SELF-ASSEMBLED PATTERNS OF BLOCK COPOLYMER/HOMOPOLYMER BLENDS

A Dissertation
Presented to the
The Graduate Faculty of the University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

Dongsik Park
May, 2008
SELF-ASSEMBLED PATTERNS OF BLOCK COPOLYMER/HOMOPOLYMER BLENDS

Dongsik Park

Dissertation

Approved:  

Advisor  
Dr. Erol Sancaktar

Committee Member  
Dr. Avraam I. Isayev

Committee Member  
Dr. James L. White

Committee Member  
Dr. Bi-min Zhang Newby

Committee Member  
Dr. Fred Kat-Chung Choy

Accepted:  

Department Chair  
Dr. Sadhan C. Jana

Dean of the College  
Dr. Stephen Z. D. Cheng

Dean of the Graduate School  
Dr. George R. Newkome

Date
ABSTRACT

Many researchers have studied the orientation behavior of block copolymers (BCPs) with the most recent works directed towards nanotechnologies. Self-assembly of block copolymers is very relevant in controlling periodic nanostructures for nanotechnological applications. Nanotechnological applications of BCPs are possible due to their physical properties related to mass and energy transport, as well as mechanical, electrical, and optical properties. These properties provide substantial benefits in nanostructure membranes, nanotemplates, photonic crystals, and high-density information storage media. In many applications, such nanopatterns need to be achieved as ordered and tunable structures. Consequently, the control of orientation of such structures with defect-free ordering on larger length scales still remain as major research challenge in many cases. In addition to their pure block forms, blends of copolymers with other polymers offer productive research areas in relation to nanostructural self-assembly.

We prepared well-aligned nanocylinders into block copolymer over the enhanced sample area and scale of height without any external field applications or modification of interaction between the sample and the substrate. Self-assembled 3-dimensional perpendicular cylinder orientation was achieved mainly by blending of minority homopolymer into the blockcopolymer. Thus, this study investigated a spontaneous and simple method for the orientation of perpendicular cylinders in BCP/homopolymer mixtures on a preferential substrate, by increasing the interaction force between the homologous polymer pair at a fixed composition of minority block component. Since the
thermodynamical changes have been simply accomplished by the control of incompatibility between the block components, the intrinsic advantages of block copolymer nanopatterning, such as fast and spontaneous 3-dimensional nanopatterning with a high thermodynamic stability and reproducibility, have been completely preserved in this fabrication strategy. By exploiting thermodynamical changes using temperature variation and by blending a homopolymer with well controlled molecular weight, we illustrated that redistribution of homopolymer resulted in a shift of phase boundaries and in the stabilization of well-ordered structures to create new opportunities for nanotechnologies.
ACKNOWLEDGEMENTS

I would like to extend my upmost appreciation to my advisor Dr. Erol Sancaktar for his invaluable guidance and support during my graduate career. This research would not have been possible without his guidance and encouragement. I would also like to extend my gratitude toward my committee members, Dr. Avraam I. Isayev, Dr. James L. White, Dr. Dr. Bi-min Zhang Newby, and Dr. Fred Kat-Chung Choy for their time, advices, and suggestions on my research works.

I would like to express my special gratitude to Dr. Dae Up Ahn for his advice and leading to this great research topic and to Dr. Mark Foster and Dr. Sewoo Yang in the University of Akron’s polymer science department for allowing me to use their equipments and materials. I would also like to thank Dr. Sadan Jana, my department chair for his advice and help during my graduate school years. I would also like to thank President Steve Johnson at Advanced Coating International Inc. and Dr. Kyung Don Kim at Omnova Solutions Inc. for their supports and advices during my internship career.

Finally, I would like to give my thanks with all hearts to all those who gave me that added bit of confidence in helping me accomplish my life long goal: Kyun Ha Ban, Soo Jeoung Park, Dr. Jaein Suh, Namil Kim, Byoung Jo Lee, Dr. Wutticharoenwong Kosin, Pritam Das, Serkan Bas, and the faculties and staffs of the University of Akron’s Department of Polymer Engineering.
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Figure 6.10. AFM images of SBS1102/PS21K blend at different temperatures: (a) SBS/PS21K 120, (b) SBS/PS21K 150, (c) SBS/PS21K 170, and (d) SBS/PS21K 190. Images were obtained from ~10 \( \mu \text{m} \)-thick samples annealed on Teflon substrates at 120 °C, 150 °C, 170 °C, and 190 °C, respectively. Topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is \( 2 \times 2 \mu \text{m}^2 \)...

Figure 6.11. AFM images of SBS1102/PS27K blend at different temperatures: (a) SBS/PS27K 120, (b) SBS/PS27K 150, (c) SBS/PS27K 170, and (d) SBS/PS27K 190. Images were obtained from ~10 \( \mu \text{m} \)-thick samples annealed on Teflon substrates at 120 °C, 150 °C, 170 °C, and 190 °C, respectively. Topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is \( 2 \times 2 \mu \text{m}^2 \)...

Figure 7.1. AFM images of SIS4114/PS12K annealed at 130 °C on different substrates: (a) ~100 nm thick samples on Si substrate, (b) ~420 nm thick samples on Kapton substrate, (c) ~360 nm thick samples on Mylar substrate, and (d) ~10 \( \mu \text{m} \) thick samples on Teflon substrate. The size of the image is \( 2 \times 2 \mu \text{m}^2 \)...

Figure 7.2. AFM images of SIS4114/PS17K annealed at 130 °C on different substrates: (a) ~100 nm thick samples on Si substrate, (b) ~420 nm thick samples on Kapton substrate, (c) ~360 nm thick samples on Mylar substrate, and (d) ~10 \( \mu \text{m} \) thick samples on Teflon substrate. The size of the image is \( 2 \times 2 \mu \text{m}^2 \)...

Figure 7.3. AFM images of SIS4114/PS27K annealed at 130 °C on different substrates: (a) ~100 nm thick samples on Si substrate, (b) ~420 nm thick samples on Kapton substrate, (c) ~360 nm thick samples on Mylar substrate, and (d) ~10 \( \mu \text{m} \) thick samples on Teflon substrate. The size of the image is \( 2 \times 2 \mu \text{m}^2 \)...

Figure 7.4. AFM images of SBS1102/PS17K annealed at 120 °C on different substrates: (a) ~95 nm thick samples on Si substrate, (b) ~450 nm thick samples on Kapton substrate, (c) ~390 nm thick samples on Mylar substrate, and (d) ~10 \( \mu \text{m} \) thick samples on Teflon substrate. The size of the image is \( 2 \times 2 \mu \text{m}^2 \)....
Figure 7.5. AFM images of SBS1102/PS21K annealed at 120 °C on different substrates: (a) ~95 nm thick samples on Si substrate, (b) ~450 nm thick samples on Kapton substrate, (c) ~390 nm thick samples on Mylar substrate, and (d) ~10 µm thick samples on Teflon substrate. The size of the image is $2 \times 2 \, \mu m^2$.

Figure 7.6. AFM images of SBS1102/PS27K annealed at 120 °C on different substrates: (a) ~95 nm thick samples on Si substrate, (b) ~450 nm thick samples on Kapton substrate, (c) ~390 nm thick samples on Mylar substrate, and (d) ~10 µm thick samples on Teflon substrate. The size of the image is $2 \times 2 \, \mu m^2$.

Figure 7.7. AFM images of different samples on Kapton: (a), (b), and (c) are from ~420nm thick samples of SIS4114 blends with PS12K, PS17K, and PS27K, respectively. (d), (e), and (f) are from ~450nm thick samples of SBS1102 blends with PS17K, PS21K, and PS27K, respectively. The size of the image is $2 \times 2 \, \mu m^2$.

Figure 7.8. AFM images of different samples on Mylar: (a), (b), and (c) are from ~360nm thick samples of SIS4114 blends with PS12K, PS17K, and PS27K, respectively. (d), (e), and (f) are from ~390nm thick samples of SBS1102 blends with PS17K, PS21K, and PS27K, respectively. The size of the image is $2 \times 2 \, \mu m^2$. 
CHAPTER I
INTRODUCTION

1.1. Motivation and Objectives

Nano-science and nano-technology have grown explosively in the past decade [1]. Nanotechnology in material science starts with the material preparation, fabrication of nanostructure, and their application. Nanotechnology enables various applications including the continuing miniaturization of electronic and memory devices, the development of more potent drugs that can recognize and attack only the diseased sites, the development of more accurate and effective diagnostic procedures, and the design and synthesis of more robust catalysts.

Nanostructures can be manipulated by using various top-down high resolution lithographic methods. The lithographic approach carves a large size material into smaller pieces and is able to produce structures with dimensions approaching to a few 100 nanometers at an industrial scale. Chemists and scientists also synthesize materials and manipulate nanostructures by molecular assembly, or the bottom-up method. Block copolymers (BCPs) have been the focus of much interest during the last 40 years because of the general lack of miscibility between their constituent blocks, leading to microphase separation [2]. Triblock copolymers of polystyrene and polydienes have received the greatest attention since their introduction in 1965 [2], because their molecular structure is
relatively simple and uniform as one of the model polymers. Since 1967, the date of the first conference on BCPs [3], many researches [4-12] have been contributed to the subject of block copolymers.

Self-assembly of BCPs is an important strategy in new material science and technology, and nano-sized patterns from self-assembly are poised to replace current lithographic technologies. BCPs have become the center of attention in such self-assembly-based bottom-up processes due to the scale of the microdomains between 10 and 100 nm, and their various chemical and physical properties. The size and shape control of microdomains have proven to be quite effective in BCPs by modification of their thermodynamic states via molecular weights and compositions [13].

Self-assembled structures in BCPs can be readily spread over a large area throughout the bulk material, giving rise to long-range ordering and the formation of structures such as cubic array of spheres or hexagonally packed cylinders. However, the order in these BCPs is not as high as in crystals, and the persistence length of the ordered component is generally short (a few micrometers), especially in the case of cylinders and lamellae [14]. Control over microdomain orientations and elimination/minimization of defects play a crucial role in optimization of the resultant physical properties with nanostructures. Understanding the mechanism of defect formation has been an essential topic in controlling BCPs microstructures [15].

In order to achieve a regularly ordered structure across long range scales, the orientation can be controlled by using self-organizing materials, whose assembly is ordered and directed by various molecular interactions (and their combination) as well as by external constraints. Competing factors in controlling structure formation include
chemical differences, conformational entropy, spatial constraints (molecular shape effects) and external (electric, magnetic, hydrodynamic flow) fields. The substrate can be prepatterned on the length-scale of the polymer [16-18], or coated with a thin layer of anchored random copolymers to provide a neutral surface [19,20], equally attractive for both blocks. Application of e.g. high electric fields [21] allows one to also overcome the surface effect and to align block copolymer morphologies perpendicular to the surface. Mixtures of block copolymers and homopolymers [22-24] also provide interesting micro- and nanostructures, and thus offer additional routes for patterning.

Block copolymer/homopolymer mixtures have been of considerable interest because they can be easily modified to yield desired properties in polymeric materials such as pressure-sensitive adhesives. The phase behavior of these mixtures is generally quite complicated because two different transitions can occur at the same time, i.e. macrophase and microphase separations. If the molecular weight of the added homopolymer is sufficiently low compared with that of the block copolymer, it tends to be solubilized into one of the microdomains [25-28]. In this case, the macrophase separation is suppressed, and the microphase separation becomes dominant.

Recently, several researchers extended self-consistent mean field calculations to BCPs and homopolymer blends having ordered phases other than lamellae. Matsen [29] found that the addition of homopolymer stabilizes the complex ordered phases in the weak segregation regime. Janert and Schick [30] investigated the effect of relative homopolymer length on the phase behavior in the weak to the intermediate segregation regime considering lamellae, cylinder, and body-centered-cubic phases.
Main concerns in this study are directed toward asymmetric copolymers, especially to cylinder-structured orientation by blending of a homopolymer. The cylindrical morphology more easily allows the study of the dynamics of long-range ordering, in comparison to the lamellar structure. The usefulness of parallel cylinders in nanotechnology, however, is limited in comparison to the lamellar structure [31,32]. Cylinders perpendicular to a substrate are more interesting and essential in preparation of templates for nanoreplicated pattern formation. Russell and coworkers [33-35] investigated and reported on methods to order perpendicular cylinders on substrates by controlling the thickness of perpendicular cylinders and by adjusting the amount of blended homopolymer with asymmetric block copolymer. Even though the homopolymer was incorporated into the copolymer and the adjustment of molecular weight enhanced the orientation of perpendicular cylinders, there has been a limit to increase the dimension of the perpendicular cylinders at larger scale film thicknesses. Furthermore, control of thickness, modification of substrate-BCPs interactions, or application of external field has been necessary in combination with the blending method.

Recently, Ahn and Sancaktar [36] reported on perpendicularly ordered cylinders prepared by simply blending the asymmetric polystyrene-block-polyisoprene-block-polystyrene (SIS) triblock copolymer with polystyrene (PS) homopolymers (same minor component in SIS) having different molecular weights. Control of the homopolymer molecular weight enabled changes in the periodic spacing and hexagonal orientation of the perpendicular nanocylinders. This study assumed that PS homopolymer with a molecular weight similar to that of the PS block in the SIS generated an internal driving force converting an initially stable parallel cylinder orientation to another stable
orientation perpendicular to the substrate. Once a strong preference was achieved for the perpendicular orientation, the morphology of the BCP/homopolymer was not influenced by sample thickness and/or difference of surface interactions between the polymer and the substrate. Thus, a method to control perpendicular ordering on large scale throughout the area in asymmetric triblock copolymers was demonstrated by simply adjusting thermodynamic conditions for BCP/homopolymer blends. Furthermore, it was illustrated that the control of substrate-polymer interaction and modification of the substrate surface do not necessarily influence the perpendicular orientation process of the cylinders, especially when a thermodynamic preference for perpendicular orientation is already strongly introduced into the material by the blending, in the BCPs, of a homopolymer of an appropriate molecular weight. This work, however, has been restricted to a specific system (Vector 4113, SIS, DEXCO Polymers). Consequently, it is necessary to carry out systematic studies on different blends of asymmetric BCPs and different molecular weight homopolymers in order to be able to extend our recent discoveries to a large number of BCP/homopolymer blend systems.

The main objective of this research, therefore, is to prepare perpendicularly and hexagonally well-oriented cylinders with a consistency over a large size of sample area and thickness by using only thermodynamic controls on BCP/homopolymer blend systems. This goal will be achieved by thermodynamic control over the immiscibility between A and B blocks in BCPs (ABA) and by exploiting the compatibility between A homopolymer and A block in BCPs. Additional thermodynamic control is achieved by kinetic adjustments, i.e., by annealing BCPs/homopolymer mixtures.
To achieve the above-mentioned goals, we utilized untested systems, such as a series of SIS and polystyrene-b-polybutadiene-b-polystyrene (SBS) BCPs. Each BCP under this study has different molecular weights and compositions for each block. Thus, small angle x-ray scattering (SAXS), as well as tapping mode atomic force microscopy (AFM) were mainly employed to investigate a series of mixtures of a compositionally asymmetric BCPs and PS homopolymers. Phase behavior from various measurements was compared with theoretical predictions and discussed.
CHAPTER II
BACKGROUND AND STATE OF THE ART

2.1. Thermoplastic Elastomers

Thermoplastic elastomers, a new class of polymers of practical and theoretical interest, were announced by the Shell Chemical Company (U.S.A.) in 1965 [4]. These novel products have been formed into useful articles by modern rapid thermoplastics processing techniques, such as injection molding, and without any chemical vulcanization step still provide most of the useful properties of vulcanized rubber. High resilience, high tensile strength, highly reversible elongation, and abrasion resistance were obtained [37,38]. The thermoplastic elastomers consist of ordered block copolymers of the general structure ABA, where A is a thermoplastic block polymer and B is an elastomeric block polymer. Choice of monomers, block length, and the weight fractions of A and B are crucial in achieving elastomeric performance. An example is a polystyrene-b-polylbutadiene-b-polystyrene (SBS) block copolymer where the molecular weights of the blocks and the weight fraction of polystyrene are restricted. Block copolymers have multi-phase morphology, due to the basic incompatibility of the polymer blocks. A two-phase system is formed, with middle-block phase constituting a continuous three-dimensional elastomeric network and the dispersed end-block phase serving as multi-junction points for the ends of the middle blocks.
2.1.1. Historical Review

Efforts in the synthetic rubber industry on these block copolymers began about 1960 [2]. The main purpose of this research was the economic polymerization of polyisoprene with a high cis-1,4 structure, i.e. the production of a synthetic version of natural rubber. The research about synthesis on a semi-commercial scale using both Ziegler type catalysts [39] and lithium metal catalysts [40] stimulated rubber synthesis. About this time, workers at the Shell Development Company investigated lithium metal initiators for isoprene polymerization and found that alkyllithiums were better initiators than the metal itself, a conclusion duplicated at other industrial research laboratories [41]. There were no chain termination or chain transfer steps with the benefit of the lithium based catalysts and properly purified monomer. Consequently, when the original monomer was consumed totally, the polymer chain still remained active, which let the further initiation of polymerization if more monomer was added. In 1957, an investigation at the Shell Development Company [42] illustrated the process for manufacture of polystyrene-polydiene block copolymers using alkyllithium initiators. This research contributed to the background knowledge, even though at the time these materials were not recognized as thermoplastic elastomers. At that time, difunctional initiators were also used for the polymerization of triblock copolymers [43,44]. These were produced under condition which gave polydiene segments with relatively low 1,4 content and so the products had very poor elastomeric properties. A new SB type rubber was described subsequently for use in blends with conventional vulcanized rubbers [45]. This polymer was later revealed to be a polystyrene-polybutadiene diblock polymer [46] in which one block tapered into the other.
At the time of these investigations, the melt rheologies of polybutadiene [47] and polyisoprene [48] were being investigated, and these materials showed Newtonian behavior. Although the polybutadiene and polyisoprene behave as solid materials, these elastomers are in fact viscous materials, even at room temperature. When Shell Chemical research was directed at the serious problems associated with their storage and commercial manufacture, the polydiene elastomers were polymerized at lower molecular weights and with short blocks of polystyrene, first at only one end and later at each end. In contrast to the diene homopolymers, these block copolymers showed non-Newtonian behavior, in that their viscosities were anomalously high at other shear rates [3]. An even more striking anomaly was given by the physical properties of the triblock copolymers. When pressed into tensile sheets they showed properties in the unvulcanized state which were very similar to those of conventional elastomeric vulcanizates, that is, they had high tensile strength, high elongations and rapid and almost complete recovery after elongation. These examples of anomalous behavior led to the development of the domain theory. This theory predicts that, in the bulk state, the polystyrene short end segments of the block copolymers agglomerate. At temperatures significantly below the glass transition temperature of polystyrene, these agglomerations (domains) act as strong and multifunctional junction points, and thus, the triblock copolymers behave as though they are joined in a cross-linked network [49].
2.1.2. Structure

The basic structure of most of the polystyrene/polydiene BCPs is poly(styrene-b-butadiene-b-styrene) (SBS), or poly(styrene-b-isoprene-b-styrene) (SIS). Their most important feature is that they have phase separated structures, unlike the corresponding random copolymers. The two phases of polystyrene and polydiene retain many of the properties of the respective homopolymers. SBS and SIS BCPs have two different Tg’s at room temperature [50], which means that the polystyrene phase is strong and rigid, while the polydiene phase is soft and elastomeric. If the polystyrene phase is only a minor part of the total volume, it is reasonable to postulate a phase structure. In this structure, the polystyrene phase consists of separate spherical regions (domains). The rigid polystyrene domains act as multifunctional junction points to give a crosslinked elastomer network similar to that of a conventional vulcanized rubber, since both ends of each polydiene chain are terminated by polystyrene segments. However, in this case the cross links are formed by a physical rather than a chemical process. At room temperature, a block copolymer of this type has many of the properties of a vulcanized rubber. However, when the material is heated, the hard segments soften and the network loses its strength and eventually the block copolymer can flow. When the heated block copolymer is cooled down, the domains become hard again and the original properties are regained. Similarly, such a block copolymer will be soluble in many solvents but it will regain its original properties when the solvent is evaporated.
2.1.3. Synthesis

SBS, SIS, and similar block copolymers are made by anionic polymerization [51,52]. The reaction is limited to only three common monomers (styrene, isoprene, and butadiene). The synthesis of triblock copolymers can be accomplished using one of the following methods [2]: (a) three-step sequential addition of monomers; (b) two-step sequential additions of monomers followed by a coupling reaction with a suitable difunctional linking agent; and (c) use of a difunctional initiator and a two-step sequential addition of monomers. The purification requirements are also valid for the successful use of the three-step sequential addition. This method has the advantage that asymmetric triblock copolymers ABA, with the two A blocks having different molecular weights, can be prepared. The second method involves the synthesis of the living diblock AB, where the B block has only half of the molecular weight compared to the desired one, followed by reaction with a difunctional linking agent. The linking reaction must be efficient and fast. However, the stoichiometry of the reaction is difficult to control. Consequently, a small excess of the living diblock copolymer is used to ensure complete linking. The excess diblock copolymer has to be removed by fractionation in a later step. This technique can be only used for the synthesis of symmetric ABA triblock copolymers. The third method is limited to the synthesis of symmetric triblock copolymers, but is versatile, since it involves only a two-step reaction without fractionation or other purification steps. The main limitation of this method is the choice of the difunctional initiator, which must be able to initiate the polymerization of the desired monomer with the same rate from both directions.
2.2. Phase Behavior of Block Copolymers

Block copolymers are composed of chemically different chains. Depending on the number of different blocks, their composition, and the way they are linked together (linear, branched, star-like or cyclic), they can form a variety of ordered structures with characteristic lengths on the mesoscale. This self-organization into ordered structures (also called morphologies) has attracted considerable interest among theoreticians and experimentalists during the last few decades, as indicated by an increasing number of publications in this field. Living anionic polymerization enabled the controlled synthesis of block copolymers, and the number of accessible monomers since its inception has increased due to further developments in various types of controlled polymerization techniques. Besides the pure block copolymers, their blends with other components are also fascinating research areas. Starting with changing thermodynamics by temperature variation or by adding low molecular weight solvents, homopolymers or other block copolymers, to block copolymers, a large field has opened up for morphological transitions, i.e. manipulating block copolymer morphologies. There have been many excellent reviews on this topic [1,13,53], and for that reason the focus of this contribution will be on the developments in this area during the last few years. Consequently, this chapter will review different aspects of these researches as they relate to phase behavior and morphology of block copolymers, basically in the bulk state.
2.2.1. Linear Block Copolymers

The best-known and simplest class of block copolymers is linear diblock copolymers (AB). Being composed of two immiscible blocks, A and B, they can adopt the following equilibrium microphase morphologies, basically as a function of composition: spheres ($S$), cylinders ($C$ or $Hex$), double gyroid ($G$ or $Gyr$), lamellae ($L$ or $Lam$), (Figure 2.1) and the inverse structures. With the exception of the double gyroid, all morphologies are ideally characterized by a constant mean curvature of the interface between the different microdomains [54].

For nearly symmetric compositions the unlike blocks form domains composed of alternating layers, known as lamellar phase ($L$). Slightly off-symmetry composition results in the formation of a different layered structure. The structure is known as perforated layers ($PL$). Despite an earlier assignment as an equilibrium phase, it is now known to be in a long-lived metastable state that facilitates the transition from $L$ to $G$ phases [23,55-57]. The $PL$ structure consists of alternating minority and majority component layers in which hexagonally packed channels of the majority component extend through the minority component.

A sketch of the perforated lamellar morphology is depicted in Figure 2.2. Depending on the point of view, the 2D projection exhibits different patterns: perpendicular to the layers of the perforated lamellar structure the projection appears like a hexagonal honeycomb mesh (Figure 2.2 (a)). By contrast, the parallel view (Figure 2.2 (b)) leads to rows of spots.
Figure 2.1. Morphologies of diblock copolymers: cubic packed spheres (S), hexagonal packed cylinders (C or Hex), double gyroid (G or Gyr), and lamellae (L or Lam) [54].

Figure 2.2. Morphology of perforated layers (PL): (a) Projection direction perpendicular to layers of perforated lamellar structure appears as a hexagonal honeycomb mesh. (b) Projection parallel to layers appears as rows of dark spots resulting from cross section of parts [23].

The G phase is a complex phase possessing a bi-continuous structure which is located in or close to the compositional range of the PL phase. The minority component forms two interpenetrating three-fold coordinated network [23]. When the compositional asymmetry is further increased, the minority component assembles in hexagonally packed cylinders (C). Finally, it is organized in an array of spheres. A body-centered cubic lattice arrangement (S or bcc) is mostly observed.

2.2.2. Phase Behavior of Various Block Copolymer systems: Theory

The phase behavior of block copolymers can be described theoretically by different approaches [53]. According to mean-field theory (MFT) [58], the phase behavior of
diblock copolymers is dictated by the Flory-Huggins segment-segment interaction parameter, $\chi$, the degree of polymerization, $N$, and the composition, $\phi$, with the product $\chi N$ determining the degree of segregation. In the case $\chi N \leq 10$, the system is ruled by entropic terms, resulting in a disordered phase. Under the condition $\chi N > 10$, enthalpic terms dominate, causing an order-disorder transition (ODT) where the unlike segments segregate into a variety of ordered periodic microstructures. Leibler [58] was the first to describe microphase separation, i.e. the transition between a disordered liquid or homogeneous state, and an ordered one. He treated the microphase separation transition within the so-called weak segregation limit (WSL). The WSL approximates the composition fluctuations by a single wave function (first harmonic). Using higher degrees of segregation between the microdomains leads to a description called the strong segregation limit (SSL). Here, composition fluctuations are approximated by step functions across the microdomain boundaries. An expression of the free energies for classic morphologies in the SSL was first developed by Meier [59] to mention just a few of several groups in this field. Although providing useful insights, neither the SSL nor the WSL describes the morphological behavior completely. Matsen used a self-consistent field theory (SCFT), which also takes higher harmonics into account and could mostly bridge the gap between the weak and the strong segregation limits [60].

The morphological behavior of binary triblock copolymers (ABA) was elucidated in a subsequent work [61]. Including higher harmonics into his computation, Matsen’s SCFT is able to bridge the gap between diblock and symmetrically composed triblock copolymers. An asymmetry parameter, $\tau$, was introduced which relates the number of segments of the shorter, $\tau\phi_A N$, with that of the longer A block, $(1-\tau)\phi_A N$ (i.e. $0 \leq \tau \leq 1$).
with the limiting cases $\tau = 0$: AB-diblock and $\tau = 1/2$: symmetric ABA triblock).

The resulting phase diagrams are shown in Figure 2.3 and Figure 2.4.

Although being qualitatively in agreement with experimental results, disagreements between experiment and theory remain. Besides the composition, $f_A$, and the total degree of polymerization, $N$, all theoretical works refer to the segmental interaction parameter $\chi$. This parameter can be estimated from a relationship to the solubility parameters. The order-disorder transition (ODT, the transition from a homogeneously disordered melt to a heterogeneously ordered melt) was used as a thermodynamic measure of the incompatibility to compare a set of symmetrically composed diblock copolymers from different hydrocarbons, polydimethylsiloxane and poly(ethylene oxide) (PEO) [62]. While the behavior of hydrocarbon diblock copolymers was successfully described by a consistent set of solubility parameters, this procedure failed for systems containing PEO. The asymmetry in size of the different components was attributed to an enthalpic contribution to the $\chi$-parameter.

More complex block copolymers as triblock terpolymers have also been described. Molecular dynamics simulations were applied to the morphological behavior of triblock terpolymers, and basically the experimentally found structures were reproduced [63-65]. Using SCFT, the morphological behavior of linear triblock terpolymers was described in two dimensions. A fundamental problem in most simulation works is the definition of boundary conditions like the size and geometry of the simulation box. This can lead the simulation to a wrong equilibrium state. Using a rather flexible simulation approach, Bohbot-Raviv and Wang [66] created morphologies of terpolymers of various topologies in two dimensions without the initial assumptions of the morphology symmetry.
Figure 2.3. Mean-field phase diagrams for melts of an AB diblock copolymer $\tau = 0$ and a symmetric ABA triblock copolymer ($\tau = 0.5$) plotted in terms of segregation $\chi N$ and composition $f_A$ calculated with SCFT [61].

Figure 2.4. Mean-field phase diagrams for asymmetric ABA triblocks spanning between diblock ($\tau = 0$) and symmetric triblock ($\tau = 0.5$) limits at segregations of (a) $\chi N = 20$, (b) $\chi N = 30$ and (c) $\chi N = 40$ calculated with SCFT. Dotted curves: critical asymmetries $\tau_c$ predicted by SST beyond which short $A$ blocks are extracted from their domains [61].
2.2.3. Phase Behavior of Thin Film Block Copolymers

In addition to the previously mentioned driving forces that determine the bulk state phase behavior of block copolymers, two additional factors play roles in block copolymer thin films: the surface/interface energies, as well as the interplay between the film thickness $t$ and the natural period, $L_0$, of the bulk microphase-separated structures [67-69]. Due to these two additional factors, a very sophisticated picture has emerged from the various theoretical and experimental efforts that have been made in order to describe the phase behavior of block copolymer thin films as summarized by Fasolka et al. [68]. The picture is further convoluted by the fact that block copolymer nanofabrication processes have usually been performed on thin films with asymmetric compositions, such as 2D cylindrical [21] or 3D spherical [70] microstructures. The extra degrees of freedom inherent to off-symmetric motifs generate very complex systems for both theoretical and experimental scientists. For example, the thin film microdomain motif was found to shift from surface-parallel cylinders to volume-asymmetric lamella [71,72], due to the interplay between interfacial energies and film thickness. To fully understand and utilize these off-symmetric block copolymer thin films, continued experiments and systematic theoretical calculations are required.
2.3. Phase Transitions in Block Copolymers

Phase transitions in block copolymers can be either order-order transitions (OOT) or order-disorder transitions (ODT). The first type includes changes between the various ordered morphologies discussed in Figure 2.1, whereas the latter describes the transition between the presence and absence of long range interactions in the system. For a block copolymer of given molecular weight and composition, both transitions may be triggered by the variation of temperature and/or pressure. Blending offers another possibility to alter the system’s phase space. Besides the temperature and/or pressure, variation of different component fractions offers an elegant (and most used) possibility to tailor the system’s phase space.

2.3.1. Transition Kinetics

The viscoelastic effects on the morphology and dynamics of microphase separation of diblock copolymers was simulated by Huo et al. [73] based on Tanaka’s viscoelastic model [74] in the presence and absence of additional thermal input. Their results indicate that for a volume fraction, $\phi = 0.5$ and an identical bulk modulus of both blocks, the area fraction of the A-rich phase remains constant during the microphase separation process. For each block randomly oriented lamellae are preferred.

In the case of bulk modulus differences between the two blocks, the area fraction of the higher bulk modulus A-rich phase reaches a maximum during separation and then decreases to a steady-state value that is slightly different from $\phi$. The morphology
exhibits a thin network-like continuous phase of the A material with the lower bulk modulus B-rich droplets dispersed in the A-rich matrix. In symmetric systems, the viscoelastic effect does not cause a variation in the computed morphologies. For $\phi_A = 0.4$, the situation is different, which is due to inherent composition asymmetries. Although the minority component A possesses a higher bulk modulus, it tends to form a thin lamellar morphology. From the pattern evolution the lower bulk modulus B-rich droplets begin to emerge first, and then grow in size, with the A-rich phase being compressed to form a network-like structure. As the microphase separation proceeds further, the B-rich phase eventually forms the continuous phase and the A-rich network is partially broken up. It is obvious that the minor component A has a greater tendency to form a lamellar morphology (Figure 2.5 (a)). On the other hand, if the minority component A possesses a lower bulk modulus, the domains of the A-rich phase first emerge from the B-rich matrix and then eventually evolve into isolated A-rich droplets (Figure 2.5 (b)). The morphological differences between the absence and the presence of bulk modulus differences emphasize the importance of accounting for the viscoelastic properties. They may be responsible for the deviations between the experimentally measured and the mean-field theoretically predicted phase diagrams.

Small-angle X-ray studies indicate that long equilibration times after temperature jumps (T-jump) within the ordered state of sphere-forming PI-b-PDMS and PEP-b-PDMS copolymers are due to slow chain diffusion. The diffusion changes the number of domains (if T-jump occurs within one phase) or the symmetry of domains (if an OOT is involved). Measurements using tracers indicated that chain mobility was not rate-limiting, although variations in mobility did account for the differences between the two
investigated polymers. Moreover, the required reduction in the number density of spheres on cooling was found to be rate limiting. The disappearance of spheres, either by “evaporation” or by “fusion”, provided a large kinetic barrier. Lamellae, however, could adjust domain dimensions simply by local displacements of individual chains and for this reason occur rather rapidly [75].
Figure 2.5. Simulated pattern evolution during microphase separation for $\varphi_A = 0.4$ with A having a 10 times higher (a) and lower (b) bulk modulus than B. Black: A-rich regions; white: B-rich regions. [73]
2.3.2. Disordered and Ordered States Transitions

Usually the discussion of the ODT of highly asymmetric block copolymers in the strong segregation limit starts from a body-centered cubic (bcc) array of the minority phase. Phase transitions were calculated using SCFT accounting for both the translational entropy of the micelles in a disordered micelle regime, as well as the intermicelle free energy [76]. Results indicate that the ODT occurs between occurrence of ordered bcc spheres and disordered micelles.

Contrary to the more symmetric L or C systems which transform directly to the disordered state with thermally induced composition fluctuations at $T_{\text{ODT}}$, the highly asymmetric spherical ones undergo transformation to disordered micelles. These exhibit liquid-like short-range order disappearing at even higher temperatures, resulting in an amorphous melt. To emphasize the distinction, the transition from bcc to disordered micelles is termed the lattice disordering transition (LDT), whereas the disappearance of the micelles occurs at the demicellization temperature (DMT) [77-79]. This definition, however, leads to the conceptual difficulty of relating the DMT to the ODT, which is completely inconsistent with the requirement that the ODT is a true first-order thermodynamic phase transition taking place between an ordered and a disordered state.

The temperature-dependent phase behavior of an asymmetric PS-b-PI system was predicted independent of this definition, and reasonable agreements were found with the experimentally observed ODT and LDT temperatures [76,79].

Above the ODT, the number density of micelles decreases steadily. Over some region, termed the critical micelle temperature (cmt), the rate of decrease changes, and the free energy of the disordered micelle regime (with very low micelle concentration) is
only slightly lower than the Flory-Huggins free energy for a homogeneous melt. Hence, the cmt may be defined as the temperature which separates the disordered micelle regime (with a finite micelle concentration) from a disordered melt (with an exponentially small micelle fraction); however, it is not a true phase transition. At even higher temperatures the formation of micelles becomes thermodynamically less favorable, and their fraction decreases considerably. The micelle concentration will always be non-zero as even an infinitesimally small fraction of micelles allows the system to gain translational entropy. The exact definition of the transition process between ordered \textit{bcc} and random micelles on one hand and randomly distributed micelles and the disordered melt on the other is still under discussion. Some authors argue that the existence of the disordered micelle regime represents an essential difference between sphere-forming and more symmetric block copolymer systems, and therefore, requires a special treatment.

The architecture as well as the preparation of the test specimen has a pronounced effect on the ODT. Choi et al. [78] found that $T_{\text{ODT}}$ of the symmetric PS-b-PI-b-PS copolymer is approximately 20 °C higher than that of the corresponding PS-b-PI block copolymer. In the same study the preparation by compression molding or solvent casting was found to influence $T_{\text{ODT}}$ and demicellization transformation in the case of highly asymmetric PS-b-PI and PS-b-PI-b-PS respectively, while the ODT for lamellar or cylindrical block copolymers was less influenced [78]. Based on their findings, the researchers recommended the following practice for determining the phase-transition temperature of highly asymmetric block copolymers: (i) a slow solvent casting, instead of compression molding, should be used to prepare specimens, (ii) optimum annealing conditions in terms of temperature and the duration of annealing should be determined
and (iii) sufficiently low angular frequencies (e.g. 0.01 rad/s) should be applied to a specimen, when conducting isochronal dynamic temperature sweep experiments.

The ordering kinetics of PS-b-PI-b-PS triblock copolymers were investigated after $T$-quenches to the $S$ or $C$ phase [135]. After deep quenches, the system stays in the supercooled disordered-sphere phase for a certain incubation period. Thereafter, the grains composed of $Hex$-cylinders nucleate in the disordered-sphere phase and grow at the expense of the disordered-sphere phase, i.e. the $C$ phase is formed directly from the disordered spheres. Shallow quenches into the $C$ phase proceed via a different pathway; the system stays in the supercooled disordered-sphere phase for a certain incubation period. Then, the grains composed of $bcc$ spheres appear in the disordered-sphere phase and grow at the expense of it. The ordered volume filling $bcc$ spheres are metastable and will undergo OOT into the final $C$ morphology, when the complete sample space is filled with them.

2.3.3. Ordered States Transitions

The order-order transition (OOT) of a block copolymer is defined as the change of one type of ordered microdomain structure to another one. In the strong segregation limit it basically depends on the volume fraction of one of the constituent block chains, $\varphi$. In the WSL it is also influenced by $\chi N$ and therefore may occur by changing the temperature. The thermo-reversible OOT between $S$ and $C$ of a PS-b-PI block copolymer with a PS weight fraction of 0.20 was investigated by Kimishima et al. [80]. By using SAXS and polarized optical microscopy they observed cylindrical microdomains on a hexagonal lattice up to 114.7 °C, which changed reversibly to $bcc$ spheres above 116.7 °C.
A straightforward transition process [81] from the C to S was proposed (Figure 2.6): The cylinder breaks up into spheres with the original cylindrical axis parallel to the [111] direction of the bcc sphere lattice induced by thermodynamic instability of the cylindrical interface at $T > T_{OOT}$. The process may proceed via four subsequent steps: (i) undulation (as shown from part a to b), (ii) break-up of cylinders into ellipsoids (from part b to c), (iii) relaxation of domains from the ellipsoids into spheres (from part c to d), and (iv) relaxation in a junction distribution to attain a uniform distribution (from part d to e). These processes involve only local rearrangements of the block copolymer molecules rather than large length-scale rearrangements of block copolymer molecules or microdomains. The reverse transition involves deformation and elongation of the spheres into ellipsoids and coalescence of the ellipsoids into cylinders. These processes are driven by thermodynamic instability of spherical interfaces caused by increased segregation power at $T < T_{OOT}$.

The mean-field phase diagram in the WSL calculated by Matsen et al. [82] predicts a transition from C to the disordered state via the bcc and the fcc array with decreasing $\chi N$. Transitions from the C to S (at 115.7 °C), to the lattice-disordered sphere - where the bcc lattice was distorted by thermal fluctuations - and finally to the disordered state (estimation at $T > 180$ °C but not attained in the study) were observed. It was reasoned to consider the lattice-disordered spheres as a fluctuation-induced lattice disordered phase. This enlarges the window for the disordered one and causes the fcc phase to disappear. Even if the latter should exist, its observation will be aggravated by its narrow temperature width of about 8K and its slow formation due to the symmetry changes between fcc and bcc spheres.
The kinetics and mechanisms of the $C \rightarrow G$ transition in a concentrated solution of PS-b-PI in the PS-selective solvent di-$n$-butyl phthalate was also studied [81]. For shallow quenches into $G$, the transition proceeds directly by a nucleation and growth process. For deeper quenches, a metastable intermediate structure appears, with scattering and rheological features consistent with the hexagonally perforated layer ($PL$) state. The $C \rightarrow G$ transition follows the same pathways, and at approximately the same rates, even when the initial $C$ phase is not shear-oriented.

Phase transitions of the PS-b-PI system have been extensively studied. The morphological transition from the $L$ phase to the $G$ phase proceeds through nucleation and growth. The difference in the geometrical characteristics of these two phases induces considerable local distortion of both morphologies during the transition. The resulting strain raises the surface energy of the grains, leading to a suppression of the direct $L \rightarrow G$ transition in case of an asymmetric polymer ($\phi_{PI} = 0.3$). Instead, the $PL$ phase tends to appear as an intermediate structure capable of forming low-energy grain boundaries during the $L \rightarrow G$ transition.

The overall arrangement of the $PL$ phase retains a planar aspect reminiscent of the $L$ phase, though the minority components are already arranged in a planar, three-fold coordinated structure. Hence, the PL phase combines characteristics of the $L$ and $G$ phases, which accounts for its intermediate role [23]. The distortions grow in amplitude until channels are formed extending through the minority component domains. The $PL \rightarrow G$ transition can proceed with epitaxial relation via nucleation and growth, because both $PL$ and $G$ morphologies are constructed from a nearly identical, three-fold-coordinated minority component [83].
However, a PS-b-PI/PI blend shows direct $L \rightarrow G$ transition without appearance of the $PL$ phase. The $L$ microdomain is more favorable than the $PL$ phase since the volume fraction of the PI block component and the symmetry of microdomains are increased by the addition of PI homopolymer. Hence, the $PL$ phase may not be formed as an intermediate structure if relatively high molecular weight PI homopolymer is added. The latter is not able to effectively fill the corners of the Wigner-Seitz cells; consequently packing frustration cannot be released and the PL phase is not favored [84]. In contrast, the addition of low molecular weight PI homopolymer to the minor component of the $PL$ phase reduces the packing frustration imposed on the block copolymers and stabilizes it [85]. Hence, transition from the $PL$ to the $G$ phase indicates an epitaxial relationship between the two structures, while the direct transition between $L$ and $G$ yields a polydomain structure indicative of epitaxial mismatches in domain orientations [84].

Using selective solvents for either PS or PI, different cubic spherical phases could be generated in solutions of a symmetric PS-b-PI diblock copolymer. Using shear, an $fcc$ solution could be transformed into a mixture of $fcc$ and $hcp$. Similarities to metals were found in the mechanisms present during the transitions from $fcc$ or $hcp$ lattices to the $bcc$ lattice, when heating the system to the $bcc$ region of the phase diagram in the absence of shear [86]. Very recently, the flow-induced transition from a $G$ to a $C$ morphology was reported in a PS-b-PB-b-PS triblock copolymer (SBS). Two-dimensional SAXS measurements revealed that the $G$ structure transformed into uniaxially aligned cylinders with hexagonally close packing upon imposing the flow, where a plane of the hexagonally packed cylinders was preferentially aligned parallel to the substrate [87].
In the case of triblock terpolymers, two different interfaces have to be considered for the morphological transitions, making the description of the transition process much more demanding. The transition from $L$ to $G$ morphology of a PI-b-PS-b-P2VP triblock terpolymer has been investigated by Suzuki et al. [88]. The symmetric triblock ($\phi_{PI} = \phi_{P2VP} = 0.26$ and $\phi_{PS} = 0.46$) showed a metastable lamellar morphology directly after solvent casting. Annealing the film for 14 hours triggered the conversion to a $G$-type morphology taking more than 2 days to accomplish. It was reasoned that the lamellar structure could be formed because of a strong affinity of the P2VP to the polytetrafluorethylene material used in casting. The motif of layered lamellar structure (domain spacing 58 nm), however, guided the evolution of the $G$-type morphology, leading to its [110] orientation normal to the film surface and a repeating unit of 55 nm (Figure 2.7).
Figure 2.6. Schematic diagram of elemental process during transition from Hex cylinder to bcc sphere; (i) undulation of interface (a, b), (ii) break-up of cylinders into ellipsoids (b, c), (iii) relaxation of domains from ellipsoids into spheres (c, d), and (iv) relaxation in junction distribution to attain uniform distribution (d, e). Pole where concentration of junction points is low may work as memory of grain conservation upon reverse transition from bcc sphere to Hex cylinder. Small arrows in part (b) indicate diffusion of chemical junctions along interface in process (ii) [80].
Figure 2.7. Schematic comparison of: a) side view for lamellar structure, b) PI/PS interface for $G$ structure and c) PS/PI interface for $G$ structure. [110] direction is pointed out as arrow between b and c [88].
2.4. Ordering of Block Copolymers

The self-assembly of block polymers, in the bulk, thin film and solution states, produces uniformly sized nanostructure patterns that are very useful for nanofabrication. Optimal utilization of these nanoscopic patterns requires complete spatial and orientational control of the microdomains. However, the microdomains in the bulk state normally have grain sizes in the submicron range and have random orientations. In block copolymer thin films, the natural domain orientations are generally not desirable for nanofabrication. In particular, for composition-asymmetric cylindrical thin films, experimental and theoretical results [71,89,90] indicate that microdomains oriented parallel to the substrates are thermodynamically favored when the film surfaces are preferentially wet by either block, while the microdomains oriented perpendicular to the substrates are more desirable as templates for the fabrication of high aspect-ratio nanostructures. Therefore, various strategies have been used for inducing large area orientation of block copolymer microdomain patterns.

In the bulk state, block copolymer long-range orientation is generally achieved by mechanical shear, compression, and elongational fields on the polymer melts or solutions. Steady shear [57,91,92], capillary extrusion [93], and extensional flow [94] cause certain domain orientations to be favored so that nearly single-crystal-like textures have been produced, as exemplified in the roll-casting process [95]. Besides these mechanical orientation methods, Hashimoto and coworkers [96] showed that a single, macroscopic, lamellar grain of poly(styrene-b-isoprene) (PS-b-PI) block copolymer can be achieved using an applied temperature gradient. Due to the sharp temperature gradient $\nabla T$ and its...
slow-moving speed (2mm/day), the system underwent a “zone-refinement”-like process and a single-crystal-like lamellar grain was grown, with the lamellae normals parallel to the $\nabla T$ direction. Amundson et al. [97-99] have demonstrated that an electric field is another effective means of orienting block copolymer bulk microdomain structures from polymer melts or solutions.

In block copolymer thin films, the perpendicular orientation of microdomains relative to the substrate cannot be achieved by the shear methods developed in the bulk case. Based on the additional variables (film thickness and surface/interface interactions) in block copolymer thin films, three different strategies are generally applied for orienting block copolymer thin films:

1. Controlling the substrate physical constraints (topography) and thus the film thickness.
2. Chemical modification of the surface to change the substrate-polymer interactions.
3. Applying external fields (electric, thermal, eutectic solidification, crystallization, and solvent evaporation etc.) to induce long-range ordering in microdomains with desirable orientation.

Processes which employ combinations of these strategies have proved to be much more effective at yielding uniform long-range ordered patterns than single strategies. Table 1 describes the methods used to control the microdomain orientation of a variety of thin film block copolymers [16,17,19,20,69,100-121].
Table 1. Summary of block copolymers studied in order to control microdomain orientations in thin film states [16,17,19,20,69,100-121]

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Structure</th>
<th>Morphology</th>
<th>Orientation method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(styrene-b-isoprene-b-styrene)</td>
<td><img src="image1" alt="Structure" /></td>
<td>Cylinder</td>
<td>Electric field</td>
<td>[100]</td>
</tr>
<tr>
<td>Poly(styrene-b-isoprene)</td>
<td><img src="image2" alt="Structure" /></td>
<td>Cylinder</td>
<td>Directional crystallization with Graphoepitaxy</td>
<td>[101]</td>
</tr>
<tr>
<td>Poly(styrene-b-isoprene)</td>
<td><img src="image3" alt="Structure" /></td>
<td>Cylinder</td>
<td>Directional crystallization</td>
<td>[102]</td>
</tr>
<tr>
<td>Poly(styrene-b-butadiene)</td>
<td><img src="image4" alt="Structure" /></td>
<td>Cylinder</td>
<td>Fast solvent evaporation</td>
<td>[103]</td>
</tr>
<tr>
<td>Poly(styrene-b-butadiene)</td>
<td><img src="image5" alt="Structure" /></td>
<td>Lamella cylinder</td>
<td>Fast solvent evaporation</td>
<td>[104]</td>
</tr>
<tr>
<td>Poly(styrene-b-butadiene)</td>
<td><img src="image6" alt="Structure" /></td>
<td>Cylinder</td>
<td>Orthogonal flow field</td>
<td>[105]</td>
</tr>
<tr>
<td>Poly(styrene-b-butadiene-b-styrene)</td>
<td><img src="image7" alt="Structure" /></td>
<td>Cylinder</td>
<td>Fast solvent evaporation</td>
<td>[106]</td>
</tr>
</tbody>
</table>
Continued Table 1. Summary of block copolymers studied in order to control microdomain orientations in thin film states

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Structure</th>
<th>Morphology</th>
<th>Orientation method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(styrene-b-ethyleneoxide)</td>
<td><img src="image" alt="structure" /></td>
<td>Cylinder</td>
<td>Fast solvent evaporation</td>
<td>[107]</td>
</tr>
<tr>
<td>Poly(styrene-b-methylmethacrylate)</td>
<td><img src="image" alt="structure" /></td>
<td>Lamella, cylinder</td>
<td>Neutral surface</td>
<td>[19,69,108-111]</td>
</tr>
<tr>
<td>Poly(styrene-b-methylmethacrylate)</td>
<td><img src="image" alt="structure" /></td>
<td>Lamella</td>
<td>Control interfacial interaction</td>
<td>[20]</td>
</tr>
<tr>
<td>Poly(styrene-b-methylmethacrylate)</td>
<td><img src="image" alt="structure" /></td>
<td>Lamella</td>
<td>Chemical patterned substrate</td>
<td>[16,17,112-114]</td>
</tr>
<tr>
<td>Poly(styrene-b-methylmethacrylate)</td>
<td><img src="image" alt="structure" /></td>
<td>Cylinder</td>
<td>Electric field</td>
<td>[115-119]</td>
</tr>
<tr>
<td>Poly(styrene-b-methylmethacrylate)</td>
<td><img src="image" alt="structure" /></td>
<td>Lamella</td>
<td>Orthogonal electric field</td>
<td>[120]</td>
</tr>
<tr>
<td>Poly(styrene-b-methylmethacrylate)</td>
<td><img src="image" alt="structure" /></td>
<td>Sphere</td>
<td>Graphoepitaxy</td>
<td>[121]</td>
</tr>
</tbody>
</table>
2.4.1. Control of Film Thickness

As described in 2.2.3 block copolymer thin film phase behavior can be controlled by controlling the surface/interface energies as well as by controlling the interplay between the film thickness \( t \) and polymer natural period \( L_0 \). Depending on the nature of the surface interactions, block copolymer thin films can be separated into two general categories [67,68]:

1. Symmetric boundary conditions [14,122,123], in which the energies imposed by both film surface/interfaces are identical, such as free-standing films [72] and thin films confined between two identical substrates [19,122].

2. Asymmetric boundary conditions [14,67,123,124], in which the two surface/interfaces of the thin films have different energies, such as substrate-supported films [18,110].

Unlike the bulk morphology, block copolymer thin films are often characterized by thickness-dependent highly oriented domains, as a result of surface and interfacial energy minimization [125,126]. For example, in the simplest composition-symmetric coil-coil thin films, when \( t > L_0 \), the overall trend is for the lamellae to be oriented parallel to the plane of the film [126]. Under symmetric boundary conditions, frustration cannot be avoided if \( t \) is not commensurate with \( L_0 \) in a confined film and the lamellar period deviates from the bulk value by compressing the chain conformation [127]. Under asymmetric boundary conditions, an incomplete top layer composed of “islands” and “holes” of height \( L_0 \) forms as in the incommensurate case [128]. However, it has also been observed that microdomains can reorient such that they are perpendicular to the surface, or they can take mixed orientations to relieve the constraint [18].
In the case of $t < L_0$, it has been suggested that perpendicular lamellae are favored in the boundary-symmetric confined film, because they avoid the entropic penalty associated with the compressed chain conformations in parallel-oriented microdomains [123]. In boundary-asymmetric substrate supported films, various kinds of morphologies, including hybrid morphologies that combine surface-parallel and surface-perpendicular components, are predicted, as well as observed, depending on the film thickness difference and surface/interface energies [67,68].

2.4.2. Modification of Substrate-Polymer Interactions

For diblock copolymer films composed of cylindrical or lamellar microdomains, the interfacial interactions dictate the wetting layers at both the substrate and surface interfaces and, consequently, the orientation of the microdomains in the film [19,67,72]. Therefore, various strategies have been utilized to control the interfacial interactions to achieve large-area microdomains with desirable orientations.

One way of achieving a perpendicular orientation of microdomains is to remove or balance all interfacial interactions, i.e., use non-preferential or neutral surfaces (Figure 2.8). Under these conditions, a perpendicular orientation is favored over a parallel arrangement because of an entropic effect [109,129]. Peters et al. [20] demonstrated control of interfacial interactions by the modification of self-assembling monolayer (SAM) substrates. Symmetric, neutral, and asymmetric wetting of block copolymer thin films can be achieved on modified SAM substrates to control the block copolymer thin film orientations. Kellogg et al. [19] achieved the same objective by placing random copolymers, consisting of the same monomeric units as the diblock copolymer, at the
confining surfaces. In order to avoid potential diffusion of the random copolymers into the confined diblock layer, Mansky et al. [69,111] anchored brushes of random copolymers of PS-r-PMMA to silicon substrates, and capped surface-philic perfluorodecanoyl-terminated PS-r-PMMA random copolymers at the PS-b-PMMA block copolymer/air interface. The compositions of the random copolymers were tailored so that neutral surfaces could be achieved at both substrate and air interfaces. Symmetrical lamellae as well as asymmetrical cylindrical PS-b-PMMA block copolymer microdomains were found to orient perpendicular to the interfaces throughout the entire film thickness.

Figure 2.8. Schematic representation of control of block copolymer thin film orientations by adjusting polymer-substrate interactions: neutral interfaces [130].

2.4.3. External Field Usage

External fields have been widely used to align block copolymer microdomains. This approach relies on the ability to couple an external applied bias field to some molecular or supramolecular feature, and thus achieve directional control over the microdomains. External fields, such as an electric field [97-99], mechanical flow field [57,91,92], and
temperature gradient [131], have been utilized to control the long-range orientation of block copolymers in the bulk state.

Morkved et al. [116] examined the effect of an electric field on PS-b-PMMA block copolymer thin film morphology applied across the film through micro-fabricated electrodes. In-plane cylinders were found to be aligned parallel to the electric field lines after long annealing times. By adjusting the polymer-electrode interfacial effects, Elhadj et al. [100] also described an approach for producing a metastable state with polystyrene cylinders of poly(styrene-b-isoprene-b-styrene) (PS-b-PI-b-PS) triblock copolymers to orient perpendicular to the electric field lines. Thurn-Albrecht et al. [118,132] studied this system in further detail and demonstrated that a vertically ordered cylindrical PMMA microstructure was achieved when the electric field was applied perpendicular to the film surface (Figure 2.9). Through theoretical analysis [117,132], these researchers also proposed that the driving force for the alignment is the orientation-dependent polarizability of the original anisotropic microdomains. Recently, a sequential, orthogonal electrical field approach [119] has been used to gain biaxial control of microdomain pattern alignment, and give long-range, 3D ordered lamellar microdomains in PS-b-PMMA thin films.

Application of mechanical stress to a block copolymer thin film can be accomplished by processes associated with crystallization and solvent evaporation. Crystallization is one of the most prominent molecular self-organization processes in nature. Reiter et al. [133] and Hong et al. [134] have explored the possibility of using it to direct microdomain orientation. After spincasting a symmetrical poly(butadiene-b-ethylene oxide) (PB-b-PEO) block copolymer onto a substrate, Reiter et al. found that
crystallization of the PEO block, combined with a dewetting process, could generate well-aligned vertical lamella on a substrate over macroscopic distances as a consequence of directed growth. De Rosa et al. [102,135] studied the phenomenon of solvent crystallization-assisted orientation of various block copolymers (Figure 2.10). Through eutectic solidification of the block copolymer/solvent mixtures, epitaxial growth of the polymer microdomains was achieved by directional crystallization of a small molecule solvent. Depending on the block copolymer composition, large area surface-perpendicular cylinders or lamella were obtained.

![Figure 2.9. Schematic representation of control over block copolymer thin film orientation by applying an electric field to orient PS-b-PMMA cylinders perpendicular to the substrate [21].](image)

Controlling solvent evaporation of cast thin films has proved to be another means of inducing a flow field to align microdomain patterns. The evaporation process is typically highly directional, occurring normal to the surface. Perpendicular orientations of lamella, as well as cylinders, are favored during a fast evaporation process in a variety of block copolymer systems [103-107,136], possibly due to directional internal strain fields [136] associated with film shrinkage and anisotropic deswelling during the final stages of
solvent evaporation. This anisotropic deswelling likely results from the solvent moving through high transport pathways formed by the vertical solvent-philic microdomains to the surface, rather than serial transport through alternating solvent-philic and solvent-phobic layers, which would be present in the parallel-oriented microdomain case [103,106].

Figure 2.10. Schematic representation of control over block copolymer thin film orientation by directional eutectic solidification. The scheme shows control of polystyrene-b-polyethylene (PS-b-PE) block copolymer microdomain orientation through directional crystallization of benzoic acid (BA) [135].

This process generates a zone-refinement-like effect, which aligns the microdomains in the vertical direction. Due to the fact that the solvent improves the mobility of the
polymer chains and mediates the surface energy difference of the building blocks, which make it feasible to form long range oriented microdomain patterns, nanopatterned surfaces can be rapidly generated by simple spin or dip-casting processes with the perpendicular orientation of microdomains being possible over a wide range of thicknesses. Recently, by pinning a block copolymer solution droplet on a substrate, Kimura et al. [105] produced two orthogonal flow fields during the evaporation process: a flow field within the droplet directed towards the pinned edge, and the evaporation flow field from the surface to the droplet. Using this approach, ordered arrays of cylindrical microdomains, highly oriented parallel to the surface, were generated over large lateral distances.

2.5. Control of Block Copolymer Morphologies via Blending

In a strict sense, synthetic polymers are never one-component systems due to polydispersities in chain lengths, microstructures, tacticity, or composition (random copolymers, block copolymers). In the preceding sections blends of block copolymers with homopolymers were occasionally discussed. This section gives an overview of various aspects of influencing block copolymer morphologies by blending. In the first part the influence of polydispersity is discussed. Examples of blending block copolymers with other polymers or block copolymers will follow, and finally the incorporation of block copolymers by reactive blending in other polymers will be briefly reviewed.
2.5.1. Effects of Molecular Weight Distribution

The effects of composition distribution on the morphology of PS-b-P2VP diblock copolymers were investigated by Matsushita et al. [137]. They produced PS-b-P2VP samples with various composition distributions but with constant average composition by blending. If the polydispersity indices of each block were lower than 1.7, the expected lamellar domains were detected (Figure 2.11).

It is obvious from Figure 2.12 that the domain spacing is not merely dependent on the number-average molecular weight of the constituent block copolymers. It is also governed by the condition for polymer segments to fill the 3D space constantly. Hence, a non-uniform compositional distribution also affects the spacing for identical average chain length, as schematically sketched in Figure 2.12. In the non-uniform case (left), the segments for the longer chain compensates the shortage of the segments of the shorter ones leading to an increase in the domain spacing. Hence, the average surface area for a junction point of each block copolymer in blends with wide compositional distribution is smaller than that for regular monodisperse copolymers. As a result the spacing increases with increasing compositional distribution until macrophase separation takes place.
Figure 2.11. Composition distribution dependence of reduced domain spacing, $D/D_0$, of PS-b-P2VP with single microphase-separated structure. $D_0 = 60.8$ nm is domain spacing of parent copolymer with $Mn = 125$ kg/mol. *Hatched region*: macrophase separation [137].

Figure 2.12. Schematic comparison of microdomains formed by block copolymers with wide (*left*) and narrow (*right*) composition distributions [137].
2.5.2. Blending with Homopolymer (Binary Blends)

The effect of blending an AB diblock copolymer with an A-type homopolymer has been the subject of many research activities. On a theoretical basis the subject was investigated e.g. by Whitmore and Noolandi [138] and Matsen [139]. If a diblock exhibiting lamellae morphology is blended with a homopolymer of high molecular weight, macrophase separation between the diblock-rich lamellar phase and a homopolymer-rich disordered phase is observed, caused by an attractive interaction between diblock bilayers. In contrast, a low-molecular-weight homopolymer leads to a repulsive interaction between bilayers. Here, the homopolymer may be added to the lamellar phase indefinitely without macrophase separation. The A blocks of the block copolymer are concentrated near the interface, while the A homopolymer is preferentially located in the central region of the A-rich domains. Tension in the A blocks pushes the homopolymer toward the middle of the A-rich domains. Entropy of mixing counters this effect and favors a more uniform homopolymer distribution. The latter effect is enhanced by lowering the molecular weight of the homopolymer. To accommodate homopolymer near the interface, the microstructure may undergo a phase transition to a geometry where the interface is curved less toward the A-rich domain. Even if this effect is not strong enough to cause a phase transition, homopolymer may penetrate the interface by spreading apart the diblocks and in consequence increasing the interfacial area. This allows the B blocks to contact, leading to a reduced thickness of the B-rich domains. In summary, previous studies predicted that blending a diblock copolymer with a homopolymer would result in a shift of phase boundaries and in the stabilization of new morphologies.
A phase diagram of the symmetric PS-b-PI blended with PS homopolymer of shorter chain lengths was constructed by Bodycomb et al. [22]. The effect of blend composition on the ODT is shown in Figure 2.13 along with the results of mean-field calculations. In analogy to MFT the addition of homopolymer decreases the ODT temperature for the nearly symmetric diblock copolymer.

The phase diagram in Figure 2.13 reveals an irreversible temperature-induced OOT between $C$ and $G$, with the former being the low-temperature phase, which differs from previous studies on PS-b-PI/PS or PI blends [23]. The irreversibility of the OOT was attributed to a kinetic effect. At temperatures between ODT and OOT the system assembles in $G$ morphology. This structure is kinetically trapped and persists at temperatures below OOT, where cylinders are expected to be formed.

Recently, the effect of blending the commercially available PI-b-PS-b-PI triblock copolymer VECTOR 4111 with PS and PI on their phase behavior was investigated [24]. Addition of low-molecular-weight homopolymers to an asymmetric triblock copolymer caused contraction of the domain spacing. The addition of majority-component PI triggered the transition from a cylindrical to a spherical microdomain structure. This indicates that the increase in curvature is favored compared either to a stretching of the PI block or a contraction of the PS block because it involves less conformational entropy loss. The addition of a small concentration of minority component PS leads to an intermediate structure, a possible precursor to a lamellar phase. Addition of a 1 : 1 blend of PI and PS changed the cylindrical morphology neither in bulk nor in thin films, and led to enhanced alignment of cylinders parallel to the surface in case of thin films. This behavior could have been caused either by the segregation of PI to the substrate, resulting
in an additional “wetting layer” or by a “plasticization” of the PS by low molecular weight homopolymer. However, at one particular blend composition, the ODT dropped enormously. A similar behavior was reported for pure block copolymers [140] in blends of PS with polystyrene-b-poly(2-vinylpyridine) and with PS-b-PI copolymers [56].

Figure 2.13. Phase diagram of blend of PS-b-PI with PS. ●: $T_{ODT}$, ○: $T_{DMT}$, □: $T_{OOT}$. Vertical lines separating microdomain structures are obtained from total volume fraction PS in system. Dashed line: results of mean-field calculation for ODT. The OOT line, which exists at volume fractions $\phi_{lb} \leq \phi_{PS} \leq \phi_{ub}$ was obtained during a heating process [22].
2.5.3. Blending of Triblock (ABA or ABC) and Diblock (AB or AC) Copolymers

The effect of blending a lamellar triblock PS-b-PI-b-PS copolymer with an L or C-type PS-b-PI copolymer can either increase or decrease the long period of the parent block copolymer. Generally speaking, PS-b-PI-b-PS/PS-b-PI blends composed of PS-b-PI chains with relatively short PI blocks tend to reduce the thickness of the PI lamellae. Here, the PI blocks from the PS-b-PI copolymer fill the space close to the interface. Such block arrangement forms a bi-disperse polymer layer, forcing the PI blocks from the PS-b-PI-b-PS copolymer to reside near the lamellar midplane and promoting the formation of midblock bridges [141].

Some work has been done on blends of ABC and AB or AC or AB’C block copolymers, such as polystyrene-b-polybutadiene-b-poly(methylmethacrylate) (PS-b-PB-b-PMMA) triblock terpolymers with PS-b-PB or PB-b-PMMA or other systems. Besides known morphologies for these block copolymers (though at other overall compositions with respect to the different chemical repeating units), other morphologies could also be obtained, which do not exist in the pure block copolymers. These works have been reviewed [54]. In particular, a non-centrosymmetric lamellar superstructure was found in various blends of ABC- and AC-block copolymers [142,143]. An example of another unusual superstructure is shown in Figure 2.14 for a blend of lamellar PB-b-PS-b-P2VP and PS-b-P2VP [144].
2.6. Combination of Top-Down and Bottom-Up Methods

The development of top-down lithographic imaging technologies has been one of the most critical and active areas for the fabrication of new generations of large-area integrated patterns. Polymeric materials have played an important role in lithographic processes by allowing the continued reduction of the minimum feature size through the development of new chemically amplified resist materials that function at shorter exposure wavelengths. Interestingly, the lithographic requirements imposed on polymeric resists, such as sensitivity, adhesion, etch resistance, and solvent developability can rarely be met by simple homopolymers. Copolymers have proved to be useful in this context because they allow the properties of the final material to be tuned by incorporating different monomers together in a variety of ratios.
Block copolymer nanofabrication can provide large-area periodic functional patterns or objects with feature sizes on the order of tens of nanometers. However, in many practical applications, such as multifunctional on-chip bioseparations, the desired block copolymer microdomains are only required in specific areas on the substrate, while the remaining areas on the substrate should be entirely devoid of polymer. In order to satisfy this requirement, a strategy for exerting spatial control over the microdomains is necessary in addition to the usual formation of simple periodic nanostructures. Also, it has been demonstrated that multiaxial guiding forces can generate much improved control of the microstructure order, as compared with a uniaxial aligning force. For these purposes, the convergence of the lithographic top-down approach with the bottom-up, block copolymer self-assembly nanofabrication within the same system has received attention.

There are generally two strategies for achieving spatial control of nanostructures: first, the substrates are patterned with lithographic techniques to generate top-down patterns, on top of which the block copolymer bottom up nanopatterns can be subsequently directed; second, the convergence of top-down and bottom-up patterning occurs because the block copolymers contain all of the necessary functionalities to allow both types of patterning.
2.6.1. Topographically Patterned Substrates

A graphoepitaxy method has been developed in which a topographic top down defined pattern is used on a substrate to direct the epitaxial growth in an overlaying block copolymer bottom-up nanostructure by creating a periodic thickness profile (Figure 2.15). Fasolka and coworkers [18] employed a faceted silicon substrate, which has sawtooth-profile corrugations in the nanometer scale, in the study of symmetric poly(styrene-\textit{b}-butylmethacrylate) (PS-\textit{b}-PBMA) thin films. A flat block copolymer/air surface was observed in the thin film, which implies a periodic thickness profile: thinner above corrugation peaks, thicker above troughs. If the average film thickness is chosen correctly, such that these thickness modulations occur about a critical thickness at which a morphological transition takes place, a lateral microdomain pattern could be developed that mirrors the substrate topology. Through the use of substrate topography, diverse film patterns with a range of length scales have been created, which are consistent with theoretical calculations [67,145].
Figure 2.15. Schematic cross-sections of thin film morphologies of the topographic pattern grown by a graphoepitaxy method. A micropattern with different lamellar domain orientation is shown. (A) Surface-parallel lamellae, typical of film thickness \( t \) greater than the natural equilibrium period \( L_0 \). (B) Surface-perpendicular lamellae, typical of film thickness \( t \) less than \( L_0 \) [67].

2.6.2. Chemically Patterned Substrates

By modifying the surface/interface energies in a periodic manner, chemically patterned surfaces have also been widely used to control the orientation of nanostructures over large areas (Figure 2.16). Theoretical [146-148] and experimental [16,17,113,114,149,150] results have indicated that with the appropriate surface grating and boundary conditions, lateral control over nanostructures propagates microns away from the surface (deep into the film), thus providing true 3D control of the self-assembly process. Russell and coworkers [17,113] published the first observation of the orientation of a symmetric PS-b-PMMA block copolymer cast on a nanoscopic heterogeneous surface composed of alternating stripes of nonpolar gold and polar silicon oxide. Commensurability of the block copolymer natural period \( L_0 \) with the substrate stripe period was found to be essential for production of a surface-directed morphology. When the commensurate condition is fulfilled, the PS and PMMA blocks are attracted to the
gold and silicon oxide regions respectively. Lamellar microdomains orient themselves perpendicular to the substrate plane and parallel to the striping. However, a mismatch in length scale of only ±10% is sufficient to cause loss of domain orientation.

Nealey and coworkers [16,114,151] took a similar approach and applied lithographically defined self-assembled monolayers as substrates to direct the orientation of block copolymer thin films. After EUV interferometric lithography on octadecyltrichlorosilane (OTS) or phenylethyltrichlorosilane (PETS) monolayers, PS-b-PMMA block copolymers were deposited and annealed on the substrates. Due to the selective wetting of PS and PMMA on the unexposed and exposed regions, respectively, they were able to obtain large areas of perpendicular lamella when the commensurate condition was fulfilled.

The use of top-down substrate patterns to direct bottom-up block copolymer patterns has proved to be very efficient in creating oriented hierarchical patterns. However, introduction of yet another structure-directing element to these systems has allowed even more control over the patterning process. Recently, by applying a directional solidification process to a topographically patterned substrate, Park et al. [101] have been able to apply an additional driving force into the graphoepitaxial growth of the bottom-up block copolymer pattern onto the top-down substrate pattern. By confining a PS-b-PI block copolymer thin film between the solvent crystal and the topographic patterned substrate, they have been able to induce two types of PI cylinder domain orientations in the same precise lateral patterns (Figure 2.17).
Figure 2.16. Schematic representation of the strategy used to create chemically nanopatterned surfaces and investigate the epitaxial assembly of block-copolymer domains. a, A SAM of PETS was deposited on a silicon wafer. b, Photoresist was spin-coated on the SAM-covered substrate, and c, patterned by EUV-IL with alternating lines and spaces of period \( L_s \). d, The topographic pattern in the photoresist was converted to a chemical pattern on the surface of the SAM by irradiating the sample with soft X-rays in the presence of oxygen. e, The photoresist was then removed with repeated solvent washes. f, A symmetric, lamella-forming PS-b-PMMA copolymer of period \( L_o \) was spin-coated onto the patterned SAM surface and g, annealed, resulting in surface directed block-copolymer morphologies. Chemically modified regions of the surface presented polar groups containing oxygen and were preferentially wetted by the PMMA block, and unmodified regions exhibited neutral wetting behavior by the block copolymer [16].
Figure 2.17. Schematics of the PS/PI block copolymer microstructure, directionally solidified on the patterned substrate (a) before and (b) after O$_2$-RIE. Note the difference in magnification between the vertical and in-plane directions. (a) Block copolymer films confined between the BA crystal and the prepatterned substrate undergo thickness variations, leading to two different orientations. Preferential PI and PS wetting on silicon and the BA surface, respectively, are assumed. (b) O$_2$-RIE generates a vertically ordered cylindrical hole structure on the mesa regions. On the plateau regions, the original film thickness is reduced by approximately 15%, so only part of cylindrical PI layer is modified due to limited etching [101].
2.6.3. Convergence of Top-Down and Bottom-Up in Block Copolymer Design

The convergence of top-down and bottom-up fabrication in the same block copolymer architecture has been demonstrated using e-beam lithography by Bal et al. [152] and Spatz et al. [153,154]. Through SEM-e-beam exposure of cylindrical PS-b-PMMA films, Bal et al. [152] have been able to create cylindrical nanochannels at defined locations from PS-b-PMMA on the substrate, and thereby demonstrated its potential to generate integrated magnetoelectronic devices. In this process, the PS matrix is crosslinked in the exposed area, thus making the block copolymer system behave as a negative tone e-beam resist, in which the unexposed material is removed in a development step. In a similar manner, by using metal precursor loaded PS-b-P2VP block copolymer micellar monolayers as a negative e-beam resist, Spatz et al. created metallic nanodots in microscopically defined locations [153,154]. In this system, the patternability is proposed to arise from crosslinking of the PS block as well as chemical modification of P2VP/metal salts due to e-beam exposure.

Although e-beam lithography can give excellent spatial control of functional microdomains, this direct-write patterning process is not time-efficient for large-area integration of functional devices. Techniques for rapid patterning of functional nanostructures are thus needed for real-time applications. Ober et al. [155-157] have successfully developed a novel block copolymer system using poly(α-methylstyrene-b-4-hydroxystyrene) (PαMS-b-PHS) to achieve spatial control through high-resolution deep UV lithographic processes. Through the incorporation of high-resolution PHS photoresist and PαMS in the block architecture, large-area uniform nanometer-sized cylinders were generated in submicron-sized patterns through simple fabrication processes (Figure 2.18).
Additionally, this block copolymer was automatically spincoat aligned with vertical orientations over a wide range of film thicknesses (40 nm – 1 µm), thereby avoiding tedious alignment procedures. Furthermore, this block copolymer system was designed such that the thermodegradable PαMS block could be removed to make a nanoporous material.

Figure 2.18. Novel nanofabrication process of obtaining spatially controlled nanopores: (a) spin-coat PRMS-b-PHOST/CL/PAG mixture onto a silicon wafer to form vertical cylinders of PRMS in the PHOST matrix, (b) irradiate using a 248 nm stepper with a photomask and bake, (c) develop with a mixed solvent to form micron-sized patterns on top of substrate, (d) irradiate using a 365 nm lamp under vacuum, and (e) form patterns with nanoporous channels [157].
2.7. Patterning with Block Copolymer Templates

All of the material discussed to this point has dealt with patternable block copolymer systems in which a pattern is defined in the polymer, whether by self-assembly of the blocks into microdomain patterns, or by lithographically defined patterns. While the processes for transferring top-down patterns to the underlying substrates have been well-established, there is also great deal of interest in transferring the self-assembled bottom-up patterns to other materials. Patterning with block copolymers using bottom-up nanostructures as templates in this way opens the door to a variety of nanotechnological applications, which require patterned materials with properties much different to polymeric matrices, such as inorganic networks and metals. High-resolution nanopatterned substrates, patterned nanoparticles, nanoporous monoliths, as well as nanoreplicated materials have been generated from block copolymer templates.

2.7.1. Nanolithography Templates

Composition-asymmetric diblock copolymer thin films have been shown to be good candidates for use as nanolithographic templates because two-dimensionally large area periodic patterns can be produced on a nanometer-size scale with either a monolayer film of close-packed spheres, or with a thin film containing an array of cylinders oriented perpendicular to the substrate. The periodic nanostructure patterns can be subsequently transferred to various kinds of substrates through a lithographic ion-etching process because of the different etching sensitivities of the two building blocks.
Park et al. [70,158] were the first researchers to demonstrate the template nanolithographic process with well-ordered spherical or cylindrical PS-b-PB or PS-b-PI diblock copolymers (Figure 2.19). Through ozone removal of either the PB or PI minor phase or via selective staining, these block copolymer films were employed as positive and negative resists for a subsequent phase-selective reactive ion etching process. Using this approach, an extremely high-density array \( \sim 10^{11} \text{ holes/cm}^2 \) of holes and dots were produced on silicon [158], germanium [158], and silicon nitride [70] substrates. By combining block copolymer nanolithography with a multilayer resist technique, they were also able to further demonstrate the generation of high density metal [101] and GaAs [159] nanodots, using the patterned silicon nitride layer as a mask. Using a similar approach, Russell’s group [160] has also demonstrated pattern transfer in PS-b-PMMA thin films. After UV-degradation of the PMMA minor phase, the nanoporous polymer template structures were successfully transferred to the underlying substrates through a subsequent etching process.
Figure 2.19. Schematic representation of block copolymer nanolithography process. (A) Schematic cross-sectional view of a nanolithography template consisting of a uniform monolayer of PB spherical microdomains on silicon nitride. PB wets the air and substrate interfaces. (B) Schematic of the processing flow when an ozonated copolymer film is used as a positive resist, which produces holes in silicon nitride. (C) Schematic of the processing flow when an osmium-stained copolymer film is used as a negative resist, which produces dots in silicon nitride [70].
2.7.2. Nanoparticle Templates

BCPs have also been utilized not only as surfactants to inhibit coalescence and aid in dispersion of nanoscale particles such as metal, metal oxide, inorganics, molecular chromophores and quantum dots, but also to spatially pattern the particles [161-172]. The selective dispersion of quantum dots into a target set of microdomains within functionalized polynorbornene BCPs was first achieved by controlling the affinity between the selective block and quantum dot surface (Figure 2.20 (a)) [165,166]. A photonic crystal with improved dielectric contrast was made by selective deposition of CdSe nanocrystals to the 2-vinyl pyridine (2VP) microdomains of a self-assembled poly(styrene-b-isoprene-b-2-vinyl pyridine) triblock copolymer (Figure 2.20 (b)) [173]. In another approach to patterning nanoparticles with BCPs, the BCP domain structure has been used as a ‘nano-reactor’, where nanoscale particles are induced to nucleate and grow through the chemical reactions [161-163,174]. For example, nanometer scale platinum and palladium catalysts were generated and stabilized within the polystyrene core of poly(styrene-b-ethylene oxide) BCP spherical domains [174]. Electrolysis deposition of metals into selected micro-domains has been recently performed to provide continuous material loading [168,169,175]. The tendency of selective adsorption of metals in BCPs has also been used. Gold nanoparticles were selectively patterned on cylinder-forming poly(styrene-b-methylmethacrylate) (PS/PMMA) BCP thin film via thermal evaporation [176]. Recently, Bockstaller et al. demonstrated a hierarchically patterned microstructure of ternary mixtures of two different-sized nanoparticle species (gold and silica) and a BCP by strategic design of the size and the respective surface coatings of the nanoparticles (Figure 2.21 (c)) [171,172]. The authors also showed that a
homogeneous sequestering of nanocrystals into self-assembled BCP is a more advantageous morphology than interfacial segregation and center alignment of nanocrystals for engineering block copolymer based photonic materials with high reflectivity, since it allows one to incorporate a larger amount of nanocrystals, while preventing enhanced light absorption by the electrodynamic coupling effect between neighboring metallic nanocrystals [172].
Figure 2.20. (a) TEM micrograph of 45 Å CdSe nanoclusters in a thin film of diblock copolymer of phosphine oxide functionalized monomers (NBE-CH$_2$O(CH$_2$)$_3$P(oct)$_2$ and methyhtetracyclododecene (MTD), slow-cast after 30 min equilibration time [165]. (b) TEM micrograph of 1D self-assembled dielectric lattice made of poly(isoprene-b-2vinyl pyridine-b-isoprene) (PI/P2VP/PI) with TOPO coated CdSe nanocrystals sequestered in the 2VP phase [173]. (c) TEM micrograph of a ternary blend of PS-PEP + AuR$_1$ + SiO$_2$R$_2$ with inorganic filling fraction f = 0.02, respectively, after micro-sectioning normal to the layer direction (no stain). Gold nanocrystals appear as dark spots along the IMDS, silica nanocrystals reside in the center of the PEP domain. Inset: Schematic of the particle distribution (size proportions are changed for clarity) [171].
2.7.3. Nanoreplicated Pattern Formation

One of the most important applications of nanoporous membranes is as “nanoscaffolds” in template synthesis, to replicate the structural features of the nanopores, or patterns, into metals [177], carbons [178], semiconductors [179], conductive polymers [180], and other materials [181]. The important characteristics of template synthesis have been best reviewed by Martin [182,183]. In short, it is a robust, general method suitable for the replication of nanoscale features into almost all kinds of materials, which can be retrieved afterwards without structural damage.

The Russell group has applied the template synthesis approach to nanoporous films generated from UV-treated PS-b-PMMA copolymers [21,152,177,179,184], which were pre-aligned perpendicular to the substrate by an electric field. Through direct current electrodeposition, they fabricated high-density vertical arrays of ferromagnetic cobalt nanowires (Figure 2.21) [21]. Through subsequent work, they also demonstrated the successful replication of nanoscale features with the formation of silicon dioxide posts [179], metal nanodots [177], nanoporous metal films [184,185], nanoelectrode arrays [184] as well as surface-patterned PDMS elastomers [181].
Figure 2.21. Schematic representation of the growth of high-density nanowires from a nanoporous block copolymer thin film. (A) An asymmetric PS-b-PMMA diblock copolymer was aligned to form vertical PMMA cylinders under an electric field. (B) After removal of the PMMA minor component, a nanoporous film is formed. (C) By electrodeposition, an array of nanowires can be replicated in the porous template [21].
CHAPTER III
OBJECTIVES, MATERIALS, AND EXPERIMENTAL PROCEDURES

From the previous results in our research group, blending homopolymers with BCPs and controlling their molecular weights were suggested as a convenient method to lower the transition energy required for changing the cylinder orientation from a stable parallel orientation to a stable perpendicular orientation, especially when the homopolymer had a molecular weight that is similar to the corresponding block-copolymer component. In case of SIS4113 (Vector 4113, DEXCO Polymers), with the addition of lower PS molecular weight homopolymer than that of PS block in neat SIS, the entropic increase in the PS domains enhanced the tendency to maintain the initial parallel orientation in neat SIS4113 while the enthalpic increase induced by the increased amount of PS molecules intrinsically unfavorable with PI molecules was not favorable to the initial parallel orientation in neat SIS [36]. Therefore, achieving more favorable thermodynamic conditions by blending with homopolymer and controlling a molecular weight was the critical factor to orient perpendicular cylinders.

We investigate the spontaneous method with a block copolymer which has the same chemical structure, a similar composition of PS block, but different information of molecular weight with those of SIS4113 in the previous mixtures [36]. We also report on an untested system with a block copolymer having the same chemical structure, but
different composition of PS block and different information of molecular weight. After that, we employ another block copolymer as a material which has different chemical structure, composition of PS block, and information of molecular weight to investigate the spontaneous and effective method of self-assembly systematically.

This study illustrates and investigates the favorable thermodynamic conditions by blending with homopolymer. For the purpose, we control the thermodynamic information by adjusting the molecular weight of the added homopolymer into block copolymer and by varying the annealing temperatures. We also study the effect of the interfacial interaction between the mixture and the surface of the substrates on the micro domain orientation using various preferential substrates. During the investigations, the spatial distribution of the chains of homopolymer and the structure parameters of the microdomains are also characterized and then the experimental results are compared with the theoretical interpretations. Study of new orientation methods and their effects will offer more effective pathways of the ordering process into self-assembly of block copolymer.

3.1. Materials and Experimental Procedures

The structures of the block copolymers are shown in Table 1. Polystyrene-b-polyisoprene-b-polystyrene (SIS) and polystyrene-b-polybutadiene-b-polystyrene (SBS) were used without further purification as received from DEXCO Polymers and KRATON polymers, respectively. The series of each BCP are summarized in Table 2. Highly purified solvents, toluene, dodecane, and heptane were obtained from Aldrich.
Dimethylformamide (DMF) was also supplied from Fisher Scientific. These solvents were highly pure and used without purification. A number of PS homopolymers with different molecular weights were received from Sewoo Yang of Dr. Foster’s group (U of Akron, Department of Polymer Science). The PS homopolymers were synthesized by anionic polymerization using sec–butyllithium as initiator, benzene as solvent, and standard high-vacuum techniques. The materials are summarized in Table 2. A PS with a molecular weight (17 kg/mol) was received from Polymer Source.

Gel Permeation Chromatography instruments were used to characterize the average molecular weight and molecular weight distribution of the precursor materials. The weight average molecular weight, $M_w$ and the polydispersity index (PDI, $M_w/M_n$) of SIS, SBS triblock copolymer and PS homopolymers were determined from the gel permeation chromatography (GPC, Waters) data based on the calibration with the PS standard of known molecular weight and PDI. The PS weight percent of the block copolymer was determined by proton nuclear magnetic resonance (1H-NMR, Varian VXR 200) spectroscopy.

The glass transition temperatures (Tg) were measured by differential scanning calorimeter (DSC) (Q1000, TA instruments). The data were taken from second scan performed under a stream of nitrogen gas by cooling to -100 °C with refrigerated cooler (TA instruments) and then to 250 °C at scanning rate of 10 °C/min. The first scan was run for the removal of previous thermal history. The value of Tg was taken as the temperature at which half of the specific heat change has been accomplished during the glass transition.
A number of different PS samples with various molecular weights were blended into BCPs. The solution samples were prepared in toluene as a solvent. Different composition of PS homopolymers and BCPs were dissolved in toluene (2 ~ 5 wt % in solution) with 0.05 wt % of antioxidant (Irganox 1010, Ciba-Geigy Group). Thin films of BCPs/homopolymer mixture were spun cast from the filtered solution directly in the 3 in. diameter substrate at 1000 to 2000 rpm. Before spin coating, the silicon substrates were cleaned with a mixture solution (7/3) of sulfuric acid and hydrogen peroxide, and were etched with hydrofluoric acid (49 wt % solution) to remove the native oxide layer. The control of thickness of film on substrate was performed according to the concentration of solution and the speed of spinning. Film thickness values of 50 to 150 nm were measured with a Gaertner model L116C ellipsometer using a He-Ne laser (wavelength = 632.8 nm) and a fixed angle of incidence of 70°. Thicker film samples between 500 nm and a few tens of micrometers were prepared by solution casting onto selected substrates. The solvent in BCPs/homopolymer solutions was slowly evaporated at ambient condition for 2 days and then in a vacuum oven at 50°C for a day. Finally, all the samples were annealed in a vacuum oven at different annealing temperatures, which was well above glass transition temperatures (T_g’s) of PS block and PS homopolymers.

Topographic images of the samples were obtained under ambient conditions. The surface morphologies of the samples deposited on different substrates were recorded with a Nanoscope III from Digital Instruments. The atomic force microscope (AFM) was operated in the tapping mode under ambient conditions using commercial silicon microcantilever probe tips (Veeco, RTESP5) with spring constants ranging between 20 and 80 N/m as specified by the manufacturer. Almost same topographic and phase images
were obtained simultaneously using a resonance frequency of ~280 kHz for the probe oscillation.

Small-angle scattering (SAS) is a powerful technique for examining nanostructures formed by the self-assembly of block copolymers, whether in the melt, solution or crystal state. This study focused on small-angle X-ray scattering studies. Bulk samples for SAXS experiments were prepared by coating on a polytetrafluorethylene substrate. The Rigaku MicroMax-002+ X-ray generator was the microfocus source produced by coupling a high performance Osmic Confocal Max-Flux® (CMF) optic with a sealed tube microfocus X-ray source. The SAXS patterns were recorded on the 2-dimensional detector manufactured by Rigaku Innovative Technologies and it used a CMF optic to condition the beam through a series of 3 collimating pinholes. A source spot size was 20 µm. This Cu source operates at 40W power with 45kV voltage and 0.88mA current. The wavelength of X-ray radiation was 1.5405Å. SAXS is used for the determination of the microscale or nanoscale structure of particles in terms of average particle size, shape, distribution, and surface-to-volume ratio. The main use of SAXS in this study was to confirm the microdomain morphologies and structure, its structure parameters, and segmental distribution of homopolymer chains. In this study, the structure parameters of each microdomain were calculated only from SAXS profiles, where we assume complete mixing of PS homopolymer with PS microdomains in BCPs. Since AFM images only describe the morphology at the surface of each sample and the end of each microdomain at the surface may not homogeneously come toward the air, there is possibility of misinterpreting the microdomain’s structure parameters and morphologies, when using only AFM measurements. Particularly, in case of parallel orientation on the substrate, the
surface image from AFM measurement may not show the complete cylinder distribution, as some of them are expected to be hidden slightly below the surface of the sample.

Table 2. Summary of block copolymers and homopolymers and their characteristics

<table>
<thead>
<tr>
<th>Material Name</th>
<th>Styrene (wt %)</th>
<th>M.W. (kg/mol)</th>
<th>PDI (Mw/Mn)</th>
<th>Tg (°C)</th>
<th>Source</th>
</tr>
</thead>
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<tr>
<td>SIS4111</td>
<td>18</td>
<td>S (12.8)-b-I (116)- b-S (12.8), 141.6</td>
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<td>-</td>
<td>Dexco Polymers</td>
</tr>
<tr>
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<td>15</td>
<td>S (11.4)-b-I (129.2)- b-S (11.4), 152</td>
<td>1.05</td>
<td>-</td>
<td>Dexco Polymers</td>
</tr>
<tr>
<td>SBS1102</td>
<td>28.6</td>
<td>S (16.8)-b-B (84)- b-S (16.8), 117.6</td>
<td>1.1</td>
<td>-</td>
<td>Kraton Polymers</td>
</tr>
<tr>
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<td>4</td>
<td>1.08</td>
<td>78</td>
<td>Synthesized</td>
</tr>
<tr>
<td>PS12.2k</td>
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<td>1.05</td>
<td>90</td>
<td>Synthesized</td>
</tr>
<tr>
<td>PS17K</td>
<td>-</td>
<td>17</td>
<td>1.05</td>
<td>92</td>
<td>Polymer Source</td>
</tr>
<tr>
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<td>93</td>
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</tr>
<tr>
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<td>24</td>
<td>1.02</td>
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<tr>
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<tr>
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<td>43.1</td>
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<td>98</td>
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</table>
3.2. Thermodynamic Control over the Immiscibility between the Blocks: Different Molecular Weights of Homopolymer

Earlier work by Ahn and Sancaktar revealed that further increases of PS molecular weight over 27 kg/mol results in severe macrophase separation between the SIS (Vector 4113, DEXCO Polymers) and PS homopolymer even at the homopolymer weight fraction of 5 wt %. [36]. The series of SIS and SBS in this study, however, have different thermodynamic information (lower molecular weights, different block compositions and components). Thus, higher molecular weights of PS were also added in this study and additional thermodynamic information regarding BCPs and homopolymers interactions are expected, possibly with different phase behaviors.

Consequently, we believe that the incompatibility between the blocks can be modified by the change of homopolymer molecular weights. Thus, different samples were prepared and these were individually named, for example for SIS4114, we have:

(1) Neat SIS4114;
(2) SIS4114/PS4k(90/10, weight ratio), PS with 4000 g/mol of weight average molecular weight, $M_w$;
(3) SIS4114/PS12k(90/10), PS with $M_w$ (12200 g/mol);
(4) SIS4114/PS17k(90/10), PS with $M_w$ (17000 g/mol);
(5) SIS4114/PS21k(90/10), PS with $M_w$ (21300 g/mol);
(6) SIS4114/PS27k(90/10), PS with $M_w$ (26700 g/mol);
(7) SIS4114/PS40k(90/10), PS with $M_w$ (40300 g/mol).

SIS4111, SBS1102 BCPs were modified in similar fashion.
It is notable that further increase of PS homopolymer weight fraction is restricted by the macrophase separation between the BCPs and PS homopolymer. In the previous study by our group, two different effects of homopolymer volume fraction were observed on the arrangement of block copolymer cylinders. When the homopolymer molecular weight is sufficiently smaller than that of the corresponding block component, the straightness of the parallel cylinders along the substrate plane are gradually enhanced, as the volume fraction of homopolymer is increased, due to the gradual decrease of incompatibility between the blocks. When the homopolymer molecular weight is similar to or larger than that of corresponding block component, and as its volume fraction increases, the size and periodic spacing of perpendicular cylinders gradually decrease due to the proportional increase of incompatibility.

The goal of this part of our study is to explore the phase behavior, which can be controlled by the molecular weights of homopolymer, as a function of different BCPs. This investigation from various angles expects that the cylinder orientation with a persistency and higher scale of periodic size and spacing can be adjusted simply by controlling the molecular weight of the blended homopolymer.

3.3. Thermodynamic Control over the Immiscibility between the Blocks: Different Annealing Conditions: SIS Triblock Copolymer

The objective of this part of our study is to investigate the effects of the variation of annealing temperature on the ordering of BCPs/homopolymer mixtures. The morphologies of orientation are studied by changing the annealing conditions at a fixed homopolymer molecular weight and volume fraction, which results in well-ordered
structure with a persistency. We note that the degree of incompatibility (i.e. the preference for perpendicular cylinder orientation) will gradually decrease as the temperature increases. Thus, the perpendicular cylinders achieved at relatively lower temperature can be transferred to parallel ones at higher temperature if their preference for perpendicular orientation is not strong enough to overcome the entropic effects arising from the increase of temperature. In case of the parallel cylinders formed at relatively lower temperature, the straightness of their arrays is expected to be enhanced with the increase of temperature due to the decrease of incompatibility.

At a fixed molecular weight and volume fraction of blended homopolymer, the variation of annealing temperature of block copolymer mixture can also modify the segregation forces between the heterogeneous block components. The thermal histories of the specimens used in this study are summarized in Table 3.

3.4. Thermodynamic Control over the Immiscibility between the Blocks: Different Annealing Conditions: SBS Triblock Copolymer

At a fixed molecular weight and volume fraction of blended homopolymer, the variation of annealing temperature of block copolymer mixture can also modify the segregation forces between the heterogeneous block components. The thermal histories of the specimens used in this study are summarized in Table 4.
Table 3. Thermal Histories of the SIS Block Copolymer Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>thermal history</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat SIS, SIS/PS4K, SIS/PS12K, SIS/PS17K, SIS/PS21K, SIS/PS27K, SIS/PS40K, and SIS/PS43K at 130°C</td>
<td>annealed at 130°C for 48 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SIS, SIS/PS4K, SIS/PS12K, SIS/PS17K, SIS/PS21K, SIS/PS27K, SIS/PS40K, and SIS/PS43K at 150°C</td>
<td>first annealed at 130°C for 45 h and then heated to 150°C and held there for 1 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SIS, SIS/PS4K, SIS/PS12K, SIS/PS17K, SIS/PS21K, SIS/PS27K, SIS/PS40K, and SIS/PS43K at 170°C</td>
<td>first annealed at 130°C for 45 h and then heated to 150°C and held there for 1 h and then heated to 170°C and held there for 2 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SIS, SIS/PS4K, SIS/PS12K, SIS/PS17K, SIS/PS21K, SIS/PS27K, SIS/PS40K, and SIS/PS43K at 190°C</td>
<td>first annealed at 130°C for 45 h and then heated to 150°C and held there for 1 h and then heated to 170°C and held there for 1 h and then heated to 190°C and held there for 1 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SIS, SIS/PS4K, SIS/PS12K, SIS/PS17K, SIS/PS21K, SIS/PS27K, SIS/PS40K, and SIS/PS43K at 210°C</td>
<td>first annealed at 130°C for 45 h and then heated to 150°C and held there for 0.5 h and then heated to 190°C and held there for 0.5 h and then heated to 210°C and held there for 1 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SIS, SIS/PS4K, SIS/PS12K, SIS/PS17K, SIS/PS21K, SIS/PS27K, SIS/PS40K, and SIS/PS43K at 230°C</td>
<td>first annealed at 130°C for 45 h and then heated to 150°C and held there for 0.5 h and then heated to 190°C and held there for 0.5 h and then heated to 210°C and held there for 0.5 h and then heated to 230°C and held there for 1 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SIS, SIS/PS4K, SIS/PS12K, SIS/PS17K, SIS/PS21K, SIS/PS27K, SIS/PS40K, and SIS/PS43K at 250°C</td>
<td>first annealed at 130°C for 45 h and then heated to 150°C and held there for 0.5 h and then heated to 170°C and held there for 0.5 h and then heated to 190°C and held there for 0.5 h and then heated to 210°C and held there for 0.5 h and then heated to 230°C and held there for 0.5 h and then heated to 250°C and held there for 0.5 h and then rapidly quenched in liquid nitrogen</td>
</tr>
</tbody>
</table>
Table 4. Thermal Histories of the SBS Block Copolymer Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>thermal history</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat SBS, SBS/PS4K, SBS/PS12K, SBS/PS17K, SBS/PS21K, SBS/PS27K, SBS/PS40K, and SBS/PS43K at 130°C</td>
<td>annealed at 120°C for 48 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SBS, SBS/PS4K, SBS/PS12K, SBS/PS17K, SBS/PS21K, SBS/PS27K, SBS/PS40K, and SBS/PS43K at 150°C</td>
<td>first annealed at 120°C for 45 h and then heated to 150°C and held there for 3 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SBS, SBS/PS4K, SBS/PS12K, SBS/PS17K, SBS/PS21K, SBS/PS27K, SBS/PS40K, and SBS/PS43K at 170°C</td>
<td>first annealed at 120°C for 45 h and then heated to 150°C and held there for 1 h and then heated to 170°C and held there for 2 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SBS, SBS/PS4K, SBS/PS12K, SBS/PS17K, SBS/PS21K, SBS/PS27K, SBS/PS40K, and SBS/PS43K at 190°C</td>
<td>first annealed at 120°C for 45 h and then heated to 150°C and held there for 1 h and then heated to 170°C and held there for 1 h and then heated to 190°C and held there for 1 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SBS, SBS/PS4K, SBS/PS12K, SBS/PS17K, SBS/PS21K, SBS/PS27K, SBS/PS40K, and SBS/PS43K at 210°C</td>
<td>first annealed at 120°C for 45 h and then heated to 150°C and held there for 0.5 h and then heated to 190°C and held there for 0.5 h and then heated to 210°C and held there for 1 h and then rapidly quenched in liquid nitrogen</td>
</tr>
<tr>
<td>neat SBS, SBS/PS4K, SBS/PS12K, SBS/PS17K, SBS/PS21K, SBS/PS27K, SBS/PS40K, and SBS/PS43K at 230°C</td>
<td>first annealed at 120°C for 45 h and then heated to 150°C and held there for 0.5 h and then heated to 170°C and held there for 0.5 h and then heated to 190°C and held there for 0.5 h and then heated to 210°C and held there for 0.5 h and then heated to 230°C and held there for 1 h and then rapidly quenched in liquid nitrogen</td>
</tr>
</tbody>
</table>
3.5. Investigation of Effects of Substrate-Polymer Interactions: Various Substrates with Different Interfacial Interactions

This part of our study explores the control of orientation by the variation of interaction between the polymer and the substrate to achieve large-area microdomains with desirable orientations. To investigate the effects of interfacial interaction on the orientation, various substrates were selected: poly(tetrafluoroethylene) (Teflon), HF-treated silicon wafer, polyimide (Kapton), and poly(ethylene terephthalate) (PET, Mylar). On a preferential substrate, one of the block components possessing stronger affinity to the substrate than any other components is expected to preferentially enlarge its interfacial area in contact with the substrate. Thus, the parallel cylinder orientation may be attributed to the presence of preferential interaction between the substrate and one of the block components. For the SIS4113/PS system, the previous investigation [36] in our group, reported that once a strong preference for each orientation type was achieved by controlling the thermodynamic information of the blend, the interaction modification by employing special interface between substrate and polymer was not a significant factor to affect the cylinder orientation of the block copolymer.

Consequently, we will continue to investigate useful and convenient strategies (without any modification on substrate surfaces) for possible changes in the orientation structure by simply blending the homopolymer into the BCPs and modifying the thermodynamics of the blends as a function of different surface tensions of the substrate and different BCPs.
CHAPTER IV
SELF-ASSEMBLED MICRODOMAIN AND ITS ORIENTATION
BEHAVIOR OF BLOCK COPOLYMER/HOMOPOLYMER
BLEND: PS-PI-PS TRIBLOCK COPOLYMER, VECTOR 4114

4.1. Introduction

Block copolymers (BCPs) have been the focus of much interest during the last 30 years because of the miscibility between their constituent blocks, leading to microphase separation [15]. Self-assembly of BCPs is an important strategy in new material science and technology, and nano-sized patterns from self-assembly are poised to replace current lithographic technologies. BCPs have become the center of attention in such self-assembly-based bottom-up processes due to the scale of the microdomains between 10 and 100 nm, and their various chemical and physical properties. Size and shape control of microdomains have proven to be quite effective in BCPs by modification of their thermodynamic states via molecular weights and compositions [13].

Control over microdomain orientations and elimination/minimization of defects play a crucial role in optimization of the resultant physical properties with nanostructures. Understanding the mechanism of defect formation has been an essential topic in controlling BCPs microstructures [15]. In order to achieve a regularly ordered structure across long range scales, the orientation can be controlled by using self-organizing
materials, whose assembly is ordered and directed by various molecular interactions (and their combination) as well as by external constraints. Competing factors in controlling structure formation include chemical differences, conformational entropy, spatial constraints (molecular shape effects) and external (electric, magnetic, hydrodynamic flow) fields. The substrate can be prepatterned on the length-scale of the polymer [16-18], or coated with a thin layer of anchored random copolymers to provide a neutral surface [19,20], equally attractive for both blocks. Mixtures of block copolymers and homopolymers [22-24] also provide interesting micro- and nanostructures, and thus offer additional routes for patterning.

Recently, we employed the rapid method to induce vertically oriented cylindrical microdomain by blending BCPs with homopolymer (same structure with a minor component in triblock copolymer [36]. Control of the homopolymer molecular weight enables changes in the periodic spacing and hexagonal orientation of the perpendicular nanocylinders. Thus, the method to control perpendicular ordering on large scale throughout the area in asymmetric triblock copolymers is demonstrated by simply adjusting thermodynamic conditions for BCP/homopolymer blends. Furthermore, it is illustrated that the control of substrate-polymer interaction and modification of the substrate surface do not necessarily influence the perpendicular orientation process of the cylinders, especially when a thermodynamic preference for perpendicular orientation is already strongly introduced into the material by the blending, in the BCPs, of a homopolymer of an appropriate molecular weight.

The main objective of this research, therefore, is to prepare perpendicularly and hexagonally well-oriented cylinders with a consistency over a large size of sample area
and thickness by only using thermodynamic controls on BCP/homopolymer blend systems. It is achieved by thermodynamic control over the immiscibility between A and B blocks in BCPs (ABA) and by exploiting the compatibility between A homopolymer and A block in BCPs. Additional thermodynamic control is achieved by kinetic adjustments, i.e., by annealing BCPs/homopolymer mixtures.

In this chapter, we report on a system untested in the previous research of Ahn and Sancaktar [36], SIS4114 (Vector 4114, DEXCO Polymers), having a molecular weight of 152 kg/mol with a PS block of 22.8 kg/mol and a PI block of 129.2 kg/mol. The SIS4114 triblock copolymer used in this study was chosen as a material which has the same chemical structure, a similar composition of PS block, but different molecular weight with those of SIS4113 in the previous mixtures [36] to investigate the method of self-assembly systematically. The molecular weight of homopolymer (PS) is varied in the range between 4 kg/mol and 43 kg/mol. The bulk microdomain of SIS4114 orientation is that of hexagonally oriented parallel cylinder PS domains. We show that a simple and fast method can be employed to orient the cylinders in perpendicular direction.

4.2. Experimental Methods

A commercially available polystyrene-polyisoprene-polystyrene (SIS) block copolymer Vector 4114 (Dexco Polymers Co.) was used. Vector 4114 contains 15 wt % (13 vol %) PS and has a weight-average molecular weight ($M_w$) of 152000 g/mol and a polydispersity ($M_w/M_n$) of 1.05. Various molecular weights of polystyrene (PS) were
used in the blends. All the polymers and chemicals were used without further purification. All information about the polymers used in this study is summarized in Table 2.

Different molecular weights of PS were blended into SIS4114. The solution samples were blended with toluene as a solvent. 10 wt % of PS homopolymers and 90 wt % of BCPs were dissolved in toluene (2 wt % in solution) with 0.05 wt % of antioxidant (Irganox 1010, Ciba-Geigy Group). Information on blended samples such as the molecular weight ratio of PS homopolymer to PS block in the SIS4114 ($\alpha$), the weight fraction of PS phase ($W_{PS}$), and the volume fraction of PS phase ($\Phi_{PS}$) in SIS4114 and SIS4114/PS blends are summarized in Table 5. Thin films of BCPs/homopolymer mixture were spin cast from the filtered solution directly on the 3 in. diameter substrate at 2000 rpm. Film thickness values of 90 to 110 nm were measured with a Gaertner model L116C ellipsometer using a He-Ne laser (wavelength = 632.8 nm) and a fixed angle of incidence of 70°. Thicker film samples between 500 nm and a few tens of micrometers were also prepared by solution casting onto selected substrates. The solvent in BCPs/homopolymer solutions was slowly evaporated at ambient condition for 2 days and then in a vacuum oven at 50 °C for a day. Finally, all the samples were annealed in a vacuum oven at different annealing temperatures well above the glass transition temperatures ($T_g$’s) of PS block and PS homopolymers.

Bulk samples for small-angle X-ray scattering (SAXS) experiments were prepared by coating the mixture solutions on the Teflon substrate. The Rigaku MicroMax-002+ X-ray generator was the microfocus source produced by coupling a high performance Osmic Confocal Max-Flux® (CMF) optic with a sealed tube microfocus X-ray source. The SAXS patterns were recorded on the 2-dimensional detector manufactured by
Rigaku Innovative Technologies and it used a CMF optic to condition the beam through a series of 3 collimating pinholes. A source spot size was 20 μm. This Cu source operates at 40W power with 45kV voltage and 0.88mA current. The wavelength of X-ray radiation was 1.5405Å. SAXS measurements were performed at ambient temperature.

Topographic images of the samples were obtained under ambient conditions. The surface morphologies of the samples deposited on different substrates were recorded with a tapping mode AFM (Nanoscope III, Digital Instruments). AFM was operated under ambient conditions using commercial silicon microcantilever probe tips (Veeco, RTESP5) with spring constants ranging between 20 and 80 N/m as specified by the manufacturer. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 280 kHz for the probe oscillation; however, only the phase images were presented as they have more contrast.
Table 5. Summary of the information of the molecular weight and volumetric ratio in the SIS4114 and SIS4114/PS blends

<table>
<thead>
<tr>
<th>sample name</th>
<th>$\alpha$</th>
<th>$W_{PS}$</th>
<th>$\Phi_{PS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS4114</td>
<td>-</td>
<td>0.150</td>
<td>0.129</td>
</tr>
<tr>
<td>SIS4114/PS4K</td>
<td>0.35</td>
<td>0.152</td>
<td>0.131</td>
</tr>
<tr>
<td>SIS4114/PS12K</td>
<td>1.05</td>
<td>0.157</td>
<td>0.136</td>
</tr>
<tr>
<td>SIS4114/PS17K</td>
<td>1.49</td>
<td>0.160</td>
<td>0.138</td>
</tr>
<tr>
<td>SIS4114/PS21K</td>
<td>1.84</td>
<td>0.163</td>
<td>0.140</td>
</tr>
<tr>
<td>SIS4114/PS27K</td>
<td>2.37</td>
<td>0.166</td>
<td>0.144</td>
</tr>
<tr>
<td>SIS4114/PS40K</td>
<td>3.51</td>
<td>0.174</td>
<td>0.150</td>
</tr>
<tr>
<td>SIS4114/PS43K</td>
<td>3.77</td>
<td>0.176</td>
<td>0.152</td>
</tr>
</tbody>
</table>

$\alpha$: the molecular weight ratio of PS homopolymer to PS block in the BCP, $W_{PS}$: the weight fraction of PS phase, and $\Phi_{PS}$: the volume fraction of PS phase.
4.3. Transition in Microdomain Orientation of SIS4114 Triblock Copolymer with the Addition of PS Homopolymer

Figure 4.1 shows AFM images of SIS4114 triblock copolymer and its homopolymer blends annealed at 130 °C for 48 h on Si substrate. The AFM images of the samples annealed on Teflon substrate with a same condition are shown in Figure 4.2. The AFM images determined by tapping mode under ambient conditions show the identical height and phase images. It is determined that the cylinder orientation behavior of block copolymer and its blends spin-coated on HF-treated silicon wafer with a film thickness of ~100 nm is identical to that of samples solution-cast on Teflon substrate with a film thickness of ~10 µm. In addition, the AFM measurement also reveals that the images on the interface between the sample and Teflon substrate are not much different from the orientation behavior on the top surface of each sample. These observations reveal that the film thickness of the blending system with SIS4114 and PS homopolymer blends does not significantly affect the cylinder orientation behavior in the range of sample thickness from the sample-substrate interface to ~10 µm when deposited on commercial substrates, which are HF-treated Si wafer and Teflon without any modification. The effect of blending BCPs with homopolymer on the cylinder orientation overcomes the interplay between the film thickness \( t \) and the natural period, \( L_0 \), of the bulk microphase-separated structures [67-69] and the limitation of interfacial interaction between block copolymer and the substrate [19,20].

In Figure 4.2 (a) and (b), the image of SIS4114/PS4K, (b) is compared to that of SIS4114 (a). A relatively longer-range parallel cylinder orders were detected in
SIS4114/PS4K in comparison to the microdomain orientation in neat SIS4114 sample. Since the more straightly aligned parallel cylinders in SIS4114/PS4K originate from the decrease of interfacial area between the block domains after the blending PS4K, we expect that the blended PS homopolymer with low molecular weights will reduce the segregation force between the block components. The 2D fast Fourier transforms (FFT’s) included as insets in Figure 4.2 clearly demonstrate that the order of parallel cylinders in the $x,y$-plane is enhanced by the addition of PS4K.

On the same unmodified Si and Teflon substrates, however, perpendicular cylinders are spontaneously produced in SIS4114/PS12k (the molecular weight ratio of the PS homopolymer to its corresponding PS block in neat SIS4114, $\alpha = 1.05$), SIS4114/PS17K ($\alpha = 1.49$) and SIS4114/PS27K ($\alpha = 2.37$) throughout the whole sample area without any external field application (Figure 4.1 (c), (d), (e), Figure 4.2 (c), (d), and (e)). In addition, it can also be confirmed from the comparison of the 2D FFT’s of images in Figure 4.1 (c), (d), (e), Figure 4.2 (c), (d), and (e) that the hexagonal ordering of perpendicular cylinders is enhanced with the increase of blended PS homopolymer molecular weight. Such overall perpendicular cylinder orientation disappears and macro-phase separation occurs when the molecular weight of blended homopolymer is increased further.
Figure 4.1. AFM images of neat SIS4114 and its mixtures with PS homopolymer annealed at 130 °C on the Si substrate: (a) neat SIS4114, (b) SIS4114/PS4K, (c) SIS4114/PS12K, (d) SIS4114/PS17K, and (e) SIS4114/PS27K. Sample images were obtained from ~100 nm thick samples, and the topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is $2 \times 2 \, \mu\text{m}^2$. 

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Figure 4.2. AFM images of neat SIS4114 and its mixtures with PS homopolymer annealed at 130 °C on the Teflon substrate: (a) neat SIS4114, (b) SIS4114/PS4K, (c) SIS4114/PS12K, (d) SIS4114/PS17K, and e) SIS4114/PS27K. Sample images were obtained from ~10 μm thick samples, and the topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is $2 \times 2 \mu m^2$. 
4.4. Microdomain Structures of SIS4114 Triblock Copolymer with the Addition of PS Homopolymer

It is well-known that BCPs have multiple interparticles scattering peaks, Bragg reflection peaks, due to its ordered structure. [27] Based on the information of multiple peaks, the microdomain structures can be determined. The Bragg peaks exhibit different arrays depending on the shape of the microdomain structure, e.g., relative positions of each peak \( (q/q_{\text{max}}) = 1, 2, 3, 4, \ldots \) for Lamellae (LAM), \( 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \sqrt{9}, \ldots \) for hexagonal array (HEX), \( 1, \sqrt{2}, \sqrt{3}, \sqrt{4}, \sqrt{5}, \ldots \) for spheres in body centered-cubic arrays (BCC), and others. \( q = (4\pi / \lambda)\sin(\theta / 2) \), where \( \lambda \) is the wavelength of the X-ray, \( \theta \) is the scattering angle, \( q \) is scattering wave number, and \( q_{\text{max}} \) is on the position of the first-order peak.

To confirm the microdomain morphologies and structure of SIS4114/PS blends, we carried out SAXS for the same samples used in the AFM studies and shown in Figure 4.2. All the measurements were taken for the samples quenched to room temperature after annealing at 130 °C for 48 hr in a vacuum oven. Figure 4.3 reveals the ordered structures and orientation as obtained in SAXS patterns for SIS4114 and its blends with different molecular weights of PS homopolymer. The results for SIS4114/PS blends are presented in a vertically shifted plot of scattered intensity as a function of scattering wave number \( q \). Irradiating normal to the plane of the samples (SIS4114/PS12K, SIS4114/PS17K, SIS4114/PS21K, and SIS4114/PS27K) result in weak scattering and no evidence of an ordered morphology. The SAXS profiles of these samples are obtained by irradiating in the planar direction of the same samples by constructing samples with multiple layers.
(about 20) of transverse slices from the film samples. A fixed concentration (10 wt %) of PS homopolymers with different molecular weight in SIS4114 blends does not change the hexagonal packing of PS microdomains. Five peaks exist as hexagonally arrayed cylinders ($q/q_{\text{max}} = 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \text{ and } \sqrt{9}$, Figure 4.3).

AFM investigations for SIS4114/PS blends revealed a transition of cylinder orientation on increasing the molecular weight of PS in the blends. The perpendicular cylinders for the blends determined in Figure 4.1 and Figure 4.2, however, could equally be interpreted as the end of spheres at the interface between air and BCP blends, since the AFM investigation can show only the surface of the films. The strong evidence from the SAXS measurements, however, reveals that hexagonally packed cylinders and their transition from parallel to perpendicular orientation are not spheres or the end of spheres.
Figure 4.3. SAXS profiles of SIS4114 and SIS4114/PS blends as a function of molecular weight of PS homopolymer. The SAXS profiles were shifted vertically to avoid overlapping.
Based on the SAXS results, we calculated structure parameters for each microdomain of SIS4114 and SIS4114/PS blends annealed at 130 °C. The calculated results are summarized in Table 6.

The radius of hexagonally packed cylinders of PS can be determined by the following equation [186],

$$ r_{PS} = d \left( \frac{2}{\sqrt{3} \pi} \Phi_{PS} \right)^{\frac{1}{2}} $$  \hspace{1cm} (4.1)

where we assume perfect packing and complete solubilization of PS homopolymer into the PS microdomain of block copolymer, and the domain periodicity ($d$) can be calculated as $d = \frac{2\pi}{q_{\text{max}}}$. Therefore, on the basis of geometrical considerations, the distance between the outer surfaces of nearest PS microdomains, $L_{\text{major}}$, is calculated as [187]

$$ L_{\text{major-component}} = \frac{2}{\sqrt{3}} d - 2r_{PS} $$  \hspace{1cm} (4.2)

$L_{\text{major-component}}$ is closely related to PI chain stretching, since a large portion of our triblock copolymers can form bridge structures through this distance, connecting the PS microdomains.
Table 6. Structure parameters for microdomains of SIS4114 and SIS4114/PS blends obtained from SAXS measurement

<table>
<thead>
<tr>
<th>Sample (90/10 w/w)</th>
<th>PS domain structure</th>
<th>$\Phi_{PS}$</th>
<th>$q_{max}$ (nm$^{-1}$)</th>
<th>$d$ (nm)</th>
<th>$r_{PS}$ (nm)</th>
<th>$L_{PI}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS4114</td>
<td>CYL.</td>
<td>0.129</td>
<td>0.211</td>
<td>29.75</td>
<td>6.48</td>
<td>21.39</td>
</tr>
<tr>
<td>SIS4114/PS4K</td>
<td>CYL.</td>
<td>0.131</td>
<td>0.200</td>
<td>31.40</td>
<td>6.90</td>
<td>22.46</td>
</tr>
<tr>
<td>SIS4114/PS12K</td>
<td>CYL.</td>
<td>0.136</td>
<td>0.150</td>
<td>41.87</td>
<td>9.35</td>
<td>29.64</td>
</tr>
<tr>
<td>SIS4114/PS17K</td>
<td>CYL.</td>
<td>0.138</td>
<td>0.140</td>
<td>44.86</td>
<td>10.12</td>
<td>31.56</td>
</tr>
<tr>
<td>SIS4114/PS21K</td>
<td>CYL.</td>
<td>0.140</td>
<td>0.129</td>
<td>48.83</td>
<td>11.10</td>
<td>34.19</td>
</tr>
<tr>
<td>SIS4114/PS27K</td>
<td>CYL.</td>
<td>0.144</td>
<td>0.121</td>
<td>51.85</td>
<td>11.92</td>
<td>36.04</td>
</tr>
</tbody>
</table>
4.5. Segmental Distributions of Added Homopolymer into the Nanocylinders of Block Copolymer/Homopolymer Blends

The above study investigated the orientation and its structure of SIS4111/PS mixtures and discussed the effects of the added PS homopolymer molecular weight on the microdomain orientation based on SAXS and AFM measurements. Tanaka and coworkers [27,188,189] investigated and discussed the dependence of the molecular weight of added homopolymer on the segmental distribution within the PS microdomains of the SI diblock copolymer using SAXS and TEM methods. Mayes and coworkers [26] also investigated the segmental distribution of added PS homopolymer or poly(methylmethacrylate) (PMMA) homopolymer within PS-block-PMMA copolymer in spin-coated thin films using scattering methods. Their investigation found that (1) when the molecular weight of added PMMA was comparable to that of the corresponding copolymer block, it was not distributed uniformly within the PMMA microdomains, localizing at the center of the microdomains, and (2) as the molecular weight of added PMMA was decreased, it was distributed more uniformly within the PMMA microdomains of the PS-block-PMMA copolymer. Such experimental observations were found to be in agreement with theoretical prediction [190] and consistent with results reported for bulk film specimens [27,188,191].

Based on these above investigations of other research groups and the resulted structure parameters determined in this study, Figure 4.4 illustrates a diagram of the domain distribution of the added PS homopolymer into the blocks of SIS4114. Figure 4.4 (a) is a diagram of a homogeneously blended sample. The chains of SIS block (ABA) and
PS homopolymer ($A_h$) are homogeneously mixed well in the mixtures. Figure 4.4 (b) shows a microphase separated domains with a homogeneous distribution of PS homopolymer into PS block. Figure 4.4 (c) illustrate a microphase separated domains with an inhomogeneous distribution of PS homopolymer into the center of PS block. Macrophase separated microdomains between the block copolymer and the PS homopolymer are illustrated in Figure 4.4 (d). When macrophase separation occurs in the mixture, the chains of PS homopolymer separate from the chains of the A-block-B-block-A copolymer and form macroscopic domains of PS homopolymer. When the added PS homopolymer is solubilized into the microdomains of the block copolymer and the molecular weight of homopolymer is relatively low, the chains of PS homopolymer are mixed on the molecular level with the chains of PS block (as illustrated by (b) in Figure 4.4). When the added PS homopolymer is solubilized into the microdomains of the block copolymer and the molecular weight of homopolymer is relatively high, the chains of PS homopolymer are not uniformly mixed with the chains of PS block and localize at the center of the microdomains (i.e., localized solubilization, as illustrated by (c) in Figure 4.4).

When the chains of PS homopolymer are uniformly mixed together with the PS microdomains and the PS microdomains swell (Figure 4.4 (b)), the average distance between the neighboring chemical junctions of the block copolymer increases and the interfacial area between the block domains is decreased. Thus, the straightness of parallel cylinders is increased in SIS4114/PS4K ($\alpha = 0.35$) (Figure 4.2 (b)), in comparison of that of parallel domains in SIS4114 (Figure 4.2 (a)). The domain periodicity and diameter also increase slightly due to the same reason as summarized in Table 6.
When the molecular weight of PS homopolymer is increased more as in SIS4114/PS12K ($\alpha = 1.05$) and its chains tend to localize at the center of the microdomains, the size of PS block domain and its periodicity increase suddenly as shown in Figure 4.4 (c). This is confirmed with the results of SAX measurements summarized in Figure 4.3 and Table 6. Domain periodicity and diameter also increase slightly as the molecular weight of the added PS homopolymer (PS17K ($\alpha = 1.49$), PS21K ($\alpha = 1.84$), PS27K ($\alpha = 2.37$)) is increased. When the molecular weight of PS homopolymer increases, the contribution of combinatorial entropy to the free energy decreases, because the combinatorial entropy is related to the inverse of degree of polymerization (N) of the homopolymer [188]. Thus, the chains of the added PS homopolymer are not homogeneously solubilized and tend to be localized at the center of the microdomains of the PS block or forms separate macroscopic domains. When the chains of the added PS homopolymer have a molecular weight of 40K ($\alpha = 3.51$) and 43K ($\alpha = 3.77$), the macrophase separations occurs as illustrated in Figure 4.4 (d).
Figure 4.4. Schematic illustration of the domain distribution of the added PS homopolymer ($A_H$) into SIS4114. (a) homogeneously blended sample, (b) microphase separated sample with a homogeneous distribution of $A_H$ into PS block (A) in SIS4114, ($\alpha \leq 0.35$) (c) microphase separated sample with a localization of $A_H$ into the center of A, ($1.05 \leq \alpha \leq 2.37$) (d) macrophase separated sample between A-B-A (PS-b-PI-b-PS) and $A_H$, ($\alpha \geq 3.51$)
4.6. Temperature-Dependent Microdomain Behaviors of Block Copolymer and its Mixture with Homopolymer

Figure 4.5 shows the microdomain structure and its behavior of SIS4114/PS4K blend as a function of different annealing temperatures. This AFM observation reveals that temperature-dependent microdomains and their orientation behaviors for parallel cylinder-forming SIS4114/PS4K blends are more uniform and straight than those of neat SIS4114 because SIS4114/PS4K does not experience the OOT from cylinder to sphere, which would be observed at higher annealing temperatures for SIS4114. This is because the volume fractions of PS block component become higher than the critical volume fraction for the cylinder microphase over the experimental temperature ranges. We note that the OOT temperature of neat SIS, determined by rheological and small angle X-ray measurements, was ~185 °C [192]. In case of SIS4113/PS2K, the absence of OOT from cylinder to sphere, was confirmed by rheological SAXS experiments [192]. As shown in the AFM images of Figure 4.5 (a), (b), and (c), in the temperature range from 130 °C to 190 °C, the straightness of parallel cylinders in SIS4114/PS4K is enhanced with increasing annealing temperature due to the temperature-proportional preference for reducing the interfacial area between the block domains. It is also notable that the ordering of parallel cylinders in SIS4114/PS4K (Figure 4.2 (b)) is more enhanced than those in neat SIS at 130 °C, owing to the relatively lower molecular weight of blended PS homopolymer than that of PS block in the neat SIS4114 (Figure 4.2 (a)), which enhances the mixing entropy to reduce the interfacial area between the block components. After the parallel cylinder straightening process, the parallel cylinders in SIS4114/PS4K abruptly
disappeared without any notable OOT and composition fluctuations, and homogeneous melt state is observed above 200 °C (Figure 4.5 (d)).

The perpendicular microdomain orientation of SIS4114/PS12K at different annealing temperatures is investigated by the AFM results shown in Figure 4.6. A gradual transition from perpendicular to parallel orientation is observed as the annealing temperature is increased at the range between 130 °C and 210 °C. The overall perpendicular cylinder orientation at 130 °C is mainly transferred to parallel cylinder orientation at 190 °C, via the orientation transition process starting from ~170 °C. After achieving mainly parallel cylinders, composition fluctuations of block components lasted until ~220 °C, and then homogeneous melt states are observed at 230 °C. The long-lived composition fluctuations detected in perpendicular cylinder-forming SIS4114/PS12K are not observed in the parallel cylinder-forming SIS4114/PS4K. Thus, we conclude that the stability of transient phases arising from the composition fluctuations at the temperatures above the ODT is largely dependent on the intrinsic segregation forces between the block domains.

The perpendicular microdomain orientation of SIS4114/PS17K with relatively strong segregation forces between the block domains is observed using the AFM as shown in Figure 4.7 for different annealing temperatures. More stable perpendicular microdomain orientations are observed at temperatures ranging from 130 °C to 170 °C, and then hexagonal lattice disordering of perpendicular cylinders is observed at the range of the annealing temperature between 190 °C and 210 °C compared to the case of SIS4114/PS12K. Thus, we conclude that the preference for perpendicular orientation in SIS4114/PS17K is stronger than that in SIS4114/PS12K. After the termination of
hexagonal lattice disordering process, composition fluctuation-driven phases last until ~220 °C, and homogeneous melt states are observed at ~230 °C.

SIS4114/PS27K also shows relatively strong microdomain segregation behavior between the block domains, as the annealing temperature is increased in the temperature range from 130 °C to 170 °C, as shown in Figure 4.8. After the disordering process between 190 °C and 210 °C, a composition fluctuation-driven phase is detected at ~220 °C, and a homogeneous melt state is then observed at ~230 °C.

Based on the AFM studies, we can categorize the following three different temperature-dependent phase behaviors for cylinder-forming miscible block copolymer mixtures: 1) In case of parallel cylinder-forming SIS4114/PS4K, parallel cylinder straightening/lengthening process is observed before homogeneous melting, and there are no long-range composition fluctuations before melting due to the inherently weak segregation forces between the block domains; 2) In case of perpendicular cylinder-forming SIS4114/PS12K, long-range orientation transition from perpendicular to parallel is observed before composition fluctuations. In comparison to the case of SIS4114/PS4K, SIS4114/PS12K displays longer-lived composition fluctuation before its homogeneous melting due to its relatively stronger segregation forces between the block domains; and 3) In case of perpendicular cylinder-forming SIS4114/PS17K and SIS4114/PS27K, long-range hexagonal lattice disordering is identified before composition fluctuation, and there are also long-lived composition fluctuations before melting due to the strong segregation forces between the block domains. Thus, we realize that SIS4114/PS17K and SIS4114/PS27K have stronger preferences for perpendicular orientation. We note that the parallel cylinder orientation of neat SIS4114 is spontaneously transferred to a
perpendicular one as the molecular weight ratio between the homologous PS pair (i.e., PS homopolymer to PS block) approaches to unity (SIS4114/PS12K, $\alpha = 1.05$), as long as the ratio is approximately up to 2.37. In addition, it is also notable that such orientation transition corresponds to the temperature-dependent phase behavior of SIS4114/PS12K, which would occur by lowering the annealing temperature. Therefore, we realize that thermodynamic driving forces involved in temperature-dependent phase behaviors are similar to those involved in homopolymer molecular weight-dependent phase transition.
Figure 4.5. AFM images of SIS4114/PS4K blend at different temperatures: (a) SIS/PS4K 130, (b) SIS/PS4K 170, (c) SIS/PS4K 190, and (d) SIS/PS4K 210. Images were obtained from ~10 µm-thick samples annealed on Teflon substrates at 130 °C, 170 °C, 190 °C, and 210 °C, respectively. Topographic and phase AFM images were the same. The size of the image is $2 \times 2 \ \mu m^2$. 
Figure 4.6. AFM images of SIS4114/PS12K blend at different temperatures: (a) SIS/PS12K 130, (b) SIS/PS12K 150, (c) SIS/PS12K 170, (d) SIS/PS4K 190 and (e) SIS/PS4K 230. Images were obtained from ~10 µm-thick samples annealed on Teflon substrates at 130 °C, 150 °C, 170 °C, 190 °C, and 230 °C, respectively. Topographic and phase AFM images were the same. The size of the image is $2 \times 2 \, \mu \text{m}^2$. 

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Figure 4.7. AFM images of SIS4114/PS17K blend at different temperatures: (a) SIS/PS17K 130, (b) SIS/PS17K 170, (c) SIS/PS17K 190, and (d) SIS/PS17K 210. Images were obtained from ~10 µm-thick samples annealed on Teflon substrates at 130 °C, 170 °C, 190 °C, and 210 °C, respectively. Topographic and phase AFM images were the same. The size of the image is $2 \times 2 \mu \text{m}^2$. 
Figure 4.8. AFM images of SIS4114/PS27K blend at different temperatures: (a) SIS/PS27K 130, (b) SIS/PS27K 170, (c) SIS/PS27K 190, and (d) SIS/PS27K 210. Images were obtained from ~10 μm-thick samples annealed on Teflon substrates at 130 °C, 170 °C, 190 °C, and 210 °C, respectively. Topographic and phase AFM images were the same. The size of the image is 2 × 2 μm².
4.7. Theoretical Consideration of Transition to Perpendicular Orientation: Increased Incompatibility by Homopolymer Addition

If we assume that the contributions of homologous PS pair (i.e., PS block and PS homopolymer) to the domain-domain incompatibility routinely depend on their average molecular weight and their individual compositional fraction, we can estimate the $\chi N$ values (where $\chi$ is the Flory-Huggins segmental interaction parameter and $N$ is the degree of polymerization) of block copolymers by using the following equations: [193-195]

\[
\chi = -0.0419 + \frac{38.54}{T} \quad (4.3)
\]

\[
N = \frac{1}{v_{\text{ref}}} \left( M_{w,PS} v_{PS} + M_{w,PI} v_{PI} \right) \quad (4.4)
\]

\[
v_{PS} = 0.9199 + 5.098 \times 10^{-4} (T - 273) + 2.354 \times 10^{-7} (T - 273)^2 \\
+ (32.46 + 0.1017 (T - 273)) / M_{w,PS}
\]

\[
v_{PI} = 1.0771 + 7.22 \times 10^{-4} (T - 273) + 2.46 \times 10^{-7} (T - 273)^2
\]

\[
v_{\text{ref}} = \left( M_{S} v_{PS} M_{I} v_{PI} \right)^{0.5}
\]

Here, $v_{\text{ref}}$ is the molar volume of a reference component, $v_{PS}$ and $v_{PI}$ are the specific volumes of PS and PI, respectively, and $M_{S}$ and $M_{I}$ are the molecular weights of the styrene and isoprene monomers, respectively. At the annealing temperature of 130 °C, the calculated $\chi N$ values are 62.99, 56.80, 57.04, 57.13, and 57.49 for neat SIS4114,
SIS4114/PS4K, SIS4114/PS12K, SIS4114/PS17K, and SIS4114/PS27K, respectively. Such mutually similar $\chi_N$ values, however, neither provide a critical explanation on the homopolymer-driven cylinder orientation transition transition phenomenon nor reasonably explain the different temperature-dependent phase behaviors of perpendicular cylinder-forming block copolymers. Note that the perpendicular cylinder orientation is not obtained when the molecular weight of blended homopolymer (i.e., the incompatibility between the block domains) is routinely increased; rather it is achieved when the molecular weight ratio between the homologous PS pair approaches to unity, as long as the ratio is approximately larger than 1.05. Furthermore, the exceptionally strong preference for perpendicular orientation in SIS4114/PS17K cannot be described by its $\chi_N$ value nearly identical to that of SIS4114/PS4K and SIS4114/PS12K. Therefore, we provide an alternative thermodynamic consideration for the block copolymer orientation transition phenomena at a fixed composition.

If we consider a parallel-to-perpendicular cylinder orientation transition at a fixed total sample volume and volume fraction of minority block component (Figure 4.9), i.e.,

$$r_0^2 \pi LN_0 = r^2 \pi tN$$

$$\frac{N}{N_0} = \frac{L}{t} \left( \frac{r_0}{r} \right)^2$$

$$\begin{cases} N_0 = 4nm \\ N = \frac{8n^2}{\sqrt{3}} \left( \frac{r_0}{r} \right)^2 \end{cases}$$

$$\frac{A}{A_0} = \frac{2\pi rtN}{2\pi r_0 LN_0} = \frac{r_0}{r},$$

the ratio between perpendicular and parallel domain-domain excess free energies ($G/G_0$) is given by:
Here, $A/A_0$ is the ratio between perpendicular and parallel domain-domain interfacial areas and $\gamma$ is the interfacial energy between the block components, depending on the average molecular weights of block components and the annealing temperature, $T$. In addition, the ratio of interfacial area between the minority domain and the substrates (or supersubstrates) $(A_{\text{minor}}/A_{\text{minor},0})$ and its corresponding ratio of excess free energy $(G_{\text{minor}}/G_{\text{minor},0})$ are given by:

$$
\frac{G_{\text{minor}}}{G_{\text{minor},0}} \sim \frac{A_{\text{minor}}}{A_{\text{minor},0}} = \frac{2\pi r^2 N}{2r_0 2nd 4n} = \frac{\pi r_0}{d\sqrt{3}} = a
$$

The ratio of interfacial area between the majority domain and the substrates (or supersubstrates) $(A_{\text{major}}/A_{\text{major},0})$ and its corresponding ratio of excess free energy $(G_{\text{major}}/G_{\text{major},0})$ are also given by:

$$
\frac{G_{\text{major}}}{G_{\text{major},0}} = \frac{A_{\text{major}}}{A_{\text{major},0}} = \frac{2\left(4n^2d^2 - \frac{4n^2 2\pi r_0}{d\sqrt{3}} - r_0 d\right)}{2\left(4n^2d^2 - 8n^2r_0 d\right)} = \frac{d - 2ar_0}{d - 2r_0}
$$
For parallel cylinder orientation, the fractions of interfacial areas, \( f_0 \)'s are given by:

\[
\begin{align*}
  f_{\text{domain-domain},0} &= \frac{A_0}{A_{\text{total},0}} = \frac{2m\pi r_0}{d + 2m\pi r_0} \\
  f_{\text{domain-minor},0} &= \frac{A_0}{A_{\text{total},0}} = \frac{2m\pi r_0}{d + 2m\pi r_0} \\
  f_{\text{major-substrate},0} &= \frac{A_{\text{major},0}}{A_{\text{total},0}} = \frac{d - 2r_0}{d + 2m\pi r_0} \\
  f_{\text{minor-substrate},0} &= \frac{A_{\text{minor},0}}{A_{\text{total},0}} = \frac{2r_0}{d + 2m\pi r_0}
\end{align*}
\]  

Here, \( A_{\text{total},0} \) is the total interfacial area of parallel cylinder-forming sample (i.e., \( A_{\text{total},0} = A_0 + A_{\text{major},0} + A_{\text{minor},0} \)). In addition, for perpendicular cylinder orientation, the fractions of interfacial areas, \( f \)'s are given by:

\[
\begin{align*}
  f_{\text{domain-domain}} &= \frac{A}{A_{\text{total}}} = \frac{2m\pi r_0 \left( \frac{r_0}{r} \right)}{d + 2m\pi r_0 \left( \frac{r_0}{r} \right)} \\
  f_{\text{major-substrate}} &= \frac{A}{A_{\text{total}}} = \frac{d - 2ar_0}{d + 2m\pi r_0 \left( \frac{r_0}{r} \right)} \\
  f_{\text{minor-substrate}} &= \frac{A}{A_{\text{total}}} = \frac{2ar_0}{d + 2m\pi r_0 \left( \frac{r_0}{r} \right)}
\end{align*}
\]  

Here, \( A_{\text{total}} \) is the total interfacial area of perpendicular cylinder-forming sample.

The relative interfacial area changes after the orientation conversion process from parallel to perpendicular can be determined by using experimentally determined cylinder dimensions based on the microdomain parameters from the SAXS profiles in Table 6 and...
the above equations. Here, it is noted that we do not consider any types of thermodynamic driving forces involved in the cylinder orientation transition in order to estimate the above equations since we use the experimentally (i.e., thermodynamically and kinetically) obtained microdomain dimensions to calculate the changes of the interfacial areas and the excess free energies owing to the geometric transition from parallel to perpendicular.

As shown in the changes of microdomain parameter in Table 6, the domain periodicity and the radius of PS domain slightly increase when PS4K is blended in SIS4114. With PS12K addition, however, sudden increases are observed in the domain periodicity and radius (Table 6), which enable the transition from the parallel orientation (SIS4114/PS4K, the molecular weight ratio of PS homopolymer to PS block in SIS4114, $\alpha = 0.35$) into the perpendicular orientation (SIS4114/PS12K, $\alpha = 1.05$). Addition of PS homopolymer with molecular weights higher than 12 kg/mol slightly increases the PS domain periodicity and radii and holds the perpendicular orientation in the SIS4114/PS blends. Above the 27 kg/mol molecular weight range, the samples show macro-phase separations.

During the calculations of these equations using the domain parameters from SAXS measurements, we designate the dimensional parameters of SIS4114/PS4K as reference dimensional values for parallel cylinders in order to compare the interfacial areas and energies of perpendicular cylinders to those of parallel cylinders, because the PS block composition of SIS4114/PS4K is similar to those of SIS4114/PS12K, SIS4114/PS17K and SIS4114/PS27K. Therefore, the calculation fixes the reference ratio between perpendicular and parallel domain-domain excess free energies at 1, since there is no
parallel to perpendicular transition free energy in the parallel microdomain orientation of SIS4114/PS4K. The calculated values in the third column of Table 7 ($A/A_0$) show the changes of the ratio between perpendicular and parallel domain-domain excess free energies as a function of different molecular weights of PS homopolymer added in SIS4114/PS blends having a perpendicular microdomain structure. We note that these ($A/A_0$) values decrease when the homopolymer PS12K and others with higher molecular weights are blended into SIS4114 and the parallel structure transfers into perpendicular orientation. We also note that the decrease in ($A/A_0$) is rather large for PS12K addition and further increases of molecular weight of added PS homopolymer result in smaller decreases in the ratio of excess free energy and result in the desirable perpendicular microdomain structure. Therefore, based on the microdomain parameters obtained by SAXS measurements, and the above equations, the addition of PS12K ($\alpha = 1.05$) into SIS4114 decreases the perpendicular domain-domain excess free energy abruptly in comparison to the reference value in SIS4114/PS4K ($\alpha = 0.35$), thus resulting in the parallel to perpendicular transition.

The fourth column of Table 7 shows the changes in the ratio of the majority component-substrate interfacial areas between the perpendicular and the parallel microdomain structures, $A_{\text{major}}/A_{\text{major,0}}$, and its corresponding ratio of excess free energy. This value increases abruptly when the PS12K is blended into SIS4114, since all perpendicular minority microdomains orient normal to the substrates and the many portions of minority-substrate interfacial areas are replaced by those of majority-substrate. After the parallel to perpendicular microdomain transition, the corresponding ratio of excess free energy decreases as the higher molecular weight of PS homopolymer is added.
into SIS4114, which results in stronger preference for the perpendicular microdomain structures. As shown in the fifth column of Table 7, the calculated results show the changes in the ratio of the minority component-substrate interfacial areas between the perpendicular and the parallel microdomain structures, $A_{\text{minor}}/A_{\text{minor,0}}$, and the corresponding ratio of excess free energy. The value decreases abruptly when the PS12K is blended into SIS4114, since the perpendicular minority microdomain starts orienting in the direction normal to the substrates. Stronger preferences for the perpendicular microdomain structures are expected as higher molecular weights of PS homopolymer are added into SIS4114 and the corresponding ratios of excess free energy decrease. In addition, we geometrically realize that the change of interfacial area between the block domains is the most critical factor for the cylinder orientation transition due to its largest fraction (see the sixth, seventh, and eighth columns of Table 7). Considering the calculated results together with our experimental results, therefore, we conclude that perpendicular orientation-inducing thermodynamic conditions such as the blending of minority homopolymer with appropriate molecular weight ($1.05 \leq \alpha \leq 2.37$) and the lowering of annealing temperature should involve sufficient lowering of excess free energy in the block domains to obtain parallel to perpendicular microdomain transitions. Thus, such unusual cylinder orientation transition occurs spontaneously in the block copolymer mixtures used in this study, when the molecular weight ratios and the annealing temperature conditions are right. We note that our proposed intermolecular interaction is different from the well-known secondary forces such as electrostatic, hydrogen bonding and van der Waals interactions. There would not be significant charge-charge, charge-dipole and hydrogen bonding interactions between the homologous PS
pair due to the absence of charges and hydrogen bonding-generating functional groups in the PS components. In addition, the dipole-dipole and van der Waals interactions of PS pair that generally increase with increasing the molecular weight of polymer components might not be a candidate for the thermodynamic compensation since the amount of compensation depends on the molecular weight ratio between the polymer pair, rather than their absolute molecular weight.

The results with SIS4114/PS4K show that the interaction energy between the homologous PS pair is low due to the low molecular weight of PS homopolymer, ($\alpha = 0.35$) and hence the initial parallel cylinders in neat SIS4114 are straightened after the blending of PS4K (or after the increase of annealing temperature) simply owing to the decreased incompatibility between the block components. The interaction force (i.e., significant amount of heat of mixing) between the homologous PS pair, however, will be generated in SIS4114/PS12K ($\alpha = 1.05$) owing to the high enough molecular weight similar to the molecular weights of PS block in SIS4114. Since the homologous pair interaction induces an additional enhancement of incompatibility between the PS and PI components by virtue of strong segregation between the homologous PS pair, the actual incompatibility of SIS4114/PS12K will be much higher than the incompatibility predicted by the Flory-Huggins theory.

The calculated results in this part can also be used to investigate the effects of the variation of annealing temperature on the ordering of BCPs/homopolymer mixtures and the results determined here can be compared to those of the study at different annealing temperatures as described Section 4.6. The morphologies of orientation are studied by changing the annealing conditions at a fixed homopolymer molecular weight and volume.
fraction, which result in well-ordered and persistent structures. We note that the degree of incompatibility (i.e. the preference for perpendicular cylinder orientation) will gradually decrease as the temperature increases. Thus, the perpendicular cylinders in SIS4114/PS12K ($\alpha = 1.05$) mixture achieved at relatively lower temperature can be transferred to parallel ones at higher temperature if the incompatibilities between the blocks and their preference for perpendicular orientation are not strong enough to overcome the entropic effects arising from the increase of annealing temperature. In case of perpendicular cylinder-forming SIS4114/PS17K ($\alpha = 1.50$) and SIS4114/PS27K ($\alpha = 2.37$), the interaction energies between the homologous PS pair will increase significantly due to the increased molecular weights of the corresponding PS homopolymers, and hence the cylinders display exceptionally strong preference for perpendicular orientation even at high annealing temperatures (i.e., even at an extremely unfavorable condition for a perpendicular cylinder orientation). In case of the parallel cylinders in SIS4114/PS4K ($\alpha = 0.35$) formed at relatively lower temperature, the straightness of their arrays is expected to be enhanced with the increase of temperature due to the decrease of incompatibility.
Figure 4.9. Simple model for the cylinder orientation conversion from parallel to perpendicular: $d$ is the center-to-center spacing between the cylinders, $t$ is the sample thickness, $m$ and $n$ are the multiplying factors ($n \geq m$), $W$ is the sample width, $L$ is the sample length, $r_0$ is the radius of initial parallel cylinders, $r$ is the radius of perpendicular cylinders, $N_0$ is the number of initial parallel cylinders, and $N$ is the number of perpendicular cylinders.
Table 7. Changes of domain-domain interfacial area and excess free energy after the parallel-to-perpendicular cylinder orientation transition in SIS414/PS blends

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Sample</th>
<th>$A/A_0$</th>
<th>$A_{major}/A_{major,0}$</th>
<th>$A_{minor}/A_{minor,0}$</th>
<th>$f_{domain}$</th>
<th>$f_{majority}$</th>
<th>$f_{minority}$</th>
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<td>m = 1</td>
<td>SIS414/PS12K</td>
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<td>1.345</td>
<td>0.299</td>
<td>0.433</td>
<td>0.511</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.580*)</td>
<td>(0.347*)</td>
<td>(0.074*)</td>
</tr>
<tr>
<td></td>
<td>SIS414/PS17K</td>
<td>0.682</td>
<td>1.320</td>
<td>0.279</td>
<td>0.397</td>
<td>0.551</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>SIS414/PS27K</td>
<td>0.579</td>
<td>1.275</td>
<td>0.241</td>
<td>0.326</td>
<td>0.631</td>
<td>0.043</td>
</tr>
<tr>
<td>m = 5</td>
<td>SIS414/PS12K</td>
<td>0.738</td>
<td>1.345</td>
<td>0.299</td>
<td>0.792</td>
<td>0.187</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.873*)</td>
<td>(0.104*)</td>
<td>(0.022*)</td>
</tr>
<tr>
<td></td>
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<td>0.241</td>
<td>0.707</td>
<td>0.274</td>
<td>0.019</td>
</tr>
</tbody>
</table>

*the corresponding fraction of interfacial area for SIS414/PS4K
4.8. Concluding Remarks

In this study, we developed and investigated a spontaneous and simple method for the orientation of perpendicular cylinders with a triblock copolymer (SIS4114) possessing an initial orientation preference for parallel structures on a preferential substrate, by increasing the interaction force between the homologous polymer pair at a fixed composition of minority block component. This is achieved without any external field application or modification of interfacial energy between the sample and the substrate. When the chains of PS homopolymer are uniformly distributed together with the PS microdomains and the PS microdomains swell, the average distance between the neighboring chemical junctions of the block copolymer stretches and the interfacial area between the block domains is decreased. Thus, the domain periodicity slightly increases and the straightness of parallel cylinders is increased in SIS4114/PS4K ($\alpha = 0.35$). The additional increases of molecular weight of PS homopolymers ($1.05 \leq \alpha \leq 2.37$) could enable the ratio of the excess free energy to decrease and result in the perpendicular microdomain orientation. The microphase separated samples with a localization of the chains of these homopolymers into the center of the PS block results in abrupt increases in the domain periodicity and radius, which enables the transition from the parallel to perpendicular orientation. Further increases of molecular weight of PS homopolymers result in macrophase separations. The perpendicular-to-parallel cylinder orientation transition occurs at higher annealing temperatures if the incompatibilities between the blocks and their preference for perpendicular orientation are not strong enough to overcome the entropic effects arising from the increase of annealing temperature. In case
of perpendicular cylinder-forming mixtures \(1.50 \leq \alpha \leq 2.37\), the interaction energies between the homologous PS pair increase significantly due to the highly increased molecular weights of corresponding PS homopolymer, and hence its cylinders display an exceptionally strong preference for perpendicular orientation even under unfavorable conditions for perpendicular cylinder orientation. From the viewpoint of nano-science and nano-technology of block copolymers, this spontaneous and simple method should provide an effective pathway and play a crucial role in optimization of the ordering process for self-assembly of block copolymers.
CHAPTER V
SELF-ASSEMBLED MICRODOMAIN AND ORIENTATION
BEHAVIOR OF BLOCK COPOLYMER/HOMOPOLYMER
BLENDs: PS-PI-PS TRIBOCK COPOLYMER, VECTOR 4111

5.1. Introduction

Block copolymers (BCPs) are composed of chemically different chains. Depending on the number of different blocks, their composition, and the way they are linked together (linear, branched, star-like or cyclic), they can form a variety of ordered structures with characteristic lengths on the mesoscale. For example, an AB or ABA symmetric block copolymer has a mesophase structure of lamellae. For the asymmetric block copolymer (AB or ABA), there are two different types, which are cylinder and sphere microdomains if the amount of a minority microdomain has a range 20~40 % and lower than 15 %, respectively. [15] This self-organization into ordered structures (also called morphologies) has attracted considerable interest among theoreticians and experimentalists during the last few decades, as indicated by an increasing number of publications in this field.

Recently, we explored that the addition of PS homopolymer into SIS block copolymer also changes the direction of orientation in the cylindrical microdomains as described in previous chapter. The key parameters controlling the microdomain
morphology and the orientation transition in blends of block copolymers with two different blocks (A and B) and a homopolymer A (HA) are $\alpha_A(M.W._{HA}/M.W.A_{in\, BCP})$. Three extremes of the possible mixing states after phase separation are possible: (1) the range of low molecular weight of homopolymer when $\alpha_A < 1$; (2) the range of high molecular weight of homopolymer when $\alpha_A \geq 1$; and (3) macrophase separation region when $\alpha_A$ is too high. These three regions have different features and orientation behavior.

In the regime (1) low molecular weight homopolymer tends to be homogeneously solubilized into the corresponding block copolymer microdomain, swelling the block chains, and keep the initial microdomain orientation. In the second regime (2), the addition of homopolymer induces the sudden increases in the domain periodicity and radius, which enables the transition from the parallel orientation into the perpendicular orientation. As a result, the excess free energy between the block domains and that between the majority block and the substrate is decreased after the parallel-to-perpendicular orientation transition. The addition of higher molecular weight of homopolymer tends to show the macro-phase separation in the regime (3).

We’ve investigated and illustrated that the system with a SIS4114 triblock copolymer (Chapter 4) is successfully employed to induce vertically oriented cylindrical microdomain by blending BCPs with a homopolymer (same structure with a minor component in triblock copolymer.) In this chapter, we report on a system untested in the previous results, SIS4111((Vector 4111, DEXCO Polymers), having a molecular weight of 141.6 kg/mol with a PS block of 25.6 kg/mol and a PI block of 116 kg/mol, which has more stable range for the orientation of the cylindrical microdomain. The SIS4111 triblock copolymer used in this study is chosen as a material which has the same...
chemical structure, but a different composition of PS block and different information of molecular weight with those of SIS4114 in the previous mixtures (Chapter 4) to investigate the method of self-assembly systematically. The molecular weight of homopolymer (PS) is varied in the range between 4 kg/mol and 46 kg/mol. The bulk microdomain of SIS4111 orientation is that of hexagonally oriented parallel cylinder PS domains. Therefore, here we show that a simple and fast method can be employed to orient the cylinders in perpendicular direction and overcome two major driving forces that determine the bulk state orientation of block copolymers: the surface/interface energies, as well as the interplay between the film thickness $t$ and the natural period, $L_0$, of the bulk microphase-separated structures [67-69]. In this case of BCP/homopolymer blend, only thermodynamic modification is applied. Study of new orientation methods and their effects will offer more effective pathways of the ordering process into self-assembly of block copolymer.

5.2. Experimental Methods

This chapter employed a commercially available polystyrene-polysoprene-polystyrene (SIS) block copolymer Vector 4111 (Dexco Polymers Co.). Vector 4111 contains 18 wt % (16 vol %) PS and has a weight-average molecular weight ($M_w$) of 141600 g/mol and a polydispersity ($M_w/M_n$) of 1.1. Various molecular weights of polystyrene (PS) were used in the mixtures of SIS4111/PS. All the polymers and chemicals were used without further purification. All information about the polymers used in this study is summarized in Table 2.
PS homopolymers having different molecular weights were blended with SIS4111. The solution samples were prepared into toluene as a solvent. A fixed composition of 10 wt % of PS homopolymers and 90 wt % of BCPs was prepared and the mixtures were dissolved in toluene (2 wt % in solution) with 0.05 wt % of antioxidant (Irganox 1010, Ciba-Geigy Group). All Information on mixtures such as the molecular weight ratio of PS homopolymer to PS block in the SIS4111 (α), the weight fraction of PS phase (W_{PS}), and the volume fraction of PS phase (\Phi_{PS}) in SIS4111 and SIS4111/PS mixtures are summarized in Table 8. Thin films of BCPs/homopolymer mixture were prepared by spin-coating on the 3 in. diameter Si substrate at 2000 rpm. The solution was filtering during spin-coating on the Si substrate. 90 to 110 nm thickness of the samples on Si substrate was measured with a Gaertner model L116C ellipsometer using a He-Ne laser (wavelength = 632.8 nm) and a fixed angle of incidence of 70°. Relatively thicker film samples between 500 nm and a few tens of micrometers were also fabricated by solution casting onto selected substrates. Many amount of the solvent in BCPs/homopolymer solutions was slowly evaporated at ambient condition for 2 days and then in a vacuum oven at 50 °C for a day. Finally, all the samples were annealed in a vacuum oven at different annealing temperatures well above the glass transition temperatures (Tg’s) of PS block and PS homopolymers, and small amount of the residual solvent in the mixtures was also removed at this time.

The SIS4111/PS samples for SAXS measurement were prepared by coating on the Teflon substrate and the BCPs/PS samples were annealed at 130 °C. The SAXS measurement used the Rigaku MicroMax-002+ X-ray generator which has the microfocus source produced by coupling a high performance Osmic Confocal Max-Flux™.
(CMF) optic with a sealed tube microfocus X-ray source. The SAXS profiles were recorded on the 2-dimensional detector (Rigaku Innovative Technologies), which used a CMF optic to condition the beam through a series of 3 collimating pinholes. A source had a spot size of 20 µm. SAXS measurement was performed with the X-ray radiation wavelength of 1.5405Å at ambient temperature.

The surface morphologies of the samples coated on different substrates were recorded with a tapping mode AFM (Nanoscope III, Digital Instruments) under ambient conditions. AFM was performed using commercial silicon microcantilever probe tips (Veeco, RTESP5) with spring constants ranging between 20 and 80 N/m as recommended by the specification of the manufacturer. Topographic and phase images were obtained at the same time and these images showed identical morphologies; however, only the images from the phase mode were presented for the interpretation of the orientation behavior.
Table 8. Summary of the information of the molecular weight and volumetric ratio in the SIS4111 and SIS4111/PS blends

<table>
<thead>
<tr>
<th>sample name</th>
<th>$\alpha$</th>
<th>$W_{PS}$</th>
<th>$\Phi_{PS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS4111</td>
<td></td>
<td>0.181</td>
<td>0.156</td>
</tr>
<tr>
<td>SIS4111/PS4K</td>
<td>0.31</td>
<td>0.183</td>
<td>0.159</td>
</tr>
<tr>
<td>SIS4111/PS12K</td>
<td>0.94</td>
<td>0.188</td>
<td>0.163</td>
</tr>
<tr>
<td>SIS4111/PS17K</td>
<td>1.33</td>
<td>0.192</td>
<td>0.166</td>
</tr>
<tr>
<td>SIS4111/PS21K</td>
<td>1.64</td>
<td>0.194</td>
<td>0.168</td>
</tr>
<tr>
<td>SIS4111/PS27K</td>
<td>2.11</td>
<td>0.198</td>
<td>0.172</td>
</tr>
<tr>
<td>SIS4111/PS40K</td>
<td>3.13</td>
<td>0.206</td>
<td>0.179</td>
</tr>
<tr>
<td>SIS4111/PS43K</td>
<td>3.36</td>
<td>0.208</td>
<td>0.180</td>
</tr>
</tbody>
</table>

$\alpha$: the molecular weight ratio of PS homopolymer to PS block in the BCP, 

$W_{PS}$: the weight fraction of PS phase, and $\Phi_{PS}$: the volume fraction of PS phase
5.3. Transition in Microdomain Orientation of SIS4111 Triblock Copolymer with the Addition of PS Homopolymer

Figure 5.1 and Figure 5.2 show AFM images of SIS4111 triblock copolymer and its homopolymer blends annealed at 130 °C for 48 h on Si substrate and Teflon substrate, respectively. The bottom surface cylinder orientation of each sample deposited on Teflon substrate is not much different from its top orientation.

As shown in Figure 5.1 (a) and (b), relatively longer-range parallel cylinder orders are detected in SIS4111/PS4K in comparison to the case of neat SIS4111. Furthermore, the AFM image of Figure 5.1 (c) shows the more enhanced straightness of parallel cylinder orientations in the SIS4111/PS12K compared to that in the SIS4111/PS4K (Figure 5.1 (b)). Since the more straightly aligned parallel cylinders in SIS4111/PS4K originate from the decrease of interfacial area between the block domains after the blending PS4K, we expect that the blended PS homopolymer with low molecular weights will reduce the segregation force between the block components. The 2D fast Fourier transforms (FFT’s) included as insets in Figure 5.1 (a), (b), and (c) clearly demonstrate that the order of parallel cylinders in the x,y-plane is enhanced by the addition of the relatively low molecular weight of PS.

On the preferential Si substrates, on the other hand, perpendicular cylinders are spontaneously produced in SIS4111/PS17K (the molecular weight ratio between the PS homopolymer and its corresponding PS block in neat SIS4111, i.e., molecular weight of homo PS component / molecular weight of PS component in SIS, \( \alpha = 1.33 \)), SIS4111/PS21K \( \alpha = 1.64 \) and SIS4111/PS27K \( \alpha = 2.11 \) throughout the whole
sample area without any external field application (Figure 5.1 (c), (d), and (e)). In addition, it can also be confirmed from the comparison of the 2D FFT’s of images in Figure 5.1 (c), (d), and (e) that the hexagonal ordering of perpendicular cylinders is enhanced with the increase of blended PS homopolymer molecular weight. Such overall perpendicular cylinder orientation disappears and macro-phase separation occurs when the molecular weight of blended homopolymer is increased further.

On the preferential Teflon substrate, however, the microdomain orientation has a different behavior with that of the orientation on the Si substrate as shown in Figure 5.2. As shown in Figure 5.2 (a) and (b), relatively longer-range parallel cylinder orders are detected in SIS4111/PS4K in comparison to the case of neat SIS4111. The AFM image of Figure 5.2 (c) shows the more enhanced straightness of parallel cylinder orientations in the SIS4111/PS12K compared to that in the SIS4111/PS4K (Figure 5.2 (b)). Since the more straightly aligned parallel cylinders in SIS4111/PS4K originate from the decrease of interfacial area between the block domains after the blending PS4K, we expect that the blended PS homopolymer with low molecular weights will reduce the segregation force between the block components. The 2D fast Fourier transforms (FFT’s) included as insets in Figure 5.2 (a), (b), and (c) clearly demonstrate that the order of parallel cylinders in the x,y-plane is enhanced by the addition of the relatively low molecular weight of PS. Furthermore, the adding of higher molecular weight of PS homopolymer into SIS4111 keeps the parallel microdomain orientations, even though the molecular weight of PS homopolymer (PS17K (α = 1.33), PS21K (α = 1.64) and PS27K (α = 2.11)) is higher than the PS block in SIS4111. The interplay between the film thickness t and the natural period, L_0, of the bulk microphase-separated structures [67-69] significantly limits into.
the perpendicular microdomain orientation at the relatively thick film (t =10µm). The straightness of parallel microdomains increases as the molecular weight of added homopolymers increases as shown in the AFM images of Figure 5.2 (d), (e), and (f). The 2D fast Fourier transforms (FFT’s) included as insets in Figure 5.2 (d), (e), and (f) also demonstrate that the order of parallel cylinders in the x,y-plane is enhanced by the addition of the relatively high molecular weight of PS. The different behavior will be characterized with various structure parameters according to the different mixtures by the SAXS measurement and discussed with the early results in Chapter 4 and the next results in Chapter 6.
Figure 5.1. AFM images of neat SIS4111 and its mixtures with PS homopolymer annealed at 130 °C on the Si substrate: (a) neat SIS4111, (b) SIS4111/PS4K, (c) SIS4111/PS12K, (d) SIS4111/PS17K, (e) SIS4111/PS21K, and (f) SIS4111/PS27K. Sample images were obtained from ~100 nm thick samples, and the topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is $2 \times 2 \mu$m$^2$. 
Figure 5.2. AFM images of neat SIS4111 and its mixtures with PS homopolymer annealed at 130 °C on the Teflon substrate: (a) neat SIS4111, (b) SIS4111/PS4K, (c) SIS4111/PS12K, (d) SIS4111/PS17K, (e) SIS4111/PS21K, and (f) SIS4111/PS27K. Sample images were obtained from ~10 µm thick samples, and the topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is 2 × 2 µm².
5.4. Microdomain Structures of SIS4111 Triblock Copolymer with the Addition of PS Homopolymer

It is well-known that BCPs have multiple interparticles scattering peaks, Bragg reflection peaks, due to its ordered structure. [27] Based on the information of multiple peaks, the microdomain structures can be determined. To confirm the microdomain morphologies and structure of SIS4111/PS blends, we carry out SAXS for the same samples used in the AFM studies shown in Figure 5.2. All the measurements were taken for the samples quenched to room temperature after annealing at 130 °C for 48 hr in a vacuum oven. In Figure 5.3, one ordered structure and orientation are obtained in SAXS patterns for SIS4111 and its blends with different molecular weights of PS homopolymer at a fixed composition (SIS4111/PS, 90/10 (wt/wt)). The results for SIS4111/PS blends are presented in a vertically shifted plot of scattered intensity as a function of scattering wavenumber $q$. Scattering peaks normal to the plane of the all samples have strong scattering. A fixed concentration (10 wt %) of PS homopolymers with different molecular weight in SIS4111 blends does not change the hexagonal packing of PS microdomains. Five peaks exist as hexagonally arrayed cylinders ($q/q_{\text{max}} = 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \text{ and } \sqrt{9}, \text{ Figure 5.3}$). The strong evidence from the SAXS measurement reveals that the hexagonally packed cylinders are not sphere or lamellae.

Based on the SAXS results and the equations in Section 4.4, this study also calculated structure parameters for each microdomain of SIS4111 and SIS4111/PS blends annealed at the same temperature of 130 °C. The calculated results are summarized in Table 9.
Figure 5.3. SAXS profiles of SIS4111 and SIS4111/PS blends as a function of molecular weight of PS homopolymer. The SAXS profiles were shifted vertically to avoid overlapping.
Table 9. Structure parameters for microdomains of SIS4111 and SIS4111/PS blends obtained from SAXS measurement

<table>
<thead>
<tr>
<th>Sample (90/10, w/w)</th>
<th>PS domain structure</th>
<th>$\Phi_{PS}$</th>
<th>$q_{max}$ (nm$^{-1}$)</th>
<th>$d$ (nm)</th>
<th>$r_{PS}$ (nm)</th>
<th>$L_{PI}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS4111</td>
<td>CYL.</td>
<td>0.156</td>
<td>0.198</td>
<td>31.78</td>
<td>7.62</td>
<td>21.45</td>
</tr>
<tr>
<td>SIS4111/PS4K</td>
<td>CYL.</td>
<td>0.159</td>
<td>0.189</td>
<td>33.25</td>
<td>8.03</td>
<td>22.33</td>
</tr>
<tr>
<td>SIS4111/PS12K</td>
<td>CYL.</td>
<td>0.163</td>
<td>0.174</td>
<td>36.18</td>
<td>8.86</td>
<td>24.05</td>
</tr>
<tr>
<td>SIS4111/PS17K</td>
<td>CYL.</td>
<td>0.166</td>
<td>0.152</td>
<td>41.23</td>
<td>10.19</td>
<td>27.24</td>
</tr>
<tr>
<td>SIS4111/PS21K</td>
<td>CYL.</td>
<td>0.168</td>
<td>0.148</td>
<td>42.55</td>
<td>10.58</td>
<td>27.96</td>
</tr>
<tr>
<td>SIS4111/PS27K</td>
<td>CYL.</td>
<td>0.172</td>
<td>0.140</td>
<td>44.76</td>
<td>11.24</td>
<td>29.20</td>
</tr>
</tbody>
</table>
5.5. Segmental Distributions of Added Homopolymer into the Nanocylinders of Block Copolymer/Homopolymer Blends

Using SAXS and AFM measurements, the ordered structure of BCPs/homopolymer mixtures are investigated and the effects of the added PS homopolymer molecular weight on the microdomain orientation are discussed in the previous Sections. Tanaka and coworkers [27,188,189] investigated and discussed the dependence of the molecular weight of added homopolymer on the segmental distribution within the PS microdomains of the SI diblock copolymer using SAXS and TEM methods. Mayes and coworkers [26] also investigated the segmental distribution of added PS homopolymer or poly(methyl methacrylate) (PMMA) homopolymer within PS-block-PMMA copolymer in the spin-coated thin films. Their investigation found that (1) when the molecular weight of added PMMA was comparable to that of the corresponding copolymer block, it was not distributed uniformly within the PMMA microdomains, localizing at the center of the microdomains, and (2) as the molecular weight of added PMMA was decreased, it was distributed more uniformly within the PMMA microdomains of the PS-block-PMMA copolymer. Such experimental observations were found to be in agreement with theoretical prediction [190] and consistent with results reported for bulk film specimens [27,188,191].

Based on these above results of other research groups, Figure 5.4 shows a Schematic illustration of the domain distribution of the added PS homopolymer. In a homogeneously blended sample, its block components and homopolymer are illustrated in Figure 5.4 (a). Figure 5.4 (b) and (c) illustrate a microphase separated domains with a homogeneous
distribution of PS homopolymer into PS block and a microphase separated domains with an inhomogeneous of PS homopolymer into the center of PS block, respectively. Macrophase separated microdomains between block copolymer and PS homopolymer are illustrated in Figure 5.4 (d). When macrophase separation occurs in the mixture, the chains of PS homopolymer separate from the chains of the A-block-B-block-A copolymer and form macroscopic domains of PS homopolymer. When the added PS homopolymer is solubilized into the microdomains of the block copolymer and the molecular weight of homopolymer is relatively low, the chains of PS homopolymer are mixed on the molecular level with the chains of PS block (as illustrated by (b) in Figure 5.4) When the added PS homopolymer is solubilized into the microdomains of the block copolymer and the molecular weight of homopolymer is relatively high, the chains of PS homopolymer are not uniformly mixed with the chains of PS block and localize at the center of the microdomains (i.e., localized solubilization, as illustrated by (c) in Figure 5.4).

The schematic illustration is compared with the AFM images in Figure 5.1. When the chains of PS homopolymer are uniformly mixed together with the PS microdomains and the PS microdomains swell (Figure 5.4 (b)), the average distance between the neighboring chemical junctions of the block copolymer increases and the interfacial area between the block domains is decreased. Thus, the straightness of parallel cylinders is increased in SIS4111/PS4K ($\alpha = 0.31$) and SIS4111/PS12K ($\alpha = 0.94$) (Figure 5.1 (b) and (c)) in comparison of that of parallel domains in SBS1102 (Figure 5.1 (a)). Domain periodicity and diameter also increase slightly according to the molecular weight of PS homopolymer due to the same reason as summarized in Table 9.
When the molecular weight of PS homopolymer (PS17K, \( \alpha = 1.33 \)) increases more and its chains are localized at the center of the microdomains, the size of PS block domain and its periodicity increase suddenly as shown in Figure 5.4 (c). This is confirmed with the results of SAX measurement summarized in Figure 5.3 and Table 9. Domain periodicity and diameter also increases slightly as the molecular weight of the added PS homopolymer (PS21K (\( \alpha = 1.64 \)), PS27K (\( \alpha = 2.11 \))) increase. When the molecular weight of PS homopolymer increases, the contribution of combinatorial entropy to the free energy decreases, because the combinatorial entropy is related to the inverse of degree of polymerization (N) of the homopolymer. [188]. Thus, the added PS homopolymer tends to be localized at the center of the microdomains of the PS block or forms separate macroscopic domains. The higher molecular weight of PS homopolymer (PS40K (\( \alpha = 3.13 \)), PS43K (\( \alpha = 3.36 \))) results in the macrophase separations as illustrated in Figure 5.4 (d).
Figure 5.4. Schematic illustration of the domain distribution of the added PS homopolymer ($A_H$) into SIA4111. (a) homogeneously blended sample, (b) microphase separated sample with a homogeneous distribution of $A_H$ into PS block (A) in SIS4111, ($\alpha \leq 0.94$) (c) microphase separated sample with a localization of $A_H$ into the center of A, ($1.33 \leq \alpha \leq 2.11$) (d) macrophase separated sample between A-B-A (PS-b-PI-b-PS) and $A_H$, ($\alpha \geq 3.13$)
5.6. Theoretical Consideration of Transition to Perpendicular Orientation: Increased Incompatibility by Homopolymer Addition

If we assume that the contributions of homologous PS pair (i.e., PS block and PS homopolymer) to the domain-domain incompatibility routinely depend on their average molecular weight and their individual compositional fraction, we can estimate the $\chi^N$ values (where $\chi$ is the Flory-Huggins segmental interaction parameter and $N$ is the degree of polymerization) of block copolymers by using Eq. 4.3 and Eq. 4.4 [193-195]. At the annealing temperature of 130 °C, the calculated $\chi^N$ values are similar according to the different PS homopolymer blended into SIS4111 as reported in Chapter 4. Such mutually similar $\chi^N$ values, however, neither provide a critical explanation on the homopolymer-driven cylinder orientation transition phenomenon nor reasonably explain the different temperature-dependent phase behaviors of perpendicular cylinder-forming block copolymers. Note that the perpendicular cylinder orientation is not obtained when the molecular weight of blended homopolymer (i.e., the incompatibility between the block domains) is routinely increased; rather it is achieves when the molecular weight ratio between the homologous PS pair approached to unity, as long as the ratio is approximately larger than 1.00. Furthermore, the exceptionally strong preference for perpendicular orientation in SIS4111/PS17K cannot be described by its $\chi^N$ value nearly identical to that of SIS4111/PS4K and SIS4111/PS12K. Therefore, we provide an alternative thermodynamic consideration for the block copolymer orientation transition phenomena at a fixed composition.
Using experimentally determined cylinder dimensions based on the microdomain parameters from the SAXS profiles in Table 9 and the previous equations (4.5-4.9) as suggested in Chapter 4, we can estimate the relative interfacial area changes after the orientation conversion process from parallel to perpendicular. It is notable that, in order to estimate above equations, we do not need to consider any types of thermodynamic driving forces involved in the cylinder orientation transition because we use the experimentally (i.e., thermodynamically and kinetically) already determined cylinder dimensions to calculate the changes of interfacial areas and excess free energies due to the geometric transition from parallel to perpendicular.

The changes of microdomain structure parameter in Table 9 reveals that the periodicity and the size of PS domain slightly increase when PS4K and PS12K is blended into SIS4111. With PS17K addition, however, shows the sudden increases in the domain periodicity and radius (Table 9), which enable the transition from the parallel orientation (SIS4111/PS12K, the molecular weight ratio of PS homopolymer to PS block in SIS4111, α = 0.94) into the perpendicular orientation (SIS4111/PS17K, α = 1.33) as indicated in the AFM images of Figure 5.1 (c) and (d). As shown in the structure parameters in Table 9 and the AFM images of Figure 5.1 (e) and (f), addition of PS homopolymer molecular weight higher than 17 kg/mol slightly increases the PS domain periodicity and radius and holds the perpendicular orientation in the SIS4111/PS blends, respectively. Furthermore, the microdomain disappears and the macrophase separation occurs in the mixture above the 27 kg/mol molecular weight range.

To compare the interfacial areas and energies of perpendicular cylinders to those of parallel cylinders, we designate the dimensional characteristics of SIS4111/PS12K as
reference dimensional values of parallel cylinders because the PS block composition of SIS4111/PS12K is most similar to those of SIS4111/PS17K, SIS4111/PS21K and SIS4111/PS27K. The reference ratio between perpendicular and parallel domain-domain excess free energies, therefore, is fixed at 1, since there is no parallel to perpendicular transition free energy in the parallel microdomain orientation of SIS4111/PS12K. As shown in the third column of Table 10 \( (A/A_0) \), the calculated values determine the changes of the ratio between perpendicular and parallel domain-domain excess free energies as a function of different molecular weights of added PS homopolymer into SIS4111/PS blends having a perpendicular microdomain structure. We note that these \( (A/A_0) \) values decrease when the homopolymer PS17K and others with higher molecular weights are blended into SIS4111 and the parallel structure transfers into perpendicular orientation. We also note that the decrease in \( (A/A_0) \) is rather larger for PS17K addition and further increases of molecular weight of added PS homopolymer result in smaller decreases in the ratio of excess free energy and result in the desirable perpendicular microdomain structure. Based on the SAXS measurement, its microdomain parameters, and the equations (4.5-4.9), therefore, the addition of PS17K \( (\alpha = 1.33) \) into SIS4111 decreases the perpendicular domain-domain excess free energy abruptly in comparison to the reference value in SIS4114/PS12K \( (\alpha = 0.94) \), thus resulting in the parallel to perpendicular transition.

As shown in the fourth column of Table 10, the calculated values determines the changes in the ratio of the majority component-substrate interfacial areas between the perpendicular and the parallel microdomain structures, \( A_{\text{major}}/A_{\text{major,0}} \), and its corresponding ratio of excess free energy. This value increases abruptly when the PS17K
is blended into SIS4111, since all perpendicular minority microdomains orient normal to the substrates and the many portions of minority-substrate interfacial areas are replaced by those of majority-substrate. After that, the corresponding ratio of excess free energy decreases as the higher molecular weight of PS homopolymer is added into SIS4114, which results in stronger preference for the perpendicular microdomain structures. The calculated results in the fifth column of Table 10 show the changes in the ratio of the minority component-substrate interfacial areas between the perpendicular and the parallel microdomain structures, $A_{\text{minor}}/A_{\text{minor},0}$, and the corresponding ratio of excess free energy. The value decreases abruptly when the PS17K is blended into SIS4114, since the perpendicular minority microdomain starts orienting in the direction normal to the substrates. Stronger preference for the perpendicular microdomain structures are expected as the higher molecular weights of PS homopolymer are added into SIS4114 and the corresponding ratios of excess free energy decrease. As shown in the third, forth, and fifth columns of Table 10, the excess free energy between the block domains and that between the majority block and the substrate decreases after the parallel-to-perpendicular orientation transition. In addition, we geometrically realize that the change of interfacial area between the block domains is the most critical factor for the cylinder orientation transition due to its largest fraction (see the sixth, seventh, and eighth columns of Table 10). Considering the calculated results together with our experimental results, therefore, we conclude that perpendicular orientation-inducing thermodynamic conditions such as the blending of minority homopolymer with appropriate molecular weight ($1.33 \leq a \leq 2.11$) and the lowering of annealing temperature should involve sufficient lowering of excess free energy into the block domains. Thus, we can expect that a strong
thermodynamic compensation should be involved in the process of parallel-to-perpendicular cylinder orientation transition to overcome the domain-domain excess free energy. Note that such unusual cylinder orientation transition occurs spontaneously in the block copolymer mixtures used in this study, when the molecular weight ratios and the annealing temperature conditions are right. As an exothermic interaction force surpassing the domain-domain excess free energy (i.e., generating an additional increase of incompatibility between the block components), we propose an interaction between the homopolymer and its corresponding block component, whose strength depends on the molecular weight difference between them. Our proposal implies that a homologous polymer pair with mutually different molecular weights does not recognize each other as an identical counterpart. Thus, the heat of mixing will be generated in the blend of such homologous polymer pair, whose amount is proportional to the degree of identity between them, as long as their molecular weights are mutually different. We note that our proposed intermolecular interaction is different from the well-known secondary forces such as electrostatic, hydrogen bonding and van der Waals interactions. There would not be significant charge-charge, charge-dipole and hydrogen bonding interactions between the homologous PS pair due to the absence of charges and hydrogen bonding-generating functional groups in the PS components. In addition, the dipole-dipole and van der Waals interactions of PS pair that generally increase with increasing the molecular weight of polymer components might not be a candidate for the thermodynamic compensation, since the amount of compensation depends on the molecular weight ratio between the polymer pair, rather than their absolute molecular weight, as mentioned in Chapter 4.
In case of parallel cylinder-forming SIS4111/PS4K, the interaction between the homologous PS pair is small due to the low molecular weight of PS homopolymer, (α = 0.31) and hence the initial parallel cylinders in neat SIS4111 are straightened after the blending of PS4K (or after the increase of annealing temperature) simply owing to the decreased incompatibility between the block components. On the other hand, the interaction force (i.e., significant amount of heat of mixing) between the homologous PS pair will be generated in SIS4111/PS17K (α = 1.33) owing to the highly enough molecular weight similar to the molecular weights of PS block in SIS4111. Since the homologous pair interaction induces an additional enhancement of incompatibility between the PS and PI components by virtue of strong segregation between the homologous PS pair, the actual incompatibility of SIS4111/PS17K will be much higher than the incompatibility predicted by the Flory-Huggins theory. In case of perpendicular cylinder-forming SIS4111/PS21K, the interaction between the homologous PS pair will extremely increase due to the highly increased molecular weights, and hence its cylinders display an exceptionally strong preference for perpendicular orientation even at high annealing temperature (i.e., even at an extremely unfavorable condition for a perpendicular cylinder orientation).

This observation based on the samples annealed on Si substrate (Figure 5.1) is not identical to that based on the samples annealed on Teflon substrate (Figure 5.2). The perpendicular microdomain orientation at the relatively thick film (t =10µm) is significantly restricted by the interplay between the film thickness t and the natural period, \( L_0 \), of the bulk microphase-separated structures [67-69]. The different behavior should be characterized with various structure parameters according to the different mixtures by the
SAXS measurement and compared to the early results in Chapter 4 and the next results in Chapter 5. The jump rate in the domain periodicity after parallel to perpendicular is 33.33% between SIS4114/PS4K and SIS4114/PS12K as described in the structure parameters from the SAXS profiles in Chapter 4. The structure parameters of SBS1102/PS mixtures in Chapter 6 determine that the jump rate of the periodicity between domains is 24.53% between SBS1102/PS12K and SBS1102/PS17K. The jump rate in the domain periodicity, however, is just 13.99% between SIS4111/PS12K and SIS4111/PS117K, which enables the parallel to perpendicular orientation transition on the relatively thin film, but limits in the perpendicular orientation on the relatively thick film. Thus, perpendicular block copolymer cylinders in a relatively thick film sample would lose their perpendicular orientation, since the compensation between the limitation of film thickness and the strong interaction force of homologous PS pair is not enough to thoroughly overcome the total excess free energy; mainly due to the increased corresponding free energy between the block domains at a thick film (the sixth column in Table 10 at m =5).
Table 10. Changes of domain-domain interfacial area and excess free energy after the parallel-to-perpendicular cylinder orientation transition in SIS4111/PS blends

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Sample</th>
<th>(A/A_\text{0} )</th>
<th>(A_{\text{major}}/A_{\text{major,0}} )</th>
<th>(A_{\text{minor}}/A_{\text{minor,0}} )</th>
<th>(f_{\text{domain-domain}} )</th>
<th>(f_{\text{majority-substrate}} )</th>
<th>(f_{\text{minority-substrate}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>m = 1</td>
<td>SIS4111/PS17K</td>
<td>0.870</td>
<td>1.460</td>
<td>0.390</td>
<td>0.540</td>
<td>0.383</td>
<td>0.077</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.606*)</td>
<td>(0.308*)</td>
<td>(0.086*)</td>
</tr>
<tr>
<td></td>
<td>SIS4111/PS21K</td>
<td>0.837</td>
<td>1.444</td>
<td>0.378</td>
<td>0.523</td>
<td>0.402</td>
<td>0.075</td>
</tr>
<tr>
<td></td>
<td>SIS4111/PS27K</td>
<td>0.788</td>
<td>1.420</td>
<td>0.359</td>
<td>0.495</td>
<td>0.433</td>
<td>0.072</td>
</tr>
<tr>
<td>m = 5</td>
<td>SIS4111/PS17K</td>
<td>0.870</td>
<td>1.460</td>
<td>0.390</td>
<td>0.854</td>
<td>0.121</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.885*)</td>
<td>(0.090*)</td>
<td>(0.025*)</td>
</tr>
<tr>
<td></td>
<td>SIS4111/PS21K</td>
<td>0.837</td>
<td>1.444</td>
<td>0.378</td>
<td>0.846</td>
<td>0.130</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>SIS4111/PS27K</td>
<td>0.788</td>
<td>1.420</td>
<td>0.359</td>
<td>0.831</td>
<td>0.145</td>
<td>0.024</td>
</tr>
</tbody>
</table>

*the corresponding fraction of interfacial area for SIS4111/PS12K
5.7. Concluding Remarks

We illustrated a spontaneous and simple method for the orientation of perpendicular cylinders with a triblock copolymer (SIS4111) possessing an initial orientation preference for parallel structures on a preferential substrate, by increasing the segregation forces between the homologous polystyrene pairs at a fixed blending composition of PS homopolymer. This is obtained without any external field usages or modification of substrate interfacial interaction with the block components. When the molecular weight of homopolymer is relatively lower than that of the corresponding minority block component \((a \leq 0.94)\), the added PS homopolymer is homogeneously solubilized into the microdomains of the block copolymer and the chains of PS homopolymer are mixed on the molecular level with the chains of PS block. Thus, the domain periodicity slightly increases and the straightness of parallel cylinders is increased due to the swelling of microdomain and the increase of the average distance between the neighboring chemical junctions of the block copolymer. The addition of the higher molecular weight of the homopolymer chains \((1.33 \leq a \leq 2.11)\) enables the ratio of perpendicular domain-domain excess free energy to decrease and result in the perpendicular microdomain orientation only into the relatively thin films. The addition of PS homopolymer with a higher range of molecular weight results in macrophase separations. Thus, the fabrication strategy using the simple method by blending of block copolymer with homopolymer having an appropriate molecular weight creates new opportunities for the fabrication of low-cost and high-throughput ordering process into the self-assembly of block copolymer materials with highly controlled 3-dimensional nanopatterns.
CHAPTER VI
SELF-ASSEMBLED MICRODOMAIN AND ORIENTATION
BEHAVIOR OF BLOCK COPOLYMER/HOMOPOLYMER
BLENDS: PS-PB-PS TRIBOOCK COPOLYMER, KRATON D1102K

6.1. Introduction

BCP/homopolymer Blends have been of many attentions due to its easy and fast modification for the desired properties in polymeric materials. It is clearly determined that blending homopolymer in a BCP may cause changes in cylindrical microdomain structure in the block copolymer [53]. Recently, we investigated that blending homopolymer into BCP also induced the transition of the parallel orientation into the perpendicular orientation on the preferential substrate as determined in previous chapters. The most important factor controlling the cylinder orientation into the self-assembly of the BCPs/homopolymer mixture are the ratio of the molecular weight between the homologous PS pairs, i.e. $\alpha_A (M.W_{HA} / M.W_{A \text{ in } BCP})$. When the range of molecular weight of homopolymer is low ($\alpha_A < 1$), the homopolymer chains with low molecular weight tends to be homogeneously mixed together with the PS microdomain in the BCP and the initial parallel structure and its orientation do not change. When the high molecular weight of homopolymer ($\alpha_A \geq 1$) are added into the BCPs, the localization of
the homopolymer chains at the center of the PS microdomains enable the periodicity and size of the microdomains increases suddenly. Thus the unusual cylinder orientation occurs spontaneously with a perpendicular structure on the preferential substrate. Further increases of molecular weight of homopolymer result in the macro-phase separation.

The previous studies have investigated that the addition of PS homopolymer into the BCPs results in the perpendicular orientation into the PS homopolymer blending systems with SIS4114 and SIS4111 triblock copolymer as described in Chapter 4 and 5, respectively. In this chapter, we also investigate a different system untested in the previous results, with SBS1102((KRATON D1102K, KRATON Polymers), having a molecular weight of 117.6 kg/mol with a PS block of 33.6 kg/mol and a PB block of 84 kg/mol. The SBS1102 triblock copolymer in the mixtures used in this study is chosen as a material which has different chemical structure, composition of PS block, and information of molecular weight with those of SIS4114 and SIS4111 in the previous mixtures (Chapter 4 and 5, respectively) for the investigation of the simple method into self-assembly process into BCPs/homopolymer mixtures. The molecular weight of PS homopolymer is employed with various ranges between 4 kg/mol and 46 kg/mol to investigate the effect of the molecular weight of homopolymer on the microdomain orientation. The bulk microdomain of the relatively thin film of SBS1102 is that of hexagonal cylinder PS microdomains with both parallel and perpendicular orientation. For the relatively thick film, the PS microdomain has a parallel orientation [90]. Therefore, here we illustrate that the spontaneous method studied in the previous two chapters is also effective way for the cylinder orientation into the different blending system with a normal direction on the preferential substrate.
6.2. Experimental Methods

A polystyrene-polybutadiene-polystyrene (SBS) block copolymer, Kraton D1102K, was supplied as a commercial sample from the Kraton Polymers Co. Kraton D1102K contains almost 29 wt % (24 vol %) PS and has a weight-average molecular weight ($M_w$) of 117600 g/mol and a polydispersity ($M_w/M_n$) of 1.10. PS homopolymers having different molecular weights were used in the blending system in this study. All chemicals were used without further purification. All information about the BCPs and homopolymers used in this study are illustrated in Table 2.

Different molecular weights of PS were mixed into SBS1102. A fixed composition with 90 wt % of BCPs and 10 wt % of PS homopolymers were blended with 0.05 wt % of antioxidant (Irganox 1010, Ciba-Geigy Group) and all materials were dissolved into toluene (2 wt % in solution). Table 11 shows the information on samples of BCPs/PS mixtures such as the molecular weight ratio ($\alpha$) of PS homopolymer to PS block in the SBS1102, the weight fraction of PS phase ($W_{PS}$), and the volume fraction of PS phase ($\Phi_{PS}$) in SBS1102 and SBS1102/PS blends. Thin films (~100 nm) of BCPs/homopolymer mixture were spin cast from the filtered solution directly in the 3 in. diameter Si substrate at 2000 rpm. Film thickness was measured with a Gaertner model L116C ellipsometer using a He-Ne laser (wavelength = 632.8 nm) and a fixed angle of incidence of 70°. Relatively thicker film samples between 500 nm and a couple of micrometers were also prepared by a method of solution casting onto selected substrates. The thickness of thick film over 1 um was measured by the micrometer. The solvent in BCPs/homopolymer solutions was slowly removed at ambient condition for 2 days and then in a vacuum oven.
at 50°C for a day. The remained solvent into the BCPs/homopolymer mixtures was removed during annealing the samples in a vacuum oven at different annealing temperatures well above glass transition temperatures (Tg’s) of PS block component and PS homopolymers.

The samples of BCPs/homopolymer mixture for SAXS experiments were prepared by coating on the Teflon substrate and were annealed at a fixed annealing temperature of 130 °C. The SAXS patterns were recorded on the 2-dimensional detector (Rigaku Innovative Technologies) with a Rigaku MicroMax-002+ X-ray generator, the microfocus source. The beam source with a spot size of 20 µm was produced by coupling a high performance Osmic Confocal Max-Flux® (CMF) optic with a sealed tube microfocus X-ray source for conditioning the beam through a series of 3 collimating pinholes. SAXS measurement was performed under the condition of a Cu source with 40W of power, 45kV of voltage and 0.88mA of current at ambient temperature. The wavelength of X-ray radiation was 1.5405Å.

The AFM measurement was performed to obtain the topographic images of the samples under ambient conditions. A tapping mode AFM (Nanoscope III, Digital Instruments) recorded the topographical data of the morphologies of the structure and its orientation on the surface of BCPs/PS mixtures coated on different substrates. Commercial silicon microcantilever probe tips (Veeco, RTESP5) were used for the operation of AFM measurement using with spring constants ranging between 20 and 80 N/m as that of the manufacturer’s specification. The images from the phase mode measurement was presented in this chapter, because height and phase modes were performed at the same time and showed the identical images.
<table>
<thead>
<tr>
<th>sample name</th>
<th>$\alpha$</th>
<th>$W_{PS}$</th>
<th>$\Phi_{PS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS1102</td>
<td></td>
<td>0.286</td>
<td>0.240</td>
</tr>
<tr>
<td>SBS1102/PS4K</td>
<td>0.24</td>
<td>0.288</td>
<td>0.242</td>
</tr>
<tr>
<td>SBS1102/PS12K</td>
<td>0.71</td>
<td>0.294</td>
<td>0.247</td>
</tr>
<tr>
<td>SBS1102/PS17K</td>
<td>1.01</td>
<td>0.297</td>
<td>0.250</td>
</tr>
<tr>
<td>SBS1102/PS21K</td>
<td>1.25</td>
<td>0.300</td>
<td>0.252</td>
</tr>
<tr>
<td>SBS1102/PS27K</td>
<td>1.61</td>
<td>0.303</td>
<td>0.256</td>
</tr>
<tr>
<td>SBS1102/PS40K</td>
<td>2.38</td>
<td>0.312</td>
<td>0.263</td>
</tr>
<tr>
<td>SBS1102/PS43K</td>
<td>2.56</td>
<td>0.314</td>
<td>0.265</td>
</tr>
</tbody>
</table>

$\alpha$: the molecular weight ratio of PS homopolymer to PS block in the BCP, $W_{PS}$: the weight fraction of PS phase, and $\Phi_{PS}$: the volume fraction of PS phase
6.3. Transition in Microdomain Orientation of SBS1102 Triblock Copolymer with the Addition of PS Homopolymer

Figure 6.1 and Figure 6.2 show an AFM image of ~100 nm thick sample of SBS1102 triblock copolymer. Both of parallel and perpendicular orientation and cylinder structure are observed. It was reported that the limitation of thickness in SBS1102 triblock copolymer is ~42nm to manipulate the perpendicular cylinder orientation on whole area and both mesophase orientations were reported above the thickness of ~42nm. [90] Figure 6.2 shows an AFM image of larger scan (5 × 5 µm²) of the same sample; the scan (2 × 2 µm2) of Figure 6.1 is indicated by a square. In the valleys (darker area), the cylinders are oriented perpendicular to the substrate and on the hills (brighter area) the cylinders are oriented parallel to the surface.

As shown in Figure 6.3 and Figure 6.4, AFM measurement reveals the topographic images of SBS1102 triblock copolymer and its homopolymer mixtures annealed at 120 °C for 48 hr on Si substrate and Teflon substrate, respectively. It is also observed that the cylinder orientation of BCPs spin-coated on HF-treated silicon wafer (thickness, t = ~100 nm) is identical to that of BCPs solution-cast on Teflon substrate with a film thickness of ~10 µm as shown in the results of SIS4114/PS mixtures in Chapter 4. In addition, the bottom surface cylinder orientation of each sample deposited on Teflon substrate is not much different from its top orientation. Thus, we expect that the thickness limitation of the perpendicular orientation in neat SBS1102 and its miscible homopolymer blends does not significantly affect their cylinder orientation in the range of sample thickness from the sample-substrate interface to ~10 µm when deposited on commercial substrates, which
are HF-treated Si wafer and Teflon without any modification. The effect of blending BCPs with homopolymer on the cylinder orientation overcomes the interplay between the film thickness $t$ and the natural period, $L_0$, of the bulk microphase-separated structures [67-69] and the limitation of interfacial interaction between block copolymer and the substrate [19,20]. In the cases of SBS1102/PS40K and SBS1102/PS43K, the AFM measurement shows the disappearance of microdomains as well as the microphase separation between the PI and PS components.

As shown in Figure 6.4 (a), (b), and (c), relatively longer-range parallel cylinder orders are detected in SBS1102/PS4K and SBS1102/PS12K in comparison to the case of SBS1102. Since the more straightly aligned parallel cylinders in SBS1102/PS4K originate from the decrease of interfacial area between the block domains after the blending PS4K, we expect that the blended PS homopolymer with low molecular weights will reduce the segregation force between the block components. The 2D fast Fourier transforms (FFT’s) included as insets in Figure 6.4 clearly demonstrate that the order of parallel cylinders in the x,y-plane is enhanced by the addition of PS4K. In comparison to SBS1102/PS4K, SBS1102/PS12K shows the similar trend of enhanced alignment in Figure 6.4 (b), (c), and each FFT’s image in inset.

On the preferential fluorine substrates, on the other hand, perpendicular cylinders are spontaneously produced in SBS1102/PS17k (the molecular weight ratio of the PS homopolymer to its corresponding PS block in SBS1102, i.e., molecular weight of homo PS component / molecular weight of PS component in SBS1102, $\alpha = 1.01$), SBS1102/PS21K ($\alpha = 1.25$) and SBS1102/PS27K ($\alpha = 1.61$) throughout the whole sample area without any external field application (Figure 6.3 (d), (e), (f), Figure 6.4 (d),
(e), and (f)). The comparison of the 2D FFT’s of images in Figure 6.3 (d), (e), (f), Figure 6.4 (d), (e), and (f) also confirms that the hexagonal ordering of perpendicular cylinders is enhanced with the increase of blended PS homopolymer molecular weight. Such overall perpendicular microdomain orientation disappears and macrophase separation occurs when the molecular weight of blended homopolymer is increased further (SBS1102/PS40K, \( \alpha = 2.38 \), and SBS1102/PS43K, \( \alpha = 2.56 \)).
Figure 6.1. AFM images of SBS1102 annealed at 120°C on the Si substrate. Sample image were obtained from the white square area in Figure 6.2. The size of the image is $2 \times 2 \, \mu\text{m}^2$. 
Figure 6.2. AFM images of SBS1102 annealed at 120°C on the Si substrate. Sample image were obtained from ~100 nm thick samples, and the topographic and phase AFM images were the same. The size of the image is $5 \times 5 \mu m^2$. 
Figure 6.3. AFM images of SBS1102 and its mixtures with PS homopolymer annealed at 120°C on the Si substrate: (a) SBS1102, (b) SBS1102/PS4K, (c) SBS1102/PS12K, (d) SBS1102/PS17K, (e) SBS1102/PS21K, and (f) SBS1102/PS27K. Sample images were obtained from ~100 nm thick samples, and the topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is $2 \times 2 \mu m^2$. 
Figure 6.4. AFM images of SBS1102 and its mixtures with PS homopolymer annealed at 120°C on the Teflon substrate: (a) SBS1102, (b) SBS1102/PS4K, (c) SBS1102/PS12K, (d) SBS1102/PS17K, (e) SBS1102/PS21K and (f) SBS1102/PS27K. Sample images were obtained from ~10 µm thick samples, and the topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is 2 × 2 µm².
6.4. Microdomain Structures of SBS1102 Triblock Copolymer with the Addition of PS Homopolymer

It is well-known that BCPs have multiple interparticles scattering peaks, Bragg reflection peaks, due to its ordered structure. [27] Based on the information of multiple peaks, the microdomain structures can be determined. To confirm the microdomain morphologies and structure of SBS1102/PS blends, we carry out SAXS for the same samples used in the AFM studies shown in Figure 6.4. All the measurements were taken for the samples quenched to room temperature after annealing at 120 °C for 48 hr in a vacuum oven. In Figure 6.5, one ordered structure and orientation are obtained in SAXS patterns for SBS1102 and its blends with different molecular weights of PS homopolymer at a fixed composition (SBS1102/PS, 90/10 (wt/wt)). The results for SBS1102/PS blends are presented in a vertically shifted plot of scattered intensity as a function of scattering wavenumber \( q \). Irradiating normal to the plane of the samples (SBS1102/PS17K, SBS1102/PS21K, and SBS1102/PS27K) result in weak scattering and no evidence of an ordered morphology. The SAXS profiles of these samples are obtained from the direction of in the plane of same samples. A fixed concentration (10 wt %) of PS homopolymers with different molecular weight in SBS1102 blends does not change the hexagonal packing of PS microdomains. Five peaks exist as hexagonally arrayed cylinders (\( q/q_{\text{max}} = 1, \sqrt{3}, \sqrt{4}, \sqrt{7}, \text{and} \sqrt{9} \), Figure 6.5).

AFM investigations for SBS1102/PS blends reveal a transition of cylinder orientation on increasing the molecular weight of PS in the blends. The perpendicular cylinders for the blends determined from the AFM images in Figure 6.3 and Figure 6.4,
however, could equally be interpreted as the end of spheres or lamellae at the interface between air and BCP blends, since the AFM investigation can show only the surface of the films. The strong evidence from the SAXS measurement reveals that hexagonally packed cylinders and its transition from parallel to perpendicular orientation are not spheres or lamellae and the end of those.

Figure 6.5. SAXS profiles of SBS1102 and SBS1102/PS blends as a function of molecular weight of PS homopolymer. The SAXS profiles were shifted vertically to avoid overlapping.
Based on the SAXS results and the equations in Section 4.4, this study also calculated structure parameters for each microdomain of SBS1102 and SBS1102/PS blends annealed at the same temperature of 120 °C. The calculated results are summarized in Table 12.

### Table 12. Structure parameters for microdomains of SBS1102 and SBS1102/PS blends obtained from SAXS measurement

<table>
<thead>
<tr>
<th>Sample (90/10, w/w)</th>
<th>PS domain structure</th>
<th>$\Phi_{PS}$</th>
<th>$q_{max}$ (nm$^{-1}$)</th>
<th>$d$ (nm)</th>
<th>$r_{PS}$ (nm)</th>
<th>$L_{PI}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS1102 CYL.</td>
<td>0.240</td>
<td>0.221</td>
<td>28.43</td>
<td>8.45</td>
<td>15.94</td>
<td></td>
</tr>
<tr>
<td>SBS1102/PS4K CYL.</td>
<td>0.242</td>
<td>0.218</td>
<td>28.83</td>
<td>8.61</td>
<td>16.08</td>
<td></td>
</tr>
<tr>
<td>SBS1102/PS12K CYL.</td>
<td>0.247</td>
<td>0.213</td>
<td>29.46</td>
<td>8.88</td>
<td>16.25</td>
<td></td>
</tr>
<tr>
<td>SBS1102/PS17K CYL.</td>
<td>0.250</td>
<td>0.171</td>
<td>36.68</td>
<td>11.12</td>
<td>20.11</td>
<td></td>
</tr>
<tr>
<td>SBS1102/PS21K CYL.</td>
<td>0.252</td>
<td>0.163</td>
<td>38.43</td>
<td>11.71</td>
<td>20.96</td>
<td></td>
</tr>
<tr>
<td>SBS1102/PS27K CYL.</td>
<td>0.256</td>
<td>0.158</td>
<td>39.67</td>
<td>12.17</td>
<td>21.47</td>
<td></td>
</tr>
</tbody>
</table>
6.5. Segmental Distributions of Added Homopolymer into the Nanocylinders of Block Copolymer/Homopolymer Blends

The orientation and its structure of SBS1102/PS mixture were investigated and the effects of the added PS homopolymer molecular weight on the microdomain orientation were discussed based on the results of SAXS and AFM measurement in the previous Sections. This study focuses on the distribution of the chains of PS homopolymer into the microdomains of SBS1102.

Figure 6.6 illustrates a diagram of the domain distribution of the added PS homopolymer into the blocks of SBS1102. A diagram of a homogeneously blended sample is illustrated in Figure 6.6 (a). The chains of SBS block (ABA) and PS homopolymer (A\textsubscript{H}) are homogeneously mixed well in the mixtures. Figure 6.6 (b) and (c) illustrate a microphase separated domains with a homogeneous distribution of PS homopolymer into PS block and a microphase separated domains with an inhomogeneous of PS homopolymer into the center of PS block, respectively. Macrophase separated microdomains between block copolymer and PS homopolymer are illustrated in Figure 6.6 (d). The chains of PS homopolymer separate from the chains of the A-block-B-block-A copolymer and form macroscopic domains of PS homopolymer, when macrophase separation occurs in the mixture. When the added PS homopolymer is solubilized into the microdomains of the block copolymer and the molecular weight of homopolymer is relatively low, the chains of PS homopolymer are mixed on the molecular level with the chains of PS block (as illustrated by (b) in Figure 6.6) When the added PS homopolymer is solubilized into the microdomains of the block copolymer and the molecular weight of
homopolymer is relatively high, the chains of PS homopolymer are not uniformly mixed with the chains of PS block and localize at the center of the microdomains (i.e., localized solubilization, as illustrated by (c) in Figure 6.6).

When the chains of PS homopolymer are uniformly mixed together with the PS microdomains and the PS microdomains swell (Figure 6.6 (b)), the average distance between the neighboring chemical junctions of the block copolymer increases and the interfacial area between the block domains is decreased. Thus, the straightness of parallel cylinders is increased in SBS1102/PS4K ($\alpha = 0.24$) and SBS1102/PS12K ($\alpha = 0.71$) (Figure 6.4 (b) and (c)) in comparison of that of parallel domains in SBS1102 (Figure 6.4 (a)). Domain periodicity and diameter also increase slightly according to the molecular weight of PS homopolymer due to the same reason as summarized in Table 12.

The addition of the PS homopolymer having a molecular weight of 17K ($\alpha = 1.01$) enables the localization at the center of the microdomains and the size and periodicity of PS microdomain increase suddenly as shown in Figure 6.6 (c). This is confirmed with the results of SAX measurement summarized in Figure 6.5 and Table 12. Domain periodicity and diameter also increases slightly as the molecular weight of the added PS homopolymer (PS21K ($\alpha = 1.25$), PS27K ($\alpha = 1.61$)) increase. When the molecular weight of PS homopolymer increases, the contribution of combinatorial entropy to the free energy decreases, because the combinatorial entropy is related to the inverse of degree of polymerization (N) of the homopolymer. [188] Thus, the chains of the added PS homopolymer are not homogeneously solubilized and tend to be localized at the center of the microdomains of the PS block or forms separate macroscopic domains. When the chains of the added PS homopolymer have a molecular weight of 40K ($\alpha =$
2.38) and 43 K (α = 2.56), the combinatorial entropy decreases more and the macrophase separations occurs as illustrated in Figure 6.6 (d).

Figure 6.6. Schematic illustration of the domain distribution of the added PS homopolymer (A\textsubscript{H}) into SBS1102. (a) homogeneously blended sample, (b) microphase separated sample with a homogeneous distribution of A\textsubscript{H} into PS block (A) in SBS1102, (α ≤ 0.71) (c) microphase separated sample with a localization of A\textsubscript{H} into the center of A, (1.01 ≤ α ≤ 1.61) (d) macrophase separated sample between A-B-A (PS-b-PB-b-PS) and A\textsubscript{H}, (α ≥ 2.38)
6.6. Temperature-Dependent Microdomain Behaviors of Block Copolymer/Homopolymer Mixtures

As shown in the AFM images of Figure 6.7 (a), (b), (c), and Figure 6.8 (a), (b), and (c), in the temperature range from 120°C to 170°C, the straightness of parallel cylinders in SBS1102/PS4K and SBS1102/PS12K is enhanced with increasing temperature due to the temperature-proportional preference for reducing the interfacial area between the block domains as mentioned in Chapter 4. It is also notable that the ordering of parallel cylinders in SBS1102/PS12K is more enhanced than those in SBS1102/PS4K at the same temperature, owing to the relatively higher molecular weight of blended PS homopolymer than that of PS block in the SBS1102/4K, which enhances the mixing entropy to reduce the interfacial area between the block components. After the parallel cylinder straightening process, the parallel cylinders in SBS1102/PS4K and SBS1102/PS2K abruptly disappeared without any notable OOT and composition fluctuations, and homogeneous melt state is observed above 190 °C.

The AFM images of Figure 6.9 show the phase behaviors of perpendicular cylinder-forming SBS1102/PS17K at different temperatures. In the temperature range from 120 °C to 170 °C, the gradual orientation transition from perpendicular to parallel is observed with increasing the temperature. The overall perpendicular cylinder orientation at 120 °C is mainly transferred to parallel cylinder orientation at 170 °C, via the orientation transition process starting from ~150 °C. After achieving mainly parallel cylinders, composition fluctuations of block components last until ~200 °C, and then homogeneous melt states are observed at 210°C. We recall the fact that the long-lived composition
fluctuations detected in perpendicular cylinder-forming SBS1102/PS17K are not observed in the parallel cylinder-forming SBS1102/PS4K and SBS1102/PS12K. Thus, we conclude that the stability of transient phases arising from the composition fluctuations at the temperatures above the ODT is largely dependent on the intrinsic segregation forces between the block domains.

The AFM images of Figure 6.10 show the temperature-dependent phase behaviors of SBS1102/PS21K with relatively stronger segregation forces between the block domains. In comparison to the case of SBS1102/PS17K, more stable perpendicular cylinders are observed at temperatures ranging from 120°C to 170°C, and then hexagonal lattice disordered of perpendicular cylinders is identified in the temperature range between 170°C and 190°C. During the disordered process, the perpendicular cylinders in SBS1102/PS21K merge together to decrease the interfacial area between the PS and PB domains without a perpendicular-to-parallel cylinder orientation transition. Thus, we expect that the preference for perpendicular orientation in SBS1102/PS21K is exceptionally stronger than that in SBS1102/PS17K. After the termination of hexagonal lattice disordered process, composition fluctuation-driven phases last until ~200°C, and homogeneous melt states are then observed at ~220°C.

Similar to the case of SBS1102/PS21K, SBS1102/PS27K also show relatively strong segregation behavior between the block domains, as the annealing temperature is increased in the temperature range from 120°C to 170°C, as shown in Figure 6.11. After the disordered process between 170°C and 190°C, a composition fluctuation-driven phase is detected at ~200°C, and a homogeneous melt state is then observed at ~220°C.
Based on the AFM studies, we can categorize the following three different temperature-dependent phase behaviors for cylinder-forming block copolymer mixtures: 1) In cases of parallel cylinder-forming SBS1102/PS4K and SBS1102/PS12K, domain straightening/lengthening process is observed before their homogeneous melting, and there are no long-range composition fluctuations before their melting due to the inherently weak segregation forces between the block domains; 2) In case of perpendicular cylinder-forming SBS1102/PS17K, long-range orientation transition from perpendicular to parallel is observed before their composition fluctuations. In comparison to the cases of SBS1102/PS4K and SBS1102/PS12K, SBS1102/PS17K displays longer-lived composition fluctuation before its homogeneous melting due to its relatively stronger segregation forces between the block domains; and 3) In case of perpendicular cylinder-forming SBS1102/PS21K and SBS1102/PS27K, long-range hexagonal lattice disordering is identified before composition fluctuation, and there are also long-lived composition fluctuations before melting due to the strong segregation forces between the block domains. We note that the parallel cylinder orientation of SBS1102 is spontaneously transferred to a perpendicular one as the molecular weight ratio between the homologous PS pair (i.e., PS homopolymer to PS block) approaches to unity (SBS1102/PS17K, $\alpha = 1.01$), as long as the ratio is approximately up to 1.61. In addition, it is also notable that such orientation transition corresponds to the temperature-dependent phase behavior of SBS1102/PS17K, which would occur by lowering the annealing temperature. Therefore, we realize that thermodynamic driving forces involved in temperature-dependent phase behaviors are similar to those involved in homopolymer molecular weight-dependent phase transition.
Figure 6.7. AFM images of SBS1102/PS4K blend at different temperatures: (a) SBS/PS4K 120, (b) SBS/PS4K 150, (c) SBS/PS4K 170, and (d) SBS/PS4K 190. Images were obtained from ~10 µm-thick samples annealed on Teflon substrates at 120 °C, 150 °C, 170 °C, and 190 °C, respectively. Topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is $2 \times 2 \mu m^2$. 
Figure 6.8. AFM images of SBS1102/PS12K blend at different temperatures: (a) SBS/PS12K 120, (b) SBS/PS12K 150, (c) SBS/PS12K 170, and (d) SBS/PS12K 190. Images were obtained from \( \sim 10 \mu m \)-thick samples annealed on Teflon substrates at 120 °C, 150 °C, 170 °C, and 190 °C, respectively. Topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is \( 2 \times 2 \mu m^2 \).
Figure 6.9. AFM images of SBS1102/PS17K blend at different temperatures: (a) SBS/PS17K 120, (b) SBS/PS17K 150, (c) SBS/PS17K 170, and (d) SBS/PS17K 210. Images were obtained from ~10 μm-thick samples annealed on Teflon substrates at 120 °C, 150 °C, 170 °C, and 210 °C, respectively. Topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is $2 \times 2 \mu m^2$. 
Figure 6.10. AFM images of SBS1102/PS21K blend at different temperatures: (a) SBS/PS21K 120, (b) SBS/PS21K 150, (c) SBS/PS21K 170, and (d) SBS/PS21K 190. Images were obtained from ~10 µm-thick samples annealed on Teflon substrates at 120 °C, 150 °C, 170 °C, and 190 °C, respectively. Topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is $2 \times 2 \mu m^2$. 

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Figure 6.11. AFM images of SBS1102/PS27K blend at different temperatures: (a) SBS/PS27K 120, (b) SBS/PS27K 150, (c) SBS/PS27K 170, and (d) SBS/PS27K 190. Images were obtained from ~10 μm-thick samples annealed on Teflon substrates at 120 °C, 150 °C, 170 °C, and 190 °C, respectively. Topographic and phase AFM images were the same. The inset of the AFM image is a 2D FFT of the image. The size of the image is $2 \times 2 \, \mu m^2$. 
6.7. Theoretical Consideration of Transition to Perpendicular Orientation: Increased Incompatibility with an Addition of Homopolymer

If we assume that the contributions of homologous PS pair (i.e., PS block and PS homopolymer) to the domain-domain incompatibility routinely depend on their average molecular weight and their individual compositional fraction, we can estimate the $\chi N$ values (where $\chi$ is the Flory-Huggins segmental interaction parameter and $N$ is the degree of polymerization) of block copolymers. At the annealing temperature of 120°C, the calculated $\chi N$ values are almost similar according to the different PS homopolymers blended into SBS1102 as mentioned in Chapter 4 and 5. These similar $\chi N$ values, however, neither provide a critical explanation on the homopolymer-driven cylinder orientation transition phenomenon nor reasonably explain the different temperature-dependent phase behaviors of perpendicular cylinder-forming block copolymers. Note that the perpendicular cylinder orientation is not obtained when the molecular weight of blended homopolymer (i.e., the incompatibility between the block domains) is routinely increased; rather it is achieved when the molecular weight ratio between the homologous PS pair approaches to unity, as long as the ratio is approximately larger than 1.01. Furthermore, the exceptionally strong preference for perpendicular orientation in SBS1102/PS21K cannot be described by its $\chi N$ values nearly identical to that of SBS1102/PS12K and SBS1102/PS17K. Therefore, we provide an alternative thermodynamic consideration for the block copolymer orientation transition phenomena at a fixed composition as reported in Chapter 4.
The relative interfacial area changes after the orientation conversion process from parallel to perpendicular can be determined by using experimentally determined cylinder dimensions based on the microdomain parameters from the SAXS profiles in Table 12 and the earlier equations (4.5-4.9) as suggested in Chapter 4. Here, it is noted that we do not consider any types of thermodynamic driving forces involved in the cylinder orientation transition in order to estimate above equations since we use the experimentally (i.e., thermodynamically and kinetically) obtained microdomain dimensions to calculate the changes of the interfacial areas and the excess free energies owing to the geometric transition from parallel to perpendicular.

As shown in the changes of microdomain parameter in Table 12, the domain periodicity and the radius of PS domain slightly increase when PS4K and PS12K is blended in SBS1102. With PS17K addition, however, sudden increases are observed in the domain periodicity and radius (Table 12), which enable the transition from the parallel orientation (SBS1102/PS4K, the molecular weight ratio of PS homopolymer to PS block in SBS1102, $\alpha = 0.24$, and SBS1102./PS12K, $\alpha = 0.71$) into the perpendicular orientation (SBS1102/PS17K, $\alpha = 1.01$). Adding higher molecular weights of PS homopolymer than those of 17 kg/mol slightly increases the PS domain periodicity and radius and holds the perpendicular orientation in the SBS1102/PS blends. Above the range of molecular weight of 27 kg/mol, the samples show the macro-phase separations. The behavior of PS microdomain periodicity and size has same trends as determined in SIS4114/PS blending system (Chapter 4.), after or before the microdomain orientation transitions.
In order to compare the interfacial areas and energies of perpendicular cylinders to those of parallel cylinders, we’ve designated the dimensional parameters of SBS1102/PS12K as reference dimensional values for parallel cylinders because the PS block composition of SBS1102/PS12K is most similar to those of SBS1102/PS17K, SIS4114/PS21K and SIS4114/PS27K. The calculation fixes the reference ratio between perpendicular and parallel domain-domain excess free energies at 1, since there is no parallel to perpendicular transition free energy in the parallel microdomain orientation of SBS1102/PS12K. The calculated values in the third column of Table 13 \( \frac{A}{A_0} \) show the changes of the ratio between perpendicular and parallel domain-domain excess free energies as a function of different molecular weights of PS homopolymer added in SBS1102/PS blends having a perpendicular microdomain structure. We note that these \( \frac{A}{A_0} \) values decrease when the homopolymer PS17K and others with higher molecular weights are blended into SBS1102 and the parallel structure transfers into perpendicular orientation. We also note that the decrease in \( \frac{A}{A_0} \) is rather larger for PS17K addition and further increases of molecular weight of added PS homopolymer result in smaller decreases in the ratio of excess free energy and result in the desirable perpendicular microdomain structure. Based on the SAXS measurement, its microdomain parameters, and the equations (4.5-4.9), therefore, the addition of PS17K \( (\alpha = 1.01) \) into SBS1102 suddenly decreases the perpendicular domain-domain excess free energy in comparison to the reference value in SBS1102/PS12K \( (\alpha = 0.71) \), thus resulting in the parallel to perpendicular transition.

The fourth column of Table 13 shows the changes in the ratio of the majority component-substrate interfacial areas between the perpendicular and the parallel
microdomain structures, $A_{\text{major}}/A_{\text{major,0}}$, and its corresponding ratio of excess free energy. This value increases abruptly when the PS17K is blended into SBS1102, since all perpendicular minority microdomains orient normal to the substrates and the many portions of minority-substrate interfacial areas are replaced by those of majority-substrate. After the perpendicular orientation is transited from the parallel microdomain, its corresponding ratio of excess free energy decreases as the higher molecular weight of PS homopolymer is added into SBS1102, which results in stronger preference for the perpendicular microdomain structures. As shown in the fifth column of Table 13, the calculated results show the changes in the ratio of the minority component-substrate interfacial areas between the perpendicular and the parallel microdomain structures, $A_{\text{minor}}/A_{\text{minor,0}}$, and the corresponding ratio of excess free energy. The value decreases abruptly when the PS17K is blended into SBS1102, since the perpendicular minority microdomain starts orienting in the direction normal to the substrates. Stronger preferences for the perpendicular microdomain structures are expected as higher molecular weights of PS homopolymer are added into SIS4114 and the corresponding ratios of excess free energy decrease. In addition, we geometrically realize that the change of interfacial area between the block domains is the most critical factor for the cylinder orientation transition due to its largest fraction (see the sixth, seventh, and eighth columns of Table 13). Considering the calculated results together with our experimental results, therefore, we conclude that perpendicular orientation-inducing thermodynamic conditions such as the blending of minority homopolymer with appropriate molecular weight ($1.01 \leq a \leq 1.61$) and the lowering of annealing temperature should involve sufficient lowering of excess free energy in the block domains to obtain parallel to
perpendicular microdomain transitions. Thus, such unusual cylinder orientation transition occurs spontaneously in the block copolymer mixtures used in this study, when the molecular weight ratios and the annealing temperature conditions are right. We consider the interaction between the homopolymer and its corresponding block component, with the interaction strength depending on the molecular weight difference between them, as an exothermic interaction force surpassing the domain-domain excess free energy (i.e., generating an additional increase of incompatibility between the block components). We note that our proposed intermolecular interaction is different from the well-known secondary forces such as electrostatic, hydrogen bonding and van der Waals interactions. There would not be significant charge-charge, charge-dipole and hydrogen bonding interactions between the homologous PS pair due to the absence of charges and hydrogen bonding-generating functional groups in the PS components. In addition, the dipole-dipole and van der Waals interactions of PS pair that generally increase with increasing the molecular weight of polymer components might not be a candidate for the thermodynamic compensation since the amount of compensation depends on the molecular weight ratio between the polymer pair, rather than their absolute molecular weight as mentioned in Chapter 4.

When the relatively low molecular weight of 12K of the PS homopolymer is added into SBS1102, the interaction energy between the homologous PS pair is low due to the low molecular weight of PS homopolymer, ($\alpha = 0.71$) and hence the initial parallel cylinders in neat SBS1102 are straightened after the blending of PS12K (or after the increase of annealing temperature) simply owing to the decreased incompatibility between the block components. On the other hand, the interaction force (i.e., significant
amount of heat of mixing) between the homologous PS pair will be generated in SBS1102/PS17K ($\alpha = 1.01$) owing to the high enough molecular weight similar to the molecular weights of PS block in SBS1102. Since the homologous pair interaction induces an additional enhancement of incompatibility between the PS and PB components by virtue of strong segregation between the homologous PS pair, the actual incompatibility of SBS1102/PS17K will be much higher than the incompatibility predicted by the Flory-Huggins theory.

The effects of the variation of annealing temperature on the ordering of BCPs/homopolymer mixtures can be investigated by the calculated results in this part and the investigations studied in this part can be also compared to those of the study at different annealing temperatures as determined in the previous Section 6.6. The morphologies of orientation are studied by changing the annealing conditions at a fixed homopolymer molecular weight and volume fraction, which results in well-ordered and persistent structures. We note that the degree of incompatibility (i.e. the preference for perpendicular cylinder orientation) will gradually decrease as the temperature increases. Thus, the perpendicular cylinders in SBS1102/PS17K ($\alpha = 1.01$) mixture achieved at relatively lower temperature can be transferred to parallel ones at higher temperature if the incompatibilities between the blocks and their preference for perpendicular orientation are not strong enough to overcome the entropic effects arising from the increase of temperature. In case of perpendicular cylinder-forming SBS1102/PS21K ($\alpha = 1.25$) and SBS1102/PS27K ($\alpha = 1.61$), the interaction energies between the homologous PS pair will increase significantly due to the increased molecular weights of the corresponding PS homopolymers, and hence the cylinders display exceptionally strong
preference for perpendicular orientation even at high annealing temperatures (i.e., even at an extremely unfavorable condition for a perpendicular cylinder orientation). In case of the parallel cylinders in SBS1102/PS12K ($\alpha = 0.71$) formed at relatively lower temperature, the straightness of their arrays is expected to be enhanced with the increase of temperature due to the decrease of incompatibility. These above results investigated in this part are also apparently similar to those of Chapter 4, even though the block copolymer has different chemical structure, composition, and molecular weight.

Table 13. Changes of domain-domain interfacial area and excess free energy after the parallel-to-perpendicular cylinder orientation transition in SBS1102/PS blends

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Sample</th>
<th>$A/A_0$</th>
<th>$A_{\text{major}}/A_{\text{major},0}$</th>
<th>$A_{\text{minor}}/A_{\text{minor},0}$</th>
<th>$f_{\text{domain,}0}$</th>
<th>$f_{\text{majority,}0}$</th>
<th>$f_{\text{minority,}0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SBS1102/PS17K</td>
<td>0.798</td>
<td>1.527</td>
<td>0.439</td>
<td>0.548</td>
<td>0.356</td>
<td>0.096</td>
</tr>
<tr>
<td>$m = 1$</td>
<td>SBS1102/PS21K</td>
<td>0.758</td>
<td>1.499</td>
<td>0.419</td>
<td>0.524</td>
<td>0.384</td>
<td>0.092</td>
</tr>
<tr>
<td></td>
<td>SBS1102/PS27K</td>
<td>0.730</td>
<td>1.482</td>
<td>0.406</td>
<td>0.506</td>
<td>0.404</td>
<td>0.090</td>
</tr>
<tr>
<td></td>
<td>SBS1102/PS17K</td>
<td>0.798</td>
<td>1.527</td>
<td>0.439</td>
<td>0.859</td>
<td>0.111</td>
<td>0.030</td>
</tr>
<tr>
<td>$m = 5$</td>
<td>SBS1102/PS21K</td>
<td>0.758</td>
<td>1.499</td>
<td>0.419</td>
<td>0.846</td>
<td>0.124</td>
<td>0.030</td>
</tr>
<tr>
<td></td>
<td>SBS1102/PS27K</td>
<td>0.730</td>
<td>1.482</td>
<td>0.406</td>
<td>0.837</td>
<td>0.134</td>
<td>0.030</td>
</tr>
</tbody>
</table>

**the corresponding fraction of interfacial area for SBS1102/PS12K**
6.8. Concluding Remarks

This study has also investigated a very effective method to achieve a regularly ordered structure across long range scales, the orientation can be controlled by using self-organizing materials, whose assembly is ordered and directed by various molecular interactions (and their combination). We employ a method of modifying the thermodynamic conditions with PS homopolymers and a triblock copolymer (SBS1102), possessing an initial orientation preference for parallel and perpendicular mixed structures on a preferential substrate, by increasing the interaction energies between the homologous polymer pair at a fixed blending composition. This is achieved without any external field application or modification of interfacial energy between the sample and the substrate. When the molecular weight of homopolymer is relatively lower than that of the corresponding minority block component \( a \leq 0.71 \), the chains of PS homopolymer tends to homogeneously solubilize together with the PS microdomains, the PS microdomains swell, the average distance between the neighboring chemical junctions of the block copolymer stretches, and the interfacial area between the block domains is decreased. Thus, the added PS homopolymer into SBS1102 enables the domain periodicity slightly increase and the straightness of parallel cylinders increase. As the molecular weight of the homopolymer chains \( 1.01 \leq a \leq 1.61 \) increases further, the ratio between perpendicular and parallel domain-domain excess free energies decreases. Thus, the perpendicular microdomain orientation on the preferential substrates is accomplished. The parallel to perpendicular transition is also affected with the sudden increases of the domain periodicity and size caused by a localization of the chains of
these homopolymers into the center of the PS block in the microphase separated samples. The addition of further increases of molecular weight of PS homopolymers results in macrophase separations. When the incompatibilities between the blocks and their preference for perpendicular orientation are not strong enough to overcome the entropic effects arising from the increase of annealing temperatures, the perpendicular-to-parallel cylinder orientation transition is detected at higher annealing temperatures, i.e. unfavorable condition. When the interaction energies between the PS block component and PS homopolymer increase significantly due to the highly increased molecular weights of the corresponding chains of PS homopolymer ($1.25 \leq a \leq 1.61$), an exceptionally strong segregation forces between the PS homologous pair results in more stable perpendicular orientation even under unfavorable conditions. Therefore, we conclude that the amount of segregation forces (i.e., the actual incompatibility) between the block domains is a critical factor to determine the phase behavior of BCPs/homopolymer mixtures.
CHAPTER VII
THE EFFECT OF INTERFACIAL INTERACTIONS BETWEEN BLOCKS AND SURFACE OF SUBSTRATE: PS-PI-PS TRIBLOCK COPOLYMER (VECTOR 4114) AND PS-PB-PS TRIBLOCK COPOLYMER (KRATON D1102K)

7.1. Introduction

The parallel orientation of block copolymer microstructures has been attributed to the presence of preferential interaction between the substrate (or air) and one of the block components [111,118,179]. One way of achieving a perpendicular orientation of microdomains is to remove or balance all interfacial interactions, i.e., use non-preferential or neutral surfaces. Under these conditions, a perpendicular orientation is favored over a parallel arrangement because of an entropic effect [109,129]. Peters et al. [20] demonstrated control of interfacial interactions by the modification of self-assembling monolayer (SAM) substrates. Symmetric, neutral, and asymmetric wetting of block copolymer thin films can be achieved on modified SAM substrates to control the block copolymer thin film orientations. Kellogg et al. [19] achieved the same objective by placing random copolymers, consisting of the same monomeric units as the diblock copolymer, at the confining surfaces. In order to avoid potential diffusion of the random copolymers into the confined diblock layer, Mansky et al. [69,111] anchored brushes of
random copolymers of PS-r-PMMA to silicon substrates, and capped surface-philic perfluorodecanoyl-terminated PS-r-PMMA random copolymers at the PS-b-PMMA block copolymer/air interface. The compositions of the random copolymers were tailored so that neutral surfaces could be achieved at both substrate and air interfaces. Symmetrical lamellae as well as asymmetrical cylindrical PS-b-PMMA block copolymer microdomains were found to orient perpendicular to the interfaces throughout the entire film thickness.

Rather than on neutral substrate, perpendicular cylinder microdomains have been readily achieved in thin films on a preferential substrate without the need for additional surface treatments to obtain neutral substrate [90]. In case of asymmetric block copolymers including the cylinder-forming asymmetric PS-PB-PS diblock copolymers, the orientation of the cylindrical microdomain was critically dependent on the film thickness, rather than the interfacial interactions between the blocks and the substrates. It was reported that the limitation of thickness in SBS1102 triblock copolymer is ~42nm to manipulate the perpendicular cylinder orientation on whole area and both mesophase orientations were reported above the thickness of ~42nm. In addition, theory and simulation have predicted that the perpendicular cylinder orientation may be stable in thin films on preferential substrates [196,197]. By considering the free energy difference between parallel and perpendicular cylinder orientations on a preferential substrate, it was predicted that the probability for perpendicular orientation increased as the film thickness decreased [196]. Similarly, a Monte Carlo simulation for cylinder-forming asymmetric ABA triblock copolymer also predicted that perpendicular cylinders were stably formed in a thin film on a preferential substrate over a wide-range of substrate-block interaction,
even though the range of interaction gradually decreases with increasing film thickness [197]. Thus, the equal interfacial interactions between the blocks and the substrates cannot be considered as an essential requirement for the perpendicular orientation of block copolymer cylinders, because the perpendicular cylinders are readily formed in thin films on a preferential substrate, and the cylinder orientation achieved on a neutral substrate also depends on film thickness. It is notable that the perpendicular cylinder orientation achieved on a neutral substrate should remain invariant regardless of the film thickness if the equal interfacial interaction is critical for the perpendicular cylinder orientation. Therefore, it can be concluded that eliminating a preferential interaction is not an effective approach for the perpendicular orientation of cylinder microdomain due to its insignificant influence on block copolymer microstructures in comparison with the effect of film thickness.

We have illustrated a rapid method to induce perpendicularly oriented cylindrical microdomain by blending various BCPs with homopolymer of the same structure with a minor component in the triblock copolymer. Control of the homopolymer molecular weight enables changes in the periodic spacing and hexagonal orientation of the perpendicular nanocylinders. Thus, the method to control perpendicular ordering on large scale throughout the area in asymmetric triblock copolymers is demonstrated by simply adjusting thermodynamic conditions for BCP/homopolymer blends.

Furthermore, it is determined that the control of substrate-polymer interaction and modification of the substrate surface do not necessarily influence the perpendicular orientation process of the cylinders, especially when a thermodynamic preference for perpendicular orientation is already strongly introduced into the material by the blending,
in the BCPs, of a homopolymer of an appropriate molecular weight. In this chapter, we employ systems untested in previous efforts of my research group [36]. Vector 4114 (Dexco Polymers Co.) and polystyrene-polybutadiene-polystyrene (SBS) block copolymer Kraton D1102K (Kraton Polymers Co.) are used for this purpose. Each sample is annealed on Si, Kapton, Mylar, and Teflon substrates, which have different interfacial energies with block components. The objectives of this part of the study are to investigate the interplay of the substrate interfacial interaction energies with the blocks and the domain-domain excess free interfacial energy and their effect on the perpendicular microdomain orientation.

7.2. Experimental Methods

A commercially available polystyrene-polyisoprene-polystyrene (SIS) block copolymer Vector 4114 (Dexco Polymers Co.) and polystyrene-polybutadiene-polystyrene (SBS) block copolymer Kraton D1102K (Kraton Polymers Co.) were used. Vector 4114 contains 15 wt % (13 vol %) PS and has a weight-average molecular weight ($M_w$) of 152000 g/mol and a polydispersity ($M_w/M_n$) of 1.05. Kraton D1102K contains 29 wt % (24 vol %) PS and has a weight-average molecular weight ($M_w$) of 117600 g/mol and a polydispersity ($M_w/M_n$) of 1.10. Various molecular weights of polystyrene (PS) were used in the BCPs/PS blends. All the polymers and chemicals were used without further purification. Information about the polymers used in this study is summarized in Table 2.
PS homopolymers having different molecular weight were mixed into SIS4114 and SBS1102 with 0.05 wt % of antioxidant (Irganox 1010, Ciba-Geigy Group). Two different series of blending mixture (SIS4114/PS and SBS1102/PS) were blended with toluene as a solvent. The blending composition was fixed at 10 wt % of PS homopolymers and 90 wt % of BCPs. Information on blended samples, such as the molecular weight ratio of PS homopolymer to PS block in the BCPs ($\alpha$), the weight fraction of PS phase ($W_{PS}$), and the volume fraction of PS phase ($\Phi_{PS}$) in BCPs and BCP/PS blends are summarized in Table 14 (SIS4114/PS mixtures) and Table 15 (SBS1102/PS mixtures). BCPs/homopolymer films on the 3 in. diameter Si substrate were prepared by spin-coating the filtered solution directly. A Gaertner model L116C ellipsometer measured the film thickness values of 90 to 110 nm on the Si substrate. Relatively thicker film samples between 300 nm and a few tens of micrometers were also prepared by solution casting onto selected PI, PET, and Teflon substrates. The solvent in BCPs/homopolymer solutions was slowly evaporated at ambient condition for 2 days and then in a vacuum oven at 50 °C for a day. Finally, the residual solvent was removed and at the same time, all the samples were annealed in a vacuum oven at different annealing temperatures of 120 °C (SIS4114/PS mixtures) and 130 °C (SBS1102/ps mixtures).

The orientation behavior and structures at the surface of the samples on different substrates were determined with a tapping mode AFM (Nanoscope III, Digital Instruments) under ambient conditions using commercial silicon microcantilever probe tips (Veeco, RTESP5). Height and phase modes were recorded simultaneously using spring constants ranging between 20 and 80 N/m and a resonance frequency of ~280 kHz.
Table 14. Summary of the molecular and volumetric information in the SIS4114/PS blends

<table>
<thead>
<tr>
<th>sample name</th>
<th>$\alpha$</th>
<th>$W_{PS}$</th>
<th>$\Phi_{PS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIS4114/PS12K</td>
<td>1.05</td>
<td>0.157</td>
<td>0.136</td>
</tr>
<tr>
<td>SIS4114/PS17K</td>
<td>1.49</td>
<td>0.160</td>
<td>0.138</td>
</tr>
<tr>
<td>SIS4114/PS21K</td>
<td>1.84</td>
<td>0.163</td>
<td>0.140</td>
</tr>
<tr>
<td>SIS4114/PS27K</td>
<td>2.37</td>
<td>0.166</td>
<td>0.144</td>
</tr>
</tbody>
</table>

$\alpha$: the molecular weight ratio of PS homopolymer to PS block in the BCP, $W_{PS}$: the weight fraction of PS phase, and $\Phi_{PS}$: the volume fraction of PS phase
<table>
<thead>
<tr>
<th>sample name</th>
<th>$\alpha$</th>
<th>$W_{PS}$</th>
<th>$\Phi_{PS}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBS1102/PS17K</td>
<td>1.01</td>
<td>0.297</td>
<td>0.250</td>
</tr>
<tr>
<td>SBS1102/PS21K</td>
<td>1.25</td>
<td>0.300</td>
<td>0.252</td>
</tr>
<tr>
<td>SBS1102/PS27K</td>
<td>1.61</td>
<td>0.303</td>
<td>0.256</td>
</tr>
</tbody>
</table>

$\alpha$: the molecular weight ratio of PS homopolymer to PS block in the BCP, $W_{PS}$: the weight fraction of PS phase, and $\Phi_{PS}$: the volume fraction of PS phase.
7.3. Interfacial Interactions between the Blocks and the Substrates: Vector 4114/PS Blends

At the minimum sample thickness \( m = 1 \), a thermodynamic compensation overcomes the excess free energy between the block domains, which occurs after the parallel-to-perpendicular cylinder orientation transition. The sixth, seventh and eighth columns of Table 7 show the fractional changes of interfacial areas between each of the block domains and the substrate after the cylinder orientation transition. In cases of thin film samples, therefore, the perpendicular domain-domain free energy can also be relieved by the excess free energy between each of the block components and the substrate, i.e., 1) by enlarging the fraction of the interfacial area between the substrate and its relatively majority block component, and at the same time, 2) by reducing the fraction of the interfacial area between each microdomain and the fraction of the interfacial area between the substrate and its minority block component. The perpendicular domain-domain free energy, originating from the parallel-to-perpendicular cylinder orientation transition, will be relieved on the fluorine substrates, which are less preferential to the PI block because the fraction of the interfacial area between the fluorine substrates and the minority PS domain will decrease after achieving perpendicular cylinder orientation (See the eighth column of Table 7). However, the changes in the fraction of the interfacial area between the minority microdomain and the substrate are small compared to those of the fraction of the interfacial area between each microdomain or the fraction of the interfacial area between the substrate and its relatively majority block component. Furthermore, the fraction of the interfacial area is almost the
same at m = 5. Thus, the increasing fraction of the interfacial area between its relatively majority block component and the substrate is the most critical factor in reducing the interfacial area fraction between the blocks and it enables the decreases of the perpendicular domain-domain excess free energies. In addition, the compensational effects of strong homologous PS pair interaction results in the perpendicular microdomain orientations. Thus, perpendicular block copolymer cylinders in a thin film sample would partially lose their perpendicular orientation on a substrate which has a higher interfacial interaction to the majority block if the homologous pair interaction is not strong enough to thoroughly overcome the total excess free energy between the block domains in addition to that originating from the substrate and the majority component interaction.

Figure 7.1 shows the AFM images of SIS4114/PS12K annealed at 130 °C on Si substrate (a), Kapton substrate (b), Mylar substrate (c), and Teflon substrate (d), respectively. As shown in Figure 7.1 (b) and (c), SIS4114/PS12K sample has some amount of parallel cylinders on Kapton and Mylar substrates, which are relatively favorable to the majority PI block, due to the insufficient strength of homologous pair interaction, since the interfacial energy between the PI and the Kapton substrate is ~6 mJ/m² and that between the PI and the Mylar is ~9 mJ/m² at 130 °C [198]. On the other hand, complete perpendicular cylinder orientation is observed with a higher sample thickness on the Teflon substrates, which are much less favorable to the majority PI block, with the interfacial energy between the PI and the Teflon being ~2 mJ/m² at 130 °C [198]. We note that the amount of parallel cylinders is proportional to the interfacial energy between the majority block component and the substrate, i.e., apparently larger amount of
parallel cylinders is observed on the Mylar substrate in comparison to the Kapton substrate. However, it is notable that the overall perpendicular cylinder orientation is still maintained in the thin film sample of SIS4114/PS12k on the Kapton and the Mylar substrates in spite of the small amount of parallel cylinders. The AFM results in Figure 7.1 (b) and (c) were obtained with the film thicknesses up to ~420 nm on Kapton substrate and ~360 nm on Mylar substrate, respectively. When each sample has a thickness higher than ~600 nm on both substrates, the limitation of the sample thickness effects on the microdomain orientations into the samples on Kapton and Mylar substrate and the overall parallel microdomain orientations are observed.

Figure 7.2 shows the AFM images of SIS4114/PS17K annealed at 130 °C on Si substrate (a), Kapton substrate (b), Mylar substrate (c), and Teflon substrate (d), respectively. As shown in Figure 7.2 (b), SIS4114/PS17K sample does not have any parallel cylinders on the Kapton while they are observed with the SIS4114/PS12K on the same substrate. However, SIS4114/PS17K still has some amount of parallel cylinders on Mylar substrates (more favorable to the majority PI block than Kapton substrate), as shown in Figure 7.2 (c). The homologous PS pair interaction is not enough to overcome the higher interfacial interaction energy between the block and the Mylar substrate. Here, we also note that the amount of parallel cylinders is proportional to the interfacial energy between the majority block component and the substrate, i.e., apparently some amounts of parallel cylinders are observed on the Mylar substrate, while none are observed on the Kapton substrate.

Figure 7.3 also shows the AFM images of SIS4114/PS27K annealed at 130 °C on Si substrate (a), Kapton substrate (b), Mylar substrate (c), and Teflon substrate (d),
respectively. As shown in Figure 7.3 (b), SIS4114/PS27K also does not produce any parallel microdomain orientation on the Kapton. However, SIS4114/PS27K still keeps some amount of parallel cylinders on Mylar substrates (more favorable to the majority PI block than Kapton substrate), as shown in Figure 7.3 (c). The interfacial interaction energy between the block and Kapton substrate can still be overcome by the strong homologous PS pair interaction in the microdomains in SIS4114/PS27k on Kapton substrate. The homologous PS pair interaction in SIS4114/PS27k, however, is not still enough to overcome the higher interfacial interaction energy between the block and Mylar substrate, even though the microdomain interaction has a stronger preference for the perpendicular orientation in comparison to that of the SIS4114/PS12K.

In the presence of a considerable interaction between the homologous PS pair on the substrates with a relatively higher interfacial interaction energy, i.e. between PI and Kapton substrate, therefore, the interfacial energy between each of the block components and the substrate would be overcome by the interplay of the strong interaction between the homologous PS pair, the decreased excess free interfacial energy of perpendicular domain-domain, and the reduced interfacial area fraction between the blocks.
Figure 7.1. AFM images of SIS4114/PS12K annealed at 130 °C on different substrates: (a) ~100 nm thick samples on Si substrate, (b) ~420 nm thick samples on Kapton substrate, (c) ~360 nm thick samples on Mylar substrate, and (d) ~10 µm thick samples on Teflon substrate. The size of the image is $2 \times 2 \, \mu m^2$. 
Figure 7.2. AFM images of SIS4114/PS17K annealed at 130 °C on different substrates: (a) ~100 nm thick samples on Si substrate, (b) ~420 nm thick samples on Kapton substrate, (c) ~360 nm thick samples on Mylar substrate, and (d) ~10 µm thick samples on Teflon substrate. The size of the image is $2 \times 2 \ \mu m^2$. 
Figure 7.3. AFM images of SIS4114/PS27K annealed at 130 °C on different substrates: (a) ~100 nm thick samples on Si substrate, (b) ~420 nm thick samples on Kapton substrate, (c) ~360 nm thick samples on Mylar substrate, and (d) ~10 μm thick samples on Teflon substrate. The size of the image is $2 \times 2 \ \mu m^2$. 
7.4. Interfacial Interactions between the Blocks and the Substrates: Kraton D1102K/PS Blends

Figure 7.4 shows the AFM images of SBS1102/PS17K annealed at 120 °C on Si substrate (a), Kapton substrate (b), Mylar substrate (c), and Teflon substrate (d), respectively. As shown in Figure 7.4 (c), SBS1102/PS17K sample has some amount of parallel cylinders on Mylar substrates (relatively favorable to the majority PB block, the interfacial energy between the PB and the Mylar is ~7 mJ/m² at 120 °C [198]) due to its insufficient strength of homologous pair interaction, even though its complete perpendicular cylinder orientation is observed with a higher sample thickness on the Kapton substrate (relatively less favorable to the majority PB block, the interfacial energy between the PB and the Kapton is ~5 mJ/m²) and Teflon substrate (relatively much less favorable to the majority PB block, the interfacial energy between the PB and the Teflon is ~2 mJ/m² at 120 °C [198]). Here, we also note that the amount of parallel cylinders is proportional to the interfacial energy between the majority block component and the substrate, i.e., apparently larger amount of parallel cylinders is observed on the Mylar substrate in comparison to the Kapton substrate. The AFM measurement and its results in Figure 7.4 (b) and (c) are determined with the film thickness up to ~450 nm on Kapton substrate and ~390 nm on Mylar substrate, respectively. When each sample has a thickness higher than ~1000 nm (1 µm) on both substrates, the limitation of the sample thickness effects on the microdomain orientations into the samples on Kapton and Mylar substrate and then the overall parallel microdomain orientations are observed.
Figure 7.5 shows the AFM images of SBS1102/PS21K annealed at 120 °C on Si substrate (a), Kapton substrate (b), Mylar substrate (c), and Teflon substrate (d), respectively. As shown in Figure 7.5 (c), SBS1102/PS21K sample does not have any parallel cylinders on the Mylar substrate which is observed in the SBS1102/PS17K on the same substrate (Figure 7.4 (c)); owing to its strong homologous PS pair interaction overwhelming the domain-substrate interfacial interactions. In addition, SBS1102/PS21K still has the perpendicular cylinders on the whole area of Kapton substrates (more unfavorable to the majority PB block than Mylar substrate), as shown in Figure 7.5 (b).

Figure 7.6 also shows the AFM images of SBS1102/PS27K annealed at 120 °C on Si substrate (a), Kapton substrate (b), Mylar substrate (c), and Teflon substrate (d), respectively. As shown in Figure 7.6 (b) and (c), SBS1102/PS27K sample still has no parallel microdomain orientation on Kapton substrate and Mylar substrate, respectively. The interfacial interaction energy between the block and Kapton substrate and Mylar substrate can still be overcome by the strong homologous PS pair interaction in the microdomains in SBS1102/PS27k.

As shown in the sixth, seventh and eighth columns of Table 13, after the cylinder orientation transition, the fractional changes of interfacial areas between each of the block domains and the substrate are determined with a similar trend as mentioned in the above Section 7.3 and shown in Table 7. The changes of the fraction of the interfacial area between minority microdomain and substrate are still small compared to those of the fraction of the interfacial area between each microdomain or the fraction of the interfacial area between the substrate and its relatively majority block component. Furthermore, the fraction of the interfacial is same at m = 5. (See the eighth column of Table 13) Thus, the
increasing fraction of the interfacial area between its relatively majority block component and the substrate is the most critical factor to reduce the interfacial area fraction between the blocks and enables the decreases of the perpendicular domain-domain excess free energies as determined in the study of SBS1102/PS mixtures. Here, the compensational effects of strong homologous PS pair interaction also results in the perpendicular microdomain orientations. Therefore, the investigation of the changes of domain-domain interfacial area and excess free energy after the parallel-to-perpendicular cylinder orientation transition in SBS1102/PS blends also agree that the perpendicular block copolymer cylinders in a thin film sample would partially lose their perpendicular orientation on a substrate which has a higher interfacial interaction to the majority block if the homologous pair interaction is not strong enough to thoroughly overcome the total excess free energy; one is mainly due to that between the block domains, and the other additionally originates from that between the substrate and the majority component.

It is notable that the investigations in this part also agree that the interplay of the strong interaction between the homologous PS pair, the decreased excess free interfacial energy of perpendicular domain-domain, and the reduced interfacial area fraction between the blocks would also overcome the limitation of the relatively higher interaction between majority block component and the substrate into the perpendicular microdomain orientation.
Figure 7.4. AFM images of SBS1102/PS17K annealed at 120 °C on different substrates: (a) ~95 nm thick samples on Si substrate, (b) ~450 nm thick samples on Kapton substrate, (c) ~390 nm thick samples on Mylar substrate, and (d) ~10 μm thick samples on Teflon substrate. The size of the image is $2 \times 2 \, \mu m^2$. 
Figure 7.5. AFM images of SBS1102/PS21K annealed at 120 °C on different substrates: (a) ~95 nm thick samples on Si substrate, (b) ~450 nm thick samples on Kapton substrate, (c) ~390 nm thick samples on Mylar substrate, and (d) ~10 μm thick samples on Teflon substrate. The size of the image is 2 × 2 μm².
Figure 7.6. AFM images of SBS1102/PS27K annealed at 120 °C on different substrates: (a) ~95 nm thick samples on Si substrate, (b) ~450 nm thick samples on Kapton substrate, (c) ~390 nm thick samples on Mylar substrate, and (d) ~10 μm thick samples on Teflon substrate. The size of the image is 2 × 2 μm².
7.5. Interfacial Interactions between the Blocks and the Substrates: Summary

In Sections 7.3 and 7.4, AFM results on each blended sample were interpreted based on different interfacial energies between each majority block component and the substrate. Here, the interplay of the reduced interfacial area fraction between the blocks and the decreased excess free energy of perpendicular domain-domain, and their effect on the perpendicular microdomain orientation are described according to different interactions between the homologous PS pair. Figure 7.7 and Figure 7.8 show the AFM images on the same substrate (Kapton or Mylar) as a function of different samples by reorganizing the determined results on Kapton and Mylar substrates from Figure 7.1 to Figure 7.6 for additional interpretations.

Figure 7.7 shows the AFM images of different samples on Kapton substrate: (a), (b), and (c) are from ~420nm thick samples of SIS4114 blends with PS12K, PS17K, and PS27K, respectively. (d), (e), and (f) are from ~450nm thick samples of SBS1102 blends with PS17K, PS21K, and PS27K, respectively. SIS4114/PS12K on Kapton substrate has the mixed orientation, as shown in Figure 7.7 (a). SIS4114/PS17K and SIS4114/PS27K on the same substrate show the overall perpendicular microdomain orientations in Figure 7.7 (b) and (c). SBS1102/PS blends also have the overall perpendicular microdomain orientation, as shown in Figure 7.7 (d), (e), and (f).

Figure 7.8 shows the AFM images of different samples on Mylar substrate: (a), (b), and (c) are from ~360nm thick samples of SIS4114 blends with PS12K, PS17K, and PS27K, respectively. (d), (e), and (f) are from ~390nm thick samples of SBS1102 blends with PS17K, PS21K, and PS27K, respectively. All SIS4114/PS mixtures on Mylar
substrate have the mixed orientation, as shown in Figure 7.8 (a), (b), and (c). Only SBS1102/PS17K shows the mixed orientation in Figure 7.8 (e), and SBS1102/PS21K and SBS1102/PS27K on the same substrate show the overall perpendicular microdomain orientations in Figure 7.8 (f) and (g).

In cases of thin film samples, the perpendicular domain-domain free energy could also be relieved from the reduced excess free energy between each of the block components and the substrate by enlarging the fraction of the interfacial area between the substrate and its majority block component and also by reducing the fraction of the interfacial area between each microdomain at the same time. Insufficient strength of homologous pair interaction in SIS4114/PS12K on Kapton substrate restricts the perpendicular microdomain orientation due to the relatively higher interfacial energy between the PI and Kapton (~ 6 mJ/m$^2$ at 130 °C), and its interplay with the reduced interfacial area fraction between the blocks and the decreased excess free interfacial energy of perpendicular domain-domain, as shown in Figure 7.7 (a). Insufficient strength of homologous pair interaction in SBS1102/PS17K on Mylar substrate also limits the perpendicular microdomain structure due to the same reasons, where the interfacial energy between the PB and the Mylar is ~7 mJ/m$^2$ at 120 °C, as shown in Figure 7.8 (d). Furthermore, the unfavorable interfacial interaction between PI block and Mylar substrate (~ 9 mJ/m$^2$ at 130 °C) restricts the perpendicular microdomain orientation even at the relatively strong homologous pair interaction which was determined in the study with the samples annealed at different temperature on Teflon, as shown in Figure 7.8 (a), (b), and (c).
Thus, the results in this part also reveal that the increasing fraction of the interfacial area between the majority block component and the substrate is a critical factor in reducing the interfacial area fraction between the blocks to enable the decrease of the perpendicular domain-domain excess free energies. In addition, the compensational effects of strong homologous PS pair interaction results in the perpendicular microdomain orientations.
Figure 7.7. AFM images of different samples on Kapton: (a), (b), and (c) are from ~420nm thick samples of SIS4114 blends with PS12K, PS17K, and PS27K, respectively. (d), (e), and (f) are from ~450nm thick samples of SBS1102 blends with PS17K, PS21K, and PS27K, respectively. The size of the image is $2 \times 2 \mu m^2$. 
Figure 7.8. AFM images of different samples on Mylar: (a), (b), and (c) are from ~360nm thick samples of SIS4114 blends with PS12K, PS17K, and PS27K, respectively. (d), (e), and (f) are from ~390nm thick samples of SBS1102 blends with PS17K, PS21K, and PS27K, respectively. The size of the image is $2 \times 2 \, \mu m^2$. 
7.6. Concluding Remarks

In this chapter, we have illustrated a spontaneous parallel-to-perpendicular orientation transition of block copolymer nano-cylinders on various preferential substrates by increasing the interaction force between the homologous polymer pair at a fixed composition of minority block component, without any external field application or modification of substrate. For the fabrication of perpendicular block copolymer cylinders on various preferential substrates without a significant influence of film thickness, therefore, we expect that a compensational and direct control of the interaction between the homologous pairs on the relatively low interfacial interaction between the block and the substrate will be more effective than that indirectly modifying the domain-substrate interfacial energies, such as neutralization of substrate surface.

The mixed cylinder microdomain orientation exists in block copolymer mixtures even with a relatively strong homologous polymer pair interaction and a decreased domain-domain excess free energy ($\alpha > 1$), when the interfacial interaction between the majority component and the substrate is high enough to restrict the perpendicular microdomain orientation. In case of overall perpendicular cylinder-forming block copolymer mixture (especially, SIS4114 with PS17K and PS27K, and SBS1120 with PS21K and PS27K), on the other hand, the strong homologous PS pair interaction would overcome the limitation from the relatively high domain-substrate interfacial interactions. Thus, this study also concludes that the exceptional strong segregation force between the homologous pairs is the most important factor to orient the nanocylinder structure normal to the preferential substrate.
8.1. Conclusions

In the first systematic study with a triblock copolymer (SIS4114) and its mixtures with PS homopolymer, this study illustrated a spontaneous and simple method for the orientation of perpendicular cylinders, by increasing the interaction force between the homologous polymer pair at a fixed composition of minority block component without any external field application or modification of interfacial energy between the sample and the substrate. When the molecular weight of homopolymer is relatively lower than that of the corresponding minority block component \((a = 0.35)\), the chains of PS homopolymer tends to be homogeneously solubilized together with the PS microdomains, the PS microdomains swell, the average distance between the neighboring chemical junctions of the block copolymer stretches, and the interfacial area between the block domains decreases. Thus, the added PS homopolymer into SIS4114 enables the domain periodicity slightly increase and the straightness of parallel cylinders increase. As the molecular weight of the homopolymer chains \((1.05 \leq a \leq 2.37)\) increases further, the ratio between perpendicular and parallel domain-domain excess free energies decreases. Thus, the perpendicular microdomain orientation on the preferential substrates is accomplished. The parallel to perpendicular transition is mainly affected by the
exceptionally strong segregation force between the homologous PS pair, which was caused by a localization of the chains of these homopolymers into the center of the PS block in the microphase separated samples. When the incompatibilities between the blocks and their preference for perpendicular orientation are not strong enough to overcome the entropic effects arising from the increase of annealing temperatures, the perpendicular-to-parallel cylinder orientation transition occurs at higher annealing temperatures, i.e. unfavorable condition. When the interaction energies between the homologous PS pair increase significantly due to the highly increased molecular weights of the corresponding chains of PS homopolymer ($1.50 \leq \alpha \leq 2.37$), an exceptionally strong preference for perpendicular orientation is determined even under unfavorable conditions for perpendicular cylinder orientation.

In the second and third systematic studies, we employed same method for the control of the thermodynamic conditions by blending PS homopolymer into SIS4114 and SBS1102, respectively. The investigation with these different blending systems shows same orientation behavior with the results of the first systematic study with SIS4114/homopolymer mixtures. Thus, the domain periodicity slightly increases and the straightness of parallel cylinders is increased in SIS4111/PS mixtures ($\alpha \leq 0.94$) and SBS1102/PS mixtures ($\alpha \leq 0.71$). At the additional increases of molecular weight of PS homopolymers in SIS4111/PS mixtures ($1.33 \leq \alpha \leq 2.11$) and SBS1102/PS mixtures ($1.01 \leq \alpha \leq 1.61$), the perpendicular domain-domain excess free energy decreases and thus the perpendicular microdomain orientation occurs. Further increases of molecular weight of PS homopolymers also result in macrophase separations. In case of perpendicular cylinder-forming mixtures of SBS1102 with PS homopolymer ($1.25 \leq \alpha \leq 2.37$),
the higher interaction energies between the homologous PS pair also displays an exceptionally strong preference for perpendicular orientation even under unfavorable conditions for perpendicular cylinder orientation.

This study has also shown a spontaneous parallel-to-perpendicular orientation transition of block copolymer nano-cylinders on various preferential substrates having different interfacial interaction between block components and substrate. A direct control of the segregation force between the homologous pairs on the relatively low interfacial interaction between the block and the substrate is suggested as a better way to fabricate the perpendicular and cylindrical structures on various preferential and commercial substrates. When the interaction between homologous PS pair is high enough (especially, SIS4114 with PS17K, PS21K, and PS27K, and SBS1120 with PS21K and PS27K), it overcomes the limitation of the relatively high domain-substrate interfacial interactions.

Consequently, this dissertation has shown that the redistribution of a compatible homopolymer blended in certain block copolymers results in a shift of phase boundaries and in the stabilization of well-ordered structures to create new opportunities for nanotechnologies by exploiting thermodynamical changes using temperature variation and by blending a homopolymer with well controlled molecular weight. The addition of homopolymer (A) into an asymmetric triblock copolymer (ABA) increases the periodic orientation normal to substrate, enabling directed self-assembly of the block copolymers into arrays of highly oriented, high-aspect-ratio cylindrical nanostructures over large areas.
8.2. Recommendations

The spontaneous and simple method investigated in this study would be recommended as one of the most effective candidates for the ordering process into self-assembly of block copolymers. The results of this investigation should have substantial benefits and potential to be utilized as a basis in many areas, such as nanostructure membranes, nanotemplates, photonic crystals, and high-density information storage media: owing to its extremely simple fabrication procedure for highly ordered block copolymer nanopatterns, as well as their excellent thermodynamic stability. Patterning with the block copolymer/homopolymer mixture using bottom-up nanostructures as templates in this way opens the door for future works towards a variety of nanotechnological applications, which require patterned materials with properties much different to polymeric matrices, such as inorganic networks and metals. Direct modification of one of the block components would be recommended for the applications in electronic industries. These self-assembling concepts combined with a top-down method, which would be a current lithography technique, may lead to new developments in nanotechnology.
REFERENCES


