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Free Surface Confinement of Diblock Copolymer Multilayers

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ABSTRACT: Thin films of symmetric diblock copolymers self-assemble into multilayered structures, due to the strong interactions of one of the blocks with the substrate and/or free surface. If the film thickness, t, is not an integral or half-integral multiple of the bulk period L_0, depending upon the boundary conditions, then islands or holes form on the free surface with a step height of L_0 to relieve the frustration imposed by the film thickness. It is shown here, however, that a well-ordered multilayer can form prior to hole formation, with a period L that deviates significantly from L_0. This structure can be stable for weeks. Topographic features eventually appear on the surface, however, allowing the period to attain its equilibrium value. This indicates that free surface confinement is a kinetic, rather than equilibrium, effect. Confinement of compressed periods is much more effective than for expanded periods, indicating that the activation barrier for the nucleation of holes is larger than that for islands.

Introduction

Many recent studies have focused on the behavior of thin films of diblock copolymers.[1-7] In the case of symmetric diblock copolymers, the preferential interaction of one of the blocks with the substrate and the difference in the surface energies of the blocks cause the formation of a multilayered structure when the film is heated above the glass transition temperature. The lamellar period of a multilayered film with a flat surface can equal the bulk equilibrium period, L_0, only for discrete values of the film thickness. In the case of antisymmetric adsorption, one block interacts strongly with the substrate and the second block has the lower surface energy, as in the case of copolymers of polystyrene and poly(methyl methacrylate) P(S-*b*-MMA) on silicon oxide. The preferred values of the film thickness for this case are given by $(n + {}^1\!/_2)L_0$, where n is an integer. If the initial film thickness does not conform to this condition, i.e., if the initial film thickness is $(n + {}^1\!/_2 + \epsilon)L_0$, then islands or holes form on the surface with a step height of L_0 to relieve the frustration imposed by the incommensurate film thickness. Thus, the resulting film has two different thicknesses, each of which satisfies the $(n + {}^1\!/_2)L_0$ condition. The kinetics of the formation and growth of this surface topography has been studied extensively in the past.[8-13]

Recently, Lambooy et al.[14-16] and Koneripalli et al.[17] have developed techniques to suppress the formation of surface topography by confining copolymer films between two hard walls. It was found that well-ordered multilayers formed with an integral or half-integral number of layers confined between the two walls, depending upon the boundary conditions. The strong interactions of the blocks with the walls were sufficient to force the period of the copolymer to expand or compress by as much as 50% in some cases. Theoretically, Kickuchi and Binder,[18,19] Turner[20] and Walton et al.[21] have examined the problem of confined lamellar diblock copolymers. In these studies it was found that the frustration of the diblock copolymer by film thickness constraints depended strongly upon the strength of the interactions of the blocks with the substrate. In the case of strong interactions, stretched or compressed copolymer multilayers were predicted. However, as the interactions of the copolymer with the confining walls become weaker, the copolymer domains can change their orientation with respect to the substrate under conditions of maximal frustration. Only recently has this latter mechanism of frustration relief been observed experimentally.[22]

In this article, the observation of confinement effects on P(S-*b*-MMA) multilayers on silicon oxide is reported *without* hard-wall constraints, i.e., *free surface confinement*. It is found that if the initial film thickness t is as much as 10% less than the quantized value of $3.5L_0$, no topographic features form initially. Instead, a well-ordered multilayer forms with the period L obeying $L = t/3.5$ and deviating from L_0. However, we find that this confinement effect is kinetic, as opposed to thermodynamic, in origin. While the confinement is effective over time scales much longer than that required for the copolymer to self-assemble into a multilayered structure, holes form in all samples after extended annealing, and the period assumes the equilibrium value. Nonetheless, the results reported show a simple and potentially useful means of studying the effect of confinement on the structure and phase transitions of thin copolymer films.

Experimental Section

Experiments were performed on thin films of a symmetric diblock copolymer of polystyrene and poly(methyl methacrylate), denoted P(S-*b*-MMA), having a weight-average molecular weight of 1.08×10^5, a polydispersity of 1.1, and a polystyrene volume fraction of 0.48. PS homopolymer impurity generated during the synthesis of the copolymer was removed via Soxhlet extraction with cyclohexane. Solutions of the copolymer in toluene (3% w/v) were spin coated onto cleaned Si substrates having a diameter of 5 cm and a thickness of 5 mm. The sample thickness was varied by increasing the spinning speed from 1500 to 2500 rpm in small increments. Multiple measurements of each sample thickness were made using ellipsometry, ensuring that the film thickness was uniform over the entire sample to within ±20 Å. The sample thickness was varied from ~1100 to 1700 Å in increments of 30–60 Å.

The samples were annealed in a vacuum oven at 170 °C for a total of 6 weeks. They were removed from the oven and quenched to room temperature after 1 day, 1 week, 2 weeks, 4 weeks, and 6 weeks for X-ray reflectivity and/or reflection microscopy studies. After 1 day, a series of discrete, uniform interference colors with sharp boundaries were present at the edges of all of the samples, where large thickness variations occur as a result of the spin-coating process. This indicates

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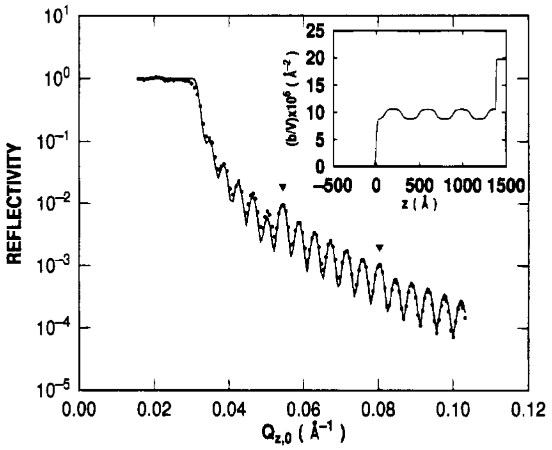

Figure 1. X-ray reflectivity for one of the optically flat samples after 1 week of annealing at 170 °C: points, data; line, fit based on the scattering length density profile shown in the inset. Arrows mark the third- and fifth-order Bragg peaks.

that the copolymer has self-assembled into a multilayered structure after 1 day.

After 1 week, observation in a reflection microscope divided the samples into three categories: the thinnest and three thickest samples exhibited surface features (islands or holes) while those of intermediate thickness still showed no surface topography; i.e., they were optically flat. Nine samples were chosen for X-ray reflectivity measurements: three with islands, one with holes, and five that were optically flat. The samples were then put back into the vacuum oven. After 2 weeks, all of the optically flat samples were unchanged. After 4 weeks, all but one of these samples had developed holes on the surface, with the area coverage of holes increasing with decreasing film thickness. The remaining flat sample, whose thickness was closest to the quantized value of $3.5L_0$, developed holes on the surface after 6 weeks. After 6 weeks, reflectivity measurements were again made on all nine samples.

X-ray reflectivity measurements were performed using an 18 kW Rigaku rotating-anode generator with a copper target at a power of 50 kV and a current of 200 mA. X-rays from the anode impinged upon a channel-cut Si monochromator which delivered monochromatic X-rays with a wavelength, λ, of 1.542 Å. Reflectivity data were obtained by rocking the sample by an angle θ with respect to the incident beam and rotating the detector by 2θ. The reflected X-rays were collected with a scintillation counter and pulse height analyzed to discriminate unwanted radiation and electronic noise. The reflectivity results are reported as a function of the momentum transfer normal to the surface $Q_{z,0}$, which is given by $(4\pi/\lambda)\sin\theta$. Background was determined by offsetting the detector by ±0.1° in 2θ and averaging the two measurements. Over the $Q_{z,0}$ range of interest, the background was insignificant.

Results and Discussion

A typical X-ray reflectivity profile is shown in Figure 1. These data are for a specimen that was optically flat by reflection optical microscopy after a 1 week anneal at 170 °C. Below the critical angle, the X-rays are totally externally reflected at the surface. However, above the critical angle, the reflectivity drops off rapidly and exhibits Kiessig fringes, characteristic of the total film thickness.[23] A second, more subtle, feature is the enhancement of the interference fringes at $Q_{z,0}$ values of 0.054 Å^{-1} and 0.08 Å^{-1} (marked by the two arrows in the figure). These are Bragg peaks arising from the multilayering of the PS and PMMA domains. The electron density difference between the PS and PMMA is sufficiently large to yield third- and fifth-order Bragg reflections. The position of the nth-order reflection is related to the period of the multilayer by a modified Bragg equation

$$n\lambda = 2L\sin\theta_i \tag{1}$$

where θ_i is the angle of the X-rays within the sample. This includes refraction effects at the air/polymer interface, and θ_i is therefore not equal to the external incidence angle θ. The period L can thus be determined directly from the positions of the Bragg peaks, without further analysis.

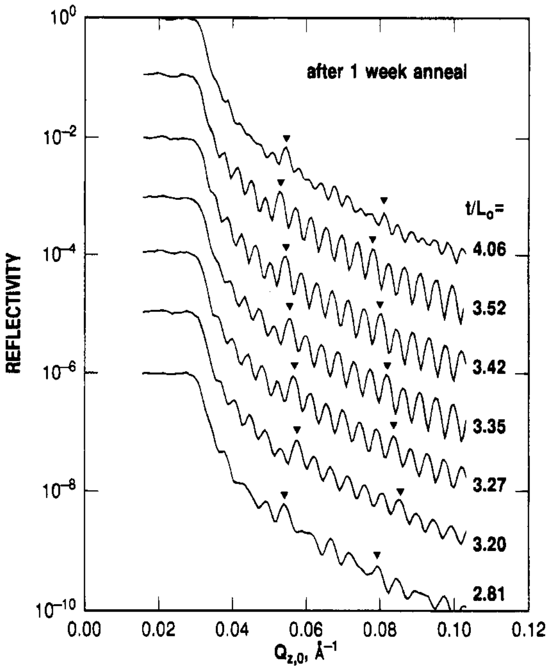

Figure 2. Measured reflectivity curves for seven of the samples, after 1 week of annealing at 170 °C. The initial film thickness decreases from top to bottom. The third- and fifth-order Bragg peaks are marked by arrows for each curve. The curves are labeled by the reduced initial film thickness t/L_0, with L_0 = 405 Å.

The solid line in the figure is a fit to the experimental data, calculated using the scattering length-density profile, b/V, shown in the inset. For X-rays, the scattering length density is $r_0\rho_{el}$, where r_0 is the classical electron radius and ρ_{el} is the electron density. As can be seen, the measured and calculated reflectivity profiles are in good agreement over the entire scattering vector range studied. This film is comprised of 3.5 complete layers with a period of 398 Å, made up to 199 Å thick alternating layers of PS and PMMA. Due to the small b/V difference between the PS and PMMA layers, in comparison to the larger b/V changes at the air and substrate interfaces, it is not possible to determine accurately the interfacial width between the PS and PMMA layers. In these calculations a value of 50 Å was therefore used, in keeping with the results of previous studies.[3,4,24-26]

The reflectivity profiles obtained after 1 week for seven of the samples studied are shown in Figure 2 as a function of $Q_{z,0}$. The reflectivity profiles for the different samples have been offset vertically for clarity; the data for the thickest sample are at the top and the thickness decreases monotonically for each successive curve. The sample thickness divided by the equilibrium bulk period, t/L_0, is given for each profile. The uppermost profile is for a sample that showed island formation after 1 week, while the bottom profile is for a sample that exhibited holes. In these cases, a beating

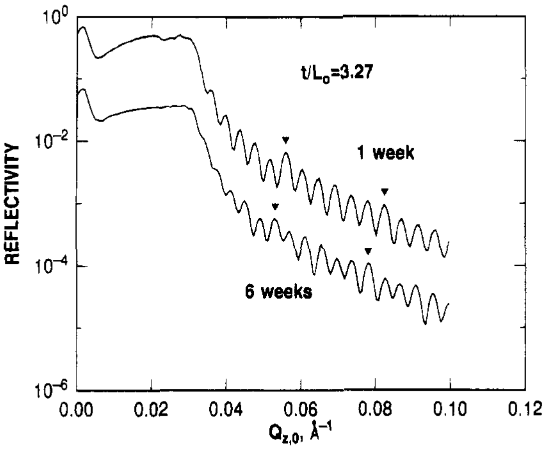

Figure 3. X-ray reflectivity profiles of a sample with $t/L_0 = 3.27$. The uppermost profile is for the sample annealed for 1 week, prior to the formation of surface features, i.e., kinetically confined, and the lower profile was obtained after annealing for 6 weeks whereupon surface features were observed. Note the shift in the Bragg peaks to lower $Q_{z,0}$ and the onset of beating.

of the oscillations is seen which arises from the two different thicknesses characterizing each film ($3.5L_0$ and $4.5L_0$ for the top curve, and $2.5L_0$ and $3.5L_0$ for the bottom curve). The peaks arising from the internal multilayers of the film are still evident. The middle five profiles are for samples which showed no surface topography, i.e., which were optically flat. These reflectivity profiles show oscillations arising from the film thickness as well as the third- and fifth-order Bragg reflections arising from the internal multilayered structure.

The positions of the third- and fifth-order Bragg peaks are marked by arrows for each of the curves in Figure 2. Rather than being constant, the peak positions shift dramatically and in a systematic way as the film thickness is varied. The peak positions are roughly the same for samples with islands and holes (top and bottom profiles), with third- and fifth-order reflections occuring at 0.054 and 0.080 Å^{-1}, respectively. From the position of these reflections, a period of ~398 Å is found. However, the peaks for the five optically flat samples (middle five curves) shift systematically to higher $Q_{z,0}$ as the film thickness is reduced and occur at $Q_{z,0}$ values both lower and higher than the peak positions of the thickest and thinnest samples. The reflectivities of all five of these samples could be fit quite well using scattering length density profiles similar to that shown in Figure 1, indicating that these samples all have a similar multilayered structure.

Thus, for the optically flat samples, it can be concluded that the films have been effectively confined by the solid substrate and the free surface. The lamellar period expands or compresses in response to the thickness constraint in a manner that is identical to that observed for copolymer films confined between two solid surfaces.[14,16,17]

After six weeks, the five samples which were flat after 1 week had all developed holes. Typical changes in the reflectivity profiles are shown in Figure 3, where the reflectivity profiles for a single sample annealed for 1 week (upper profile) and for 6 weeks (lower profile) are shown. As can be seen, there is a clear shift in the position of the Bragg peaks—i.e., the period of the multilayer has changed—and the onset of beating due to the presence of two sample thicknesses is evident.

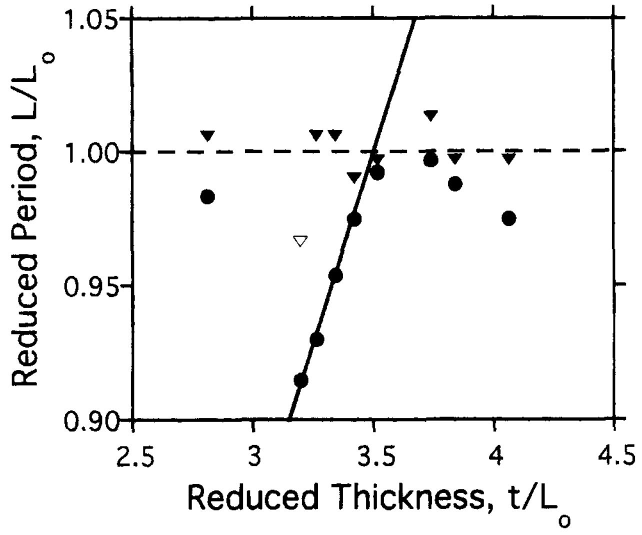

Figure 4. Reduced period L/L_0 vs reduced film thickness t/L_0 after 1 week (circles) and 6 weeks (triangles). The solid line is the equation $L = t/3.5$, the expected result for confined samples with 3.5 layers, while the dashed line is $L = L_0 = 405$ Å. The deviation of one point from the dashed line (open triangle) may be due to sample degradation, but this sample still experienced a shift of the period in the same direction as the others.

After 6 weeks of annealing, all of the Bragg peaks in the reflectivity profiles occurred at approximately the same $Q_{z,0}$ values, indicating that the periods of all of the samples are now nearly identical.

In Figure 4, the reduced period L/L_0 is plotted against the reduced film thickness t/L_0, for all samples studied by X-ray reflectivity, and with annealing times of 1 week and 6 weeks. After 1 week of annealing, samples with $3.2 < t/L_0 < 3.5$ have periods which obey $L = t/3.5$ (solid line), the relationship for a confined film 3.5 layers thick. After 6 weeks, all of the samples but one have the same period $L = L_0 = 405$ Å (dashed line). Figure 4 summarizes the main conclusions of this paper. First, a copolymer multilayer can be effectively confined by the substrate and free surface for periods of up to several weeks, if the film thickness is close to the ideal value. Second, this confinement is apparently much more effective for compressed periods than for stretched periods, indicating that the activation energy for hole formation is much higher than for island formation. This result is in keeping with recent arguments of Williams,[27] who found that a copolymer multilayer with a stretched period is unstable against the occurrence of undulations, while a compressed multilayer is stable against such undulations. Finally, the confinement of PS/PMMA on SiO_2 by a free surface is a kinetic effect and does not represent an equilibrated state.

The driving force for the formation of surface topography is the stretching or compression of the copolymer chains, due to an incommensurate film thickness. It has previously been shown that, beginning with a disordered spin-cast film, order propagates into the film from both surfaces during annealing, driven by the surface interactions.[6] Until order has propagated throughout the sample, so that the two surfaces can "communicate", this driving force cannot be effective in inducing surface topography. Once order has propagated throughout the film, free surface confinement can be expected to occur if the time scale for vertical redistribution of chains between layers is significantly shorter than the time required for island or hole formation, which involves the lateral redistribution of large amounts of material over large distances on the surface. The driving force for topography formation should vanish approximately as $(L - L_0)^2$ since L_0 represents a minimum in the free energy and we can expand the free energy about L_0. Thus, free surface confinement should occur over longer time scales as the film thickness approaches the ideal value.

The maximum possible frustration occurs for film thicknesses of $t = nL_0$, for which $\Delta L/L_0$ is approximately $1/2n$. For example, for films approximately 10 layers thick, a thickness change of only 10% is sufficient to drive the multilayer from the $n = 10$ configuration into the $n = 9$ or $n = 11$ states. The period change due to confinement will never exceed $\Delta L/L_0 = 5\%$. Therefore, the driving force for the formation of surface topography diminishes with an increasing number of layers, and kinetically trapping a film in a confined state becomes more likely. Although the driving force for the formation of surface features can become quite large for very thin films, the interactions of the copolymer with the surface and substrate can slow down the formation of surface features as shown by Coulon et al.[13]

Finally, we point out that these results may be quite important for practical applications in which one desires a multilayer with a flat surface. Since it is impossible to repeatedly spin cast films with a perfectly uniform and specified thickness, it is important to quantify the degree of process lattitude in the initial thickness and the annealing time, which will yield a film with a flat surface, free of islands and holes.

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