Interfacial Interaction Dependence of Microdomain Orientation in Diblock Copolymer Thin Films

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ABSTRACT: The dependence of the orientation of lamellar microdomains in thin films of symmetric diblock copolymers of polystyrene-*b*-polymethyl methacrylate was quantitatively investigated by small angle neutron scattering, transmission electron microscopy (TEM), and reflectance optical microscopy. A mixed orientation of the lamellar microdomains was found when the difference in the interfacial energies between each block and the substrate was not strong enough to force the orientation of the lamellae parallel to the substrate throughout the film. A limiting film thickness was found, below which a parallel alignment of the lamellar microdomains was seen throughout the film. This film thickness was found to depend on the strength of the interfacial interactions of each block with the substrate. TEM images indicate that the surface field suppresses the fluctuations in the microdomain, reduces defects, and consequently, propagates the orientation of the domains parallel to the surface into the film.

Introduction

In block copolymer thin films, the presence of a surface or interface can strongly influence the microdomain morphologies and the kinetics of microdomain ordering. Much work has appeared on the influence of surfaces and interfaces on the ordering properties of symmetric diblock copolymers.[1−4] Fredrickson studied the surface-ordering phenomena in symmetric diblock copolymers near the microphase separation transition using mean field arguments. An oscillatory profile was found normal to the substrate where the amplitude of the oscillations decayed exponentially from the surface with a decay length that increased with increasing proximity to the microphase separation temperature, i.e., $\chi N - (\chi N)_s$, where χ is the segmental interaction parameter, $(\chi N)_s$ is the value of χN at the microphase separation transition, and N is the number of the repeat units.[5,6] In disordered diblock copolymer thin films, the concentration of one block at the substrate interface is dictated by the difference in interfacial energies of the blocks with the substrate and the strength of segmental interactions. Experiments of Menelle et al.[7] and Mansky et.al.[8] quantitatively described the concentration profiles of phase-mixed symmetric diblock copolymers and found general agreement with the mean field arguments.

Experiments on the thin films of ordered symmetric diblock copolymer have typically focused on the behavior of copolymers at the interfaces where the surface field strength is either large[9,10] or zero.[11,12] In the cases of a strong surface field, one block has much lower interfacial energy with the substrate and this block wets the substrate, inducing an orientation of the microdomains parallel to the substrate that propagate through the film. When the surface is neutral, i.e., where the interfacial interactions of both blocks with the substrate are the same, there is no preferential wetting and the microdomains orient normal to the substrate interface. This orientation persists a few periods from the interface before a randomization of the microdomain orientation occurs. While these phenomena result from the surface field, there is no quantitative study on the extent to which interfacial energies can induce the propagation of microdomain orientation into a block copolymer film.

Here, the influence of interfacial interactions, a surface field, on the propagation of lamellar microdomain orientation parallel to the substrate in thin films of symmetric diblock copolymer polystyrene-*b*-polymethyl methacrylate (PS-*b*-PMMA) thin films was quantitatively studied. By anchoring a random copolymer of styrene and methyl methacrylate onto a silicon substrate, the interfacial energy, i.e., the strength of the surface field, was precisely tuned by varying the composition of the random copolymer. It was found that the stronger the surface field, i.e., the larger the difference in the interfacial energies between the blocks with the substrate, the further the orientation of the microdomains propagate into the films. For a specific surface field strength, a film thickness limit was found beyond which the orientation of the microdomains parallel to the surface was found throughout the film and above which there was a loss of orientation. This thickness limit was found to be proportional to the strength of the surface field. In addition, the surface field was found to suppress the fluctuations at the interfaces between the microdomains in the vicinity of the interface, thereby retarding the formation of the defects and promoting the alignment of the microdomains parallel to the substrate interface.

Experimental Section

Diblock copolymers of polystyrene and polymethyl methacrylate, denoted as PS-*b*-PMMA, were made by conventional anionic polymerization procedures and were characterized by size exclusion chromatography using polystyrene as a standard. The molecular weight was M_n = 71 900 g/mol with a polydispersity (PDI) of 1.06. For small angle neutron scattering studies, the PS block was deuterated and the copolymer was denoted as dPS-*b*-PMMA. The molecular weight of dPS-*b*-PMMA was M_n = 70 500 g/mol (PDI = 1.05). The preparation of the narrow-molecular-weight-distribution random copolymers of styrene and methyl methacrylate and modification of

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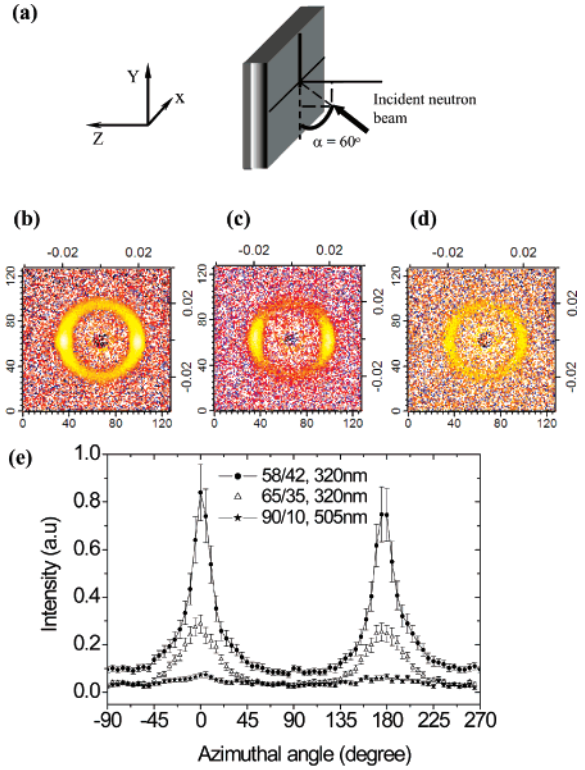

Figure 1. (a) Schematic drawing of the experimental setup. SANS profiles of dPS-*b*-PMMA thin films on Si substrate modified with random copolymers of (b) 58/42 (~320 nm), (c) 65/35 (~320 nm), and (d) 90/10 (~505 nm) after annealing at 170 °C under vacuum for 72 h. The samples were tilted at 60° with respect to the incident beam. (e) Azimuthal angle integration of the SANS intensity in (b), (c), and (d).

the silicon substrates have been described elsewhere.[8,13,14] The volume fractions of styrene in the random copolymers were 0.30, 0.58, 0.65, 0.7, and 0.90 with interfacial energy differences between PMMA and PS with the modified surface ($\Delta\gamma = |\gamma_{PS/substrate} - \gamma_{PMMA/substrate}|$) of approximately 0, 0.25, 0.45, 0.5, and 0.75 ergs/cm^2, respectively.[8,14] Details on the substrate modifications and measurements of the interfacial energy differences have been published previously.[8] Films with thickness ranging from 100 to 900 nm were spin-coated from toluene solutions onto modified Si wafers and annealed at 170°C under vacuum for 3 days. SANS experiments were performed on the 30-m NG3-SANS instrument at National Institute of Standard Technology (NIST) with a 1.25-cm pinhole at the sample defining a beam with a wavelength of $\lambda = 6$ Å and $\Delta\lambda/\lambda = 15\%$. The sample surface was either normal to the incident beam or tilted an angle of 60° with respect to the incident beam. A schematic diagram is shown in Figure 1a. A thin layer of carbon (10−20 nm) was coated onto the surface of the copolymer film; then, the film was embedded with epoxy and cured at 60 °C for 12 h. The film was removed from the substrate by being dipped into liquid N_2. The substrate was examined by ellipsometry and a film of less than 5 nm was left for all the samples shown here. Thin cross sections were microtomed at room temperature and were exposed to ruthenium tetroxide that preferentially stained PS blocks for 35 min. The TEM images were taken on a JEOL 100CX at an accelerating voltage of 100 kV.

Results and Discussions

The microdomains in block copolymer thin films are oriented parallel to the surface due to the preferential wetting of one block with the substrate. Islands and holes will form on the surface if the film thickness is not equal to nL_o or $(n + 1/2)L_o$ (where n is an integer and L_o is the equilibrium period of the copolymer), depending on the boundary condition.[15] This surface topography is a simple, yet quantitative, indicator of the orientation of the microdomains parallel to substrate interface. Four samples with similar thickness (~$10.3L_o$) were prepared on the substrates modified with random copolymers having styrene fractions of 0.58, 0.65, 0.30, and 0.90, where the differences in the interfacial energies were were 0, 0.25, 0.45, and 0.75 ergs/cm^2 respectively. No islands and holes were observed on the surface modified with 58/42 ($\Delta\gamma \approx 0$ ergs/cm^2) and 65/35 ($\Delta\gamma \approx 0.25$ ergs/cm^2) random brushes, whereas islands and holes were clearly seen on the surfaces modified with 30/70 ($\Delta\gamma \approx 0.45$ ergs/cm^2) and 90/10 ($\Delta\gamma \approx 0.75$ ergs/cm^2) random brushes. By variance of the film thickness, the absence of a surface topography on films prepared on substrates with a 58/42 random copolymer brush can be attributed to an orientation of the microdomains normal to the surface. In the case of the 65/35 surface, the PS block preferentially wets the substrate. However, the strength of the surface field is weak and the preferential orientation of the microdomains parallel to the interface is lost with increasing distance from the substrate. In both cases, the orientation of the microdomains normal the surface, or at least orientations that are not parallel to the surface, removes commensurability constraints between the film thickness and L_o, and consequently, the surface of the film remains smooth.

A series of tilting SANS experiments was used to study the internal microdomain orientation. The azimuthal angle dependence of the scattering reflects the different microdomain orientations and was explained in detail previously.[16] For the samples tilted at α degree with respect to the incident beam, the scattering arises from microdomains oriented at angles more than α away from the surface planes. Shown in Figure 1b (58/42), c (65/35), and d (90/10) are the SANS pattern of three films on substrates with different surface fields. The samples were tilted at 60° with respect the incident beam, as shown in Figure 1a. The overall intensities decrease with increasing surface field strength. Even with much thicker films (~500 nm vs 320 nm), the intensity of scattering for the film on the 90/10 substrate is much lower than that for films on either the 58/42 or 65/35 substrates. Thus, the extent to which the orientation of the microdomains is maintained parallel to the surface increases with increasing strength of the surface field. Figure 1e shows the integration of the SANS intensity over q as a function of the azimuthal angle. In all three cases, the majority of the microdomains that are not parallel to the surface have orientations close to being normal to the surface. This may very possibly be due to the longer lifetime of the '*T*' junction defects as described for bulk diblock copolymers.[17,18] It is particularly obvious for the film on the 90/10 substrate (Figure 1d, ~505 nm), where the lamellae were parallel to the surface throughout the film in a slightly thinner film.

SANS was performed with the beam normal to the substrate surface to assess the microdomain orientation, focusing on the limiting film thickness above which the lamellar microdomains are no longer oriented parallel to the surface throughout the film. Since the diffraction vector is oriented parallel to the surface, no scattering will be observed for the films where the lamellar microdomains are oriented parallel to the substrate throughout the films. The intensity of the scattering

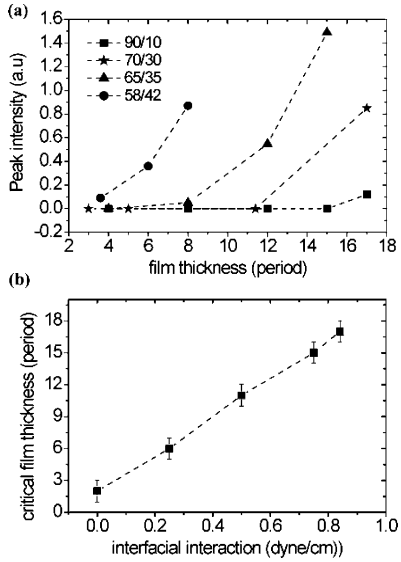

Figure 2. (a) SANS peak intensities of the annealed dPS-*b*-PMMA thin films on Si substrates modified with different random copolymers, 58/42, 65/35, 70/30, and 90/10. (b) Plot of the critical film thickness vs interfacial interactions. The dotted line is to guide the eye.

maximum is proportional to the number of lamellar microdomains oriented normal to the substrate surface. Figure 2a shows the peak intensity for diblock copolymer thin films with different thicknesses on substrates modified with different random copolymers. For films with a similar thickness, the peak intensity decreases as the strength of the surface field increases, suggesting more lamellar microdomains are oriented parallel or close to parallel to the substrate. The film thickness dependence of the SANS on any given surface shows that no SANS is observed until a specific thickness is reached. Then, with increasing film thickness, the peak intensity increases. Thus, for very thin films, the lamellae are oriented parallel to the film surface throughout the entire film. However, above a limiting film thickness, the influence of the surface is lost and the lamellae orient normal to the interface in the film interior. This limiting film thickness is directly related to the surface field strength. Defining the limiting film thickness for each surface field strength as the thickness above which the scattering intensities are higher than 0.005 (a.u) and the islands and holes are absent on the film surfaces, the relationship between the limiting film thickness and the surface field strength are shown in Figure 2b, where essentially a linear relationship is seen.

Figure 3 shows typical cross-sectional TEM images of the samples in this study. Figure 3a shows an ~400 nm film on a neutral surface (58/42). From the TEM sample preparation, the top surface corresponds to the copolymer/substrate interface. The lamellae orient normal to the interface, and this orientation propagates into the film. At the air/polymer surface, the microdomains are parallel due to the lower surface tension of PS. Figure 3b is an ~430 nm film on the substrate modified with a 70/30 random copolymer. As seen before, the lamellae are oriented parallel to the substrate due to the preferential wetting of PS (dark) on the modified substrate. This orientation propagates through the entire film for the thinner films (no shown). However, for thicker films, the parallel orientation is lost after a given distance from the copolymer/substrate interface,

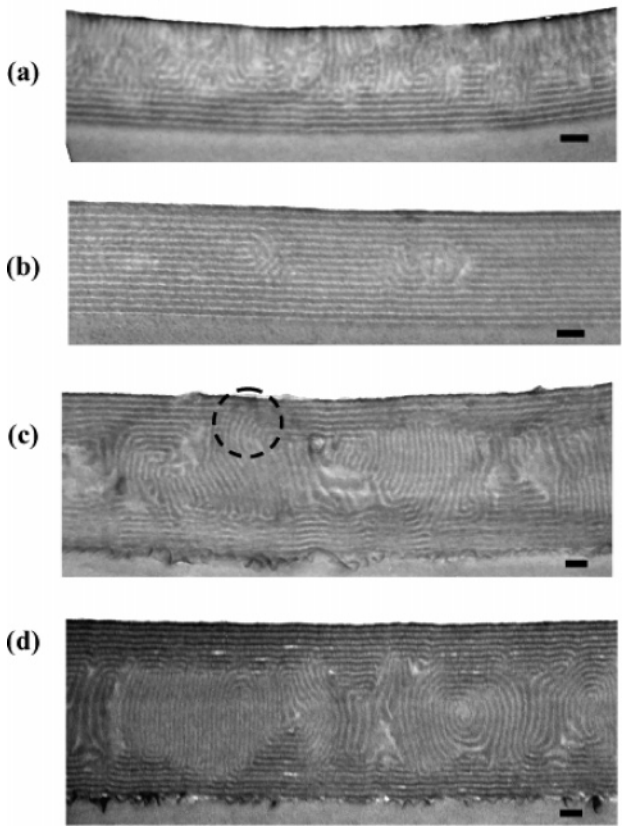

Figure 3. Cross-sectional TEM images of the annealed PS-*b*-PMMA thin films on Si substrates modified with random copolymers: (a) 58/42 (~400 nm), (b) 70/30 (~430 nm), (c) 70/30 (~800 nm), and (d) 90/10 (~800 nm). From the TEM sample preparation, the top surface corresponds to the copolymer/substrate interface. Scale bar: 100 nm.

and in the middle of the film, different microdomain orientations appear as shown in Figure 3b. Mixed orientations become obvious when the film gets thicker, as shown in Figure 3c. The coherence of the parallel orientation across the films is lost after $\sim 3L_o$. Defects in the structure appear (highlighted by the circles), and lamellae with mixed orientations are dominant in the center of the film. Figure 3d shows the cross-section TEM image of a film with a thickness similar to that of the sample in Figure 3c prepared on a substrate modified with the 90/10 random copolymer. The parallel alignment of the lamellae propagates further into the film. In the center of the films, a mixed orientation is seen. The microdomain orientation in the film did not change significantly with further annealing (up to a week). In keeping with the SANS results, the TEM images show that there is a distance from the substrate where the orientation of the microdomains persists and this distance increases with increasing strength of the interactions between the copolymer and the modified substrate surface.

The TEM images were used to quantify the persistence of the microdomain orientation as a function of distance from the copolymer/substrate surface. By projecting the contrast of the TEM image onto a line oriented normal to the interfaceface, the projected amplitude of the contrast is a direct measure of the copolymer orientation. An alternate approach used here was to determine the linear fraction of lamellae oriented parallel to the surface of the TEM images as a function of distance from the surface, as shown in Figure 4. Films (~800 nm) on three substrates modified with 30/70 ((Δγ

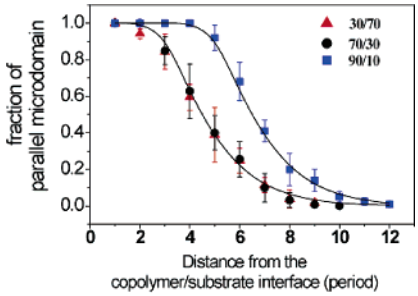

Figure 4. Fraction of parallel lamellae microdomains vs the distance from the copolymer/substrate interface. The solid lines were plotted to guide the eye.

≈ 0.45 ergs/cm^2), 70/30 ($(\Delta\gamma \approx 0.5$ ergs/cm^2), and 90/10 ($(\Delta\gamma \approx 0.75$ ergs/cm^2) random copolymers were analyzed. The lamellar microdomains oriented parallel to the copolymer/substrate interface within $\pm 5°$ were counted in each TEM image and divided by the overall film length to obtain the parallel fraction of the lamellae. Each point was obtained from $\sim$20-μm wide cross-section TEM images. The results in Figure 4 are quite revealing. First, the shapes of the profiles are similar. Adjacent to the copolymer/substrate interface, the profiles are flat, indicating the parallel alignment of copolymer microdomains. The distance over which the orientation persists depends on the strength of the interfacial interactions. This distance is the same for the 70/30 and 30/70 cases, extending $\sim$3 periods from the surface. For the 90/10 case, the parallel alignment extends $\sim$5 periods from the interface, as would be expected from the stronger interfacial iinteractions. The decay of the orientation is essentially the same in all cases, i.e., the profiles can be superimposed. Such behavior has been predicted theoretically and indicates that the decay in orientation is a characteristic of the copolymer.

Conclusion

It is well known that the preferential wetting of one block with the substrate induces an alignment of the lamellar microdomains parallel to a surface. Here, by modifying a surface with random copolymers, interfacial energies were controlled and the influence of interfacial energy on the lamellae orientation of PS-*b*-PMMA thin films was studied quantitatively. Mixed lamellae orientations were found when the surface field, i.e., the difference in the interfacial energies between each block with the substrate, is not strong enough to orient the lamellae parallel to the substrates throughout the film. The limiting film thickness, below which the lamellae orient parallel to the substrate surface, is proportional to the surface field strength. TEM images indicate that the presence of a surface field suppresses microdomain fluctuations and, consequently, the defects, promoting the propagation of orientation into the film. A linear relationship is seen between the strength of interfacial interactions and the distance over which the orientation of the microdomains persists. These results have direct bearing on the strength of applied fields necessary to orient microdomains in thin block copolymer thin films.[19] It is evident that field strength needs to be high enough to induce the fluctuations close to the copolymer/substrate interface to orient the microdomains normal to the surface.[20] This, as shown here, depends on the interfacial interactions, and for films below a critical thickness, parallel alignment of the microdomains will occur regardless of the strength of the applied field.

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