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Phase Behavior of Thin Film Blends of Block Copolymers and Homopolymers: Changes in Domain Dimensions

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ABSTRACT: We used atomic force microscopy to examine the phase behavior of thin film mixtures of a symmetric A−B diblock copolymer of degree of polymerization $N_{A-B} = 650$ with (i) two homopolymers ($N_A = 20$ and 250) and (ii) a symmetric A−B diblock copolymer ($N_{A-B} = 200$). Thin film symmetric diblock copolymers are known to undergo a transition from a disordered phase to an ordered lamellar phase in which the lamellae orient parallel to the plane of the substrate. We examined films sufficiently thin in order to determine the effect of the substrate on the phase behavior. Homopolymer volume fractions of up to 50% were studied. The interlamellar spacing increased with the addition of both low- and high-molecular-weight homopolymers, although it was less extensive for the lower molecular weight homopolymer. Both situations could be well-described by theory relying on assumptions about the homopolymer distribution in the domains and the areal densities occupied by the copolymer junctions. In contrast to the homopolymers, the lamellar spacing of blends formed with the second diblock copolymer ($N_{A-B} = 200$) decreased with increasing volume fraction of this shorter chain copolymer. This behavior could be described by assuming that $L \propto N_w^{2/3}$, where N_w is the weight-average degree of polymerization of the mixture. We also show that the degree of swelling of the domains depends on the proximity of the domain to the substrate.

Introduction

Diblock copolymers are known to exhibit different microphase-separated morphologies, including spheres, hexagonally packed cylinders, lamellae, and bicontinuous "gyroid" structures.[1] The phase structure is determined by the Flory−Huggins interaction parameter (χ), the number of segments per copolymer chain (N), and the volume fraction of each phase.

The phase behavior exhibited by mixtures of an A−B diblock copolymer with an A or B homopolymer has been the subject of considerable interest.[2−21] This body of work has focused on either mapping out phase diagrams[8−13] or investigating changes in domain dimensions[14−21] of ordered block copolymers with the addition of the homopolymers. In these blends, the free energy is reduced when the homopolymers segregate to the appropriate domains of the ordered microstructure, reducing the number of unfavorable segmental A/B contacts. The microdomains swell in order to accommodate the homopolymers. This situation typically arises when the degree of polymerization of the homopolymer is on the order of or less than the degree of polymerization of the appropriate component of the copolymer chain. Transitions from one type of microstructure to another or the formation of separate phases or both are also possible depending on the relative chain lengths of the copolymer and homopolymers, the χ parameter, and the volume fraction.

The behavior of thin film diblock copolymers differs from that of bulk copolymers in distinct ways. Symmetric diblock copolymers, for example, undergo an isotropic-to-lamellar transition below an order−disorder transition temperature T_{ODT}, defined by the condition $\chi N > 10.495$.[1] The lamellae typically orient parallel to the plane of the substrate because one component of the A−B diblock exhibits a preferential affinity for the substrate. Because of this relative attraction, ordering of the copolymer generally proceeds from the substrate. An alternate way of considering this behavior is that the effective A/B interactions become more repulsive in the vicinity of the substrate, $\chi_{\mathrm{substrate}} > \chi_{\mathrm{bulk}}$. In essence, the effective temperature at which this transition occurs is increased appreciably above the bulk value, $T_{ODT}{}^{\mathrm{substrate}} > T_{ODT}{}^{\mathrm{bulk}}$. Consequently, the substrate can induce ordering in the sample, as shown earlier. By implication, the degree of segregation, particularly for weakly ordered copolymers, should be enhanced near the substrate.

In the ordered state, thin film block copolymers are known to exhibit terraces of height L, equivalent to the interlamellar spacing in the bulk. The formation of these terraces, often described as islands or holes, is dictated by the commensurability between the interlamellar spacing and the thickness of the film.[22] Atomic force microscopy (AFM) has proven to be an effective method by which the dimensions of these terraces could be imaged.[22] The results compare favorably with neutron reflectivity measurements of interlamellar spacings in the same systems.[23]

In view of these clear differences between thin film and bulk block copolymers, it is natural to examine the influence of the substrate on the phase behavior of block copolymer/block copolymer mixtures and block copolymer/homopolymer mixtures. In this paper we show that AFM is a viable method for examining the changes in domain dimensions of these mixtures in the ordered state. We will restrict our attention to films of thickness on the order of a few L or less in order to examine the effect of the substrate on the behavior of the mixture. We also compare our results with mean field theory[20,28] and the behavior of bulk mixtures.

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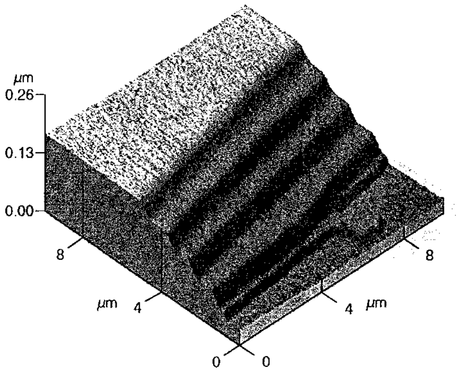

Figure 1. Steps which develop at the edge of an ordered diblock copolymer film when the film is scratched and the substrate is exposed (subsequently annealed above T_g).

Experimental Section

Two poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymers with total molecular weights of $M = 20\,500$ ($M_{PS} = 9\,800$, $M_{PMMA} = 10\,700$, $\phi_{PS} \approx 0.48$, $M_w/M_n < 1.09$) and $M = 65\,500$ ($M_{PS} = 33\,000$, $M_{PMMA} = 32\,500$, $\phi_{PS} \approx 0.50$, $M_w/M_n < 1.06$) were purchased from Polysciences, Inc. In addition, polystyrene (PS) homopolymers with molecular weights of 2 500 and 25 000, with polydispersity indices $M_w/M_n < 1.06$, were obtained from Pressure Chemical.

Solutions of 65K PS-*b*-PMMA blended with PS were prepared in toluene with homopolymer volume fractions, φ, ranging from 0.01 to 0.5. Additionally, blends of varying volume fractions, 0.02 to 0.1, of a 20.5K PS-*b*-PMMA diblock with the 65K diblock were prepared. The solutions were used to spin-cast the films onto polished silicon wafers which were covered with ~20 Å thick native oxide layers.

We examined films of thickness $t < 4L$. All films were scored and subsequently annealed at 179 °C for periods in excess of 24 h under vacuum. After they were annealed; the films were examined by AFM.

Results

The edges of ordered copolymer/homopolymer and copolymer/copolymer blend films were imaged in several locations. Figure 1 shows that steps develop at the edges of the films which were scored and annealed. This image is typical of all of the blends we examined. We can construct a diagram of the ordered film based on numerous measurements near the edge of the film. This is shown in Figure 2. Here the steps occur at the interface between the layers of the lower surface energy polystyrene component. Figure 3a shows an image of the surface of the blend containing a volume fraction of 50% of the 2K homopolymer, and Figure 3b shows the surface of a film containing 4% homopolymer. Both surfaces exhibit similar topographies.

On the basis of multiple scans taken of the edges of each sample, the layer in contact with the substrate, L_1, was determined to be relatively insensitive to the volume fraction of homopolymer. Typical line scans are shown in Figure 4 for varying concentrations of homopolymer in the copolymer. In this figure L_1 is approximately 157 Å, comparable to the value in the pure copolymer. This is clearly less than one-half of the value of the subsequent layers. The L_1 layer for the 2K homopolymer blend generally was found to be slightly higher than that determined for the 25K homopolymer blend.

Moreover, as a general trend, the degree of swelling depended on the proximity of the layer to the substrate.

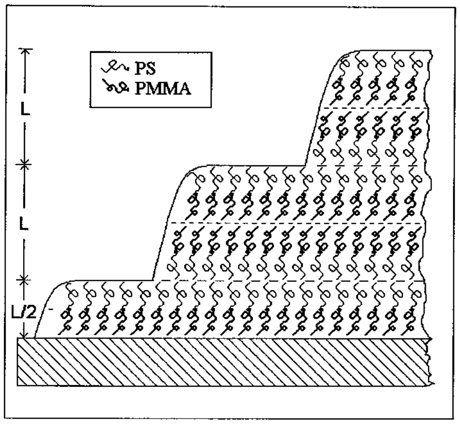

Figure 2. Simplified schematic of a cross section of the steps at the edge of a PS-*b*-PMMA copolymer film. The lower surface energy PS component is exposed to the free surface. Others (see: Carvalho, B. L.; Thomas, E. L. *Phys. Rev. Lett.* **1994**, *73*, 3321 (1994) have shown, using transmission electron microscopy, that the edges of droplets on carbon substrates form steps. At the *edges* of these droplets, lamellae were observed to undergo significant contortions to accommodate the transition from one height to another. This schematic ignores this complication.

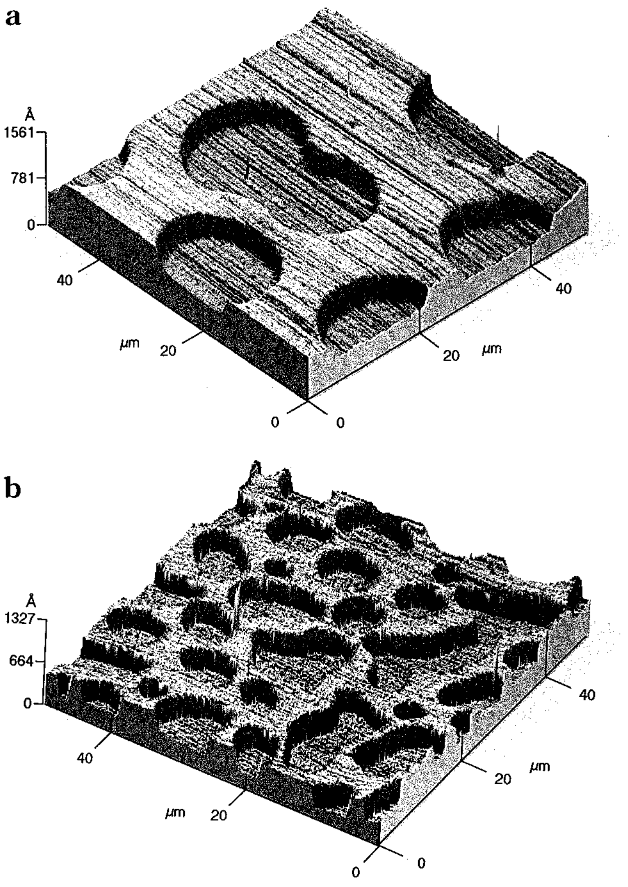

Figure 3. Images of the surfaces of two blends (a) 50% and (b) 4% 2K polystyrene.

It is clear from the scans shown in Figure 4 that the layers become somewhat thicker with increasing distance from the substrate. We determined an average layer spacing by taking the average value for L from the layers L_2–L_4 from numerous scans of each sample. These data are plotted in Figure 5.

The circles and squares in Figure 5 indicate that the interlamellar periods, L(2K) and L(25K), for the 2K and

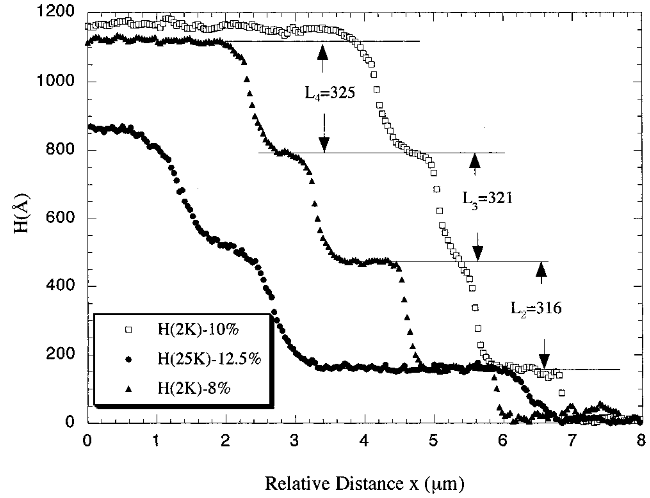

Figure 4. Line scans of the step heights of the ordered mixtures for blends containing the 2K and 25K homopolymers.

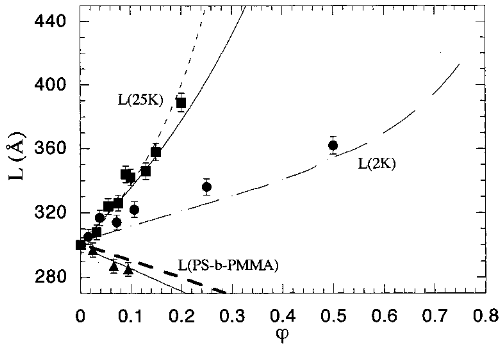

Figure 5. Interlamellar spacing versus volume fraction of PS homopolymers and PS-*b*-PMMA diblock copolymers. The solid line drawn through the 25K PS data was computed using eq 7, the broken line was computed using eq 5, and the line drawn through the L(2K) data was computed using eq 8. The line drawn through the triangles was computed as described in the text.

25K homopolymer blends, respectively, increase appreciably with φ. L(2K) exhibits a weaker dependence on φ than L(25K), as expected. However, as discussed later, L(2K) has a stronger dependence on φ than might be anticipated on the basis of the behavior of bulk systems with comparable or smaller $\chi_{\mathrm{bulk}}N$. The copolymer/copolymer blends involving short diblocks exhibited behavior significantly different than the copolymer/homopolymer blends. The interlamellar spacing decreased with the addition of the 20.5K diblock copolymer. The lines drawn through the data sets in Figure 5 are discussed later.

Discussion

The equilibrium lamellar spacing in a symmetric diblock copolymer can be determined from a simple balance of the elastic free energy and interfacial energy contributions,[24]

$$\Delta F_{\mathrm{b}} \approx (^3/_2)k_{\mathrm{B}}T(\mathrm{Na}^3/\Sigma^2) + \Sigma\gamma_{\mathrm{A/B}} \qquad (1)$$

where $\gamma_{\mathrm{A/B}}$ is the interfacial energy between A and B components of the copolymer chain. The area per copolymer chain is identified by $\Sigma = \mathrm{Na}^3/D$, where D is one-half of the interlamellar spacing. Minimization of this free energy with respect to Σ provides the equilibrium lamellar spacing

$$2D_{\mathrm{eqb}} = L \propto (\gamma_{\mathrm{A/B}}/k_{\mathrm{B}}T)^{1/3}N^{2/3} \propto \chi^{1/6}N^{2/3} \qquad (2)$$

In the above equation, we used the fact that $\gamma_{\mathrm{AB}} \approx (k_{\mathrm{B}}T/a^2)\chi^{1/2}$.

Equation 1 might be rewritten to account for the additional interfacial energy contributions. The free-energy change with respect to the substrate, assuming that the A component has a preferential affinity for the substrate and the B component for the free surface, is[25]

$$\Delta F \approx (^3/_2)k_{\mathrm{B}}T(2n + 1)(\mathrm{Na}^3/\Sigma^2) + \Sigma[(2n + 1)\gamma_{\mathrm{A/B}} + \gamma_{\mathrm{lv}}{}^{\mathrm{B}} + \gamma_{\mathrm{sl}}{}^{\mathrm{A}} - \gamma_{\mathrm{sv}}] \qquad (3)$$

Minimization of this equation with respect to Σ shows that

$$2D_{\mathrm{eqb}}(2n + 1) = L_{2n+1} \propto \{[\gamma_{\mathrm{AB}} + (\gamma_{\mathrm{lv}}{}^{\mathrm{B}} + \gamma_{\mathrm{sl}}{}^{\mathrm{A}} - \gamma_{\mathrm{s}})/(2n + 1)]/k_{\mathrm{B}}T\}^{1/3}N^{2/3} \qquad (4)$$

Here we assumed that the film is of uniform thickness $t = (n + {}^1/_2)L$. It is further assumed that Σ is constant in each layer. In light of this analysis, it follows that the effective interaction parameter is altered as a result of interactions with the substrate and with the surface.

We now examine the wetting properties of the copolymer film on the substrate. The copolymer did not spread on the substrate after it was scored. In fact, the film remained stable and formed steps at the edges. It is known that thin films of PS and PMMA are unstable on silicon and will dewet the substrate because of capillary forces, long-range van der Waals forces, or both. We, in fact, observe these instabilities regularly on these substrates. In the case of an unstable homopolymer film, there would be a net force, F_{k},[26] acting on the edge of the film, $F_{\mathrm{k}} = \gamma_{\mathrm{lv}}{}^{\mathrm{A}} + \gamma_{\mathrm{sl}}{}^{\mathrm{A}} - (\rho g h^2/2) - \gamma_{\mathrm{sv}}$. In this equation, the third term is the hydrostatic pressure, ρ is the density, g is the gravitational constant, and h is the film thickness. In contrast to the homopolymer constituents, the copolymer film is stable on the substrate, suggesting that interfacial tension between PS and PMMA has a significant impact on the wetting properties of the copolymer. For the ordered copolymer to dewet the substrate, it would have to create additional A−B monomer contacts, which is energetically unfavorable. The interfacial tension for PS/PMMA is small, ~2 dynes/cm, compared with the surface energies of the pure components, which are over an order of magnitude larger.[27] The general question of wetting of copolymer droplets on substrates is discussed elsewhere.[25] The role of the interfacial tension of the spreading coefficient of copolymer droplets on substrates is addressed quantitatively. We will not address this point further in this paper because it is a secondary issue here.

We will now briefly discuss the general behavior of bulk block copolymer/homopolymer mixtures in order to provide a context for the subsequent discussion of results from our thin film experiments. It is known from bulk samples that the A homopolymer can be completely solubilized in the A domains of a lamellar A−B diblock copolymer structure when the homopolymer molecular weight is less than, or comparable to, that of the corresponding block. For a given molecular weight, increasing the concentration of the homopolymer A increases L_A and decreases L_B, where L_A and L_B are the thicknesses of the A and B domains, respectively; the equilibrium lamellar thickness L is given by $L = L_A + L_B$. In general, the increase in L_A is greater than the decrease in L_B, which results in an overall increase in L, although a decrease in L has been observed in *bulk* blends with low-molecular-weight homopolymers.[10,16,17] For a fixed blend concentration, homopolymers with high molecular weights expand L_A more and contract L_B less than those with lower molecular weights. Thus, increasing the molecular weight of the homopolymer in the blend generally increases the lamellar period.

The effect of the homopolymer molecular weight on the swelling can be understood by examining the distributions of the homopolymers in the solubilizing domains. Experiments[10,17] in bulk samples indicate that homopolymers with considerably lower molecular weights are dissolved comparatively uniformly in the microdomains but those with higher molecular weights, comparable to that of the corresponding block of the copolymer, tend to be localized between the ends of blocks (middle of the domains) instead of intermingled with them. This difference in the degree of penetration into the copolymer block can be directly correlated to the relative translational and conformational entropy losses associated with the confinement of the short and long homopolymer chains. For short chains, gains in the translational entropy due to uniform solubilization in the domains outweigh the minor losses in conformational entropy that occur when the chains adjust their configurations in order to fit between copolymer blocks. By contrast, the conformational entropy penalty associated with perturbing long homopolymer chains sufficiently to integrate them among the copolymer blocks is relatively high in comparison with the translational entropy loss accompanying the localization of the chains at the centers of the domains. Thus, higher molecular weight homopolymers locally segregate toward the middle of the microdomains instead of intermixing with the copolymer blocks.

Torikai and co-workers have shown[20] that if the homopolymer chains are localized at the center of the lamellae without changing the conformations of the block copolymer chains or the distances between the copolymer junctions, then the lamellae should be extended only along the axial direction, perpendicular to the interface, and the domain spacing can be expressed by

$$L = L_0 \left[\frac{2 - f_{PS}}{2(1 - f_{PS})}\right] \tag{5}$$

where L is the equilibrium lamellar period for the mixture, L_o is the equilibrium lamellar period of the pure copolymer, and f_{PS} is the weight fraction of the PS homopolymer in the PS domains of the ordered copolymer. By contrast, if the homopolymer is distributed uniformly throughout the domains, then the lamellae should be extended uniformly, and the domain spacing is predicted as follows:

$$L = L_0 \left[\frac{2 - f_{PS}}{2(1 - f_{PS})^{1/3}}\right] \tag{6}$$

This equation predicts that L should decrease with f_{PS}. It is assumed here that the penetration of the low-molecular-weight homopolymers into the copolymer "brushes" can induce lateral swelling and hence an increase in σ_J, the average interfacial area per copolymer junction. Therefore, bulk copolymer blends with low-molecular-weight homopolymers swell more in the lateral direction and less in the axial direction in comparison with their high-molecular-weight counterparts. As a result, the neighboring domains in low-molecular-weight systems also contract to a greater extent than their higher molecular weight counterparts.

Hamdoun et al. recently examined the effect of nanosized inorganic particles on the change in domain dimensions of diblock copolymers.[28] This theory is not specific to inorganic particles and should also provide insights into the effect of homopolymers on the domain dimensions. If the material added to the block copolymer is confined to the middle of the domains, then

$$L = L_0\,(1/1 - \varphi) \tag{7}$$

In this equation, φ is the volume fraction of the homopolymer in the entire sample. On the other hand, if the homopolymers penetrate between the copolymer brushes and are therefore more widely distributed than their higher molecular weight counterparts, then

$$L_u = L_0\,[g(f, \varphi)]^{-1/3}/(1 - \varphi) \tag{8}$$

where

$$g(f,\varphi) = \frac{f + (1 - f)\varphi^2}{f(1 - \varphi)^2}$$

In this equation, f is the volume fraction of the A component of the copolymer which is $^1/_2$ for symmetric diblock copolymers. It should be noted that eq 8, in contrast to eq 6, predicts that L must increase. This increase is necessarily smaller than those predicted by eqs 5 and 7 because it describes the situation in which the homopolymers are more broadly distributed throughout the domains.

We can now discuss the data in Figure 5 in light of these predictions (eqs 5−8). The broken line drawn through the L(25K) PS data was computed using eq 5, whereas the solid line was computed using eq 7. Over the range of concentrations considered, both equations yield reasonable predictions, suggesting that the homopolymer chains are confined exclusively to the middle of the domains. The behavior observed here for thin films is identical to that observed in bulk samples, which is not surprising, because for these higher molecular weight homopolymers, $N_{PS} \approx N_{PS-PMMA}/2$.[10,17,29] We consistently observed that $L_1 < {}^{L}/_{2}$, in fact $\Delta = {}^{L}/_{2} - L_1$ increased with increasing φ. The layer in contact with the substrate has a large effective χ parameter because of the preferential affinity for the PMMA segment. This layer forms a dense brush which excludes the large homopolymer chains. One might imagine that the PMMA layer would have to shrink to maintain a constant segmental density when the adjacent PS layer incorporates homopolymer chains comparable to its own length. This suggests that it is entropically more favorable for the homopolymer chains to preferentially wander into the layers away from the substrate. The fact that the axial dimensions of the L_1 layer were

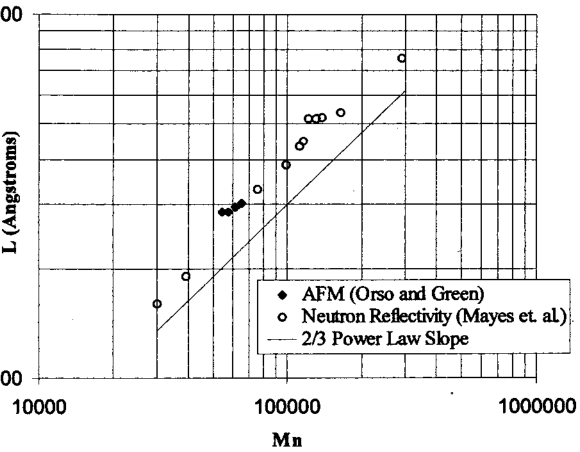

Figure 6. Our data obtained using AFM versus data obtained using neutron reflectivity (Mayes et al.).

somewhat more sensitive to the fraction of 2K homopolymer than that of the 25K homopolymer is consistent with this. The constraints of the substrate place inherent limitations on this process.

The discussion above indicates that adding 25K PS homopolymer chains to the 65K PS-*b*-PMMA swells the lamellar domains. By contrast, adding the 20.5K PS-*b*-PMMA diblock copolymer chains to the 65K PS-*b*-PMMA diblock results in a contraction of the lamellae. The bulk PS/PMMA interaction parameter is $\chi_{\text{bulk}} = 0.037$,[30] indicating that the 65K diblock would be ordered in the bulk, whereas the shorter diblock would be disordered. The triangles in Figure 5 show how the dimensions of the ordered layers decrease with the volume fraction of the smaller diblock. The trend exhibited in the figure is consistent with the notion that when symmetric short diblocks are added to the longer diblocks, there is a decrease in the interfacial tension and an increase in the stretching energy which results in a decrease in the equilibrium lamellar spacing as observed here.[31] The solid line drawn through the data was computed by first calculating the weight-average degree of polymerization, N, of the mixture of both copolymers and using the fact that $L = kN^{2/3}$ [where k is a constant determined from $L = 300$ Å $= k(650)^{2/3}$]. The broken line was computed by assuming that $L \propto N^{1/2}$. The former assumption obviously yields better agreement.

Mayes et al.[23] studied PS-*b*-PMMA diblock copolymer mixtures with neutron reflectivity and found that the variation in the lamellar spacing with the number-average molecular weight of the system scales as $L \propto M_n^{2/3}$. We converted our data in order to make a comparison. Figure 6 shows our data and that of Mayes et al. The agreement shown here is a strong indication that measurement of step height is a viable method to determine the domain swelling in these systems. The $^2/_3$ power law suggests that all of the systems are in the strong segregation regime.

We can now discuss the behavior of the diblock copolymer blends with the low-molecular-weight homopolymer. The effect of the substrate on the phase behavior is more apparent here than for the mixture containing the 25K homopolymer. Figure 5 shows that L(2K) increases with φ but to a lesser degree than L(25K). This suggests that these 2K homopolymers are more widely distributed throughout the PS domain than their 25K analogues. The dependence of domain swelling on volume fraction of the low-molecular-weight homopolymers exhibits a trend similar to that predicted by eq 8 and not eq 6.

As discussed earlier, experiments and theory on bulk copolymer systems show that low-molecular-weight polymers are uniformly distributed throughout the domains and can induce an increase in the average distance between copolymer junctions. In some situations, the interlamellar spacings are observed to decrease.[17] There is no evidence of this in our data. More importantly, evidence of changes in the blend morphology from lamellar to spherical morphologies, for example, have been documented.[10] This blend corresponds to a volume fraction of 75% PS, indicating that a change in morphology might be expected. We, however, see no evidence of changes in morphology. The fact that the images shown in Figures 3a and b, containing 4% and 50% homopolymer, respectively, yield identical topological features suggests that they have similar structures. Other morphologies, such as cylinders, are clearly identifiable using AFM.[33] There was no evidence of such morphologies. We should mention however that for samples which are thicker, $t > 3L$, the surface features become very diffuse. In cases for which the homopolymer solubility limit is exceeded, the homopolymer segregates to either the free surface or the substrate, depending on the interfacial energetics. For example, when the solubility limit of 100K PS is reached, the excess PS segregates to the outer surface. Experiments in our lab using a homopolymer poly(norbornene-methyl-d_3-carboxylate) show that when this polymer exceeds the solubility limit in the copolymer, it segregates to the substrate. It has a stronger affinity for the substrate than that of either PS or PMMA.[32]

Let us now examine further the effect of $\chi_{\text{substrate}}$ on the phase behavior. One should recall that the effective value of χ in the bulk, χ_{bulk}, should be smaller than the value near the substrate, $\chi_{\text{substrate}}$. This means that ordered thin films on substrates are more strongly segregated than bulk polymers of identical molecular weight. On the basis of the block copolymer phase diagram,[1] samples with large values of χN maintain lamellar structures over a larger composition than those closer to $\chi\text{N} = 10.5$. These results suggest that in the presence of a surface, transitions from the lamellar to other morphologies should be suppressed because of the large effective interaction parameter.

In this final section of this paper, we address important questions regarding the behavior of films which are much thicker. There are limitations on the use of features on the free surface depending on the film thickness. Consider Figure 7a, which shows the surface of a PS-*b*-PMMA film of nominal thickness $t \approx 0.62$ μm (i.e., $t \approx 21L$), which varied considerably. This film was annealed for 66 h at 180 °C, and the surface shows no signs of islands or holes. In fact, a line scan of the surface indicates that the uniformity in that 50 × 50 micron region varies by more than L. Clearly there is no variation of the topology with local thickness across the image, i.e., an absence of surface structures. It is noteworthy that a thinner region, $t \approx 0.5$ μm, of this sample (Figure 7b) exhibits well-defined surface relief structures. The accompanying line scan for this image is shown. Clearly, despite the fact that $T < T_{\text{ODT}}$, the appearance of the surface features is dependent on the local thickness of the films. Moreover, the steps become “washed out” when the film becomes thick. Experiments

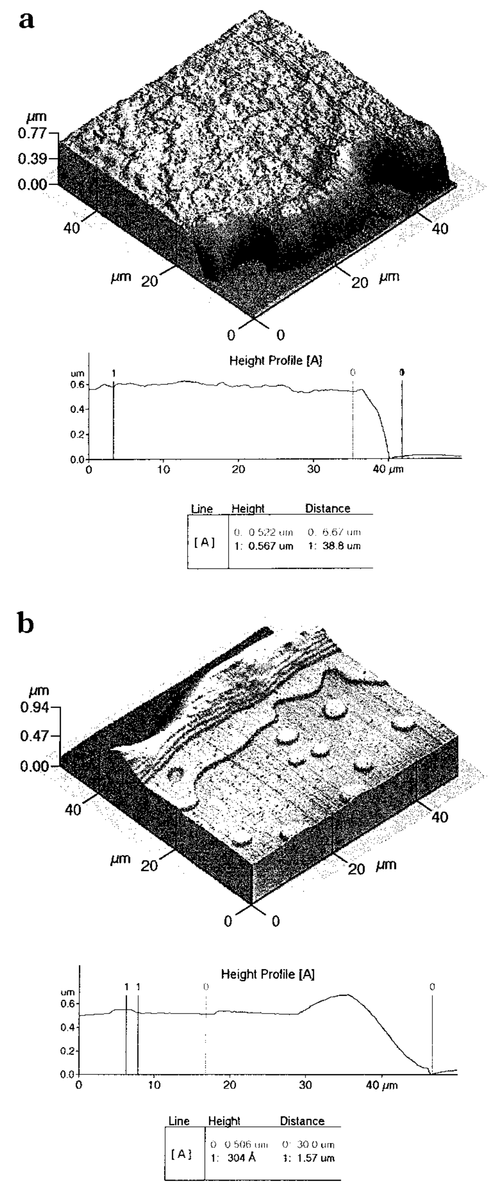

Figure 7. (a) Surface of a film of nominal thickness $t \approx 0.62$ μm ($t \approx 21L$) which was annealed at 179 °C for 66 h under vacuum. (b) Surface of a slightly thinner region ($t \approx 17L$) of this sample.

are underway to examine the effect of other substrates on the phase behavior.

Conclusions

We have shown that AFM provides a very convenient means by which domain swelling and contraction in block copolymer/block copolymer and block copolymer/homopolymer mixtures can be studied. The utility of this technique rests on the fact that the dimensions of the steps and the topological features of the block copolymer thin films provide a useful measure of the dimensions of the internal equilibrium structure. Finally, because PMMA had a stronger affinity for the substrate, the effective value of the PS/PMMA segmental interactions was enhanced, ($\chi_{\text{substrate}} > \chi_{\text{bulk}}$) resulting in a more immiscible system near the substrate. These effects were observed to alter the phase behavior of the mixtures in relation to the bulk. One effect of the substrate is to suppress transitions between morphologies that would normally be expected in bulk mixtures of comparable χN. We also showed that the swelling of the layers depended on the proximity of the layer to the substrate.

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