify the differences in the rates of crystallization between the SsPS3.2H*Random and SPS3.2H*Blocky copolymers, crystallization half-times, $t_{1/2}$, were extracted from each of the crystallization isotherms. In addition, a complete Avrami analysis of the crystallization isotherms is provided in the Supplemental Information, included in Figures IV-8R, IV-8B and Table IV-1. It is clear from the data in Figure IV-7 that the crystallization half-times for the SPS3.2H*Blocky copolymer are significantly shorter (i.e., a faster rate of overall crystallization) than that for the SsPS3.2H*Random copolymer, especially at higher crystallization temperatures. The faster rates of bulk crystallization for the SPS3.2H*Blocky copolymer may be attributed to a higher population of long sequences of unsulfonated sPS runs between sulfonated units that more readily associate
into crystallites compared to the random analog containing a statistically lower population of long sPS sequences. Upon cooling from the melt, as the polymer chains attempt to pack into crystalline structures, sulfonic acid groups act as defects in the polymer chain and are rejected from the growing crystalline interface. With a homogeneous distribution of defects (as expected for the SsPS3.2H*Random copolymer), it is reasonable to suspect that the probability of encountering a “defective stem” diffusing to the crystal growth front is higher when compared to a blocky distribution of defects. Rejection of these encountered defects increases the time required for crystallization to occur and leads to longer crystallization half-times, as observed for the SsPS3.2H*Random copolymer. Given the polymorphic nature of sPS, it is also of interest to note that the faster crystallization kinetics for the blocky copolymer occurs despite a greater population of the slower crystallizing β-form relative to the kinetically favored α-form, which is discussed in depth in Chapter V.

Table IV-1: Kinetic parameters at 220, 225, 230 and 235 °C for SsPS3.2H*R and SsPS3.2H*B.

<table>
<thead>
<tr>
<th>SsPS Kinetic Parameter</th>
<th>220 °C</th>
<th>225 °C</th>
<th>230 °C</th>
<th>235 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SsPS3.2H*R</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t½ (min)</td>
<td>4.64</td>
<td>9.56</td>
<td>32.51</td>
<td>65.99</td>
</tr>
<tr>
<td>n</td>
<td>2.53</td>
<td>2.41</td>
<td>1.74</td>
<td>1.69</td>
</tr>
<tr>
<td>K (min⁻¹)</td>
<td>7.9 x 10⁻³</td>
<td>2.1 x 10⁻³</td>
<td>1.4 x 10⁻³</td>
<td>5.4 x 10⁻³</td>
</tr>
<tr>
<td><strong>SsPS3.2H*B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>t½ (min)</td>
<td>2.89</td>
<td>4.57</td>
<td>7.16</td>
<td>36.45</td>
</tr>
<tr>
<td>n</td>
<td>2.65</td>
<td>2.48</td>
<td>2.08</td>
<td>1.78</td>
</tr>
<tr>
<td>K (min⁻¹)</td>
<td>3.2 x 10⁻²</td>
<td>2.2 x 10⁻²</td>
<td>1.3 x 10⁻²</td>
<td>3.1 x 10⁻³</td>
</tr>
</tbody>
</table>
Figure IV-8: ln [-ln (1-Xc(t))] versus ln t at 220, 225, 230, and 235 °C for (R) SsPS3.2H^+R and (B) SsPS3.5H^+B. Fit lines are shown in black in the graph used to determine the Avrami parameters shown in Table IV-1.

Glass transition temperature analysis

As mentioned in the introduction, Weiss and coworkers found that changes in the glass transition temperature with increasing sulfonate content could be used to distinguish between random and blocky architectures of sulfonated atactic polystyrene produced by the conventional post-polymerization route and an emulsion polymerization route, respectively. In their study,
the random SaPS system showed a linear increase in glass transition temperature \( (T_g) \) with sulfonate content over all compositions, while the \( T_g \) of the blocky SaPS system was found to become independent of sulfonate content at high degrees of functionalization.\(^{31}\) Assuming that the intermolecular interactions that affect the glass transition (i.e., the aggregation of polar sulfonate groups yielding physical cross-links that restrict chain mobility)\(^{32}\) are operative in both \textit{atactic} SaPS and the \textit{syndiotactic} SsPS systems, it is of interest to see if a similar analysis would provide evidence of blockiness with the gel-state sulfonated SsPS.

\textbf{Figure IV-9} shows a plot of the glass transition temperature versus mol\% sulfonation for both the random and blocky SsPS systems. Up to about 4 mol\% sulfonation, both systems show a linear increase in the glass transition temperature with increasing degree of sulfonation. Beyond 4 mol\% sulfonation, the random system continues to display the expected linear trend, while the blocky SsPS deviates significantly. In contrast to the random system, the glass transition temperature for blocky SsPS reaches at maximum at 104 °C at 4 mol\% sulfonation and then becomes independent of the degree of sulfonation at higher contents. Since quench rescans were used to obtain the \( T_g \) values in \textbf{Figure IV-9}, the observed behavior is a purely amorphous response, without influence from a crystalline contribution. As such, the long runs of unsulfonated sPS units along the chains of the blocky SsPS are expected to possess dynamics more comparable to that of amorphous chains in the parent sPS homopolymer (having a \( T_g \) near 100 °C). Therefore, in perfect agreement with the earlier results for SaPS, this comparison of the influence of sulfonate content on \( T_g \) between the random and blocky SsPS systems lends strong support for the blocky architecture of SsPS produced via the gel-state sulfonation process.
Conclusion

We have demonstrated a very simple post-polymerization method to produce a blocky sulfonated sPS that preserves crystallizability in highly functionalized copolymers. By performing the sulfonation reaction in the gel-state, long sequences of pure sPS units within the crystallites are effectively shielded from the reactive reagents. The longer sequences of unsulfonated material of the blocky SsPS facilitates the ability of these crystallizable stems to pack efficiently into crystalline structures relative to that of the randomly sulfonated sPS analog. At relatively low degrees of sulfonation (3 mol%), the blocky copolymer crystallizes significantly faster than that of the random copolymer. At high ion contents of 9.2 mol%, the randomly sulfonated ionomer is rendered totally amorphous due to the presence of homogeneously distributed defects along the polymer backbone. In contrast, however, the highly sulfonated SsPS10.5H*B copolymer is able to achieve a high degree of crystallinity during isothermal annealing.
Additionally, further evidence has been presented showing that for gel-state functionalized copolymers the glass transition temperature becomes independent of the degree of sulfonation above 4% sulfonation, which is consistent with previous studies conducted by Weiss and coworkers on sodium styrene sulfonate block copolymer systems. Enhanced lamellar SAXS scattering contrast of the crystallized blocky copolymer suggests that the polar sulfonate groups are distributed within the amorphous, inter-lamellar domains.

It is important to note that the gel-state functionalization approach described here is not expected to be limited to sulfonation. Other chemistries, such as halogenation, are quite possible, provided the reaction is not inhibited by the solvent chosen to sustain the gel state. Halogenated copolymers produced from this facile approach will greatly broaden the scope of this methodology in creating precursory blocky architectures that could be further modified with a wide range of useful functionality. In proton exchange membrane fuel cells (PEMFC) applications, the crystalline component within the membrane can enhance mechanical durability and limit water solubility. However, conventional post-polymerization sulfonation used to create efficient membranes, such as sulfonated poly(ether-ether-ketone) (SPEEK), yields a random copolymer that profoundly prohibits crystallizability. To effectively decouple crystallization from functional group aggregation, blocky architectures created through controlled copolymerization methods are becoming state-of-the-art. With the facile approach described in this report, the process of crystallization within the blocky architecture also inherently increases the functional group concentration in the amorphous phase. This crystallization-induced concentration of the functional groups may then lead to enhanced aggregation, and thus improved transport properties in applications such as PEMFC. Recently, we have discovered that this gel-state
functionalization approach is applicable to new thermo-reversible gels of poly(ether ether ketone),\textsuperscript{33} which extends this platform of facile blocky copolymer synthesis to materials (i.e., blocky SPEEK) ideally suited to the harsh chemical environments encountered in PEMFC operations.
References


Chapter V:
Crystalline Morphology of Blocky and Random Sulfonated Syndiotactic Polystyrene

Abstract

Small angle x-ray scattering measurements were used to illuminate the effects that using a random versus a blocky architecture has on the crystalline morphology in SsPS copolymers. It has been shown that at low percentages of sulfonation that these copolymer systems appear to be quite similar to each other, although there is a notable difference in the contrast seen between phases, where the blocky functionalization appears to have a higher contrast between phases. When compared to the homopolymer both random and blocky functionalized samples have much greater contrast, implying that there must be ions intercalated between lamellae within the crystalline structures. This is additionally confirmed when higher sulfonation percentages are used and the blocky system still retains the high contrast observed at lower percentages. In fact, the effect of measurement temperature is actually inverted compared to the homopolymer, where the peak becomes unobservable when the temperature is elevated. The effects of annealing temperature were also characterized, which appears to have little effect on the lamellar size observed in SAXS (according to peak position). WAXD analysis shows that the crystalline morphology of random and blocky SsPS are quite different with respect to polymorphic composition, where the blocky copolymer yields a significantly greater composition of the beta polymorph. Enhanced lamellar SAXS scattering contrast of the
crystallized blocky copolymer suggests that the polar sulfonate groups are distributed within the amorphous, inter-lamellar domains.

**Introduction**

Small angle x-ray scattering (SAXS) experiments have been performed on these random and “blocky” sulfonated syndiotactic polystyrene systems in order to compare the morphology of both the ionic and crystalline components in these materials. As described in **Chapter III**, SAXS can provide both qualitative and quantitative comparisons of the shape, size, and distribution of phases in phase separated materials. In this chapter the acid form of the randomly sulfonated and gel-state, “blocky”, sulfonated sPS are compared in order to discover any critical differences in the arrangement of the polar sulfonate groups and the non-polar sPS homopolymer crystallites. This has allowed for our research group to gain a more fundamental understanding of the morphological arrangement of these phases. This morphological analysis will provide greater context for how these two sulfonation procedures allow for different morphologies and ultimately how these differing morphologies impact the large observed differences in the thermal properties that have were described in **Chapter IV**. Additionally, this chapter provides a brief description of how the sPS homopolymer, randomly functionalized SsPS, and blocky functionalized SsPS can have an extensive impact on the polymorphic composition in these systems. This provides crucial information on how these structures can be used to manipulate a variety of crystal forms, which can also be used to tune the thermal and mechanical properties in these materials. Wide angle x-ray diffraction was used order to compare these differences in melt crystallized samples, where it has been observed that blocky functionalized copolymers tend
to favor the thermodynamically stable crystal forms, compared to randomly functionalized copolymers that tend to favor the kinetically favored crystal forms.

**Experimental**

**Small angle x-ray scattering**

SAXS experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-rays with a wavelength of 0.154 nm (Cu Kα). The sample-to-detector distance was 1605 mm, and the q-range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector with an exposure time of 2 hours. All SAXS data were analyzed using the SAXSGUI software package to obtain radially integrated SAXS intensity versus scattering vector \( q \), where \( q = \left( \frac{4\pi}{\lambda} \right) \sin(\theta) \), \( \theta \) is one half of the scattering angle, and \( \lambda \) is the X-ray wavelength.

**Wide angle x-ray diffraction**

WAXD experiments were performed using a Rigaku MiniFlex II x-ray diffractometer emitting X-rays with a wavelength of 0.154 nm (Cu Kα). Samples were scanned from 5 to 35 degrees 2\( \theta \) at a scan rate of 0.25 degrees 2\( \theta \)/min, and a sampling window of 0.050 degrees 2\( \theta \) at a potential of 30 kV and current of 15 mA. All WAXD data were analyzed using the PDXL 2 software package to obtain WAXD intensity versus 2\( \theta \) profiles. WAXD profiles were vertically shifted to facilitate a comparison of the peak positions.
Preparation of X-ray Scattering Samples

Films were prepared by thermally pressing each sample between Kapton sheets at 200 °C and 3000 psi for 3 min using a Carver laboratory press. The SsPS films were allowed to cool to RT under ambient conditions after removal from the press. Samples from the thermally pressed films were die cut and placed within aluminum DSC pans. The weight for each film was maintained between 6 – 8 mg. Samples were heated from 50 °C to 330 °C at 10 °C/min and held at 330 °C for 5 min. Samples were then rapidly quenched to the desired isothermal crystallization temperature, and isothermal crystallizations were carried out at 220, 225, 230, and 235 °C for 60 min for WAXD analysis and 200 °C for 2 hours for SAXS analysis. After isothermal crystallization the films were quenched to room temperature at the maximum cooling rate. All samples for SAXS analysis were prepared to have a degree of crystallinity of approximately 20%, DSC scans of heat flow versus temperature are shown in Figure IV-5 in the previous chapter.

Results and Discussion

Characterization of Phase Distributions in Sulfonated Syndiotactic Polystyrene using Small Angle X-ray Scattering

Small-angle X-ray scattering (SAXS) has been used to develop an understand of the ordering of crystallites within the material. Figure V-1 contains one-dimensional SAXS profiles of SsPS3.2H*R, SsPS3.2H*B, and the sPS homopolymer. From the SAXS data it is clear that there are fundamental differences between the homopolymer and the sulfonated samples in the high q region. The observation of a diffuse peak at high q can be attributed to the presence of hydrogen
bonded crosslinks being present in the system. The presence of a diffuse peak in the region of 1.5 – 2.5 nm\(^{-1}\) is consistent with the interference peak observed for sulfonated polystyrene ionomers \(^1\) although to our knowledge there are no reports on the acid form of SsPS published.

There are also significant differences in the peak that appears at near 0.3 nm\(^{-1}\) that is associated with the morphology of crystallites in these systems. The incorporation of sulfonate groups appears to increase the average separation of crystallites, indicated by a shift of the peak maxima to lower q. Blocky sulfonation gives rise to an average intercrystallite spacing at some intermediate crystallite separation compared to homopolymer and the randomly sulfonated polymer. There is as expected a large difference in the apparent contrast of the peaks, where the incorporation of the sulfonic acid functionality should enhance the electron density difference between the low density α-crystalline phase and the matrix phase. The enhanced contrast in the sulfonic acid form suggests that the higher electron density styrene sulfonate groups are likely isotropically distributed throughout the amorphous matrix and are intercalated between crystallites. Additionally, when comparing the blocky and random samples it is important to note the change in the small angle upturn for scattering vectors of q < 0.2 nm\(^{-1}\), where the blocky sample appear to have a pronounced upturn, which can be observed in the inset of Figure V-1. It has been proposed by Ding and coworkers that this small angle upturn is due to a nonhomogeneous distribution of ion long pairs existing in the matrix material surrounding the ionic aggregates.\(^2\) Tentatively, the more pronounced upturn in these blocky systems may be due to a higher concentration of ion lone pairs in this matrix in the blocky samples, since the distribution of ions will be more concentrated in blocky systems than in their randomly
functionalized counterparts. However, a more in depth investigation, possibly with the aid of theoretical models would be needed to confirm this hypothesis.

**Figure V-1**: One dimensional SAXS profiles for SsPS3.2H+B (B), SsPS3.5H+R (R), and the sPS homopolymer (H). SAXS profiles have been vertically offset to facilitate comparison between curves.

Small-angle X-ray scattering (SAXS) is used here to probe the ordering and scattering contrast of crystallites within the SsPS copolymers. **Figure V-2** contains SAXS profiles of the SsPS9.2H+Random and SsPS10.5H+Blocky copolymers in comparison to that of the sPS
homopolymer. In order to provide a comparable volume of phase separated structures in this analysis, all samples were isothermally crystallized at 200 °C, prior to analysis. The crystallization time was controlled to yield an equivalent degree of crystallinity of approximately 20% for both the sPS homopolymer and the SsPS10.5H*Blocky copolymer. Note that the SsPS9.2H*Random copolymer remained completely amorphous as shown in Figure V-2. The SAXS profile for the SsPS10.5H*Blocky copolymer shows a prominent scattering maximum at $q = 0.39 \text{ nm}^{-1}$, which is attributed to an inter-lamellar long period of ca. 16 nm. As expected, the SAXS profile for the completely amorphous SsPS9.2H*Random copolymer is featureless within this $q$-range, consistent with the absence of stacked lamella. While the sPS homopolymer certainly contains crystalline lamella of a composition comparable to that of the SsPS10.5H*Blocky copolymer, the sPS SAXS profile also shows a featureless, monotonic decrease in intensity over this $q$-range. As demonstrated by Barnes and McKenna, this behavior is attributed to a lack of scattering contrast between the crystalline and amorphous components of sPS.\textsuperscript{3} The crystalline densities of the $\alpha$ and $\beta$ forms are 1.033 g/cm\textsuperscript{3} and 1.067 g/cm\textsuperscript{3}, respectively, while the density of amorphous sPS is 1.04 g/cm\textsuperscript{3}.\textsuperscript{4} With an expected mixed composition of both $\alpha$ and $\beta$ polymorphs in the isothermally-crystallized sPS sample, it follows that the electron density contrast in sPS is very weak regardless of polymorphic composition. At elevated temperatures, however, a differential coefficient of thermal expansion between the amorphous and crystalline components yields sufficient contrast to observe a scattering maximum.\textsuperscript{3} Based on this fundamental principle of scattering contrast, we propose that the prominent scattering maximum observed at room temperature for the SsPS10.5H*Blocky copolymer is attributed to the presence of relatively electron dense sulfonate groups dispersed within the amorphous layers between the lamella.
Upon crystallization, the sulfonate groups are concentrated within the amorphous domains, intercalated between the lamella, thus yielding a relatively high electron density contrast between the correlated amorphous and crystalline components of the SsPS10.5H+Blocky copolymer. If the sulfonate groups were somehow isolated to regions well removed from the crystalline domains, then the electron density contrast between the amorphous and crystalline layers would be expected to be identical to that of the homopolymer.

**Figure V-2:** One dimensional SAXS profiles for sPS homopolymer (H), SsPS10.5H*B (B), SsPS9.2H*R (R) copolymers. All samples were isothermally crystallized at 200 °C prior to analysis. SAXS profiles have been vertically offset to facilitate comparison between curves.

Differences can be seen in the morphology of the SsPS3.5H*B and the SsPS10.5H*B samples in the contrast observed in the crystalline scattering. In this case this further confirms the hypothesis that these sulfonate groups are arranged in between the crystalline structures. It
can be seen in Figure V-1 that the crystalline peak intensity is enhanced by incorporating more ionic groups into these blocky systems. This enhanced crystalline peak intensity can only occur if there is a large difference between electron density of the crystallites and the surrounding amorphous matrix, this difference in the amorphous matrix electron density is proposed to arise from the incorporation of highly electron dense sulfonate groups. These sulfonate groups are intercalated between these crystallites, thus with increasing ion content the contrast between the amorphous matrix and the crystallites themselves will be increased.

Temperature effects on the crystalline morphology have also been investigated in these systems in order to compare the randomly functionalized copolymer, the blocky copolymer, and the sPS homopolymer, a demonstration of this can be seen in Figure V-3. In both the copolymers and the sPS homopolymer it can be noted that the peak position and shape is fundamentally similar in all of these systems, except in the sPS homopolymer where the crystalline peak (c.a. 0.3 nm⁻¹) appears to be significantly lower in intensity compared to both the randomly functionalized copolymer and the sPS homopolymer. However, the peak and shape and position being similar between all of these indicate a fundamentally similar shape and distribution of crystallites in these systems at low sulfonate group incorporation.

The differences in intensity in the between the sPS homopolymer and the SsPS copolymers is indicative of a larger difference in the contrast between the amorphous matrix and the crystallites. The crystallite density and the amorphous matrix density are extremely similar at room temperature in the sPS homopolymer. When sulfonic acid groups are incorporated the contrast is significantly increased, where the sulfonic acid groups will raise the average electron density in the amorphous matrix, and the density of crystallites will only be affected by changed
in the polymorphic composition. This leads to the observed intensity increase in these systems.

A representation of the changes in the contrast between the amorphous matrix is shown in

**Figure V-4.** As can be seen from the $\Delta \rho^2$ values, the square of the contrast (which the intensity scales linearly with) increases by almost an order of magnitude when comparing the homopolymer to the sulfonated copolymers. Additionally, the randomly functionalized copolymer and the blocky have nearly the same contrast.
Figure V-3: 1D SAXS profiles of sPS (H), SsPS3.2H*Blocky (B), and SsPS3.2H*Random (R) post-isothermal crystallization at 220°C, 225°C, 230°C, and 235°C for 1 hour.
Figure V-4: Representation of the contrast between the amorphous matrix and the crystallites using the sPS homopolymer, SsPS3.5H*R, and SsPS3.2H*B.

A much more profound effect on the contrast can be seen when considering SsPS5.1Cs*B in Figure V-5. In this sample it was observed that there is actually an inversion of the contrast behavior compared to what would be expected for the sPS homopolymer. Barnes observed that when syndiotactic polystyrene is measured at room temperature the contrast between crystallites and the surrounding matrix is extremely low, which does not allow for a clear observation of the crystallite scattering. However, when samples are measured above the glass transition temperature scattering becomes readily apparent. In this experiment Barnes measured these samples at 50°C and observed almost no contribution to the scattering profile from crystallites, in spite of evidence of crystallinity present in the wide angle x-ray diffraction profile based on the observation of crystalline reflections. Barnes hypothesized that the lack of crystalline scattering in the SAXS profile was due to the fact that the density of crystallites and the amorphous matrix are nearly identical. In order to get pronounced contrast in these samples Barnes measured these samples at higher temperature in order to utilize the differences in the

\[ \Delta \rho^2 \approx 3.12 \times 10^{17} \text{ cm}^{-4} \]

\[ \Delta \rho^2 \approx 6.48 \times 10^{18} \text{ cm}^{-4} \]

\[ \Delta \rho^2 \approx 4.51 \times 10^{18} \text{ cm}^{-4} \]
coefficient of thermal expansion between crystallites and the amorphous matrix and saw that the crystalline interference peak became visible when the sample is measured above the glass transition temperature.

![Graph showing SAXS profiles](image)

**Figure V-5:** SAXS profiles SsPS5.0Cs*Blocky melted at 300 °C and then isothermally crystallized at 200 °C for 2 hours. The measurements were taken at two different temperatures during the SAXS measurement.

**Figure V-6** shows a pictorial description of the previously described effect for the inversion of the contrast dependence on temperature. In the case shown on the left for the blocky SsPS copolymer, we can see that there is an additional ionic contribution included. This ionic component is dispersed with the amorphous matrix, thus their individual contributions can be averaged. In this case the amorphous chains have an overall lower electron density as the amorphous chains expand due to thermal expansion at higher temperatures, but still possess the contribution from the ionic components. The system in this case has a higher electron density in
the amorphous matrix compared to the crystalline component at low temperatures and at high temperatures the ionic and amorphous components combined have a similar electron density to the crystalline component. When compared to the homopolymer, where at room temperature the amorphous and crystalline component have similar electron densities, we can see the difference in behavior. This description gives a clear picture into the physical rationale for the differences in the contrast dependence on material temperature, and shows that the hypothesis that makes the most sense is for the ions to be intercalated between crystallites.

Figure V-6: Pictorial diagram of the change in contrast due to the material temperature comparing SsPS5.1Cs*Blocky and the sPS homopolymer. $\rho_c$ is the electron density of crystalline lamellae, $\rho_a$ is the electron density of the amorphous chains, and $\rho_i$ is the electron density of ions.

Quantitative Analysis of Sulfonated Polystyrene Crystallites

A quantitatively analysis has also been performed in order to approximate the dimensions of these crystallite arrangements. In order to properly predict the dimensions of these systems a script has been written in Mathematica that can fit the scattering curves of these systems.
Crystallites in polymer systems possess an anisotropic structure, where the differences in the fold surface and the lateral surface possess a different Gibbs free energy of interaction with amorphous matrix and different kinetic processes for assembly. Typically, these crystal systems will adopt a geometry with an elongated fold surface and a smaller lamellar thickness due to kinetic processes. In these systems it is important to understand the geometry of these crystallites because the crystallite shape and distribution will allow us to determine the overall sequencing of the ion rich phase because they will overall not participate in the crystallographic assembly.

To simulate a reasonable geometry for these systems a liquid-like distribution of hard spheres with an elliptical core has been used for several reasons. The elliptical shape allows one to determine a reasonable gauge on the aspect ratio of these crystallites in respect to lateral and lamellar thickness. Additionally, this shape can properly reflect differences in thickness throughout the lamellar thickness, where the edges of crystals may be thinner than the central core of these crystals. Using a liquid-like ordering also reflects the fact that there should be some minimum distance between crystallites due to the rigid amorphous fraction and the notion that crystals physically cannot occupy the same space.

Table V-1 and V-2 shows the dimensions that have been calculated from this model using SAXS data collected from annealed samples at both 220°C and 235°C. It should be first noted that these models almost certainly reflect the approximate dimensions of these materials, as there is no polydispersity included in the crystallite size, which is likely to contribute significantly to the dimensions. In this model $R_a$ reflects to the lamellar thickness, $R_b$ is the lateral thickness, $R_{ca}$ is the radius of closest approach, and the $V_p$ is is the average volume occupied per particle. First
the comparison of SsPS3.2H*R and SsPS3.5H*B is considered. It is quite apparent that this calculation predicts larger crystals that are farther apart for the random copolymer compared to the blocky copolymer. This clearly shows some of the short comings of this model, where it appears to have little predictive power of the exact crystallite dimensions, clearly a more complex model may be more appropriate. It should be noted that the thermal data predicts a higher melting point in the blocky systems compared to random systems, which implies a higher lamellar thickness. However, the local environments may be different in these two systems due to differences in the distribution of sulfonate groups, which may change the enthalpy of melting at the interface between the crystallites and the matrix material. In essence. These numbers may serve as useful approximations for the size and distribution in these systems, but may not necessarily correspond exactly with the thermal differences seen in these samples, where the blocky samples tend to melt at higher temperatures. The sPS homopolymer was not able to be used for any calculations of the crystallite distribution at an annealing temperature of 220°C due to a lack of contrast, but is considered for the calculations done for samples annealed at 235°C.

When these samples have been modeled at 235°C the dimensions again show a disparity between the melting points and the calculated lamellar thickness. However, it can be seen that the difference in the SsPS3.5H*B and the sPS homopolymer actually correspond well with the observed melting point depression. SsPS3.5H*B shows a lamellar thickness of 9.4 nm and the sPS homopolymer has a lamellar thickness of 11.1 nm, based on calculating the lamellar thickness from the melting point. Additionally, the predicted volume fractions appear to accurately describe the approximate crystallinity calculated from DSC (X_c = 35% for SsPS3.2H*R and X_c = 36% for the sPS homopolymer). In contrast, the degree of crystallinity of the SsPS3.5H*R copolymer
is significantly reduced ($X_c = 26\%$). It can be seen again that the random copolymer is predicted to have a larger crystallite size than either the blocky SsPS and the sPS homopolymer, which does not account for the melting point depression observed in DSC data. It can be seen in all of these samples that similar center-to-center distances are calculated for the B-SsPS copolymer and the sPS homopolymer.

This model however appears to be successful at predicting that the crystallite sizes become smaller as the sulfonic acid content, when SsPS.S0H*B has been modeled using this anisotropic liquid-like hard-sphere model. While a comparable total crystallinity cannot be obtained for this sample due to both thermal and kinetic considerations, the dimensions of the crystallite are predicted to be notably smaller in all dimensions, as can be seen in Table V-3. The crystallite is predicted to be ~1 nm smaller on each dimensions, including the radius of closest approach.

It is clear through these calculations that while they may provide useful approximation for the dimensions in crystallites, but may only provide a relative comparison in order to qualitatively compare the form factor for the crystallite size and shape. There are several reasons that are not able to be adequately built into this model that may explain these shortcomings, most importantly would be the lack of inclusion of a polydispersity in the crystallite sizes and not being able to account for the presence of multiple polymorphic structures. In order to be able to include both of these factors a new method for determining the size and shape of polymers with multiple polydisperse crystalline polymorphs is described in the next section. This method using the peak broadening in wide angle x-ray diffraction to be able to separate the contribution from each individual polymorph in order to provide a more accurate calculation of the crystallite
dimensions, which would be useful in more accurately predicting the relationship between the crystallite morphology and the thermal properties of these materials. This analysis calculates the size and distribution of crystallites within the matrix can allow for an approximation of the block structure of the polymer chains in terms of distribution of ionic blocks and homopolymer blocks. This calculation is detailed in Chapter VII.

**Table V-1:** Fit Parameters from sPS (H), SsPS3.2H*Blocky (B), and SsPS3.2H*Random (R) post-isothermal crystallization at 220°C for 1 hour.

<table>
<thead>
<tr>
<th>220°C</th>
<th>(R_a) (nm)</th>
<th>(R_b) (nm)</th>
<th>Aspect ratio</th>
<th>(R_{ca}) (nm)</th>
<th>(V_p) (nm(^3))</th>
<th>Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-SsPS</td>
<td>6.0</td>
<td>9.5</td>
<td>1.6</td>
<td>9.1</td>
<td>8704</td>
<td>0.36</td>
</tr>
<tr>
<td>B-SsPS</td>
<td>4.5</td>
<td>6.6</td>
<td>1.5</td>
<td>8.7</td>
<td>6037</td>
<td>0.46</td>
</tr>
</tbody>
</table>

**Table V-2:** Fit Parameters from sPS (H), SsPS3.2H*Blocky (B), and SsPS3.2H*Random (R) post-isothermal crystallization at 235°C for 1 hour.

<table>
<thead>
<tr>
<th>235°C</th>
<th>(R_a) (nm)</th>
<th>(R_b) (nm)</th>
<th>Aspect ratio</th>
<th>(R_{ca}) (nm)</th>
<th>(V_p) (nm(^3))</th>
<th>Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS</td>
<td>5.6</td>
<td>7.2</td>
<td>1.3</td>
<td>8.4</td>
<td>6125</td>
<td>0.41</td>
</tr>
<tr>
<td>R-SsPS</td>
<td>6.3</td>
<td>10.1</td>
<td>1.6</td>
<td>9.7</td>
<td>11416</td>
<td>0.34</td>
</tr>
<tr>
<td>B-SsPS</td>
<td>4.7</td>
<td>7.5</td>
<td>1.6</td>
<td>8.8</td>
<td>8174</td>
<td>0.35</td>
</tr>
</tbody>
</table>

**Table V-3:** Fit Parameters for SsPS5.1H*Blocky

<table>
<thead>
<tr>
<th>235°C</th>
<th>(R_a) (nm)</th>
<th>(R_b) (nm)</th>
<th>Aspect ratio</th>
<th>(R_{ca}) (nm)</th>
<th>(V_p) (nm(^3))</th>
<th>Volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-SsPS</td>
<td>3.7</td>
<td>6.0</td>
<td>1.6</td>
<td>7.7</td>
<td>6125</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Consideration Sequence Lengths and Sequence Length in Gel-state Functionalized Semi-Crystalline Ionomers

Currently a set of model dependent equations have been developed in order to describe the average block length from these systems. The equations used are in analogy to the equations
used by Eisenberg to compare the block length of copolymers studied by SANS and have
determined that the chain dimensions of polystyrene can be modeled effectively using a free
polystyrene chain. Here it is proposed that the average block length can be described using the
morphological parameters determined for crystallites to approximate the average block length.
Space filling calculations are shown in Figure V-7 show that it is necessary for these ionic
aggregates to be intercalated in between crystallites in both random and non-random systems
in order to be able to correctly account for the number of ionic aggregates.

If the ions are isotropically distributed in between crystals, the average block length is
determined by the average path length of a chain that ties two crystallites together. While this
does not take into account very short chains that reenter the same crystallite or very long chain
that never enter crystals at all, these two effects are expected to be nearly equal in likelihood,
thus the average block length can be described using the average length between crystallites.
However, in order to establish a chain length between crystallites, the average radius of
crystallite needs to be taken into account, since the ionic portion should not exist inside the
crystallite. Several approximations exist for approximating the average radius of an ellipsoid as a
sphere with an “effective” elliptical radius. Of particular use here for ellipsoids with a high aspect
ratio the quadratic elliptical radius can be used which gives a reasonable estimate for the average
radius. Thus the average surface to surface distance ($D_{ss}$) between crystallites can be adjusted
by the twice the quadratic radius ($R_e$):

$$R_e = \sqrt{\frac{a^2 + b^2}{2}}$$

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\[ D_{ss} = 2(R_{ips} - R_e) \]  \hfill (16)

\[ R_{ips} = \left( \frac{3}{4\pi} V_p \right)^{1/3} \]  \hfill (16)

**Figure V-7:** Pictoral representation of the crystallite distribution. The purple translucent sphere represents the average inter-crystallite distance derived from model fits.

In order to account for the random directionality of polymer chains traversing the matrix one can use a polystyrene free chain to estimate the number of monomer units it would take to traverse a distance of \( D_{ss} \). In this case to estimate the distance a chain travels the root mean square end to end distance can be used, and the chain number of monomer units (N) required to travel a distance \( D_{ss} \) can be calculated using the following relation:

\[ D_{ss} = \sqrt{R^2} = l \sqrt{C_\infty N} \]  \hfill (17)
\[ N = \left( \frac{D_{ss}}{\sqrt{C_{\infty} l}} \right)^2 \frac{l}{0.254 \text{ nm}} \]  

(18)

In order to convert from number of Kuhn segments to number of monomers a factor of \( l/0.254 \) was added. The factor of 0.254 nm accounts for two carbon-carbon bonds placed along the backbone of polystyrene. If we use the numbers derived from the fits we find that the average segment size of the ionic block in terms of the number of monomer units, \( N \), is 225.5. The number of chains participating in crystalline lamellae can be assumed in this case to occupy the space between structures. Using the original molecular weight of our polymer 310,000 g/mol we find that there are 1489 monomer units in each polymer chain on average. This means that at most four ionic block chains can exist within a chain according to this calculation. If it is assumed a given chain starts with an ionic segment, this allows for three full ionic segments, three crystalline segments, and a partial ionic segment. Of course combinatorically different arrangements can be imagined, but since this is an approximation this assumption will be used to say that the block structure could potentially consist of eleven blocks (alternating homopolymer and ion containing blocks). A more complete version of this calculation that would require significant modeling work and would likely best be represented using some type of coarse grain molecular modeling would be to include the thermodynamic and morphological differences between the different polymorphic structures within the matrix. A discussions of the polymorphic composition in these materials is provided in the next section.

**Characterization of Polymorphism in Sulfonated Syndiotactic Polystyrene**

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WAXD was used to probe the polymorphic composition of the copolymers in comparison to the sPS homopolymer. Using WAXD, the polymorphic composition of each system can be determined by comparing the relative peak areas of the diffraction peaks appearing at 11.6° and 12.2° using the following empirical relationship derived by Guerra,

\[
P_\alpha = \frac{1.8 \frac{A_{11.6}}{A_{12.2}}}{1 + 1.8 \frac{A_{11.6}}{A_{12.2}}} \times 100
\]  

(3)

where \(P_\alpha\) represents the fraction of crystallites in the \(\alpha\)-form and \(A_{11.6}\) and \(A_{12.2}\) are the integrated areas of the diffraction peaks occurring at \(2\theta = 11.6\) and 12.2 degrees respectively.\(^5\)

**Figure V-8:** Representations of the crystal structures for melt crystallized and solvent crystallized syndiotactic polystyrene. Reprinted with permission of the Elsevier. Copyright 2009 Elsevier.\(^6\)

Syndiotactic polystyrene has many different crystal forms that can be adopted depending on the processing conditions, a pictorial representation is shown in **Figure V-8**. These crystal forms include two melt crystallized forms \(\alpha\) and \(\beta\), and three solution crystallized forms \(\delta\), \(\gamma\), and \(\varepsilon\). **Figure V-9** shows the WAXD data for sPS and the SsPS3.5H\(^{+}\)Random and SsPS3.2H\(^{+}\)Blocky
copolymers that were isothermally crystallized at temperatures ranging from 220 °C to 235 °C. Figure V-10 compares the polymorphic compositions of the polymers over the same range of isothermal crystallization temperatures. For pure sPS, a decrease in $P_\alpha$ with increasing crystallization temperature is commonly observed, and this trend is clearly observed for each of the samples in this study. In agreement with our previous studies, the incorporation of sulfonic acid functionalization is found to promote the formation of the $\beta$ polymorph in both the random and blocky SsPS copolymers. This behavior was attributed to restricted segmental mobility in the melt due to the interacting sulfonate groups, thus inhibiting the formation of the kinetically favored $\alpha$-form crystals.
Figure V-9: WAXD profiles of sPS, SsPS3.2H*R (R), and SsPS3.2H*B (B) post-isothermal crystallization at 220°C, 225°C, 230°C, and 235°C for 1 hour.
Figure V-10: Percentage of α-crystallites ($P_\alpha$) versus isothermal crystallization temperature; samples were crystallized for 1 hr. Polynomial fit lines have been added as visual guide.

In comparing the polymorphic composition of the sulfonated copolymers, it is surprising to note that the SsPS3.2H*Blocky sample displays a much stronger tendency to promote the formation of the β polymorph, relative to the random analog at an equivalent sulfonate content. Given the proposed blocky architecture for the gel-state sulfonate copolymer, it is reasonable to expect that the local mobility of the crystallizable segments (well separated from the functionalized units) would be somewhat greater than that of the statistically shorter crystallizable segments in the random analog (containing a more homogeneous distribution of sulfonate groups). Thus, the mobility argument (used to rationalize the inhibited formation of the kinetically favored α-form crystals for each of the SsPS copolymers over that of pure sPS) is not feasible to explain the enhanced β form composition observed for the SsPS3.2H*Blocky
sample. As an alternative hypothesis, we consider the metastable nature of the α-polymorph.\(^9\) Woo and coworkers found that sufficiently small α-form lamella can gradually transform into the β phase during isothermal crystallization provided that the crystal thickness is limited to below a critical size.\(^{10}\) Moreover, this α to β transformation was proposed to occur through a lamellar thickening process. If the blocky architecture of the SsPS3.2H\(^+\)Blocky copolymer limits the size of the α-form lamella over that of pure sPS, then these small metastable crystallites could be susceptible to solid-solid transformation, leading to an increase in the composition of the thermodynamically stable β phase.

Of course, this size restriction is also likely to occur for the SsPS3.5H\(^+\)Random copolymer. However, it is also reasonable to expect that lamellar thickening would be limited in the random analog due to structural pinning from the local proximity of defects (i.e., the sulfonated units) along the statistically shorter crystallizable chain segments. With limited lamellar thickening, the α-form lamella in the SsPS3.2H\(^+\)Random would persist, and perhaps grow laterally, leading to higher P\(_{\alpha}\) composition, relative to the blocky analog. Clearly, this prospective argument will require further analysis (beyond the scope of this initial study) in order to support the link between the polymer architecture and polymorphic composition.

**Conclusion**

We have demonstrated a very simple post-polymerization method to produce a blocky sulfonated sPS that preserves crystallizability in highly functionalized copolymers. By performing the sulfonation reaction in the gel-state, long sequences of pure sPS units within the crystallites are effectively shielded from the reactive reagents. This change in the architecture of chain is
evident in the scattering behavior of these systems where it can be seen that significant
differences are seen in the contrast observed for these systems, where the sulfonated samples
show a significant increase in the amplitude of the scattering peak associated with the crystalline
component. This implies the existence of electron dense sulfonate groups intercalated between
crystalline lamellae. This is further supported by the observation of an inversion in the thermal
dependence of the amplitude of the crystalline scattering. Fitting of these data sets using the
ellipsoidal hard-sphere model provided some relative gauge of the size and shape of the
crystallites in these samples. However, the sizes predicted do not have good agreement with the
results seen in the previous chapter where the thermal properties are analyzed. It should be
noted however that this does give preliminary evidence that the crystallites are indeed
anisotropic in shape, but a more robust model may provide more quantitative predictions of
these dimensions. Using these fits however we can approximate the block structure in terms of
the number of blocks, which predicts that these samples may exist as hepta-block copolymers in
the case of blocky samples. WAXD analysis has shown additional differences exist between
random and blocky copolymers with respect to polymorphic composition, where the blocky
copolymer yields a significantly greater composition of the beta polymorph, which indicates a
large difference in the thermodynamics and kinetics of crystallization, further supporting the
stark differences imbibed by using these two different reaction procedures.

It is important to note that the gel-state functionalization approach described here is not
limited to sulfonation. Recently, we have discovered that other chemistries, such as
halogenation, are quite applicable. Halogentated copolymers produced from this facile approach
that will greatly broaden the scope of this new methodology in creating blocky architectures with
a wide range of useful functionality. With respect to the morphological consequence of this new gel-state blocky functionalization approach, it is also of interest to consider the technological benefit of developing a highly sulfonated polymer with high crystallizability. In proton exchange membrane fuel cells (PEMFC) applications, the crystalline component within the membrane can enhance mechanical durability and limit water solubility. However, conventional post-polymerization sulfonation used to create efficient membranes, such as sulfonated poly(ether-ether-ketone) (SPEEK), yields a random copolymer that profoundly prohibits crystallizability. To effectively decouple crystallization from functional group aggregation, blocky architectures created through controlled copolymerization methods are becoming state-of-the-art. With the facile approach described in this report, the process of crystallization within the blocky architecture also inherently increases the functional group concentration in the amorphous phase. This crystallization-induced concentration of the functional groups may then lead to enhanced aggregation, and thus improved transport properties in applications such as PEMFC. Recently, we have discovered that this gel-state functionalization approach is applicable to new thermo-reversible gels of poly(ether ether ketone),¹¹ which extends this platform of facile blocky copolymer synthesis to materials (i.e., blocky SPEEK) ideally suited to the harsh chemical environments encountered in PEMFC operations.
References


Chapter VI:
Introduction to USAXS and Applications of USAXS to Long-Range Phase Separation in Ionomers

Abstract

Blocky sulfonated syndiotactic polystyrene (SsPS) copolymers were produced using a post-polymerization functionalization procedure conducted in the gel-state. The Morphological structure has been probed using a combination of small angle x-ray scattering (SAXS) and ultra-small angle x-ray scattering (USAXS) to provide a description of both the differences in ionic aggregate structure and the higher order structure of clusters of these aggregates. It has been found that at low degrees of sulfonation (circa 3%) that there are large differences in the size of these clusters. At higher degrees of sulfonation a more profound difference is observed, where in randomly sulfonated samples higher order clustering still exists compared to in blocky sulfonated polymers the appearance of a large cluster phase does not persist, indicating a diminished presence of the cluster phase. This is additionally supported by a large decrease in the contrast observed between these two sulfonation architectures, where for the same counter-ion there is a significant decrease in the contrast of this higher order peak in blocky sulfonated polymers, indicating a lower number density of these collections of multiplet structures compared to the randomly sulfonated counterpart.

Introduction
Ultra small angle x-ray scattering is fundamentally similar to small angle x-ray scattering with the exception of the size scale that is probed. Typically, SAXS measures sizes that are within the size range of 1 nm – 100 nm within typical laboratory systems, such as the Rigaku S-max system in the Moore research group. In order to obtain information about scattered x-rays at smaller angles the Bragg condition must be satisfied with a high degree of precision. The common techniques used to explore smaller angles using normal SAXS of adjusting the sample to detector distance or by using a beam with a smaller volume fails to improve the resolution sufficiently to observe these scattered x-rays. The most crucial condition to observing ultra-small angles in scattered x-rays is how well one can align the incident beam to exactly satisfy the Bragg condition of the (220) crystal reflection in highly silicon crystals with a very low degree of imperfections. Here we have used the Bonse-Hart camera apparatus, which allows the user to study size scales from 100 nm to several microns. Resolution of x-rays corresponding to this size scale will allow for us to study the behavior of collections of particles, in this case it has been used to study the clustering of ions, which has been observed to be in this research to occur between $q = 0.003$ Å$^{-1}$ and 0.03 Å$^{-1}$.

Previous work has been conducted by Li, Peiffer, and Chu concerning the ultra-small angle x-ray scattering behavior of sulfonated atactic polystyrene.$^1$ In their work they only observed a characteristic upturn in the x-ray scattering as can be seen in Figure VI-1, however there is no distinct peak that arises from the clustering of multiplets. This could be due to the fact that in this work they have used the divalent Zn$^{2+}$ counter ion, which may not induce clustering effects or may possess insufficient contrast compared to the surrounding matrix. In order to
approximate a cluster size Chu and coworkers used a fitting approach to attempt to assign a correlation length to these clusters using the Debye-Bueche model, which is defined as follows: \[ I(q) = \frac{I(0)}{(1 + q^2 \xi^2)^2} \]

, where \( \xi \) defines the correlation length of inhomogenities, and \( I(0) \) is the interpolated scattering at zero-angle in order to normalize the function. In their study they present several correlation lengths for each sample depending on which region of the curve was used for fitting. When using 0.004 nm\(^{-1} \) to 0.045 nm\(^{-1} \) they have calculated a correlation length of 130 nm, however when using 0.045 nm\(^{-1} \) to 0.12 nm\(^{-1} \) they have obtained a correlation length of 40 nm. Clearly this approach does not produce consistent results and is subject to significant user bias. It is suggested in the paper that using the former fitting range of 0.004 nm\(^{-1} \) to 0.045 nm\(^{-1} \) produces a more accurate interpretation of the correlation length, whereas using a range of q-values that are at higher angles produces artificially low estimations. Chu and coworkers have also analyzed this data using the relationship derived by Guinier, which describes particulate systems with a negligible particle-particle interference and can be used to obtain a spherical radius of gyration via the following relationship: \[ I(q) = I(0) \exp \left( -\frac{R_g^2 q^2}{3} \right) \]

, where \( R_g \) is the spherical radius of gyration of the inhomogeneity, and \( I(0) \) is the zero-angle scattering previously described for the Debye-Bueche equation. Using this analysis, they obtain similar results, when fitting from 0.004 nm\(^{-1} \) to 0.026 nm\(^{-1} \), \( R_g \) is estimated to be 120-160 nm. However, if the fit is performed from 0.055 to 0.12 nm\(^{-1} \) then \( R_g \) is estimated to be 25-28 nm. This
clearly presents a problem with user bias again in these systems, where the range used for fitting can dramatically affect the estimation of these clusters. In the current work that was done at the Advanced Photon Source in Argonne National Labs we have observed a clear peak that shows a significant amount of coherence in these clusters. This has allowed for a more reliable analysis of an appropriate size and distribution of these clusters.

Figure VI-1: Raw USAXS profiles measured at room temperature. The SaPS7.4Zn$^{2+}$ sample was compression-molded at 200 OC and fast cooled to room temperature (-3 min). Reprinted from the American Chemical Society. Copyright 1993 American Chemical Society.$^1$

It is additionally important to introduce an observation from their work concerning the lack of temperature dependence of the ultra-small angle scattering behavior. Overall the authors note that there was a small dependence on the intensity of the USAXS profiles depending on the temperature that these samples were measured at. However, there was no apparent differences in the slope of the upturn, which fundamentally dictates the correlation lengths that are
calculated using the Debye-Bueche and Guinier models. Thus, it appears as if the cluster morphology depends not on temperature, but rather on the chemical interactions in these systems. The data from this paper is shown in Figure VI-2, shows these atatic polystyrene ionomers measured at various temperatures. The authors propose that the invariance of the upturn with respect to temperature are due to the strong electrostatic crosslinks created by the multiplets, which are stable up to approximately 250°C. Even when these samples are measured at temperatures above the ion-rich phase glass transition temperature the scattering behavior remains unchanged, possibly due to the high melt viscosity of these systems. This could help explain the superior properties at high temperatures of these ionomers. A similar experiment is presented in this chapter, however, instead of comparing the samples measured at a given temperature we have performed these experiments by annealing the samples at various temperatures then measuring the scattering behavior in the USAXS region.
Figure VI-2: USAXS profiles of a SaPS7.4Zn\textsuperscript{2+} sample measured at different temperatures. Reprinted from the American Chemical Society. Copyright 1993 American Chemical Society.\textsuperscript{1}

Experimental

Materials

Syndiotactic polystyrene (Questra 102) having a weight average molecular weight (M\textsubscript{w}) of 310,000 g/mol was obtained from the Dow Chemical Company. Reagent grade 1,2,4-trichlorobenzene (TCB), methanol, sulfuric acid, and potassium monophthalate were obtained from Fisher Scientific. Hexanoic anhydride, benzyltrimethylammonium hydroxide, and benzoic acid were received from Sigma Aldrich.
**Preparation of Sulfonation Reagent**

A mild sulfonation reagent (hexanoyl sulfate) was prepared according to previously published procedures\(^4\) using TCB as the solvent. TCB was added to a volumetric flask containing 0.03 moles of hexanoic anhydride per mL of sulfuric acid. The TCB/hexanoic anhydride solution was cooled in an ice bath for 1 hour, and then 1-10 mL (depending on the target degree of sulfonation) of concentrated sulfuric acid was added to the chilled solution and shaken vigorously to allow for complex formation. Additional TCB was then added to the fill the remaining space in the volumetric flask.

**Random Sulfonation of Syndiotactic Polystyrene**

sPS was dissolved in TCB under reflux for 1.5 h to yield a 10% w/v solution. After 1.5 h, the solution was cooled to 70 °C and then additional TCB was added to yield a 1% w/v sPS solution. The sPS solution was allowed to equilibrate at 70 °C under a nitrogen purge for 1.5 hr. After equilibration, the appropriate amount of sulfonating reagent was added, and the reaction was allowed to proceed for 1 hour at 70 °C under a nitrogen purge. After 1 h, 10 mL methanol was added to the solution to terminate the reaction. The solution was poured into a large excess of methanol (c.a. 2 L) to precipitate the copolymer, followed by filtration and washing with deionized water. For the random copolymers containing higher than 5 mol% sulfonation, ethyl ether was used to precipitate the polymer instead, and water was used for the entire washing process in order to avoid dissolution of the polymer into methanol. The random SsPS precipitates were filtered and washed with deionized water repeatedly until all remaining traces of TCB, sulfonating reagent, and methanol were removed. The resulting polymer was dried under vacuum at 100 °C for 12 h.
Blocky Sulfonation of Syndiotactic Polystyrene

Syndiotactic polystyrene was dissolved in TCB under reflux for 1.5 h to yield a 10% w/v solution. After 1.5 h, the solution was cooled to room temperature. Upon cooling, the 10% w/v sPS solution was allowed to remain at room temperature for 24 hours. During this cooling process, the sPS solution crystallizes and forms a physical gel. The solid gel was manually broken in small, submillimeter-scale particles using a spatula. The sPS gel particles were diluted in additional TCB to yield a 1% w/v sPS suspension. The sPS gel-particle dispersion was allowed to equilibrate at 70 °C under a nitrogen purge for 1.5 hr. After equilibration, the appropriate amount of sulfonating reagent was added and the reaction was allowed to proceed for 1 hour at 70 °C under a nitrogen purge. No visible change in the solvent-suspended gel particles was observed during the course of the reaction. After 1 h, 10 mL methanol was added to the dispersion to terminate the reaction. The dispersion was poured into a large excess of methanol in order to precipitate the polymer. The SsPS particles were filtered and washed with deionized water repeatedly until all remaining traces of TCB, sulfonating reagent, and methanol were removed. The resulting polymer was dried under vacuum at 100 °C for 12 h.

Determination of Degree of Sulfonation

The randomly and blocky sulfonated SsPS copolymers were redissolved in 95/5 v/v TCB/methanol for 1.5 h to yield 0.5% w/v solution. These 0.5% w/v solutions were used to determine the degree of sulfonation via non-aqueous titration with methanolic benzyltrimethylammonium hydroxide. The benzyltrimethylammonium hydroxide was standardized using benzoic acid. SsPS ionomers of low sulfonic acid content and high ion content were prepared. Low sulfonic acid content SsPS containing 3.2 to 3.5 mol% sulfonate groups are
identified as SsPS3.5H*Random and SsPS3.2H*Blocky, where the H* denotes the copolymers are in the acid-form. The Random and Blocky nomenclature denotes homogeneous functionalization of SsPS in solution and functionalization of SsPS in the gel-state, respectively. High sulfonic acid content SsPS random and blocky copolymers were also prepared for this study containing 9.2 and 10.5 mol% sulfonate groups, respectively. These copolymers are identified as SsPS9.2H*Random and SsPS10.5H*Blocky.

Neutralization of SsPS

The SsPS Ionomers were neutralized using either NaOH, KOH, RbOH, or CsOH in order to create the SsPS ionomers. Solutions that were 0.05 M in methanol were created using either the NaOH pellets, KOH pellets, RbOH solutions in water, or a CsOH in water solution to create the Na+, K+, Rb+ or Cs+ neutralizing reagent, respectively. SsPS ionomers were dissolved in chloroform and a 1:1 molar ratio of the neutralizing reagent was added.

Morphological Characterization by Ultra Small Angle X-ray Scattering

Ultra small angle x-ray scattering (USAXS), small angle x-ray scattering (SAXS), and wide angle x-ray diffraction data (WAXD) were collected at Argonne National Laboratory beamline 9ID-C, using a photon energy of 24 keV [1]. Scattering profiles are plotted as absolute intensity versus q, where \( q = \left( \frac{4\pi}{\lambda} \right) \sin(\theta) \), \( \theta \) is one half of the scattering angle, and \( \lambda \) is the X-ray wavelength. USAXS measurements were performed using a Bonse-Hart camera. Small-angle x-ray scattering (SAXS) measurements were taken using the Pilatus 100k camera.\(^5\) Data reduction has been performed using the Irena\(^6\) and Nika,\(^7\) data reduction software provided by Argonne National Laboratory.
Sample Preparation for USAXS samples

In order to probe this a series of samples were prepared by annealing these samples in a DSC pan at a variety of temperatures. For the first part of this discussion samples were heated from room temperature at 20°C/min and annealed at 190°C for 1 hour to allow the samples to reach a kinetic equilibrium. The samples were then quenched at 80°C/min to room temperature. Samples have also been annealed at 190°C, 205°C, 220°C, and 235°C for 1 hour in order to study the effects of annealing temperature on the behavior of the ionic multiplets and the clustering of these aggregates.

Results and Discussion

Comparison of Random and Blocky SsPS Functionalization Percentage

In the first part of this study the effect of concentration has been studied. Of particular interest in to compare the randomly functionalized ionomer to establish the morphology features of both ionic multiplets and ionic clusters. Qualitatively from Figure VI-3 there are two prominent features to note. There are two major peaks that appear in these systems at approximately 0.11 Å⁻¹ and 0.005 Å⁻¹, which correspond to the interference peaks for multiplets and what are proposed to be here as the clusters respectively.

The multiplet peak in this case shows no obvious changes in the shape and position, however there is a significant change in the intensity of this peak. The intensity of this peak can either be related to the total number of ionic aggregates in these systems or the contrast in these systems. It is apparent that these two effects can not necessarily be distinguished in this case, although the most logical explanation is that the major contributing factor would be an increase
in the total number of aggregates formed, since there should be a higher number of aggregates formed in these systems with increasing concentration. Additionally, this is supported by the fact that if the number of multiplets remained the same in these systems, then it is necessary for many of the ionic functionalities to exist as free ion pairs in the amorphous matrix. If these ions are present in higher concentrations in the amorphous matrix, then this should actually lower the difference between the electron density multiplets and an ion-rich amorphous matrix. Thus, the only reasonable conclusion is that we must be forming a higher number of multiplets. The clustering peak shows an interesting trend, where with increasing concentration this peak appears to shift to higher q-values, indicating a smaller calculated Bragg spacing with increasing concentration. A more in depth quantitative analysis is shown in the next discussion to compare this. Qualitatively this peak shows some amount of structure, however it does not have possess any significant higher order scattering reflections. This lack of higher order “Bessel-like” reflections does not allow for the calculation of any structure between these clusters, however the use of a polydisperse form factor allows for the determination of an approximate size based on the position and shape of this peak.
Figure VI-3: USAXS data of SsPSCs*R at several different concentrations annealed at 190°C for 1 hour using the DSC conditions described in the experimental section.

For comparison blocky ionomers were also measured and show distinctly different behavior with both the ionic multiplet peaks and the clustering behavior. If the multiplet peaks are qualitatively described it can be seen that the peak increases in intensity, indicating again that a higher number of multiplets are formed by the same logic used when discussing the randomly functionalized counterpart. However, the appearance of these peaks is strikingly different than the randomly functionalized counterpart when comparing the trends with peak position, where in the blocky functionalized ionomers the peak position shifts to higher q-values, indicating larger multiplets that are spaced closer together. SsPS10.5Cs*B shows a different multiplet peak scattering, further analysis of this is shown later, but the general conclusion from
this peak is that the multiplets in blocky systems may adopt an asymmetric geometry, in contrast to the all other analyzed samples at lower concentrations, which appears to be described extremely well by liquid-like hard spheres.

When considering the geometry of the ionic clusters that were extremely apparent in the case of the random ionomer, there is a significant difference in the blocky functionalized polymers. The cluster peak in fact appears to only be present for ion contents of 3 mol% of lower. If the ion content is increased to higher levels the cluster peak is missing entirely. Even when considering the 3 mol% functionalized blocky polymer the cluster peak appears at a larger q-value than even the highest concentration randomly functionalized sample measured. This indicates that even for low ion contents that the blocky ionomers form significantly smaller clusters. This effect can be seen in Figure IV-4, where a peak can be seen in the sample SsPS3.2Cs*B at \( q = 0.03 \text{ Å}^{-1} \). In order to explore this further a distribution of dilute spheres has been used to model these peaks in the next section in comparison to the randomly functionalized counterpart.
Figure VI-4: USAXS data of SsPSCs+B at several different concentrations.

The Cluster Size of Randomly Functionalized SsPS

In order to make quantitative comparisons between the randomly functionalized ionomers a several models can be used, however in the absence of any supporting information concerning the cluster shape it seems most appropriate to use a model with a high degree of symmetry. In this case a set of dilute spheres has been used with a lognormal distribution in sizes. While it is possible to model these curves using a number of different asymmetric form factors,
such as cylinders, ellipsoids, finite lamellae, or any other form factor it may prove artificial to attempt to distinguish between these shapes without corroborating data that shows that these clusters adopt a non-spherical shape. Shown below in Figure VI-5 (a), is a highlight of the concentration series of SsPSCs+R ionomers that has been shown previously. As was noted earlier the scattering peak near 0.002 Å⁻¹ shifts to higher q with increasing ion content. Quantitatively this can be seen in Figure VI-5 (b) where the size of these clusters has been modeled according to the distribution function. There are two primary features that are incorporated into the size distribution analysis, a mean size and the lognormal standard deviation. The mean size shows where the most probable cluster size will be, and the standard deviation gives a relative gauge on the polydispersity of these cluster sizes, however, this standard deviation corresponds to the breadth of a logarithmic distribution instead of the more commonly used Gaussian distribution that uses the full-width half max approach.

As can be seen in Table VI-1, the mean cluster radius decreases from 38 nm to 19.7 nm when increasing the ion content from 3.2 mol% to 9.2 mol %, while the standard deviation only appears to increases significantly for the 9.2 mol% sample. No information about the structure factor of these clusters can be obtained with high certainty, as this data can only be accurately assessed in this model when there is either sharper peaks or secondary reflections. However, the fact that clusters become much smaller with increasing ionic content, while the contrast appears to remain similar leads to the conclusion that these clusters are most likely becoming both smaller and closer together. A pictorial representation of the change in the cluster structure of randomly functionalized ionomers is shown in Figure VI-6 However, the conclusion cannot be directly confirmed through this data without other supporting evidence and the techniques for
measuring this cluster size is previously not described in the literature with the exception of the work done by Chu and coworkers using the Debye-Bueche model, which does not provide a direct comparison to the work shown here. This phenomenon could potentially be explored in future work, however at this time orthogonal analytical methods to describe these cluster sizes to compliment the data determined by light scattering must be developed.

**Figure VI-5:** (a) USAXS data of a concentration series of SsPSCs^R. (b) Size distribution analysis of the cluster morphology using a lognormal distribution of dilute spheres.
Table VI-1: Calculated parameters using a polydisperse set of dilute spheres for the “cluster peak observed in randomly functionalized samples.

<table>
<thead>
<tr>
<th>Concentration of Ionic Groups</th>
<th>3.5%</th>
<th>6.5%</th>
<th>9.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{\text{mean}}$ (Å)</td>
<td>380.0</td>
<td>328.8</td>
<td>197.3</td>
</tr>
<tr>
<td>Std. Dev. (Å)</td>
<td>0.40</td>
<td>0.38</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Table VI-2: Calculated parameters using the Kinning and Thomas Hard-Sphere model to model the multiplets.

<table>
<thead>
<tr>
<th></th>
<th>$R_1$ (nm)</th>
<th>$R_{ca}$ (nm)</th>
<th>$V_p$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SsPS3.5Cs*R</td>
<td>0.81</td>
<td>1.43</td>
<td>93.9</td>
</tr>
<tr>
<td>SsPS6.5Cs*R</td>
<td>1.03</td>
<td>1.70</td>
<td>97.9</td>
</tr>
<tr>
<td>SsPS9.2Cs*R</td>
<td>1.05</td>
<td>1.62</td>
<td>64.6</td>
</tr>
<tr>
<td>SsPS3.2Cs*B</td>
<td>1.01</td>
<td>1.63</td>
<td>108.6</td>
</tr>
<tr>
<td>SsPS6.3Cs*B</td>
<td>1.48</td>
<td>2.04</td>
<td>1128.7</td>
</tr>
</tbody>
</table>

Figure VI-6: Pictorial representation of the cluster morphology with changing ion content.

When considering the multiplet sizes of the randomly functionalized ionomers the size of the spherical aggregate appears to increase slightly from 3 mol% to 6 mol% and then remains constant, additionally the shell size of these aggregates increases as well, maintaining a shell that is approximately 0.6 nm larger than the corresponding core. It is also important to note that the
aggregates appear to become closer together when the ionomer goes from an ion content of 6.5 mol% to 10.5 mol%, which indicates that while the aggregates remain a similar size, they begin to get closer together with increasing ion content. The blocky ionomers however have a much more profound effect on the ionomer architecture in terms of the size and shape of these multiplets. For the SsPS3.2Cs*B sample it is apparent that there is most likely a very low intensity reflection present, which gives an aggregate size similar to that seen in the randomly functionalized samples. However, it is important to note that with increasing ion content from 3.2 mol% to 6.3 mol% causes this multiplet scattering peak appears to shift to lower q-values, which arises due to multiplets that are larger in size, yet are farther apart. An interesting feature to note in this case is the drastically different peak shape present in the 10.5 mol% ionomer. The shape of this cannot be modeled satisfactorily using the same liquid-like hard sphere model used for all other ionomers. A discussion of the possible geometry of these multiplets is provided next.

**Scattering of SsPS10.5Cs*B**

Several different models were attempted in order to describe the morphological arrangement of ionic multiplets in high ion content blocky ionomers. In order to make a proper comparison to the previous fits that were performed that first model that was attempted was again the liquid-like hard sphere model. As can be seen below in **Figure IV-7**, this model fails to address most of the important features in this curve. Firstly, it does not match the data at low q-values. It also fails to properly describe the position of the first and second peak in the data, while it tends to provide far too many second order reflections. Clearly this model is not adequate to describe these morphological features and an anisotropic model must be attempted.
Figure VI-7: Fit of the multiplet feature in SsPS10.5Cs*B using the Kinning and Thomas liquid-like hard sphere model (KT-model).

Table VI-3: Fit parameters extracted using the KT-model from Figure VI-7.

<table>
<thead>
<tr>
<th>Spherical Model</th>
<th>Parameter Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>2.74 nm</td>
</tr>
<tr>
<td>$R_{CA}$</td>
<td>2.01 nm</td>
</tr>
<tr>
<td>$V_P$</td>
<td>3358.4 nm$^3$</td>
</tr>
</tbody>
</table>

The next model and arguably the model that describes these systems the most accurately according to how well to the fit matches the data is where we use a cylinder as the form factor with a hard-sphere structure factor. This model describes a morphology where we have cylinders with a spherical shell surrounding it, with liquid-like ordering. While it is most likely that the ions do not adopt cylindrical shape, this may provide a very close approximation to the type anisotropy and aspect ratio of these multiplets. Although it is obvious the shell is slightly smaller
than the width of the cylinder, this is most likely an artifact of the fact that the shell would not be spherical. However, it is quite difficult to provide a shell with fixed orientations, as would be needed to provide a cylindrical shell or even an elliptical shell. However, the shell in this case is not meant to provide much physical interpretation like it gives for the Kinning and Thomas model, but rather to provide a reasonable restriction on the proximity of adjacent multiplets. The most important insight that this model appears to provide is the fact that anisotropic models describe this system well, especially those that have a larger dimension perpendicular to the axis of rotation as will be seen later with the comparison between the oblate spheroid and prolate spheroid. Additionally, it gives an approximate value of the average volume per particle for these multiplets.

Figure VI-8: Fit of the multiplet feature in SsPS10.5Cs*B using a cylindrical form factor with a liquid-like hard-sphere structure factor.
<table>
<thead>
<tr>
<th>Cylinder Model</th>
<th>Parameter Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius</td>
<td>2.52 nm</td>
</tr>
<tr>
<td>Length</td>
<td>0.90 nm</td>
</tr>
<tr>
<td>$R_{CA}$</td>
<td>2.45 nm</td>
</tr>
<tr>
<td>$V_P$</td>
<td>771.3 nm$^3$</td>
</tr>
</tbody>
</table>

The Oblate spheroid fit provides similar insight to the cylindrical model, it shows that we have one axis that is approximate 3.1 nm and the axis of rotation is 0.5 nm. While the aspect ratio here is significantly different compared to the cylindrical model, it does show that in order to properly model this curve using an ellipsoidal morphology that the data is best described when the size in the direction perpendicular to the axis of rotation is larger. The length in the direction of the axis of rotation is significantly smaller, much like was seen in the cylindrical model. Again, the radius of closest approach in this model is not physical, but provides a useful boundary for a minimum distance that adjacent multiplets must be separated by. Lastly, the volume per multiplet is 588.7 nm$^3$ is very close to the prediction provided using the liquid-like cylinders.
**Figure VI-9:** Fit of the multiplet feature in SsPS10.5Cs⁺B using a oblate spheroid form factor with a liquid-like hard-sphere structure factor.

**Table VI-5:** Fit parameters extracted using the model from Figure VI-9.

<table>
<thead>
<tr>
<th>Oblate Spheroid</th>
<th>Fit Parameter Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_1 )</td>
<td>3.10 nm</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>0.15</td>
</tr>
<tr>
<td>( R_{CA} )</td>
<td>2.51 nm</td>
</tr>
<tr>
<td>( V_P )</td>
<td>571.9 nm³</td>
</tr>
</tbody>
</table>

A final example is provided where the axis of rotation is much larger than the axis perpendicular to this axis. Shown below is an example of this fit. Much like the liquid-like hard sphere model it can be seen that the fit clearly inadequately describes nearly every feature in the data. Additionally, it can be seen that almost every value provided by this fit must be considered to be non-physical, since the radius of closest approach is significantly smaller than both axes,
and the center-to-center distance is far too small to allow for any separation between these ellipsoids. Clearly this model provides unrealistic results.

**Figure VI-10:** Fit of the multiplet feature in SsPS10.5Cs+Br using a prolate spheroid form factor with a liquid-like hard-sphere structure factor.

**Table VI-6:** Fit parameters extracted using the model from **Figure VI-10**.

<table>
<thead>
<tr>
<th>Prolate Spheroid</th>
<th>Parameter Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₁</td>
<td>1.86 nm</td>
</tr>
<tr>
<td>Aspect Ratio</td>
<td>3.17</td>
</tr>
<tr>
<td>R_CA</td>
<td>1.36 nm</td>
</tr>
<tr>
<td>Vₚ</td>
<td>33.0 nm³</td>
</tr>
</tbody>
</table>

The models used here provide a great deal of important information regarding the morphology of these aggregates in blocky systems when the ion content is increased to a high functionalization level (10 mol%). These aggregates are most likely anisotropic, where they adopt
a shape with smaller axis of rotation than the perpendicular axis, a pictorial representation of this shape is shown below in Figure VI-11. Additionally, the center-to-center distance is approximately 5 nm (based on the volume occupied per particle). While these models may only describe the approximate shape and dimensions of these multiplets, it is important to note that the cylinder model and oblate ellipsoidal model provide information that is reasonable.

Figure VI-11: Representation of the anisotropic multiplet, specifically the oblate spheroid model.

Further study of this particular system would be necessary in order to elucidate the structure of blocky ionomers with a high ion content (>10% sulfonation). It seems that using a hard-shell structure may provide valuable insight into these systems, however, a fundamental change to these models could be made. Instead of using an asymmetric shape with a spherical shell, a model could be specifically developed that includes an asymmetric hard-shell. This hard-shell should be incorporated to rotate in tandem with the inner core. Significant work would need to be done to develop and implement this model into the current analysis package that was provided by Argonne National Labs that was used to process the data.
Effect of Neutralization on Ionic Morphology

In order to further ascertain the different parameters that can effect both the multiplet structure of ionic aggregates and the clustering of these multiplets the effect of different counter ions have been investigated. Two different ion contents are presented in the Na\(^+\) and Cs\(^+\) SsPS salt to understand if these different counter-ions have any effect on the morphology of the ion-rich phases in these copolymers. By using both Na\(^+\) and Cs\(^+\) monovalent counter-ions the morphology is compared in environments that contain strong electrostatic interaction and weak electrostatic interactions for Na\(^+\) and Cs\(^+\), respectively.

Ionomers functionalized with 2 mol% seem to show very little difference in either the blocky or randomly functionalized copolymers. If we consider the ionic multiplets themselves there appears to be a difference in the intensity of these aggregates, where the Cs\(^+\) counter-ion provides a higher amount of contrast between the aggregates and the surrounding ion deficient amorphous matrix. In fact, in the SsPS2.4Na\(^+\)R ionomers the multiplet peak is nearly invisible due to a low contrast with the amorphous matrix. This potentially provides a method to screen the ability to resolve ionic aggregates in these systems, allowing for one to determine the effects of the crystalline morphology independent of effects from ionic scattering. If the scattering due to clusters is compared it is apparent that the randomly functionalized ionomers appear at different q-values, where SsPS2.4Na\(^+\)R has a smaller cluster radius, however the physical rationale for the smaller cluster radius is not proposed here and would require further study. The clusters for the blocky SsPS appear to be fundamentally similar. While qualitatively the slope seems to be slightly different, it is not clear if these effects are an artifact of the data processing (background subtraction and intensity calibration) or if these effects are due to a different morphology.
However, it is seen in the scattering data that the interference peak is at almost the same position for both SsPS2.1Na+B and SsPS2.4Cs+B. In order to see if these counter-ion dependent morphological changes are consistent higher ion-content ionomers have also been analyzed.

![Graph showing scattering behavior of SsPS with differing counter-ions at low functionalization percent.](image)

**Figure VI-12**: Comparison of the different scattering behavior of SsPS with differing counter-ions at low functionalization percent.

Qualitatively the high ion-content appear to have almost the same morphological features, regardless of whether the Na⁺ or Cs⁺ salt forms are considered, which are shown in **Figure VI-12**. If the multiplet structures are compared both the random and blocky functionalized ionomers have the same peak position, shape, and intensity. The type of counter-ion does not appear to have as profound of an effect on any feature of these curves when considering high ion-content SsPS, especially in respect to the intensity, compared to the low ion-content ionomers seen in **Figure VI-12**. Comparing the cluster morphology is only relevant when
considering the randomly functionalized polymers, as there does not appear to be any evidence that large clusters exist in the blocky copolymers at 10.5 mol% sulfonate groups, however this does appear to indicate that clusters do not appear to be resolved in scattering experiments when the electron density contrast is changed in these systems. When comparing the randomly functionalized ionomers, it can be seen in Figure VI-13 that SsPS9.2Na'R does not have an interference peak corresponding to clusters, whereas, SsPS9.2Cs'R has a very clear peak that be used to identify geometric features of these clusters such as the size. There are two possible explanations for why there is a difference in the appearance of these peaks in the Cs'-form and does not appear in the Na' form. The first and most plausible explanation is that the increase in ionic strength may cause these clusters to decrease in size, which is observed in the SsPS3.5Cs'R samples, where the peak shifts to higher q-values, indicating a smaller cluster domain for the SsPS3.5Na'R sample. If we consider this explanation for the SsPS9.2Cs'R and SsPS9.2Na'R samples we may approach the same situation that was seen with the cluster dependence for the SsPSCs'B concentration series, where the cluster appears to become smaller and then eventually creates a nearly homogeneous distribution of ions at increasing concentration. If using the Na' counter ion decreases the cluster size of the already small cluster seen in the SsPS9.2Cs'R sample, then it is plausible that the cluster becomes so small in this case that the distribution of ions has become homogeneous. Another possible explanation for the lack of a cluster peak in the high ion content samples is that if these ions are distributed amongst this system, that the contrast may be very low for the Na' counter ion compared to the Cs' counter ion, due to the fact that Na' has a much lower charge density. However, this is less likely, due to the fact that the multiplet peaks appear to have a very similar intensity. While there is obviously some change in contrast effect ed
by exchanging counter ions, it is not readily apparent that this would change drastically on large size scales, thus it is most plausible that the use of the Na\(^+\) counter ion is actually shifting these clusters to smaller dimensions and at very high ion contents the cluster is so small that it becomes a homogeneous matrix.

![Graph](image)

**Figure VI-13:** Comparison of the different scattering behavior of SsPS with differing counter-ions at high functionalization percent.

**Effect of Annealing Temperature on Ionic Structure**

The last parameter that was analyzed at during these USAXS studies was the possibility of temperature effects on the ionic morphology in these ionomer systems. In order to compare these annealing effects samples have been melted and then isothermally annealed at the indicated temperature for 1 hour. Two temperature, 205\(^\circ\)C and 235\(^\circ\)C, have been chosen to compare any effect on the both the multiplet and cluster morphology. Additionally, any effect
on the morphological features have been compared at a low ion content of 3 mol% and a high
ion content of 10 mol%. Qualitatively there are not any large differences between samples
prepared at different annealing temperature for both random and blocky samples, where the
peak positions, intensity, and shape are all fundamentally similar at both low and high ion
content. This leads to conclusion that annealing at a given temperature has almost no effect on
the arrangement of ions in these systems, and any small observed differences in these data sets
appear only when considering the crystalline reflections in the 3 mol% ionomers. This also
supports the fact the annealing temperature appears to have very little influence on the
morphological ordering of the ion-rich phase. This confirms the conclusions made previously by
Chu and coworkers, who also observed little effect on the morphology of clusters in their
USAXS study when considering randomly functionalized sulfonated polystyrene with Zinc as the
counter-ion.
**Figure VI-14:** USAXS data on the effect of annealing temperature on the morphology of SsPS3.5Na*R, SsPS3.5Cs*R, SsPS3.2Na*B, and SsPS3.2Cs*B.

**Figure VI-15:** USAXS data on the effect of annealing temperature on the morphology of SsPS9.2Na*R, SsPS9.2Cs*R, SsPS10.5Na*B, and SsPS10.5Cs*B.
Conclusion

Random and Blocky functionalized ionomers have been compared using SAXS and USAXS to describe the morphology of the ion-rich multiplet and cluster structures. Several different parameters have been compared to assess their effect on both the morphology of ionic multiplets and ionic clusters. When comparing the effects of concentration, it was found that in randomly functionalized copolymers clusters are seen to become much smaller with increasing ion content. In blocky copolymers it has been found that the clusters are much smaller than the randomly functionalized counterpart and then appear to become homogeneous when the ion content is increased above 3 mol%. The effect of concentration on multiplets is also remarkably different in the random and blocky functionalized ionomers, where the multiplet size and distribution is not effected by ion content, but in blocky functionalized copolymers the multiplets change in size, shape, and average volume occupied by a given multiplets. In fact, in these blocky systems the multiplets may likely adopt an asymmetric shape when the ion content is increased to 10 mol%. Counter ions have been determined to not significantly affect either the multiplet of cluster morphology, however the type of counter ion used can significantly affect the contrast of both multiplets and the cluster phase, where the Na⁺ functionalized ionomers appear to have a much lower contrast with the amorphous matrix compared to Cs⁺ functionalized ionomers. Lastly, the effects of annealing temperature have also been compared, which indicates that annealing temperatures have virtually no effect on the ionic morphology. This allows for the crystalline morphology and polymorphic composition of these samples to be altered independent of the ionic morphology. The lack of change in the ionic morphology appears to primarily be controlled by the architecture of these polymers and the total ion content. Blocky
and random systems bear a vastly different ionic morphology, however these morphologies can be tuned based on the ion content, type of ion used, and sequencing of ions, allowing for customizable morphological features in these systems. Future studies could focus on the blending of these systems in order to provide even more control over the ionic structure in these systems for use in high-performance ion-transport applications.
References


Chapter VII:
Peak Broadening Analysis to Determine Crystallite Dimensions in Polymorphic Syndiotactic Polystyrene

Abstract

Peak broadening analysis was performed on several samples in order assess the determination of crystallite sizes in samples with mixed polymorphic compositions in the sPS homopolymer, R-SsPS, and B-SsPS. This analysis was carried out using two different methods including the Scherrer method and the Williamson-Hall method, which attempt to assess the size in both cases and in the case of the Williamson-Hall method incorporates a strain component. The Scherrer method in this case was found to produce more reliable results based on the consistency of results determined by error analysis. The Williamson-Hall method based on analysis of the fitting error produced unreliable results when considering both the size and strain. Additionally, it was found that the low angle peaks provided inconsistent results when compared to other reflections (even those in the same crystallographic plane). This has established the Scherrer method to be adequate in determining crystallite sizes in these systems, even in the presence of multiple polymorphs with poorly resolved peaks. This analysis shows that these systems depending on the conditions used to crystallize these samples have sizes in the range of 35 nm – 70 nm, this could potentially be used to study the effects of various different thermal processing conditions in order to impart higher mechanical and thermal stability in these systems.
Introduction

In order to determine the parameters associated with the crystallite size, which includes the average value and standard deviation of crystal sizes the width of peaks in wide-angle x-ray scattering data can be analyzed. There are two approaches that are presented here to determine a crystallite size, which is likely in this case to be the of several lamellae stacked linearly. The first and most common approach is to use an analysis method called the Scherrer equation. This type of analysis treats the broadening of peaks in the wide angle x-ray scattering spectrum as an effect that is created strictly by the size of crystallites. The second approach that has been used here is called with Williamson-Hall method, which expands upon the Sherrer equation by including a component from dislocations within the crystal structure, which will cause stacking defects and ultimately cause a signal that is not as well refined. The theoretical basis for these two types of analysis are presented below.

First the Scherrer equation is described here as a basis for both analyzes. The Scherrer equation was defined by Paul Sherrer as follows1-7:

$$ L = \frac{K \lambda}{\beta \cos \theta} $$

where L is the length of the crystallite, K is a dimensionless constant which has a value that is ~0.9 for spherical crystals (but depends on the shape of the crystallite), λ is the wavelength of x-ray used, and β is the full width half max (FWHM) of a crystalline reflection, and θ is the scattering angle that the reflection is centered upon. β in this case is defined in terms of radians for the purposes of this calculation. In order to correct for instrumental effects, the line broadening that is associated with the measurement must be subtracted. This effect is caused by several
contributions including the shape of the x-ray beam, broadening of the beam as it travels through space, imperfections in pinholes used to columnate the beam, as well as any other potential effects from the detector. The instrumental broadening can be measured by using a material that forms crystals of sufficient size (several microns), as well as, has been prepared in a way that the sample with have very little strain introduced into the crystal structure (lattice dislocations). In this case a line broadening standard purchased from NIST is used. Once the instrumental line broadening is measured it can fit using a Gaussian curve to determine the parameter $\beta_{\text{instrument}}$. In the case of using a Gaussian curve to fit both the peaks in the data to be analyzed and the standard used to remove the convolved signal from the instrumental broadening a sum of the squares of the two convolved signal components approximates the total peak width as follows$^7$:

$$\beta_{\text{total}}^2 = \beta_{\text{size}}^2 + \beta_{\text{instrument}}^2$$  \hspace{1cm} (2)

This equation can be rearranged to solve for the broadening due to the size of the crystal giving the follow equation:

$$\beta_{\text{size}} = \sqrt{\beta_{\text{total}}^2 - \beta_{\text{instrument}}^2}$$  \hspace{1cm} (3)

The peak width with the instrumental signal removed can now be used to calculate the size of the crystallite using equation (1).

Further expanding upon this approach the Williamson-Hall method introduces the concept of broadening that is due to strain in the lattice due to imperfections and distortions in crystal structure. The simplest form for calculating the strain is defined as follows$^7,8$:
\[ \varepsilon = \frac{\beta}{4 \tan \theta} \quad (4) \]

where \( \varepsilon \) is strain within the crystalline structure.

Next it is assumed that the contributions from size and strain are independent of each other and the observed line broadening can be treated as a summation of these two effects. This gives rise to the equation:

\[ \beta = \frac{K \lambda}{L \cos \theta} + 4 \varepsilon \tan \theta \quad (5) \]

This equation can be recast to provide a convenient form for plotting and determining the parameters \( L \) and \( \varepsilon \) by multiplying both sides of the equation by \( \cos \theta \) giving a new form to this equation:

\[ \beta \cos \theta = \frac{K \lambda}{L} + 4 \varepsilon \sin \theta \quad (6) \]

In order to extract parameters from this a plot can be constructed where the y-axis is \( \beta \cos \theta \) and the x-axis is \( \sin \theta \). An example of this plot is shown below in Figure VII-1. From this plot the y-intercept equals \( \frac{K \lambda}{L} \) and the slope equals \( 4 \varepsilon \).

**Experimental**

**Preparation of Wide-Angle X-ray Scattering Samples**
Samples have been prepared using a Carver melt press to make films that can be placed into a differential scanning calorimetry pan. A series of samples were prepared by annealing these samples in a DSC pan at a variety of temperatures. For the first part of this discussion samples were heated from room temperature at 20°C/min to above the melting temperature for 5 minutes and then annealed at different annealing temperatures for 1 hour to allow the samples to reach a kinetic equilibrium. The samples were then quenched at 80°C/min to room temperature. The melting temperature used and crystallization temperature are indicated in the results and discussion.

**Wide-Angle X-ray Diffraction Measurements**

WAXD experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting x-rays with a wavelength of 0.154 nm (Cu Kα). The sample-to-detector distance was 82.5 mm for WAXD and the q-range was calibrated using a silver behenate standard. WAXD 2D diffraction patterns were obtained using an image plate with an exposure time of 1 h. All WAXD data were analyzed using the SAXSGUI software package to obtain radically integrated WAXD intensity versus the scattering vector \( q \), where \( q = (4\pi/\lambda) \sin(\theta) \), \( \theta \) is one half of the scattering angle and \( \lambda \) is the x-ray wavelength. The instrumental line broadening has been determined using a LaB₆ line broadening standard purchased from NIST and using the reflection nearest to the data being analyzed.

**Data Processing and Fitting**
In order to process the data, the most recent version of Origin Pro 2020 SR1 version 9.7 has been used. A prepackaged peak finding and fitting method has been used and has been used with custom fitting options for both determining the background subtraction and the identification of peaks. For the background subtraction two different functions have been used based on which appropriately represents the background, in some cases a cubic spline interpolation has been used to connect points that were marked to be part of the background and in other cases these background points were fit using a 4th order polynomial. Peak finding is done manually based on the established positions of these crystallographic reflections. Further details about the procedure are provided in the results and discussion section. Peaks were identified based on several references that have analyzed both the α and β polymorphs.9-14

Results and Discussion

Samples have been analyzed using both the Scherrer method and the Williamson-Hall method to calculate the size of crystallites and in the case of the Williamson-Hall method the average strain is measured. The goals of this analysis was to see if the crystallite sizes could be accurately determined when there are multiple crystal structures present, in this case the α and β polymorphs of syndiotactic polystyrene. Ultimately the “accuracy” of these measurements is assessed here based on the standard deviation obtained from doing a basic error analysis. For the Scherrer equation a standard deviation of sizes determined from each reflection, and in the case of the Williamson-Hall method Excel’s Linest function was used to obtain errors on the slope and intercept of the fit.
Figure VII-1: Example of raw data input for fitting. Note the data has been reduced to just consider scattering angles between 4° and 15° in order reduce the background complexity.

Figure VII-2: Example of the fit data using an interpolating function for the background and Gaussian peaks for the peaks.

First the fitting procedure used will be described here with examples to establish a method to establish a method for correcting these data sets for the background of the spectrum and ultimately determine the FWHM of the various reflections that are to be analyzed in this
discussion. Figures from the program used are shown above in Figures VII-1 and VII-2, which is a representative figure of the fits that have been done for all samples. In this case Gaussian peaks have been used because they appear to give a fit of sufficient quality to represent the peak breadth and position of the peak.

In the case of the Scherrer analysis, a simple average of the crystal sizes was taken, which is used because this version of the Scherrer equation assumes a spherically symmetric crystallite, thus all directions in the crystallite can be treated similarly. A standard deviation of these quantities was also computed, which helps show the variation between crystalline reflections. For all of the samples analyzed here crystallite sizes that were 35 nm and 80 nm were obtained with varying degrees of relative error. Clearly these crystallite sizes determined here are far too large to be a measurement of a single crystalline lamellae, which should be closer to 10-20 nm in length. Based on this it can be reasonably concluded that these numbers correspond to a stack of connected lamellae that are arranged in the same direction within the sample. For the samples that are unfunctionalized syndiotactic polystyrene the goal was to create control samples that were representative of a sample that contained mostly α-crystals, mostly β-crystals, and a sample that contained a mixture of the two polymorphs. The reason these samples were created was to ensure that the method of determining the peak breadth is consistent in a model system that does not include the presence of other phase separated structures.

Clearly in the case of this analysis the sizes appear to have a large relative standard deviation, but could provide a relative gauge to compare between samples, values for these fits have been tabulated in Table VII-1. To remedy this a higher resolution may be necessary, since in this case the peaks are relatively sharp the peaks are only comprised of 10-20 data points.
Additionally, the resolution between peaks is certainly limited in this system, which makes the variation in the fitting procedure less reliable. This can be seen especially in the determination of the (020) \( \beta \) reflection, which in all cases appears to be much larger than the other peaks associated with the \( \beta \) polymorph, even when compared to the (040) reflection in the same plane, which should produce similar results. In fact if this reflection were to be removed from the process the determination of a size for the \( \beta \) polymorph would actually produce results with very little variability. In the case of the \( \alpha \) polymorph the standard deviation appears to have a similar problem, where the (110) reflection appears to be much larger than the other two reflections and can similarly be compared to the (220) reflection, which is in the same plane. This could also be an artifact of poor resolution between peaks, since the (020) \( \beta \)-reflection and the (110) \( \alpha \)-reflection have significant overlap in the data set. However, the fit actually appears to be quite good for both of these peaks, and currently there is little explain why both of these peaks would be artificially less broad unless this is an artifact of the measurement. Broadening at very low angles due to the instrument was not able to be assessed at this point because the line broadening standard does not contain any peaks that are near these two peaks. However, it is feasible to use samples that would produce sharp scattering peaks in this region that would be suitable for analysis of these low-angle WAXD peaks. One possibility with this is that the expectation is that the instrumental broadening at low angles should actually become larger, which should produce artificially large crystallite dimensions, however this has not been confirmed with a different line broadening standard. Clearly for these peaks to be suitable further analysis should be done.
Table VII-1: Tabulated results of crystallite sizes derived by using the Scherrer equation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt Temperature (°C)</th>
<th>Crystallization Temperature (°C)</th>
<th>Polymorph</th>
<th>Crystal Reflection</th>
<th>Crystal Size (nm)</th>
<th>Average Crystal Size (nm)</th>
<th>σ (nm)</th>
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</thead>
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<td>sPS</td>
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<td></td>
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<td>35.2</td>
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<td></td>
<td></td>
<td>(040)</td>
<td>55.1</td>
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<td>(130)</td>
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<td>SsPS3.2H'R</td>
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<td>235</td>
<td>α</td>
<td>(110)</td>
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<td>59.1</td>
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<td>(040)</td>
<td>48.5</td>
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<td></td>
<td>(130)</td>
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<td>β</td>
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<td>(040)</td>
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<td>(130)</td>
<td>51.7</td>
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</table>

As can be seen in Table VII-2 the standard deviation that is produced from determining the average crystallite size is greatly reduced when the low angle (110) α reflection and the (020) β reflection. Although this removes some of the data, it can be seen that the consistency of these reflections is much better than the original data set. It should be noted that the removal of these
reflections should be further justified in order discover the source of error introduced into these two peaks that have been removed. It is possible that there is some amount of error introduced in either the measurement itself, the fitting procedure used, or the choice of line broadening standard.

**Table VII-2:** Tabulated results of crystallite sizes derived by using the Scherrer equation with the low angle reflections removed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt Temperature (°C)</th>
<th>Crystallization Temperature (°C)</th>
<th>Polymorph</th>
<th>Crystal Reflection</th>
<th>Crystal Size</th>
<th>Average Crystal Size (nm)</th>
<th>σ (nm)</th>
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<td>sPS</td>
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<td>α</td>
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<td>41.0</td>
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<td></td>
<td>(220)</td>
<td>47.0</td>
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<td></td>
<td></td>
<td>β</td>
<td>(040)</td>
<td>35.4</td>
<td>35.2</td>
<td>0.2</td>
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<td>(130)</td>
<td>35.1</td>
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<td>sPS</td>
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<td>235</td>
<td>β</td>
<td>(110)</td>
<td>64.5</td>
<td>67.8</td>
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<td>SsPS3.2H*R</td>
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<td>51.7</td>
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</table>

The Williamson-Hall method proved to provide results that have high variation and results that appear to be unreasonable especially in the case of determining the size of the crystallites. There are several reasons why this analysis may have provided inadequate results. The first
reason could be that there are not enough crystalline reflections that can isolated and accurately fit in this particular polymer system. In the case of the α polymorph only three data points are able to be used for this analysis, one of which bears the same problem discussed in the previous section on the Scherrer analysis where the first peak appears to be artificially narrow. In the case of the β polymorph only four separate reflections are able to be used, which also provides a poor data set, even in the case of a linear fit. A second reason that the sizes determined using this analysis are quite far away from the y-intercept of the graph are clustered together. An example of this is shown below in Figure VII-3 and VII-4. This means that in order to determine the size the data must be extrapolated far from the origin of the x-axis, which will also exacerbate the error when determining this feature.

Table VII-3: Tabulated results using the Williamson-Hall analysis method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt Temperature (°C)</th>
<th>Crystallization Temperature (°C)</th>
<th>Polymorph</th>
<th>Average Crystal Size (nm)</th>
<th>σ (nm)</th>
<th>ε</th>
<th>Strain σ</th>
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<td>sPS</td>
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<td>0.0008</td>
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<td>β</td>
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In order to improve the analysis using the Williamson-Hall method several improvements could be made. Firstly, a higher resolution dataset could be obtained with the availability of high resolution powder diffraction instruments such as those available at beamline facilities. In fact, with higher resolution it may be the case that other crystalline reflections could be measured,
which would improve the number of data points that can be included in the data set. Another consideration would be to improve the determination of the widths of the low angle peaks that are present in the spectrum, which appears to be inconsistent with the higher angle peaks in the terms of the width. An additional improvement could be made by trying to separate the reflections by using strain to separate the peaks into different direction by aligning the crystal structures into separate directions. This type of sample preparation however would not necessarily representative of the unstrained sample, since this process of stretching the samples could alter both the size and almost certainly the measured strain component within the crystals. However, this could certainly be used to verify if the increased error is due to poor resolution between peaks or if there are other problems that reduce the quality of the results obtained. There also exist more sophisticated versions of the Williamson-Hall method that could more accurately model the types of strain in the crystal structure, however, without orthogonal techniques such as electron microscopy to verify the different types of crystalline defects that are present the choice of model becomes ambiguous.
Figure VII-3: Example for data used for fitting the α polymorph is sPS.

Figure VII-4: Example for data used for fitting the β polymorph is sPS.

In both of the versions of the Scherrer analysis it appears to show that the blocky form of SsPS has larger crystallites. The results provided by using Scherrer analysis will be used to tentatively draw conclusions about the difference between the randomly functionalized polymer versus the blocky functionalized polymer. For the blocky functionalized polymer, only the β crystallite is observed, which is consistent with previous results in Chapter IV where the relative amounts of the two polymorphs were characterized. This crystallite in the blocky system is notably larger in size than either of the polymorphs measured for the randomly functionalized system. The theory proposed based on previous results is that there are longer sections in the polymer where unfunctionalized material could crystallize, which could potentially allow larger
lamellar stacks to form uninterrupted. This would support the idea that the ionic groups have been segregated in the blocky system and are more homogeneously distributed in the random system. It should be noted that in order to make broader conclusions about the propensity of blocky systems to form larger crystallites that a more robust experiment that includes several percentages where both of the systems are able to crystallize well and could be prepared at a similar degree of crystallization. Additionally, an experiment could potentially be designed where there is a mixture of the two different polymorphs present in the blocky system, where the weight percentage of each polymorph would be similar.

Conclusion

An analysis was performed to find a suitable method to determine the crystallite size in sPS, B-SsPS, and R-SsPS. Two different methods were used in this case. The simplest version being the commonly used Scherrer method, which attributes the line broadening as a product of the size of a crystallite. A slightly more sophisticated version called the Williamson-Hall method considers an additional contribution from the strain within a crystal arising from dislocations within the crystal structure. Based on this analysis the Scherrer analysis provides a consistent method to analyze both polymorphs of syndiotactic polystyrene. However, the lowest angle reflections proved to provide a crystallite size that was inconsistent with the other reflections that were present in the system. In fact, removal of those reflections from the analysis greatly improved the standard deviation obtained for the size data. The size of these crystallites ranged from 35nm – 70 nm depending on the processing parameters used to prepare the samples.
the case of the sulfonated polymers, the blocky polymers were observed to produce larger crystal sizes than the randomly functionalized counterpart. However, further analysis could be done to prove that if a similar composition of polymorphs was produced in these two systems that this trend would still hold true. This method of analysis provides a base for a method to obtain consistent results in these systems that can be used for cross comparison. It should be noted that Scherrer analysis should fundamentally underestimate the crystallite size if there is an expectation that there is strain in the crystal structure.

The Williamson-Hall method in this case has proved to be inadequate to analyze crystal sizes and the strain in these systems. Several changes could potentially be made to improve the data that is used for analysis, including obtaining higher resolution data, which could potentially obtain a more accurate description of the peak widths and possibly elucidate previously unseen crystal reflections in these systems. The method of fitting could potentially have a large effect in these systems, however in this current analysis it is not suspected that the main deficiency in this analysis is due to the fitting procedure used. It is possible that this particular polymer system is not suitable for this type of analysis due to the small amount of crystalline reflections able to be resolved and the presence of peaks with significant overlap. Additionally, this analysis could be improved by using an orthogonal method such as electron microscopy that could help provide information on the type of strain that exists in the system and to help validate the sizes obtained from this analysis. Overall, Scherrer analysis using the sample preparation procedure and instrumentation described here provides a much more reliable method to determine crystal sizes that can be compared and help elucidate some of the properties of these materials.
References


Chapter VIII:
Conclusion and Future Work

Conclusion

In this dissertation the effects of gel-state functionalization has been assessed using syndiotactic polystyrene as a model system to study both the effects of this synthetic procedure on both the thermal behavior of these materials and the impact on the structuring of the ion-rich phase. In order to provide a protocol for creating advanced materials that are thermally and mechanically robust, that is also able to efficiently transport ions across a membrane it is desirable to create a material that contains both a high ion content, as well as, a high crystallinity. The high ion content will provide a dense network of charges, which will allow for the transportation of ions from one side of the membrane to the other. The crystalline network can impart both thermal stability when using these types of materials for applications that will function at high temperatures. In addition to thermal stability, this crystalline network can provide mechanical stability to materials, which is crucial to providing materials that can withstand harsh conditions that are encountered when using membranes, including the necessary pressures that will be exerted on the material.

The first section of this dissertation detailed that using gel-state sulfonation that the crystallization properties can be greatly improved by creating a blocky structure, which is created using a semi-crystalline organo-gel that will serve as a template for creating the blocky structure. It was seen that very little crystallization can occur when the polymer backbone is functionalized.
with as little as 3% by monomer of the sulfonic acid functionality. In contrast to this, when using a blocky architecture, it can be seen that the polymer can be crystallized when the polymer is functionalized up to 10% sulfonic acid groups. In addition to the improved ability to crystallize, the rate of crystallization and spherulitic growth is also greatly improved. Furthermore, the use of a blocky architecture created in this manner also increases the melting point, providing higher thermal stability even at high functionalization percentages. This leads to the conclusion that the architecture has been significantly altered using this procedure and more importantly that this architecture improves the crystallization behavior.

After establishing that the desired thermo-mechanical properties had been improved by using the gel-state functionalization procedure, it was of interest to look at how this blocky architecture affects the ion-rich phase morphology when comparing randomly functionalized polymers versus the blocky counterpart. There were two main features that were analyzed in order to assess the critical differences. On the small scale, the ionic multiplets were analyzed using several models, most importantly the liquid-like hard-sphere model. It was found that at low levels of incorporated ions that the morphology on this small scale was relatively similar for the randomly functionalized polymers and the blocky functionalized polymers, regardless of the counter-ion system used. However, when more ions were incorporated the multiplet structure became markedly different when considering the blocky functionalized polymer. Tentatively, the conclusions from this analysis was that the multiplets actually may become more crowded and adopt a larger shape at intermediate functionalization content and most likely adopts a different geometry when high ion content is considered (10% functionalization). The exact geometry that has been adopted at high functionalization percentages is unclear at this point, however, several
models have been used to attempt to approximate the shape of these models and it is likely that some type asymmetric multiplet is likely based on the goodness of fit when using these different scattering models. In fact, the cylindrical model and oblate spheroid proved to be good candidates, and logically the shape should be confined in 3-dimensions so an ellipsoidal geometry is likely a more physically relevant prediction.

On a larger scale to our research groups knowledge, this is the first instance that a potential candidate for the cluster network has been identified in the ultra-small angle x-ray scattering spectrum. Additionally, substantial differences were observed when considering randomly functionalized polymers versus the blocky functionalized polymers. Even at low functionalization percentages the blocky functionalized polymer appeared to have a smaller cluster network. When considering the random copolymer the cluster size appeared to decrease in size with increasing functionalization percentage. This observation shows that both the ion content has a profound impact on the morphology of clusters most likely due to a higher density of ions, which is consistent with the hypothesis that blocky functionalization provides a higher ion density, which could explain the smaller cluster size at low ion content. Another very interesting observation that can be seen in the blocky functionalized polymer is that the peak associated with the cluster network is absent at functionalization percentages above 6% sulfonation. This would support that the clusters become smaller and closer together at higher functionalization percentages and eventually can become a homogeneous network throughout the material. This effect is observed again when considering the blocky copolymer at 10% functionalization, where the scattering peak associated with the cluster network is absent and
there appears the be an additional effect from creating such a high localized ion density that forces the multiplet structure to adopt an anisotropic geometry.

Finally, in order to deconvolute the crystallite size contributions from different mixed polymorphic compositions in these systems an analysis was carried out using line broadening analysis of WAXD data. This analysis showed that the simplest method of performing these size estimates provided the most reliable characterization of the size of lamellar stacks. This method has been compared to both the Williamson-Hall method and the Warren-Averbach method (not presented in this dissertation) and was shown to produce superior results based on the statistical error of the analysis. Based on the Scherrer method crystallites were found to have a size between 35 nm and 70 nm in the processing conditions explored. This analysis has provided a method to characterize the two melt-processed polymorphs present in sPS and could potentially be extended to any polymeric system that contains multiple crystal structures.

**Future Work**

Future studies could be done on these materials to assess a wealth of different information. One of the most obvious things that could be studied is functionalization percentages that are even higher than 10%. This could be relevant both in the real world applications of this material type if it is used in an industrial or commercial application and would support the conclusions drawn here about the trends observed for the effects on the thermal behavior, mechanical behavior, and morphological structure.
Another future study could be done that could tie these observation and conclusions made about the ion network structure to the ion conductivity properties of these systems. This would allow a systemic comparison between random and blocky functionalized polymers in a well-studied system, that can be finely tuned in regards to molecular weight, crystallinity, ion content, and architecture. These studies would require making membranes that are representative of the conditions used for current ionic membrane technologies so that this could be benchmarked against other materials, as well as benchmarked against the random counterpart (at least in the case where the random counterpart can be formed into stable membranes).

Based on the gel-state functionalization procedure new polymer backbones could be used if these polymers are able to form an organo-gel or even a nanoporous aerogel. Currently, studies have been performed by the Moore research group to investigate Poly (ether ether ketone) sulfonated copolymers. This particular polymer could provide a material that is both mechanically and thermally robust, while providing the added benefit of being chemically resistant to degradation from the harsh conditions that these membranes would be subject to when being used in fuel cell applications. Additional polymer backbones could also be used that could even have different chain architectures (branched, telechletitic, star, bottle-brush, etc.). In fact, to commercialize this type of material another material would almost certainly need to be used to be competitive with “gold standard” materials such as Nafion®.

In addition to different polymer backbones, different functional groups that can attached to provide ionic functionality could be looked into. Currently in the Moore research group a bromination procedure has been developed that would allow for easier exchange of functional group, which could be used to make any ionomer system have a much higher performance. This
type of side-chain substitution has additionally been looked at using Nafion® derivatives and could certainly applied to any systems that could be functionalized in the gel-state if the chemistry is compatible and allows these types of chemical transformations to occur.

Further characterization of the crystallite size and strain structure could certainly provide new insight into the effect of the ionomer architecture on the crystallization properties of these materials. In this current study a method for analyzing different peaks has been established using both Scherrer analysis and the Williamson-Hall method. An additional method that could provide insight the Warren-Averbach method, which was attempted, but gave results that were not satisfactory for presentation here. Future studies could use high resolution powder diffraction techniques with samples that can be strained in various ways to give insight into the effects of ion incorporation on the growth of lamellar stacks.

Lastly, another future study could be performed to assess the mechanical properties of these materials This could be characterized in a variety of, but mostly in terms of using DMA or rheology if the solution state is of concern. This would allow for the determination of the impact of the architecture, ion-type, functional group type, and the ion content. The mechanical properties in these systems will be critical to implementing these materials into both commercial and industrial applications. Certainly there are many studies that can be branched off of both this research directly and the class of materials that can be created using this gel-state sulfonation procedure. In fact, there needs to be much more work done on the fundamental research to help understand the structure-morphology-property relationships, as well as, the development of novel advanced materials and their applications.
Chapter IX:
Collaborative Studies on Block Copolymer Systems

Imidazole-containing triblock copolymers with a synergy of ether and imidazolium sites

Authors: Chainika Jangu, Jing-Han Helen Wang, Dong Wang, Gregory Fahs, James R. Heflin, Robert B. Moore, Ralph H. Colby, and Timothy E. Long

Figure IX-1: Ionomeric A–BC–A triblock copolymer poly[Sty-b-(MVBIm-Tf₂N-co-DEGMEMAm)-b-Sty].

Reversible addition–fragmentation chain transfer (RAFT) polymerization enabled the synthesis of well-defined A–BC–A triblock copolymers containing a synergy of pendant ether and imidazolium sites. The soft central BC block comprises low \( T_g \) di(ethylene glycol) methyl ether methacrylate (DEGMEMAm) and 1-(4-vinylbenzyl) methyl imidazolium units. External polystyrene blocks provide mechanical reinforcement within a nanoscale morphology. In order to characterize the morphology of the triblock copolymers AFM and SAXS have been performed to provide complimentary morphological data.
SAXS experiments complemented AFM morphological findings and determined the presence of bulk microphase-separation (Figures IX-2 and IX-3). X-ray scattering data plotted as intensity, I(q), vs. the momentum transfer vector, q, confirmed microphase-separation in the A–BC–A triblock copolymers. For all three triblock copolymers, scattering maxima were observed, indicating the presence of microphase-separation in the A–BC–A triblock copolymer films. The triblock copolymers with 18 mol% ion content exhibited peak maxima at q*, 2q*, 3q* and 4q*, indicating a well-ordered, lamellar morphology. The triblock copolymer with 26 mol% ion content, second peak maxima was still observed, which diminishes at 36 mol% ion content, indicating phase mixing.

Figure IX-2: Atomic force microscopy (AFM) of ionomeric A–BC–A triblock copolymer poly[Sty-b-(MVBlm-Tf₂N-co-DEGMEMA)-b-Sty] going from (a) 18 mol% (b) 26 mol% (c) 36 mol% ion content. With an increase in VBIm composition in the central block, we observed a less ordered system, since the styrenic comonomer was presumably more compatible to polystyrene external blocks, inducing phase mixing. The SANS results agreed well with AFM images and DMA analysis of the triblock copolymer. Furthermore, there was no peak observed for ionic aggregation at q of 1.0–2.0 nm, indicating the A–BC–A triblock copolymer system behaving as single ion
conductors with superior ion-transport properties as opposed to a “channel-network morphology” in Nafion®.

Figure IX-3: Small angle X-ray scattering (SAXS) of ionomeric A–BC–A triblock copolymer poly[Sty-b-(MVBlm-Tf2N-co-DEGMEMA)-b-Sty] with various ion contents 18, 26 and 36 mol%.

Nucleobase-functionalized ABC triblock copolymers: self-assembly of supramolecular architectures²

Authors: Keren Zhang, Gregory B. Fahs, Motohiro Aiba, Robert B. Moore, and Timothy E. Long

RAFT polymerization has been used to synthesize poly(thymine acrylate-b-n-butyl acrylate-b-adenine acrylate) (poly(ThA-b-nBA-b-AdA)) ABC triblock copolymers with self-
complementary nucleobase-functionalized external blocks and a low-Tg soft central block. Figure IX-4 shows a chemical structure of the ABC triblock copolymers. ABC triblock copolymers self-assembled into well-defined lamellar microphase-separated morphologies for potential applications as thermoplastic elastomers. Complementary hydrogen bonding within the hard phase facilitated self-assembly and enhanced mechanical performance. SAXS has been run on these samples in order to determine the morphology of these ABC triblock copolymers.

**Figure IX-4:** Chemical structure of poly(ThA-b-nBA-b-AdA) ABC triblock copolymers.

Complementary hydrogen bonding within the hard phase contributed to a remarkably ordered microphase separated morphology of the ABC triblock copolymers. Small angle X-ray scattering (SAXS) was used to elucidate the microphase-separated bulk morphology of all three PTBA copolymers in **Figure IX-5**. The phaseseparated morphologies of asymmetric ABC
copolymers are usually more complex than symmetric ABA triblock and AB diblock copolymers. However, all three PTBA triblock copolymers showed distinctive lamellar scattering profiles. SAXS profiles of PTBA2 and PTBA3 both exhibit primary scattering peaks and four additional secondary peaks, indicating well-organized lamellar morphologies with long-range order. The distinctive scattering peaks for ABC triblock copolymers resulted from the complementary molecular recognition, which combined two chemically different blocks into a single, precisely-ordered hard phase. Consequently, self-assembly of an ABC triblock copolymer with complementary external blocks resembled the self-assembly behavior of a symmetric ABA triblock copolymer. However, in sharp contrast, PABA with 38 wt% nucleobase content (similar to PTBA2 with 35 wt%) showed a less-ordered cylindrical microphase-separated morphology with broader SAXS scattering peaks. These analogous ABA triblock copolymers will be discussed in more detail in a forthcoming publication on nucleobase-functionalized symmetric ABA triblock copolymers. The degree of polymerization (N) difference provided one possible explanation for the morphological difference according to the phase diagram, since the morphology varies as a function of N. However, the highly ordered phase separation of PTBA copolymers was still unique for an ABC or ABA triblock copolymer, considering the presence of the complementary hydrogen bonding between two dissimilar external blocks.
Figure IX-5: SAXS profiles of poly(ThA-b-nBA-b-AdA) triblock copolymers.

The domain spacing of the lamellae were 25.9 nm, 25.0 nm, and 23.4 nm for PABT3, 2, and 1, respectively. Increasing central block lengths resulted in an increased spacing between lamellae. The SAXS profile of PTBA1 (Figure IX-5) showed broader scattering peaks with fewer highly ordered peaks compared to the other two compositions, suggesting a broader distribution of lamellar thicknesses and/or interlamellar dimensions, and thus less ordered domains. Two hypotheses may account for the difference in self-assembled morphologies for PTBA triblock copolymers with various compositions. The less ordered phase separation of PTBA1 was possibly a consequence of a shorter central block. The central block length was insufficient to induce well-defined microphase separation. Secondly, the highly ordered lamellar packing possibly resulted from the fact that thymine: adenine molar ratios of PTBA2 and 3 were close to 2. In the second
hypothesis, each thymine functionalized block statistically paired with two adenine blocks, facilitating the aligning of alternating soft phase and hard phase lamellae. In the latter case, the phase separated morphology would not follow the general phase diagram of ABA triblock copolymers.\textsuperscript{4} Both inter-and intra-chain hydrogen bonding were presumably present according to the second hypothesis at a 2 : 1 thymine : adenine molar ratio. The inter-chain complexion also provided an explanation for enhanced mechanical performance compared to PABA and PTBT, resulting from increased apparent chain lengths. However, elucidation of inter-and intrachain hydrogen bonding in the solid state is challenging due to the complexity of polymer structure compared to low molar mass molecules. Preliminary atomic force microscopic (AFM) results did not reveal a well-defined surface morphology for copolymer films, differing from the observed lamellae bulk morphology in SAXS profiles. Tuning film casting conditions and applying transmission electron microscopy (TEM) will further elucidate the morphology of nucleobase-functionalized ABC triblock copolymers. Further investigations are underway to validate two hypotheses mentioned above and understand the details of self-assembly of ABC triblock copolymers with complementary external blocks.

Nucleobase-functionalized acrylic ABA triblock copolymers and supramolecular blends\textsuperscript{2}

Authors: Keren Zhang, Motohiro Aiba, Gregory B. Fahs, Amanda G. Hudson, William D. Chiang, Robert B. Moore, Mitsuru Ueda, and Timothy E. Long
An optimized, two-step, RAFT polymerization afforded ABA tri-block copolymers with either adenine acrylic (AdA) or thymine acrylic (ThA) external blocks and a PnBA central block, the chemical structure is shown in Figure IX-6. Poly(AdA-b-nBA-b-AdA) and poly(ThA-b-nBA-b-ThA) were melt pressed at 120 °C for 1 h and annealed at 120 °C in vacuo for 24 h. Morphological analysis of both the individual block copolymers and the blend have been performed using both atomic force microscopy (AFM) and small angle x-ray scattering (SAXS).

SAXS results were used to probe the bulk morphology of solution-cast poly(AdA-b-nBA-b-AdA), poly(ThA-b-nBA-b-ThA), and blends (Figure IX-7). The SAXS profile for each of the samples contains relatively broad scattering maxima with periodic intensity oscillations, indicative of a morphology with a distribution of characteristic dimensions (in agreement with the AFM data in Figure IX-8 a, b, and e). Poly(AdA-b-nBA-b-AdA) and the blend show periodic scattering maxima that roughly match the expected $q$, $\sqrt{3} q$, $\sqrt{4} q$, $\sqrt{7} q$, and $\sqrt{12} q$ peak positions that are characteristic of hexagonally packed cylinders, where $q$ is the position of the first maximum.
contrast, for poly(ThA-b-nBA-b-ThA), both Figure IX-7 and Figure IX-8b indicate a much less ordered morphology. The well-assembled cylindrical phase separation morphology of poly(AdA-b-nBA-b-AdA) and the blend was attributed to enhanced ordering originating from $\pi-\pi$ stacking and complementary hydrogen bonding, respectively. Purine rings of poly (AdA-b-nBA-b-AdA) were shown to afford a stronger $\pi-\pi$ interaction than pyrimidine rings in poly(ThA-b-nBA-b-ThA).\(^5\) However, the WAXD profile only shows a broad diffraction peak characteristic of interchain correlations (amorphous halo) of the PnBA block.\(^5\) The absence of a signature diffraction peak for $\pi-\pi$ stacking is presumably due to the small, nanometer-scale size of the packed AdA domains, as compared to much longer range order of packed AdA units in the homopolymers.\(^5,\)\(^6\) The d spacings were 60.4 nm, 63.4 nm, and 58.7 nm for poly(AdA-b-nBA-b-AdA), poly(ThA-b-nBA-b-ThA), and the blend, respectively. These d spacings were attributed to the inter-particle distance between the phase separated domains, which also corresponded well with inter-particle distances observed in AFM. All average spacings were close to 60 nm due to the similar volume fractions of the external and internal blocks for all three samples. Overall, noncovalent interactions within the hard phase facilitated the self-assembly of block copolymers at the equilibrium self-assembled morphology. The bulk morphology and surface morphology agreed well, and both demonstrated the positive effect of noncovalent interactions on block copolymer self-assembly.
Figure IX-7: SAXS of solution-cast nucleobase-functionalized triblock co-polymers and their blend. For clarity, data were vertically shifted by arbitrary factors.

Figure IX-8: Tapping mode AFM phase image of (a) solution-cast poly(AdA-b-nBA-b-AdA), (b) solution-cast poly(ThA-b-nBA-b-ThA), (c) melt-pressed poly(AdA-b-nBA-b-AdA), (d) melt-pressed poly(ThA-b-nBA-b-ThA), and (e) solution-cast supramolecular blend.
SAXS results also agreed with the trend in dynamic mechanical analysis of the solution-cast poly(AdA-b-nBA-b-AdA), poly(ThA-b-nBA-b-ThA), and the blend. Poly(ThA-b-nBA-b-ThA) exhibited the lowest order–disorder transition temperature due to the least ordered microphase-separation. **Figure IX-9** depicts the self-assembled morphology of the supramolecular blend. The complementary hydrogen bonding facilitated self-assembly of supramolecular block copolymer blends and enhanced the mechanical performance as a function of temperature. The thermal dissociation of hydrogen bonding led to a disruption of the physically cross-linked network in the hard phase, which resulted in a modulus drop. Overall, a synergy between the noncovalent interactions within the hard phase and the equilibrium, self-assembled morphology contributed to enhanced supramolecular polymer properties. Better phase separation led to more physical crosslinking within the hard phase and higher modulus when comparing solution-cast to melt-pressed samples. Stronger physical crosslinking within the hard phase facilitated self-assembly and reinforced the microphase-separated morphology when comparing solution-cast supramolecular blend with poly(AdA-b-nBA-b-AdA) and poly(ThA-b-nBA-b-ThA). However, noncovalent interactions decreased the rate of self-assembly in the melt.
Doubly-Charged Ionomers with Enhanced Microphase-Separation\textsuperscript{7}

Authors: Keren Zhang, Gregory B. Fahs, Kevin J. Drummey, Robert B. Moore, and Timothy E. Long*

Two styrenic DABCO salt monomers allowed the synthesis of DABCO salt-containing random copolymers with two quaternized nitrogen cations on each ionic pendant group. Triethyl-(4-vinylbenzyl) ammonium chloride (VBTEACl) containing random copolymers served as singly charged controls. DABCO salt-containing copolymers with 20 mol % or lower ionic contents exhibited microphase-separated morphologies, agreeing with the multiplet-cluster model for random ionomers. Morphological analysis of these copolymers has been performed using small angle x-ray scattering.
Small angle X-ray scattering (SAXS) elucidated the bulk morphology of DABCO salt containing copolymers in Figure IX-10 in comparison to the VBTEA analogues. SAXS experiments were conducted on the same solution-cast films for DMA experiments. SAXS profiles of DABCO salt-containing copolymers exhibited a relatively broad scattering maxima, indicative of a microphase-separated morphology with a distribution of characteristic dimensions, correlated to the interaggregate distances. To further elucidate the morphological features of the ionic domains, the SAXS curves were fit using a liquid-like hard sphere model according to Kinning and Thomas (Table IX-1), following a formulation for the SAXS modeling interference terms (structure factors) defined by Winey et al. These fits provided quantitative insight concerning the center-to-center distance between ionic domains and the size of aggregates. The liquid-like hard sphere model describes collections of aggregates with respect to three principle spatial parameters: the radius of the spherical aggregate ($R_1$), the radius of closest approach ($R_{ca}$), and the average center-to-center aggregate separation ($2R_{is}$). The fitting data in Table IX-1 provide reasonable explanations for the observable trends in Figures IX-11a and 11b. In Figure IX-11a, the q-value of the scattering maximum for VBD$_6$BrCl-containing copolymers increases as the ionic
content increases from 12 to 42 mol %. The fitting data for VBD$_6$BrCl containing copolymers suggested that both aggregate size $R_1$ and average interparticle separation $R_{1\sigma}$ decreased with increasing ion content, consistent with the observed scattering peak shift to higher $q$-value. Overall, poly(VBDC$_6$BrCl-co-nBA) copolymers tended to form a larger number of smaller aggregates that were closer together with higher ion content.

Poly(VBDC$_{14}$BrCl-co-nBA) exhibited a different trend with increasing ion content. In Figure IX-11b, the $q$-value of the scattering maximum for VBD$_{14}$BrCl-containing polymers remains near 1.9 nm$^{-1}$, independent of varying DABCO salt concentrations from 8 to 38 mol %, more commonly observed for random ionomers with relative high ionic contents.$^{11, 12}$ The constant $q$-value pertained to a nearly constant interaggregate dimension with varying ion content. However, the size of the aggregates ($R_1$) significantly increased, accommodating the increased ion content. SAXS profiles of VBDC$_{14}$ salt-containing copolymers exhibited sharper scattering peaks compared to VBDC$_6$ salt-containing copolymers, reflecting the effect of alkyl chain length on the formation of ionic aggregates. Longer alkyl chains likely enhanced mobility of ions and facilitated the formation of aggregates, leading to a narrower distribution of interaggregate spacing for poly(VBDC$_{14}$BrCl-co-nBA) compared to poly(VBDC$_6$BrCl-co-nBA).$^{13, 14}$
Figure IX-11: (a) SAXS of solution-cast poly(VBDC₆BrCl-co-nBA), poly(VBDC₆BF₄-co-nBA), and poly(VBDC₆Tf₂N-co-nBA); (b) SAXS of solution-cast poly(VBDC₁₄BrCl-co-nBA), poly(VBDC₁₄BF₄-co-nBA), and poly(VBDC₁₄Tf₂N-co-nBA). For clarity, data were shifted by arbitrary factors vertically.
**Figure IX-12:** Pictorial representation for aggregation of DABCO salt units, multiplets, and ionic domains of poly(VBDC₆BrCl-co-nBA) with halide counterions.

**Table IX-1:** Fitting Parameters from the Kinning and Thomas Model for SAXS Curves of DABCO Salt-Containing Copolymers with Various Counterions

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<th>Ionic monomer mol%</th>
<th>R₁ (nm)</th>
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<td>12 mol% poly(VBDC₆BrCl-co-nBA)</td>
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<td>20 mol% poly(VBDC₆BrCl-co-nBA)</td>
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<td>42 mol% poly(VBDC₆BrCl-co-nBA)</td>
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<td>20 mol% poly(VBDC₆BF₄-co-nBA)</td>
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<td>8 mol% poly(VBDC₁₄BrCl-co-nBA)</td>
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</tr>
<tr>
<td>20 mol% poly(VBDC₁₄BrCl-co-nBA)</td>
<td>0.92 ± 0.01</td>
<td>1.58 ± 0.01</td>
<td>2.19 ± 0.01</td>
</tr>
<tr>
<td>38 mol% poly(VBDC₁₄BrCl-co-nBA)</td>
<td>1.00 ± 0.01</td>
<td>1.60 ± 0.01</td>
<td>2.20 ± 0.01</td>
</tr>
<tr>
<td>20 mol% poly(VBDC₁₄BF₄-co-nBA)</td>
<td>0.79 ± 0.01</td>
<td>1.44 ± 0.01</td>
<td>2.10 ± 0.01</td>
</tr>
</tbody>
</table>

*₂R₁ represents the radius of the spherical aggregate, R₉A represents the radius of closest approach, and 2R₉S pertains to the average center-to-center aggregate separation.

The q-value at the scattering maximum for copolymer with 20 mol% DABCO salt increased with anions varying from Cl⁻, Br⁻ to BF₄⁻ to TF₂N⁻ in both parts a and b of Figure IX-11. This was due to size increase and charge density decrease of these associated counterions.

Table IX-1 indicates that the VBDC₆⁻ containing copolymer with halide counterions contained smaller aggregates with shorter interaggregate distance compared to the copolymer with BF₄⁻, consistent of the q-value change. A similar change existed for VBDC₁₄ containing copolymer, where the bulkier anion contributed to smaller aggregates with less spacing in-between. This phenomenon likely resulted from the dipole–dipole interaction diminishing with bulkier anions,
which led to the formation of smaller aggregates. The fitting for samples with TF₂N⁻ proved inaccurate due to poor agreement between the Kinning and Thomas model and the data.

**Figure IX-12** depicts the spatial arrangement of DABCO salt units in random copolymers over a range of length scales, agreeing with typical ionomer behavior. **Figure IX-11** describes (a) aggregation of ions driven by dipole–dipole (columbic) interactions, (b) spatial arrangement of multiplets, note some ion pairs not able to associate with a specific multiplet, (c) spatial heterogeneity of ionic domains (hard phase) containing a high density of ions and multiplets dispersed with neutral domains (soft phase). Within a typical aggregate, the number of DABCO salt units ranges from 10 to 60, calculated based on space filling of DABCO salt unit (assuming a volume per unit of \(6.23 \times 10^{-3} \text{ nm}^3\)) into an aggregate volume of \(V = \frac{4\pi R_1^3}{3}\). The DABCO salt unit was approximated as a sphere of diameter 0.559 nm, determined using the distance between two carbons adjacent to the two quaternary ammonium cations of the DABCO salt unit in the crystallography data of a dialkylated DABCO salt.

**Phosphonium containing diblocks copolymers from living anionic polymerization of 4-diphenylphosphino styrene**

Authors: Alison R. Schultz, Gregory B. Fahs, Chainika Jangu, Mingtao Chen, Robert B. Moore, and Timothy E. Long

Living anionic polymerization of 4-diphenylphosphino styrene (DPPS) achieved well-defined homopolymers, poly(DPPS-b-S) styrenic block copolymers, and poly(I-b-DPPS) diene-
based diblock copolymers. Poly(I-b-DPPS) diblock copolymer provided a balance of hard (DPPS, high $T_g = 120 \, ^\circ C$) and soft (I, low $T_g = 50 \, ^\circ C$) block sequences to fabricate a mechanically robust, free-standing film. Post-alkylation with bromohexane and bromododecane achieved phosphonium based derivatives (Figure IX-13), poly(I-bC6DPPS)+ Br and poly(I-b-C12DPPS)+ Br, and small angle X-ray scattering analysis (SAXS) was employed to reveal the microphase-separated bulk morphologies of the neutral and charged samples (Figure IX-14).

All SAXS measurements were performed at room temperature, and all films were slowly cast from toluene and annealed at 120 $^\circ$C under reduced pressure (5 mmHg) to facilitate phase separation of the blocks. The neutral poly(I-bDPPS) block copolymer sample exhibited an ordered scattering profile with peak maxima at $q^*$, $2q^*$, $3q^*$, and $4q^*$, indicating a lamellar morphology. Bragg’s law was used to approximate lamellar spacing from the primary scattering maximum at $q^*$, revealing a Bragg distance of 28 nm. The scattering profile for both poly(I-b-C6DPPS)$^+$ Br and poly(I-b-C12DPPS)$^+$ Br exhibit broader scattering maxima compared to the neutral copolymer, presumably due to the incorporated ion associations that prohibit sufficient thermal annealing in these samples. Scattering maxima are observed at $q^*$, $2q^*$, $3q^*$, $4q^*$ for poly(I-b-C6DPPS)$^+$ Br and $q^*$, $2q^*$ for poly(I-b-C12DPPS)$^+$ Br, suggesting a less ordered lamellar morphology for both samples compared to the neutral copolymer. The lamellar spacing for both poly(I-b-C6DPPS)$^+$ Br and poly(I-bC12DPPS)$^+$ Br is calculated to be 38 nm. Increasing the alkyl length also gave rise to a broad scattering peak at approximately $q = 2.1 \, \text{nm}^{-1}$, corresponding to the interdigitated packing of dodecyl chains on the phosphonium cation. A similar phenomenon was observed in earlier reports involving random copolymers containing trioctyl phosphonium styrenic ionic liquids.19
Figure IX-13: phosphonium containing diblock copolymers, poly(I-\text{-b-}C_6\text{DPPS})^+\text{Br}^- and poly(I-\text{-b-}C_{12}\text{DPPS})^+\text{Br}^-.

Figure IX-14: Small Angle X-Ray Scattering profiles reveal bulk morphologies for poly(I-\text{-b-DPPS}), poly(I-\text{-b-C}_6\text{DPPS})^+\text{Br}^-, and poly(I-\text{-b-C}_{12}\text{DPPS})^+\text{Br}^- diblock copolymers. The appearance of broad peak in poly(I-\text{-b-C}_{12}\text{DPPS})^+\text{Br}^- scattering profile corresponds to interdigitated bilayers.
Living anionic polymerization of 4-diphenylphosphino styrene for ABC triblock copolymers

Authors: Alison R Schultz, Mingtao Chen, Gregory B Fahs, Robert B Moore, and Timothy E Long

Living anionic polymerization of styrene, isoprene, and 4-diphenylphosphino styrene (DPPS) achieved unprecedented poly(S-b-I-b-DPPS) ABC triblock copolymers with predictable molecular weights and narrow polydispersities (chemical structure in Figure IX-15). AFM and SAXS were used as complementary techniques for characterizing the surface and bulk morphological features of the poly(S-b-I-b-DPPS) triblock copolymers. In a typical AFM phase image of a microphase-separated block copolymer, the hard domains appear as lighter regions and the soft phase appears as darker regions. Figure IX-16 shows the AFM tapping mode phase images for the triblock copolymers with 25 wt%, 50 wt% and 60 wt% polystyrenic external blocks, revealing tunable microphase-separated morphologies for each composition. SAXS experiments revealed the microphase-separated bulk morphologies of the ABC triblock copolymer samples as a complement to the AFM surface morphology analysis (Figure IX-17). Poly(S_{25k}-b-I_{50k}-b-DPPS_{25k}) exhibited an ordered scattering profile with peak maxima at q*, 2q*, 3q* and 4q*, which is indicative of one-dimensional packing symmetry corresponding to a lamellar morphology. Bragg's law was used to approximate lamellar spacing from the primary scattering maximum at q*, revealing a Bragg distance of 27 nm. The scattering profile for both poly(S_{50k}-b-I_{50k}-b-DPPS_{25k}) and poly(S_{20k}-b-I_{120k}-b-DPPS_{20k}) revealed significantly less ordered bulk morphologies with a lack of long range periodicity. Poly(S_{50k}-b-I_{50k}-b-DPPS_{25k}) exhibits peak maxima at q*, 2q* and 3q*, which could be indicative of a disordered lamellar morphology with a Bragg spacing of 29 nm. Based on the weak, broad SAXS scattering maxima, the morphological structure for
poly(S_{20}k-b-I_{120}k-b-DPPS_{20}k) is less clear. For this sample, it is reasonable to consider the two peaks present at 0.4 nm\(^{-1}\) and 0.7 nm\(^{-1}\) as the symmetry elements \(q^*\) and \(\sqrt{3}q^*\), indicative of either spherical domains or bicontinuous phase separation with close packed liquid-like ordering on the scale of approximately 17 nm. Earlier literature involving poly(S-b-I) and poly(I-b-DPPS) block copolymers reveal a similar morphology.\(^{18}\) The observation of phase separation from AFM and SAXS correlated well with observations in DMA experiments, which indicated a microphase-separated morphology for all compositions.

Figure IX-15: Phosphonium containing diblock copolymers, poly(I-b-C_{6}DPPS)\(^+\)Br\(^-\) and poly(I-b-C_{12}DPPS)\(^+\)Br\(^-\).
**Figure IX-16:** AFM images reveal surface morphologies for (A) poly(S\textsubscript{25k}-b-I\textsubscript{50k}-b-DPPS\textsubscript{25k}), (B) poly(S\textsubscript{50k}-b-I\textsubscript{50k}-b-DPPS\textsubscript{25k}) and (C) poly(S\textsubscript{20k}-b-I\textsubscript{120k}-b-DPPS\textsubscript{20k}).

**Figure IX-17:** SAXS profiles reveal oriented bulk morphologies for poly(S\textsubscript{25k}-b-I\textsubscript{50k}-b-DPPS\textsubscript{25k}), poly(S\textsubscript{50k}-b-I\textsubscript{50k}-b-DPPS\textsubscript{25k}) and poly(S\textsubscript{20k}-b-I\textsubscript{120k}-b-DPPS\textsubscript{20k}).

**Imidazolium-Containing ABA Triblock Copolymers as Electroactive Devices**\textsuperscript{21}
Authors: Evan Margaretta, Gregory B. Fahs, David L. Inglefield, Jr., Chainika Jangu, Dong Wang, James R. Heflin, Robert B. Moore, and Timothy E. Long

Two-step reversible addition–fragmentation chain transfer (RAFT) polymerization and two subsequent postpolymerization modification steps afforded well-defined ABA triblock copolymers featuring mechanically reinforcing polystyrene outer blocks and 1-methylimidazole-neutralized poly(acrylic acid)-based central blocks. The ionic liquid (IL) 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][OTf]) was incorporated at 30 wt % into polymeric films, Figure IX-18 shows the chemical structure of both the ABA triblock copolymer and ABA triblock copolymer with the ionic liquid incorporated. Atomic force microscopy, small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM) determined surface and bulk morphologies, and poly(Sty-b-AA(MeIm)-b-Sty) exhibited a change from packed cylindrical to lamellar morphology in SAXS upon IL incorporation.

![Figure IX-18: Chemical Structure of (a) Poly(styrene-b-(nBA-co-AA)-b-styrene) and (b) Subsequent Neutralization with 1-Methylimidazole](image)

AFM (Figure IX-19 a and b) revealed the surface morphologies of poly(Sty-b-AA(MeIm)-b-Sty) and poly(Sty-b-[nBA_{4%}-co-AA(MeIm)_{96%}]-b-Sty) in the absence of IL and confirmed the phase-separated nature of the materials suggested with DSC. Poly(Sty-b-AA(MeIm)-b-Sty) exhibits hexagonally packed cylinders on the surface of the membrane, and poly(Sty-b-[nBA_{4%}-co-}]}
AA(MeIm)$_{96\%}$-b-Sty) displays well-defined lamellar surface morphology. In particular, SAXS (Figure IX-19 c, Table IX-2) indicated the presence of an ordered morphology, consistent with packed cylinders rather than spheres in poly(Sty-b-AA(MeIm)-b-Sty), with broad scattering peaks at $q^*:\sqrt{3}:3$. The SAXS profile of poly(Sty-b-[nBA$_{4\%}$-co-AA(MeIm)$_{96\%}$]-b-Sty) illustrates the presence of reflections indicative of microphase separation, but in contrast with the AFM results (Figure IX-19 b) it does not conclusively reveal any long-range order in the bulk. Because central block molecular weights remained similar, nBA incorporation into the central block likely affected the Flory–Huggins interaction parameter $\chi$ sufficiently enough to induce significant change in morphology. However, the present investigation did not include determination of this parameter.

**Table IX-2: Summary of form factors from SAXS analysis**

<table>
<thead>
<tr>
<th>sample</th>
<th>scattering peaks</th>
<th>morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(Sty-b-AA(MeIm)-b-Sty)</td>
<td>$q^*, \sqrt{3}q, 3q$</td>
<td>cylindrical</td>
</tr>
<tr>
<td>with 30 wt % IL</td>
<td>$q^*, 3q, 5q$</td>
<td>lamellar</td>
</tr>
<tr>
<td>poly(Sty-b-[nBA$<em>{4%}$-co-AA(MeIm)$</em>{96%}$]-b-Sty)</td>
<td>$q^*$</td>
<td>ND</td>
</tr>
<tr>
<td>with 30 wt % IL</td>
<td>$q^*, \sqrt{3}q, \sqrt{8}q$</td>
<td>ND</td>
</tr>
</tbody>
</table>
Figure IX-19: AFM phase images of (a) poly(Sty-b-AA(Melm)-b-Sty) and (b) poly(Sty-b-[nBA4%-co-AA(Melm)96%]-b-Sty) reveal differences in surface morphologies, and (c) SAXS profiles indicate bulk morphologies similar to those observed in AFM.

SAXS also probed bulk morphology of IL-containing membranes (Figure IX-20), further confirming the phase separation indicated in DMA and DSC. Scattering peaks at ratios $q^*:3:5$ suggest lamellar morphology upon the incorporation of IL into poly(Sty-b-AA(Melm)-b-Sty) (Table IX-2). Microphase structure critically affects ionic conductivity of membranes, with films possessing lamellar morphology exhibiting higher ionic conductivity than those having hexagonally packed cylinders.22 When polymer samples approach 50:50 vol %, structure and form factors in the scattering may overlay and reduce peak intensity at even integral reflections.23, 24 The primary scattering peak position at 0.125 nm$^{-1}$ correlated to $d$-spacing of 50.3 nm. The change from packed cylinders to lamellae ostensibly resulted from varying both $\chi$
and volume fraction of the central block. Meanwhile, the SAXS profile for poly(Sty-b-[nBA4%-co-AA(Melm)96%]-b-Sty) cast with 30 wt % IL indicates microphase-separated bulk morphology with some degree of long-range order; however, the broad secondary scattering peaks of $q^* : v3 : v8$ do not directly correlate to geometries commonly observed for ABA triblock copolymers.

Figure IX-20: SAXS profiles of poly(Sty-b-AA(Melm)-b-Sty) (solid) and poly(Sty-b-[nBA4%-co-AA(Melm)96%]-b-Sty) (dotted) reveal microphase separation when cast with 30 wt % [EMIm][OTf] ionic liquid. Transmission electron micrographs of OsO4-stained poly(Sty-b-AA(Melm)-b-Sty) at (a) 7500× and (b) 96 000× magnification and (c) poly(Sty-b-[nBA4%-co-AA(Melm)96%]-b-Sty) at 96 000× magnification. All samples have 30 wt % [EMIm][OTf] incorporated.

TEM clearly revealed the bulk morphologies of poly(Sty-b-AA(Melm)-b-Sty) and poly(Sty-b-[nBA4%-co-AA(Melm)96%]-b-Sty), further confirming the SAXS data (Figure IX-20). The micrographs clearly showed the lamellar bulk morphology of poly(Sty-b-AA(Melm)-b-Sty). The images revealed interlamellar spacing of $51.15 \pm 4.79$ nm, which correlated well with the $d$-
spacing as determined using SAXS. **Figure IX-20 a** demonstrates the small grain size of the lamellar domains, which explains the broad nature of the peaks in the SAXS profiles. Increasing the magnification (**Figure IX-20 b**) better reveals the well-defined order of the lamellar domains. The small grain size may provide some explanation for the conductivity of the film. Balsara demonstrated the inverse correlation of lamellar domain grain size with ionic conductivity in block copolymer electrolyte samples.25

**High-Performance Segmented Liquid Crystalline Copolyesters**26

Authors: Ashley M. Nelson, Gregory B. Fahs, Robert B. Moore, and Timothy E. Long

![Chemical structure of poly(BB-HD)$_x$-ran-poly(BB-P10R5$_x$)$_y$ (BB$_6$P10R5$_y$ series).](image)

**Figure IX-21:** Chemical structure of poly(BB-HD)$_x$-ran-poly(BB-P10R5$_x$)$_y$ (BB$_6$P10R5$_y$ series).

All polymers were synthesized using a similar melt transesterification procedure.27,28 For the various compositions the charged weight percent SS ranged from 24% to 25%, 52% to 54%, and 64% to 66% referred to as 25, 50, and 60 wt% throughout. For example, in preparation of poly(BB-HD)$_{47}$-ran-poly(BB-P10R5$_{2k}$)$_{53}$, where the subscript corresponds to the weight percent of each segment charged and is further referred to as the 50 wt% SS (soft segment) composition, 4.16 g of BB (4,4′-biphenyldicarboxylate), 2.18 g of HD (methylene spacer for the hard segment), and 5.01 g of P10R5$_{2k}$ (Pluronic 10R5). The chemical structure is shown in **Figure IX-21**.
Small angle X-ray scattering (SAXS) was used to gain insight into the nanometer scale morphology of these polymers. Scattering maxima resulting from ordered domains allows for an estimation of characteristic dimensions using \( d = \frac{2\pi}{q} \) where \( d \) corresponds to the Bragg spacing and \( q \) is the scattering vector at the peak maximum. SAXS analysis was performed on compression molded films of the BB<sub>6</sub> homopolymer and BB<sub>6</sub>P10R5<sub>y</sub> series at 25 °C. The scattering profiles, depicted in Figure IX-22 exhibit a peak for each composition and diffuse scattering for the segmented copolyesters at lower \( q \) values. Table IX-3 contains the maximum \( q \) values for each peak and corresponding Bragg spacing. The calculated Bragg spacing values correlated well with previously reported BB<sub>6</sub> homopolymer lamellar spacing values of 225–294 Å.\textsuperscript{29} 30 The consistent spacing between BB<sub>6</sub> and BB6P10R5<sub>y</sub> series suggested the scattering peak corresponds to the hard segment and further confirmed the microphase-separated morphology of these segmented copolyesters.

WAXD probes the crystalline structure of materials on a smaller scale than SAXS and is capable of providing exact crystal lattices and polymer chain lengths.\textsuperscript{31} WAXD utilizes the Bragg equation, \( d = \frac{2\pi}{q} \), to determine crystal size and length scales. WAXD was performed on compression molded films of the BB<sub>6</sub>P10R5<sub>y</sub> series and the overlaid curves, shifted vertically for ease of comparison, are displayed in Figure IX-23. The lack of an amorphous halo for the BB<sub>6</sub> homopolymer (100 wt% HS) indicated a highly crystalline material, congruent with previous literature.\textsuperscript{32} 33 An amorphous halo appeared upon incorporation of the soft segment and increased with increasing flexible content. The segmented copolyesters maintained many peaks similar or identical to BB<sub>6</sub>, as visible in Figure IX-23. Interestingly, increasing the soft segment also introduced structure not observed in the homopolymer. These new peaks are attributed to soft
segment induced polymorphs and show a distinct difference from WAXD profiles. Takahashi and Nagata\textsuperscript{32} reported for BB\textsubscript{6}PTMO segmented copolyesters with varying wt\% soft segment.

**Table IX-3:** Scattering vector maxima and calculated Bragg spacing from the SAXS profiles of the BB\textsubscript{6}P10R5\textsubscript{y} series

<table>
<thead>
<tr>
<th>HS [wt%]</th>
<th>q [nm\textsuperscript{-1}]</th>
<th>d [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0.18</td>
<td>34</td>
</tr>
<tr>
<td>50</td>
<td>0.18</td>
<td>35</td>
</tr>
<tr>
<td>75</td>
<td>0.19</td>
<td>34</td>
</tr>
<tr>
<td>100</td>
<td>0.19</td>
<td>33</td>
</tr>
</tbody>
</table>

**Figure IX-22:** SAXS profiles for BB\textsubscript{6}P10R5\textsubscript{y} series (vertically shifted) which coupled with DSC further supports a microphase-separated morphology.
**Figure IX-23**: WAXD profiles of the BB₆P₁₀R₅ᵧ series highlighting the highly crystalline hard segment and appearance of polymorphs upon soft segment incorporation.

**Synthesis and Characterization of Polysulfone-Containing Poly(butylene terephthalate) Segmented Block Copolymers**

Authors: Joseph M. Dennis, Gregory B. Fahs, Robert B. Moore, S. Richard Turner, and Timothy E. Long*

**Figure IX-24**: Chemical structure of PSU–PBT Segmented Block Copolymers

A segmented block copolymer has been synthesized using melt transesterification polymerization (**Figure IX-24**). 1,4-Butanediol and dimethyl terephthalate afforded poly(butylene...
terephthalate) (PBT) segments upon chain extension of the polysulfone (PSU) oligomer. Small-angle X-ray scattering (SAXS) provides insight into the bulk morphology and reveals a phase ordering consistent with crystallinity.\textsuperscript{35, 36} Figure IX-25 compares the scattering profiles of quench-cooled films, where compositions of less than 40\% PSU exhibited a distinct Bragg’s reflection. The domain spacing determined from the peak maximum increases with increasing PSU. This observation complements an exclusion of the PSU to the edge of the growing lattice, leading to an increase in spacing between crystallized PBT. As a result, PSU acts as an impurity during crystallization and remains excluded from the crystal structure of PBT.

The thermal history of these polymer films significantly impacts their mechanical analyses due to restricted crystallization of the PBT segments. As such, the polymer films were annealed at 160 °C \textit{in vacuo} for 3 days. A temperature was chosen above the $T_g$ of the oligomeric PSU ($T_g = 147$ °C) to promote long-range segmental motion and was used consistently for all compositions. Figure IX-26 overlays the resulting scattering profiles for the polymer films. As expected from the DMA results, the annealed films show a single Bragg’s reflection at values similar to those observed in the nonannealed, semicrystalline copolymers. Furthermore, the nonannealed, semicrystalline copolymers showed a reduction in the domain spacing postannealing and approached the crystallite spacing of neat PBT (Table IX-4).
Figure IX-25: SAXS intensity plots of PSU–PBT segmented copolymers varying in polysulfone incorporation before annealing.

Figure IX-26: SAXS intensity plots of PSU–PBT segmented copolymers varying in polysulfone incorporation after annealing at 160 °C for 3 days.
Table IX-4: Domain spacing of PESu-PBT samples as synthesized and annealed.

<table>
<thead>
<tr>
<th>Polysulfone (wt%)</th>
<th>Domain Spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Charged Not Annealed</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
</tr>
<tr>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>40</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

Synthesis of Polysulfone-containing Poly(butylene terephthalate) Segmented Block Copolymers: Influence of segment length on thermomechanical performance

Authors: Joseph M. Dennis, Gregory B. Fahs, Nicholas G. Moon, Ryan J. Mondschein, Robert B. Moore, Garth L. Wilkes, and Timothy E. Long

A facile synthesis of hydroxyethyl-functionalized poly(ether sulfone) (PESu) oligomers permitted subsequent melt transesterification into segmented block copolymers with poly(butylene terephthalate) (PBT). In agreement with a relatively constant $T_m$ and phase separation observed with DSC and DMA, respectively, small-angle x-ray scattering identified a compositionally independent lamellar thickness, while the amorphous layer thickness increased with PESu incorporation. Figure IX-27 shows a chemical structure of the PBT-PESu segmented block copolymer.
Figure IX-27: Chemical structure of the PBT-PESu segmented block copolymer.

Samples for SAXS analysis were prepared by compression molding at 270 °C and annealed at 160 °C under vacuum for 24 h. Quenched samples were also prepared by compression molding at 300 °C and immediately cooled in a liquid nitrogen bath, resulting in optically clear films. SAXS profiles were analyzed using the linear correlation function via the following relationship in order to extract characteristic dimensions associated with the lamellar crystallites:

\[
\gamma(r) = \frac{\int_0^\infty l(q) \cos(qr)q^2 dq}{\int_0^\infty l(q)q^2 dq}
\]  

(1)

Although physically limited to a finite scattering angle, extrapolation to high and low-q regions using Porod and Guinier functions, respectively, enabled the application of Equation 1.

The real space dimension, r, provided the shift factor in the intensity spectrum via the cosine transform (Equation 1). The correlation between the shifted and unshifted spectra originated a solution \(\gamma(r = 0) = 1\), and behaved as a decaying oscillation about \(\gamma(r) = 0\) with increasing r for periodic systems (e.g. stacked lamella). Furthermore, a comparable model system for an “ideal” lamellar lattice, as described by Vonk, enabled extraction of the characteristic dimensions. In summary, a linear extrapolation of the initial decay to intersect with the tangent of the first minimum identified the minimum thickness for the minor phase (S) (e.g. crystallite thickness) in nanometers. The long period (\(L_p\)) is extractable as the first maxima away from \(r = 0\).
Using both the minimum crystallite thickness and the long period, the local crystallinity (\(L_c\)) is defined as follows:

\[
L_c = \frac{S}{L_p}
\]  
(2)

Small angle x-ray scattering (SAXS) explored nanoscale order of the novel segmented block copolymers. Figure IX-28 provides representative \(q\) scattering plots of copolymers with a constant 10 kg/mol PESu segment length and varying compositions. The single, primary peak across compositions >80 wt.% PESu correlated well with previous literature\textsuperscript{39, 40} on the inter-crystallite distance of PBT. In comparison to the PBT homopolymer control, the d-spacing increased from 12.3 to 16.4 nm upon 40 wt.% incorporation of 10 kg/mol PESu, indicating a small fraction of soluble PESu segments in the amorphous PBT phase. Further incorporation of 10 kg/mol PESu resulted in minimal change to the inter-crystallite distance (16.0 ± 0.7 nm). However, the reduction in the PBT segment length inhibited the copolymer’s propensity to crystallize and resulted in a lower peak intensity, presumably due to a decrease in the crystallinity. At 80 wt.% incorporation of 10 kg/mol PESu, the material did not display any phase separation.
Figure IX-28: Small angle x-ray scattering of PESu-PBT segmented block copolymers at a constant PESu segment length of 10 kg/mol.

In order to provide a more in-depth comparison of the PBT homopolymer and the PBT-PESu segmented block copolymers, the linear correlation function was computed and analyzed using the method as described by Vonk\textsuperscript{38} and later extended upon by Ruland\textsuperscript{41}. The correlation function provided estimates of the lamellar thickness, amorphous thickness, long period of crystallites, and local crystallinity (crystallinity within an assembly of stacked crystallites). The lamellar thickness (\textit{circa} 3.0 nm) changed minimally when comparing the PBT homopolymer and each of the PESu\textsubscript{10k}-PBT copolymers, which is consistent with the observed small deviation in melting points for all samples measured. The correlation function analysis also indicated that the amorphous thickness increased from 6.3 nm in the homopolymer to \(~9.0~\text{nm}~\) for all copolymer compositions of PESu\textsubscript{10k}-PBT. The local crystallinity shows that with increasing PESu content the local crystallinity decreases, indicating that the packing density of crystallites decreases as larger
non-crystallizable PESu blocks are incorporated between the crystallizable PBT blocks. **Figure IX-29** and **Table IX-5** provides plots of the autocorrelation function and the calculated parameters respectively. Quenching samples from above the melting point eliminated all peaks in WAXS and SAXS scattering (**Figures IX-30** and **IX-31**, respectively), indicating that the origin of the SAXS peaks in the annealed samples resulted from the periodicity of the crystalline domain without a contribution from phase separation.

![SAXS linear correlation function of PESu-PBT segmented block copolymers with 10 kg/mol PESu segments.](image)

**Figure IX-29**: SAXS linear correlation function of PESu-PBT segmented block copolymers with 10 kg/mol PESu segments. Curves have been offset vertically (by 0.5 each) to facilitate comparison.
Table IX-5: Calculated parameters for the linear correlation function of PESu-PBT segmented block copolymers with 10 kg/mol PESu segments using a paracrystalline (ideal) lattice.

<table>
<thead>
<tr>
<th></th>
<th>Crystal Lamellar Thickness (nm)</th>
<th>Amorphous Interlamellar Thickness (nm)</th>
<th>Long Period (Lp) (nm)</th>
<th>Local Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>3.3</td>
<td>6.3</td>
<td>9.6</td>
<td>34.0</td>
</tr>
<tr>
<td>20PESu_{10k} -80PBT</td>
<td>3.6</td>
<td>7.8</td>
<td>11.5</td>
<td>31.7</td>
</tr>
<tr>
<td>40PESu_{10k} -60PBT</td>
<td>3.3</td>
<td>8.7</td>
<td>12.0</td>
<td>27.8</td>
</tr>
<tr>
<td>50PESu_{10k} -50PBT</td>
<td>3.2</td>
<td>8.8</td>
<td>12.0</td>
<td>26.4</td>
</tr>
<tr>
<td>60PESu_{10k} -40PBT</td>
<td>2.5</td>
<td>9.1</td>
<td>11.6</td>
<td>21.3</td>
</tr>
</tbody>
</table>

Figure IX-30: Wide-angle x-ray scattering of PESu-PBT copolymers a). After annealing at 160 °C for 24 h b). After quench-cooling from 300 °C.
Figure IX-31: Small-angle x-ray scattering of PESu-PBT copolymers after quench-cooling from 300 °C.

Synthesis and Properties of Segmented Polyurethanes with Triptycene Units in the Soft Segment

Authors: Zhengmian Chang, Gregory B. Fahs, Amanda G. Hudson, E. Bruce Orler, Robert B. Moore, Garth L. Wilkes, and S. Richard Turner

Segmented polyurethanes based on poly(tetramethylene glycol) soft segments (SS) containing aromatic units are synthesized. Hydroquinone bis(2-hydroxyethyl) ether and 4,4’-methylenebis(phenyl isocyanate) are used as the chain extender and the diisocyanate, respectively. Effects of incorporation of hydroquinone (HQ) and triptycene hydroquinone into
the soft segments on the morphology and properties of the undeformed segmented polyurethanes are investigated. A chemical structure of these polymers is shown in Figure IX-32.

![Chemical structure of segmented polyurethane](image)

**Figure IX-32:** Chemical structure of segmented polyurethane.

WAXD was used to further confirm the crystallization of the soft segments after DSC experiments. It was proposed that strain induced crystallization can partially contribute to strain hardening and consequently enhance the mechanical properties for crystallizable thermoplastic polymers.\textsuperscript{43-45} In our study, all of the compression molded samples except PTMGTH-PU showed some sign of hardening behavior. As previously discussed in the thermal properties section, the bulky triptycene units can minimize thermally induced crystallization. This prompted us to therefore also investigate the effect of these same bulky aromatic structures upon strain induced crystallization of the soft segments. WAXD was used to analyze the unstrained samples and the samples that were uniaxially stretched to 150%, 300%, and 370% (PTMGTH-PU). None of the unstrained samples exhibited diffraction peaks characteristic of PTMG crystallization (Figure IX-33). This is because the soft segment crystal structure of four of the samples melts below room temperature. At strains of 150%, PTMG2K-PU and PTMGHQ-PU started to show crystalline reflection at 2\(\theta\) = 19.9° and 2\(\theta\) = 24.2°, which are attributed to the Bragg spacing of the (020) and (110) planes, respectively. The monoclinic form of PTMG has unit cell dimensions of \(a = 0.559\) nm, \(b = 0.890\) nm, \(c = 1.207\) nm, and \(\beta = 134.2°\).\textsuperscript{46} The intensity of both peaks increased as the
strain increased to 300%. Although overlapping with the broad amorphous peak, the peak around 19.9° was observed to become sharper and more intense when the strain increased from 150% to 300%. In PTMG2K-PU and PTMGHQ-PU, three additional crystalline reflections were also observed at 2θ = 36.7°, 2θ = 40.6°, and 2θ = 42.9° (not shown in Figure IX-33), which become more intense when the strain is increased from 150% to 300%. However, no diffraction peaks were observed from the PTMGTH-PU sample, even when the strain was increased up to 370% (Figure IX-33 and Figure IX-34). This provides evidence that the triptycene units prevent strain induced crystallization at strains up at least to 370% under these conditions. In addition, the PTMG1K-PU sample lacks the ability to promote strain induced crystallization at strains of 300% due to the short soft segments.

SAXS was also used to probe the morphology of the compression molded films. The scattering intensities and the scattering vector q values are plotted in Figure IX-35. All SAXS profiles display a single interference peak that strongly supports the presence of microphase separation in the four samples. As expected, the interference peak of PTMG1K-PU appears at a higher q value than other samples, which indicates a shorter interdomain spacing around 10.1 nm (Table IX-6). With soft segment molecular weights higher than 2000 g mol⁻¹, the interdomain spacings of PTMG2K-PU, PTMGHQ-PU, and PTMGTH-PU increased to 13.3, 16.0, and 16.2 nm and the order is consistent with their increasing soft segment molecular weights.⁴⁷

Unlike the bulk morphologies studied by SAXS, tapping mode AFM provides a direct view of morphology on the surface of the materials. It is worth mentioning that the free air surface of the solution cast films was used in the AFM analysis to avoid surface contamination from substrate, while the compression molded films were used in other characterizations. As shown
in Figure IX-36, all of the samples exhibit a distinct microphase separation with well-defined bright regions (hard domains) dispersing in the dark regions (soft domains), which confirms that the microphase separation is not significantly reduced by the presence of the aromatic units in the soft segments. The triptycene containing PTMGTH-PU sample even showed a long-range order of hard segment connectivity.
**Figure IX-33:** WAXD profiles of segmented polyurethanes at strains.

**Figure IX-34:** WAXD patterns of segmented polyurethanes at strains (films were stretched in vertical direction).
Figure IX-35: SAXS profiles of the studied polyurethane samples.

Table IX-6: SAXS calculated Bragg spacings of polyurethanes based on different soft segments.

<table>
<thead>
<tr>
<th>Polyurethane samples</th>
<th>Scattering vector $q_{\text{max}}$ [nm$^{-1}$]</th>
<th>Interdomain spacings $d$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG1K-PU</td>
<td>0.621</td>
<td>10.1</td>
</tr>
<tr>
<td>PTMG2K-PU</td>
<td>0.472</td>
<td>13.3</td>
</tr>
<tr>
<td>PTMGHQ-PU</td>
<td>0.393</td>
<td>16.0</td>
</tr>
<tr>
<td>PTMGTH-PU</td>
<td>0.389</td>
<td>16.2</td>
</tr>
</tbody>
</table>
Figure IX-36: AFM phase images of the studied PU samples.

New semicrystalline block copolymers of poly(arylene ether sulfone)s and poly(1,4-cyclohexylenedimethylene terephthalate)\textsuperscript{48}

Authors: Zhengmian Chang, Gregory B. Fahs, Bin Zhang, Hans E. Edling, E. Bruce Orler, Robert B. Moore, and S. Richard Turner

Figure IX-37: Chemical structure of PAES-PCT multiblock copolymers
Multiblock copolymers of poly(arylene ether sulfones) (PAESs) and poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) were synthesized via melt-phase polymerization (Figure IX-37). WAXS was used to characterize the crystallization and microphase separation of the copolymers. Before the analyses, the samples were annealed at 200 °C for 24 h to promote crystallization. As shown in Figure IX-38, reflection peaks appear at 14.5°, 16.1°, 18.5°, 22.3°, and 24.8° for the samples with 40wt% or higher PCT components. These peaks are attributed to the crystallized PCT segments in the copolymers. It is reported that tPCT has a triclinic crystal structure, with the unit cell dimension as a = 0.646 nm, b = 0.665 nm, c = 1.422 nm, α = 89.45°, β = 47.03°, and γ = 114.95°. The peaks at 14.5°, 16.1°, 18.5°, 22.3°, and 24.8° correspond to (011), (010), (11̅0), (100), and (11̅1) planes of triclinic crystal structure. As expected, the relative intensities of the crystalline reflections decrease with increasing PAES content.

Only a broad amorphous peak was observed for the copolymers with less than 40wt% of PCT, and the intensity of this broad peak decreased as the PCT content increased, which corresponded to an increasing crystallinity in agreement with the thermal studies. The PAES-tPCT copolymers showed a similar trend as the PAES-PCT series. Crystallization peaks were observed when PCT content was 40wt% or higher, and the positions of peaks were essentially identical to the peak positions of PAES-PCT sample (Figure IX-39), which is similar to results reported in the previous work.
**Figure IX-38:** WAXS profiles of annealed PAES-PCT copolymers. (a. PCT; b. PAES-PCT-80; c. PAES-PCT-60; d. PAES-PCT-50; e. PAES-PCT-40; f. PAES-PCT-20; g. PAES).

**Figure IX-39:** WAXS profiles of annealed PAES-tPCT copolymers. (a. PAES-tPCT-60; b. PAES-tPCT-50; c. PAES-tPCT-40; d. PAES-tPCT-20; e. PAES).
SAXS was used to investigate the long range periodicity of the lamellar structure of these samples. As shown in Figure IX-40, all the samples except PAES homopolymer and PAES-PCT-20 exhibited a scattering peak in the range of $q = 0.4$ to $0.6 \text{ nm}^{-1}$, corresponding to lamellar spacing of 10.5–15.7 nm. Moreover, as PCT composition decreased, scattering peak of these samples shifted to lower $q$ values, which suggested a trend of increasing interlamellar dimension (i.e. greater amorphous content between lamellae). Although copolymers with tPCT segments have higher crystallinity than their cis/trans PCT-based analogues, no significant increase in the scattering behavior was observed in these SAXS measurements (Figure IX-41). Previous work suggested the high level of microphase separation of polysulfone-polyester copolymers was obtained by using higher molecular weight polyester segments ($\sim 6000 \text{ g/mol}$).\textsuperscript{34}

Figure IX-40: SAXS profiles of PAES-PCT copolymers.
**Multiblock Copolymers Based upon Increased Hydrophobicity Bisphenol A Moieties for Proton Exchange Membranes**

Authors: Jarrett R. Rowlett, Yu Chena, Andrew T. Shaver, Gregory B. Fahs, Benjamin J. Sundell, Qing Li, Yu Seung Kim, Piotr Zelenay, Robert B. Moore, Sue Mecham, and James E. McGrath

**Figure IX-41:** SAXS profiles of PAES-tPCT copolymers.

**Figure IX-42:** Chemical structure $6F_{50}X_{50}$PAEB-BPS100 multiblock copolymers.
A series of nitrile-containing hydrophobic oligomers consisting of bisphenol A (Bis A), dimethylbisphenol A (DMBPA), and tetramethylbisphenol A (TMBPA) moieties were reacted with a disulfonated poly (arylene ether sulfone) hydrophilic segment to form the multiblock copolymer series (chemical structure shown in Figure IX-42). SAXS was performed in order to investigate the effects of bisphenol A methyl substitution on the morphological features of multiblock copolymer membranes (Figure IX-43). All of the SAXS profiles showed a primary peak at \( q_{\text{max}} \) (Table IX-8) and also a secondary peak at \( 2q_{\text{max}} \), which is consistent with a lamellar organization of the phase-separated domains in these multiblock copolymers. The most significant difference between these profiles was the smaller domain spacing (larger \( q_{\text{max}} \)) observed for the tetramethyl multiblock copolymers. In addition, the primary SAXS peak for the tetramethyl series was found to be significantly sharper compared to the dimethyl and bisphenol A based multiblock copolymers (see FWHM, Table IX-8). Similarly, the secondary peak for the tetramethyl series was also observed to be more prominent and well-resolved. This scattering behavior suggests that the phase separated morphology of the tetramethyl based multiblock copolymers exhibits a more refined order in comparison to the dimethyl and bisphenol A based multiblock copolymers.
Based upon self-consistent mean-field theory (SCFT), the Bragg spacing for the primary scattering peak ($d_1$) for a lamellar phase separated block copolymer may be correlated to the effective segment-segment interaction parameter ($\chi_{\text{eff}}$) by the following relationship:

$$d_1 = 1.10 a N^{2/3} \chi_{\text{eff}}^{1/6}$$

where $a$ is the statistical segment (Kuhn) length, and $N$ is the number of Kuhn segments within a diblock sequence.\textsuperscript{53, 54} For the multiblock copolymers studied here, the statistical segment
length was approximated using the Kuhn segment length of polycarbonate, with \( a = 2.94 \text{ nm} \) and
the Kuhn length of each multiblock assumed to be identical based on studies of bisphenol A and
tetramethyl bisphenol A polycarbonates.\(^{55}\) The value for \( N \) was computed by considering the
segment length to correspond to two adjacent polycarbonate monomers, resulting in a value of
\( N = 29 \) segments within a single 10 K-10 K AB diblock sequence.\(^{56}\) These assumptions have been
used for simplicity due to the structural similarity between each multiblock copolymer
considered. Following these calculations, the observed increase in \( q_{\text{max}} \) with increasing methyl
group content corresponds to a decrease in the effective interaction parameter between the
blocks of the multiblock copolymers (Table IX-8). With increasing hydrophobicity (and likely an
increase in steric constraints) imposed by the addition of methyl substituents, the driving force
for phase separation increases, leading to a more ordered phase separated morphology. This
increase in lamellar organization of the highly hydrophobic tetramethyl multiblock copolymers
may also be a factor in the observed increase in elongation over that of the bis A and dimethyl
systems. Future studies will focus on morphological transformations during in-situ tensile/SAXS
experiments. Similarly, the more ordered morphology could have restricted the swelling of the
hydrophilic domain, thus contributing to the observed reduction in water uptake of the
multiblock copolymer membranes.
References


*Materials 2010*, 3 (12), 5097-5110.


*Polymer 2012*, 53 (21), 4614-4622.


52. Lee, M.; Park, J. K.; Lee, H.-S.; Lane, O.; Moore, R. B.; McGrath, J. E.; Baird, D. G. Effects of block length and solution-casting conditions on the final morphology and properties of


Appendix A:

Note: All code presented here was written in Mathematica and is stable in Mathematica 11.3.

Code for Kinning and Thomas Fits

Kinning and Thomas Fitting Routine
Import Data
ClearAll["Global`*"]
workingdirectory = SetDirectory[];
filedirectory=SystemDialogInput["FileOpen",workingdirectory];
Data=Import[filedirectory];
Data[[All,1]]=Data[[All,1]]*10;
DataPlot=ListLogPlot[Data[[All,1;;2]],PlotRange->Full]

The Kinning - Thomas Model
Defining the functions for the Kinning and Thomas scattering intensity

\[ \eta[1,1] = \frac{(4 \pi)}{3} \]
\[ \Phi[x_] := \frac{3}{x^3} (\sin[x] - x \cos[x]) \]
\[ \eta[Rca_,Vp_] := \frac{4}{3 \pi} Rca^3 \frac{1}{Vp}; \]
\[ B[q_,Rca_] := 2 q Rca; \]
\[ G[B_,Rca_,Vp_] := \frac{(1 + 2 \eta[Rca,Vp])^2}{(B^2 (1 - \eta[Rca,Vp])^4)} (\sin[B] - B \cos[B]) - (6 \eta[Rca,Vp] (1 + \eta[Rca,Vp]) (\sin[B] - B \cos[B])^2) \]
\[ \frac{(2 B \sin[B] + (2 - B^2) \cos[B])}{ (2 B^5 (1 - \eta[Rca,Vp])^4)} \]
\[ (-B^4 \cos[B] + 4((3B^2 - 6) \cos[B] + (B^3 - 6B) \sin[B] + 6)) \]
IKT[q_, R1_, Rca_, Vp_, ρ1_] := ρ1 Φ[q R1]^2 (1/(1 + 24 η[Rca, Vp]/B[q, Rca]))
BGScattering[q_, a1_, a2_, k_, d_] := a1 + a2 q + k q^6 d

Plotting of Functions
Initial Guesses
4/3π 2.7^3
82.448
gR1 = 1.0;
gRca = 1.7;
gVp = 80;
gρ1 = 0.01;
ga1 = -0.028;
ga2 = 0.003;
ga3 = 0;
gk = 0.008;
gd = 4;

LogPlot[IKT[q, gR1, gRca, gVp, gρ1] + BGScattering[q, ga1, ga2, gk, gd], {q, .008, 2.5}]

Manipulate[
  fitguesses = {R1, Rca, Vp, ρ1, a1, a2, k, d};
  Show[ListLogPlot[Data[[All, 1 ;; 2]]], LogPlot[IKT[q, R1, Rca, Vp, ρ1] + BGScattering[q, a1, a2, k, d], {q, Data[[1, 1]], Data[[-1, 1]]}, ImageSize -> Large, PlotRange -> {0.001, 10}, PlotStyle -> {Red, Thick}], {{R1, gR1, "Sphere Radius"}, 0, 5}, {{Rca, gRca, "Radius of Closest Approach"}, 0, 10}, {{Vp, gVp, "Interparticle Distance"}, 30, 500}, {{ρ1, gρ1, "Contrast"}, 0.01, 1}, {{a1, ga1, "Background"}, -1, 1}, {{a2, ga2, "Background b"}, -0.05, 1}, {{k, gk, "Porod Invariant"}, 0, 0.01}, {{d, gd, "Fractal Dimension"}, 1, 4}]

Show[ListLogPlot[Data[[All, 1 ;; 2]]], LogPlot[IKT[q, R1, Rca, Vp, ρ1] + BGScattering[q, a1, a2, k, d], {q, Data[[1, 1]], Data[[-1, 1]]}, ImageSize -> Large, PlotRange -> {0.001, 10}, PlotStyle -> {Red, Thick}], {{R1, gR1, "Sphere Radius"}, 0, 5}, {{Rca, gRca, "Radius of Closest Approach"}, 0, 10}, {{Vp, gVp, "Interparticle Distance"}, 30, 500}, {{ρ1, gρ1, "Contrast"}, 0.01, 1}, {{a1, ga1, "Background"}, -1, 1}, {{a2, ga2, "Background b"}, -0.05, 1}, {{k, gk, "Porod Invariant"}, 0, 0.01}, {{d, gd, "Fractal Dimension"}, 1, 4}]
Fitting Procedure

(**Runs the actual fit and then plots the resulting function and variable estimates with a 95% confidence interval**) (**)nlm=NonlinearModelFit[Data[[All,1;;2]], {IKT[q,R1,Rca,Rip,ρ1]+BGScattering[q,a1,a2,k,d], 0<R1<2,0<Rca<3,0<Rip<10,0<ρ1<1,0<k<0.03,2<d<4}, {{R1,fitguesses[[1]]},{Rca,fitguesses[[2]]},{Rip,fitguesses[[3]]},{ρ1,fitguesses[[4]]},{a1,fitguesses[[5]]},{a2,fitguesses[[5]]},{k,fitguesses[[7]]},{d,fitguesses[[8]]}}, q, Weights -> 1/Data[[All,3]]^2]**

nlm=NonlinearModelFit[Data[[All,1;;2]], {IKT[q,R1,Rca,ρ1]+BGScattering[q,a1,a2,k,d], 0.5 <R1<2,0<Rca<3,0<ρ1<400,0<k<0.5,1<d<4}, {{R1,fitguesses[[1]]},{Rca,fitguesses[[2]]},{ρ1,fitguesses[[3]]},{a1,fitguesses[[4]]},{a2,fitguesses[[5]]},{k,fitguesses[[7]]},{d,fitguesses[[8]]}}, q, Weights -> 1/Data[[All,3]]^2]

ExtractedParameters=nlm["ParameterConfidenceIntervalTable"]

R1fit=nlm[[1,2]][[1,2]]; Rcafit=nlm[[1,2]][[2,2]]; Ripfit=nlm[[1,2]][[3,2]]; ρ1fit=nlm[[1,2]][[4,2]]; a1fit=nlm[[1,2]][[5,2]]; a2fit=nlm[[1,2]][[6,2]]; kfit=nlm[[1,2]][[7,2]]; dfit=nlm[[1,2]][[8,2]];

Show[LogPlot[IKT[q,R1fit,Rcafit,Ripfit,ρ1fit]+BGScattering[q,a1fit,a2fit,kfit,dfit], {q,.8,2.5}], ListLogPlot[Data[[All,1;;2]], PlotStyle -> Red]]

{
{ R1, 0.717201, 0.932549, {-1.11496,2.54936}},
{ Rca, 1.41942, 0.275366, {0.878411,1.96042}},
{ Vp, 187.976, 323.394, {-447.391,823.342}},
{ ρ1, 0.0240651, 0.0117749, {0.000931231,0.0471999}},
{ a1, 0.0330071, 0.0138835, {0.00573038,0.0602837}},
{ a2, -0.00488913, 0.0063718, {-0.0174077,0.00762942}},
{ k, 0.00172901, 0.0000667836, {0.00159583,0.00186218}},
{ d, 2.97473, 0.0186126, {2.93816,3.0113}}
}
Show[LogPlot[IKT[q,R1fit,Rcafit,Ripfit,ρ1fit]+BGScattering[q,a1fit,a2fit,kfit,dfit],{q,.08,2.5}],
ListLogPlot[Data[[All,1;;2]],PlotStyle->Red]]

FitData=Data[[All,1;;2]];
FitData[[All,2]]=Array[IKT[Data[[#,1]],R1fit,Rcafit,Ripfit,ρ1fit]+BGScattering[Data[[#,1]],a1fit,a2fit,kfit,dfit]&,&Length[Data]];
ListLogPlot[FitData]
Ellipsoidal Hard-Sphere Model Fit Code

Loading in Data
ClearAll["Global`*"]
workingdirectory = SetDirectory[NotebookDirectory[]];
filedirectory=SystemDialogInput["FileOpen",workingdirectory];
Data=Import[filedirectory];
IVsqData=Data[[All,1;;2]];
IVsqData[[All,1]]=Data[[All,1]]*10;
ExperimentalData=ListLogPlot[IVsqData,PlotRange->Full]
Cropping the data (For sPS or SsPS derivatives use a range of 0.2 nm\(^{-1}\)-2.4 nm\(^{-1}\))

Background Matrix Scattering

Define the background matrix scattering as a fractal like matrix scattering with fractal dimension \(D\)

Matrix Scattering \(\rightarrow a+K/q^{6-D}\)

\[\text{BGScattering}[q_, \text{bg}_-, k_, d_] := \text{bg}+k/q^d\]

The Kinning - Thomas Model for Ionic Scattering

Defining the functions for the Kinning and Thomas scattering intensity

\[\Phi[x_] := \frac{3}{x^3} (\sin[x] - x \cos[x])\]

\[\eta[Rca_, Rip_] := \frac{4}{3} \pi \frac{Rca^3}{1/(4/3 \pi Rip^3)}\]

\[B[q_, Rca_] := 2 q Rca\]

\[G[B_, Rca_, Rip_] := (1+2\eta[Rca,Rip])^2/(B^2 \ (1-\eta[Rca,Rip])^4) \ (\sin[B]-B \cos[B]-
(6\eta[Rca,Rip])^2/(B^3 \ (1-\eta[Rca,Rip])^4) \ (2B \sin[B]+(2B^2)\cos[B]-2)+
(\eta[Rca,Rip])^2/(B^2 \ (1-\eta[Rca,Rip])^4) \ (-B^4\cos[B]+4((3B^2-6)\cos[B]+(B^3-6B)\sin[B]+6))\]

\[S[q_, Rca_, Rip_, \rho1_] := (1/(1+24 \eta[Rca,Rip]) \ (G[B[q,Rca],Rca,Rip]/B[q,Rca]))\]

\[\text{IKT}[q_, R1_, Rca_, Rip_, \rho1_] := \rho1 \ \Phi[q, R1]^3 \ S[q,Rca,Rip]\]

Crystalline Scattering of sPS

Ellipsoidal Form Factor

NIST form factor

\[Xf[z_, a_, b_] := (\sin[z]-z \cos[z])/z^3\]

\[P[q_?\text{NumericQ}, a_?\text{NumericQ}, b_?\text{NumericQ}] := \text{NIntegrate}[(3*(4\pi)/3 \ a \ b^2) \ NIntegrate[(3*(4\pi)/3 \ a \ b^2 \ Xf[q \ b \ (1+x^2 \ ((a/b)^2-1))))^2, \{x,0,1\}], \text{Method}->\{\"SymbolicPreprocessing",\"OscillatorySelection\"->\text{False}\}]\]
\[ P[q_\text{?NumericQ}, a_\text{?NumericQ}, b_\text{?NumericQ}] := \text{NI}ntegrate[(3 \text{SphericalBesselJ}[1, q (a^2 \mu^2 + b^2 (1-\mu)^(1/2))]/(q (a^2 \mu^2 + b^2 (1-\mu)^(1/2)))^2, \{\mu, 0, 1\}, \text{Method->}\{"SymbolicPreprocessing","OscillatorySelection"\->False\}] \]

Liquid like hard sphere structure factor from Tsao 1999, volume 271 page 322

\[ \text{XtalIntensity}[q_-, a_-, b_-, RcaX_-, RipX_-, \rho1_-] := \rho1 \ P[q, a, b] S[q, RcaX, RipX] \]

Total Combined Intensity Plots

Manipulate[
  Show[ExperimentalData, LogPlot[+BGScattering[q, bg, k, d], \{q, IVsqData[[1, 1]], IVsqData[[-1, 1]]\}], PlotRange->Full, ImageSize-> Large], \{\{bg, 0.1\}, \{k, 0.002\}, \{d, 2.4\}, Frame->True, FrameLabel-> \{"Scattering Vector q", "Intensity"\}] 
]

Manipulate[
  InitialGuess={a, b, RcaX, RipX, \rho1 X, bg, k, d};
  Show[ExperimentalData, LogPlot[(XtalIntensity[q, a, b, RcaX, RipX, \rho1 X] + BGScattering[q, bg, k, d]), \{q, IVsqData[[1, 1]], IVsqData[[-1, 1]]\}], PlotRange->Full, ImageSize-> Large], \{\{bg, 0.1\}, \{a, 0.5, 2\}, \{b, 0.5, 2\}, \{RcaX, 5, 5\}, \{RipX, 1, 10\}, \{k, 0.05\}, \{d, 0.4\}, Frame->True, FrameLabel-> \{"Scattering Vector q", "Intensity"\}] 
]

Fitting the Data

XtalParams=NonlinearModelFit[IVsqData, XtalIntensity[q, a, b, RcaX, RipX, \rho1 X] + BGScattering[q, bg, k, d], \{\{a, InitialGuess[[1]]\}, \{b, InitialGuess[[2]]\}, \{RcaX, InitialGuess[[3]]\}, \{RipX, InitialGuess[[4]]\}, \{\rho1 X, InitialGuess[[5]]\}, \{bg, InitialGuess[[6]]\}, \{k, InitialGuess[[7]]\}, \{d, InitialGuess[[8]]\}\}, q, PrecisionGoal->4, Weights->1/Data[All, 3]^2]

\[ \text{FittedModel}\[\text{XtalParams}[^\text{"ParameterConfidenceIntervalTable"}]\] 

\{ Estimate, Standard Error, Confidence Interval\}
\{ bg, 0.00903769, 0.000110643, \{0.00882058, 0.00925481\}\},
\{ k, 0.01875, 0.000228532, \{0.0183015, 0.0191984\}\},
\{ d, 3.74425, 0.0121163, \{3.72048, 3.76803\}\}
\}

\{ Estimate, Standard Error, Confidence Interval\}
\{ a, 6.27519, 0.248136, \{5.78828, 6.76211\}\},
\{ b, 26.1624, 1.4172, \{23.3814, 28.9433\}\},
\{ RcaX, 6.50901, 0.129558, \{6.25478, 6.76325\}\},
\{ RipX, 10.3403, 0.176797, \{9.9934, 10.6873\}\},
\{ \rho1 X, 0.000757546, 0.0000562209, \{0.000647224, 0.000867868\}\} 
\}

Show[LogPlot[XtalIntensity[q, XtalParams["BestFitParameters"][[1, 2]], XtalParams["BestFitParameters"][[2, 2]], XtalParams["BestFitParameters"][[3, 2]], XtalParams["BestFitParameters"][[4, 2]],]...
XtalParams["BestFitParameters"][[5, 2]] + BGScattering[ q, XtalParams["BestFitParameters"][[6, 2]], PorodParams["BestFitParameters"][[7, 2]], PorodParams["BestFitParameters"][[8, 2]], { q, Data[[1, 1]], Data[[-1, 1]] }, PlotRange -> Full, ImageSize -> Large], ExperimentalData

Combining and Exporting Fit Parameters
Export["3RSsPS235CIsoXtal(3).xlsx", ParameterList]
3RSsPS235CIsoXtal(3).xlsx

Monte-Carlo Modeling of Ionomer Crystalline Morphology

ClearAll["Global`*"]
Remove[Ellipsoid]
<< MultivariateStatistics`
boxsize = 35;
A = 3.7;
B = 6;
Rca = 7.7;
Te = {{A, B, boxsize {0, 0, 0}, 0, {1, 5, 0.735911056086342}}};
Do[
  NewCoordinate = Table[
    {A, B, boxsize {x - 1/2, x - 1/2, x - 1/2}, π*x, {x, x, x}} / . x :> RandomReal[], {1}][[1]];
  If[
    MemberQ[Table[EuclideanDistance[Te[[All, 3]][[i]], NewCoordinate[[3]]], {i, 1, Length[Te]]], x_ /; x <= Rca + B], Te = Te,
    Te = Insert[Te, NewCoordinate, Length[Te] + 1]
\[ \{j, 100000\} \]

TeSphere = Te;
TeSphere[[All, 1 ;; 2]] = Rca;
ellipsoid[a_, b_, center_, ?VectorQ, rotation_, around_, ?VectorQ] := Fold[GeometricTransformation, Ellipsoid[{0, 0, 0}, {a, b, b}], {RotationTransform[rotation, around], TranslationTransform[center]}]

Graphics3D[{Lighter[Blue, .5], Glow[Darker[Blue, .2]], Specularity[Cyan, 20], ellipsoid @@ @ Te, Opacity[.2], Gray, Lighting -> "Neutral", ellipsoid @@ @ TeSphere}, Boxed -> False, ImageSize -> Large, PlotRange -> boxsize/2 + 2Rca]

Graphics3D[{Lighter[Blue, .5], Glow[Darker[Blue, .2]], Specularity[Cyan, 20], ellipsoid @@ @ Te}, Boxed -> False, ImageSize -> Large, PlotRange -> boxsize/2 + 2Rca]

RcaIon = 1.9;
IonRadius = 1.2;
IonicCoordinates = {{0, 0, 0}};
Do[
    NewIonCoordinate = boxsize{x - 1/2, x - 1/2, x - 1/2}/.x :> RandomReal[];
    If[
        MemberQ[Table[RegionDistance[Ellipsoid[{0, 0, 0}, {A, B, B}], RotationTransform[-Te[[i, 4]], Te[[i, 5]]]][NewIonCoordinate - Te[[i, 3]]]], {i, 1, Length[Te]}], {i, 1, Length[Te]}], z_ /. z <= 2RcaIon - IonRadius] || MemberQ[

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Table[EuclideanDistance[IonicCoordinates[[i]], NewIonCoordinate], {i, 1, Length[IonicCoordinates]}], y_/;y<=2RcaIon],
IonicCoordinates=IonicCoordinates,
IonicCoordinates=Insert[IonicCoordinates, NewIonCoordinate, Length[IonicCoordinates]+1]]
,{j,10000}]/Timing
IonicCoordinates=Drop[IonicCoordinates, 1];
{678.844, Null}
Graphics3D[{Lighter[Blue,.5], Glow[Dark[Blue,.2]], Specularity[Cyan,20], Sphere[IonicCoordinates, RcaIon]}, Boxed->False, ImageSize->Large, PlotRange->boxsize/2+2Rca];
Graphics3D[{Opacity[.75], Lighter[Blue,.5], Glow[Dark[Blue,.2]], Specularity[Cyan,20], ellipsoid@@Te, Glow[Dark[Green,.75]], Red, Sphere[IonicCoordinates[[1;;100]], IonRadius]}, Boxed->False, ImageSize->Large, PlotRange->boxsize/2+2Rca]
Graphics3D[{Opacity[.5], Lighter[Blue,.5], Glow[Darken[Blue,.2]], Specularity[Cyan,20], ellipsoid @@Te, Opacity[.75], Glow[Darken[Green,.75]], Red, Sphere[IonicCoordinates[[1;;100]], IonRadius]}, Boxed->False, ImageSize->Large, PlotRange->boxsize/2+2Rca]
Graphics3D[{Opacity[.1], Lighter[Blue,.5], Glow[Darken[Blue,.2]], Specularity[Cyan,20], ellipsoid @@Te, Opacity[.75], Glow[Darken[Green,.75]], Red, Sphere[IonicCoordinates[[1;;100]], IonRadius]}, Boxed->False, ImageSize->Large, PlotRange->boxsize/2+2Rca]
Glatter and Lake Method for WAXD Deconvolution

Glatter Desmearing Algorithm for SAXS Detector
ClearAll["Global*"]
Load Experimental Data
workingdirectory = SetDirectory["C:\Users\Greg\Desktop\"];
filedirectory=SystemDialogInput["FileOpen",workingdirectory];
OriginalData=Import[filedirectory];
Data=OriginalData;
Data[[All,1]]=OriginalData[[All,1]]*10;
I0=1.5*Max[OriginalData[[All,2]]];
background=0;
Load Beam Data (If needed)
workingdirectory = SetDirectory["C:\Users\Greg\Desktop\"];
filedirectory = SystemDialogInput["FileOpen", workingdirectory];
BeamData = Import[filedirectory];
BeamData[[All, 1]] = BeamData[[All, 1]]*10;

Interpolation of Data end points
Fit With Constant
BeginFit = NonlinearModelFit[Data[[1, 1;;2]], {a, {a > 0}}, {a}, q] // Quiet;
FitBegin = Length[Data] - 2;
EndFit = NonlinearModelFit[Data[[FitBegin;;-1, 1;;2]], {a, {a > 0}}, {a}, q] // Quiet;
Plot[BeginFit[x], {x, 0, .01}]

Joining The Data Sets
DataSpacing = Data[[2, 1]] - Data[[1, 1]];
DataBeginNumPoints = Floor[Data[[1, 1]]/DataSpacing];

Data[[All, 2]] = OriginalData[[All, 2]] + background;
ListPlot[Data[[All, 1;;2]], PlotRange -> Full]
Defining The Fitting Functions

\[ nlmbeamstop = \text{NonlinearModelFit}[[\text{BeamData[[All,1;;2]]}, \{B1*(1+a)/(a+\text{Exp}(x^2)/b))\}, \{a, b, B1\}, x]\); \
\[ a1 = nlmbeamstop[[1,2]][[1,2]]; \]
\[ b1 = nlmbeamstop[[1,2]][[2,2]]; \]
\[ B = nlmbeamstop[[1,2]][[3,2]]; \]
\[ \text{Plot}[B*(1+a1)/(a1+\text{Exp}(x^2)/b1)), \{x, 0, 5\}, \text{PlotRange}\to \text{Full}] \]
\[ \text{Show}[\text{ListPlot}[\text{BeamData[[All,1;;2]]}, \text{PlotRange}\to \text{Full}], \text{Plot}[B*(1+a1)/(a1+\text{Exp}(x^2)/b1)), \{x, 0, 1\}]] \]
Defining the Smoothing Intensity Functions

```math
\text{v}[x_] := \left(\frac{a_1}{2(1+a_1)b_1 \log(1+a_1)}\right)\left(\frac{1+a_1}{a_1+\exp\left((x^2)^{1/2}/b_1\right)}\right)
```

```math
\text{Plot}[v[x], \{x, 0, 5\}, \text{PlotRange} \rightarrow \text{Full}]
```

NumberSmoothPoint = 7;
SGWindow = SavitzkyGolayMatrix[{numberSmoothPoint}, 3];
SmoothData = TotalData[[All, 1 ;; 2]];
SmoothData[[All, 2]] = ListConvolve[SGWindow, PadRight[PadLeft[TotalData[[All, 2]], Length[TotalData]] + numberSmoothPoint, TotalData[[1, 2]], Length[TotalData] + 2 numberSmoothPoint, TotalData[[1 - 1, 2]]];
ExtrapData = TotalData[[All, 1 ;; 2]];
ExtrapData[[All, 1]] = Array[TotalData[[1 - 1, 1]] + # DataSpacing &, {Length[TotalData]}];
ExtrapData[[All, 2]] = SmoothData[[1 - 1, 2]];
SmoothInterpData = Join[SmoothData, ExtrapData];
SmoothInterpolation[SmoothInterpData, InterpolationOrder -> 0];
IssArray = TotalData[[All, 1 ;; 2]];
Do[
  IssArray[[j, 2]] = With[{q = j}, NIntegrate[v[x] InterpData[[q, 1]] - x, \{x, -\infty, \infty\}, Method -> {"Trapezoidal", "SymbolicProcessing" -> False}]
    , {j, Length[TotalData]}] // Timing
{5.5, Null}
The Lake Algorithm (width desmearing)
NumberIterations = 5;
Clear[I1, li]
Iss = Interpolation[IssArray, InterpolationOrder -> 1];
I1[q_] := InterpData[q]^2/Iss[q]
li = I1;
IterationArray = TotalData[[All, 1 ;; 2]];
Do[
    Do[
        IssArray[[j, 2]] = With[{q = j}, NIntegrate[v[x]li[TotalData[[q, 1]] - x], {x, -Endpoint, Endpoint}, Method -> {"GlobalAdaptive", "SymbolicProcessing" -> False}, PrecisionGoal -> 4]]
        , {j, Length[TotalData]}] // Timing;
    IterationArray[[All, 2]] = Array[li[TotalData[[#, 1]]] + SmoothData[[#, 2]] - IssArray[[#, 2]]&, {Length[TotalData]}];
    SmoothIteration = IterationArray;

SmoothIteration[[All, 2]] = ListConvolve[SGWindow, PadRight[PadLeft[IterationArray[[All, 2]], Length[IterationArray]] + numberSmoothPoint, IterationArray[[2, 1]]], Length[IterationArray] + 2 numberSmoothPoint, IterationArray[[2, 1]]];
    li = Interpolation[SmoothIteration, InterpolationOrder -> 0];
    , {i, NumberOfIterations}] // Timing // Quiet
{9.5625, Null}
Plot[{Interpolation[IisArray][x], SmoothInterp[x]}, {x, 5, 30}]
Plot[li[x], {x, 5, 30}]
NumberIterations=1;
IisArray=SmoothData;
Do[
  Do[
    IisArray[[j,2]]=With[{q=j},NIntegrate[v[y]Ii[((TotalData[[q,1]]-y)^2)^(1/2)],{y,-
      Infinity,Infinity},PrecisionGoal->3,Method->{"GlobalAdaptive","SymbolicProcessing"->False }]]
    .{j,Length[TotalData]-1}]/Timing;
  IterationArray[All,2]=Array[Ii[TotalData[[#,1]]+TotalData[[#,2]]-IisArray[[#,2]]]&,{Length[TotalData]}];
  SmoothIteration=IterationArray;
  SmoothIteration[All,2]=ListConvolve[SGWindow,PadRight[PadLeft[IterationArray[All,2],Length[IterationArray]]+numberSmoothPoint,IterationArray[[2,1]]],Length[IterationArray]]+2numberSmoothPoint,IterationArray[[2,-1]]]
  Ii=Interpolation[SmoothIteration,InterpolationOrder->1];
  {i,NumberIterations }]/Timing//Quiet
{6.48438,Null}
The Glatter Algorithm (width desmearing)
IisArray=SmoothData;
Ii=SmoothData[[All,1;;2]];

ListPlot[{SmoothIteration[[100;;400,2]],LowpassFilter[SmoothIteration[[100;;400,2]],.5]},PlotRange->Full]

ListPlot[IisArray]
CQ=TotalData[[All,2]]; 
Sip=$MaxMachineNumber^2; 
Sim=\infty; 
i=0; 
While[i<1000&&Sip<Sim, 
  Sim=Sip; 
iInterp=Interpolation[Ii,InterpolationOrder->1]; 
Do[ 
  IisArray[[j,2]]=With[{q=j},NIntegrate[v[y]iInterp[((TotalData[[q,1]]-y)^2)^1/2],{y, 
    Endpoint,Endpoint},PrecisionGoal->5,Method->"GlobalAdaptive","SymbolicProcessing"->False]/Quiet] 
  ,{j,Length[TotalData]}] 
  CQ=Array[(SmoothData[#,2]-IisArray[#,2])^2/SmoothData[#,2]^2 (100(1-
    TotalData[#,3]/SmoothData[#,2]))^2&,{Length[TotalData]}]; 
  Sip=Sum[CQ[[i]],{i,Length[CQ]}]; 
  Di=Array[(SmoothData[#,2]-IisArray[#,2])Sqrt[CQ[#]]&,{Length[TotalData]}]; 
  Ci=ListConvolve[SGWindow,PadRight[PadLeft[Di,Length[Di]+numberSmoothPoint,Di[[1]]],Length[Di]+2numberSmoothPoint,Di[[-1]]]]; 
  Ii[[All,2]]=Array[Ii[#,2](1+Ci[#])&,{Length[Ii]}]; 
  i++; 
]/Timing 
{411.609,Null} 
i 
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ListPlot[{Ii,TotalData[[All,1;;2]]},PlotRange->Full,ImageSize->Large]
Plot[
  {SmoothInterp[x], Interpolation[IisArray, InterpolationOrder -> 1][x]},
  {x, Data[[1, 1]], TotalData[[-1, 1]]}, PlotRange -> Full, ImageSize -> Large]

Results
Plot[
  {IiInterp[x]},
  {x, Data[[1, 1]], Data[[-1, 1]]}, PlotRange -> Full]

Plot[
  {IiInterp[x], InterpData[x]},
  {x, Data[[1, 1]], Data[[-1, 1]]}, PlotRange -> Full, ImageSize -> Large]
Code for Models for Lamellar Morphologies

Concentrated Lamellar Form Factor
Calculates the scattering form factor from a lyotropic lamellar phase. Form factor is calculated for lamellae of uniform scattering length density that are randomly distributed in solution (a powder average). The lamellae thickness is polydisperse. The model can also be applied to large, multi-lamellar vesicles (MLV's).

δ = bilayer thickness
σ = bilayer distribution of thickness
Δρ = electron density contrast
q = momentum transfer vector
Form Factor for concentrated lamellae
LamellarForm[q_, Δρ_, δ_, σ_] := (2Δρ^2)/q^2 (1 - Cos[q δ]Exp[-(q^2 σ^2)/2])

Dilute Solution Intensity Function
Calculates the scattering intensity from a lyotropic lamellar phase. Form factor is calculated for lamellae of uniform scattering length density that are randomly distributed in solution a powder average. The lamellae thickness is polydisperse. The model can also be applied to large multi-lamellar vesicles (MLV's).

Concentrated Lamellar Intensity Function

Manipulate[LogPlot[{LamellarIntensity[q, Δρ, δ, σ], LamellarForm[q, Δρ, δ, σ]}, {q, 0, 2.5}, PlotRange -> Full, ImageSize -> Large, AxesLabel -> {"q(Å^-1)", "Intensity (a.u.)"}, PlotLegends -> {"Intensity","Form Factor"}, PlotLabel -> "Dilute Solution"], {Δρ, 1, 10}, {δ, 1, 100}, {σ, 0, 10}]

Concentrated Lamellar Intensity Function
Concentrated Lamellar Structure Factor

\( \eta_{cp} = \text{Caille parameter} \)

\( \gamma_E = \text{Euler's constant} \)

\( q = \text{momentum transfer vector} \)

\( \Delta \rho = \text{scattering length density contrast} \)

\( \delta = \text{bilayer thickness} \)

\( d = \text{repeat spacing} \)

\( n_{tot} = \text{number of lamellar stacks} \)

\( \Delta q = \text{Instrument resolution (set to \( \Delta q=0 \) for theoretical results)} \)

\( \eta_{cp}=0.1; \)

\( \gamma_E=0.577256649; \)

\[ \alpha[n] := \frac{\eta_{cp}}{(4\pi^2)} \left( \log(n) + \gamma_E \right) \]

\[ \text{LamellarStructure}[q, \Delta \rho, \delta, d, n_{tot}, \Delta q] := 1 + 2 \sum_{n=1}^{n_{tot}-1} \left( \frac{1-n/n_{tot}}{1+2\Delta q^2 d^2 n^2} \cos \left( \frac{q d n}{1+2\Delta q^2 d^2 n^2} \right) \exp \left( \frac{-\left( 2q^2 d^2 \alpha[n] + \Delta q^2 d^2 n^2 \right)/\left( 2(1+2\Delta q^2 d^2 n^2) \right) }{1+2\Delta q^2 d^2 n^2 \alpha[n]} \right) \right) \]

Concentrated Lamellar Intensity

\[ \text{ConcLamellarIntensity}[q, \Delta \rho, \delta, \sigma, d, n_{tot}, \Delta q] := \frac{2\pi}{dq^2} \text{LamellarForm}[q, \Delta \rho, \delta, \sigma, d, n_{tot}, \Delta q] \]

\[ \text{Manipulate[LogLogPlot[{ConcLamellarIntensity[q, \Delta \rho, \delta, \sigma, d, n_{tot}, 0], \text{LamellarForm}[q, \Delta \rho, \delta, \sigma, d, n_{tot}, 0], \text{LamellarStructure}[q, \Delta \rho, \delta, d, n_{tot}, 0], \{q, 0.008, 25\}, \text{PlotRange->Full}, \text{PlotLabel->"Concentrated Solution Lamellar"}, \text{AxesLabel->{"q(A-1)","Intensity (a.u.)"}, \text{PlotLegends->{"Intensity","Form Factor","Structure Factor"}}}, \{\Delta \rho, 1*10^6, 1*10^5\}, \{\delta, 1, 100\}, \{\sigma, 0, 1\}, \{d, 100, 1000\}, \{n_{tot}, 1, 100\}]}] \]

ParaCrystalline Stack

Variable Definitions

\( \delta = \text{bilayer thickness} \)

\( d = \text{lamellar thickness} \)

\( n = \text{number of lamellar stacks} \)

\( X_n = \text{composition of component 1} \)

\( \Gamma_m = \text{density} \)

\( \sigma = \text{lamellar thickness distribution} \)

\( \Delta \rho = \text{electron density contrast} \)

\( q = \text{momentum transfer vector} \)

Defining Functions for the Form Factor and Structure Factor for paracrystalline stacks.

Paracrystalline Form Factor

\[ \text{ParaCrystalForm}[q, \delta] := (\sin(q \delta)/(q \delta))^2 \]

Paracrystalline Structure Factor

\[ w[q, \sigma] := \exp\left[ -\left( \frac{(\sigma^2 + q^2)}{2} \right) \right] \]

\[ \text{An}[q, d, \sigma, n] := 4w[q, \sigma]^2 - 2w[q, \sigma]^3 \cos[n q d] + w[q, \sigma]^4 + 2w[q, \sigma]^5 + 2w[q, \sigma]^6 + \cos[(n+1)q d] \]

\[ \text{Sn}[q, d, \sigma, n] := \text{An}[q, d, \sigma, n] - (n+1)w[q, \sigma]^2 \cos[n q d] \]

\[ \text{Zn}[q, d, \sigma, n] := (1-w[q, \sigma]^2)/(1+w[q, \sigma]^2 - 2w[q, \sigma] \cos[q d]) + \text{Xn} \text{Sn}[q, d, \sigma, n+1] \]

Paracrystalline Intensity

\[ \text{ParaCrystalIntensity}[q, d, \delta, \sigma, n, X_n, \Delta \rho, \Gamma_m] := 2\pi \Delta \rho^2 \Gamma_m \text{ParaCrystalForm}[q, \delta]/q^2 \]

\[ \text{Zn}[q, d, \sigma, n, X_n] \]
The actual plot for the Intensity, Structure Factor, and Form Factor
Manipulate[LogLogPlot[{ParaCrystalIntensity[q,d,δ,σ,n,Xn,Δρ,Γm],ParaCrystalForm[q,δ],Zn[q, d,σ,n,Xn]},{q,.008,.25},PlotRange->Full,ImageSize->Large,AxesLabel->"{q(Å⁻¹)","Intensity (a.u.)"},PlotLabel->"ParaCrystalline Stacks",PlotLegends->{"Intensity","P(q)","S(q)"}],{d,1,400},{δ,1,100},{σ,0,100},{n,1,100},{Xn,0,1},{Δρ,10⁻⁶,10⁻⁵},{Γm,.1,1}]

Artifically Perturbed Paracrystalline Stacks
ParaCrystalForm2[q_,Δρ_,δ_,σf_]:=2(1-Cos[q δ]Exp[-((q² σf²)/2)])
ParaCrystalIntensity2[q_,d,δ,σ,σf_,n_,Xn_,Δρ_,Γm_]:=2π Δρ² Γm
ParaCrystalForm2[q,Δρ,δ,σf]/q² Zn[q,d,σ,n,Xn]
Manipulate[LogLogPlot[{ParaCrystalIntensity2[q,d,δ,σf,n,Xn,Δρ,Γm],ParaCrystalForm2[q,Δρ ,δ,σf],Zn[q,d,σ,n,Xn]},{q,.008,.25},PlotRange->Full,ImageSize->Large,AxesLabel->"{q(Å⁻¹)","Intensity (a.u.)"},PlotLabel->"ParaCrystalline Stacks with Form Factor Dampening",PlotLegends->{"Intensity","P(q)","S(q)"}],{d,1,400},{δ,1,200},{σ,0,100},{σf,0,100},{n,1,100},{Xn,0,1},{Δρ ,10⁻⁶,10⁻⁵},{Γm,.1,1}]

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