Surface-Induced Ordering in Asymmetric Block Copolymers

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ABSTRACT: The surface-induced ordering in thin films of asymmetric deuterated polystyrene (dPS)-poly(vinylpyridine) (PVP) diblock and triblock copolymers of comparable polymerization index and PVP volume fraction ($f \sim 0.25$) was studied using transmission electron microscopy, atomic force microscopy, secondary ion mass spectrometry, and neutron reflectivity. The morphology of both di- and triblock copolymer films was found to be cylindrical except for the layer adjacent to the silicon oxide surface, which due to the strong interaction of silica with PVP, was lamellar. The spacing between adjacent cylindrical layers was found to be consistent with mean field theory predictions. In the triblock copolymer films the cylindrical layers were oriented parallel to the silicon oxide surface, and no decay of the ordered structure was observed for at least 12 periods. If the total film thickness t' deviated from $t = [(n + 0.71)210 + 182]$ Å, where n is an integer, islands or holes formed at the vacuum interface. The height of the holes or islands reached its equilibrium value, 210 Å, after annealing 24 h at 180 °C. In contrast, it was far more difficult to orient parallel to the silicon oxide surface the microphase-separated cylindrical domains in the diblock copolymer films. As a result no islands or holes were observed even after annealing for 5 days at 180 °C. We concluded that the difference in ordering behavior was due to the ability of the triblock copolymer to form an interconnected micelle network while the diblock copolymer formed domains that were free to move with respect to each other. This conclusion was further confirmed by diffusion measurements which showed that the PS homopolymer penetrated easily into the ordered diblock copolymer films and was excluded from the ordered triblock copolymer films.

Introduction

Phase-separated melts of polymer molecules composed of two or more chemically distinct blocks of monomer units have been shown to have unique properties not found in simple melts of the individual components. These properties arise from the fact that, since the blocks are joined covalently, they cannot form macroscopic phases and are thus forced to form periodically ordered microdomains. The phase diagrams of these microdomains have been studied extensively both theoretically and experimentally.[1-12] The main parameters controlling the morphology of the segregated phases were found to be f, the fraction of monomers of type A in an A-B block copolymer, and the product χN, where χ is the Flory interaction parameter between A-B segments and N is the total number of monomer units in the block copolymer chain. When the interaction between the two types of monomers is highly unfavorable, i.e., $\chi N \gg 10$, the system is strongly segregated; the size of the microdomains is much larger than the interfacial width.[4,5] For symmetric ($f = 1/2$) block copolymers the interfacial tension is minimized by arranging the copolymers in a lamellar structure. As f decreases, the morphologies with the minimum interfacial free energy change[3-5] from bicontinuous double diamond ($0.28 < f < 0.34$)[11,12] to cylindrical ($0.13 < f < 0.28$) to spherical ($f < 0.13$). When a block copolymer melt is in contact with a surface, the component with the lowest surface energy will preferentially segregate to that surface. If the difference in surface energy is sufficiently high, this segregation has the effect of orienting the microdomains parallel to the surface.[6-10] Furthermore, if the orienting potential is strong, then only film thicknesses corresponding to a multiple of the domain spacing are stable.[3,6-8] Any excess material is pushed out, forming islands on the surface approximately one lamella in height.[13,14] These phenomena were first observed in a series of elegant experiments by Russell and co-workers[9,10] and the surface morphology was studied in detail by Russell, Coulon, and co-workers.[13,14]

The case of asymmetric block copolymer films is more complicated and has not been studied extensively. Theoretically, the complications arise from the three-dimensional nature of the potential which can now only be solved numerically.[6-15] Furthermore, the surface interaction not only orders the individual domains but can also induce phase transitions between the various morphologies.[15] To understand the effect of the surface on asymmetric block copolymer films, experiments involving both in and out of plane profiling must be performed. Previous experiments,[16] using transmission electron microscopy (TEM), demonstrated that either cylindrical or spherical domain structures could be induced to order parallel to a surface. These experiments though were performed on polymer droplets of nonuniform thicknesses cast on carbon-coated

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Table 1. Summary of Block Copolymers Used

	composition	polymerization index	f
diblock	PVP–dPS	220–580	0.28
	PVP–dPS	510–540	0.49
	PVP–dPS	800–800	0.50
triblock	PVP–dPS–PVP	85–550–85	0.24

glass surfaces without a well characterized preferential attraction for either of the block components. Furthermore, since the experiments focused on diblock copolymers, the interplay between the block morphology, i.e., brush vs loop adsorption, and the surface ineraction could not be probed.

In this paper, we present a comprehensive study comparing the surface-induced ordering between asymmetric deuterated polystyrene (dPS) and poly(vinylpyridine) (PVP) diblock and triblock (PVP–dPS–PVP) copolymers of similar total N and f. This system was chosen since the two components are highly immiscible and, for the temperatures studied, both bulk copolymer melts are predicted in all the theoretical treatments[3–8] to be strongly segregated into cylindrical microdomains.[3–5] The nature of any further orientation parallel to a surface when the cylinders are confined in thin films was studied using neutron reflectometry (NR) and secondary ion mass spectrometry (SIMS). The associated surface topology was studied with atomic force microscopy (AFM) in conjunction with X-ray reflectometry (XR), and the in-plane morphology was studied using transmission electron microscopy (TEM).

Experimental Section

The polymers used in this study are listed in Table 1. The triblock was composed of a dPS midblock with PVP end blocks. The copolymers were synthesized via anionic polymerization in tetrahydrofuran under an argon atmosphere at −55 °C. The diblock copolymer, poly(styrene-d_8-b-2-vinylpyridine), was synthesized using cumylpotassium as the initiator.[17] The triblock copolymer, poly(2-vinylpyridine-b-styrene-d_8-b-2-vinylpyridine), was synthesized using a difunctional initiator, (α-methylstyrene)-potassium.[18] The PVP fractions f = 0.24 for the triblock copolymer and f = 0.28 for the diblock copolymer were determined from mass microanalysis, and ^{13}C nuclear magnetic resonance. The Flory interaction parameter, χ, for this system was measured previously to be[19]

$$\chi = -0.033 + .63/T \qquad (1)$$

Consequently, for the relevant temperatures studied in this paper, $\chi N \approx 80$, placing both the triblock and diblock copolymers in the strong segregation cylindrical regime.

Uniform films of block copolymers of thicknesses ranging from 300 to 3000 Å were spun cast from toluene solution onto native oxide covered polished silicon substrates. The samples were then annealed at T = 180 °C for times ranging from 15 min to 14 days in a vacuum of 10^{-4} Torr. The samples used for SIMS were prepared by floating, on top of the sample, a "sacrificial" layer of PS, approximately 300 Å thick, prior to analysis. This extra "sacrificial" layer allows the ion beam sputtering rate to come to a steady state before the sample surface is reached. The sputtering was performed on an Atomika 3000-30 ion microprobe using a 2 keV, 20 nA beam of Ar^+ ions at 30° off normal incidence, rastered over a 0.25 mm^2 region. Negative ions of C, D, CN, CH, CD, and O were monitored. At a sputtering rate of approximately 500 Å/h, we obtained a depth resolution corresponding to a Gaussian with full width half-maximum of 100 Å. Further details on the technique and the data analysis procedure can be found in the general review by Schwarz et al.[20]

The samples studied with TEM were floated off the silica substrates after annealing and were picked up onto Cu mesh grids. The floating procedure was done in KOH solution (pH = 12) at ~90 °C which removes the polymer film by etching away the silicon oxide layer beneath it. After staining in I_2 vapor for 12 h, the samples were mounted on a double-tilt stage and imaged with a Philips CM12-T scanning transmission electron microscope using a voltage of 120 kV.

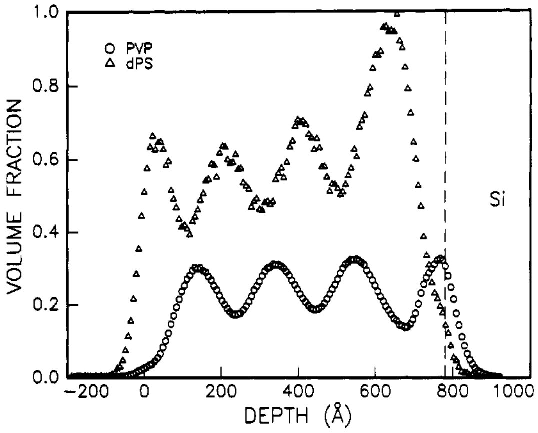

Figure 1. SIMS depth profiles of the PVP and dPS volume fractions (proportional to the CN^- (○) and D^- (△) ion intensities) in a triblock sample, 756 Å thick, annealed for 5 days at 180 °C.

Measurements of the neutron reflectivity were done at the POSY II reflectometer using the IPNS facility at Argonne National Laboratory. The instrument and the data analysis techniques are reviewed by Russell.[10] Atomic force microscopy of the sample surface was performed using a Digital Nanoscope III instrument in the contact mode, using a Si_3N_4 tip and a force of approximately 18 nN. The X-ray reflectivity measurements were performed on beam line X22C at the Brookhaven National Laboratory NSLS facility.

Results

A. Surface-Induced Ordering. The SIMS depth profiles for a PVP–dPS–PVP triblock film annealed for 5 days at 180 °C are shown in Figure 1. The PVP and dPS volume fractions are assumed to be proportional to the CN^- and D^- ion yields, respectively. From the figure it can be seen that the sample is well ordered in a direction perpendicular to the Si surface. As previously observed,[22] the more polar PVP block is adsorbed to the Si interface and the dPS component, whose surface tension is slightly lower than that of PVP, is present at the vacuum interface. From Figure 1 it is also evident that the PVP layer is narrower than the dPS layer and that the spacing of all the other dPS and PVP layers, except the one adjacent to the Si interface, is regular.

To obtain a more accurate determination of the widths of the respective layers and the interface between them, we measured the neutron reflectivity of the same sample. The data are shown in Figure 2a, where we plot the reflectivity R, the ratio of reflected to incident neutron intensity, vs k_z, the component of the neutron wave vector normal to the surface. Since the reflectivity is the square of the amplitude of the reflected neutron wave function, the phase information is lost. As a result, a general inversion of the data to obtain a unique profile is not possible.[10] To circumvent this problem, we confined our fits only to trial functions that when convoluted with the appropriate resolution function were consistent with the SIMS profile. In addition, the total film thickness, 756 Å, as well as the vacuum polymer interfacial roughness, σ = 12 Å, were measured independently with X-ray reflectometry. Within these constraints, the profile that provided the best fit to the data (χ^2 = 3) is shown in Figure 2, and the fit parameters are tabulated in Table 2.

From the table it is clearly seen that layer 1 is indeed different from the subsequent layers. The sublayer adjacent to the silica interface (1A) is almost pure PVP and somewhat narrower than half the thickness of the

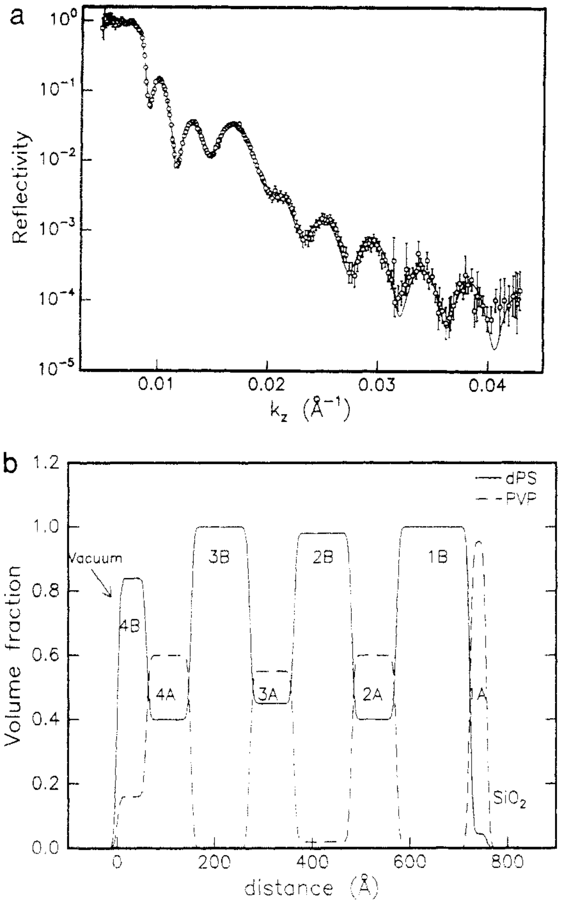

Figure 2. (a) Neutron reflectivity vs k_z corresponding to the sample in Figure 1. (b) Concentration profile used to fit the data with the parameters listed in Table 2.

Table 2. Parameters Used To Fit the Neutron Reflectivity Spectrum

layer[a]	sublayer	thickness (Å)	volume fraction dPS	volume fraction PVP	roughness (Å)
1	A (PVP)	35	0.045	0.955	43
	B (dPS)	149	1.00	0.00	74
2	A (PVP)	92	0.40	0.60	74
	B (dPS)	119	1.00	0.00	74
3	A (PVP)	90	0.45	0.55	74
	B (dPS)	120	1.00	0.00	74
4	A (PVP)	93	0.40	0.60	74
	B (dPS)	58	0.84	0.16	12[b]

[a] Layers 1A and 4B are at the silica and vacuum interfaces, respectively. [b] Determined from X-ray reflectivity.

other PVP sublayers while the corresponding dPS sublayer (1B) is wider than the others. The subsequent two and a half layers (2, 3, and 4A) are similar to each other, consisting of a dPS component 120 Å wide and a PVP component 90 Å wide. These values correspond to roughly 4 times the radius of gyration of the PVP block and twice the radius of gyration of the dPS block. The surface sublayer (4B) is almost pure dPS and exactly half as thick as the bulk dPS sublayers. The integrated volume fraction of PVP in the sample is 0.25, in agreement with the XPS and mass analysis values. Figure 3 shows the TEM micrograph of a typical sample, 498 Å thick, floated from the silica substrate onto a Cu microscope grid after annealing for 24 h at 180 °C. The dark regions correspond to the iodine-stained PVP blocks and the light sections to dPS blocks. As will be discussed later, the broad light and dark areas correspond to single- and double-ordered micelle layers. Inspection of the micrographs shows that the diameter of the micelle structure is the same in the single- and double-layer regions and remains unchanged under rotation of −40° and +40° about the axis in the sample plane as shown in the figure. We therefore conclude that the in-plane morphology has cylindrical symmetry as would be expected from the diblock copolymer phase diagram at this temperature.[3-5] From the figure it can be seen that only the single layer shows high contrast when viewed along the sample normal. In the single-layer region rotation of the sample through either +40° or −40° changes the spacing of the cylinders lying parallel to the axis of rotation, while the spacing of the cylinders lying perpendicular remains unchanged. In the two layer regions, rotation of the sample through ±40° aligns the cylinders whose axis has a component along the rotation axis so they can be viewed more clearly. Cylinders lying perpendicular to the rotation axis (region A) are not affected and are still difficult to resolve. This behavior under rotation is the same as that previously reported for cylindrically ordered diblock copolymers[16] and indicates that stacking is most probably hexagonal.

This is further confirmed by the NR data, from which we measured the distance between layers in the direction normal to the sample surface to be approximately 210 Å. If the stacking were body centered, then the separation between adjacent cylinders in the plane would be approximately 420 Å. The distance measured from the TEM micrograph, 220 ± 20 Å, is closer to 240 Å or the value expected for hexagonal packing. The diameter of the cylinders, as measured from the TEM micrograph, 100 ± 20 Å, is also in good agreement with the PVP sublayer thickness listed in Table 2. Using this value to estimate the volume fraction of PVP in the PVP sublayers, one obtains approximately 0.4 and 0.2 for the hexagonal and body centered stacking, respectively. As can be seen from Table 2, the hexagonal packing estimate is in reasonably good agreement with the neutron reflectivity data.

The curved structure of the cylinders is reflected in the broad, 75 Å, interface measured in all the dPS/PVP layers not adjacent to the Si interface. It is interesting to note though that this curvature is not reflected at the polymer/vacuum interface, which is as flat as that obtained for a homopolymer film.[9,10] The additional energy needed to form an undulating surface is compensated by slightly deforming the triblock brush in the last dPS sublayer (4B in Table 2). In contrast to the previous measurements on symmetric diblock copolymers,[9,21] where all the layers had the same morphology, the layer adjacent to the silicon oxide substrate seems to be different from the rest. In addition to having a different thickness, the in-plane structure of this layer is consistent with pure lamellar morphology; i.e., no dPS is found in the PVP phase. Furthermore, the interfacial width between the two components, 43 Å, is very narrow and is comparable to that measured for the two homopolymers.[21,23] This result is consistent with the calculation of Shull,[3] who found that if the layer is lamellar, then in the limit of $\chi N \gg 10$, the homopolymer blend and block copolymer interfacial widths are comparable.

A surface-induced transition from cylindrical to lamellar morphology was recently predicted by Turner et al.[15] and Shull.[24] When the difference between the surface interaction energies of two components is very large, the lamellar configuration is most efficient in minimizing the surface tension.[25] On the other hand, in a strongly segregated system, this energy must be large enough to overcome the bending and compressional energies of deforming the cylinders into lamellae in the interface region. In our case the energy gained by hydrogen bonding the PVP to the

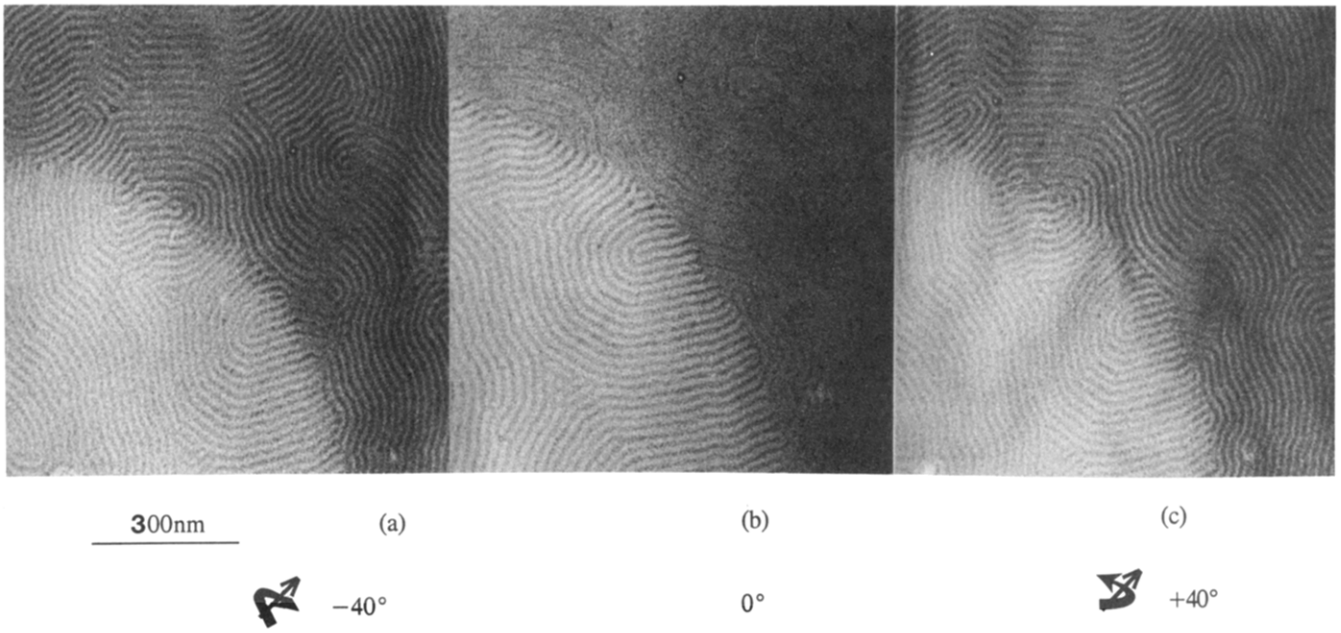

Figure 3. TEM micrographs of a triblock film, 498 Å thick, floated from the silica substrate onto a Cu grid after annealing for 24 h at 180 °C. The dark and light regions correspond to double and single layers of cylinders, respectively. The sample is imaged (a) after rotation of −40°, (b) along the normal to the sample surface, and (c) after rotation of +40°.

native silicon oxide surface is apparently sufficiently large to induce this phase transition.

Figure 4a shows the SIMS data (the CN^- intensity converted to the PVP volume fraction) for triblock films of thicknesses ranging from 450 to 2600 Å. From the figure it can be seen that progressively thicker films order layer by layer, for at least 12 layers parallel to the surface. In contrast, the order in films of the dPS–PVP diblock copolymer, annealed for an equivalent time, with a PVP fraction ($f = 0.28$) similar to that of the triblock, is shown in Figure 4b. In this case as well, the first layer adjacent to the native oxide surface has a larger PVP volume fraction and dPS spacing than the subsequent ones. Though it is not completely conclusive from SIMS data alone due to its limited resolution, the ordering of this layer is probably lamellar, as was seen in the triblock sample. On the other hand, from the figure we can clearly see that the ordering parallel to the surface does not persist when the sample becomes thicker than 2000 Å, i.e., contains more than four cylindrical layers. TEM micrographs of both the single (Figure 5) and the double (Figure 6) layer films show that the diblocks are fully segregated into microdomains, but the domains are not necessarily aligned parallel to the silicon oxide surface. In Figure 5 the film thickness corresponds to approximately one layer, and the coexisting morphologies could only be cylinders lying parallel to the surface and hexagonally packed spheres. The TEM image is therefore invariant under rotation of 40°. The thickness of the film shown in Figure 6 corresponds to two layers. Rotation of the sample through 40° (Figure 6b) shows that the "spherical" domains observed at 0° (Figure 6a) are actually short cylinders lying perpendicular to the silica surface. In addition, it should be noted that the cylinders lying parallel to the silica surface are also seen more clearly when viewed at 40° to the sample surface, indicating that they are also packed in a hexagonal arrangement.

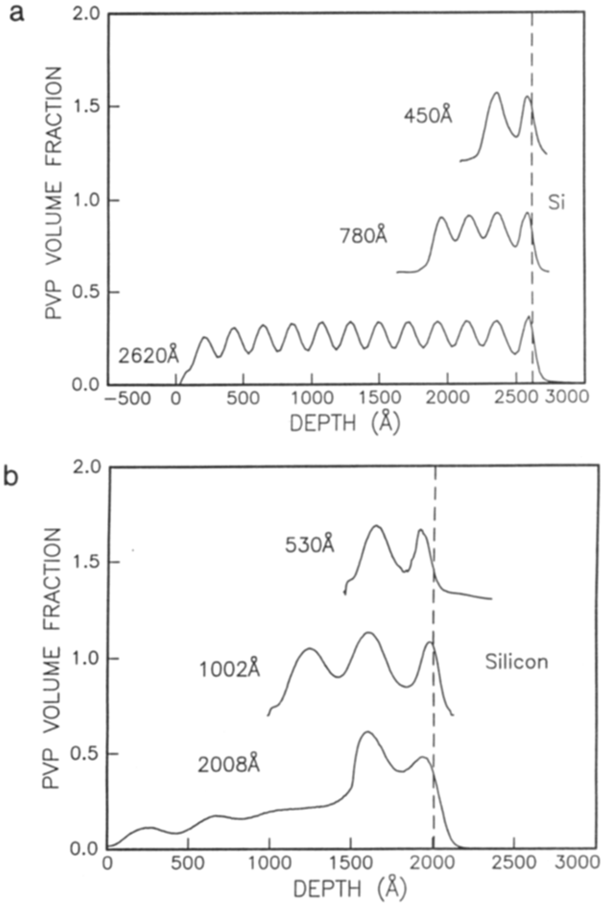

Figure 4. Volume fraction of PVP as a function of depth obtained with SIMS from copolymer films of various thicknesses annealed for 5 days at 180 °C: (a) triblock copolymer films where each upper profile offsets by 0.6 relative to the lower one; (b) diblock copolymer films where each upper profile offsets by 0.4 relative to the lower one.

The difference in the domain alignment between the di- and triblock copolymers of similar composition and morphology, we believe, is due to the difference in the conformation of the chains in the domains. Due to the "bridging" of triblock copolymer chains from one PVP microphase to another, or the entanglement of loops from adjacent micelles, the entire film becomes interconnected into a single-domain cylindrical micelle gel[26] which orients itself parallel to the surface. The consequence of a single orientation is seen in the SIMS profiles where no relaxation

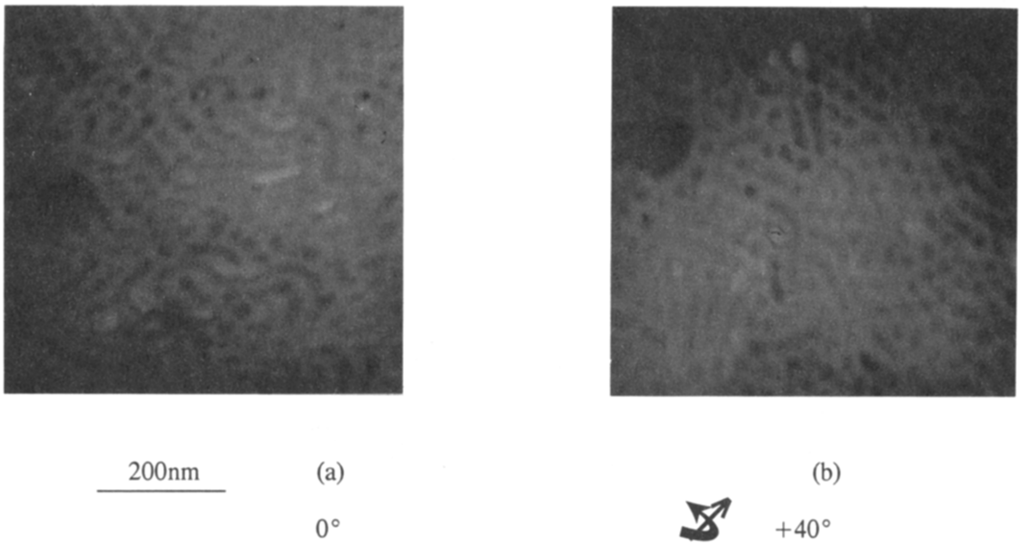

Figure 5. TEM micrographs of the 530 Å thick diblock copolymer film described in Figure 4b as viewed (a) along the sample normal and (b) after rotating 40° about an axis in the sample plane.

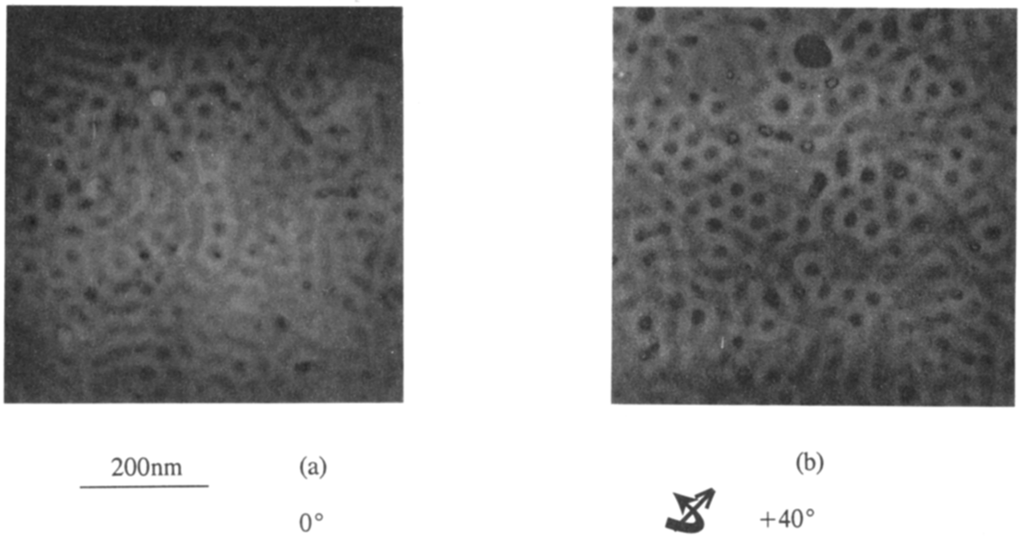

Figure 6. TEM micrographs of the 1002 Å thick diblock copolymer film as shown in Figure 4b viewed (a) along the sample normal and (b) after rotation of 40° about an axis in the sample plane.

of the layer amplitude is observed even for the thickest sample. In contrast, the interface between microdomains in the asymmetric diblock copolymer film is similar to that of two independent interpenetrating brushes. The individual cylinders can orient first into hexagonal-packed microdomains and then the domains are free to move and further orient themselves with respect to the surface. The boundary conditions on the cylindrical layers in both the di- and triblock copolymer films are such that dPS must be present at both the vacuum and the lamellar interfaces. As shown in Figure 7, in the diblock film these conditions are easily satisfied with both parallel and perpendicular orientations of the cylindrical microdomains. While we cannot present a quantitative model, the data suggest that the confinement energy of the chains into loops or bridges is higher in the triblock copolymer than in the diblock copolymer films. Any further distortions of the triblock copolymer brush which would occur if the chains had to span between domains of different orientations may extract a higher free energy penalty than the reduction of entropy which occurs when all the microdomains are oriented in the same direction.

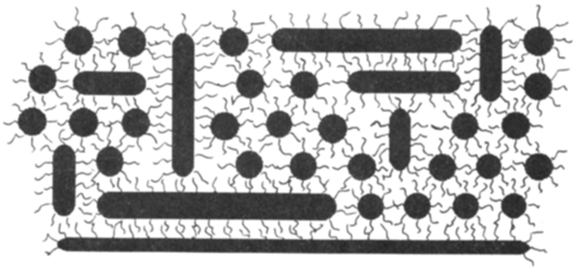

Figure 7. Schematic representation of a cross-sectional view in an annealed PS–PVP diblock copolymer film which corresponds to the SIMS profiles shown in Figure 4b of a 2000 Å thick film.

The distance between cylindrical layers in the di- and triblock copolymer samples can be computed by approximating the block copolymer melt as a collection of cylindrical micelles with PVP cores and dPS coronas. On minimizing the free energy, F, of a block copolymer melt with respect to the micelle diameter,[27,28] d, one obtains for a cylindrically ordered block copolymer

$$F_{\text{cyl}} = Q\left[\frac{(1.65 - \ln f)d^2}{64R_g^{\,2}} + \frac{4\chi N_{\text{PVP}}R_g}{d}\right] \qquad (2)$$

where Q is the number of copolymer chains in a cylindrical micelle, R_g is the block copolymer radius of gyration (R_g

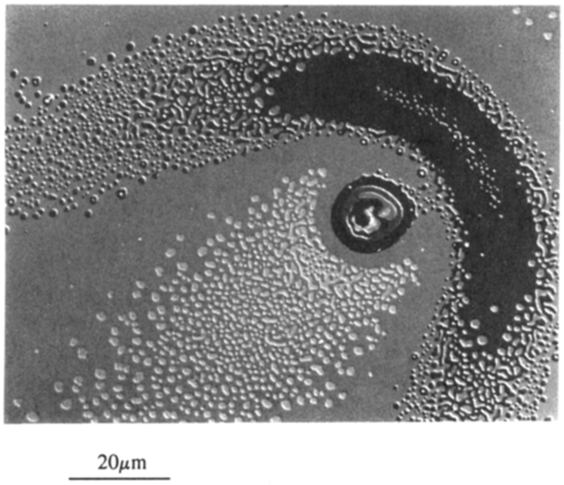

Figure 8. Optical micrograph of the area around a dust particle in an annealed, 756 Å thick, triblock copolymer film.

$= a(N/6)^{1/2}$), and a is the statistical segment length (6.7 Å for PS).[10] Minimizing F_{cyl} with respect to d, we obtain $d = 5.66R_g$, which, it is interesting to note, is independent of the precise value of f as long as the equilibrium morphology is cylindrical. If we substitute the values of N_{PVP} and N_{dPS} from Table 1 for the diblock copolymer, we obtain $d = 438$ Å, in good agreement with the value $d = 400 \pm 20$ Å determined from the SIMS and TEM data. If we approximate each triblock copolymer chain as two diblock chains of half the molecular weight,[24] then substituting the values 85 and 275 for N_{PVP} and N_{dPS}, respectively, we obtain $d = 294$ Å. This value is larger than $d = 210$ Å measured with neutron reflection and indicates that even when the chains are not very stretched,[28] the free energy associated with a polymer loop is not well approximated by eq 2 for two equivalent brushes. This result is again consistent with the other phenomena reported in this paper which demonstrate that the energy of distorting interconnected loops is higher than that of deforming brushes of equivalent size.

B. Surface Morphology. XR spectra and high-resolution optical microscopy indicated that the film studied by neutron reflection in the previous section was smooth and of uniform total thickness. Since the film ordered exactly into one lamellar and two cylindrical layers, we can define a quantization relation for the total thickness t,

$$t = (n + \alpha)L + \beta \tag{3}$$

where $n = 2$ is the number of bulk cylindrical layers, $L = 210$ Å is the layer period, $\alpha = 0.71$ is the fractional thickness of the first top cylindrical layer, and $\beta = 182$ Å is the thickness of the lamellar layer adjacent to the Si surface. This expression is similar to that obtained by Russell[9,13,14] and co-workers, Fredrickson,[6,7] and Shull,[3] except in their case the block copolymers were symmetric and all the layers were lamellar such that β and α could be set to zero and 0.5, respectively. If the total film thickness is such that n is not an integer, instabilities result which can induce the top layer to break up into islands similar to those observed previously by Coulon et al.[13,14] for lamellar morphologies. This break up of the film is illustrated in Figure 8, which is an optical microscope photograph of the region around a dust particle on the sample used to obtain the neutron reflection data. The film thickness satisfies eq 3 everywhere except around the dust particle. A progression of morphologies starting from isolated islands and converging into an interconnected structure that again breaks up into isolated islands is clearly visible. The patterns obtained for a series of films of uniform thickness annealed for 3 days at 180 °C are shown in Figure 9. The smooth films correspond to thicknesses having $n = 0$ and 1 in eq 3. For thicknesses t' greater than the nearest value of t by Δ ($t' = t + \Delta$), islands or holes form if Δ is respectively less than or greater than $L/2 \sim 105$ Å. This phenomenon is again similar to that observed in symmetric diblock copolymers,[13,14] despite the fact that in our case the interfacial width between cylindrical layers was roughly twice as large[9,21] as that measured for the lamellar block copolymers.

To accurately determine the effects of the curved interfaces on the surface roughness and the height of the islands, X-ray reflectivity measurements were performed

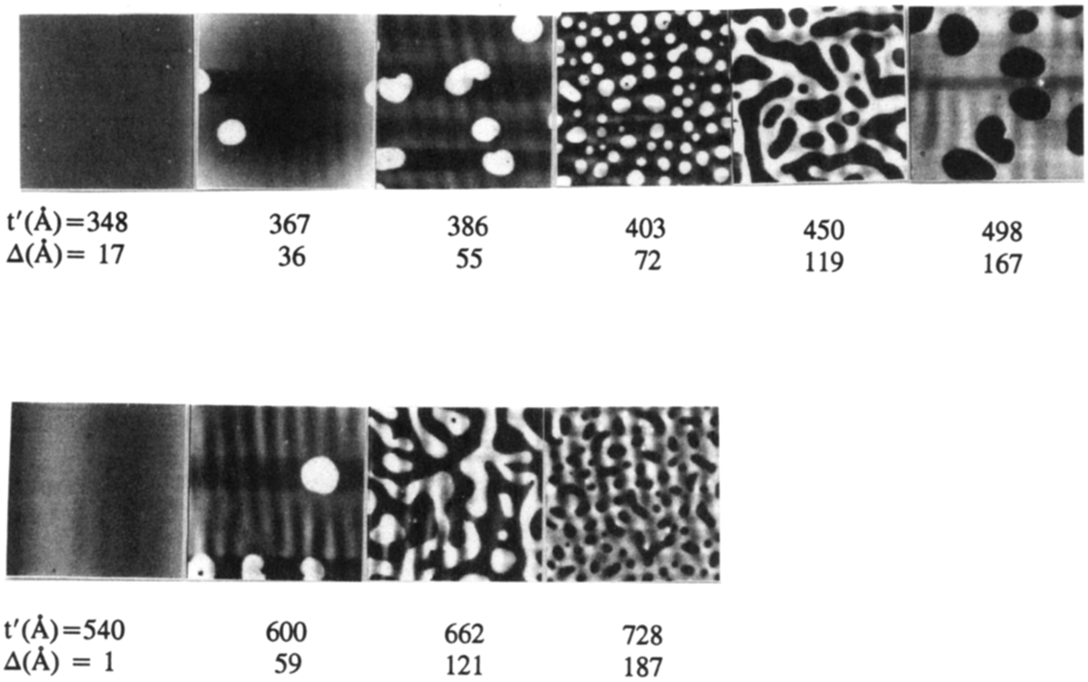

Figure 9. AFM micrographs of triblock copolymer films of various thicknesses annealed for 3 days at 180 °C.

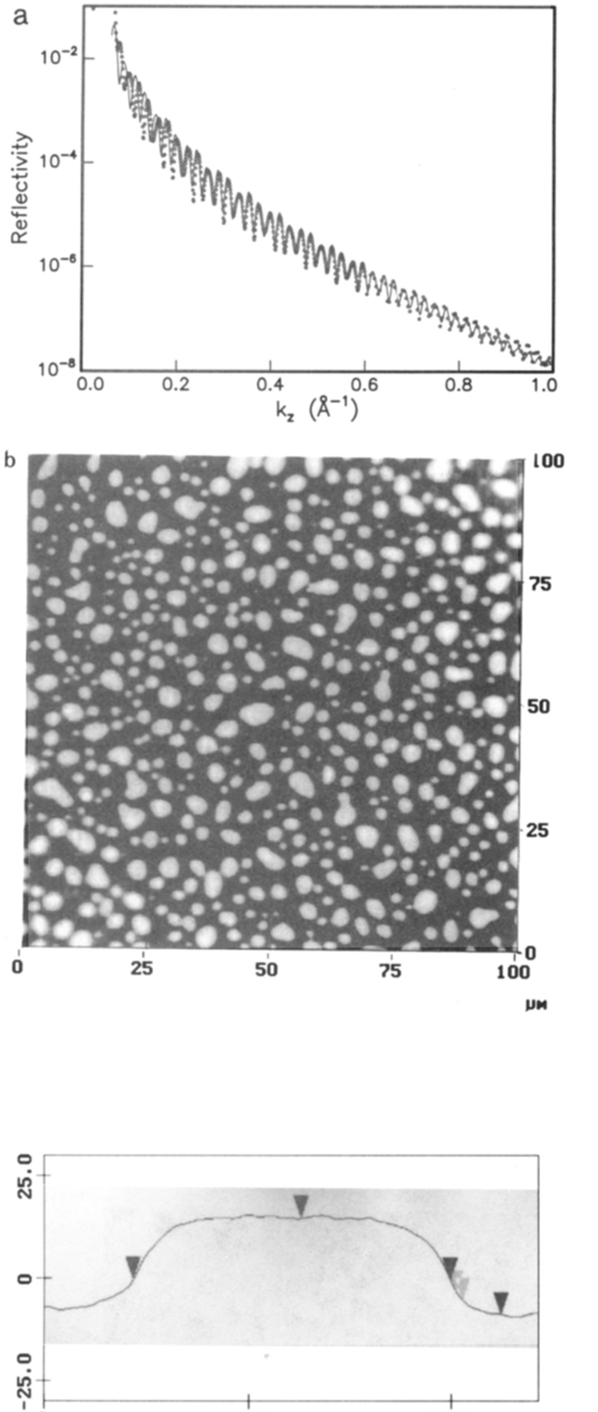

Figure 10. (a) X-ray reflectivity as a function of k_z for a 568 Å thick annealed triblock copolymer film. The solid line is a least squares fit to eq 4. (b) AFM micrograph of the film surface. (c) Horizontal cross-section of a typical island shown in (b).

(Figure 10a). The thickness of the sample, 568 Å, corresponds to one cylindrical layer and $\Delta = 27$ Å, which implies a layer of isolated islands. The predicted morphology is confirmed by the AFM image of the sample shown in Figure 10b. From the figure we can see that the island size never exceeds approximately 2 μm, which is smaller than the coherence length of 4 μm for the X-ray beam used. Assuming coherent scattering between the layer covered by islands and the bulk, we can use the Born approximation to derive an expression for the reflectivity spectra as a function of k_z. This approximation is valid in the weak, single-scattering regime and hence can only be applied at large angles, or $k_z > 0.05$ Å^{-1}. The specular reflectivity from a surface decorated with islands has been shown by Sinha[29] to be

$$R = \frac{\pi^2}{k_z^{\,4}}[\rho_1^{\,2}e^{-4k_z^2\sigma_2^2}(1 - 4\phi(1-\phi)\sin^{-2}(k_z h)) + (\rho_2-\rho_1)^2 e^{-4k_z^2\sigma_2^2} + 2\rho_1(\rho_2-\rho_1)e^{-2k_z^2(\sigma_1^2+\sigma_2^2)} (\phi\cos(2k_z(t+h)) + (1-\phi)\cos(2k_z t))] \quad (4)$$

where h is the island height, ϕ is the island fraction, and σ_1 and σ_2 are the roughness of the island and bulk layers, respectively. The solid line in Figure 10a corresponds to a least squares fit of the data with the parameters $h = 210$ Å, $\phi = 0.25$, $\sigma_1 = \sigma_2 = 9$ Å, and $t' = 568$ Å. The value obtained for h is exactly the same as the bulk layer thickness, L, measured with neutron reflection, confirming that in our case as well the island structure is essentially a "dewetting" of the surface by a layer of quantized thickness with insufficient material to span the sample surface. Analysis of the image in Figure 10b yields a fractional coverage of 0.30 and a height of 199 Å for the islands, in good agreement with the X-ray reflectivity result. Furthermore, from the AFM image (Figure 10c) we see that the islands have a broad flat top, again in good agreement with the small value of σ_2 and the distinct two-thickness beating pattern observed in Figure 10a.

Since asymmetric polymers are also ordered in the horizontal plane, it was interesting to observe the effect on the in-plane morphology when the uppermost layer breaks up into islands or holes. Figures 11–13 are a series of TEM and optical micrographs, with the corresponding SIMS depth profiles, showing the time development of the ordering for the 498 Å thick triblock copolymer sample shown in Figure 9. At equilibrium, this thickness corresponds to one lamellar and two cylindrical layers. As can be seen in Figure 9, the surface layer is broken into holes, 210 Å deep. Figure 11a is a TEM micrograph as the as-spun sample prior to annealing. From the micrograph we can see that it is already segregated into randomly oriented spherical and cylindrical domains. The SIMS profiles of the PVP volume fraction obtained from the same sample (Figure 13a) show that the lamellar layer at the silicon interface has already begun to form, and no significant out of plane orientation of the cylindrical domain has occurred. Optical micrographs of the surface show that the sample is smooth without any islands. Figure 11b shows that the sample has ordered into cylindrical domains oriented parallel to the surface after annealing only 15 min. The optical micrograph (Figure 12a) shows that small holes in the upper layer have begun to appear. The cylindrical domains can only be seen using TEM when viewed at 40° with respect to the sample normal. The SIMS profiles (Figure 13b) show that the sample is segregated into roughly two layers which, based on the TEM micrograph, have already begun to orient themselves into a hexagonal packing structure. Comparing the CN$^-$ and D$^-$ ion profiles, we can see that the chains are already segregated into the lamellar layer at the silicon interface while a significant amount of PVP is still present in the layer at the vacuum interface. Larger holes are observed to form on the sample surface after annealing for 4 h (Figure 12b). TEM micrographs now show that the "basal" layer inside the holes is composed of cylinders which are seen clearly when viewed along the sample normal (Figure 11c,(i)). The top layer becomes clear only after rotation of 40° (Figure 11c,(ii)). The depth of the holes, 170 Å, as determined from the AFM micrograph, is already close to the equilibrium value of 210 Å. After annealing for 24 h,

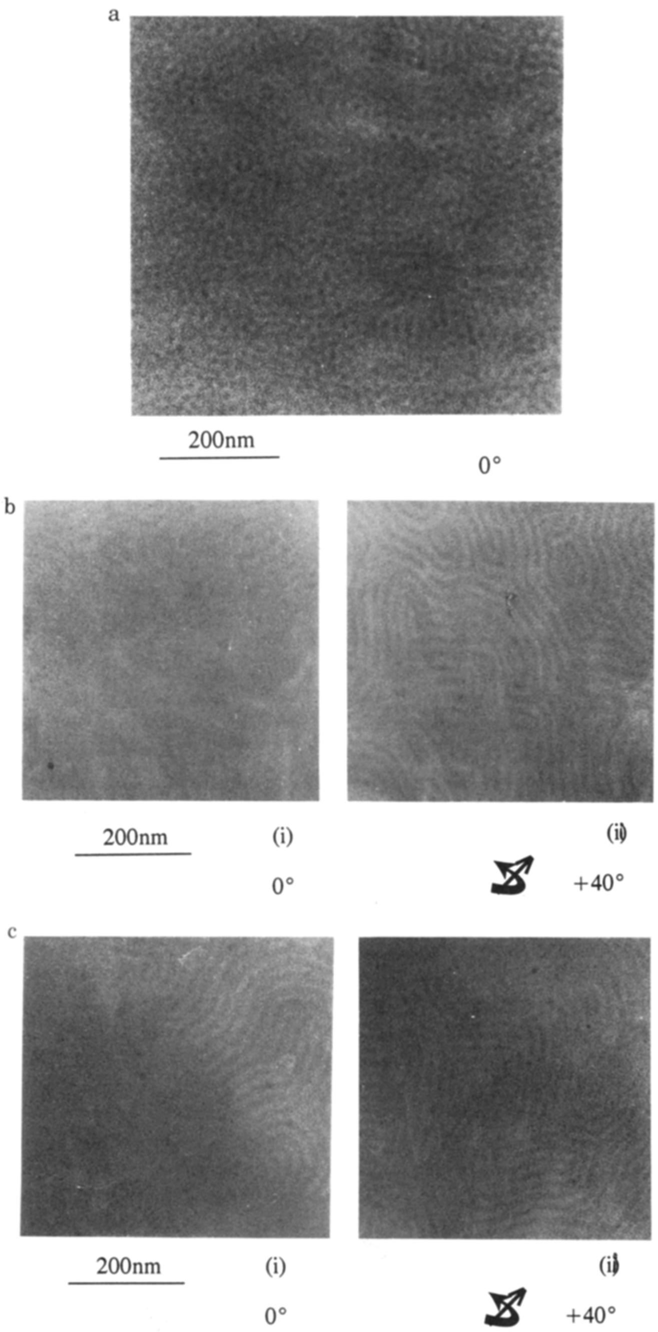

Figure 11. TEM micrographs of a 498 Å thick triblock copolymer film (a) as cast prior to annealing, (b) after annealing for 15 min and viewed at (i) 0° and (ii) 40° to the sample normal, and (c) after annealing for 4 h and viewed at (i) 0° and (ii) 40° with respect to the sample normal.

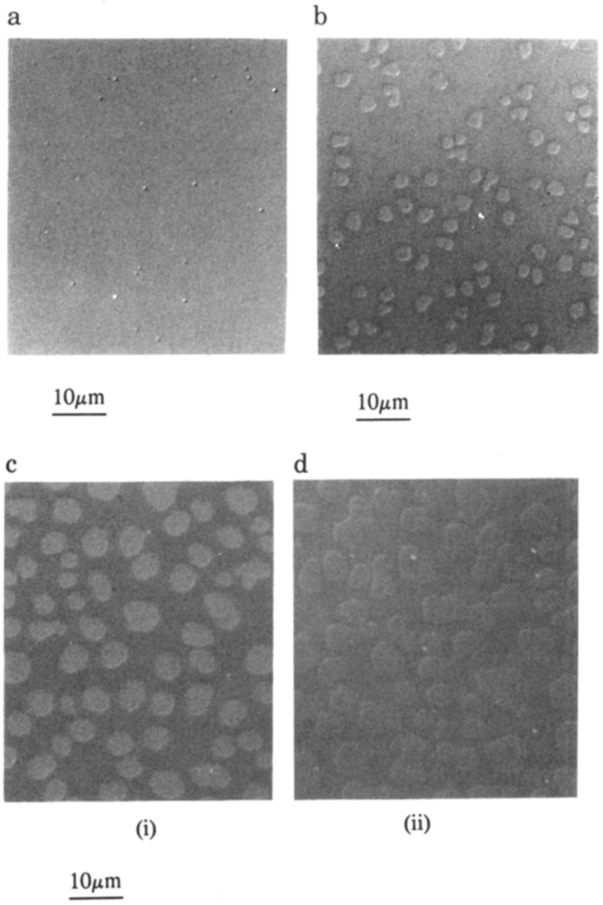

Figure 12. Optical micrographs of the films shown in Figure 11 prior to staining and after annealing for (a) 15 min, (b) 4 h, (c) 24 h, and (d) 14 days.

we can see in Figure 13c that the sublayer at the vacuum interface is pure dPS, while the PVP sublayer at the silicon oxide interface has become slightly narrower. The redistribution of material between the layers has resulted in even larger holes on the film surface (Figure 12c). No significant changes either in the hole structure (Figure 12d) or the SIMS profiles are observed after further annealing for as long as 14 days.[30] Figure 14 is an expanded view of an edge of a hole in the top layer of the sample annealed for 24 h. In the micrograph obtained at 40° (Figure 14(ii)) to the sample normal, the majority of the cylinders appear to be continuous across the boundary. If continuity were to occur, the cylinders in the lower layer would have to bifurcate and one branch would have to "climb" 210 Å to reach the upper layer. When the sample is viewed along the normal (Figure 14(i)), one can clearly see that such bifurcation does not occur since the cylinders in the upper layer are now shadowing the ones in the lower layer. The boundary between layers is sharp and no evidence of vertical orientations (which would appear as dark dots) is observed. The appearance of continuity is yet another manifestation of the high degree of ordering present in the triblock film after annealing for 24 h.

Similar studies on the time dependence of the ordering process in symmetric diblock copolymer films have recently been reported by Russell[31] and Coulon.[32] In this case, the ordering was initiated at the interfaces and was observed to decay toward the bulk, with an average lamellar period that increased with time.[31] Once the bulk was fully aligned, the fraction of surface, islands or holes, remained constant but the island or hole size continued to increase with annealing time.[32] In the case of the triblock copolymer, all the cylindrical layers appeared to order at once and no relaxation or change in lamellar spacing was observed. Similar results were also reported by Liu et al.[33] on thicker triblock copolymer films where they observed the chains to rearrange themselves between adjacent cylindrical layers rather than ordering as a decaying wave from one of the interfaces. The dynamics for the ordering process both for islands on the surface and in the bulk were shown to follow the time and temperature scaling expected for single-chain diffusion in an ordered block copolymer structure. Once the bulk was fully ordered, no further motion of either islands or holes was observed at any temperature, again consistent with the large decrease in mobility associated with an interconnected structure.

It should be noted at this point that to our knowledge this is the only case where island formation has been

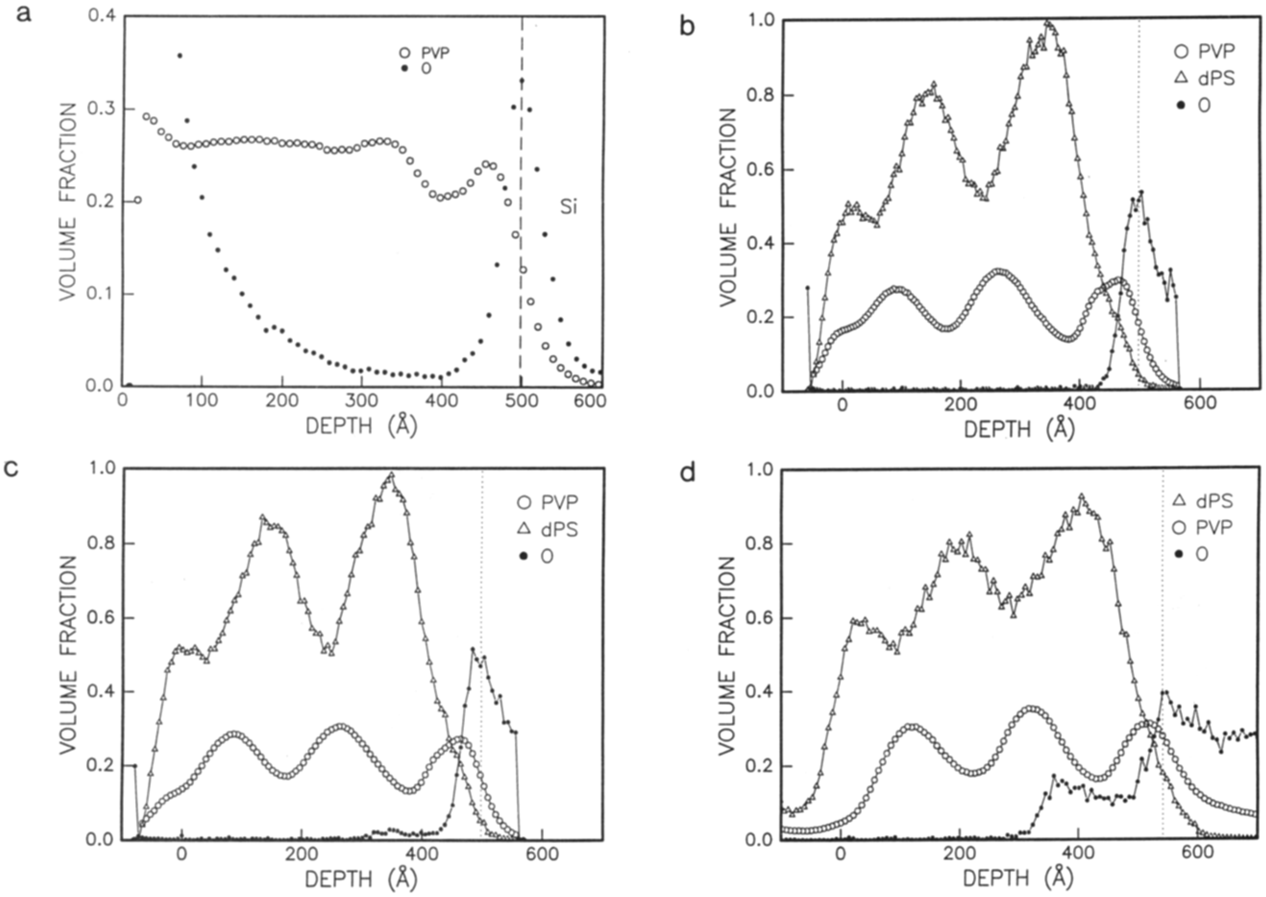

Figure 13. SIMS profiles of the PVP (○) and dPS (△) volume fraction as a function of depth corresponding to the samples shown in Figure 11 (a) prior to annealing and after annealing for (b) 15 min, (c) 4 h, and (d) 24 h. The oxygen (●) trace marks the time when the sputtering beam arrives at the silicon oxide interface. Broadening of the peak signifies the presence of polymer layers with different heights and can therefore be used as a qualitative indicator for the presence of surface holes or islands.

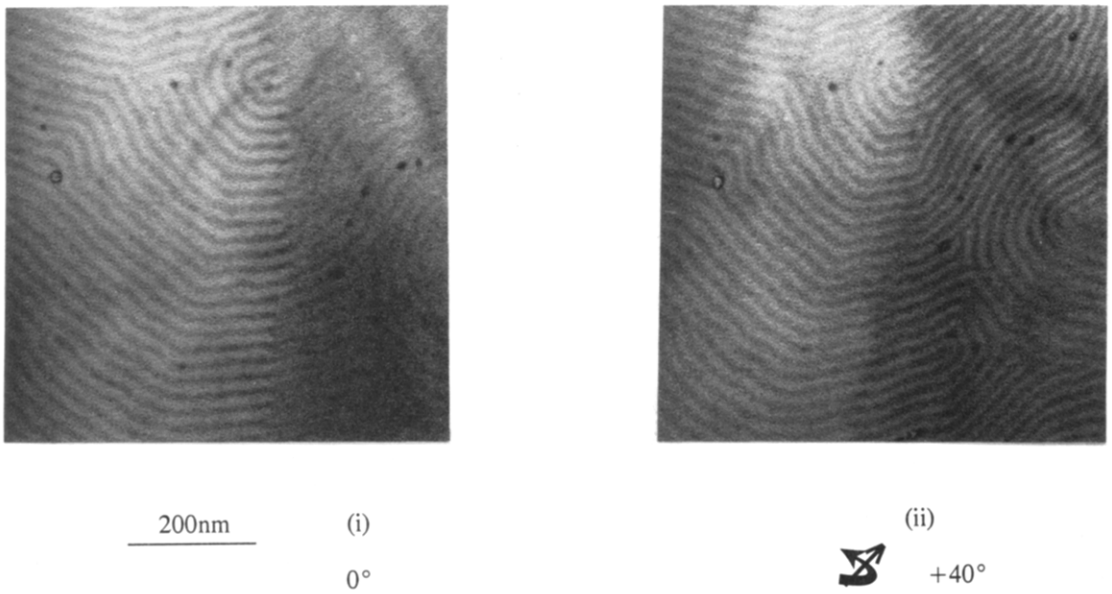

Figure 14. TEM micrographs around the periphery of a hole in the sample annealed for 24 h viewed with respect to the sample normal at (i) 0° and (ii) 40°.

observed in an asymmetric block copolymer system. The reduction in the total free energy which occurs when the microdomains in a block copolymer thin film are aligned parallel to the surface has to be weighed against the free energy cost of increasing the total surface area when islands are formed in the top layer.[3,6-8] This free energy can be dissipated by forming defects in the ordered domain lattice structure. Depending on the surface boundary conditions, this state may be of lower free energy than the perfectly aligned state with surface islands. In particular, for cylindrical diblock morphologies where, as discussed previously, the interfacial tension between microdomains may be quite small, the ordering can easily be relaxed by changing the orientation of the cylinders both in and out of the ordering plane (see Figures 6 and 7). As the sample becomes thicker, more layers become available for fault

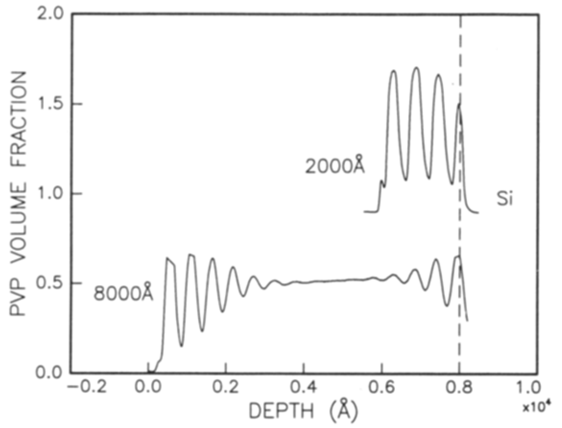

Figure 15. SIMS depth profiles of the PVP volume fraction for symmetric ($N_{\mathrm{PVP}} = 510$, $N_{\mathrm{dPS}} = 540$) diblock copolymer films, 2000 and 8000 Å thick, annealed for 5 days at 180 °C.

formation and the surface-induced ordering decays even further. Consequently, in these systems the islands will not form, even in very thin layers, since the free energy cost can easily be compensated by propagating defects through the other layers.

In the case of symmetric diblock copolymers, defects have higher free energy since the lamellae can only be deformed along the direction perpendicular to the ordering surface, i.e., only defects with Burgers vectors normal to the lamellae can form. In thin films, the energy associated with island formation is smaller than that producing a large deformation in the lamellar planes. As a result, the system is easily ordered when one component segregates strongly to a surface, and islands are formed in the strong segregation regime.[33] As the film thickness increases, each lamellar plane must distort less to accommodate the extra material in the surface layer; as a result the surface-induced orientation can decay after several lamellar periods. This decay can be seen in Figure 15, which shows the SIMS profiles of the PVP volume fraction obtained from two symmetric block copolymer films annealed for 5 days at 180 °C. (The polymerization of the dPS block, $N_{\mathrm{dPS}} = 540$, was comparable to that of the other block copolymer films discussed in this paper.) From the figure one can see that the thinner film is well ordered and optical micrographs show well-defined islands on the surface. The thicker film, with thickness corresponding to approximately 15 lamellar periods, shows no islands, and the surface-induced ordering is observed to decay from both interfaces. This picture is confirmed in the cross-sectional TEM micrograph of a thick dPS–PVP ($N_{\mathrm{dPS}} = 800$, $N_{\mathrm{PVP}} = 800$) film annealed for 5 days at 180 °C, shown in Figure 16b, while the corresponding SIMS profiles shown in Figure 16a. From the figure we see that the film is well ordered into microdomains, but only the first few lamellae are ordered parallel to the vacuum surface. It is interesting to note that the layer adjacent to the silicon oxide surface is highly ordered as well, but the lamellae are oriented perpendicular to the sample plane. A similar situation was also observed by Russell et al.[31] after annealing for only a few minutes at 170 °C in a PS/PMMA diblock copolymer thin film spin coated onto a Au-covered substrate. In this case, neither of the blocks interacts preferentially with the surface, and the perpendicular orientation provides both blocks with equal contact area. This perpendicular configuration though proved to be metastable and after a further anneal of 24 h, all the lamellae were oriented parallel to the sample surface. In our case, the perpendicular configuration seemed to be stable at least up to 5 days at 180 °C.

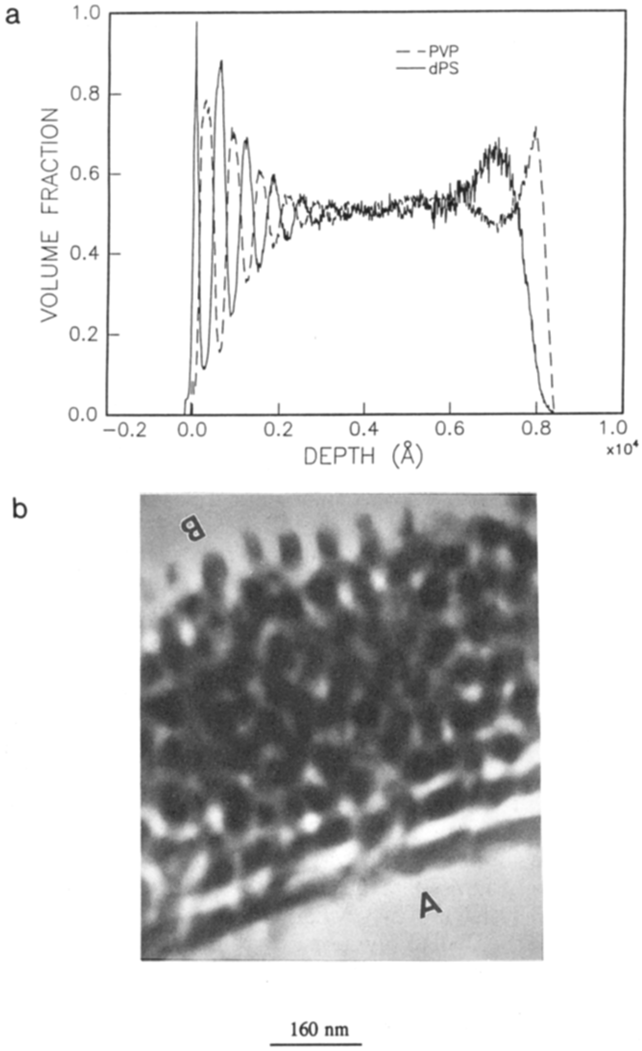

Figure 16. (a) SIMS depth profiles of the PVP volume fraction for a symmetric ($N_{\mathrm{PVP}} = 800$, $N_{\mathrm{dPS}} = 800$) diblock copolymer film, 8000 Å thick, annealed for 5 days at 180 °C. (b) TEM cross-sectional view of the film in (a).

No comparable mechanism for gradually relaxing the oriented structure to suppress island formation has been observed in the triblock copolymer. The time evolution of the ordered structure in symmetric diblock copolymer films was shown[31] to consist of a decaying wave originating at the interfaces. As the annealing time increased, the decay length increased until the entire film became uniformly ordered. In the triblock copolymer, Liu et al. show that the ordering even at early times does not decay away from any surface.[33] Rather, a uniform pattern of alternating PVP-rich and PVP-poor layers is formed throughout the film. As the annealing time increases, the amplitude of the PVP volume fraction in the layers equalizes. In the diblock case, the film rapidly segregates into ordered microdomains which then re-orient on a long time scale parallel to the surface. In the triblock case the ordering seems to proceed mainly via chain motion between adjacent layers, which obeys the usual WLF time and temperature scaling.[31] Due to the interconnected nature of the loops or bridges, in order for an entire triblock copolymer domain to move, all the chains at the interface must pull out of the cylindrical cores and form new connections. Since many chains are involved, this procedure is not energetically favored. From the fact that the triblock copolymer tends to form islands on the surface rather than faults, we infer that the energy required to produce a fault in the triblock by this process is probably higher than that required to form islands on the surface. This is further confirmed by the easy penetration of homopolymer chains into the ordered cylindrical diblock copolymer matrix and the difficult penetration of homopolymer into ordered triblock copolymer structures.[34]

Conclusion

In conclusion we have shown that it is possible to orient asymmetric triblock copolymers parallel to a surface with a high degree of both in and out of plane order. The conditions on the layer spacing as well as on the formation of surface islands are similar to those previously observed for symmetric diblock copolymers except that, due to the strong interaction of PVP and silica, the layer adjacent to the silica interface undergoes a cylindrical to lamellar transition. In contrast, a much smaller degree of ordering parallel to a surface was observed in a cylindrically segregated diblock copolymer. As a result, no island formation is observed on the diblock film surface. We conclude that the difference between the ordering behavior of the two block copolymers of comparable N and f is caused by the conformation of the chain in the micelles. The diblock copolymer forms ordered micelle domains which are free to move relative to each other, while the triblock forms an interconnected micelle network.

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