Self-Organization of Triblock Copolymer Melt Chains Physisorbed on Non-neutral Surfaces

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ABSTRACT: We here report the self-organization process of poly(styrene-b-ethylene/butadiene-b-styrene) (SEBS) triblock copolymer chains physically adsorbed on a non-neutral surface. Spin-cast SEBS thin films were prepared on silicon (Si) substrates and then annealed at a high temperature far above the bulk glass transition temperatures of the two constituent blocks. To reveal the buried interfacial structure, we utilized solvent rinsing processes and a suite of surface-sensitive techniques including ellipsometry, X-ray reflectivity, atomic force microscopy, and grazing incidence small angle X-ray scattering. We revealed that the SEBS chains form two different chain structures on the substrate simultaneously: (i) “flattened chains” with the average height of 2.5 nm but without forming microdomain structures; (ii) “loosely adsorbed chains” with the average height of 11.0 nm and the formation of perpendicularly oriented cylindrical microdomains to the substrate surface. In addition, the kinetics to form the perpendicularly-oriented cylinder was sluggish (∼200 h) and proceeded via multistep processes toward the equilibrium state. We also found that the lateral microdomain structures were distorted, and the characteristic lengths of the microdomains were slightly different from the bulk even after reaching “quasiequilibrium” state within the observed time window. Furthermore, we highlight the vital role of the adsorbed chains in the self-assembling process of the entire SEBS thin film: a long-range perturbation associated with the adsorbed chains propagates into the film interior, overwhelming the free surface effect associated with surface segregation of the lower surface tension of polystyrene blocks.

1. INTRODUCTION

Thin films of block copolymers (BCPs) self-assembled into highly ordered periodic microdomain structures with the order of 10–100 nm offer great opportunities in many nanofabrication applications. Especially, cylindrical microdomains with a perpendicular alignment to a substrate surface have been paid great attention for fabricating masks for nanolithography, templates and nanostructured membranes, photovoltaic cells, low-k dielectrics, and high-density data storage media. When BCPs are confined in a thin-film geometry, the orientation of microdomains strongly depends on molecular interactions at the interfaces (i.e., a polymer–air interface and a polymer–substrate interface) and the commensurability between film thickness and interdomain spacing of the BCP. Preferential surfaces are wet by the preferred block with the lower surface energy, resulting in parallel orientations of the microdomain structures near the interfaces.

Polymer wetting at the solid–polymer melt (SPM) interface has attracted significant attention because of its crucial roles in determining the structures and physical/mechanical properties of thin polymer films. Different research groups evidenced the formation of several nanometer-thick adsorbed polymer layers at the SPM interfaces regardless of the magnitude of attractive solid–segment interactions. It should be emphasized that irreversible adsorption used in this paper refers to physical adsorption or physisorption, where polymer chains are adsorbed on solid surfaces through dispersion, dipolar forces, or van der Waals interactions. Using a solvent rinsing procedure proposed by Guiselin in conjunction with various experimental techniques, we previously demonstrated that adsorbed layers formed at the SPM interfaces of homopolymer...
thin films are composed of an inner higher density region with the thickness of a few nanometers regardless of molecular weights ($M_w$) and an outer bulk-like density region whose thickness increases with increasing $M_w$. Although the mobility of the strongly adsorbed polymer chains (hereafter assigned as “flattened chains”) in the inner region is significantly hindered, the polymer chains in the outer region (hereafter defined as “loosely adsorbed chains”) are still mobile, flexible, crystallizable, can interact with unassembled neighboring chains, or swell in good solvents. In addition, there are many experimental results to support that the effects of the loosely adsorbed chains propagate into the film interior, resulting in long-range perturbations on the structural, dynamical, and physical properties of polymer thin films including glass transition temperature ($T_g$), local viscosity, chain diffusion/interdiffusion, crystalline structures, and thermal stability/wettability. Napolitano et al. also reported that both the nonequilibrium features of polymer thin films and the slow equilibration process of polymer chains in the vicinity of a solid surface are correlated with irreversible polymer adsorption.

Recently, we uncovered the unique structure of BCP flattened chains on a bare (non-neutral) silicon (Si) substrate. It was found that not only preferred blocks but also nonpreferred blocks adsorbed on the substrate surface by-side, forming a two-dimensional (2D) network structure with the characteristic length of about 10 nm. In spite of interfacial energetics, microdomains (at least cylinder and lamellar), or chain architectures, the network structure was formed and thermodynamically arrested because of the large number of pinning sites and was therefore considered to be long-lived at the SPM interface even when exposed to a solvent vapor. Important questions now arise: What is the structure of the loosely adsorbed BCP chains (if any)?; What is the formation process of the loosely adsorbed chains during a thermal annealing process?; How do unassembled BCP chains next to the loosely adsorbed chains self-assemble into microdomain structures?; and Does the substrate effect associated with the loosely adsorbed chains exist? If so, how far does the effect propagate into the film interior? At this point, there are no experimental and theoretical studies to address these fundamental but crucial questions in the field. In this paper, by using the aforementioned solvent rinsing approach in conjunction with a suite of surface-sensitive techniques, including ellipsometry, X-ray reflectivity (XR), atomic force microscopy (AFM), and grazing incidence small angle X-ray scattering (GISAXS), we aim to shed light on the self-assembling process of poly(styrene-ethylene/butadiene-styrene) (SEBS) thin films in the vicinity of a non-neutral Si substrate surface. Furthermore, we demonstrate the long-range perturbation of the loosely adsorbed chains on the self-assembling process of the SEBS thin film.

2. RESULTS AND DISCUSSION

2.1. SEBS Thin Films Prepared on Si Substrates. Figure 1 shows the surface morphologies of the 28 nm ($h_0 = L_{28}$; the domain spacing) and 84 nm ($h_0 = 3L_{28}$) thick SEBS films on the Si substrates after thermal annealing at 150 °C for three different annealing times ($t_{an}$): 3, 96, and 186 h. Cylinders perpendicular-oriented ($C_L$) to the film surface were formed in the 28 nm film at $t_{an} = 3$ h. We confirmed that this ordering was not present in the as-cast film and therefore induced by thermal annealing (Figure S1). Based on the cross-sectional analysis, the average diameter ($d_v$) of the cylindrical domains and the domain spacing were estimated to be $d_v = 13 \pm 2$ nm and $L_0 = 28 \pm 2$ nm, respectively. Further GISAXS analysis on the thin films will be discussed later. On the other hand, as the film thickness increased to $h_0 = 3L_{28}$ (84 nm thick), parallel-oriented ($C_{||}$) cylinders occupied the entire film at $t_{an} = 3$ h, and the surface morphologies did not show any significant changes with increasing $t_{an}$. This is attributed to surface segregation of the lower surface energy of the PS blocks, resulting in the $C_{||}$ cylinders at the topmost surface. As $t_{an}$ increased, the $C_{||}$ cylinders began to appear at the topmost surface of the 28 nm thick film at the late stage of the thermal annealing process (Figure 1b,c). Nevertheless, the observation suggests that the formation of the $C_{||}$ cylinders is hindered at the surface of the 28 nm thick film compared with that of the thicker film. This may be related to a geometric restriction against the formation of $C_{||}$ cylinders to the film surface within such a confined geometry. In our investigation, as will be discussed later, we find that the irreversible adsorption of the SEBS chains on the Si substrate plays another crucial role in determining the orientation and ordering kinetics of the cylindrical microdomains within the thin film.

Figure 2a,b show the 2D GISAXS patterns for the 84 nm thick films on the Si substrates after annealing at 150 °C for $t_{an} = 3$ h (Figure 2a) and $t_{an} = 96$ h (Figure 2b). We observed that a ringlike scattering pattern at the first-order peak position (located at $q_{cy} = 0.22$ nm$^{-1}$) became more intense as the annealing time increased. As $C_{||}$ cylinders are a majority at the topmost surface based on the AFM image (Figure 1), this suggests the formation of more $C_{||}$ cylinders underneath the topmost surface. At the same time, two streaks aligned along the $q_x$ direction at $q_{cy} = 0.22$ nm$^{-1}$ were observed in the 2D GISAXS patterns. These arise from the following two possibilities: the presence of $C_{\perp}$ cylinders (but slightly tilted) or in-plane arrays of $C_{||}$ cylinders. The key to distinguish between the two scenarios is an appearance of a $\sqrt{3}$ peak that is originated from hexagonally packed cylinders in the lateral direction. Although it was difficult to identify the peak in the GISAXS data (Figure 2c), an oxygen plasma etching method in conjunction with the
AFM experiments reveals the formation of C₃ cylinders at the surface region about 10 nm below the topmost surface of the 84 nm thick film. We will discuss this later.

Figure 2c shows the annealing time dependence of the one-dimensional (1D) GISAXS profiles for the 84 nm thick SEBS films. There is a gradual increase in the sharpness of the peaks with increasing time, indicating that the lateral ordering of cylindrical microdomains was improved during the annealing process. However, the ordering kinetics was extremely slow even at 150 °C (which is far above the T_g values of the two constituting blocks). Although it seems that the surface morphologies of the films remain unchanged regardless of t_an(Figure 1d–f), GISAXS experiments with an incident angle of 0.06° (below the critical angle of SEBS), which allowed us to probe the topmost surface region (about 9 nm in thickness), showed that the microdomain structures at the surface were also improved gradually with time (Figure S2). Hence, we anticipate that the slow rearrangement of the cylindrical microdomains take place within the entire film.

2.2. Physisorption of SEBS Chains on the Si Substrate. Figure 3a shows representative XR profiles for the SEBS residual layers after toluene-rinsing and chloroform-rinsing with t_an = 185 h. As shown in Figure 3b (and Figure 5 later), we confirmed that all residual layers (after the thermal pre-annealing and subsequent solvent rinsing processes) covered the Si substrates entirely. The best-fits (shown by the solid lines in Figure 3a) to the XR data were obtained by using a three-layer dispersion model composed of a Si substrate, a SiO₂ layer, and a SEBS layer. As seen from the figure, the different solvent leaching processes allowed us to extract two different kinds of adsorbed layers with different thicknesses (i.e., the interfacial sublayer with toluene-rinsing and the flattened layer with chloroform-rinsing; see Experimental Section for the details). However, unlike our previous findings in homopolymer interfacial sublayers, we were not able to identify that the SEBS interfacial sublayer is composed of two layers of different densities. This is possibly due to the lack of well-resolved Kiessig fringes at q_z > 3 nm⁻¹. Instead, the best-fit for the SEBS interfacial sublayer was obtained with a single-layer model having the δ value of the bulk SEBS (δ_{bulk} = 1.96 × 10⁻⁶).

As previously reported for PS-based cylinder-forming and lamellar-forming diblock and triblock copolymers, we observed similar percolating-like structure in the SEBS flattened layer (Figure 3b). The XR profile (indicated in blue in Figure 3a) for the SEBS flattened layer could not be well fit with a simple slab model, especially at q_z > 3 nm⁻¹. We postulate that this is due to the presence of the percolating network structure, which may give rise to additional diffuse scattering and makes the density and roughness determinations of the flattened layer ambiguous, whereas the thickness can be independently and accurately determined from the “period” of the oscillation fringes. Hence, it is not conclusive that the SEBS flattened layer has a higher density than the bulk, as evidenced for the homopolymer flattened layers.

Figure 4 summarizes the thicknesses (h) of the SEBS flattened layers and interfacial sublayers as a function of t_an measured by ellipsometry/XR. The growth of the flattened layer (indicated by blue circles) exhibits a linear increase, h(t_an) = h₀ + vt_an (where h₀ and v are the initial adsorbed layer thickness resulting from the spin-coating process alone and the growth rate, respectively) with v = 0.07 nm/h at the early stage of adsorption (t_an ≤ 28 h). After reaching the crossover time (t_c) of t_c = 28 h, the flattened layer reached the “quasiequilibrium” state (no more growth with time) with the thickness of h = 2.5 ± 0.4 nm. It is interesting to note...
that this $t_c$ value is much longer than those of the PS or PB flattened layers with similar molecular weights ($t_c = 2−3$ h$^{22,24,26}$).

Following the early theoretical studies on adsorption kinetics where the conformation of an adsorbed chain is governed by "piecemeal deposition", Napolitano et al. recently proposed that the adsorption kinetics for homopolymer chains from the melts can be divided into the two regimes separated by $t_c$: a linear growth at the early stage (i.e., diffusion-controlled adsorption) and a logarithmic growth at the late stage (i.e., a "reeling-in" process of the loosely adsorbed chains, which is more sluggish due to excluded-volume repulsion of the already existing adsorbed chains and chain entanglements with unadsorbed chains). In contrast to their results, the growth curve of the SEBS interfacial sublayer (indicated by red circles) can be divided into four different regimes: the early linear regime followed by two logarithmic growths with two different growth rates at $t_{an} > t_c$ and the plateau regime. According to a previous report by Eskilsson and Tiberg, the adsorption kinetics of poly(ethylene oxide-b-tetrahydrofuran-b-ethylene oxide) triblock copolymers from solution on silica substrates exhibited an intermediate logarithmic growth because of displacements between the different adsorbed blocks at the interface in a selective solution.

To gain a comprehensive insight into the formation kinetics of the SEBS interfacial sublayer, morphological changes were characterized by AFM. Figure 5 shows the time evolution of surface morphologies of the SEBS interfacial sublayers. During the initial linear growth regime (i.e., $t_{an} < t_c$), the interfacial sublayers showed irregular patch structures but with a relatively low surface roughness (root mean square roughness = 1.7 nm) (Figure 5a). It should be emphasized that $C_\perp$ cylinders existed partially at the surface at $t_{an} = 12$ h (Figure 5d). At $t_c < t_{an} < t_i$, micelle-like polymer aggregates (several hundred nanometers in average size and about 12 nm in average height) emerged and coexisted with smaller island structures with the average size of about 20 nm (Figure 5b). Here, we define $t_i$ as the intermediate time. Although the mechanism of the intermediate process is not conclusive yet, we postulate that the total number of segment-solid contacts (i.e., "effective grafting density ($\rho_T$) for adsorbed chains composed of "tails", "loops", and "trains" calculated by $\rho_T = (n_{tail} + 2n_{loop})/A$, where A is the area of a substrate and $n_{tail}$ and $n_{loop}$ are the numbers of tails and loops of adsorbed chains, respectively) is not so high during the stage. Then, the toluene rinsing and subsequent drying process for the ex situ AFM experiments, which changes the solvent quality from good to poor for SEBS, may induce phase-separated structures (i.e., polymer-rich and polymer-poor regions), as reported for an end-grafted polymer brush.

**Figure 4.** Growth of the SEBS interfacial sublayer (red circles) and flattened layer (blue circles) on the Si substrate against $t_{an}$ at $T = 150$ °C. The dashed lines correspond to the best fits of the power-law growth at the early stage. The solid lines correspond to the best fits of the two-step logarithmic growths during the late stage. The crossover time, $t_c$, and the intermediate time, $t_i$, described in the text are indicated by arrows.

**Figure 5.** (a−d) AFM height images of the SEBS interfacial sublayers at different growth stages during the irreversible adsorption process on the Si substrates. The scan sizes of the images are $5 \times 5$ μm or $10 \times 10$ μm. The height scales of all images are 0−10 nm. The corresponding zoomed-in phase images of (a,c) are shown in (d,e), respectively. The scales of the phase images are ±2°.
Further experiments are currently in progress to understand the detailed mechanism.

After reaching \( t_0 \) the reeling-in process of the loosely adsorbed chains proceeds with time \( t \) and the interfacial sublayer became relatively smooth with increased effective grafting density (Figure 5e). The expanded AFM phase image (Figure 5e) further elucidated the formation of cylindrical microdomains with a perpendicular orientation within the interfacial sublayer. At \( t < t_{an} < t_i \) (we hereafter define \( t_{an} \) as the quasiequilibrium time), although the interfacial sublayer still grows with a much slower growth rate, the surface morphologies and the ordering of cylindrical microdomains in the interfacial sublayers (with the thickness of about 10 nm) remained almost unchanged. When \( t_{an} > t_i \) (=185 h for the present case), the interfacial sublayer reached the quasiequilibrium state. We also confirmed that the in-plane ordering among C\(_z\) cylinders in the quasiequilibrium interfacial sublayers remains poor, as will be later discussed with the GISAXS results.

By adding two additional logarithmic growths at \( t_c < t_{an} < t_i \) (“Intermediate I”) and at \( t_i < t_{an} < t_q \) (“Intermediate II”), the growth of the SEBS interfacial sublayer can be categorized as follows:

\[
\begin{align*}
    h(t_{an}) &= \begin{cases} 
        h_0 + vt_{an}, & t_{an} < t_c \\
        h_c + \Pi_c \log \left( \frac{t_{an}}{t_c} \right), & t_c < t_{an} < t_i \\
        h_i + \Pi_i \log \left( \frac{t_{an}}{t_i} \right), & t_i < t_{an} < t_q \\
        h_q, & t_{an} > t_q
    \end{cases}
\]
\]

where \( h_c, h_b, \) and \( h_q \) are the thicknesses at \( t_0, t_0 \) and \( t_q \) respectively, and \( \Pi_c \) and \( \Pi_i \) are the logarithmic growth rates after reaching \( t_c \) and \( t_i \) respectively. The best fits to the data shown in Figure 4 gave \( \Pi_i = 3.90 \) nm and \( \Pi_c = 1.66 \) nm. Note that the surfaces of the interfacial sublayers during the intermediate I regime (i.e., \( t_c < t_{an} < t_i \)) were inhomogeneous and roughened (Figure 5). Hence, the thicknesses obtained by ellipsometry/XR represent the average values. The thickness of the quasiequilibrium interfacial sublayer was \( h_q = 11.0 \pm 0.4 \) nm based on the XR experiments shown in Figure 3a.

GISAXS data further characterized the cylindrical microdomain formed in the quasiequilibrium interfacial sublayer at \( t_{an} > t_q \). Figure 6 shows the 2D GISAXS data (Figure 6a) for the quasiequilibrium interfacial sublayer with \( t_{an} = 185 \) h and the corresponding 1D profile (Figure 6b) measured at room temperature. The 2D image showed a streak at \( q_{sy} = 0.20 \) nm\(^{-1}\). In conjunction with the AFM image shown in Figure 5e, it is reasonable to conclude that the streak is attributed to the presence of C\(_z\) cylinders within the quasiequilibrium interfacial sublayer. The broad peak at \( q_{sy} \approx 0.4 \) nm\(^{-1}\) in the 1D profile (Figure 6b) then suggests the \( 1/4 \) peak of hexagonal packed cylindrical microdomains in the quasiequilibrium interfacial sublayer. However, further studies are needed to clarify the domain packing. Interestingly, \( L_0 \) calculated from the first-order peak position was 30.8 \pm 0.5 nm, which is slightly larger than that in the thin film or the bulk (\( L_{32m} = 28 \) nm). Additionally, the very broadened peaks suggest the low degree of in-plane ordering among C\(_z\) cylinders in the quasiequilibrium interfacial sublayers. It is likely that the strong pinning of the SEBS segments on the Si substrate prevents the self-assembly into well-ordered microdomain structures. Meanwhile, the average size of the cylinders (\( R_{cyl} \)) in the quasiequilibrium interfacial sublayer was estimated to be about \( R_{cyl} = 9 \) nm based on the AFM result (Figure 5e), which is quite smaller than that in the 28 nm or 84 nm thick film (\( R_{cyl} = 13 \) nm). This may arise from the additional entropic penalty of stretching the adsorbed chains that affects phase separation into PS microdomains in the PEB matrix.

2.3. Correlation between SEBS Microdomains and Irreversible Chain Adsorption. Having revealed the formation of the SEBS interfacial sublayer on the non-neutral solid substrate, we now focus on the effect on the formation of cylindrical microdomains in the SEBS thin film. As clarified above, the microdomain structures formed in the interfacial sublayer are distorted, and both the domain spacing and cylinder size are different from those in the bulk. We therefore hypothesize that, during the thermal annealing process, unadsorbed neighboring chains, which are in contact with the loosely adsorbed chains within the interfacial sublayer, phase-separate into cylindrical microdomains having the same orientation (C\(_z\)) as that of the loosely adsorbed chains so as to maximize the contact area, thereby lowering the interfacial energy. However, the “incommensurability” in the microdomain structures between the loosely adsorbed chains and neighboring unadsorbed chains would cause unwanted high interfacial energy. Furthermore, the incommensurability effect can propagate into the film interior through chain entanglements between the loosely adsorbed chains and unadsorbed neighboring chains, as will be discussed below.

On the other hand, as shown in Figure 1, when the film is sufficiently thick (e.g., 84 nm thick), the morphology of the

![Figure 6](image-url)

Figure 6. (a) 2D GISAXS image of the quasiequilibrium SEBS interfacial sublayer (11 nm thick) and (b) corresponding 1D GISAXS profile along the \( q_{sy} \) direction.
topmost surface is typically governed by the surface effect because of lower surface tension of the PS blocks (i.e., a parallel orientation). To discuss the competition between free surface effect and substrate effect within the SEBS thin film, we uncovered the subsurface internal microdomain structures using an oxygen plasma etching method. The experiments were conducted using oxygen plasma (20 W, 100 mTorr) in a reactive ion etcher (CS-1701, March Plasma, Inc.). Two 84 nm thick SEBS films on the Si substrates were prepared and then annealed at 150 °C for 3 and 96 h, separately. With 5 s etching, we could remove an about 10 nm thick layer from the topmost surface of the film. As shown in Figure 7a, the etched SEBS film with pre-annealing of 3 h showed C\textsubscript{I} cylinders. On the other hand, C\textsubscript{I} cylinders were dominant at the etched surface of the 84 nm thick film after pre-annealing of 96 h (Figure 7b). These data suggest that the effect of the loosely adsorbed chains (i.e., the formation of C\textsubscript{I} cylinders) propagates at least 70 nm into the film from the substrate surface, overwhelming the free surface effect that favors C\textsubscript{II} cylinders. In addition, the results imply that the distance of the long-range perturbation associated with the loosely adsorbed chains is strongly correlated with the adsorption process: as the loosely adsorbed chains grow with annealing time, the substrate effect propagates further into the film interior. It is interesting to mention that for the 28 nm thick SEBS film where the substrate effect is dominant, the orientation of the microdomain structure at the topmost surface tends to switch from perpendicular to parallel with time (Figure 1). This suggests that the formation of C\textsubscript{I} cylinders is first provoked at the topmost surface because of the substrate field effect, but the free surface effect gradually becomes dominant at the topmost surface. As shown in Figure 1, the kinetics to switch to C\textsubscript{II} cylinders at the topmost surface is very sluggish, although the more enhanced segmental mobility is anticipated at the free surface compared to the bulk.\textsuperscript{32,51} Such mixed microdomain orientations within BCP thin films were previously reported when one of the blocks has a preferential interaction at one interface and a nonpreferential interaction at the other interface.\textsuperscript{34–57} As also indicated from Figure 1, when the thickness of the SEBS thin film is beyond the distance of the long-range perturbation (~70 nm), the surface effect is dominant at the topmost surface even after the short annealing time. We expect that the propagation distance is system-dependent.\textsuperscript{58–62} Detailed studies on a correlation among the long-range propagation of the substrate field effect, the growth of the loosely adsorbed chain, and the polymer—solid/polymer—air interactions deserve future work to establish a more comprehensive understanding of self-assembly of BCP thin films on non-neutral surfaces.

3. CONCLUSIONS

In conclusion, we revealed the formation mechanism of the cylindrical-forming SEBS thin film on a non-neutral solid surface. The optimized solvent rinsing approach in conjunction with XR and ellipsometry experiments allowed us to identify the formation of two different adsorbed chains: the outer loosely adsorbed chains that formed cylindrical microdomains in the direction perpendicular to the substrate surface and the inner flattened chains with a percolating-like network structure. It was also found that the kinetics is sluggish, and the cylinders formed with the loosely adsorbed chains have poor in-plane ordering among them, with the cylinder size and the interdomain spacing being different from those in the thin film. We also found that the effect of the loosely adsorbed chains propagates into the film interior via chain entanglements with the neighboring unadsorbed chains, leading to the formation of substrate-directed perpendicular-oriented cylinders for at least 70 nm from the substrate surface. This substrate field effect associated with the loosely adsorbed chains is dominant within the length scale over the free surface effect that induces parallel-oriented cylinders at the air—polymer interface. These findings suggest that the irreversible adsorption of constituent blocks on a non-neutral solid is critical for designing BCP thin film-based applications and technologies. This research is also reminiscent of the importance of surface modifications in directing well-ordered microdomain structures in BCP thin films. We are currently investigating the use of flattened chains composed of one of the constituent blocks as an alternative polymer coating for directed self-assembly of BCP thin films. The details will be summarized as a forthcoming publication.

4. EXPERIMENTAL SECTION

4.1. Sample Preparation. A cylinder-forming SEBS (M\textsubscript{w} = 85 000 g/mol, M\textsubscript{w}/M\textsubscript{u} = 2.4, donated by Asahi-Kasei Chemical Corp) triblock copolymer was used. Such a relatively large polydispersity index is often considered as an undesirable feature that complicates quantitative studies of structures and dynamics of macromolecules. According to Guiselin’s original work,\textsuperscript{21} adsorbed chains with multiple solid-segment contacts can be considered as a “very polydisperse pseudobrush”, and this was also validated experimentally.\textsuperscript{32} In addition, we proved that the structures of the physisorbed polymer layers remain unchanged with different degrees of M\textsubscript{w}/M\textsubscript{u} (at least up to M\textsubscript{w}/M\textsubscript{u} = 2.7).\textsuperscript{32} Hence, the effect of the relatively large polydispersity of SEBS on the structure of the adsorbed polymer layer can be ignored. The weight fraction of the polystyrene (PS) component was 0.18. Small angle X-ray scattering experiments at the CMS beamline (NSLS-II, BNL) verified that the bulk SEBS sample does not exhibit the order—disorder transition within a wide temperature range of 25–200 °C. The characteristic period of cylinders (or interdomain spacing, L\textsubscript{0}) in the bulk was determined to be L\textsubscript{0,bulk} = 28 nm at 25 °C (Figure S3). Silicon (Si) substrates (University Wafer Inc.) were treated with hot piranha solution for 30 min before being rinsed with deionized water. The cleaned Si wafers were then submerged in an aqueous solution of hydrogen fluoride...
(HF) for 20 s to remove the native oxide (SiO$_x$) layer. However, we confirmed that a SiO$_x$ layer (∼1 nm in thickness) was reproduced immediately after the HF etching, as reported previously.22,24,26 The HF-etched Si exhibited more hydrophobic nature compared to a non-HF Si substrate, giving a water contact angle of 82 ± 1°.26 We prepared SEBS thin films with average thicknesses $h_i = nL_0$, where $n$ is an integer, onto the HF-etched Si substrates by spin coating of a SEBS/toluene solution. The thicknesses of the spin-cast SEBS thin films were measured by XR or an ellipsometer (Rudolf Auto EL-II) with the given refractive index of 1.516. According to previous studies, polybutadiene (PB) exhibits more attraction to SiO$_x$ than PS.64–66 It is hence expected that the PEB block has a stronger affinity to the Si substrate than the PS block. On the other hand, because PS has a relatively lower surface energy compared to PEB, PS preferentially wets to the air interface. Hence, a SEBS thin film on the Si substrate is categorized as an asymmetric wetting condition, which requires the film thickness ($h_i$) of $(n + 1/2)L_0$ to prepare stable, supported thin films.70 However, as shown in Figure 1, SEBS thin films with $h_i = L_0$ and $h_i = 3L_0$ were stable during the prolonged thermal annealing process and typical topological features caused by the mismatching film thickness, such as islands, holes, or terraces, were not present at the film surfaces. Spin-cast films were thermally annealed at 150 °C for different times in an oil-free vacuum oven at a pressure below 10$^{-3}$ Torr.

To investigate the irreversible adsorption of SEBS chains on the HF-etched Si substrate, the thermally annealed SEBS thin films were rinsed with fresh toluene or chloroform at room temperature until the residual film thickness remained unchanged (typically a total of 3–5 cycles with 30 min per cycle). The choice of solvents was based on previous studies on the extraction of loosely adsorbed chains or flattened chains from homopolymer PS or PB thin films.22,24,26 The solvent-rinsing with toluene removes the unadsorbed chains but leaves both the inner flattened chains and outer loosely adsorbed chains on the Si surface. We assign the residual layer composed of both the inner flattened chains and outer loosely adsorbed chains as an interfacial sublayer. To uncover the inner flattened chains, chloroform, a better solvent for SEBS than toluene, was utilized. We refer to the resulting layer composed of the lone flattened chains as a flattened layer. This selective extraction of the two different adsorbed chains is attributed to the large difference in desorption energy between the outer loosely adsorbed chains and the inner flattened chains, which is linearly dependent on the number of segment–surface contacts.45,46 The resultant adsorbed layers (i.e., the flattened layers and interfacial sublayers) were annealed at 150 °C for 12 h in a vacuum oven at a pressure below 10$^{-3}$ Torr to remove any excess solvent trapped before further experiments.

### 4.2. GISAXS Measurements

GISAXS measurements were carried out at the X9 beamline at the National Synchrotron Light Source (NSLS, BNL). 2D scattering patterns were collected by using a MAR-CCD area detector with the sample-to-detector distance of 495 cm. Intensity profiles were measured as a function of the scattering vector, $q = (4\pi \sin \theta)/\lambda$, where $\theta$ is the scattering angle and $\lambda$ is the X-ray wavelength ($\lambda = 0.992$ nm). The incident angle was set to 0.12°, which is above the critical angle of SEBS (i.e., 0.1°) to observe the entire structure within the film. All measurements were carried out under vacuum (∼10$^{-3}$ Torr) with a temperature-controlled sample stage interfaced with a LakeShore 340 unit. The exposure time was fixed to 200 s. The 2D GISAXS patterns were transformed into 1D profiles along the $q_z$-direction at $q_z = 0.15$ nm$^{-1}$, with $q_{xy}$ and $q_z$ being the scattering vectors in the parallel and perpendicular directions to the film surface, respectively.

### 4.3. XR Measurements

XR measurements were performed at the X20A beamline (NSLS). Specular reflectivity profiles were measured as a function of $q_z = (4\pi \sin \theta)/\lambda$, where $\theta$ is the incident angle and $\lambda$ is the X-ray wavelength ($\lambda = 0.118$ nm). The XR data, corrected for the background scattering, was analyzed by comparing the observed reflectivities with calculated ones based on model profiles with three fitting parameters: film thickness, a dispersion value (δ in the X-ray refractive index), and interfacial roughness. To identify the two-layer formation within the interfacial sublayer, we used a standard multilayer fitting routine for a dispersion value in conjunction with a Fourier method.71,72 For the X-ray energy used (10.5 keV), the δ value of the SEBS is estimated to be $\delta_{\text{bulk}} = 1.96 \times 10^{-6}$ with the density of 0.95 g/cm$^3$.

### 4.4. AFM Measurements

The SEBS used in this study forms hexagonally packed PS cylinders embedded in a soft EB matrix. A phase contrast can visualize such a structure under a tapping mode AFM. Standard tapping mode AFM (Digital NanoScope III) using a cantilever with a spring constant of ∼40 N/m and a resonant frequency of ∼300 kHz was used to characterize the surface morphologies of the SEBS thin films and adsorbed layers. The scan rate was 1 Hz with the scanning density of 256 or 512 lines per frame.

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**ASSOCIATED CONTENT**

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02912.

SAXS data for the bulk SEBS film, the AFM image and GISAXS data for the as-cast SEBS film, and time dependence of the GISAXS profiles for the 84 nm thick SEBS thin films at the topmost surface (PDF)

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**Notes**

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