

To the Graduate Council:

I am submitting herewith a dissertation written by Karthika Madathil Soman Pillai entitled “Controlling self-assembled block copolymer morphologies for tailored performance.” I have examined the final paper copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.

Gila E. Stein, Major Professor

We have read this dissertation
and recommend its acceptance:

S. Michael Kilbey II

Bamin Khomami

Mark Dadmun

Accepted for the Council:

Dixie L. Thompson

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(Original signatures are on file with official student records.)

Controlling self-assembled block copolymer morphologies for tailored performance

A Dissertation Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Karthika Madathil Soman Pillai

August 2023

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Abstract

The macroscale properties of block copolymers (BCP), for given block chemistries and polymer architecture, are governed by their self-assembled morphologies. Depending on the processing method employed, the BCP may have an equilibrium morphology or a kinetically trapped, non-equilibrium structure. Thus it is important to understand the factors controlling the equilibrium morphology and the process parameters influencing the kinetics of the self-assembly process. This dissertation consists of two research thrusts, wherein the structures of two block copolymer systems are tailored for applications as membranes and elastomers, respectively.

The first research thrust addresses the structure-processing-property relationships for solution processed films of a sulfonated pentablock copolymer, poly(*tert*-butylstyrene-*b*-hydrogenated isoprene-*b*-sulfonated styrene-*b*-hydrogenated isoprene-*b-tert*-butylstyrene). The solutions contain trace amounts of water due to the hygroscopic nature of sulfonated polymer. Structural characterization studies showed accelerated self-assembly kinetics in model polymer/organic solvent systems with controlled amounts of trace water. This is attributed to the disruption of hydrogen bonds between acid groups, which likely increases the chain mobility. It is also shown that solvent-cast films show a preferential orientation of domains at the surface. Both the bulk morphology and domain orientation is influenced by solvent polarity as well as processing parameters such as drying time. Finally, water vapor transport and proton conductivity measurements show that both bulk structure and surface orientation of domains impact the through-film membrane transport properties.

In the second research thrust, the design of interaction-tuned additives to tailor the morphology and mechanical properties of a commodity thermoplastic, poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS) is studied. The polymeric additives used are either polystyrene (PS) or poly(methyl methacrylate-*co*-cyclohexyl methacrylate) (PrC) which are athermal and enthalpically-compatible additives, respectively, for the polystyrene end-blocks in SEBS. The SEBS/PS formed miscible blends only at low molecular weight and loading of PS. The SEBS/PrC blends, in contrast, formed miscible blends systems with lamellar morphology for a broad range of PrC molecular weight and additive loadings. Consequently, the PrC additives can increase the modulus and yield stress of styrenic BCPs without impacting toughness. Additionally, the PrC additives can elevate the glass transition temperature of the PS block and maintain a high modulus at elevated temperatures.

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Chapter 1

Introduction

Part of the content in this chapter has been submitted for the publication:

K. Madathil, B. Upadhyay, W.K. Ledford, S.M. Kilbey, G.E. Stein. "Structure-property relations of triblock copolymer thermoplastics with interaction-tuned polymer additives."

Block copolymers (BCPs) consist of two or more chemically-distinct polymer chains linked by covalent bonds. Above the glass transition temperature of the blocks, the BCP is in a melt state, wherein the individual polymer chains can move around and rearrange themselves. Usually, the different blocks are enthalpically incompatible, causing a process termed microphase separation. Upon microphase separation, the BCP self-assembles into different morphologies. This ability of BCPs to self-assemble into well-defined nanoscale structures makes them an interesting class of macromolecules which can be used for design of materials with multiple desirable properties. BCPs are used for many commercial applications such as in coatings, adhesives and food packaging and are promising candidates for various nanotechnology applications such as microelectronics patterning and membrane-based separations(1). The macroscale properties of BCP films are dependent on

the chemistry of the blocks as well as the morphology of the self-assembled structure, where the latter can be influenced by processing method.

Block copolymer films are commonly prepared by melt processing. The equilibrium phase behavior of BCPs in the melt state is controlled by several factors, including: 1) enthalpic incompatibility between the blocks, controlled by χN , where χ is the the Flory-Huggins interaction parameter between two blocks and N is the degree of polymerization; 2) the volume fraction of each block; and 3) the architecture of the block copolymer (2). The mechanical and thermal properties of BCPs can also be tailored by blending the BCP with a homopolymer additive(3; 4). The miscibility and equilibrium morphology of BCP/homopolymer blend systems depend on additional enthalpic parameters determined by the Flory-Huggins interaction parameter between the additive polymer and each block of the BCP, as well entropic parameters which depend on the degree of polymerization and volume fraction of the homopolymer in the blend(5; 6; 7).

There are many applications where melt processing is not practical, so solution processing is used instead. For example, when BCPs have multiblock architectures or high χ parameter between blocks, microphase separation by melt processing is kinetically limited due to the slow inter-block chain diffusion. In solvent based processing, solvent molecules are introduced into the block copolymer system, allowing the polymer chains the mobility to rearrange. There are several different methods of solvent based processing such as solvent annealing, direct immersion annealing, and solution casting. Solvent annealing involves exposing a polymer film to solvent vapors. The solvent vapors swell the polymer film, allowing the chains the mobility to rearrange(8). Direct immersion annealing involves dipping a polymer film into a marginally good solvent that swells the polymer chains, imparting the mobility for rearrangement without dissolving the polymer films(9). Solution casting involves preparing a solution by dissolving the polymer in a solvent, then casting a film using this solution, followed by drying of the cast solution to obtain a dry polymer film. With all the solvent based processing methods, the final dry film structure is

controlled by the solvent selectivity to the blocks as well as both kinetics and the changing composition of the system during solvent evaporation. Thus the resulting films have non-equilibrium, process-dependent structures.

In this dissertation, the self-assembled structure and correlated macroscale properties of two BCP systems is studied. The first research direction addresses the structure-process-property relationship for ionic block copolymers prepared by solvent processing for membrane based applications. In the second research direction, we study the structure of BCP thermoplastics when blended with interaction-tuned polymer additives and the resulting structure-dependent mechanical properties.

1.1 Structure-processing-property relations in sulfonated block copolymer films

Ion-containing polymers have garnered a lot of research interest in the past several decades for use as membranes in fuel cells, batteries(10; 11; 12; 13) and water purification modules(14; 15; 16; 17). Ionic BCPs in which one of the blocks contains ionic or strongly acidic species are particularly interesting because in the self-assembled structure, the ion-containing microdomains act as transport pathways and the non-ionic microdomains provide the membrane with good mechanical properties(18; 19).

The BCP used for my studies is a commercial polymer trademarked as Nexar from Kraton Polymers, which has been marketed for various applications such as membranes for water desalination, humidification and dehumidification applications, and high performance breathable fabrics. Nexar, or poly(*tert*-butylstyrene-*b*-hydrogenated isoprene-*b*-sulfonated styrene-*b*-hydrogenated isoprene-*b*-*tert*-butylstyrene) (tBS-HI-SS-HI-tBS), is available with different levels of sulfonation. The grade used in this work has the midblock styrene partially sulfonated to 52 mol%. The partially sulfonated mid styrene block can take up water and act as channels for water and ion

transport while the tert-butyl styrene and hydrogenated isoprene blocks on each side allows for controlled swelling of the mid block and imparts the membrane with good mechanical properties. Numerous previous works have studied solution-cast Nexar films and shown that the structure of these films depends partly on the polarity of the casting solvent(20; 21; 22; 23; 24). However, a complete picture of the broad parameter space in the solvent processing of ionic BCPs and their impact on structure and transport properties is far from understood.

The equilibrium self-assembled morphologies attained by melt processing are largely controlled by the volume fraction f , which is fixed for a given BCP. In the solution state, the BCP morphology also depends on the solvent selectivity towards each block and the polymer concentration in the solution(25). A selective solvent will preferentially swell one block which increases the incompatibility between different blocks and changes curvature at the interface. A neutral solvent has similar interactions with all blocks, and can therefore improve the compatibility between the different blocks. Therefore, by controlling the selectivity of the solvent, we can access a wide range of morphologies using the same BCP(26) and we can also manipulate certain properties. For example, studies with AB type diblock copolymers have shown that reduction in solvent selectivity reduces the core block(A)-solvent(S) interaction parameter (χ_{AS}) and thus the interfacial tension between the core block and the solvent. This effect can influence aggregation number (number of chains per micelle) and core radius in the BCP. Compared with a B selective solvent, a neutral solvent decreases the aggregation number per micelle and the critical micelle temperature (27).

Solvent casting is a commonly used method for preparing BCP films. The structure of solution cast films can sometimes be predicted from the solution structure (24), although the translation of the solution structure to the final film structure is also greatly dependent on the solvent selectivity and evaporation rate(28; 29; 30). During solvent evaporation, the polymer chains can rearrange in a changing environment, where the polymer concentration is increasing. When a critical polymer concentration

is reached during drying, where the polymer chains no longer have mobility, a non-equilibrium film structure is obtained. There are various parameters that control rearrangement of micelles during solvent evaporation such as the χ parameter between the solvent and the non-selective block, wherein a sufficiently high χ would deter chain exchange between micelles(31). Another parameter is the solvent evaporation rate, which controls the drying time from the solution state to the dry film state(32). In cases where the blocks have chemistries with vastly different polarities, it is hard to find a single solvent that dissolves all the blocks, and so a mixed solvent system containing a polar and non-polar solvent components is often used. When using solvent mixtures, the changing composition of the solvent during evaporation due to different vapor pressures of each solvent component, and the resulting change in solvent selectivity must also be taken into account(33). Thus, solution casting process has a complex parameter space which depends on the polymer and solvent chemistry and the drying process.

In Chapter 2 and 3 of this dissertation, solution processing of Nexar is discussed. In Chapter 2, the effect of trace amounts of water taken up by the hygroscopic sulfonic acid group on the self assembly of Nexar in the solution phase and during solution casting process is investigated. In Chapter 3, the effect of solvent selectivity and solvent casting method on the bulk and surface structure, as well as the orientation of block domains in the surface layer is studied. The film structure is then correlated to through-film water vapor and proton transport measurements.

1.2 Design of interaction tuned polymer additives for BCP thermoplastics

Commodity block copolymer thermoplastics consist of glassy and rubbery blocks with high and low glass transition temperatures (T_g), respectively. The glassy domains act as physical cross-links in the rubbery matrix, producing a ductile material that

can also be reprocessed above the T_g of the glassy block. The mechanical properties of BCP thermoplastics depend on the volume fractions of the glassy and rubbery domains and the BCP architecture(34; 35). ABA type triblock copolymers, consisting of glassy “A” domains as the minority phase and rubbery “B” domains as the matrix, have been extensively studied and commercially used for wide range of applications including adhesives, coatings, footwear, automobile parts and medical devices (1; 36; 37). A common ABA triblock copolymer platform has polystyrene end-blocks and polyisoprene, polybutadiene or poly(ethylene-*co*-butylene) as the midblock (38; 39; 40; 41; 42; 43; 44; 45; 46; 47). Thermoplastics based on poly(ethylene-*co*-butylene) or poly(ethylene-*co*-propylene) midblocks are particularly attractive, as the saturated rubber provides these material with high oxidative and chemical stability(45).

Numerous efforts have been directed towards understanding how the mechanical properties of BCP thermoplastics can be improved by modifying their architecture. For linear BCPs, domain bridging and looped entanglements in triblock and pentablock (ABA and ABABA) architectures will enhance the mechanical properties relative to AB diblock copolymers, wherein the domains are held together only by chain entanglements and van der Waals interactions (48; 35; 49). In $(AB)_n$ type alternating BCPs consisting of n AB block pairs, the tensile strength and modulus both increase with increasing n due to the presence of constrained, interconnected domains (50; 51). Branched architectures, such as miktoarm star polymers, can be exploited to form self-assembled structures with continuous rubbery domains at high volume fractions of the glassy polymer (52; 53; 54), resulting in materials with high elasticity along with high modulus. Another molecular design strategy is to introduce physical cross-links in one of the BCP domains by incorporating low amounts of hydrogen-bonding(55; 56; 57; 58) or ionic (59; 60) comonomers. These cross-links can be incorporated in the soft block (55; 56; 57; 59; 60) or the glassy block (58) to enhance the mechanical properties.

Relatively fewer works have explored tailoring mechanical properties of BCPs by blending with polymeric additives, despite it being a simple strategy that could

be compatible with commercially available BCPs and common processing methods. The main challenge with this strategy is finding a polymer additive that forms miscible blends with the BCP. Blends of BCPs with a homopolymer having the same chemistry as one of block are miscible only at low loading and molecular weight of the homopolymer due to conformational entropy loss arising from stretching of chains(6). Whereas a homopolymer additive having attractive interaction with one of the blocks can form miscible blends even at high molecular and loading of the homopolymer in the blend(61). In Chapter 4 of this dissertation, a systematic study on the effect of enthalpic and entropic interactions on the miscibility, morphology and additive distribution in blends of an ABA type styrenic BCP with polymeric additives is studied. The BCP used is poly(styrene-*b*-ethylene butadiene-*b*-styrene) (SEBS), a widely used BCP elastomer. The effect of enthalpic interactions is studied by using two different additive chemistries which have attractive and neutral interaction with the polystyrene block respectively and the effect of entropic interactions is studied by varying the molecular weight and volume fraction of the additives. The blend systems studied in this chapter fall within the lamellar region of the phase diagram. The effect of additive distribution, miscibility and long range order of the self-assembled morphology on the tensile properties and thermal stability is studied. In Chapter 5, an outlook based on the fundamental understandings developed in this Chapter 4 is discussed. This chapter explores a broader phase diagram with respect to additive loading and the effect of additive molecular weight, additive chemistry and blend morphology on creep behavior. The potential of blending thermal additives with cylinder and sphere forming BCPs is also discussed in this chapter.

Chapter 2

Effects of trace water on self-assembly of sulfonated block copolymers during solution processing

The work described in this chapter has been published in:

K. Madathil, K.A. Lantz, M. Stefik, G.E. Stein. "Effects of trace water on self-assembly of sulfonated block copolymers during solution processing". ACS Appl. Polym. Mater. 2020, 2 (11), 4893–4901

K.A. Lantz acquired the scattering data in Figure [2.2](#). K. Madathil acquired the remaining scattering and TEM data, analyzed the data and wrote the paper.

2.1 Introduction

Block copolymers are an interesting class of materials due to their ability to self-assemble into well-defined nanoscale structures in the melt state and in solutions. In the melt state, the equilibrium phase behavior is controlled by several factors, including: 1) enthalpic incompatibility between the blocks, controlled by χN , where χ is the the Flory-Huggins interaction parameter between two blocks and N is the

degree of polymerization; 2) the volume fraction of each block; and 3) the architecture of the block copolymer (2). However, block copolymers with highly incompatible blocks have very slow diffusion rates in melts,(62) which makes it difficult to achieve equilibrium microphase-separated morphologies by thermal annealing. Consequently, solvent-based processing is often used for such systems, and the resulting morphologies are often different from the equilibrium state produced by melt processing.

Solution processing is commonly used for preparing membranes based on ionic block copolymer films for fuel cells(11; 12; 63; 64; 65), gas separations(66; 16) and water purification(15; 14; 67). In these block copolymers, one of the blocks contains ionic or acidic moieties which provide transport pathways for water, protons and ions, while the other neutral block (or blocks) is used to tailor mechanical properties. The lamellar (LAM) morphology has been extensively studied for applications in membranes(68; 69; 70; 71). The transport properties in this phase depend on various factors such as grain sizes and defect structures, which are controlled by relative volumes of each block(68; 69), the type of solvent used in processing(24; 72), and other process-related conditions such as thermal history(71). Highly defective LAM structures are similar to network-like phases and provide improved transport properties(69; 73; 71; 24). Furthermore, the LAM morphology occupies the largest fraction of the block copolymer phase diagram, so it is not very sensitive to changes in the relative volume fractions of each block due to missed targets in synthesis or swelling by solvents. In solvent processing there are numerous variables that determine the morphology of the final dry film, including solvent selectivity towards each block, polymer concentration in solution and solvent evaporation rate. A major challenge with solution-cast ionic block copolymers is understanding how these process variables will influence the film morphology.

In this work, we studied the effects of trace water on self-assembly of a sulfonated pentablock copolymer (SPC), poly(*tert*-butylstyrene-*b*-hydrogenated isoprene-*b*-sulfonated styrene-*b*-hydrogenated isoprene-*b*-*tert*-butylstyrene) (tBS-HI-SS-HI-tBS). The solution-state self-assembly of this SPC has been studied in prior

works, and depending on the polymer concentration and solvent polarity, the SPC can either dissolve into free chains or assemble into spheres, lamellae, and disordered nanoscale aggregates.(74; 75; 76; 24; 77). The structures of solution-cast SPC films have also been studied, and morphologies such as lamellae, cylinders and spheres have been observed depending on the solvent type used for casting(20; 21; 22; 23; 24). Trace water is difficult to avoid during the solution processing of SPC into films, as the material soaks up water when stored at ambient humidity due to the hygroscopic sulfonated midblock. (78; 75) As a result, the solution will contain small amounts of water (ca. 1-5 wt%) unless the polymer is dried prior to dissolution or the solution is dried prior to use. However, to our knowledge, the effects of trace water on solution-state SPC self assembly and subsequent processing into films has not been previously considered. In polyelectrolytes with strong interactions arising from intrinsic ion pairs, water provides mobility to the polymer chains by increasing the free volume and acting as a lubricant between the chains(79). This effect of water results in plasticization of polyelectrolyte films and it is a function of relative humidity.(80; 81; 82; 83; 84; 85). In sulfonated polymers, the presence of water drives the dissociation of sulfonic acid groups(86), resulting in a similar plasticizing behavior. Therefore, the enhanced mobility of polymer chains arising from the dissociation of sulfonic acid likely impacts the kinetics of SPC self-assembly in solution and the morphology that forms during subsequent film processing.

For the purposes of this work, trace water refers to molar ratios of water to sulfonic acid (λ) in the range of $\lambda = 0 - 3.2$, corresponding to water compositions of 0-1.9 wt% relative to the solvent. The investigation was split into two parts: First, the self-assembly of SPC in solution was monitored with time-resolved small-angle X-ray scattering (SAXS) as a function of λ . Second, the structure of solution-cast films was measured with SAXS as a function of λ in the solution, relative humidity during casting, and evaporation rate/casting method. These studies show that kinetics of solution-state self assembly is accelerated in proportion to λ , but film formation is

not very sensitive to λ and is largely determined by other process conditions such as evaporation rate and humidity.

2.2 Experimental

SPC Material The SPC (tBS-HI-SS-HI-tBS) was provided by Kraton Polymers as films(87). The midblock styrene was sulfonated to 52 mol%. The weight fractions of the SPC blocks were 20-10-40-10-20 (tBS-HI-SS-HI-tBS) and the overall molecular weight was approximately 60-70 kg/mol. The as-received films had a spherical SPC morphology with an SS core, as reported by others(83; 78) and confirmed with SAXS measurements. The films were soaked in deionized water (18.2 M Ω) for 24 hrs to extract byproducts from the sulfonation reaction, then dried in air for 24 hrs.

Polymer Solution Preparation for Time-Resolved SAXS Toluene (T, ACS grade, Fisher) and 1-propanol (nP, $\geq 99.0\%$, VWR) were dried at room temperature by storage over 30% w/v of molecular sieves (3 Å, 8-12 mesh, Acros Organics) for one week.(88) The SPC was dried in a vacuum oven at 80 °C for 24 hrs. The polymer mass was determined immediately after drying, and the material was stored under continuous vacuum while solvent mixtures were prepared. Unless otherwise indicated, all solvent mixtures were prepared with a 33:67 ratio of nP:T (wt:wt) denoted as nP₃₃:T₆₇. The amount of water required to produce λ of 1.6 or 3.2 was calculated for the measured mass of the dry polymer, and then added to the solvent mixture. The SPC composition in solution was 16 wt% in all cases. These solutions were tightly sealed and left undisturbed for 24 hrs to undergo complete dissolution.

Film Formation at Low and High Humidity. All solutions were prepared and stored inside a nitrogen purged glove box to avoid exposure to water. Solvent vials containing nP, T and water were taken into a glove box after purging the head space

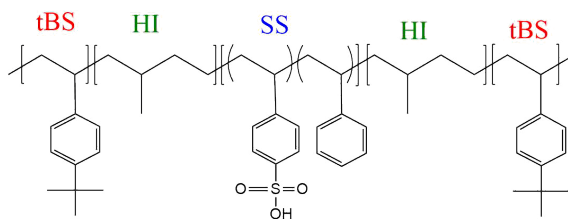


Figure 2.1: Structure of BCP, where tBS = *tert*-butylstyrene, HI = hydrogenated isoprene, and SS = partially sulfonated styrene (52 mol%). Molecular weight (pre-sulfonation): 15-10-28-10-15 kg/mol.

with argon. SPC films were loaded into a glove box immediately after drying. Two solutions were prepared with $\lambda=0$ and $\lambda=3.2$, each containing 16 wt% polymer by mass and nP₃₃:T₆₇ solvent. Films were drop cast both in the glove box (maintained below 3 ppm H₂O) as well as under ambient humidity. Drop casting was done on Kapton sheets inside a balance using 0.1 ml of solution that was aged for a specified time between 1-25 days. The mass was recorded as a function of time during the evaporation process, the solvent evaporation with time is shown in Figure A.1. For drop casting in ambient humidity, a small amount of solution was drawn from the stock solution in the glove box and taken out in a sealed vial. The thickness of drop-cast films (after solvent removal) were between 150 - 300 μm . Film preparation for studies on effect of evaporation rate/casting method were done by bar-coating on Kapton at ambient humidity using an Elcometer film applicator with gap heights ranging from 125 - 1125 μm . The thicknesses of bar-coated films (after solvent evaporation) were between 10 - 100 μm .

Small-Angle X-ray Scattering (SAXS) Time-resolved SAXS measurements of solutions were performed with a SAXSLab Ganesha at the University of South Carolina SAXS Collaborative. An 80 μL quantity of each solution was placed in a hermetically sealed sandwich cell with Kapton windows and stored under continuous vacuum maintained at 10^{-2} mbar throughout the 15 days of measurement to prevent the ingress of extraneous water. A Xenocs GeniX 3D microfocus source with a copper target was used to produce a monochromatic beam with a 0.154 nm wavelength. The sample to detector distance was 1 m. A Pilatus 300k detector (Dectris) was used to collect the 2D scattering patterns with nominal pixel dimensions of $172 \mu\text{m} \times 172 \mu\text{m}$. The data acquisition time was 30 min. All static measurements of solutions and dry films were performed at the Polymer Characterization Laboratory at the University of Tennessee, Knoxville. A Xenocs GeniX 3D microfocus source with a copper target was used to produce a monochromatic beam with a 0.154 nm wavelength. The sample to detector distance was 0.9 m for films and 1.8 m for solutions. A Pilatus3 R 300K

detector (Dectris) was used with nominal pixel dimensions of $172\text{ }\mu\text{m} \times 172\text{ }\mu\text{m}$. The data acquisition time was 3 min for films and 10 min for solutions. The two-dimensional images from each measurement (either instrument) were azimuthally-integrated with SAXSGUI to yield a one-dimensional scattering profile of intensity I (a.u) versus scattering vector q (nm^{-1}). In all the figures showing SAXS data, the plots from each data set have been offset vertically for clarity.

Transmission Electron Microscopy (TEM). TEM measurements were performed on drop cast films that were sectioned to a thickness of around 30 nm by a Leica EM FC7 microtome at $-30\text{ }^{\circ}\text{C}$. The sections were stained by sealing them in a centrifuge tube for 30 min with osmium tetroxide vapor, which segregates in HI and may reactively stain tBS. The obtained sample slices were imaged by a Zeiss Libra 200 HT FE MC transmission electron microscope.

2.3 Results and Discussions

2.3.1 Solution structure

The solution phase behavior of this SPC in polar, non-polar and mixed solvents has been studied in previous works(74; 75; 76; 24; 77). When the solution composition is 4-5 wt% polymer, the SPC structure is spherical micelles with an SS core(75; 76) at low solvent polarity, and changes to free chains(75) or inverted micelles with an SS corona(75) with increasing polarity of the solvent. In one of these examples, the SPC was dried before dissolving in the solvent,(75) but the other study did not specify the water content.(76) As polymer loading in the solvent is increased, the SPC can assemble into either ordered or disordered morphologies, depending on the solvent composition. For example, when the SPC is dissolved in nP:T solvent mixtures at a loading of 20 wt%, which includes 20 wt% water from storage at ambient humidity,

the structure after 2 days of dissolution at room temperature is lamellar (LAM) for 29-36 wt% nP and disordered (DIS) for 40-50 wt% nP.(24)

Building on these prior results, the first goal of the present study is to examine the kinetics of SPC self-assembly in nP:T solvent mixtures with and without trace water. For this purpose, we selected conditions that produce a LAM phase in solution, as this morphology is of particular interest for membranes. Unless otherwise stated, the solvent used for these studies was nP₃₃:T₆₇ (33 wt% nP, 67 wt% T) and the SPC loading in the solvent was 16 wt%. The molar ratio of water to sulfonic acid (λ) was varied in the range of 0 to 3.2. These conditions fall within the LAM region of the solution phase diagram at room temperature(24).

Figure 2.2 reports time-resolved SAXS data for solutions at room temperature with different amounts of trace water over a period of 15 days. The position of the primary peak (q^*) and its full width at half maximum (FWHM) were determined by fitting to a Voigt line shape. Figure 2.2A shows data for the nP₃₃:T₆₇ solvent with $\lambda = 0$. From 1-10 days, the SAXS spectra exhibit a single broad peak at $q^* = 0.19 \text{ nm}^{-1}$ (FWHM = 0.055 nm^{-1}), indicative of a poorly-ordered structure. By day 12, the q^* peak becomes narrower (FWHM = 0.027 nm^{-1}) and a higher-order peak emerges at $2q^*$, consistent with the formation of an ordered LAM structure. According to the Scherrer equation, grain size is proportional to $1/\text{FWHM}$, so the grain size approximately doubles over this time frame(89).

The time-resolved SAXS data were collected from solutions in tightly-sealed sandwich cells that were stored under vacuum over 15 days. To ensure that the transition from a poorly ordered structure to ordered LAM was not induced by a leak in the cell, *i.e.*, an undetectable level of solvent evaporation under the dynamic vacuum, several control experiments were implemented using solutions that were aged in sealed vials at ambient pressure for different aging times. These control experiments agree with the time-resolved studies in Figure 2.2A and confirm a transition from a poorly-ordered structure at shorter times (1, 5 and 11 days) to ordered LAM at longer times (21 days) when aged at room temperature (Figure A.2).

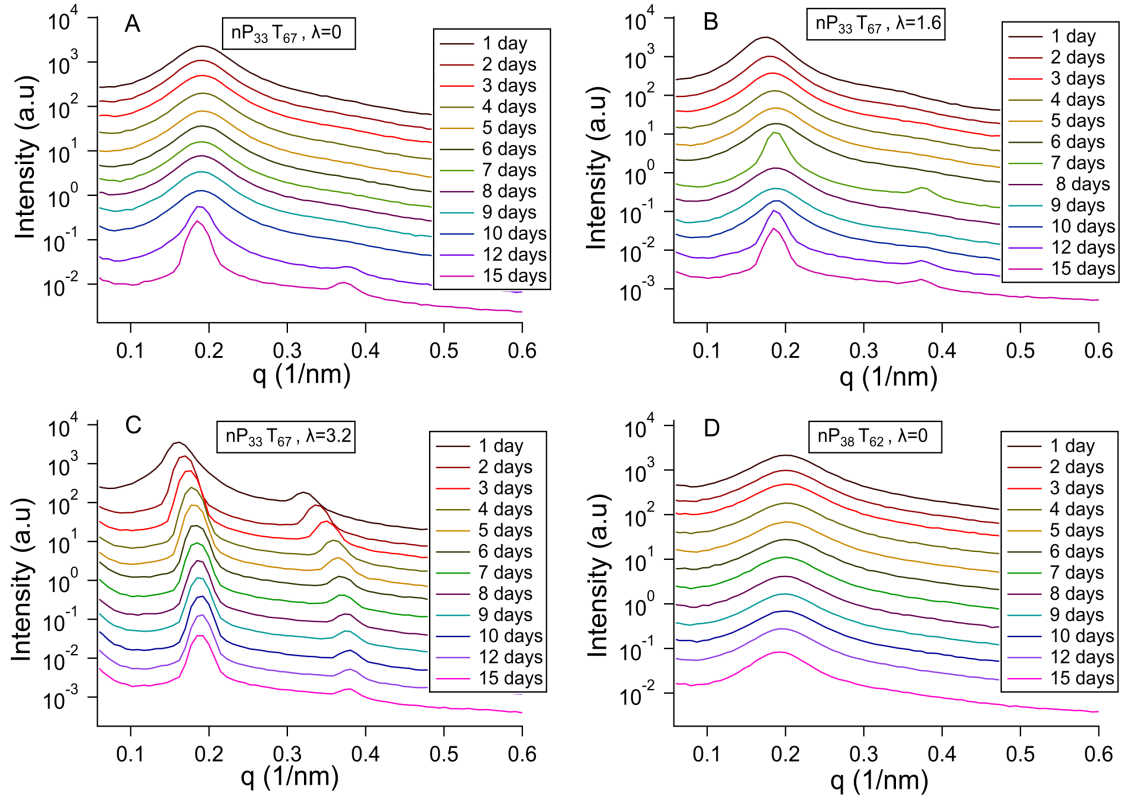


Figure 2.2: Time resolved SAXS measurements of 16 wt% SPC solutions in different solvent mixtures: A) $\text{nP}_{33}:\text{T}_{67}$, $\lambda = 0$; B) $\text{nP}_{33}:\text{T}_{67}$, $\lambda = 1.6$, C) $\text{nP}_{33}:\text{T}_{67}$, $\lambda = 3.2$, D) $\text{nP}_{38}:\text{T}_{62}$ $\text{nP}:\text{T}$, $\lambda = 0$.

The effect of water on SPC self-assembly was studied by adding trace amounts of water to the nP₃₃:T₆₇ solvent mixture. Figure 2.2B shows time-resolved data for solutions with $\lambda = 1.6$, corresponding with 0.9 wt% water in the solvent, and the results are similar to solutions with $\lambda = 0$. The initial structure is poorly ordered, as evidenced by a single broad peak at $q^* = 0.17 \text{ nm}^{-1}$ (FWHM = 0.051 nm^{-1}). By day 12, the q^* peak is sharper (FWHM = 0.019 nm^{-1}) and a higher-order peak is observed at $2q^*$, consistent with the formation of an ordered LAM phase. A second-order peak is also observed on day 7 for this sample, which then disappears by day 8 and reemerges by day 12. This behaviour was not observed for the experiments with $\lambda = 0$ or $\lambda = 3.2$ samples, which were repeated with consistent results, and the cause of this re-emergent behavior is unknown. Figure 2.2C shows time-resolved data for solutions with $\lambda = 3.2$, corresponding with 1.9 wt% water in the solvent. The SPC ordered into the LAM phase within 1 day, as evidenced by narrow peaks at $q^* = 0.16 \text{ nm}^{-1}$ (FWHM = 0.029 nm^{-1}) and $2q^*$. We also studied the solution structure for a solution with $\lambda = 8.7$ aged for 1 day, corresponding with 5.3 wt% water in the solvent, which showed LAM ordering with narrow peaks at $q^* = 0.14 \text{ nm}^{-1}$ (FWHM = 0.025 nm^{-1}) and $2q^*$. These data are included in Figure A.3.

In solutions containing trace water, the primary and higher-order peaks shift to larger q as a function of time (Figures 2.2B and 2.2C). Figure A.4 shows that the initial domain periodicity $d = 2\pi/q^*$ (at day 1) is swollen in proportion to water content. The domain periodicity remains constant with time in dry solutions, but in solutions with trace water, the domain periodicity decreases with time and converges with that of the dry solutions by day 15. This effect is only observed for solutions that were stored under vacuum for the 15-day duration of the measurement, and was not reproduced in control experiments where the solutions were aged in sealed vials at ambient pressure (Figure A.2). Thus, for solutions prepared with trace water and stored under vacuum, the reduction in domain spacing as a function of time is likely an effect of water evaporation.

The data in Figures 2.2A-2.2C demonstrate that water can accelerate the self-assembly kinetics in solution. However, it is unclear if this effect is associated with the chemistry of water rather than an increase in the solvent polarity. To test this point, a nP₃₈:T₆₂ solvent mixture with $\lambda = 0$ was prepared. As shown in the Supplemental Information (Table A.1), the Hansen Solubility Parameter of this mixture is approximately equal to that of nP₃₃:T₆₇ with $\lambda = 3.2$. Figure 2.2D reports the time-resolved SAXS data for this solvent mixture. From day 1 through day 15, the spectra show a single broad peak at $q^* = 0.12 \text{ nm}^{-1}$, similar to the data shown in Figure 2.2A for nP₃₃:T₆₇ with $\lambda = 0$. Therefore, we conclude that the accelerated kinetics of self-assembly is specific to the chemistry of water rather than changes in solvent polarity. In the absence of water, intermolecular hydrogen bonding between sulfonic acid moieties could hinder rearrangement of the polymer chains and trap poorly-ordered morphologies in the solution. With the addition of trace water to the solvent, the sulfonic acid can dissociate and provide the chains the mobility to rearrange into ordered structures. In hydrated films of sulfonated polymers, including SPC(78) and Nafion(90), infrared absorbance spectroscopy has been used to confirm the dissociation of sulfonic acid. While SAXS cannot detect sulfonic acid dissociation, the domain periodicity increases in proportion to λ (Table 2.1 and Figure A.3), providing indirect evidence that water is taken up by the SPC morphology.

To further substantiate the role of water on the solution phase self-assembly, we studied the change in solution-state structure when water is added to a dry nP₃₃:T₆₇ solution ($\lambda = 0$) with a disordered SPC structure. All solutions were aged at ambient pressure in sealed vials to avoid the complications of potential water/solvent evaporation. Figure 2.3 reports the SAXS data for these studies. The data labeled “dry solution” were acquired after aging for 1 day, and show a single broad peak at $q^* = 0.19 \text{ nm}^{-1}$ (FWHM = 0.055 nm^{-1}) that corresponds with a domain periodicity of $d = 33 \text{ nm}$. The data labeled “spiked solution” were acquired after the addition of

Table 2.1: Summary of solution-state structure as a function of solvent composition and trace water content. Solutions were aged for 1 day at room temperature. The position of the primary scattering peak is q^* , the SPC domain periodicity (or correlation length scale) is $d = 2\pi/q^*$, and FWHM is the full width at half maximum of the primary scattering peak.

nP:T	λ	q^* (nm ⁻¹)	d (nm)	FWHM (nm ⁻¹)
33:67	0	0.19	33	0.055
33:67	1.6	0.17	36	0.051
33:67	3.2	0.16	39	0.029
33:67	8.7	0.14	44	0.025
38:62	0	0.20	31	0.068

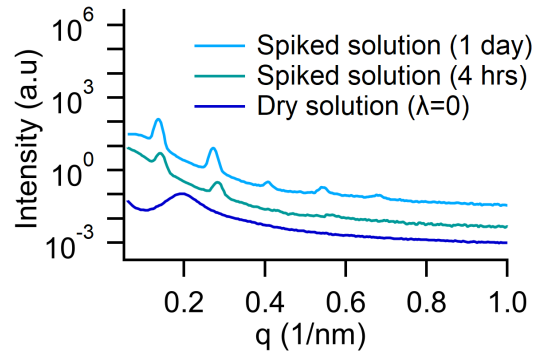


Figure 2.3: SAXS data for a dry solution with 16 wt% SPC in nP:T solvent mixture (33:67), and after “spiking” with water ($\lambda=3.2$) and aging for either 4 hrs or 1 day.

water to achieve $\lambda=3.2$. SAXS data recorded 4 hours after spiking with water showed two well-defined peaks at $q^* = 0.142 \text{ nm}^{-1}$ (FWHM = 0.022 nm^{-1}) and $2q^*$, consistent with a LAM structure having a domain periodicity of $d = 44 \text{ nm}$. After aging the spiked solution for a full day, the SAXS data show a primary scattering peak at $q^* = 0.134 \text{ nm}^{-1}$ (FWHM = 0.019 nm^{-1}) and four higher-order peaks at $2q^*$, $3q^*$, $4q^*$ and $5q^*$, consistent with a well-ordered LAM structure with domain periodicity of $d = 47 \text{ nm}$.

The SAXS data in Figure 2.2C and Figure 2.3 were both acquired from solutions with nP₃₃:T₆₇ and $\lambda = 3.2$, and the preparation differs only in regards to when water was added to the solution. For both cases, a LAM structure is observed within 1 day after the addition of water. However, the “water spiking” process produces a larger domain size and better order (more higher-order peaks) than mixing all constituents in a single step. This suggests that water is more readily taken up by the sulfonated domains when it is added after an initial SPC dissolution step.

2.3.2 Film structure

Previous works have examined the morphologies of solution-cast SPC films as a function of sulfonation level (26-52 mol%), solvent composition/polarity, and loading of SPC in the solution(20; 21; 22; 23; 24). When the solutions are prepared with 2-2.5 wt% SPC in non-polar solvents, such as cyclohexane, cyclohexane/heptane, toluene with low amounts of isopropanol, or cyclohexane/heptane with low amounts of tetrahydrofuran (THF), the resulting films have SS-rich domains in a tBS/HI matrix(20; 21; 22). This film structure appears to be partly templated by the solution-state structure, i.e., spherical micelles with an SS core and tBS/HI corona as discussed in the preceding section. The arrangement of the SS domains in the films is influenced by the solvent composition. As an example, when films are cast from mixtures of cyclohexane/heptane/THF, the connectivity of the SS domains increases with the amount of THF(22). When the solutions are prepared with 2-2.5 wt% SPC in

moderately polar solvents, such as THF, the resulting films can have coexisting LAM and hexagonally-packed cylinders (HEX) morphologies with the sulfonated midblock forming the continuous matrix (20; 22). For films cast from 16 wt% SPC in nP/T mixed solvents, a transition from LAM to network-like morphologies is observed with increasing nP content.(24). These LAM and network-like morphologies in films are produced from LAM and disordered structures in solution, respectively.

These findings suggest that the structure of the solvent-cast SPC films is correlated with the pre-assembled solution structure. However, the final film morphology of solution-cast block copolymer films is also controlled by structural transitions during the casting process(28; 29; 30; 91). In the specific case of polyelectrolyte-based block copolymers, trace water might influence the film formation process by disrupting intermolecular hydrogen bonding, as shown in the previous section for SPC in solution. To interrogate this point, we examined the film morphology as a function of λ in the casting solvent, ambient humidity during casting, and solvent evaporation rate.

Figure 2.4 shows the SAXS data of films that were prepared by drop casting from dry solutions ($\lambda=0$) and solutions with trace water ($\lambda=3.2$). The solutions were aged for 1-25 days prior to casting. The relative humidity (RH) during drop casting was either near-zero or ambient (38-55%). The evaporation rate was similar for all the drop-cast films (Figure A.1) at approximately 4 mg/min for the first 10 mins, followed by a continuously reduced rate until the films were dry.

Dry solutions aged for 1-5 days have a disordered structure with periodicity $d = 33$ nm (Figure 2.2A), and the corresponding films prepared by drop casting at near-zero RH have a poorly-ordered LAM structure with $d = 42$ nm: the SAXS data have a primary peak at $q^* = 0.15 \text{ nm}^{-1}$ with a broad secondary peak at $2q^*$ (Figure 2.4A). Dry solutions aged for more than 11 days have a LAM structure with $d = 34$ nm (Figure 2.2A), and the corresponding films prepared by drop casting at near-zero RH have a LAM structure with $d = 45$ nm: the SAXS data have a primary peak at $q^* = 0.14 \text{ nm}^{-1}$ and higher-order peaks at $2q^*$, $3q^*$ and $4q^*$ (Figure 2.4A). We note

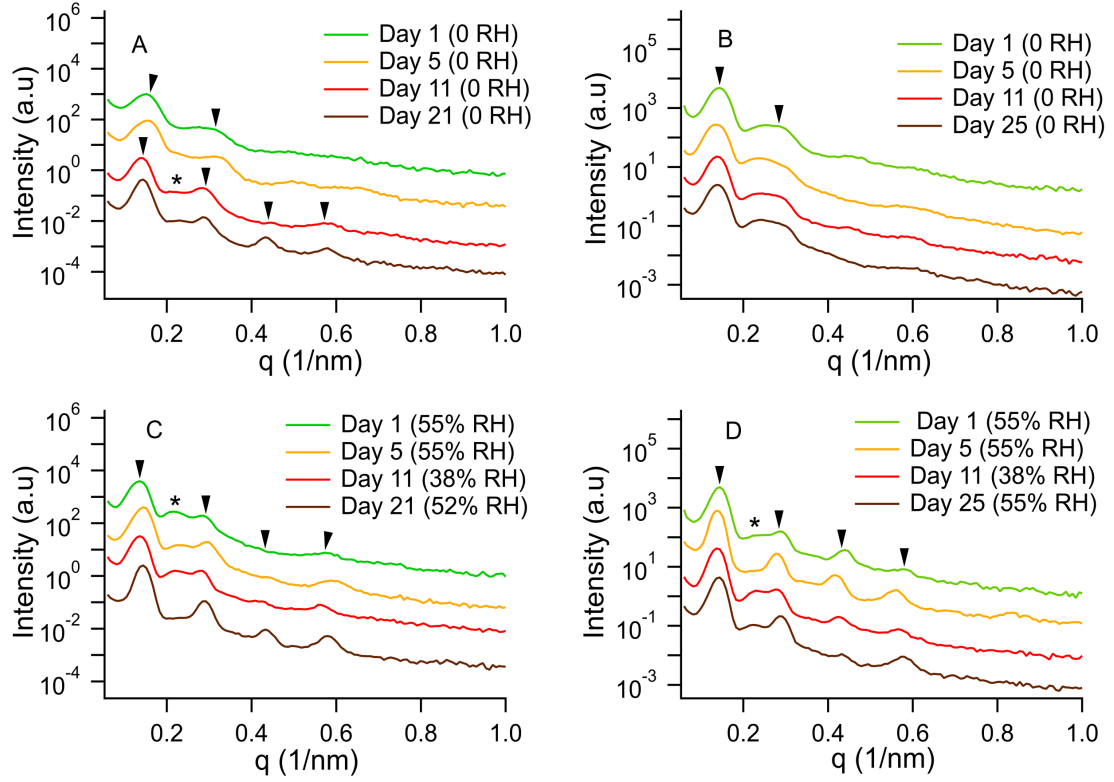


Figure 2.4: SAXS data for films produced by drop casting at near-zero relative humidity (A,B) or ambient relative humidity (C,D). Films were cast from dry solutions (A,C) and solutions containing trace amounts of water (B,D). The inverted triangles correspond to LAM peak positions, and the ‘*’ corresponds to the peak resulting from the minor HEX phase.

that the lamellar domain periodicity in films was always larger than that in solutions, which demonstrates that the nP:T mixture is a poor quality solvent for the SPC polymer and drives collapse of the chains. In films, the FWHM of the q^* peak is approximately 0.048 nm^{-1} when cast from solutions aged for 1-5 days and is reduced to 0.034 nm^{-1} when cast from solutions aged longer than 11 days.

The SPC solutions with trace water show an ordered LAM structure that does not change with aging time (Figure 2.2C). SAXS measurements of the corresponding films cast at 0% RH have a scattering peak at $q^* = 0.14 \text{ nm}^{-1}$, as well as a broad hump at higher q that appears to be the convolution of two peaks near $\sqrt{3}q^*$ and $2q^*$ (Figure 2.4B). These data are not consistent with a pure LAM or cylindrical phase: scattering from LAM will produce peak ratios of 1:2:3, while scattering from hexagonally-packed cylinders will produce peak ratios of $1:\sqrt{3}:2$. As TEM images of films cast from the 11-day aged solution show a mixture of “line” and “dot” domains (Figure 2.5A), the SAXS data likely reflect a mixture of LAM and cylindrical phases. The FWHM of the q^* peak in films is independent of the solution aging time and is approximately 0.04 nm^{-1} , which is higher than observed in the solutions with trace water (0.029 nm^{-1} for $\lambda=3.2$). These data show that adding water to the solution does not produce films with a well-ordered LAM structure if the casting is done at zero humidity. In the previous section, we noted that trace water will escape from solutions in a “sealed” cell when stored under vacuum, presumably due to a small leak in the cell. Therefore, we propose that water rapidly escapes from the wet film when cast at 0% RH. As a result, hydrogen bonds between sulfonic acid groups may inhibit the necessary chain rearrangements to maintain an ordered LAM structure as the film dries.

To examine the role of ambient humidity on film formation, a series of films were cast from solutions with and without trace water at 38-55% RH. SAXS data show an ordered LAM structure in all films, irrespective of the trace water content or aging time of the solution, as evidenced by scattering peaks at $q^* \approx 0.0136 \text{ nm}^{-1}$ and $2q^*$,

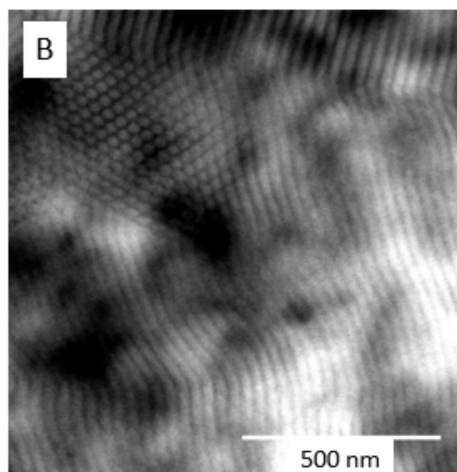
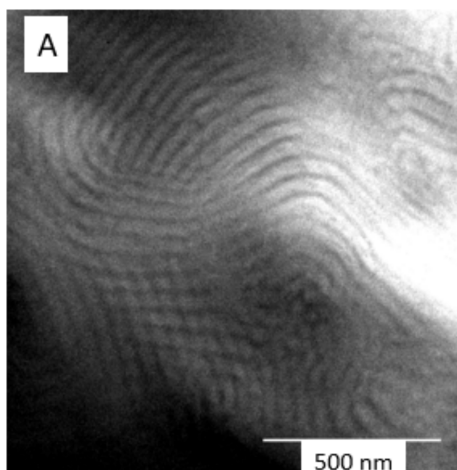


Figure 2.5: TEM images of drop cast films. A) Day 11 (0% RH) from Figure 2.4C. B) Day 11 (38% RH) from Figure 2.4D. The bright regions correspond to the SS domains, and the dark regions correspond to the tBS/HI domains after staining with osmium tetroxide.

$3q^*$ and $4q^*$ (Figures 2.4C and 2.4D). The relative peak intensities are different among the films, and in particular, there are several data sets in Figure 2.4C where the intensity of the $3q^*$ peak is very weak. Relative peak intensities are largely controlled by the form factor of the domains, i.e., the size and shape, so differences among the films could be explained by variations in water uptake and domain swelling. The SAXS data for most of the films show an additional peak at $q = 0.23 \text{ nm}^{-1}$, between q^* and $2q^*$, which is marked with a ‘ $\star$ ’ in Figures 2.4A, 2.4C and 2.4D. A TEM image for one of these cases, a film cast at 38% RH from a solution with trace water that was aged for 11 days, is consistent with a predominantly LAM structure and a minor cylindrical phase (Figure 2.5B). The minor HEX phase is likely due to changes in solution composition as the solvent evaporates.(30; 28).

All of the films develop a LAM structure, with evidence of a minor cylindrical phase in some cases, irrespective of trace water content, solution aging time, or relative humidity during film casting. The SAXS data for films processed under ambient humidity show at least four scattering peaks, indicative of a well-ordered LAM structure. In contrast, most of the SAXS data for films processed under dry conditions show few higher-order peaks. Furthermore, the FWHM of the primary SAXS peak is lower for films cast at ambient humidity as compared to films cast at 0% RH, which indicates that a humid environment produces a better defined LAM morphology than a dry environment. The TEM images are consistent with these observations: films cast under dry conditions develop a more tortuous, “fingerprint”-like LAM structure (Figure 2.5A), while films cast under humid conditions develop large ordered grains (Figure 2.5B). In order to understand how quickly the polymer can take up water under humid conditions, the increase in mass of a dry SPC film was recorded as a function of time at 38% and 55% RH. From Figure A.1 we can see that the timescale for water uptake by the dry polymer is comparable to the timescale of solvent evaporation. Therefore, a humid processing environment might facilitate the organization of a more ordered LAM phase by supplying water to the film as the organic solvents evaporate.

The effect of solvent evaporation rate on the final film structure was qualitatively examined by comparing drop-casting and bar-coating processing methods. The solution used for casting was prepared by adding trace water (to achieve $\lambda=3.2$) to a well-dissolved solution of 16 wt% SPC in nP₃₃:T₆₇ solvent, and then aging the solution for one day to obtain a highly-ordered LAM morphology. This approach is shown in Figure 2.3, where spiking an initially dry solution with water drove a rapid transition from a poorly ordered structure to the ordered LAM state. The time required for drying was varied through bar coating with a range of gap heights. The gap height controls the initial thickness and therefore volume of the wet film, so increasing the gap increases the drying time. We note that drying times could not be directly measured during bar coating, but visual inspection of the drying films confirmed the expected trend. The film cast with the smallest gap height appeared dry within seconds of casting, whereas the film cast with the largest gap height took several minutes to dry. In comparison, all the drop-cast films stayed wet for 10-15 minutes. Figure 2.6 shows the SAXS data for these bar-coated films as a function of final film thickness, as well as a drop-cast film for comparison (slowest evaporation rate). As the initial thickness of the wet film increases, producing longer drying times, a minor cylindrical phase emerges (marked by the *). The FWHM of the first-order scattering peak is in the range of 0.036 - 0.039 nm⁻¹ for the thin bar-coated films and 0.032 nm⁻¹ for the thick drop-cast films, which demonstrates that long drying times can improve lamellar order. Conversely, with the shortest drying times, the lamellar order is poorly developed and the formation of a minor HEX phase is suppressed.

The production of films with poorly-ordered LAM from the fast evaporation of solutions with well-ordered LAM seems counter-intuitive, as one might expect that fast evaporation would trap the ordered solution-state structure. However, the drying of the solution-cast film is a complex process: the film thickness contracts and the domain periodicity expands as solvent evaporates, and these processes likely disrupt the LAM ordering. When evaporation takes longer time, the chains have more time to rearrange into an ordered LAM structure.

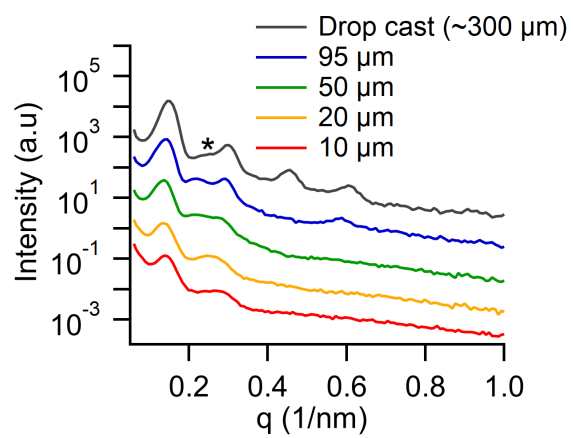


Figure 2.6: SAXS data for bar-coated films with different gap heights. The legend reports the dry film thickness, which is proportional to the initial wet film thickness.

Finally, another way to control the structure of solution-cast films is through sequential deposition of layers. When a new layer is deposited, solvent can diffuse into the underlying dry film and provide the mobility for rearrangements into a new structure. Figure 2.7 shows SAXS data for single-layer and 4-layer films. The solution was prepared by adding trace water (to achieve $\lambda=3.2$) to a well-dissolved solution of 16 wt% SPC in nP₃₃:T₆₇ solvent, and then aging the solution for one day to obtain a highly-ordered LAM morphology. Films were cast by bar-coating with a gap height of 125 μm . The dry thicknesses of the single-layer and 4-layer film were 20 μm and 65 μm , respectively. The SAXS data for the single-layer film show a primary peak at $q^* = 0.14 \text{ nm}^{-1}$ (FWHM = 0.047 nm^{-1}) and a second broad peak at $2q^*$, consistent with a poorly ordered LAM structure. The SAXS data for the 4-layer film show a primary peak at $q^* = 0.15 \text{ nm}^{-1}$ (FWHM = 0.033 nm^{-1}) and higher-order peaks at $2q^*$, $3q^*$ and $4q^*$, consistent with a well-ordered LAM structure. There are no signs of a minor cylindrical phase in either film. The process of sequentially depositing layers is similar to a direct immersion annealing process, wherein a polymer film is immersed in a marginal solvent that swells the polymer, imparting mobility to the chains for rearrangement without dissolving the entire film(9). With the immersion annealing process, the ordering of domains improved with increased immersion time. Sequential deposition of new layers increases the solvent exposure time of the previous layers, and therefore the results are similar to increasing the immersion annealing time.

2.4 Conclusions

We examined the effects of trace water on self-assembly of an SPC in solution and on the morphology of solution-cast SPC films. The SPC was dissolved at 16 wt% in a nP₃₃:T₆₇ solvent, and the molar ratio of water to sulfonic acid was varied from $\lambda = 0$ up to $\lambda = 3.2$. The structures in solutions and in films were characterized by SAXS.

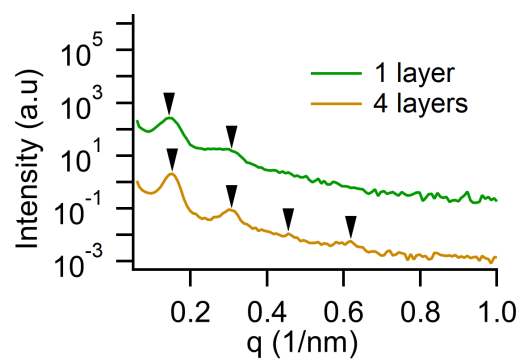


Figure 2.7: SAXS data for a single-layer and 4-layer bar-coated film.

In a dry solution, the SPC structure slowly evolves from a disordered state to ordered LAM over a period of approximately 10 days. With the addition of trace water to the solvent ($\lambda > 0$), the domain periodicity swelled in proportion to water content, demonstrating that the SPC takes up water. In solutions with $\lambda \gtrsim 3.2$, an ordered LAM structure was achieved within 1 day. The accelerated kinetics with trace water are attributed to dissociation of sulfonic acid, which likely increases the chain mobility by disrupting hydrogen bonds between acid groups. The addition of controlled amounts of water could thus be a potential technique to accelerate self-assembly kinetics and facilitate ordering in solutions of polyelectrolyte-based BCPs.

The amount of trace water in the solution was found to have little impact on the ultimate morphology of SPC films, but ambient humidity during processing did play a role. These points were demonstrated by examining the morphology of SPC films that were cast at either $\sim 0\%$ RH or ambient humidity from solutions with and without trace water. At $\sim 0\%$ RH, the SPC assembled into poorly-ordered LAM irrespective of water content in the casting solution. This outcome is explained by escape of water from the solvent to the dry atmosphere during the early stages of film drying. In contrast, when films were cast at ambient humidity from solutions with or without trace water, the ultimate morphology was well-ordered LAM. This effect is attributed to uptake of environmental water by the wet film. In addition to ambient humidity, the final film structure is also influenced by the time taken for the solvent to evaporate. Longer drying time leads to ordered LAM with a minor cylindrical phase, while shorter drying time traps a disordered LAM structure. These different outcomes are partly attributable to the timescales for water uptake by the SPC, as more water can be taken up by the SPC as evaporation rate is reduced. These findings demonstrate that water content offers a simple means to tune ordering kinetics during solution-casting of sulfonated block copolymers, providing access to both ordered and disordered morphologies. This may be useful in the design of SPC membranes, as poorly ordered LAM provide better transport pathways than well-ordered LAM.^(69; 73; 71; 24)

Chapter 3

Effects of processing methods on the morphology and domain orientation in sulfonated block copolymers

3.1 Introduction

Ionic block copolymers show promise for applications such as membranes for fuel cells and batteries(10; 11; 12; 13), water purification(14; 15; 16; 17) and gas separation(92; 16). In these polymers, one of the blocks contains ionic or strongly acidic species that provides pathways for water and ion transport, and the other non-polar block (or blocks) tailors the mechanical properties. For instance, in sulfonated block copolymers, water, methanol and proton transport is controlled by the composition and continuity of the sulfonated block (24; 16; 93). Broadly, it has been shown that transport properties in ionic block copolymers depends on the connectivity of the ionic domains(94; 95; 71; 69). For example, the gyroid morphology with 3D interconnected networks has been shown to be highly efficient for ion conduction (96; 97). Lamellar morphologies with poorly ordered, randomly oriented grains are shown to have

better domain connectivity and thus higher ionic conductivity as compared to well-ordered lamellae with large grain sizes(71; 69). In the poorly ordered lamellar morphology, high branch point defects and small grain sizes result in network like structures with well-connected domains and low tortuosity(73; 71; 69; 68). Cylindrical morphology with 1D transport pathways(98; 99) or disordered structures with poorly connected ionic domains (21), on the other hand, have poor transport properties. Ionic block copolymers films are often prepared by solvent based processing as microphase separation by thermal annealing can be difficult due to the slow inter-block chain diffusion arising from strong incompatibility between blocks and multiblock architectures. Solvent processed films have non-equilibrium structures determined by several parameters such as the polarity of the solvent and the solvent evaporation rate(24; 30; 28). Understanding process-structure relationship is thus necessary for designing efficient block-copolymer membranes.

Sulfonated block copolymers consisting of sulfonic acid groups tethered to one of the blocks is a promising material as membranes for fuel cells(18; 100). In particular, a sulfonated pentablock copolymer (SPC) with the trade name Nexar has been extensively studied as a low cost, environmentally friendly alternative to sulfonated fluorocarbon based copolymers which are the current benchmark material for proton exchange membrane fuel cells(100; 18). Nexar consists of a partially sulfonated styrene mid-block which can take up water and act as channels for water and ion transport. The sulfonated block is attached to poly(*tert*-butyl styrene) and hydrogenated polyisoprene blocks on each side which allows for controlled swelling and imparts the membrane with mechanical integrity and toughness. Previous works have studied the self-assembly of Nexar in solutions (74; 75; 76; 24; 77) of varying solvent polarity, and the final film structure(20; 21; 22; 23; 24) obtained after solvent casting and drying. These works have demonstrated that the final film structure is partly controlled by the pre-assembled structure in the solution. The translation of structure from solution to film is also dependent on the casting process. As an example, previous work from our group showed that for films prepared by bar coating,

the final film structure depends on the gap height of the bar(101). Solutions having lamellar structure produced films with poorly ordered structures when cast using a low gap height, but produced films with ordered lamellae when gap height was increased to 1000 μm . By increasing the gap height, we are essentially increasing the drying time and allowing the polymer chains longer time to translate from the solution structure to film structure. Films with lamellar structures could also be achieved by using the process of sequentially depositing layers of polymer solution after the previously deposited layers are dried. When a new layer is deposited, solvent can diffuse into the underlying dry film, re-exposing the polymer chains to the solvent thus providing mobility for rearrangements. Thus, both the gap height and the number of deposited layers impacts the final film structure(101).

Self-assembled block copolymers can also develop domains with preferred orientation during solvent processing(93). Such orientation effects are known to result in anisotropy in ion transport properties in the through-plane and in-plane direction(102; 103; 104; 105; 106; 107). Specifically, for self-assembled structures with 2D conducting pathways such as lamellae, the orientation of domains parallel to the plane of the film results in significantly lower conductivity in the through-plane direction compared to the in-plane direction(106; 107; 108; 109). Therefore, it is also important to understand how structural anisotropy is formed in films during solvent processing. Previous works have shown that the bulk structure of the film depends on both the solvent quality and the casting process, however the effect of these process parameters on the surface structure and how it defers from the bulk structure has not been explored before, to the best of our knowledge.

In this work, we show the effect of solution structure and casting process on the final film structure of Nexar, poly(*tert*-butylstyrene-*b*-hydrogenated isoprene-*b*-sulfonated styrene-*b*-hydrogenated isoprene-*b*-*tert*-butylstyrene) (tBS-HI-SS-HI-tBS). Both the bulk and surface structures of the film are studied as function of solvent quality and the film casting process, and compared with through-film measurements of proton conductivity and water vapor transport rate. Using these data, we identify

a solvent that produces "ideal" bulk and surface structures for through film transport properties.

3.2 Experimental

SPC Material The sulfonated pentablock copolymer (SPC), poly(*tert*-butylstyrene-*b*-hydrogenated isoprene-*b*-sulfonated styrene-*b*-hydrogenated isoprene-*b*-*tert*-butylstyrene) (tBS-HI-SS-HI-tBS) was provided by Kraton Polymers as films(87). The midblock styrene was sulfonated to 52 mol% per the manufacturer. The weight fractions of the SPC blocks were 20-10-40-10-20 (tBS-HI-SS-HI-tBS) and the overall molecular weight was approximately 60-70 kg/mol. The as-received films had a spherical morphology with an SS core and tBS/HI matrix, as reported by others(83; 78) and confirmed with SAXS measurements. The films were soaked in deionized water (18.2 MΩ) for 24 hours to extract byproducts from the sulfonation reaction, then dried in air for 24 hours.

Polymer Solution and Film Preparation Polymer solutions were prepared by dissolving the polymer in a mixed solvent of Toluene (T, ACS grade, Fisher) and n-Propanol (nP, ≥99.0%, VWR). The solvents are denoted as nP_X, where X is the wt% of n-propanol in the nP/T solvent mixture. Water taken up by the film under ambient humidity was determined prior to polymer dissolution, by measuring the mass of the polymers after drying and again under ambient humidity. Water was then added to the polymer solutions to adjust the value of λ to 8, where λ = moles of water:moles of sulfonic acid group. This step was done to ensure all the solutions have the same value of λ , as we saw in our previous work (Chapter 2) that self-assembly kinetics and the periodicity of the self-assembled structure in the solution depends significantly on the amount water present in the solution (101). The solutions were allowed to stand for two days before doing SAXS measurements. All films were cast on a Mylar sheet in a controlled humidity chamber maintained at $55 \pm 2\%$ RH using

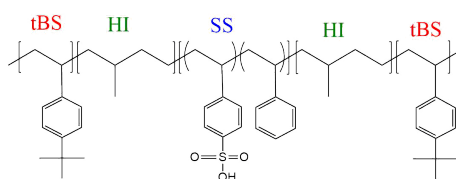


Figure 3.1: Structure of BCP, where tBS = *tert*-butylstyrene, HI = hydrogenated isoprene, and SS = partially sulfonated styrene (52 mol%). Molecular weight (pre-sulfonation): 15-10-28-10-15 kg/mol.

an Elcometer film applicator with different gap heights ranging from 100 μm to 1000 μm . Two and three layered films were prepared by sequential coating steps wherein a new layer of solution was deposited after the previous layer was allowed to dry in the controlled humidity chamber.

Small-Angle X-ray Scattering (SAXS) A Xenocs GeniX 3D microfocus source with a copper target was used to produce a monochromatic beam with a 0.154 nm wavelength. The sample to detector distance was 0.9 m. A Pilatus3 R 300K detector (Dectris) with nominal pixel dimensions of 172 $\mu\text{m} \times 172 \mu\text{m}$ was used for data acquisition. The data acquisition time was 3 min for all measurements. In all the figures showing SAXS data, the plots from each data set have been vertically offset for clarity.

Transmission Electron Microscopy (TEM) TEM measurements were performed on films that were sectioned to a thickness of around 30 nm by a Leica EM FC7 microtome at -30 °C. The sections were stained by placing them in solution of aqueous lead acetate for 7 hours, which selectively stain the sulfonated styrene domain. The obtained sample slices were imaged by a JEOL JEM 1400-Flash transmission electron microscope with an acceleration voltage of 120 kV.

Water vapor transport rate Water vapor transport rate was measured using the upright vial method at 22°C and RH below 10%. 1 ml of DI water was added to 4 ml vials, leaving head space over the water. The film samples were tightly fastened between the vial and the cap in order to create a semipermeable seal for water vapor transport. Additionally, a parafilm seal was tightly wrapped around the lower edge of the cap to minimize water escape through any pathway other than through the film. The fastening of the cap and para film was done within 10-15 s of placing the film on the vial and this vial set up was immediately placed on a weighing scale. Mass was

recorded over a period of 1 hour and then mass loss was calculated relative to the initial measurement (at 10-15 sec).

Water uptake Water uptake was calculated using Eq 3.1. W_{dry} refers to the mass of the film after drying in the oven for 12 hrs at 90°C. The films were weighed within 10 secs after taking out of the oven. W_{humid} for samples under ambient conditions refers to the mass of the samples after equilibrating to ambient temperature (25°C) and humidity (34% RH) for more than an hour. W_{humid} for samples soaked in water refers to mass of samples after equilibrating to ambient conditions, followed by soaking in DI water for 10 minutes.

$$\text{Water uptake} = \frac{W_{\text{humid}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (3.1)$$

Electrochemical Impedance Spectroscopy For measurements of samples with low water uptake (25 and 50 wt%), the films were allowed to equilibrate to ambient temperature (25°C) and humidity (34% RH) for over an hour. Samples used for measurements were obtained by cutting out circular disks ($A = 0.94 \text{ cm}^2$) from the films. Film thickness was measured using a caliper with an accuracy of 10 μm . The films were sandwiched between two stainless steel electrodes to obtain through-film configuration. Data were collected over a frequency range of 10 Hz to 1M Hz and 10 mV amplitude. Nyquist plots made using these data are shown in Figure B.6. As there weren't many points in the semicircle region of the Nyquist plot, to obtain a good fit to an electrical circuit model, the bulk resistance was estimated by extrapolating a straight line from the beginning of the semicircle to get the Z' intercept where $-Z''$ is zero, as shown in the insets of Figure B.6. For measurements of samples with high water uptake (greater than 100 wt%), the samples equilibrated at ambient humidity were soaked in water for 10 min, and this produces a water uptake in excess of 100

wt% relative to dry film mass. Thickness of these samples were measured after taking the soaked samples out of water and patting dry with a wipe.

3.3 Results and Discussions

3.3.1 Bulk structure

In a previous study we reported the structure of bar coated SPC films cast using n-Propanol/Toluene (nP_33) mixed solvent with 16 wt% SPC in solution, where the solution state structure was lamellar. The gap height for bar coating was set to 250 μm , and the films appeared dry within seconds. These ‘fast dried’ films formed a poorly ordered structure. When the gap height was increased to over 1000 μm , the drying time increase to over 30 min. These ‘slow dried’ films had a ordered lamellar morphology. Sequential depositing of four layers of casting solution on a previous layer after drying, also resulted in the formation of ordered lamellar structure(101).

In the supplementary information of this work, presented in Appendix B, we show that with the ‘fast drying’ process, the templating effect from solution to film structure is lost, wherein films cast from different solution structures result in similar poorly ordered film structure. Figure B.1 maps out the solution structure of this SPC in nP/T mixed solvent with varying solvent composition and polymer concentration, based on the solution SAXS data shown in Figure B.2. The SAXS data for the corresponding fast dried films cast from these solutions using a bar coater with a gap height of 250 μm is shown in Figure B.2. These data show that these fast dried films show a similar poorly ordered structure for a broad range of casting solution composition, despite the casting solution having distinctly different structure. TEM data for select films is shown in Figure B.4, which shows disordered structure consisting of SS domains in a matrix of tBS/HI.

Next, we study the effect of the ‘layering process’ of sequentially depositing casting solution, on films cast from two selected solution compositions, each having different

solvent selectivities towards the SPC blocks, on both the bulk as well as the surface structure of the solution cast films. All the films structures discussed in the following sections were cast from solutions containing 15 wt% SPC in the solution. For this study, SAXS experiments were done in two different configurations as shown in Figure 3.2. The ‘ $\perp$ ’ configuration is used to probe the bulk structure which is discussed in this section.

Figure 3.3 reports the SAXS data for films cast using nP/T mixed solvents with two different compositions represented as nP_30 and nP_50. The films were cast using 1000 μm or 100 μm gap height and prepared by depositing single (1000 μm), double (1000 $\mu\text{m} \times 2$) or three layers (1000 $\mu\text{m} \times 3$ and 100 $\mu\text{m} \times 3$). The nP_30 solvent is a non-polar solvent selective to the tBS and HI groups. The nP_50 solvent has neutral selectivity towards the SPC blocks(110).

The nP_30 solvent composition resulted in cylindrical solution structure with a periodicity of 49 nm and is near the border of cylinder to lamellar phase boundary wherein transition to LAM phase occurs with increase in nP content in the solvent (Figures B.1 and B.2). For the films cast using this solvent, the single layer film showed a poorly ordered structure having primary peak at $q^* = 0.136 \text{ nm}^{-1}$ corresponding to a periodicity of 46.2 nm, and a broad secondary peak. The SAXS profile and periodicity of this single layer film is same as that of the single layer film with 250 μm gap shown in Figure B.3. The double layer film showed an ordered lamellar structure with three higher order peaks and periodicity of 43.6 nm. The three layer films cast using both 1000 μm and 100 μm gap heights showed an ordered lamellar structure with a periodicity of 41.6 nm.

Figure 3.3 b shows the SAXS data for the films cast using nP_50 casting solvent. The nP_50 composition resulted in a solution structure with scattering profile characteristic of solutions composed of dissolved polymer chains that are not self-assembled (Figure B.2). The films cast with single layer (1000 μm) showed primary peak at $q^* = 0.167 \text{ nm}^{-1}$ corresponding to a periodicity of 37.5 nm. The SAXS data for all the films cast from this solution showed a disordered structure with oscillations

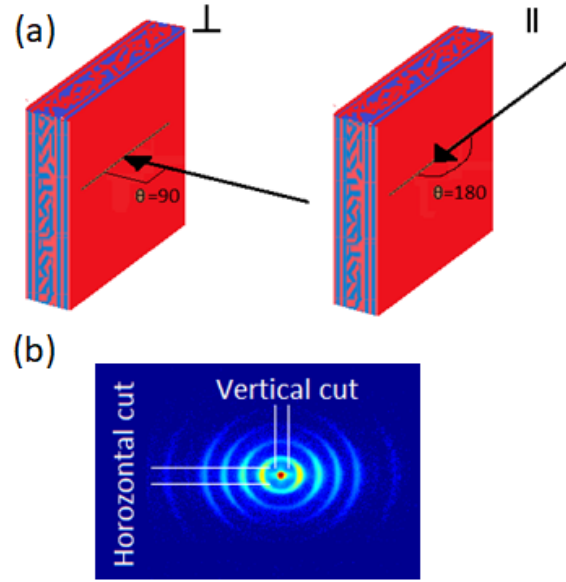


Figure 3.2: (a) Illustration for the ‘ $\perp$ ’ and ‘ $\parallel$ ’ configurations where the arrow represents the X-ray beam (b) Example of a 2D scattering profile in grazing configuration showing preferential orientation of the domains parallel to the plane of the film. Vertical cut and horizontal cut regions contain scattering from domains oriented perpendicular and parallel to the plane of the film, respectively.

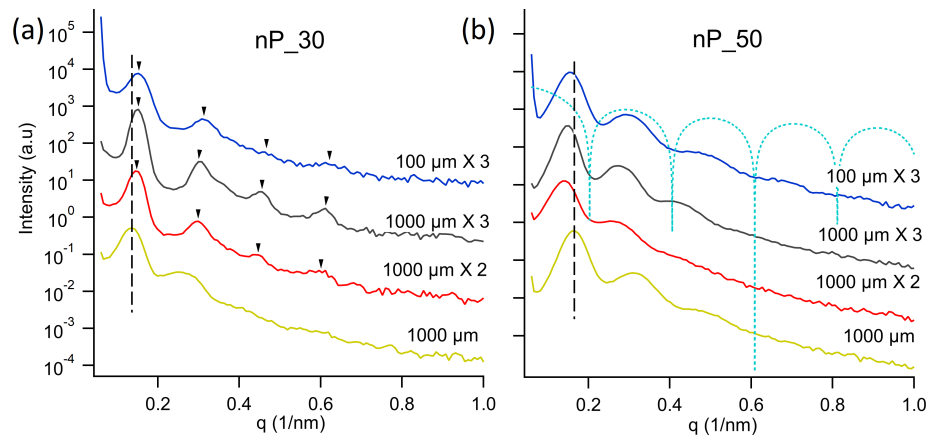


Figure 3.3: Transmission SAXS of films cast using 1000 μm gap height by depositing single, two ($\times 2$) and three ($\times 3$) layers and 100 μm gap height by depositing three ($\times 3$) layers cast using (a) nP_30 and (b) nP_50 solvents. The inverted triangles indicate peak positions for lamellar morphology.

in intensity arising from the form factor, which arises from the shape of the domain. We demonstrate this point in Figure 3.3b by plotting the lamellar form factor for the 100 $\mu\text{m}\times 3$ film using 35.4 nm as the periodicity which is calculated using $q^* = 0.159 \text{ nm}^{-1}$ from the first order peak and a domain width which is 75% of the periodicity. Figure 3.4 shows the TEM images of the 1000 $\mu\text{m}\times 3$ films cast using nP_30 and nP_50 solvents with ordered lamellar structure and poorly ordered structure, respectively. These images confirm the results from the SAXS data and show that the films prepared by sequential deposition results in structures which are dependent on the solvent selectivity.

These results show that film structure is greatly influenced by both the solvent composition and the casting process. The single layer films show a poorly ordered structure with both neutral and tBS/HI casting solvents. The three layer films with the nP_30 solvent, with the solution composition near the boundary of lamellar and cylindrical phase, forms a highly ordered lamellar morphology, whereas the films cast from the nP_50 solvent, with no self-assembled structure in solution, forms a poorly ordered network like morphology. It is worth noting that films cast using nP_50 solvent appears insensitive to processing conditions, while the films cast using nP_30 is highly sensitive. The periodicities are quite different when cast from different solvents, even when they have the same poorly ordered morphology. In the solution phase, the swelling of the blocks depends on the solvent composition and during drying the domains may expand or contract to move towards their equilibrium periodicity. The non-polar solvent composition, nP_30, is expected cause greater swelling of both the SS and the tBS/HI domains, compared to the neutral solvent composition of nP_50 (76). This could be the reason why the periodicity of the poorly ordered structure in the film cast using 1000 μm gap height from the nP_30 solvent (46.2 nm) is much larger than that of the film cast from the nP_50 solvent (37.5 nm). During sequential deposition of layers we are increasing the solvent exposure time of the previously deposited layers allowing mobility to the chains for rearrangement without dissolving the film. From Figure 3.3 we observe that for films cast from the

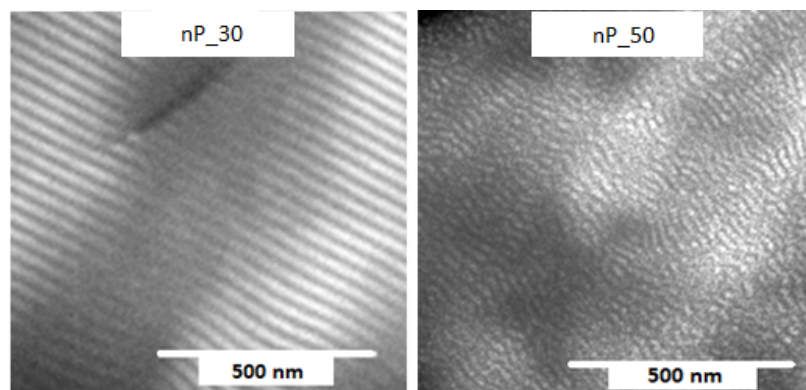


Figure 3.4: TEM images for films cast using 1000 μm gap height by depositing ($\times 3$) layers. The dark region corresponds to the SS domains and light regions correspond to the tBS/HI domains.

nP_30 solution, the sequential layering results in smaller periodicity and films cast from the nP_50 solution results in larger periodicity, compared to films cast with a single layer.

3.3.2 Surface structure

During solvent evaporation the surface layer is expected to be relatively dry with high polymer concentration due to rapid evaporation of the solvent at the air/polymer interface and the relatively slow solvent diffusion through the film (111; 112). This results in the formation of a ‘skin layer’ at the surface, and the solvent trapped in the bulk of the film depletes via diffusion through this polymer rich skin layer. We hypothesize that depending on the selectivity of the solvents to the SPC blocks, the polymer domains in the skin layer would show preferential orientation due to the sharp change in solvent concentration at the bulk/skin interface, whereas the domains in the bulk would remain unoriented. To check for orientation of domains within the films, we compare the SAXS measurements with the X-ray beam directed perpendicular to the plane of the films to measurements with the beam making a grazing angle to the plane of the film, illustrated as the ‘ $\perp$ ’ and ‘ $\parallel$ ’ configurations respectively in Figure 3.2 a. For the data obtained by SAXS measurements from the ‘ $\parallel$ ’ configuration, 1D SAXS patterns were obtained by integrating the intensities in the vertical cut and horizontal cut directions as shown in Figure 3.2 b. Note that the SAXS measurements in the $\parallel$ configuration can show the presence of oriented domains in the film, but it does not establish the location of the oriented domains within the film. Though, it is logical to assume that the oriented domains, if present, are on the surface of film.

Figure 3.5 shows the 2D SAXS pattern with measurements done in the ‘ $\parallel$ ’ configuration for single layer (1000 μm) and three layer (1000 $\mu\text{m} \times 3$ and 100 $\mu\text{m} \times 3$) films cast from both nP_30 and nP_50 solvents. All the films cast from the nP_30 solvent show higher intensity along the horizontal direction in the 2D SAXS data, indicating orientation of the domains parallel to the plane of the film. Both the three

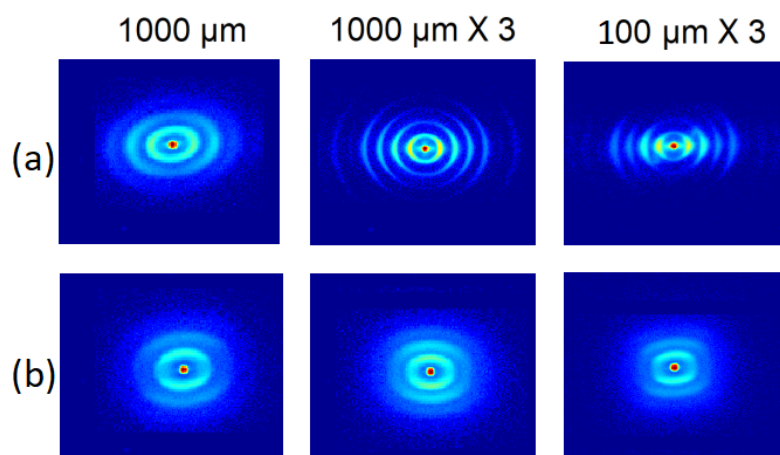


Figure 3.5: 2D scattering profiles for measurements in the ‘||’ configuration for films cast using (a) nP₃₀ and (b) nP₅₀ solvents

layer ($1000\text{ }\mu\text{m}\times 3$ and $100\text{ }\mu\text{m}\times 3$) films, which show an ordered lamellar morphology in the bulk, also show a much sharper contrast in intensity between the horizontal and vertical direction, indicating highly oriented domains, compared to the single layer ($1000\text{ }\mu\text{m}$) film which has a poorly ordered bulk structure. All the films cast from the neutral nP_50 solvent, on the other hand, show higher intensity along the vertical direction in the 2D SAXS data, indicating orientation of the domains perpendicular to the plane of the film. These intensity profiles in the SAXS patterns for the nP_30 and nP_50 solvents makes sense because the selective nP_30 solvent would cause selective wetting of the non-polar tBS/HI domain at the skin/bulk interface resulting in orientation of domains parallel to the plane of the film in the skin layer. Whereas when the solvent that has neutral selectivity to the tBS/HI and SS blocks, the block domains are expected to orient perpendicular to the plane of the film in the skin layer.

The elliptical pattern of the 2D SAXS profiles indicates the domains oriented parallel to the plane of the film shows a reduced periodicity compared to domains oriented in other directions. Such reduction in periodicity in the vertical direction (along the thickness of the film) has been observed in previous works with solvent cast films (113) and after direct immersion annealing (DIA) (114). Heinzer et al. controlled the formation of skin layer by performing solvent casting with and without a sweep gas, which allowed rapid removal solvent from the surface, and a third case where a reservoir is solvent is left in the film drying chamber which suppressed the formation of skin layer. They demonstrated that when rapid solvent removal at the surface is allowed, resulting in the formation of skin layer, a pronounced compression of domains in the vertical direction is observed(113). Longanecker et al. showed that the films formed after rapid solvent removal following DIA showed a reduced periodicity of the domains oriented parallel to the plane of the film, compared to thermal annealed films. During DIA there is reduction in the junction point density along the domain interface, and during rapid solvent removal the chains collapse in the vertical direction without significantly altering the lateral chain density resulting in the reduced periodicity(114).

In Figure 3.6 we show the 2D SAXS profiles from SAXS measurements in the ‘||’ and ‘⊥’ configurations for the 1000 $\mu\text{m}\times 3$ films cast using nP_30 and nP_50 solvents. To illustrate the distinct domain orientations captured by the ‘||’ and ‘⊥’ configurations more clearly, we plot the intensity as a function of azimuth angle for the first order ring from the 2D SAXS data, for both the configurations. The data from the ‘⊥’ configuration shows the uniform intensity as a function of azimuth angle, for films cast using both nP_30 and nP_50 solvents, indicating an unoriented bulk structure. The data from the ‘||’ configuration shows a clear variation in intensity along the azimuth, with the region showing maximum and minimum intensity flipped for the films cast from the nP_30 and nP_50 solvents, respectively. These results show the presence of oriented domains in the surface layer of solvent cast films, and that the direction of domain orientation is dependent on the solvent selectivity towards the blocks. Also, from the peaks in the intensity vs azimuthal angle plots, we note that the scattered intensity from the films cast from the nP_30 solvent is about ten times higher than the films cast from the nP_50 solvent, despite the films having similar thickness. This is due to the fact that of all the domains that are perpendicular to the plane of the film, only a fraction of them make a small angle with the X-ray beam in the ‘||’ configuration.

Figure 3.6 also shows the 1D SAXS data obtained by azimuthal integration of the 2D SAXS data in the ‘⊥’ configuration, and by integrating intensity in the vertical and horizontal cut region of the ‘||’ configuration as shown in Figure 3.2 b. The 1D SAXS data from the ‘⊥’ configuration and vertical cut region of the ‘||’ configuration shows similar profiles and periodicity for films cast from both nP_30 and nP_50 solvents. For the films cast from nP_30 solvent the vertical cut region has lower scattered intensity, which should mostly correspond to scattering from the unoriented lamellae in the bulk. For the films cast from nP_50 solvent the vertical cut region has high intensity scattering, which should correspond to scattering from domains oriented perpendicular to the plane of the film at the surface. The horizontal cut of the 1D SAXS data in the ‘||’ configuration, corresponds to the high scattered intensity region

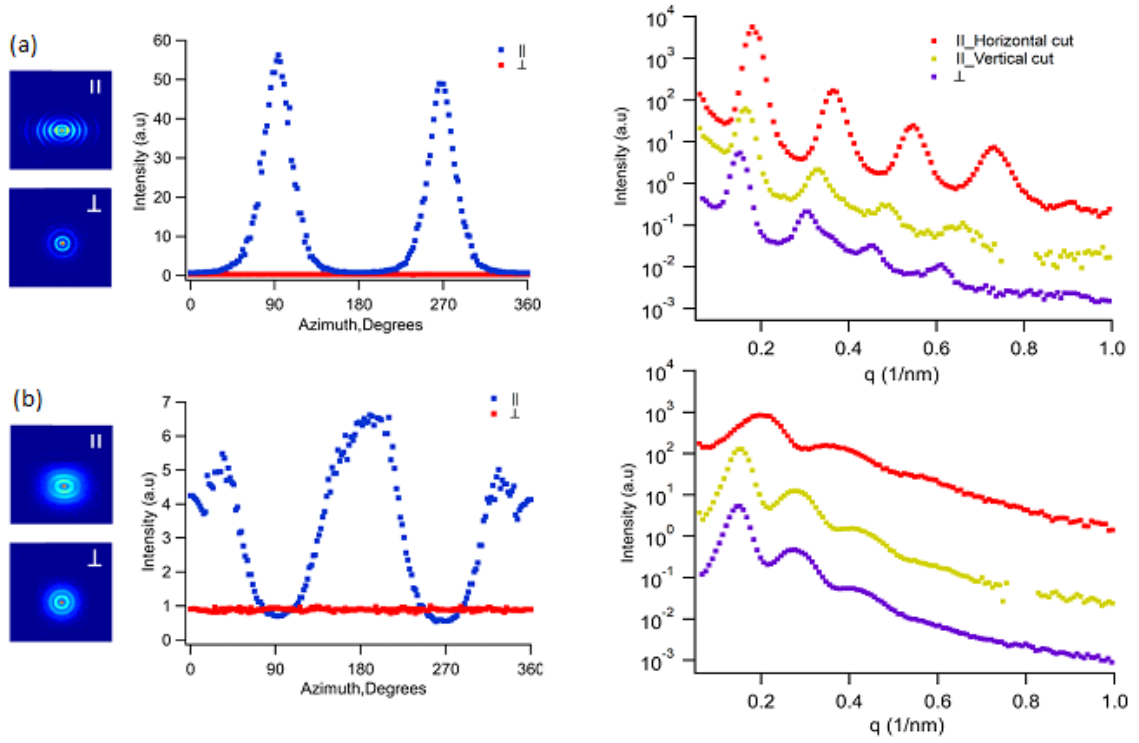


Figure 3.6: 2D scattering profiles for the 1000 $\mu\text{m} \times 3$ films, corresponding plot of Intensity as a function of azimuthal angle, and 1 D scattering profiles from azimuthal integration of intensity of the 2D scattering rings for $\perp$ configuration and intensity integration over horizontal and vertical cut region for the $\parallel$ configuration, films cast with (a)nP₃₀ and (b) nP₅₀ solvents.

for the films cast from nP_30 solvent and shows highly ordered lamellar morphology evidenced by three well defined higher order peaks. This indicates that the sequential depositing of layers using non-polar nP_30 solvent results in formation of lamellar structure in the bulk along with formation of ordered lamellar sheets parallel to the plane of the film in the skin layer. The horizontal cut of the 1D SAXS data in the ‘||’ configuration, corresponds to the low scattered intensity region for the films cast from nP_50 solvent and shows disordered structure with a broad first order peak and oscillations in intensity at higher q values.

3.3.3 Transport measurements

The water and ion transport properties through the membrane is expected to be influenced by both the morphology and orientation of domains at the surface. The morphology of the self-assembled structure would impact the connectivity of the transport channels which is an important parameter for ion transport. The orientation of domains at the surface would impact directional transport properties. Note that the domains are not necessarily oriented on both sides of the film, we only expect orientations to form at the polymer/air interface and not at the polymer/mylar interface during film drying. In Figure 3.7a we report the mass loss from vials containing water, resulting from the escape of water through a permeable seal of different films, in the upright vial set up. The mass loss shows an initial lag period followed by a linear mass loss with time. The constant slope of mass loss with time at longer times, is the steady state water vapor transport rate reported in Table 3.1. The initial lag time would be a function of the morphology, domain orientation at the surface, as well as the thickness of both the bulk and surface layers. The film thicknesses are also reported in Table 3.1. With an increase in gap height, the solvent depletion from the bulk takes much longer. For the geometry of the cast solution, where the length and breadth of the wet film are a few centimeters and the thickness is in micrometers, an increase in gap height would result in an increase in the ratio of

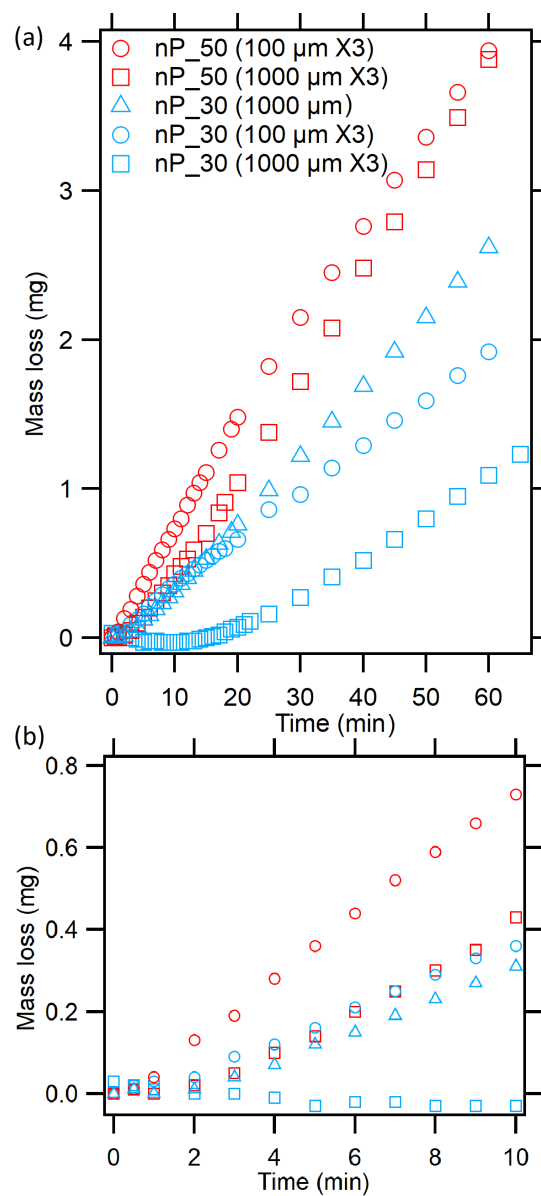


Figure 3.7: (a) Mass loss in vials with time due to water evaporation and escape through the polymer film, for the upright vial set up. (b) Enlarged plot showing mass loss in the first 10 minutes.

Table 3.1: Water vapor transport rate through different membranes

Sample	Film thicknes (μm)	WVTR (mg/hr)
nP_50 (100 $\mu\text{m} \times 3$)	34	3.5
nP_50 (1000 $\mu\text{m} \times 3$)	255	4.3
nP_30 (1000 μm)	111	2.8
nP_30 (100 $\mu\text{m} \times 3$)	47	1.9
nP_30 (1000 $\mu\text{m} \times 3$)	300	1.7

volume to surface area. For example, doubling the gap height would result in the increase in volume by two times, whereas the surface area available for solvent evaporation remains essentially unchanged. Even though we do not have a direct measurement of the thickness of the oriented layer at the film surface, we speculate that the thickness of this oriented layer increases with increase in gap height during solution casting.

The nP_30 (1000 $\mu\text{m}\times 3$) film shows the longest lag time and the mass loss only begins after over 10 mins. The mass loss through other films show a much shorter lag time and can be seen in Figure 3.7 b, which shows the mass loss in the first 10 mins. The nP_30 (100 $\mu\text{m}\times 3$) film, which has a similar bulk and surface structure and domain orientation as the nP_30 (1000 $\mu\text{m}\times 3$) film, has a lag time of about 2 mins. The much longer lag time for the nP_30 (1000 $\mu\text{m}\times 3$) film compared to nP_30 (100 $\mu\text{m}\times 3$) film can be explained by the difference in the film thickness as reported in Table 3.1. The drying time for a single layer of solution cast with 1000 μm gap height is about 30 min, Whereas the drying time for the same volume of solution cast using 100 μm gap height is about 1 min. Thus the nP_30 (1000 $\mu\text{m}\times 3$) film with 300 μm thickness has a thicker bulk as well thicker oriented surface layer compared to nP_30 (100 $\mu\text{m}\times 3$) film which has a final film thickness of 47 μm . The steady state water vapor transport rate (WVTR) which is calculated from the constant slope of mass loss with time, starting at 40 min, is reported in Table 3.1. Both the nP_30 (100 $\mu\text{m}\times 3$) and nP_30 (1000 $\mu\text{m}\times 3$) films have similar WVTR slopes, as seen in Figure 3.7 a, with values of 1.9 and 1.7 mg/hr respectively. This makes sense as the steady state WVTR should be a function of the film structure and independent of thickness, and both these films have similar bulk structure as seen in Figure 3.3, and similar surface structure and domain orientations as seen in Figure 3.6 a and Figure B.5 b.

The nP_50 (1000 $\mu\text{m}\times 3$) film shows a lag time of about 2 mins similar to that of the nP_30 (100 $\mu\text{m}\times 3$) film despite the much higher film thickness of 255 μm compared to nP_30 (100 $\mu\text{m}\times 3$) which has a thickness of 47 μm . The nP_30 films have domains oriented parallel to the plane of the film at the surface wherein the

hydrophobic domains would act as barriers to the water transport in the through film direction. The nP_50 films on the other hand has domains oriented perpendicular to the plane of the film at the surface, which should not impede transport in the through film direction. The nP_50 (100 $\mu\text{m}\times 3$) film which has a thickness of 34 μm shows a shorter lag time of less than a minute. The nP_50 (100 $\mu\text{m}\times 3$) and nP_50 (1000 $\mu\text{m}\times 3$) films have similar WVTR slopes, as seen in Figure 3.7 a, with values of 3.5 and 4.3 mg/hr respectively, which is expected as these films also have similar bulk structure and domain orientations as seen in Figure 3.3 and Figure 3.5.

The nP_30 (1000 μm) film, has a thickness of 111 μm and shows a lag time of about 2 mins and WVTR of 2.8 mg/hr. These films also shows domains oriented parallel to the plane of the film, same as the three layer nP_30 films, as can be seen in Figure 3.5, but the three layer films showed a more highly oriented lamellar structure compared to the nP_30 (100 μm) film. Thus the nP_30 (1000 μm) film, despite having a more than twice the thickness of nP_30 (100 $\mu\text{m}\times 3$) film, has a similar lag time. The intensity as a function of azimuth angle and 1D SAXS profiles integrated along the vertical and horizontal cut directions for the nP_30 (100 $\mu\text{m}\times 3$) and nP_30 (1000 μm) film is shown in Figure B.5 for comparison. The steady state WVTR for the nP_30 (1000 μm) film is lower than that of the three layer nP_50 films and higher than that of the three layer nP_30 films.

Next, we measured the water uptake and proton conductivity in the through-film direction at 35% RH. The orientation of domains on the surface of the film would impact the water uptake by the films which is a critical parameter for the dissociation of the sulfonic acid group and thus ion transport through the film. The water uptake corresponds to the wt% of water in the films left at 35% RH for over an hour. The nP_30 (1000 $\mu\text{m}\times 3$) film showed a much lower water uptake of 25 wt% compared to the nP_30 (1000 μm) and nP_50 (1000 $\mu\text{m}\times 3$) films which showed a water uptake of 50 wt%. As water uptake proceeds through the film surface, the low water uptake by the nP_30 (1000 $\mu\text{m}\times 3$) films should be due to the highly ordered lamellar domains oriented parallel to the plane of the film.

In a previous work it was shown that the through-film ion conductivity measurements are not sensitive to thin insulating interfacial layers(115). The study showed that the through-film conductivity is an accurate measurement of ionic conductivity of the bulk structure and does not capture the ion transport through the entire film. In this work we see that the proton conductivity in the through film direction, reported in Table 3.2, for the nP_50 (1000 $\mu\text{m}\times 3$) film is three times higher than that of the nP_30 (1000 $\mu\text{m}\times 3$) and the nP_30 (1000 μm) films. From the TEM images of bulk structures in Figure 3.4 we saw that the the nP_30 (1000 $\mu\text{m}\times 3$) film has a highly ordered lamellar structure and the nP_30 (1000 $\mu\text{m}\times 3$) films have a poorly ordered network like structure. This conductivity result agrees with the previous works that have shown that poorly ordered lamellar structures can have more interconnected pathways in the conducting domain as opposed to highly ordered lamellae with large grain sizes(71).

The nP_30 (1000 μm) has a much higher water uptake compared to the nP_30 (1000 $\mu\text{m}\times 3$) films, but both films show similar through film conductivity. Single layer films with similar SAXS profile of nP_30 (1000 μm) showed a poorly ordered structure with discontinuous SS domains in a matrix of tBS/HI domains as shown in Figure B.4. These results show that the poorly ordered structures formed by the single layer films result in bulk structure with poor ionic conductivity. Table 3.2 also reports the through film proton conductivity of the films after soaking in DI water. The films after soaking in water had a much higher water content which resulted in a 35-50 times increase in proton conductivity, although the films still show similar trend in conductivity with film structure, with the proton conductivity of nP_50 (1000 $\mu\text{m}\times 3$) film two to three times higher than that of the nP_30 (1000 $\mu\text{m}\times 3$) and the nP_30 (1000 μm) films. Thus, even at high moisture content in the film, the through-film conductivity measurement is dependent on the bulk structure of the film.

Table 3.2: Water content and proton conductivity through different polymer film samples

Sample	water wt%	conductivity (mS/cm)
¹ nP_50 (1000 $\mu\text{m} \times 3$)	50	0.45
¹ nP_30 (1000 $\mu\text{m} \times 3$)	25	0.14
¹ nP_30 (1000 μm)	50	0.14
² nP_50 (1000 $\mu\text{m} \times 3$)	220	15.14
² nP_30 (1000 $\mu\text{m} \times 3$)	133	6.99
² nP_30 (1000 μm)	166	5.76

¹Equilibrated at 35% RH and 25°C for 1 hr. ² Soaked in DI water at 25°C for 10 min

3.4 Conclusions

We examined the effect of solvent polarity and casting method on the bulk morphology and orientation of block domains in the surface layer of self-assembled SPC films. The effect of solvent polarity was studied using solvent mixtures with two different compositions, one that is selective to the hydrophobic tBS/HI blocks and another having neutral selectivity to all the blocks. Films formed after drying of a single layer of polymer solution, that was bar coated using a gap height of 1000 μm , resulted in the formation of a poorly ordered structure based on SAXS measurements, for both the selective and neutral casting solvents. The process of sequentially depositing three layers of solution after drying of the previous layers results in formation of different film structures that depend on the casting solvent composition. The films cast from the selective solvent resulted in highly ordered lamellar structure, whereas the films cast from neutral solvent resulted in poorly ordered network-like structure. This dependence of film structure on solvent selectivity was observed for three layer films even when a smaller gap height of 100 μm was used. The solvent selectivity also impacted the orientation of domains in the surface layer of the films. The films cast from the selective solvent showed block domains oriented parallel to the plane of the film whereas the films cast from the neutral solvent showed block domains oriented perpendicular to the plane of the film, in the surface layer. In the films cast with selective solvent, this orientation effect was also found to be more pronounced in the sequentially deposited three layer film compared to the single layer film. Finally, we show that the films with the poorly ordered network-like bulk structure shows higher proton conductivity as well as steady state WVTR in the through-film direction, compared to films having highly ordered lamellar bulk structure. The films cast from the selective solvent having highly ordered lamellar sheets oriented parallel to the plane of the film at the surface also show a much longer initial lag time before reaching the steady state WVTR, compared to films with similar thickness but having block domains oriented perpendicular to the plane of the film. These results clearly

illustrate that both the solvent selectivity and solution casting method affects both the bulk structure as well as the formation of oriented domains in the surface layer, both of which are important factors that impact the through-film membrane transport properties.

Chapter 4

Structure-property relations of triblock copolymer thermoplastics with interaction-tuned polymer additives

The work described in this chapter has been submitted for publication in macromolecules: K. Madathil, B. Upadhyay, W.K. Ledford, S.M. Kilbey, G.E. Stein. "Structure-property relations of triblock copolymer thermoplastics with interaction-tuned polymer additives".

B. Upadhyay and W.K. Ledford synthesized and characterized the random copolymers. K. Madathil prepared the blend films, performed the structural and mechanical characterizations and wrote the paper.

4.1 Introduction

Block copolymer (BCP) thermoplastics are used in a wide range of commercial products. It is well known that the mechanical performance of these materials depends

on the BCP architecture and composition, and the introduction of non-covalent interactions via comonomers can be used to tune key properties. However, tailoring the mechanics of BCPs by blending with polymeric additives is rarely explored, as most BCP/polymer blends have limited miscibility.

The phase behaviour of BCP/homopolymer blends has been well-studied over the past several decades. In a blend of an AB diblock copolymer with A homopolymer, the phase behaviour is mainly governed by entropic interactions arising from the relative chain lengths of the A homopolymer (N_h) and the A block in the BCP ($N_{A,BCP}$), given by $\alpha = N_h/N_{A,BCP}$ (116; 5; 117; 6; 118). For values of $\alpha < 1$, the A homopolymer is distributed throughout the A block of the BCP, driving both axial stretching and lateral expansion of the domain. The axial stretching of the BCP chain produces a conformational entropy loss that increases with the volume fraction of the homopolymer (ϕ) in the blend. At a certain ϕ , this entropic penalty produces a change in interfacial curvature that drives an order-order phase transition (OOT) (119; 120; 121). For $\alpha \sim 1$, there is a loss in the combinatorial entropy of mixing from the increase in homopolymer chain length, and so the homopolymer chains will accumulate at the center of the A-domain bilayer (122). For $\alpha \gg 1$, the entropic penalty drives macrophase separation of the homopolymer from the BCP system (123). For a given α , the ϕ which marks the onset of macrophase separation will depend on the structure of the pure BCP, which is a function of f and χN , where f_A is the volume fraction of the A block, χ is the Flory-Huggins parameter, and N is the degree of polymerization.

In a blend of an AB diblock copolymer or ABA triblock copolymer with type C homopolymer, where the C homopolymer is enthalpically compatible with the A block, the α and ϕ at which the OOT and macrophase separation occur are each governed by two additional enthalpic interactions captured by χ_{AC} (< 0) and χ_{BC} (> 0) (7; 124; 125; 126; 127; 128; 129; 130; 131; 61). Experimental and theoretical studies have each shown that the phase behavior depends on the molecular weight of the A block and is largely unaffected by the molecular weight of the C homopolymer.

This is because in these blend systems, macrophase separation is mainly governed by the conformational entropic penalty of the A block and the homopolymer C, which is significantly reduced with an increase in the molecular weight of the A block (132; 133). When the homopolymer additive is evenly distributed in the compatible block, which is anticipated for $\alpha < 1$, the A block undergoes axial stretching and lateral contraction at low ϕ , with an increase in the interfacial area per chain with increasing ϕ (7; 128).

Styrenic BCPs with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) homopolymer additive are a well-studied example of an ABA/C blend with $\chi_{AC} < 0$. PPO homopolymer is fully miscible with PS homopolymer, (134; 135; 136; 137; 138; 139) and blends of styrenic BCPs and PPO are miscible for $\alpha > 1$ provided the molecular weight of the PS block in the BCP is above 14 kg/mol (132; 133; 140; 3). The PPO additives tune the thermal stability and mechanical properties of the BCP (3; 141), increasing the modulus (3), tensile strength (141) and strain-at-break point (141). However, PPO has some disadvantages as an additive, both in terms of practical applications and fundamental studies. BCP/PPO blends must be processed at temperatures above 250°C due to the high T_g of PPO (141). PPO is prepared by oxidative coupling (142), which produces high dispersity in molecular weight (127). Therefore, it is difficult to investigate the effects of additive molecular weight on its distribution within the A domains of the BCP and mesoscale ordering of the self-assembled domains.

Another potential polymer additive for styrenic BCPs is the copolymer poly(methyl methacrylate-*co*-cyclohexyl methacrylate) (PrC), which is miscible with PS homopolymer provided the composition of cyclohexyl methacrylate (CHMA) exceeds approximately 21 mol% (143; 144; 145; 139). These PrC additives have T_g near that of PS (100 °C), and PS/PrC blends have a lower critical solution temperature of 220 °C, leading to a broad window for processing at moderate temperatures. Furthermore, PrC can be synthesized by controlled radical polymerization methods to achieve low dispersities ($\mathcal{D} \leq 1.2$). The enthalpic

interaction between PrC and PS can be tuned by varying the copolymer composition, with the minimum in $\chi_{\text{PrC,PS}}$ observed for approximately 70 mol% CHMA (143). To the best of our knowledge, the miscibility of CHMA-based polymers with styrenic BCPs has not been explored.

This work describes a systematic investigation of PrC miscibility in poly(styrene-*b*-ethylene-*co*-butylene-*b*-styrene) (SEBS), a widely studied class of BCP thermoplastic. The PrC composition was fixed at approximately 70 mol% CHMA, i.e., the composition that produces the strongest enthalpic compatibility with PS. The SEBS composition and molecular weight were also fixed at 26 vol% styrene and $M_n = 103.5$ kg/mol, respectively. Entropic effects that contribute to blend miscibility were explored by varying both the molecular weight of PrC, which changes α , and its loading level defined by ϕ . PS homopolymer additives, i.e., athermal additives for the PS block in SEBS, were used as a control. The knowledge acquired from this study provides a framework to design miscible polymeric additives for styrenic BCP thermoplastics that manipulate nanoscale structure, bulk mechanics, and thermal stability without compromising processability.

4.2 Experimental

Materials SEBS was obtained from Kraton Corporation. The number-average molecular weight $M_n = 103.5$ kg/mol and dispersity $\mathbb{D} = 1.05$ were determined by gel permeation chromatography (GPC) relative to PS standards. The SEBS composition of 30 mol% PS was determined from ^1H NMR. The SEBS composition on a volume basis is 26% polystyrene, assuming densities of 0.92 g/cm³ and 1.05 g/cm³ for poly(ethylene-*co*-butylene) and PS, respectively. The GPC trace and NMR spectrum for SEBS are shown in Figures C.1 and C.2, respectively.

PS samples with a range of molecular weights were purchased from Scientific Polymers and their molecular weights were verified by GPC. PrC samples were synthesized via reversible addition fragmentation chain transfer (RAFT)

polymerization, adapting procedures described previously(146). For all RAFT polymerizations, the target copolymer composition, f_{CHMA} , was fixed at 70 mol% CHMA, as it is reported as the minimum χ parameter for blends with PS(143). PrC molecular weight was varied by changing the total monomer concentration, and at the higher molecular weight, the feed ratio of CHMA:methyl methacrylate (MMA) had to be adjusted in order to hit the target composition. As an example, CHMA (64.4 mmol, 10.82 g), MMA (27.6 mmol, 2.76 g), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (1 mmol, 279 mg), and AIBN (0.1 mmol, 16.8 mg) were dissolved in 10 mL of THF and added to 25mL round bottom flask equipped with a stir bar. The flask was sealed with a septum and dissolved oxygen removed through three freeze-pump-thaw cycles. The flask was then immersed in a preheated oil bath set to 70°C. After 18 h, the reaction was quenched by opening the flask to air and freezing the crude product mixture with liquid nitrogen. After thawing, the copolymer was isolated and purified by precipitation into cold methanol and gravity filtration. The recovered PrC copolymer was dried under vacuum for 24 h prior to use. Characterization by GPC and ^1H NMR showed that this PrC had a $M_n = 2,800$ g/mol, $\text{Đ} = 1.09$, and 72 mol% CHMA. Characteristics of all PrCs synthesized are given in Table C.1, along with ^1H NMR spectra in Figure C.4 and GPC traces in Figure C.3.

Polymer characterization ^1H NMR spectroscopy was used to confirm the composition of the SEBS BCP and the PrC random copolymers. In short, 10 mg of polymer was dissolved in d-chloroform and analyzed using a Varian 500 MHz spectrometer at room temperature. Gel permeation chromatography (GPC) was used to measure the molecular weight of the SEBS BCP, PrC copolymers, and PS homopolymers. The M_n , and Đ of each polymer was determined at room temperature using an Agilent 1260 Infinity II GPC system that used THF as the mobile phase at a flow rate of 1.0 mL/min. The GPC was equipped with triple detection consisting of an Optilab T-rEX differential refractometer, a Viscostar III viscometry detector, and a Wyatt Dawn Helios multiangle light scattering detector.

All molecular weights reported were obtained via conventional calibration analysis using polystyrene standards. Samples for GPC were prepared by dissolving 12 mg of polymer in 2 mL THF and then filtering the solution using 0.2 μ M filters.

Blend preparation Blends were prepared by mixing SEBS and polymer additive at different ϕ . Densities of 0.91 g/cm³ for SEBS, 1.00 g/cm³ for PS and 1.11 g/cm³ for PrC were used for calculating ϕ , assuming there is no volume change upon mixing. The polymer mixture was then dissolved in xylenes (98.5% purity) to produce a solution with 10 wt% polymer. Polymer films were prepared by bar coating the polymer solution onto a Mylar sheet using an Elcometer film applicator with 500 μ m gap height. After drying in air at room temperature, the films were cut to obtain rectangular pieces with 1 cm width and annealed in a vacuum oven for 48 hrs at 140 °C. The final film thicknesses after drying and annealing were 70-90 μ m. Films of neat SEBS (no additive) were also prepared by the same procedure.

Small-Angle X-ray Scattering (SAXS) A Xenocs GeniX 3D microfocus source with a copper target was used to produce a monochromatic beam with a 0.154 nm wavelength. The sample to detector distance was 0.9 m. A Pilatus3 R 300K detector (Dectris) with nominal pixel dimensions of 172 μ m $\times$ 172 μ m was used for data acquisition. The data acquisition time was 5 min for all measurements. The two-dimensional images from each measurement were azimuthally integrated with SAXSGUI software to yield a one-dimensional scattering profile of intensity I (a.u) versus scattering vector q (nm⁻¹). In all the figures showing SAXS data, the plots from each data set have been vertically offset for clarity.

Transmission Electron Microscopy (TEM) TEM measurements were performed on films that were sectioned to a thickness of around 30 nm by a Leica EM FC7 microtome at -150 °C. The sections were placed on Nickel grids and stained with ruthenium tetroxide vapor for 15 min, which selectively stains the PS domain.

The sample slices were imaged by a JEOL JEM 1400-Flash transmission electron microscope with an acceleration voltage of 120 kV.

Mechanical and thermal characterizations Room temperature tensile testing was performed using an Instron 5965 instrument. Experimental setup and data acquisition were performed using Bluehill version 4.18 software. The initial separation between the grips was 20 mm. The samples were uniaxially stretched at a strain rate of 1/min, with a crosshead speed of 20 mm/min, until break point. At least five samples were measured for each blend composition, and the error bars in the plots with tensile properties denote the standard deviation.

The stress-strain curves at elevated temperature, and the T_g 's of SEBS and SEBS/additive blends were all obtained using a TA instruments Q800 dynamic mechanical analyser (DMA) in tension mode under nitrogen atmosphere. The initial separation between the grips was 1 cm. To obtain stress-strain curves, the samples were equilibrated at 80°C and stretched at a strain rate of 1/min, corresponding to a crosshead speed of 10 mm/min. To obtain T_g , the experiments were run at a heating rate of 5 °C/min from 30 °C to 140 °C and an oscillating axial force with 1% strain amplitude at a frequency of 1 Hz was applied. The T_g was taken from the maximum of the $\tan \delta$ curve.

The T_g 's of the PS and PrC additives were obtained using a TA instruments Q2000 differential scanning calorimeter (DSC). A temperature range of 25 °C to 150 °C was used for heat-cool-heat cycles at a heating and cooling rate of 10 °C/min. The T_g was taken from the mid-point of the slope in the second heating cycle.

4.3 Results and Discussion

4.3.1 SEBS morphology

Prior to preparing blends of SEBS and polymer additives, the neat SEBS morphology was characterized using both SAXS and TEM. The SAXS data showed higher-order peaks at $2q^*$, $3q^*$ and $4q^*$ positions, which are representative of an ordered lamellar (LAM) morphology, where q^* is the position of the first-order peak. TEM images for the SEBS sample, however, showed a perforated lamellar (PL) morphology having poorly ordered perforations (Figure S5). This is not surprising, as the volume fraction of the PS block in SEBS is only 26%, which likely falls within the PL or cylindrical morphology regions in the phase diagram (147). Furthermore, it has been noted in prior studies that the SAXS profile for PL morphology is not distinguishable from that of a LAM morphology when the perforations are poorly ordered (148; 149).

To check whether the structure obtained after annealing is equilibrium structure, SEBS/PS blend films prepared by using above mentioned method were compared when two different casting solvents were used: xylene, which has neutral selectivity to polystyrene and poly(ethylene-butylene) blocks, and cyclohexane, which is selective towards the poly(ethylene-butylene) block. The SAXS profiles obtained before and after annealing these films are shown in Figure C.8. Films created from both solvents form a lamellar structure after annealing, despite having different morphologies before annealing. We also note that there is a variation of up to 3.5% in the periodicity for some of the samples when the same blend preparation method is repeated as shown in Figure C.9.

4.3.2 Phase behaviour and morphology of SEBS/additive blends

Blends of SEBS with PS and PrC additives were prepared as a function of molecular weight and ϕ of the additives. Each SEBS/additive blend was defined by three

parameters: (1) the type of additive used, PS or PrC; (2) the ratio of the length of additive to the length of a single polystyrene end-block in SEBS, α ; and (3) the volume fraction of the additive in the blend, ϕ . The following equation was used to calculate α :

$$\alpha = \frac{N_{\text{additive}} \cdot V_{\text{additive}}}{N_{\text{PS,SEBS}} \cdot V_{\text{styrene}}} \quad (4.1)$$

Wherein N_{additive} and $N_{\text{PS,SEBS}}$ are the degrees of polymerization of the additives and a PS end-block in SEBS, respectively. For the SEBS used in this work, $N_{\text{PS,SEBS}}$ is 142. The v_{additive} and v_{styrene} terms are the monomer volumes for the additive and styrene, respectively, at the annealing temperature of 140 °C. The monomer volume was calculated using the M_n and density of the polymer at 140 °C. The density of the polymer at 140 °C was estimated using the density at 25 °C and a thermal expansion coefficient of $7 \times 10^{-4} / ^\circ\text{C}$ for both PS and PrC. In the case of PrC additive, v_{additive} is the average monomer volume, accounting for the number of CHMA and MMA monomers in the chain. The volume of PS and PrC monomers at 140 °C were calculated to be 0.17 nm³ and 0.23 nm³, respectively. Table 4.1 provides a summary of all polymer additives used in this work, and also reports the value of α without volume correction for reference, which is denoted as $\alpha' = N_{\text{additive}}/N_{\text{PS,SEBS}}$.

Figure 4.1a reports the phase behaviour of SEBS/additive blends over a wide range of α and ϕ , where the markers on the phase diagram represent the blend compositions that were studied. F_H corresponds to the volume fraction of the hard phase in the blend, which includes both the additive and the polystyrene blocks of SEBS. F_H was calculated using 0.26 for the volume fraction of polystyrene in SEBS and assuming volume is additive after mixing. For the range of ϕ values examined (0.1-0.4), the volume fraction of the hard phase in the blend is between 0.33-0.55, which produces a lamellar structure in linear ABA triblock copolymers with symmetric end blocks.⁽¹⁵⁰⁾ The structure of the samples was studied using SAXS and these data are shown in Figures C.6 and C.7. The samples marked as ‘LAM’ in Figure 4.1 showed higher-order

Table 4.1: Characteristics and relative sizes of additives

Additive type	f_{CHMA}	$M_n(\text{kg/mol})$	$\bar{D}$	α'	α
PS	-	1.6	1.08	0.11	0.11
PS	-	3.8	1.07	0.26	0.26
PS	-	8.0	1.05	0.54	0.54
PS	-	12.0	1.05	0.81	0.81
PS	-	15.3	1.04	1.03	1.03
PS	-	19.5	1.05	1.32	1.32
PrC	0.72	2.8	1.09	0.13	0.18
PrC	0.73	4.4	1.08	0.21	0.28
PrC	0.76	10.0	1.16	0.47	0.63
PrC	0.74	12.5	1.12	0.60	0.80
PrC	0.78	17.0	1.16	0.80	1.07
PrC	0.74	18.5	1.13	0.87	1.17
PrC	0.75	21.0	1.16	0.98	1.32
PrC	0.76	27.5	1.16	1.29	1.73
PrC	0.66	34.8	1.16	1.70	2.28
PrC	0.76	63.8	1.16	3.00	4.02

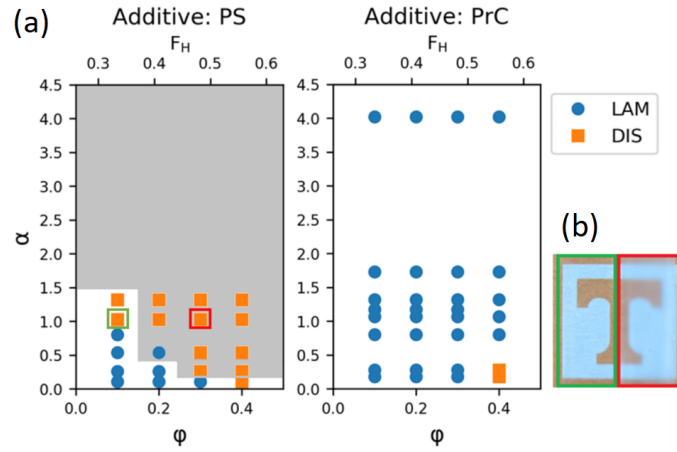


Figure 4.1: (a) Phase diagrams of SEBS/PS and SEBS/PrC blends as a function of relative chain length (α) and additive volume fraction (ϕ). (b) Films of miscible (green) and macrophase separated (red) blends, corresponding to the green and red squares in the SEBS/PS phase diagram, respectively.

peaks consistent with a lamellar structure. The ‘LAM’ symmetry was also confirmed by TEM imaging for a blend with 10 vol% of PrC additive ($\alpha = 0.28$), corresponding to $F_H=0.33$, as shown in Figure C.5. The samples marked as ‘DIS’ showed a primary peak and broad bump in intensity at higher q values, indicative of a poorly ordered structure without a clear symmetry. The grey shaded region in the SEBS/PS phase diagram marks conditions that produce macrophase separation, which were identified from the cloudy appearance of the film as shown in Figure 4.1b.

As we can see from Figure 4.1a, the SEBS/PS blend undergoes phase separation at high values of α and ϕ , as expected based on previous studies,(118; 6) whereas the SEBS/PrC blend remained miscible for all α and ϕ that were studied. The miscibility of the PrC additive with SEBS is also evident in tensile tests, as discussed in the next section. The Flory interaction parameter between PrC and PS is approximately -0.02 at 140 °C, based on the cloud point analysis of PrC/PS blends reported in previous works.(151; 152) While this is only weakly negative(143), it is evidently sufficient to overcome entropic effects that drive phase separation of polymer additive from the confined lamellar morphology. SEBS/PrC blends also showed a lamellar morphology for almost all blends, except for the lowest values of α (0.18, 0.28) at $\phi = 0.4$.

Next, we examine how α influences the distribution of additive within the polystyrene domain of SEBS by plotting the lamellar periodicity ‘ L ’ versus ϕ , as shown in Figure 4.2. This analysis is only applied to miscible blends. The value of L is calculated from the first-order peak position, $L= 2 \pi/ q^*$, where q^* is the position of the primary SAXS peak. This calculation of L is also applied for the disordered structures, where L reflects an approximate correlation length rather than the lamellar periodicity. The size of the markers in Figure 4.2 corresponds to the uncertainty in periodicity, as explained in the Experimental section. Changes in additive distribution as a function of α are inferred from changes in the dependence of L on ϕ (5). When the additive is distributed throughout the polystyrene domain, the polystyrene end-blocks stretch and the domain width increases. This process

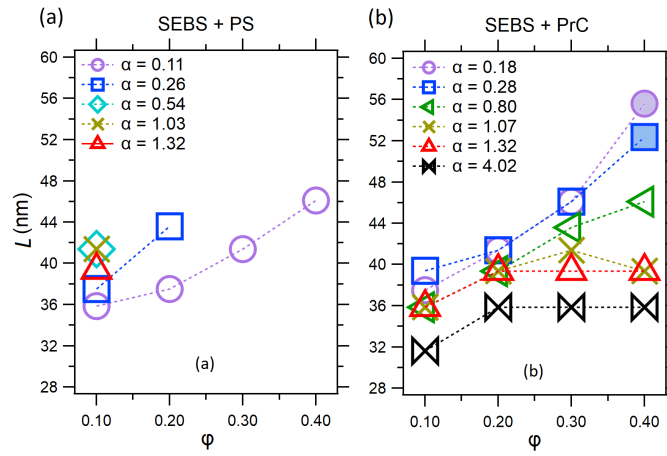


Figure 4.2: Periodicity (L) of miscible (a) SEBS/PS and (b) SEBS/PrC blends versus volume fraction of the additive (ϕ) in the blend. Unfilled markers represents blends with LAM structure, where L designates the lamellar periodicity. Filled markers represent blends with DIS structure, where L is an approximate correlation length.

either increases or decreases the width of the rubber domain, depending on how it impacts the interfacial area between junction points(7). When the additives are localized near the center of the polystyrene domain, the bilayer of polystyrene end-blocks is forced to expand and the domain width increases. This process does not impact the width of the rubber domain, so a greater increase in L is expected as ϕ increases as opposed to the situation where the additive is uniformly distributed.

For the SEBS/PS blends shown in Figure 4.2a, we observe a more pronounced increase in L with ϕ as α increases, which is seen most clearly by comparing the trends for $\alpha=0.11$ and $\alpha=0.26$. This is indicative of the additive moving towards the center of the PS domains, that is, switching from wet brush regime towards dry brush regime, with an increase in α (5; 121). No trend is identified with higher α blends because the system phase separates when $\phi>0.1$. In contrast, the SEBS/PrC blends shown in Figure 4.2b exhibit similar trends for L as a function of ϕ when α is low (0.18 and 0.28), indicating that the additive distribution in this regime is not influenced by α . However, and as seen in Figure 4.2b, for $\alpha = 0.80, 1.07, 1.32$ and 4.02 , L was reduced relative to the blends with $\alpha = 0.18$ and 0.28 . Furthermore, when α exceeded 0.8 , L was invariant with ϕ for $\phi \geq 0.2$. While this behavior might suggest that the additive was phase separating from the SEBS, the blends remained optically clear. Alternatively, this behavior can be explained by an axial swelling (along the length of the lamellar domains) that is not captured by SAXS measurements.

The increase in L with ϕ for the SEBS/PrC system when $\alpha < 1$ is comparable to the trends observed in other blends with hydrogen bonding between the additive and one of the blocks in a BCP. As an example, Sunday et al. studied blends of polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) and poly (4-vinylphenol) (PVPH), wherein PVPH forms hydrogen bonds with PMMA, for $\alpha = 0.15, 0.25$ and 0.65 and PVPH loadings up to 30 wt%(7). All blends formed a lamellar morphology. When $\alpha = 0.15$ or 0.25 , L increased by about 20% as the additive loading increased from 10 to 30 wt%, which is comparable to the swelling observed in the SEBS/PrC blends for similar α and ϕ values. To our knowledge, there are no

studies of BCP/polymer blends with attractive interactions that focused on $\alpha > 1$. Therefore, this is the first study of a BCP/polymer blend to show a constant L with increasing ϕ .

4.3.3 Mechanical properties of SEBS/additive blends

Figure 4.3a-d shows the representative tensile plots for select SEBS/PS and SEBS/PrC blends with varying α for $\phi = 0.1$ and 0.3 . The tensile behavior for SEBS with no additive is shown for comparison. The stress-strain curves for SEBS and miscible SEBS/additive blends show similar behaviour with three distinct regions: There is an initial region of elastic deformation, followed by yielding and a region of plastic deformation, and then a region showing strain hardening behavior before the sample breaks. Macroscopically, sample yielding is accompanied by formation of a distinct localized necked region which progresses through the sample with increasing strain. The necking is caused by fragmentation of the glassy domains, which allow the rubbery domains to deform elastically to a higher strain(153). Once the sample is completely necked, a further increase in strain results in strain hardening behaviour, which is associated with additional breaking of the glassy fragments. The macrophase-separated SEBS/PS blend with $\alpha=1.03$ and $\phi=0.3$, however, does not exhibit a distinct region between yielding and strain hardening (Figure 4.3b). This sample displayed uniform necking throughout the film after yielding. The localized neck formation has been observed in BCP elastomers with globally-oriented lamellae and cylinders when the deforming force is applied parallel to the domain orientation. In morphologies where there are no continuous glassy domains to break, such as spherical morphologies where the minority component is glassy, yielding and localized necking are not observed during deformation (154). The macrophase-separated SEBS/PS blend is expected to have poor continuity in the glassy domains due to the disordered mesoscale structure, as shown in SAXS measurements (Figure C.6), which explains the absence of localized necking.

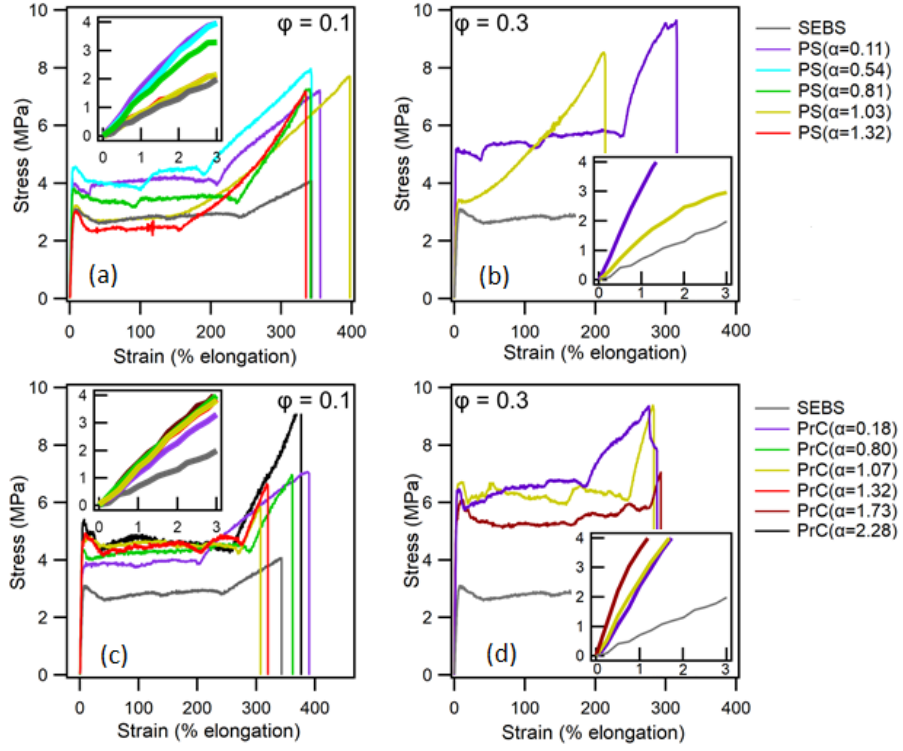


Figure 4.3: Representative tensile plots with varying α for SEBS/PS blends with (a) $\phi=0.1$ and (b) $\phi=0.3$, and for SEBS/PrC blends with (c) $\phi=0.1$ and (d) $\phi=0.3$. The inset shows the stress-strain curves for values of strain up to 3%.

Figures 4.4a-d reports the tensile properties of SEBS/PS and SEBS/PrC blends with $\phi=0.1$. For SEBS/PS blends, the blends with $\alpha = 0.11$, 0.54 and 0.81 show a higher modulus and yield stress than neat SEBS (Figures 4.4a-b). This is expected due to the increased content of glassy polymer. However, for the blends with $\alpha = 1.03$ and 1.32, the modulus and yield stress both drop to values approaching that of neat SEBS. This change in tensile properties for blends with the same ϕ can be attributed to differences in the mesoscale morphology: The blends with $\alpha = 0.11$, 0.54 and 0.81 have an ordered LAM structure, whereas the blends with $\alpha = 1.03$ and 1.32 have a disordered structure (Figure 4.1a and Figure C.6). Previous works have also reported that microphase-separated BCPs with long-range order show better mechanical performance compared to those with poorly-ordered structures(155; 156). At low α , the modulus and yield stress of SEBS/PrC blends are similar to those of SEBS/PS blends. However, the properties of the SEBS/PrC blends do not decline with increasing α , which can be attributed to the well-defined LAM structure (Figure 4.1a). The toughnesses of neat SEBS and all of the miscible SEBS/additive blends are similar within the uncertainty of the measurements.

Figures 4.3b and 4.3d shows representative tensile plots for SEBS/PS and SEBS/PrC blends with $\phi=0.3$, and Figure C.10 summarizes the tensile properties. The SEBS/PS blend with $\alpha=0.11$ is miscible and assembles into the LAM structure at $\phi = 0.3$, and compared with $\phi = 0.1$, the yield stress and modulus are increased with little impact on toughness. A similar trend is observed as ϕ is increased from 0.1 to 0.3 for SEBS/PrC blends with $\alpha = 0.18$, 1.07 and 1.73, all of which assembled into the LAM structure, despite significant differences in how L changes with ϕ (Figure 4.2b). The SEBS/PS blends with $\alpha=1.03$ are macrophase-separated at $\phi = 0.3$, and consequently, the modulus, yield stress and toughness are all reduced relative to SEBS/PS blends with $\alpha = 0.11$.

Prior studies of BCP mechanics have shown that modulus, yield stress, and toughness all depend on the interfacial curvature of the domains (157; 158; 52). BCPs

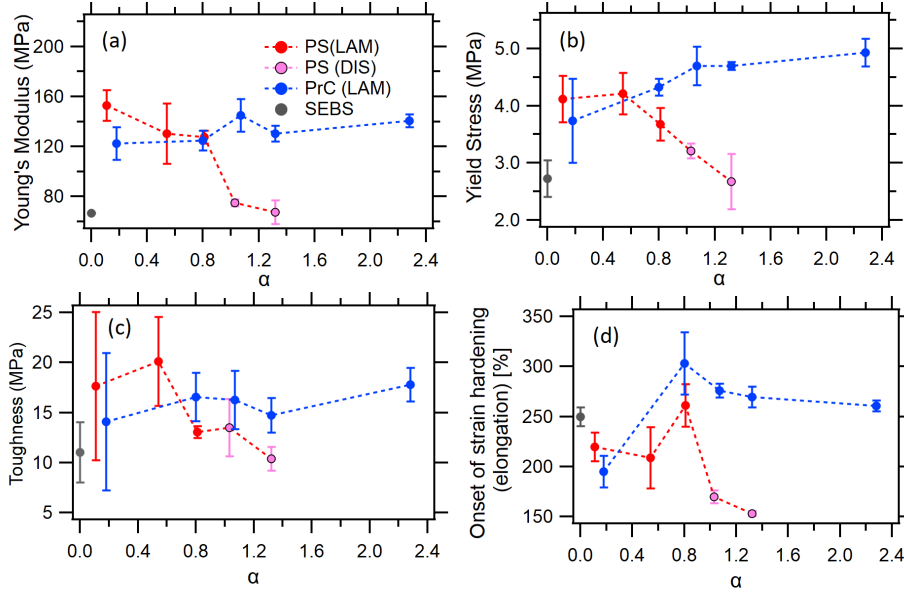


Figure 4.4: Mechanical properties as a function of α for SEBS/PS and SEBS/PrC blends, $\phi = 0.1$. The error bars denote ± 1 standard deviation based on four measurements. The properties of neat SEBS are marked by the grey circle (plotted at $\alpha = 0$).

with continuity in the rubbery domain, which happens when the minority glassy domain has convex curvature, offer ductility while discontinuity in the rubbery domains produces a brittle material. Adhikari et al. and Huy et al. compared mechanical properties of polystyrene-*b*-poly(butadiene)-*b*-polystyrene (SBS) with the same volume fraction of styrene but different morphologies.(157; 158) These works showed that SBS with discontinuous rubbery domains had a higher modulus and yield stress, but a drastic decline in toughness compared to SBS with lamellar morphology. Whether blending changes the interfacial curvature of SEBS depends on how the additive swells the domain, which is determined by how it is distributed within the domain. (61) The fact that SEBS/PrC blends have similar tensile behavior for a broad range of α (at constant ϕ) indicates that these additives do not change interfacial curvature in a way that disrupts continuity of rubber domain as ϕ is increased from 0.1 ($F_H=0.33$) to 0.3 ($F_H=0.48$). Thus, when blending SEBS with PrC additives, it is possible to create a miscible blend system with ordered lamellar structures and good continuity in the rubbery domain for a broad range of α and ϕ . This provides the opportunity to prepare blend systems that have a high modulus and high yield stress without loss of toughness.

Figure 4.4d shows the dependence of the onset of strain hardening, which happens after the sample is completely necked, with α . SEBS/PS blends with $\alpha = 1.03$ and 1.32, which have a disordered structure (Figure 4.1a), show an onset of strain hardening at a lower strain compared to the blends with LAM structures. Between yielding and the onset of strain hardening, deformation occurs through propagation of the necked region by fragmenting the PS domains(153). Thus, it makes sense that blends with poorly-ordered structures would be completely necked at lower strains, as it is easier to break apart an already fragmented glassy domain. The onset of strain hardening was also sensitive to the molecular weight of the additive, where blends with low α (< 0.8) showed the onset at lower strains than those with higher α . This observation suggests that low molecular weight additives make it easier to break apart the glassy domains under stress, perhaps due to a plasticizing effect.

From Figures 4.1, 4.3 and 4.4, we see that for higher values of α , the phase behavior and mechanical properties of SEBS/PS and SEBS/PrC blends are quite different. However, when the SEBS/polymer blends are miscible and the morphology is LAM, the same modulus, yield stress and toughness are achieved irrespective of the type of additive. In consideration of tensile properties at ambient temperature, there does not seem to be an advantage of PrC over PS additives at low loadings ($\phi = 0.1$), however, this may change at elevated temperatures: T_g is generally depressed as molecular weight is reduced, and miscible SEBS/PS blends with an ordered LAM structure are only achieved when the PS additive has a low molecular weight. Figure 4.5 reports the T_g , which was determined by DSC, of PS and PrC additives as a function of molecular weight. The T_g of PrC is higher relative to that of PS by approximately 10 K for all molecular weights in excess of 8 kg/mol. Both polymers show a drop in T_g when the molecular weight falls below approximately 8 kg/mol. Consequently, blends with low α values are expected to depress the T_g of the glassy domain.

The T_g of the glassy domain in select SEBS/additive blends, using α and ϕ values where both PS and PrC are miscible, was determined by DMA and is summarized in Table 4.2. Note that DSC could not detect T_g of the glassy domain in neat SEBS or SEBS/additive blends. Relative to neat SEBS, the T_g of the glassy domain was depressed in SEBS/PS blends with $\phi = 0.1$ and $\alpha = 0.11$, but slightly elevated as α was increased to 0.54 and 1.03. However, the T_g of the glassy domain was slightly elevated in SEBS/PrC blends with $\phi = 0.1$ and $\alpha = 0.18$, and it increased further as α was increased to 0.63 and 1.07. The slight elevation for $\alpha = 0.18$ is surprising, as the T_g of this additive (ca. 60 °C) was significantly depressed relative to that of the polystyrene block in SEBS (ca. 100 °C). However, in addition to molecular weight effects, the T_g of the glassy domain is also influenced by the strength of energetic interactions between the additive and the polystyrene block in SEBS. The attractive interaction between PrC and the polystyrene block could elevate the T_g of the glassy domain(159). To interrogate this point, we compared the predicted T_g of the glassy

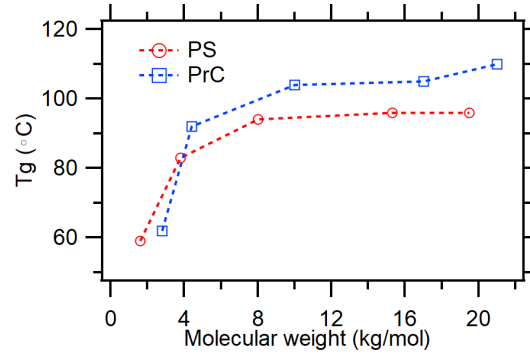


Figure 4.5: T_g of PS and PrC additives as a function of molecular weight, from DSC measurements.

Table 4.2: Experimental and predicted values of T_g for the glassy domain of SEBS/additive blends at $\phi=0.1$, and experimental modulus of SEBS and SEBS/additive blends with $\phi=0.1$ at 80°C.

Additive type	α	Experimental T_g (°C)	Predicted T_g (°C)	Modulus at 80°C (MPa)
-	-	102	102	8
PS	0.11	92	88	5
PS	0.54	106	99	50
PS	1.03	106	100	23
PrC	0.18	105	92	60
PrC	0.63	112	102	66
PrC	1.07	111	103	52

Experimental T_g is from the $\tan \delta$ peak in DMA. Predicted T_g is from the Fox equation, using the additive T_g from DSC and the polystyrene block T_g from DMA of neat SEBS.

domain using the Fox equation (Equation 4.2), which is applicable for polymer blends with weak intermolecular interactions, with the measured value for each SEBS/additive blend. The outcomes are shown in Table 4.2. The $T_{g,PS \text{ block}}$ used for the calculation is the T_g of the polystyrene block measured from neat SEBS using DMA, which was found to be 102 °C. The $T_{g,additive}$ was measured with DSC. The weight fraction of additive ($w_{additive}$) is based on the proportions of polystyrene and additive in the glassy domain, which is 0.3 and 0.325 for PS and PrC additives, respectively, for $\phi=0.1$. We note that apart from the effect of any energetic interactions, the experimental and predicted values are expected to be different as the Fox equation does not account for confinement in a self-assembled domain and the glass transitions of additive and polystyrene block are measured with different techniques. With these qualifiers in mind, the discrepancy between experimental and predicted T_g is 4-6 K for SEBS/PS blends and 9-12 K for SEBS/PrC blends, indicating that attractive interactions in the latter system may enhance the thermal stability.

$$\frac{1}{T_g(K)} = \frac{w_{additive}}{T_{g,additive}(K)} + \frac{1-w_{additive}}{T_{g,PS \text{ block}}(K)} \quad (4.2)$$

We further examined the thermal stability of SEBS/additive blends by performing tensile tests at an elevated temperature. Figure 4.6 shows stress-strain curves for blends with $\phi=0.1$ at 80°C. The modulus obtained from the linear elastic region is listed in Table 4.2. For the SEBS/PS blends, the modulus when $\alpha=0.11$ is similar to that of neat SEBS (5 MPa), despite having a higher volume fraction of polystyrene. This softening is a consequence of the depressed T_g of the glassy domain, as seen in Table 4.2. As α increases to 0.54 and 1.03, the modulus increases to 50 and 23 MPa, respectively. In these blends, the T_g of the glassy domain is similar to that of neat SEBS, so the improvement in modulus partly reflects the higher content of glassy material. As observed with room temperature tensile tests, SEBS/PS blends with LAM order ($\alpha = 0.54$) have a higher modulus than those with a disordered structure

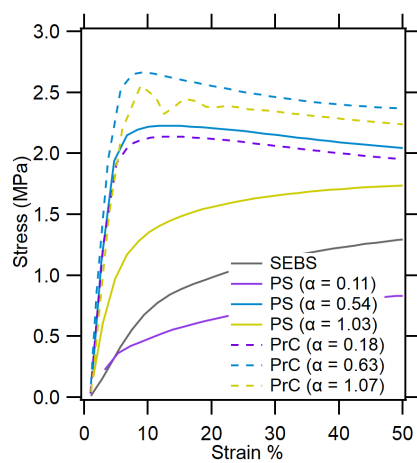


Figure 4.6: Stress-strain curves for SEBS and SEBS/additive blends ($\phi=0.1$) at 80 °C.

($\alpha = 1.03$). This can be explained by differences in the degree of structural order, where the LAM structure produces a higher modulus than the disordered structure. For the SEBS/PrC blends, the modulus is in the vicinity of 60 MPa for all α . These results show that miscible polymer additives that elevate the T_g of the glassy domain and produce a well-ordered mesoscale structure can improve the thermal stability of SEBS.

4.4 Conclusions

We tuned the enthalpic and entropic interactions between SEBS and polymeric additives to understand the impacts on phase behavior, morphology, tensile properties, and thermal stability. In the case of SEBS/PS blends, where PS is an athermal additive for the polystyrene block in SEBS, the constituents were only miscible for low ϕ and α . Consequently, there was an extremely narrow range of conditions that produced a single-phase blend with both a well-ordered morphology and a glassy T_g near 100 °C, leading to good mechanical properties at low and moderate temperatures. In SEBS/PrC blends, where PrC is a thermal additive for the polystyrene block in SEBS ($\chi_{\text{PrC/PS}} = -0.02$ at 140 °C), the constituents were miscible for the entire range of ϕ (0–0.4) and α (0.1–4) that were studied. Nearly all SEBS/PrC blends assembled into well-ordered lamellar structures with continuity in the rubber phase, so the mechanical properties were largely controlled by ϕ (independent of α), and the glassy PrC additive increased modulus and yield strength without compromising toughness. Furthermore, the PrC additive enhanced the thermal stability of the glassy domain, leading to good mechanical properties at elevated temperature. These results show that the PrCs are suitable additives to tailor the mechanical properties of styrenic BCPs over a broad temperature range.

Chapter 5

Outlook

The results in Chapter 4 clearly showed that the miscibility of SEBS/additive blend systems depend greatly on the enthalpic interaction between the polystyrene block and the additive. The attractive interaction between PrC and the polystyrene block ($\chi_{\text{PrC/PS}} = -0.02$ at 140°C) resulted in miscible blends for the entire range of ϕ (0-0.4) and α (0.1-4) that was studied. Next, we investigated the phase behavior of SEBS/PrC blend system for higher loadings (up to $\phi = 0.8$). The expanded phase diagram with the higher ϕ values is shown in Figure 5.1 a. SEBS/PrC formed miscible blends for the entire range studied and structural characterization using SAXS showed four distinct 1D scattering profiles which are indicated in the phase diagram as ‘LAM’, ‘DIS 1’, ‘DIS 2’ and ‘S’. The scattering profiles corresponding each of the four labels are shown in Figure 5.2.

At low ϕ (up to 0.3) values, all SEBS/PrC blends showed lamellar (LAM) morphology with multiple higher order peaks at lamellar peak positions. For values of ϕ between 0.3 and 0.6, the SEBS/PrC blends with short PrC additives ($\alpha=0.28$) formed a poorly ordered structure (DIS 1), with a 1D SAXS profile showing no peaks, and a bump in intensity at higher q values. Further increases in loading ($\phi=0.7,0.8$) resulted in 1D SAXS profiles with decaying intensity with increasing q , which are characteristic of solutions with dissolved polymer chains (S). At these loadings the

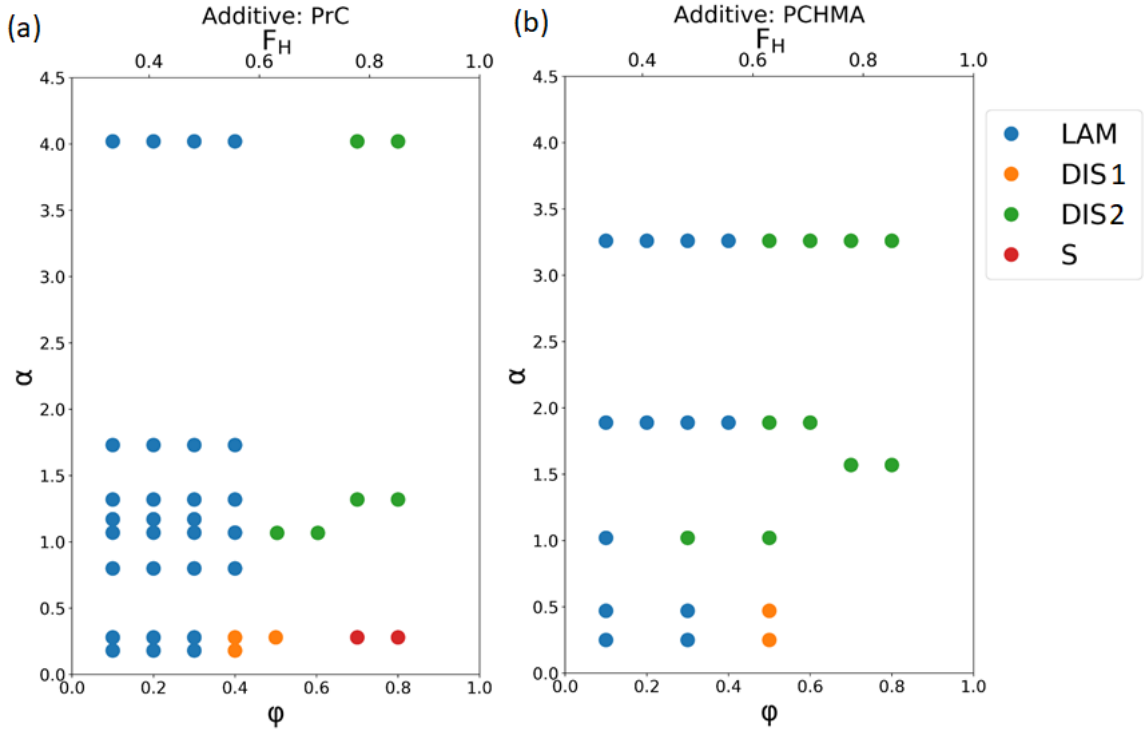


Figure 5.1: Phase diagrams of (a) SEBS/PrC and (b) SEBS/PCHMA blends as a function of relative chain length (α) and additive volume fraction (ϕ).

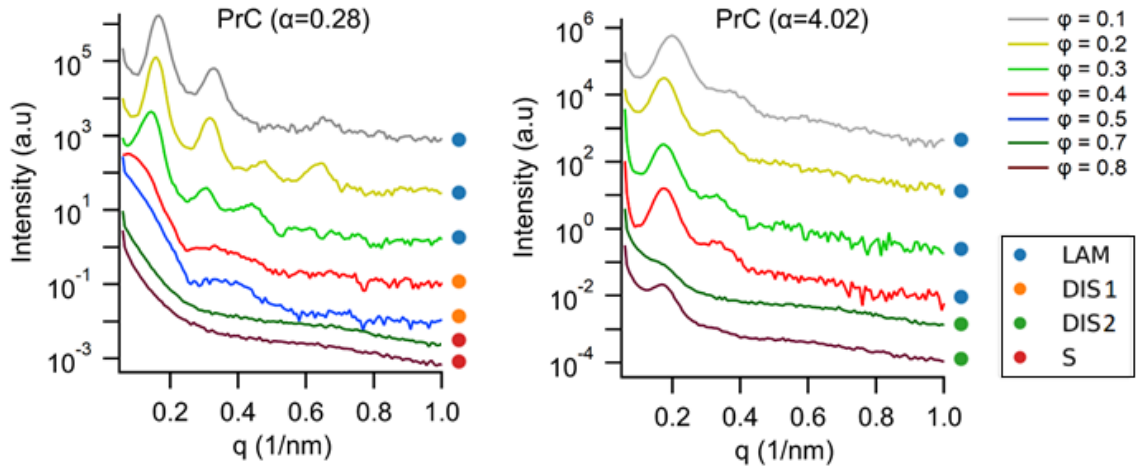


Figure 5.2: SAXS data for SEBS/PrC blends with varying ϕ for $\alpha=0.28$ and $\alpha=4.02$.

blend film is brittle and easily breaks on bending. Thus, at loading of $\phi=0.7$ and higher, the blend can be assumed to be a continuous phase of PrC with dispersed SEBS chains.

SEBS/PrC blends with higher α (1.32 and 4.02) values, and loadings of over $\phi=0.4$, formed a poorly ordered structure (DIS 2) with broad peaks, with the higher order peaks disappearing at values of $\phi=0.7$ and 0.8. The blends with higher α values did not show the ‘DIS 1’ or ‘S’ structures. This distinction in scattering profiles, seen as a function of ϕ , shows that there is a switch in additive distribution with short and long additives. Although, these X-ray scattering studies do not provide definitive information on how the additive is distributed in each case. The blends with higher α (1.32 and 4.02) values also formed brittle films which easily broke on bending at values of $\phi=0.7$ or greater. Thus, based on these simple bend tests, we did not see a difference in the minimum ϕ values where the continuity of the rubber phase is lost, for blends with short and long additives.

In the previous chapter, we chose the PrC random copolymer with 70 mol% CHMA and 30 mol% MMA as the thermal additive in our studies because the enthalpic interaction parameter between PrC and PS, $\chi_{\text{PrC/PS}}$, is the minimum at this composition based on a binary interaction model(151). Poly (cyclohexyl methacrylate) (PCHMA) homopolymer also has a slightly negative interaction parameter ($\chi_{\text{PCHMA,PS}} = -0.015$ at 140°C) and is known to form optically miscible blends with polystyrene (143). Hence, it was worth investigating the miscibility and morphology of SEBS/PCHMA blends to see if the slight difference in the χ parameter would show any significant impact on phase behavior. The phase diagram for SEBS/PCHMA blends is shown in Figure 5.1 b. SEBS/PCHMA also formed miscible blends for the entire range of α (0.25-3.26) and ϕ (0.1-0.8) studied. These blends also showed scattering profiles similar to the SEBS/PrC blends, wherein increasing ϕ resulted in change from ‘LAM’ to ‘DIS 1’ at lower α values and ‘LAM’ to ‘DIS 2’ structures at higher α values.

In the previous chapter, the additive distribution in SEBS/PrC was discussed by studying the periodicity (L) as a function of ϕ . In Figure 5.3 a, the periodicity values for blends with high α (1.32 and 4.02) and ϕ (0.7 and 0.8) values showing the ‘DIS 2’ structure is included. As seen in the figure, the ‘DIS 2’ structure showed the same peak position as the first order peak of the ‘LAM’ structures at lower ϕ values. Thus, it seems that even at higher loading, the additives continue to swell in the polystyrene domain in the axial direction, without significant contraction in the rubber domain. The presence of thermal additives at the domain interface, which is expected in the case of wet brush distribution, can have a similar effect as increase in χ parameter between the blocks, and thus impact domain periodicity. Further investigation on the impact of wet brush distribution of thermal PrC additive on the contraction and expansion of the domain widths is needed. Unlike the SEBS/PrC blends with the long chain additives, blends with short chain additives show an increase in periodicity with values of ϕ up to 0.3. This could be because the short chain additives can better swell the polystyrene domains, and have larger accumulation at the rubber/polystyrene domain interface leading to greater stretching of both the rubber and polystyrene domains. Figure 5.3 b reports the periodicity (L) as a function of ϕ for SEBS/PCHMA blends, which shows similar behavior as the SEBS/PrC blends.

Next, we performed tensile tests on SEBS/PrC blend films with high ϕ values. The blend films with $\phi = 0.7$ and greater formed brittle films, based on the bend tests, hence films with $\phi = 0.6$ was tested first. At these loadings the films were able to stretch 2-3 times their original length before breaking, but the films were stiff and curled up after annealing, and thus the tensile test results were not reproducible. Modulus of 294 and 297 MPa were obtained in two tensile tests for additives with $\alpha = 1.07$; these values are close to those obtained at $\phi = 0.3$ loading, as reported in Appendix C. The highest loading studied where the SEBS/PrC blends formed flexible films with good elastomeric behavior is $\phi = 0.5$. The representative tensile plots for the blends with $\phi = 0.5$ for two α values (0.18 and 1.07) are shown in Figure 5.4, and the corresponding tensile properties are reported in Table 5.1. The blend with ‘DIS

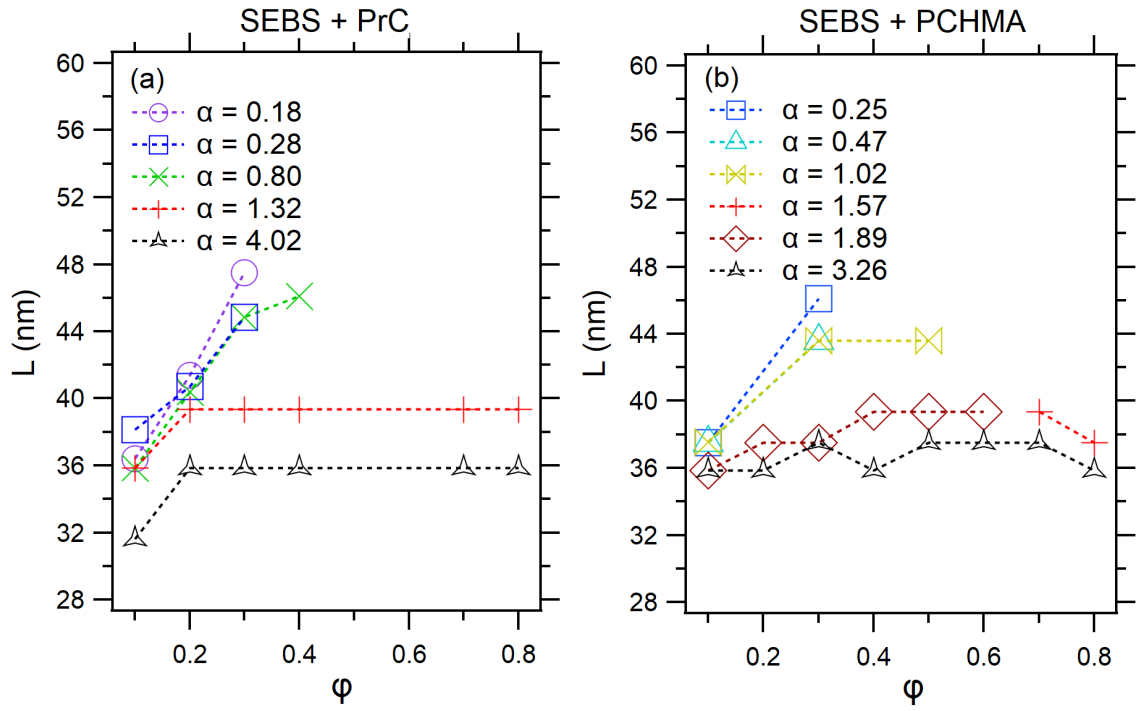


Figure 5.3: Periodicity (L) of (a) SEBS/PrC and (b) SEBS/PCHMA blends versus (ϕ) for blends with LAM and DIS 2 structures.

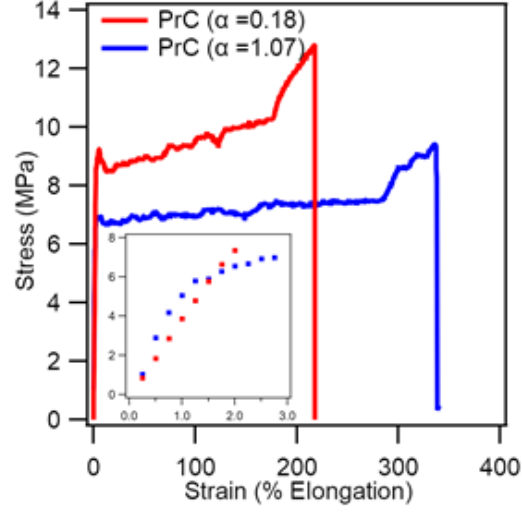


Figure 5.4: Representative tensile plots for SEBS/PrC blends with $\phi=0.5$

Table 5.1: Tensile properties for SEBS/PrC blends at $\phi = 0.5$.

α	Modulus (MPa)	Yield Stress (%elongation)	Yield Strain (%elongation)	Strain hardening onset (MPa)	Toughness (MPa)
0.18	394.4 (36.2)	9.14 (0.5)	8.82 (0.6)	160.4 (15.0)	24.73 (10.9)
1.07	635.8 (54.0)	7.57 (0.4)	7.41 (0.4)	282.7 (19.9)	27.50 (6.5)

Values in the bracket indicate ± 1 standard deviation based on three measurements.

2' structure ($\alpha = 1.07$) showed a modulus about 1.6 times that of the blend with 'DIS 1' structure ($\alpha = 0.18$). The blend with 'DIS 1' structure ($\alpha = 0.18$) showed a broader linear elastic region compared to the blend with 'DIS 2' structure ($\alpha = 1.07$) with a higher yield stress and yield strain. Thus the 'DIS 1' and 'DIS 2' structures leads to distinct differences in the hardness and elasticity of these blends. The onset of strain hardening shows a similar trend as the $\phi=0.1$ and 0.3 loading discussed in the previous chapter, wherein longer additives delays the onset of strain hardening to higher strain values.

Figure 5.5 reports the Young's modulus as a function of ϕ for SEBS/additive blends with short and long additives. SEBS/PCHMA blends were studied only for $\phi=0.1$ loading. At $\phi=0.1$, blends with both PCHMA and PrC additives show LAM structure, and have similar values for modulus with both short and long chain additives. For SEBS/PrC blends, we see an increase in modulus as ϕ goes from 0.1 to 0.5, and the blends with the short chain and long chain additives show a distinct difference only at $\phi=0.5$, where they show different structures. The modulus for SEBS/PS blends is also included in the plots, the trend for this blend system with respect to its structure was discussed in Chapter 4.

In Chapter 4, we showed that both the additive chemistry and molecular weight has a significant impact on Young's modulus at the elevated temperature of 80°C. The SEBS/PS blends showed a maximum modulus at $\alpha = 0.54$. At a low value of $\alpha=0.11$, the blend showed a depressed the T_g of the polystyrene domain compared to SEBS and at high value of $\alpha=1.03$, the SEBS/PS forms poorly ordered structure, both of which results in lowering of modulus. The SEBS/PrC blends on the other hand did not show a depression in T_g and formed an ordered LAM morphology for the range of α (0.18-1.07) studied and thus showed a high modulus value at 80 °C. It is logical to assume that blend morphology, additive chemistry and additive length would also dictate the long time creep behavior. To investigate this point creep experiments were performed on SEBS/PS blends ($\alpha=0.11$ -1.32, $\phi=0.1$), SEBS/PrC blends ($\alpha=0.11$ -4.00, $\phi=0.1$) and neat SEBS at a series of temperatures from 25 °C

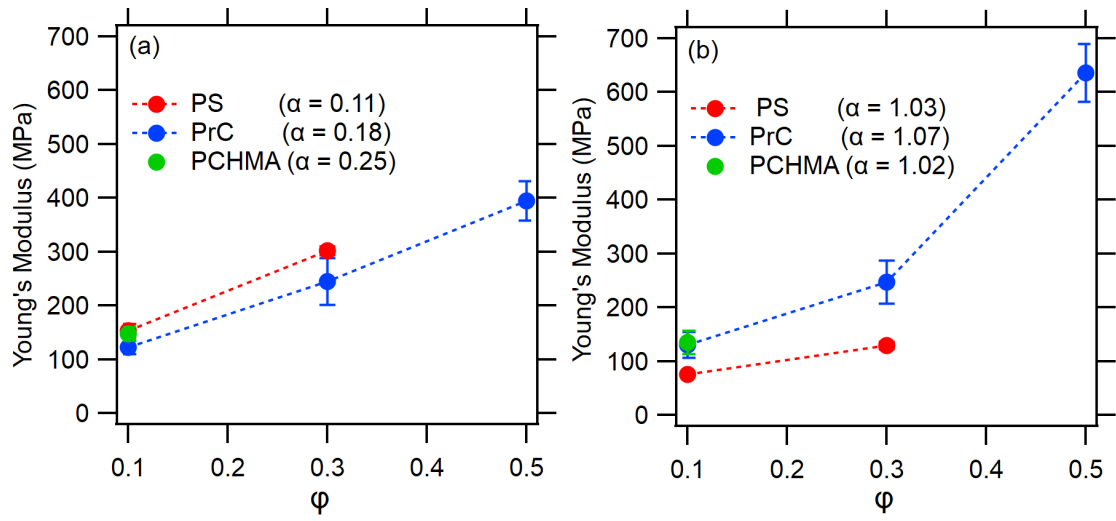


Figure 5.5: Young's modulus as a function of ϕ for SEBS/PS, SEBS/PrC and SEBS/PCHMA blends, with (a) short ($\alpha = 0.1 - 0.25$) and (b) long ($\alpha = 1$) additives. The error bars denote ± 1 standard deviation based on three measurements.

to 65 °C. The long time creep compliance (J) data obtained by performing time-temperature superpositioning (TTS) using 25 °C as the reference temperature is shown in Figure 5.6. The SEBS/PS blends with $\alpha = 0.1$, 0.54 and 1.32, showed similar long time creep curve as SEBS with no additive, with the blends showing slight improvement in resistance to long time creep deformation with increase in α . A similar pattern is seen for the SEBS/PrC blends for $\alpha = 0.18$, 0.44 and 1.32, where the resistance to long time creep deformation improves with increase in additive length, with the blend with $\alpha = 1.32$ showing significantly better resistance to deformation than all the other blends studied. These results seem to indicate that the long time creep behaviour mainly depends on the additive length. Although, the SEBS/PrC blend with $\alpha = 4.00$, shows a poorer resistance to long time creep compared to the blends with smaller α values, showing that there is an optimal value for α where we get the best creep resistance. Also note that the SEBS/PrC blends show much better creep resistance compared to SEBS/PS blends with similar α values. This study shows that the attractive interactions between PrC and polystyrene end blocks improves the long time creep resistance.

The discussions on structure-mechanical property studies so far has focused on blends with lamellar morphology which has continuity in both glassy and rubbery domain, with the neat SEBS used in these studies having a perforated lamellar morphology. For many elastomeric applications, BCPs with spherical or cylindrical morphology with discontinuous glassy domain is used. These morphologies are achieved at a lower volume fractions of the glassy domain. The discontinuity in the glassy domain leads to softer materials with better elastic recovery. It would be interesting to investigate the potential of thermal additives to tune the modulus and T_g of BCPs with discontinuous glassy domains. In order to explore this point we would need to expand this study and investigate the phase behaviour and miscibility of SEBS/PrC blends, where the neat SEBS has a spherical or cylindrical morphology.

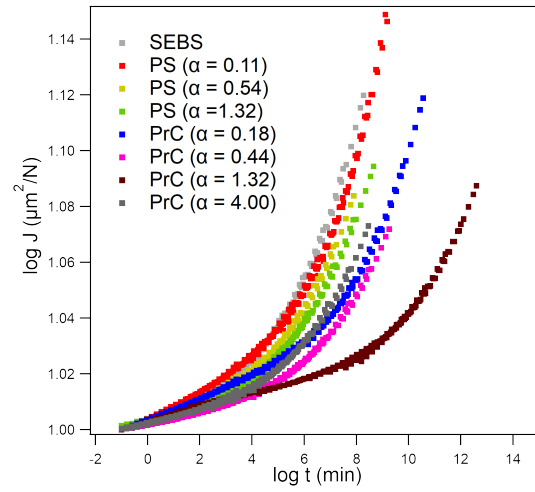


Figure 5.6: Creep TTS master curves for neat SEBS, SEBS/PS and SEBS/PrC with 25°C as the reference temperature .

The SEBS used in this work has $M_n = 103.5$ kg/mol with the polystyrene end blocks being 14.7 kg/mol. In order to have spherical or cylindrical morphologies with similar overall molecular weight BCP, the polystyrene end blocks would have shorter lengths and thus lower T_g . Also, the molecular weight of additives with respect to the α values would reduce. Thus, if miscible SEBS/PrC blends with spherical or cylindrical morphologies can be formed with high molecular weight PrC additives, it would greatly improve the T_g of the glassy domain and thus significantly expand the service window for these morphologies. However, spherical and cylindrical morphologies have a higher conformational entropy loss when blend with additives as compared to lamellar morphologies, with the spherical morphology having the highest penalty in conformational entropy. This is due to the fact that in lamellar morphology, apart from expansion in width of the domain, the additives can also be accommodated by expansion in the length and thickness of the lamellae which does not involve chain stretching. Whereas in spherical morphology, the additives can only be accommodated by stretching of the chains in the radial direction. In the cylindrical morphology on the other hand, the additives can be accommodated by expansion along the length of the cylinder which does not involve chain stretching.

With lamellae forming SEBS/PrC blends we saw possible evidence that the PrC additives accumulate along the axial direction even at high α and ϕ values. Thus it is reasonable to speculate that PrC additives would form miscible blends with cylinder forming SEBS at high α and ϕ values by expansion along the length of the cylinder. Further studies should investigate the potential of thermal additives to tune the mechanical and thermal properties of cylinder forming SEBS elastomers. We did not see any significant difference in the phase behaviour or room temperature mechanical properties between the SEBS/PCHMA and SEBS/PrC blends. PCHMA also has similar T_g values as PrC, hence we do not see any particular interest in using the PrC over PCHMA homopolymer as the thermal additive, for these investigations with styrenic block copolymers.

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Appendices

Appendix A

Supporting Information for: Effects of
trace water on self-assembly of
sulfonated block copolymers during
solution processing

I: Solvent evaporation rate during casting process

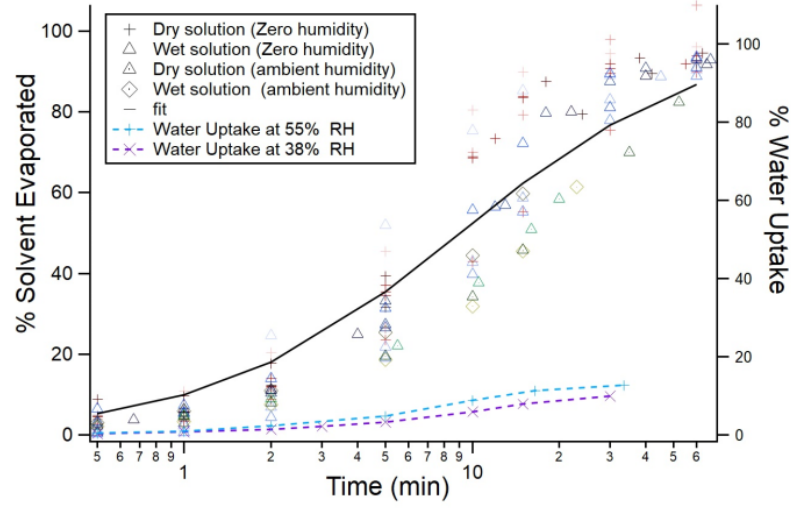


Figure A.1: Evaporation rates of solvent from dry ($\lambda=0$) and wet ($\lambda=3.2$) solutions when drop cast in near zero humidity and under ambient humidity. The different colors used for the same symbol corresponds to solution that were aged for different number of days before casting. The dashed lines correspond to the water uptake by a dry film at 38% and 55% RH. The film was dried by placing it in a vacuum oven for 24 hours at 80 °C. The evaporation rate follows the trend: $\% \text{ Solvent Evaporated} = \text{Time}/(\text{Time}+k) \times 100$, $k \sim 9$ min, when time is in minutes.

II: Time resolved SAXS on solutions

The dry solutions showed a similar behaviour for both the series of solution SAXS measurements. For the wet solutions, the one standing in dynamic vacuum during the measurement period showed a gradual decrease in domain periodicity which was not seen for the one standing in a vial under ambient conditions, as seen in the SAXS data in Figure [A.2](#). Thus, we conclude that the lowering of domain periodicity over time observed for the samples standing in vacuum was an effect of loss of water and not an effect of self-assembly kinetics.

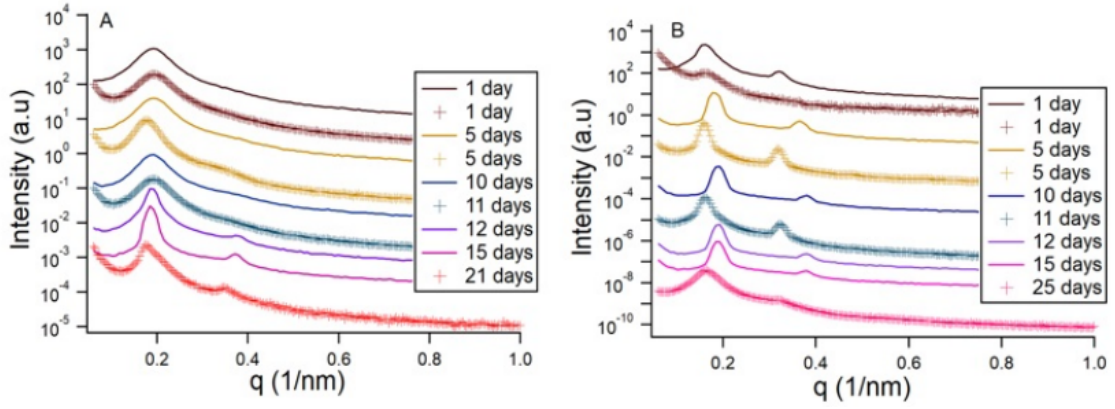


Figure A.2: Time resolved SAXS measurements of 16 wt% SPC solutions in different solvent mixtures: A) $\text{nP}_{33}:\text{T}_{67}$, $\lambda = 0$; B) $\text{nP}_{33}:\text{T}_{67}$, $\lambda = 3.2$. The solid line plot corresponds to the SAXS data on solutions that were placed in a sealed sandwich cell and stored under dynamic vacuum throughout the measurement time. The marker(+) plot corresponds to the SAXS data on samples that were drawn on different days from solutions standing in a vial under ambient conditions.

III: SAXS data for solutions aged for 1 day

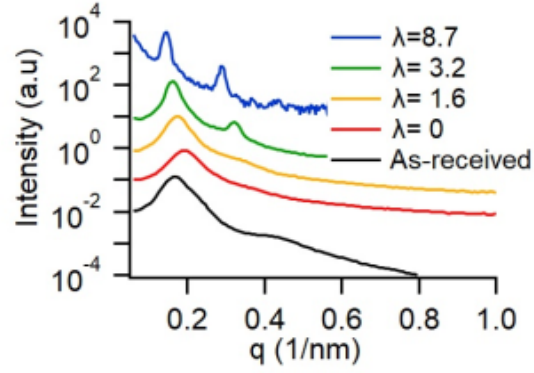


Figure A.3: SAXS data for as-received film and solutions with different λ values after aging for 1 day

IV : Change in domain periodicity with time from time resolved SAXS measurements for samples stored in vacuum during the measurement.

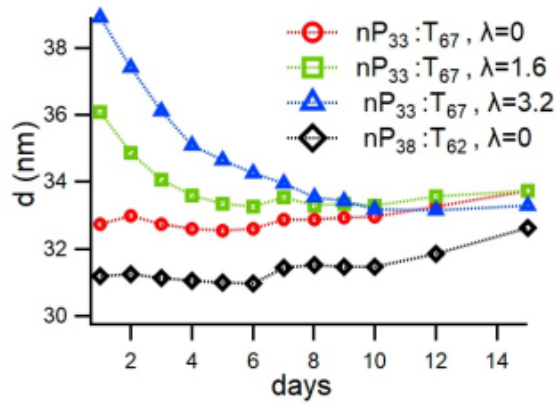


Figure A.4: Domain periodicity for solutions with time

V : Solvent selectivity estimated from Hansen solubility parameters (HSP)

The HSP has three components: dispersive δ_d , polar δ_p , and hydrogen bonding δ_h . A closer value of these components for the polymer and solvent results in better mixing and thus higher selectivity of the polymer in the solvent. The solubility of the polymer in the solvent is calculated with $R_a = 4(\delta_{d1}-\delta_{d2})^2 + (\delta_{p1}-\delta_{p2})^2 + (\delta_{h1}-\delta_{h2})^2$, which is the HSP distance between two molecules, where the subscripts 1 and 2 denote the polymer and the mixed solvent, respectively. As can be seen from the table, the solvent mixtures nP₃₃:T₆₇ with $\lambda = 3.2$ and nP₃₈:T₆₂ with $\lambda = 0$ have nearly identical R_a values.

Table A.1: Calculated Hansen solubility parameters for different solvent mixtures and the interaction distance R_a between the mixed solvents and each polymer block.

Solvent mixture		Solubility parameters			R_a		
nP _x :T _y	λ	δ_d	δ_p	δ_h	tBS	HI	SS
nP ₃₃ :T ₆₇	0	17.3	3.2	7.1	5.6	5.9	10.2
nP ₃₃ :T ₆₇	1.6	17.3	3.3	7.4	5.9	6.2	9.9
nP ₃₃ :T ₆₇	3.2	17.3	3.4	7.8	6.3	6.5	9.7
nP ₃₈ :T ₆₂	0	17.2	3.5	7.9	6.4	6.6	9.7

Appendix B

Supporting Information for: Effects of
processing methods on the
morphology and domain orientation
in sulfonated block copolymers

I: Solution structures

Figure B.1 shows the map of solution structure with respect to solvent polarity and polymer concentration when the SPC is dissolved in a propanol/toluene mixture with $\lambda = 8$. The vertical axis corresponds to the wt% of propanol in the propanol/toluene mixture, therefore solvent polarity increases as we go up in the phase diagram. The SAXS data corresponding to the solution phase diagram is given in Figure B.2. The SAXS data for solutions that fall in the region marked 'free chains' showed an intensity curve without any peaks, characteristic of scattering from individual polymer chains dissolved in a solution. The SAXS data for solutions that fall in the region marked 'spherical' fit well with Hard Sphere model. The region marked 'disordered', showed scattering profiles with a broad primary peak, characteristic of disordered aggregates and fluctuations in intensity at higher q values coming from the form factor. The regions marked 'lamellae' and 'cylindrical' showed SAXS profiles with peaks positions corresponding to lamellar and hexagonally packed cylinders respectively. The SAXS data for solutions with 50 and 60 wt% propanol in the propanol/toluene mixture is also included in Figure B.1. For 50 wt% propanol in the organic solvent mixture, the SAXS profile showed attributes of independent polymer chains. The solution structure with 60 wt% propanol in the organic solvent mixture is likely inverted micelles but the SAXS profile couldn't be definitively fit with a spherical core-shell model.

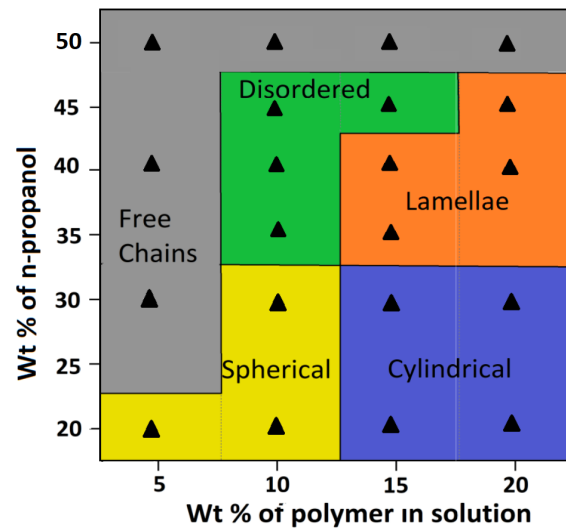


Figure B.1: Solution phase diagram. Black triangles indicate the compositions that were measured by SAXS.

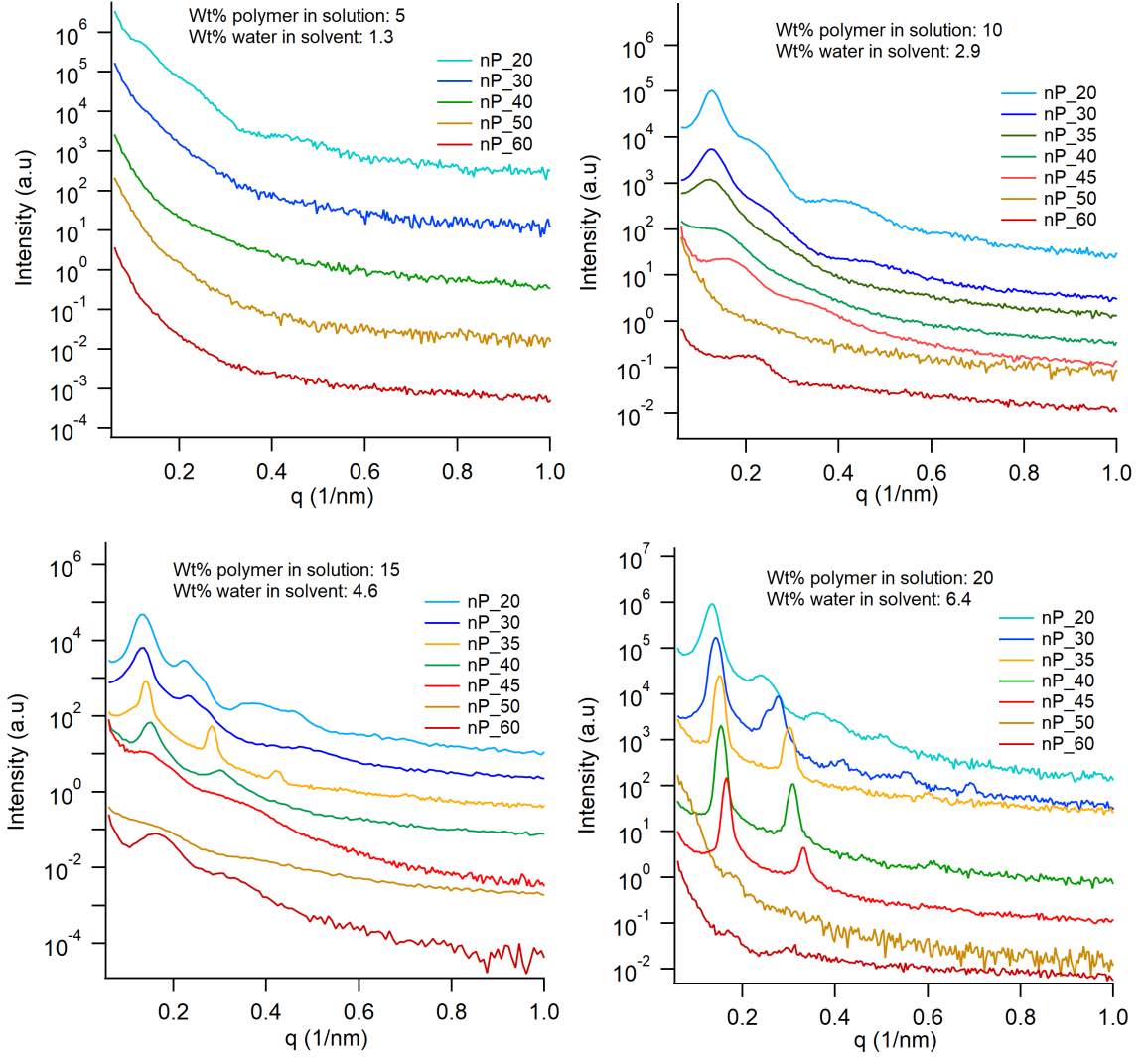


Figure B.2: SAXS data for solutions with 5,10,15 and 20 wt% polymer. These solutions also contained water with the value of $\lambda = 8$, where $\lambda =$ moles of water: moles of sulfonic acid group. Wt% water in the nP/T/water solvent mixture corresponding to $\lambda=8$ in the solution is also indicated in the plots.

II: Film structures

Films were cast from solutions with 20,30,40,50 and 60 wt% propanol in the organic solvent mixture and with 5,10,15 and 20 wt% polymer in the solution for each of the solvent compositions. The solutions containing 10,15 and 20 wt% polymer were bar coated with a gap height of 250 μm and the solutions with 5 wt% polymer was drop cast as it was too dilute for bar coating. The SAXS data for the complete set of cast films is shown in Figure B.3. Figure B.4 shows the TEM images for select films along with the SAXS data for the corresponding film and casting solution. From Figure B.4 we can see that the film structure does not show any correlation to the solution structure. All four of the film samples show similar SAXS profiles, whereas in solution, nP_30 (5 wt% polymer in solution) shows scattering characteristic of free chains in solution, nP_40 (10 wt% polymer in solution) shows disordered aggregates and nP_40 (15 wt% polymer in solution) & nP_40 (20 wt% polymer in solution) show lamellae. The film SAXS profile for all the four samples shows a broad primary peak and a weak secondary peak, indicating poorly ordered structure with an increase in correlation length with increase in polymer concentration decrease in propanol content in casting solvent as observed in Figure B.3. The TEM images corroborates with the SAXS data showing a random distribution of SS domains within the films as seen in Figure B.4.

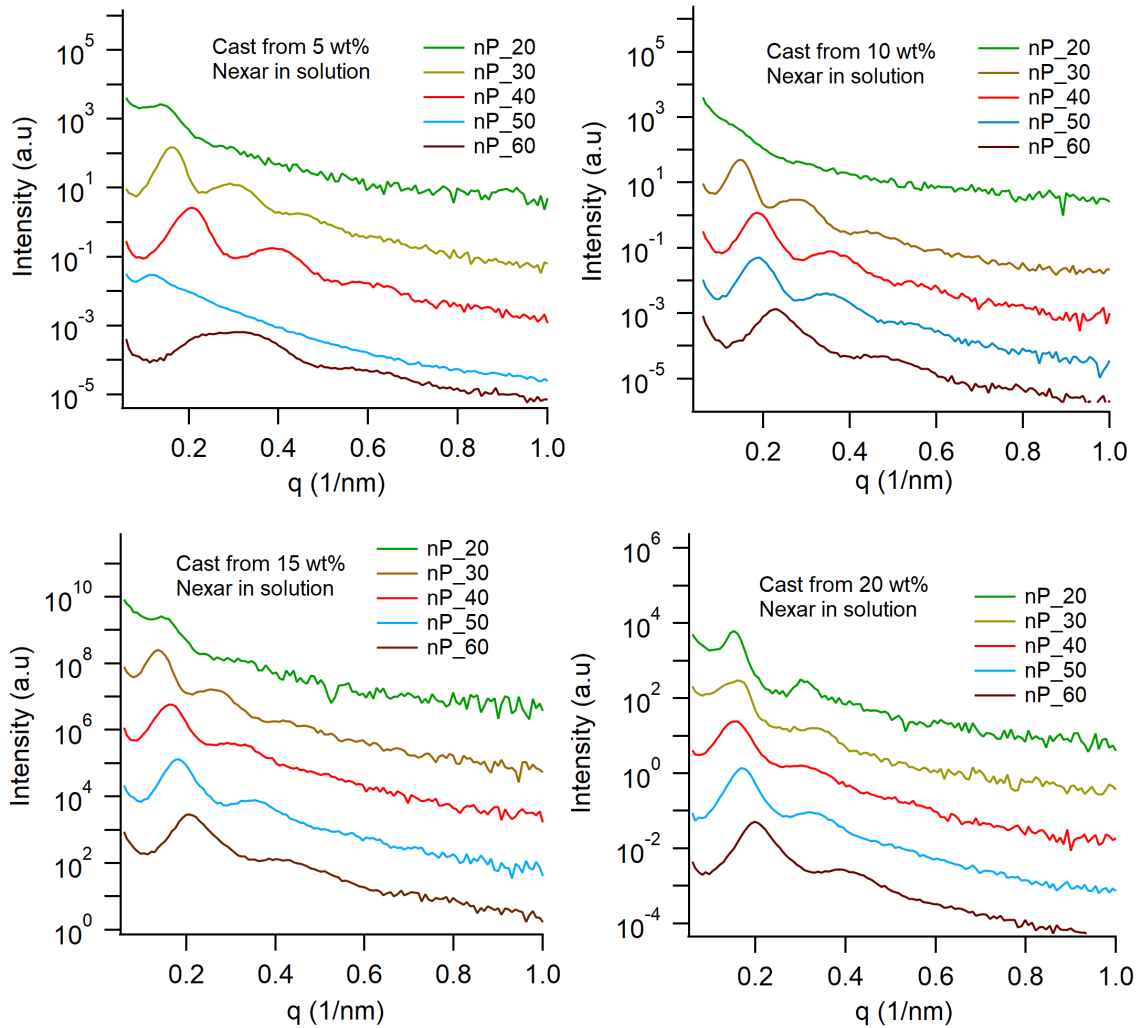


Figure B.3: SAXS data for films cast from solutions reported in the previous figure. The films were prepared by bar coating a single layer with a gap height of 250 μm .

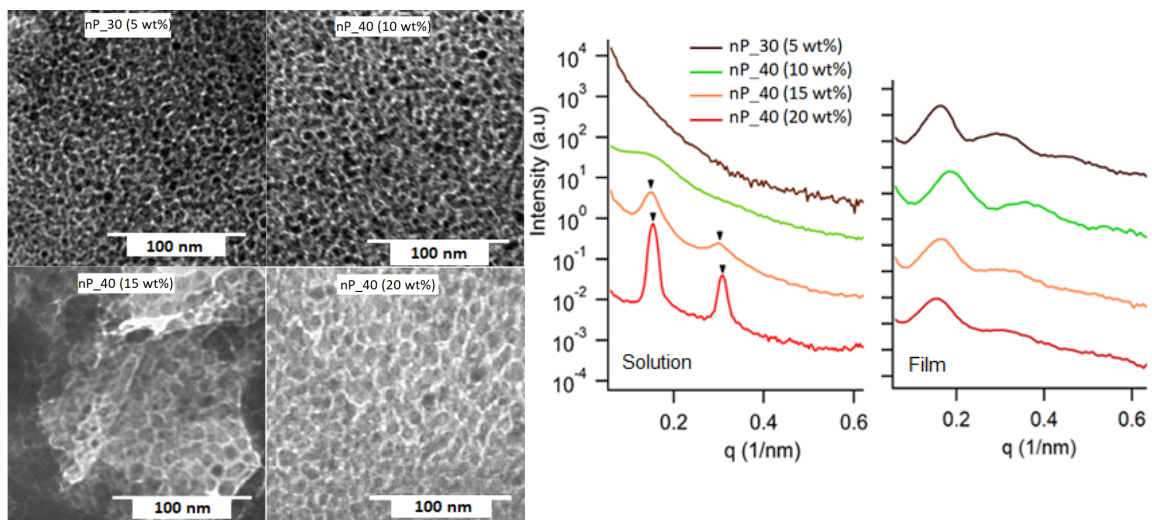


Figure B.4: TEM images of films cast with 250 μm gap height and corresponding solution and film SAXS data from Figures S2 and S3. The number in the bracket indicates the wt% of polymer in the casting solution.

Figure B.5 illustrates how sequential deposition of solution results in the formation of highly ordered and oriented structure when cast from solution having ordered structure. The main document discussed the bulk structure and domain orientation observed in films cast using 1000 μm gap height. Here we show that even using a lower gap height of 100 μm , with a selective casting solvent, we still observe highly ordered and oriented domains in the surface layer by sequential deposition of layers. Both the intensity vs azimuth degree figures are plotted to the same scale of intensity to show enhanced orientation of domains in the 100 μm X 3 films.

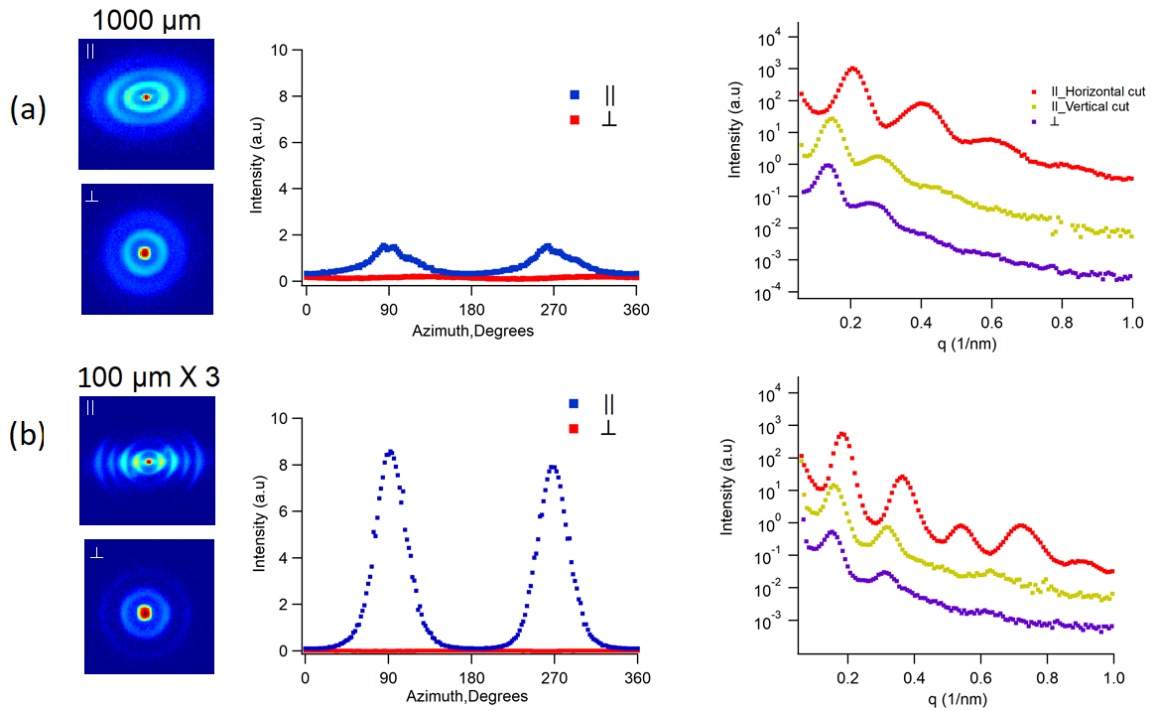


Figure B.5: 2D scattering profiles for films cast using nP₃₀ solvent, corresponding plot of Intensity as a function of azimuth degrees, and 1 D scattering profiles from azimuthal integration of intensity of the 2D scattering rings for $\perp$ configuration and intensity integration over horizontal and vertical cut region for the $\parallel$ configuration, for (a)1000 μm and (b) 100 μm X 3 films.

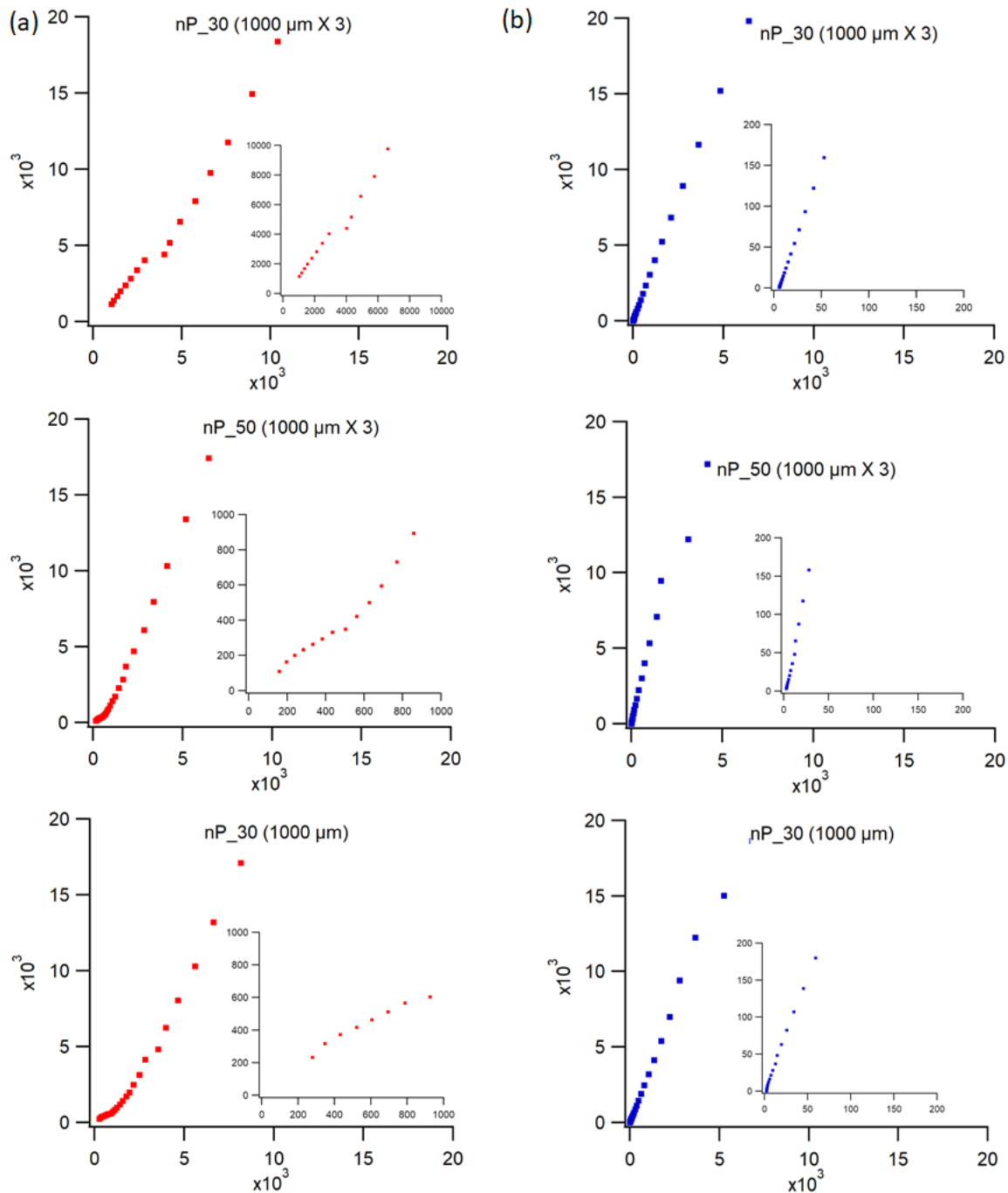


Figure B.6: Nyquist for films (a) at 35% RH (b) after soaking in DI water. The inset shows the initial high frequency region of the Nyquist plot. The bulk resistance was estimated by extrapolating a straight line from the beginning of the semicircle to get the Z' intercept where $-Z''$ is zero.

Appendix C

Supporting Information for:
Structure-property relations of
triblock copolymer thermoplastics
with interaction-tuned polymer
additives

I: Characterization of SEBS received from Kraton

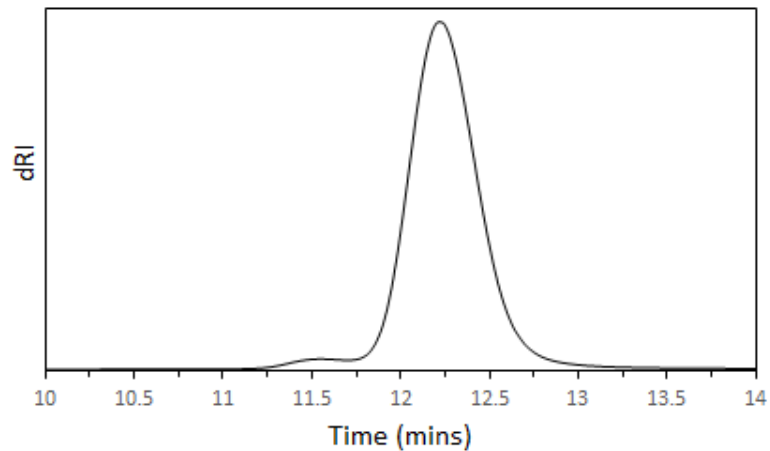


Figure C.1: GPC trace for SEBS

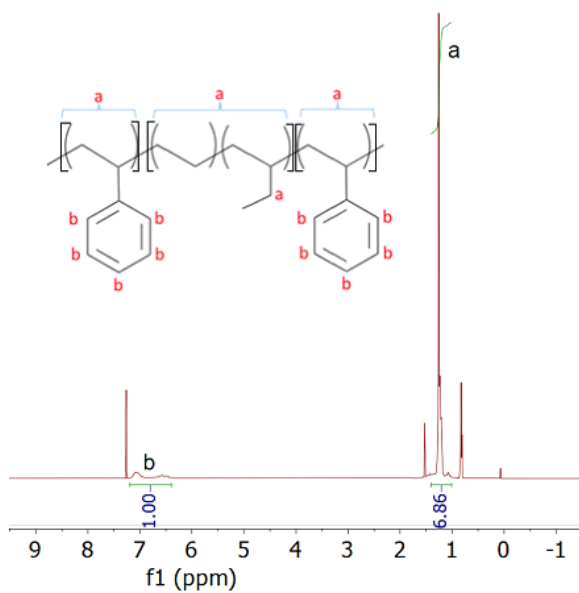


Figure C.2: ¹H NMR spectrum for SEBS. Mole % styrene calculated based on integrated peak area ratio of aromatic protons of styrene (at 6.39-7.19 ppm; labeled b) and aliphatic protons of chain backbone plus methylene protons resulting from 1,2 addition butadiene because these signals overlap (at 1.00-1.40 ppm; labeled a).

II: Characterization of synthesized random copolymers (PrCs)

Table C.1: Macromolecular Characteristics of PrC Copolymers.

Sample	f_{CHMA}	$M_n(\text{kg/mole})^{\text{a}}$	$\bar{D}$	$N_{\text{MMA}}^{\text{b}}$	$N_{\text{CHMA}}^{\text{b}}$
Sample 1	0.72	2.8	1.09	5	14
Sample 2	0.73	4.4	1.08	8	22
Sample 3	0.76	10	1.13	17	52
Sample 4	0.74	12.5	1.12	23	61
Sample 5	0.78	17	1.13	25	86
Sample 6	0.74	18.5	1.13	33	91
Sample 7	0.75	21.2	1.14	35	106
Sample 8	0.76	28.5	1.06	45	143
Sample 9	0.66	34.8	1.16	81	159
Sample 10	0.76	65.5	1.11	103	329

^a Determined by GPC

^b Determined based on ^1H NMR

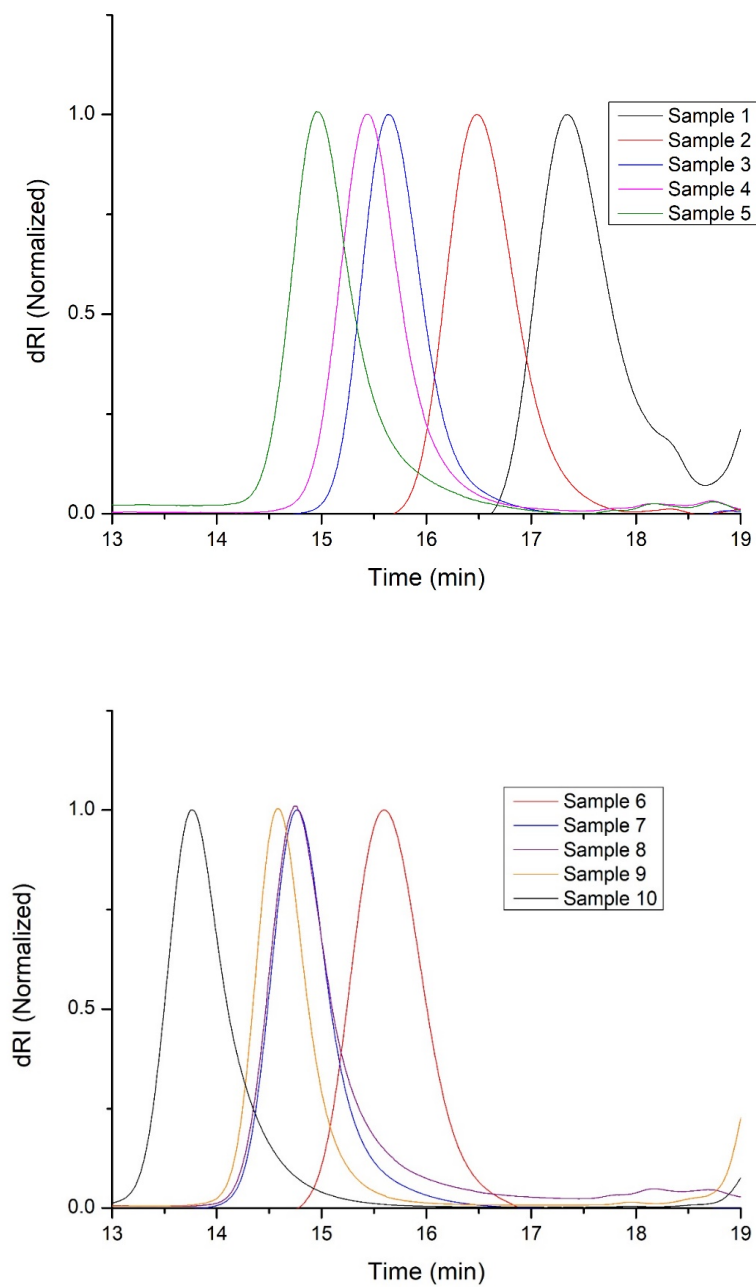


Figure C.3: GPC traces of PrC copolymers (Samples 1-10). The legend identifies each PrC by the naming used in Table S1.

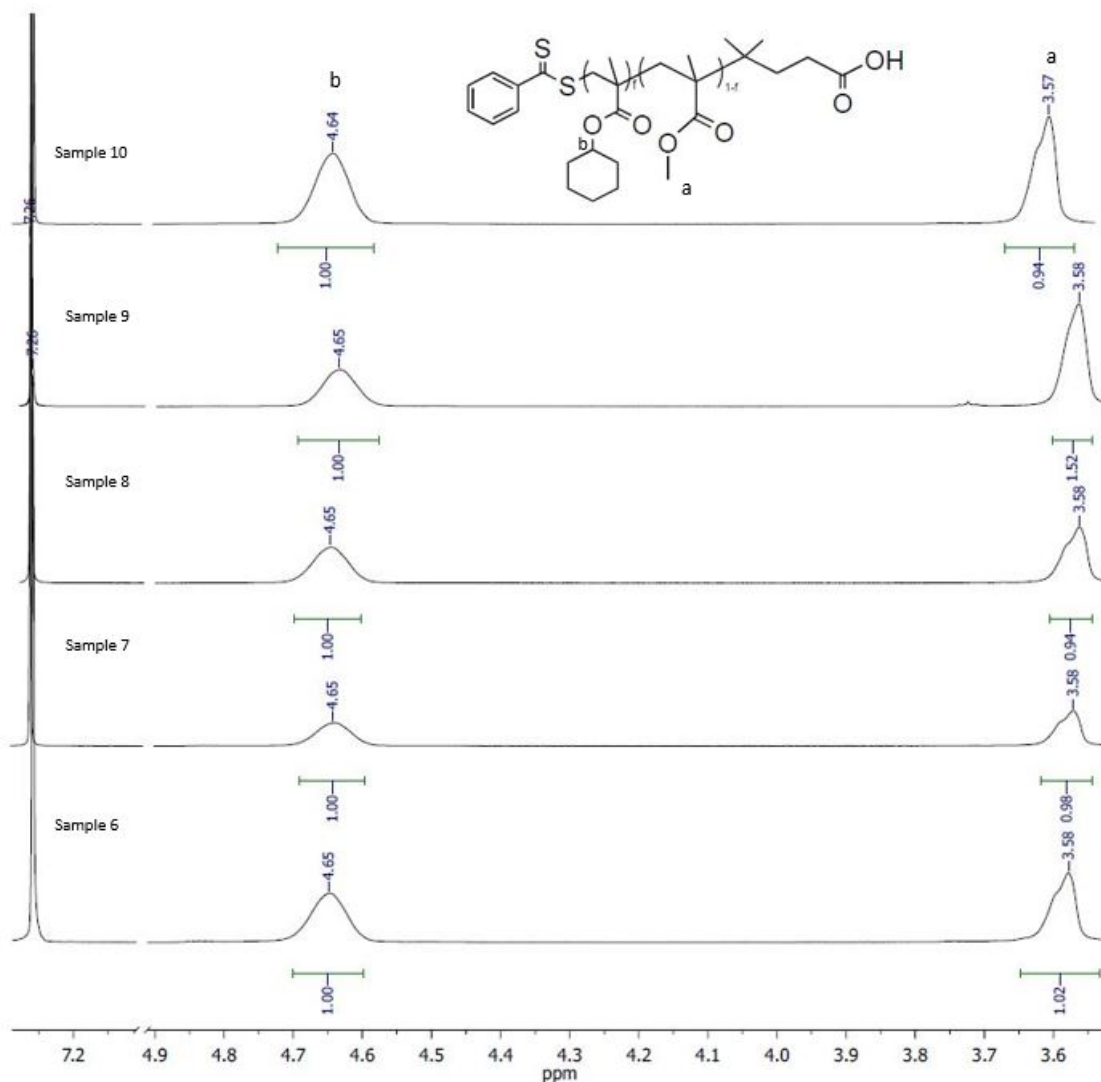


Figure C.4: Stacked ^1H NMR spectra of PrCs, (Samples 1-10) arranged such that molecular weight increases up the stack. (Labels on each spectrum at the left is consistent with naming in Table S1.) Copolymer composition was calculated from integrated peak areas corresponding to the methyl ester of MMA (at 3.57-3.58 ppm; labeled a) and the proton at the bridgehead of CHMA (at 4.63-4.65 ppm; labeled b). Spectra were acquired in CDCl_3 , as evidenced by the residual solvent peak at 7.26 ppm.

III: Structure of SEBS and blends

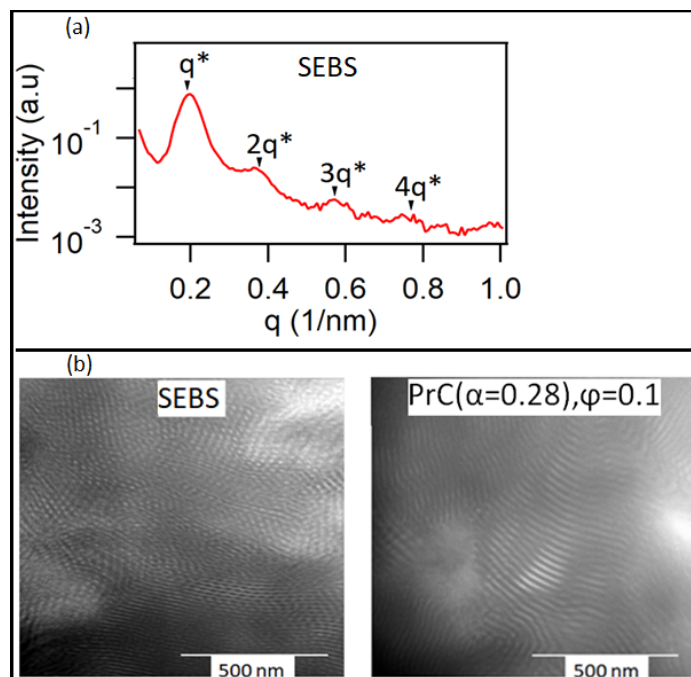


Figure C.5: (a) SAXS data for SEBS (b) TEM images for SEBS and SEBS/PrC blend with 10 volume% additive loading. The dark region corresponds to the styrene domain and the bright region corresponds to the rubber domain after staining with ruthenium tetroxide.

IV: SAXS data for blends

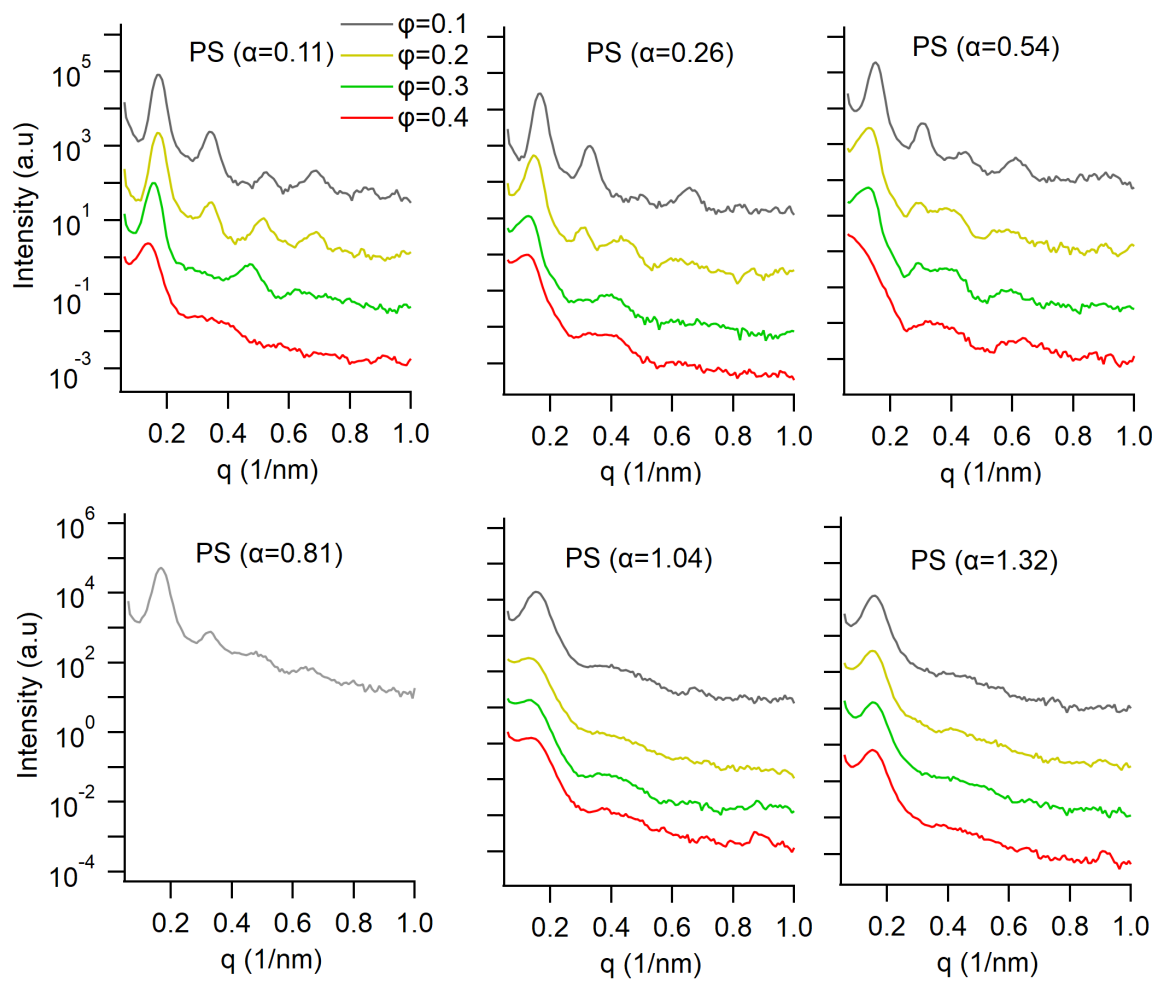


Figure C.6: SAXS for SEBS/PS blends

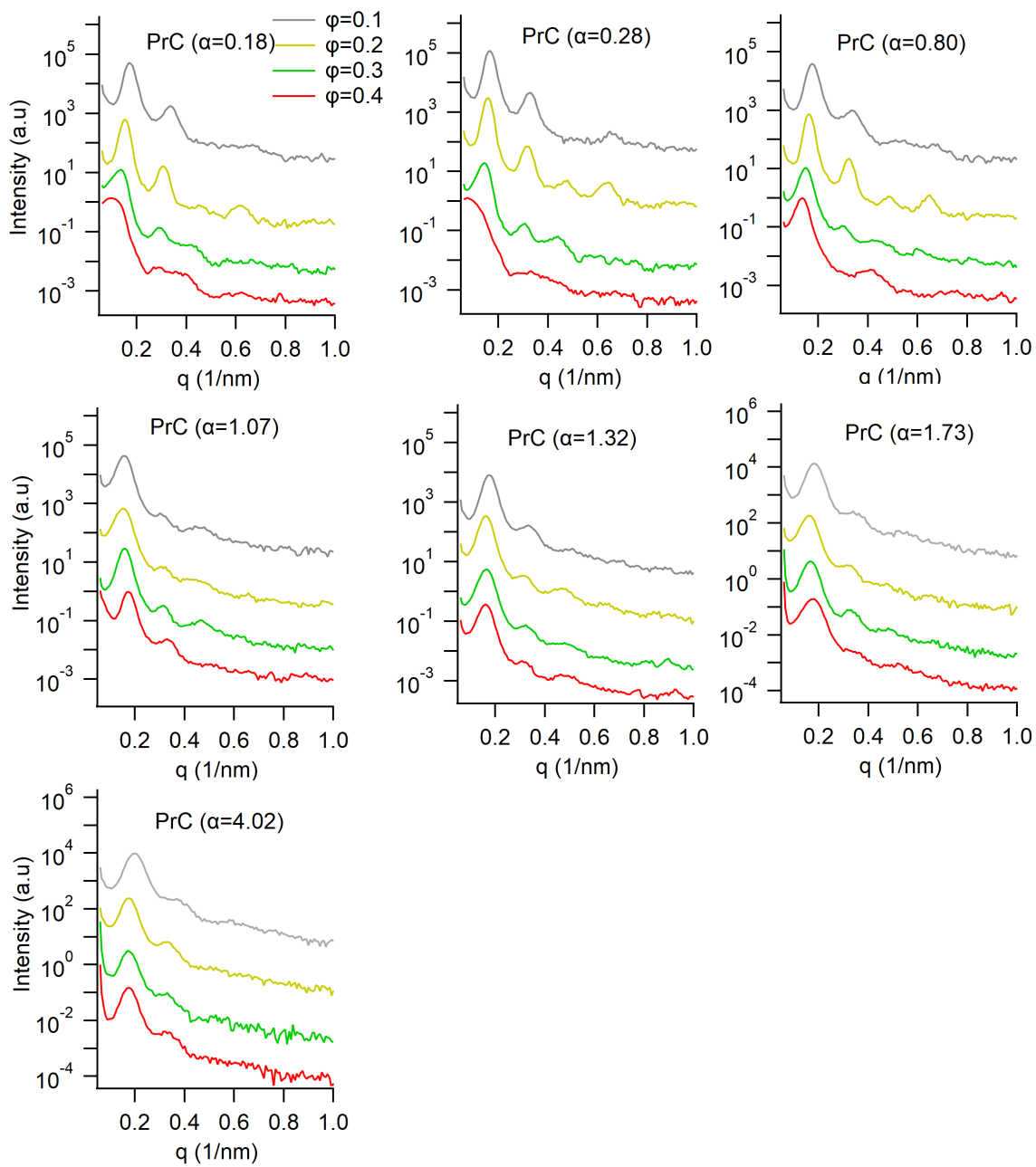


Figure C.7: SAXS for SEBS/PrC blends

V: Structure of as-cast and annealed blends prepared using different casting solvents

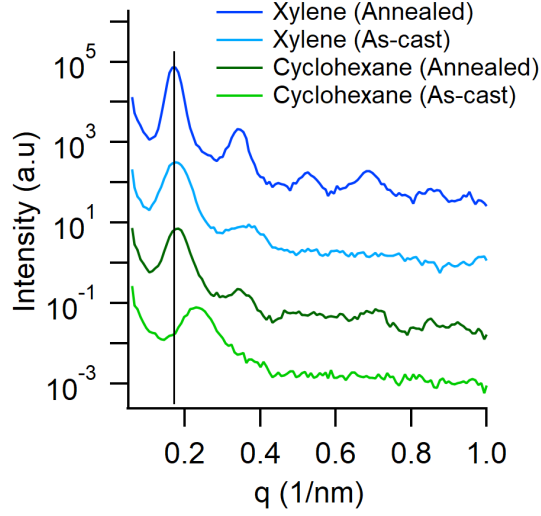


Figure C.8: SAXS data for SEBS/PS blends with $\alpha=0.11$ and $\phi=0.1$. As-cast samples were prepared using xylene and cyclohexane as solvents. Annealed samples were prepared by thermal annealing of the as-cast samples at 140 °C for 48 h. Vertical line is to enable comparison of the position of the first order peak. The higher order peaks for both of the annealed samples are in accordance with a lamellar structure.

VI: Reproducibility of the blend structure by thermal annealing

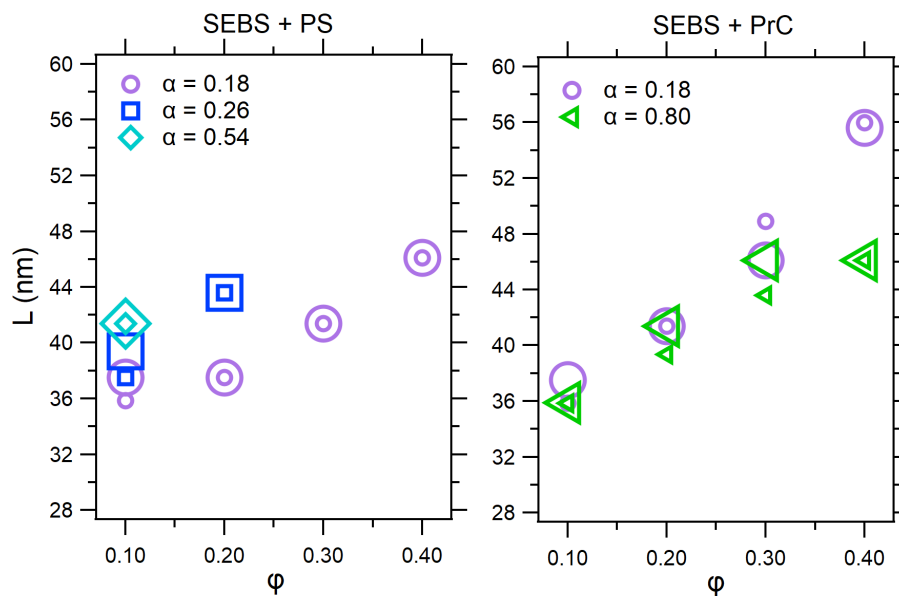


Figure C.9: Periodicity of SEBS/PS and SEBS/PrC samples with different additive loadings (ϕ) as determined from SAXS. The markers with the same shape but of different size for the same composition correspond to two different attempts of making the same blend sample.

VII: Trends in tensile property for blend samples with additive loading of $\phi=0.3$

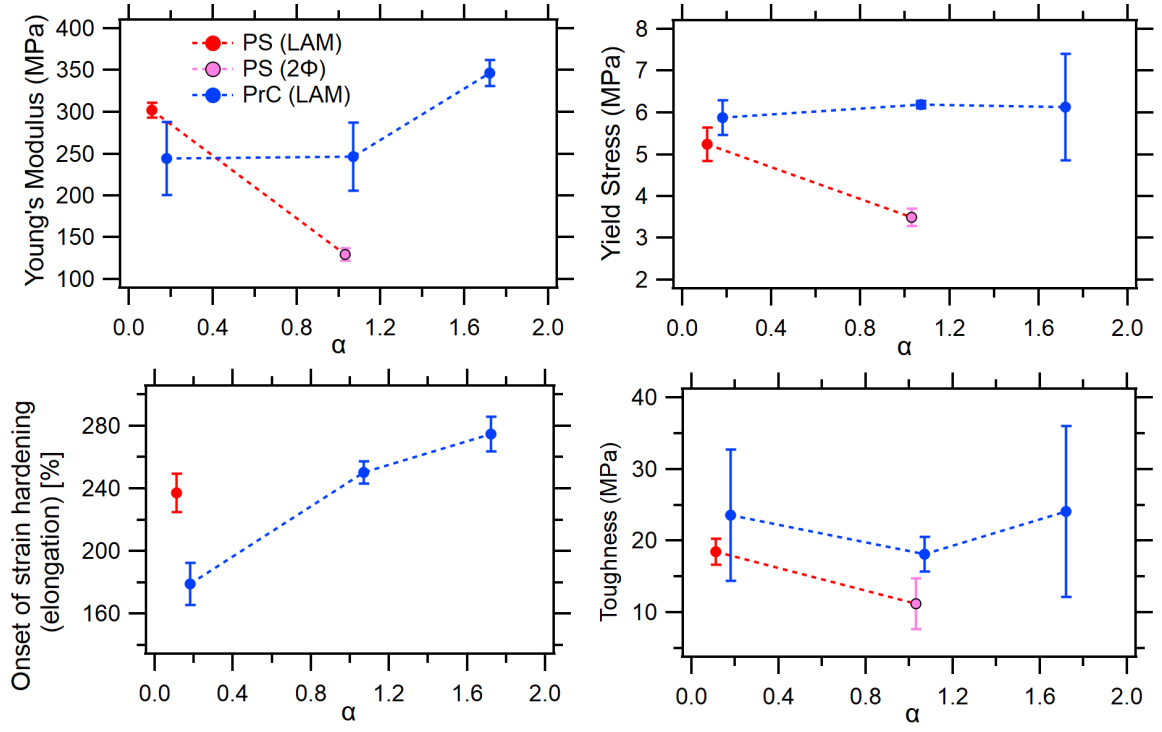


Figure C.10: Trend in tensile properties for SEBS/PS and SEBS/PrC samples with α

Vita

Karthika Madathil was born in Mumbai, India. She attended Visvesvaraya National Institute of Technology in Nagpur, India, where she earned her bachelor's degree in Chemical Engineering. She then joined Arizona State University where she worked in the lab of Prof. David Nielsen. After completing a Master's degree in Chemical Engineering from ASU, she moved to University of Tennessee where she began her PhD work under the guidance of Prof. Gila Stein. Her doctoral research has focused on understanding the thermodynamics and kinetics of self-assembly process in block copolymers with the goal of designing materials with tailored performance. After graduation, she plans to continue her research career in the field of soft and functional materials.