Structure of Asymmetric Diblock Copolymers in Thin Films

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ABSTRACT: The structure of asymmetric poly(styrene-*b*-2-vinylpyridine) (PS-PVP) diblock copolymers allowed to order in a thin film is observed by a combination of secondary ion mass spectrometry and scanning force microscopy. The surface/interface-induced ordering persists over a surprisingly long range (more than 1 μm). The 2-D structure in the layer parallel to a surface is mainly a distorted hexagonal structure similar to that of the (110) plane of a body-centered cubic structure. In contrast to the long-range order in the direction perpendicular to the surfaces, the in-plane structure shows only short-range order. The surface has a very strong effect on the structure only in the direction perpendicular to it. The development of the layered structure induced by the surfaces was also investigated as a function of temperature. When the molecular weight of PS-PVP is low but the copolymer still forms the spherical structure, the layered structure decays more rapidly with distance from the free surface as the temperature is increased. We find that the layered structure changes from an order that is nearly liquid-like near the surface to a long-range-ordered structure continuously as the temperature is decreased, which suggests that the ultimate range of order of the layered structure is governed by thermodynamics. When the molecular weight of PS-PVP is high, the propagation of the layered structure is kinetically limited due to slow diffusion. Similar to symmetric diblock copolymers with a lamellar structure, asymmetric diblock copolymers with a layered spherical domain structure form islands or holes at the free surface when the film is thin and the film thickness does not correspond to an integral number of layers of spheres. As the film becomes thick, the shape of the edge of the island or hole structure changes from a step function to a tanh function, and finally these islands or holes disappear.

Introduction

Diblock copolymers show a variety of ordered domain structures from spherical to lamellar as the block fraction, f, increases from 0 to 1/2.[1] It is known that asymmetric diblock copolymers with very small f (approximately less than 0.15) form ordered spherical domain structures. Theoretically[2] the body-centered cubic (bcc) structure for the spherical block copolymer domains is the most favorable structure, and experimentally the bcc structure is observed.[1] However, recent experimental studies of the spherical domain structure suggest there is a region in which the microphase-separated spherical domains have a fluid-like packing between the bcc phase and a completely disordered phase.[3−6] While lamellar block copolymers have been extensively investigated, spherical block copolymers have received much less attention.

Recently, self-assembling materials such as diblock copolymers have been considered as possible thin film masks for producing nanometer-scale patterns on surfaces. The structure of the diblock copolymer film can be transferred to substrates by etching procedures to produce regular patterns in the substrate, creating for example an array of quantum dots.[7] However, the ordered structure in such a thin film may not be the same as that in the bulk due to the influence of film surfaces. Certainly for the lamellar structure, the surface induces an orientation of the lamellae parallel to the surface.[8−13] A low surface energy component wets the surface to lower the surface energy, and the parallel orientation of the lamellar structure propagates from the surface into the bulk. A substrate may also induce a preferred component of a diblock copolymer to wet the substrate. For a lamellar structure, a fairly simple physical picture may be used due to the 1-D nature of the structure. For the same reason theoretical predictions are also available for the lamellar structure. On the other hand, we still do not know much about the ordering of asymmetric diblock copolymers in thin films. Cylinder domains often prefer to align parallel to a surface to reduce the number of cylinder ends. Experimentally such a parallel orientation does not propagate very far from the surface, with mixed orientations of cylinders being observed even within several cylinders of the surface.[14] However, the layering of cylinders may be kinetically limited by the slow diffusion of the diblock copolymer in the ordered structure. For a spherical domain structure, an earlier study[16] observed by transmission electron microscopy (TEM) that the spherical domains have a layered structure near the surface of very thin films.

Our previous work[17] showed that a bcc spherical domain structure of an asymmetric block copolymer, poly(styrene-*b*-2-vinylpyridine) (PS-PVP), exhibits an exceptional texture in which planes of spheres in the bcc structure are aligned parallel to the surfaces of thin films. The spacing between layers and the packing in them are consistent with those ordered layers being (110) planes of the bcc structure. The earlier experiments showed that this surface-induced epitaxial order persists over 10 layers or more.

For lamellar and cylindrical[14] block copolymer structures, the topology of the free surface of the film can depend on the thin film thickness.[11,18−20] Films with smooth surfaces are observed only when the thickness of the film matches a natural thickness of block copolymer (integer or half-integer number of lamellae or

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cylinders depending on whether the same block or different blocks wet the surface and the substrate). If the film thickness exceeds a natural thickness by less than a half-layer, the excess material is accommodated by forming islands on the film surface. If the film thickness undershoots a natural thickness by less than a half-integer, the deficit is made up by forming holes in the layer at the surface of the film. Given the existence of layered spherical domain structures, it seems logical that these may also show island/hole formation if the thickness of the initial film is not equal to a natural thickness.

Supplementary information in addition to that from a depth profiling technique such as secondary ion mass spectrometry (SIMS) is necessary to understand how spherical domains are aligned by a surface since depth profiling cannot reveal structure parallel to a surface. Traditionally, TEM has been used for this purpose. Since TEM images the structures in projection, it is difficult to identify the structure of a particular layer.

Reactive ion etching (RIE) has proved useful to remove material from the surface at a controlled rate without destroying the internal structure. Using RIE, we are able to mill down to a plane in the internal spherical domain structure and employ surface analytical techniques such as low-voltage scanning electron microscopy (LVSEM) (Harrison et al.)[21−23] or scanning force microscopy (SFM) (this work). The LVSEM method reported by Harrison et al. uses staining to reveal the microdomains; however, we found that staining of PS-PVP (with I_2 vapor) is not very useful for LVSEM perhaps because of the volatility of the I_2 stain and the resolution of LVSEM (5−10 nm), which is not much smaller than our domain size.

We developed an alternate way of observing the exposed surface structure by swelling the PVP core of the spherical domains by the vapor of a selective solvent followed by SFM observation of the swollen surface. Methanol or propanol vapor seems to selectively swell the PVP core of the spherical domain and create a small height difference between the core and the surrounding PS block that can be detected by SFM with excellent resolution. Since both methanol and propanol are nonsolvents for PS, the ordered domain structure should be conserved after exposure to the vapor of these solvents.

In this paper, we investigate the structure of spherical domains in the presence of surfaces from several points of view. The long-range ordering of such a spherical domain structure induced by the presence of a surface is demonstrated. The persistence length of such ordering from a vacuum surface is determined as a function of temperature and molecular weight using fairly thick specimens. The temperature and molecular weight dependence of the surface-induced structure allows us to discuss the thermodynamics and kinetics of layering. The topology of the free surface in a thin film on a silicon substrate is investigated. In an intermediate film thickness regime, for nominal thicknesses where islands or holes should form, they do not, but neither does a perfectly layered spherical domain structure. The internal structure of these films is discussed.

Experimental Section

Materials. A series of poly(styrene-*b*-2-vinylpyridine) (PS-PVP) block copolymers were polymerized by anionic polymerization. Styrene and 2-vinylpyridine were purchased from Aldrich. Both of them were dried using CaH_2 and distilled under a vacuum. Styrene was further purified using dibutylmagnesium (Aldrich) as a drying agent followed by distillation under a vacuum. A small amount of a hexane solution of triethylaluminum (Aldrich) was added to 2-vinylpyridine to remove residual water and alcohols followed by distillation under a reduced pressure of argon gas. These monomers were stored under an argon atmosphere. *sec*-Butyllithium was used as an initiator. Polystyrene was polymerized first, and its molecular weight was measured by gel permeation chromatography. Then, 2-vinylpyridine monomer was added and allowed to polymerize. The volume fraction of PVP, f_{PVP}, was measured by elemental analysis, and the total molecular weight was calculated. The results of the characterization are listed in Table 1. The polydispersities of the diblock copolymers are less than 1.1.

Table 1. Characteristics of Block Copolymers and Homopolymers

code	M_n	f_{PVP}	code	M_n	f_{PVP}
PS-PVP36	35 500	0.11	PS-PVP70	69 800	0.13
PS-PVP50	50 000	0.12	PS-PVP97	97 000	0.11

Sample Preparation. Specimens for dynamic SIMS were prepared by spin-casting a toluene solution of PS-PVP onto a silicon substrate covered by a thick (~500 nm) silicon oxide layer. The thickness of the PS-PVP films was adjusted by changing the concentration of PS-PVP in the toluene solution and the rotational speed of the sample. The solution was also spin-cast onto silicon substrates covered with a thin (~1.5 nm) native oxide immediately after spin-casting onto silicon oxide substrates under the same conditions for us to measure the film thickness by ellipsometry. We assumed that the films on the different substrates have the same thickness. The specimens for SFM are prepared on silicon substrates in the same way. To produce thick films (>1 μm) for the SIMS measurements, the toluene solution was cast onto silicon oxide substrates and slowly evaporated.

The silicon oxide layer (~500 nm) on the silicon oxide/silicon substrate was deposited by evaporating silicon oxide using a four-pocket electron beam evaporator (Sharon Vacuum Co., Inc.). This SiO_x layer is sufficiently insulating that the conditions for charge neutralization using the low-energy electron gun do not change as the SIMS crater approaches the polymer/substrate interface. Prior to the SIMS analysis, a sacrificial deuterated PS (dPS) thin film (30−50 nm thick) was spin-cast, floated off on distilled water, and picked up on top of the specimens. The deuterated PS was used so that the original surface could be identified. This procedure also ensured that steady-state sputtering conditions were achieved before the SIMS sputtering crater reached the original surface. For very thick films whose thicknesses were difficult to measure by ellipsometry, the signal from the sacrificial layer with known thickness was used to convert the time of SIMS sputtering into the SIMS crater depth. The sputtering rate of the sacrificial layer was assumed to be the same for PS-PVP as for dPS since PVP has a structure very similar to that of PS and the PVP fraction of our samples was only ~0.1.

Secondary Ion Mass Spectrometry. Dynamic SIMS measurements were done with a Physical Electronics 6650 dynamic SIMS using a 3 keV, 20−50 nA beam of O_2^+ ions at 60° off normal incidence, which was rastered over a 0.09 mm^2 region. Charge neutralization was accomplished using a static, defocused, 0.7−1 keV electron beam. Negative ions of H, ^2H (D), C, CH, C^2H, CN, and Si were monitored as a function of time from an electrically gated area that was less than 10% of the rastered area. Under such conditions, we obtain a depth profile with a Gaussian resolution, full width at half-maximum, of about 15 nm. A useful discussion of the important parameters for optimum dynamic SIMS depth profiling of polymers has been given by Schwarz et al.[24] By measuring the thickness of the polymer film using an ellipsometer, we convert sputtering time into depth (assuming a steady rate of sputtering). Combining this depth scale with information on the overall chemical composition and volume fraction of each block, we are able to convert the intensities of negative ions into the volume fraction of each block as a function of depth. The CN^- signal was normalized to provide a depth profile of the PVP spherical domain cores.

Reactive Ion Etching. We followed the scheme developed by Harrison et al.[21] for etching polymer films using RIE. A reactive ion etching system from Applied Materials, Inc. was operated with 10 standard cm^3/min of CF_4 flow, a pressure of 2 mTorr (0.27 Pa), and a bias voltage of 290 V. Under these conditions, RIE etches away approximately 10 nm of the PS-PVP film/min. The etching rate was constant over a typical sample area of 1 cm × 1 cm. CF_4 gas was used for etching PS-PVP films since Harrison et al. reported that the etching rates of CF_4 for PS and PVP are the same.[21] Such nonselective etching is not typical for the oxygen RIE commonly used to etch polymers.

Scanning Force Microscopy. A Digital Instruments SFM D3000 was used in the tapping mode. For the observation of islands and holes, SFM was performed without further etching or methanol vapor treatment.

Results and Discussion

Layered Structure of Spherical Domains in Thin Films. Recently it was shown that the presence of a surface induces an asymmetric PS-PVP diblock copolymer to form a layered structure of PS-PVP spheres parallel to the surface[17] similar to the surface-induced ordering of lamellae in lamellar block copolymers parallel to the surface of thin films.[8-13] The layered structure of PS-PVP diblock copolymer spheres was observed to persist for at least 200 nm (six layers). It is analogous to the order observed for lamellar block copolymer structures induced by surfaces but contrasts with reports of cylinder structures with the cylinders parallel to surfaces that do not propagate more than a few layers from the surface.[14]

To study this surface ordering phenomenon in more detail, we prepared PS-PVP97 diblock copolymer films with a variety of film thicknesses and annealed them for 3 days at 180 °C under a vacuum. We selected those films without any island/hole formation for SIMS analysis to avoid confusion caused by rough surfaces.

From the SIMS depth profile the intensity $I(x)$ of CN^- ions (mass 26) was converted into the volume fraction of PVP, ϕ_{PVP}, by the normalization scheme given by eq 1,

$$\phi_{PVP}(x) = hf_{PVP}I(x)/\int_0^h dx\, I(x) \qquad (1)$$

where x is a coordinate perpendicular to the surface of the film, f_{PVP} is the fraction of PVP (average volume fraction of PVP in the specimen), and h is the thickness of the sample. The notation $\phi_{PVP}(x)$ emphasizes that ϕ_{PVP} is a local volume fraction of PVP as a function of the x coordinate perpendicular to the surface. This volume fraction is however averaged laterally over a distance of about 100 μm, many times larger than the lattice parameter of the bcc spherical structure, which is about 30 nm.

All films, ranging from 600 nm to 1.3 μm thick, show the same layered structure with the same periodicity all the way across the film. As an example of the layered structures observed by SIMS, the depth profile of PVP in the thickest film is shown in Figure 1. The local volume fraction of PVP, ϕ_{PVP}, is plotted against the depth from the vacuum surface. This PS-PVP (PS-PVP97) has the highest molecular weight in our set of PS-PVP diblock copolymers. Surprisingly, the layered structure propagates 1.3 μm, all the way from a vacuum surface to a silicon oxide substrate with 42 PVP local maxima. The extreme ϕ_{PVP} maximum at the silicon oxide interface is due to a wetting layer of PVP against that interface. The extreme minimum of ϕ_{PVP} just above the PVP wetting layer indicates a brush of PS that excludes PVP segments from this region. It should be noted that the amplitude of the oscillation of ϕ_{PVP} is very small (0.07−0.15) in contrast to that of a lamellar structure oriented in a thin film, which nearly oscillates from 0 to 1. The smaller amplitude of oscillation indicates that discrete PVP spherical domains are aligned in layers, thus resulting in a value of $\phi_{PVP} \ll 1$ in each layer.

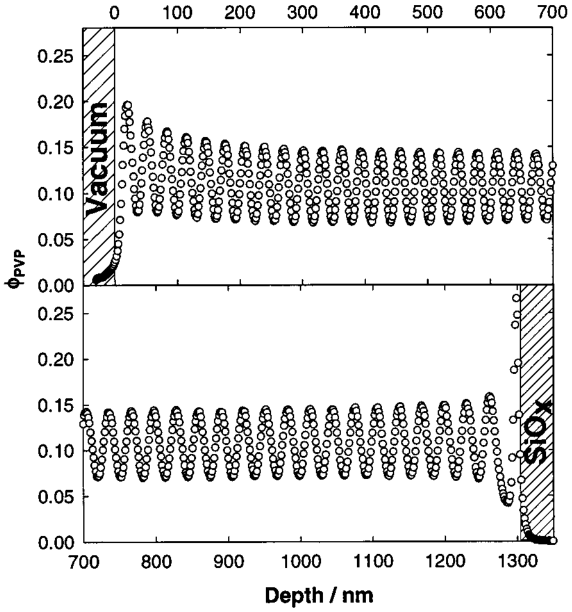

Figure 1. A depth profile of the volume fraction of PVP, ϕ_{PVP}, of a PS-PVP97 1.3 μm film on a silicon oxide substrate after being annealed for 3 days at 180 °C under a vacuum and quenched to room temperature. Each peak corresponds to a layer of PVP spheres.

The layered spherical structure in a thinner film (~200 nm) has been reported to be well fit by a bcc structure with (110) layers of spheres parallel to the surfaces. The structure observed in this study is consistent with that inferred in the previous study and extends through from the surface to the substrate without significant decay.

Structure of a Layer of Spheres. To understand this layered structure completely, information on the ordering of spheres in the plane parallel to the surface is essential. We used the RIE/SFM technique to observe the 2-D structure of such planes. RIE was used to remove 30 nm of the PS-PVP diblock copolymer from a surface. The depth of 30 nm cuts through the PVP spherical cores in the first layer according to the SIMS depth profile in Figure 1 and exposes them at the new surface. After exposing the surface to methanol vapor, we used SFM to observe the surface topological structure. PVP regions are swollen by the methanol and become higher than the PS surroundings, giving a good contrast. We confirmed the structure observed with SFM with low-voltage scanning electron microscopy following the method of Harrison et al. (with poor resolution for our specimens); therefore, the structure observed by SFM is not an artifact.

A typical 2-D structure in the first layer is shown in Figure 2. An amplitude image[15] is shown here. A height image is also similar but has slightly poorer resolution.

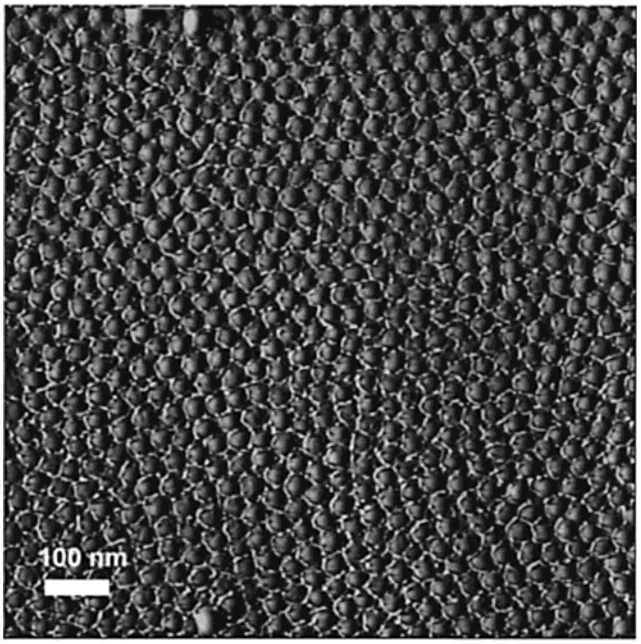

Figure 2. An in-plane structure of the PS-PVP97 block copolymer in a thin film observed by SFM after RIE etching 30 nm from a vacuum surface. The film was annealed at 180 °C for 72 h and quenched to room temperature before etching. The film was exposed to methanol vapor for 15 min after etching to enhance the topology of the surface.

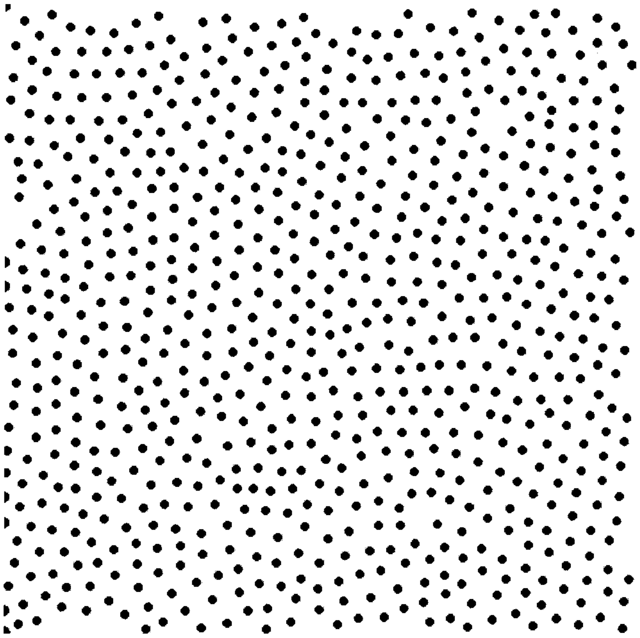

Figure 3. Digitized in-plane structure of the PS-PVP97 block copolymer in a thin film observed by SFM after RIE etching 30 nm from a vacuum surface. The dots represent the centers of the spherical domains in Figure 2.

The spheres shown in Figure 2 are the PVP cores swollen selectively by methanol and are higher than the surrounding PS. The force on the scanning force microscope tip was minimized so that the topological image could be observed without the different moduli of the PS and PVP regions influencing the results. (With a high tapping force, the image became inverted due to the difference in moduli.) In contrast to the layered structure in the direction perpendicular to the surface, the in-plane structure does not seem to have long-range order. We find a lot of defects and small grains oriented in different directions. However, most of the spheres form a distorted hexagonal packing in the plane. A distorted hexagonal pattern of spheres is characteristic of the (110) plane of the bcc structure, and is, in turn, consistent with the detailed analysis of our SIMS depth profiles.

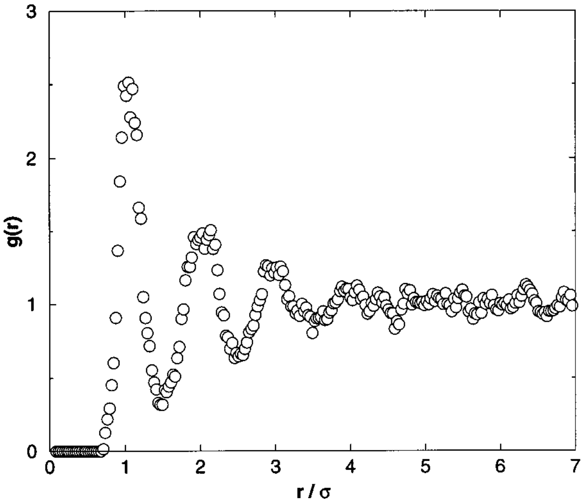

Figure 4. Radial distribution function $g(r)$ of spherical domains in a plane calculated from Figure 3. σ is 35 nm to fit the first peak of the function.

We determined the coordinates of the centers of the spheres in Figure 2 and show these as dots in Figure 3. Since the structure observed has a lot of defects and a small grain size, it is similar to the structure of a liquid. From the coordinates of the sphere centers in the plane, we can compute the in-plane radial distribution of these spheres. The computed radial distribution function is shown in Figure 4. Beyond a weak third nearest-neighbor peak, there is little order in contrast to the long-range order (the layered structure) observed in a direction perpendicular to the film surfaces. The radial distribution function $g(r)$ in the plane is similar to that of a liquid, but with more short-range order. The ordering of spherical domains is quite different in the plane of the film than normal to it.

The layered structure therefore consists primarily of a stack of (110) bcc planes with many defects in each plane. The surprising thing is that such a poorly ordered layer can stack and construct a very long range order in the direction perpendicular to the surfaces. If a liquid molecule organizes next to a flat surface, there is a local order normal to that surface, but the order decays in a few molecular spacings similar to the $g(r)$ in Figure 4.[25] On the other hand, if the block copolymer structure were analogous to an epitaxial atomic crystal,[26] such a defect structure in a plane should propagate normal to the plane; therefore, we would not expect to observe a long-range-ordered structure perpendicular to the surface. The difference in the diblock copolymer spherical structure from atomic liquids or solids is that a local density of the diblock copolymer must be nearly constant. For an atomic system a different packing or different spacing between atoms ends up providing a variation of local density. In the spherical structure of a diblock copolymer significant density variations on the scale of the spheres are not possible (it costs too much free energy to have voids with a size of ~30 nm). On the other hand, the variation of the local sphere size (micelle aggregation number) or packing geometry may be possible depending on the interaction energy of the two blocks. These fundamental differences may make the defect structure of the bcc block copolymer quite different from that of a bcc atomic crystal. Presumably, the interesting long-range-layered structure with poor in-plane order is related to such differences.

Block copolymers with a lamellar structure also can order to produce a layered structure parallel to the surfaces.[8−13] Such order would seem to be more strongly favored than that for spheres due to its 1-D character. Nevertheless, such order of lamellar block copolymers has not been observed to have such a long range. The disorder observed in thick films is primarily due to lamellae perpendicular to the surfaces in the middle of the film. Once such perpendicular lamellae are formed, it seems almost impossible to flip these lamellae into an orientation parallel to the surfaces even though such an orientation is the thermodynamically most stable one. On the other hand, for the spherical domain structure, the spheres in the middle of the film may initially form a local bcc structure, with the (110) plane perpendicular to the surfaces, but can flip the (110) plane parallel to the surfaces by only small movements of the spheres. This difference makes the kinetics of layering of spheres quite different from that of layering of lamellae.

Molecular Weight Dependence of the Layered Structure of Spheres. We investigate here the molecular weight dependence of the layered structures at fixed annealing conditions (temperature 180 °C, time 72 h). Since the order−disorder transition for a fixed fraction, f, of the minority block is controlled by the product of the Flory interaction parameter, χ, and the total number of segments, we expect that the layered structure also has an N dependence. We show the layered structure of three other PS-PVP diblock copolymers in Figure 5. PS-PVP70 with an M_n of 70 000 has a layered structure similar to that of PS-PVP97 shown in Figure 1. The spacing of the layers of PS-PVP70 is ∼27 nm, while PS-PVP97 has a spacing of ∼32 nm. We find a wetting layer of PVP at the silicon oxide substrate, the same as for PS-PVP97. Since PS has a lower surface energy than PVP, the vacuum surface consists of a PS block layer.

The diblock copolymer PS-PVP50 shows a qualitatively different behavior. The PVP block still wets the silicon oxide surface as shown by the maximum of the PVP volume fraction there, but the oscillation of the PVP volume fraction decays as we move toward the bulk of the film. A similar decay of a layered structure can be observed from the vacuum surface toward the center of the film. The decay of the layering is complete for both the surface and substrate after four layers. The period of this decaying oscillation is ∼20 nm. The oscillation due to the layering from both the vacuum and silicon oxide substrates does not persist for more than a few layers in contrast to those of PS-PVP97 and PS-PVP70.

For PS-PVP36, there is no evidence of layering except in the vicinity of the silicon oxide interface. The silicon oxide interface still seems to induce a wetting layer of PVP and to form a weakly aligned layer of spheres next to the wetting layers. Since PS-PVP36 shows no evidence of ordered structure in the bulk, the structure in the middle of the film is a disordered structure. For PS-PVP36, the surface-induced ordering, which is observed for disordered symmetric diblock copolymers,[10] is limited to the vicinity of the silicon substrate.

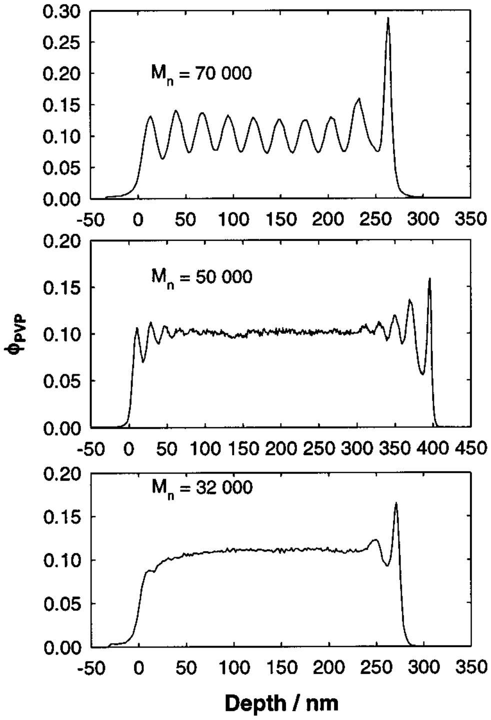

Figure 5. Molecular weight dependence of the layered structure of spherical domains of PS-PVP diblock copolymers. The volume fraction of PVP, ϕ_{PVP}, is plotted as a function of the depth from the vacuum surface. The film is on a silicon oxide substrate, which attracts the PVP block. The largest peak of ϕ_{PVP} is the wetting layer of PVP at the substrate followed by a brush of PS.

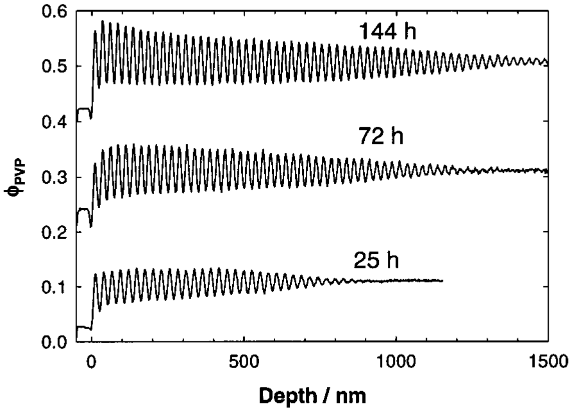

Figure 6. Annealing time dependence of layering of PS-PVP97 in a very thick film annealed at 180 °C and quenched to room temperature. The volume fraction of PVP, ϕ_{PVP}, is plotted as a function of the depth from the vacuum surface. ϕ_{PVP} is shifted vertically by 0.2 for easy comparison between curves.

Ordering of the Spherical Domain by a Single Surface. To understand the layering of spherical domains induced by surfaces, very thick films (≫10 μm) of PS-PVP97, PS-PVP70, and PS-PVP50 were prepared and annealed at different temperatures. The very thick film ensures that the structure of the film observed by SIMS is influenced only by the vacuum surface.

The dependence of the development of the layered structure of PS-PVP97 spherical domains on annealing time at 180 °C is shown in Figure 6. The depth profiles for ϕ_{PVP} at different annealing times are shifted vertically by 0.2 for comparison. Unlike the structure observed in the 1.3 μm thick film, we find that the

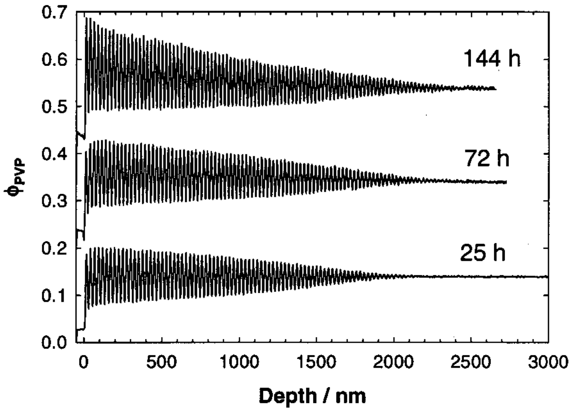

Figure 7. Annealing time dependence of layering of PS-PVP70 in a very thick film annealed at 180 °C and quenched to room temperature. The volume fraction of PVP, ϕ_{PVP}, is plotted as a function of the depth from the vacuum surface. ϕ_{PVP} is shifted vertically by 0.2 for easy comparison between curves.

oscillating depth profile of ϕ_{PVP} decays from the surface into the bulk. The reason for the difference in behavior is that the 1.3 μm film has a silicon oxide substrate in proximity to the surface and both this substrate and vacuum surface act as templates for the layering order of the 1.3 μm film. The oscillating depth profile continues to extend to greater depths even between 72 and 144 h of annealing at a temperature substantially above the glass transition temperature. For this particular sample we can conclude that the extent of the layering below the surface is limited due to the kinetics of layering. A possible factor controlling the kinetics of layering is the self-diffusion of the diblock copolymers that make up the domains. Our recent study[17,27] on the diffusion of diblock copolymers in the spherically ordered structure showed that the diffusion coefficient decreases exponentially with the product of the interaction parameter χ and the number N_{PVP} of segments of the core block relative to the diffusion of the PS or PVP homopolymer. Such diffusion is controlled by hopping of single diblock copolymers, from one domain to another. The characteristic time of hopping of dPS-PVP117 (a deuterated analog of the copolymer PS-PVP97) is 50 000 s.[17] Thus, such a copolymer could only hop 10 times during 144 h of annealing. Such short-range diffusion may not be sufficient to achieve ordering over micrometer length scales.

The time dependence of the development of the layered structure of PS-PVP70 at 180 °C is shown in Figure 7. A damped oscillation of ϕ_{PVP} is observed similar to that seen for PS-PVP97, but the decay rate of the oscillation with depth is slower than for PS-PVP97. This result is a further indication that the development of the surface-induced layering of PS-PVP97 is kinetically limited. The diffusion of PS-PVP70 is much faster (about 10 times) than that of PS-PVP97 ($\chi N_{PVP} = 9$ for PS-PVP70 vs $\chi N_{PVP} = 11$ for PS-PVP97 at 180 °C); therefore, the kinetics of ordering of PS-PVP70 is also expected to be much faster than that of PS-PVP97. We still see the range of surface-induced ordering for PS-PVP70 increases with increasing annealing time, but it is difficult to conclude much more since the layering reaches a depth over 2 μm, a depth at which the resolution of SIMS may become comparable to the spacing between layers.

The time dependence of the development of the layered structure of PS-PVP50 spherical domains on annealing time at 180 °C is shown in Figure 8. The profiles after 5 h and after 25 h are almost identical, suggesting that an "equilibrium" structure has been achieved at this temperature. The surface-induced layering of PS-PVP50 is of much shorter range than that of the other two PS-PVPs (PS-PVP70 and PS-PVP97). In addition the amplitude of the oscillation in ϕ_{PVP} even at the surface is significantly less than those for the two longer copolymers. The self-diffusion of PS-PVP50 is very close to that of the homopolymer PS[27] and much faster than that of the other two PS-PVPs, and hence the short-range surface-induced order should not be limited kinetically.

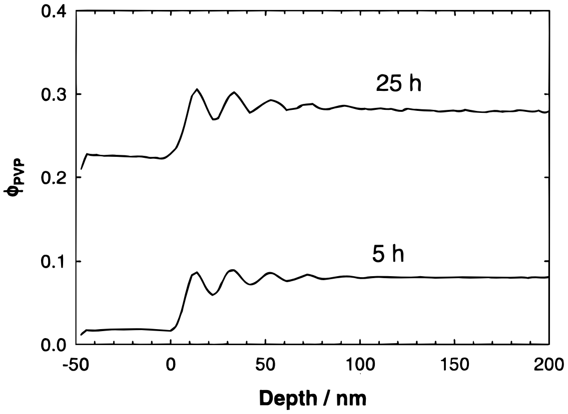

Figure 8. Annealing time dependence of layering of PS-PVP50 in a very thick film annealed at 180 °C and quenched to room temperature. The volume fraction of PVP, ϕ_{PVP}, is plotted as a function of the depth from the vacuum surface. ϕ_{PVP} is shifted vertically by 0.2 for easy comparison between curves.

From these experiments we find that the best order occurs for a block copolymer of intermediate length. For PS-PVP97, the ordering kinetics seems to be limited by diffusion, consistent with the fact that the range of the surface-induced order is still growing even at the longest annealing time. On the other hand, clearly fast self-diffusion is not sufficient to achieve long-range surface-induced order since PS-PVP50 has a very limited range of (equilibrium) order induced by the surface.

There are two possibilities that may limit the number of layers in the structure. One of them is a defect structure that persists for kinetic reasons, e.g., grain boundaries, analogous to the defect structure of atomic solids. Even though a single crystal is favored over a polycrystal thermodynamically, the growth of grains is kinetically limited. The other possibility is a thermodynamic limitation due to the fluctuation in size of spherical domains as well as fluctuations of (110) planes and orientation in a surface-induced layered structure. If the limitation is kinetic (perhaps for PS-PVP97), raising the temperature or perhaps reducing N_{PVP} slightly should increase the number of layers for a given annealing time. If the limitation is thermodynamic (perhaps for PS-PVP50), raising the temperature and reducing N_{PVP} will reduce the number of layers. Investigating the temperature dependence of the extent of the layered structure below the surface will give us information on whether the limitation is kinetic or thermodynamic.

Temperature Dependence of the Layered Structure of Spherical Domains. The layered structure of spherical domains of PS-PVP50 induced by a vacuum surface showed no annealing time dependence, indicat-

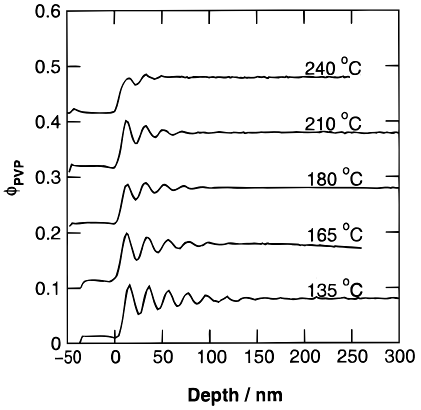

Figure 9. Temperature dependence of a layered structure of PS-PVP50 induced by a vacuum surface. The film was annealed at the various temperatures indicated for 24 h and quenched to room temperature. ϕ_{PVP} is shifted vertically by 0.1 for easy comparison between curves.

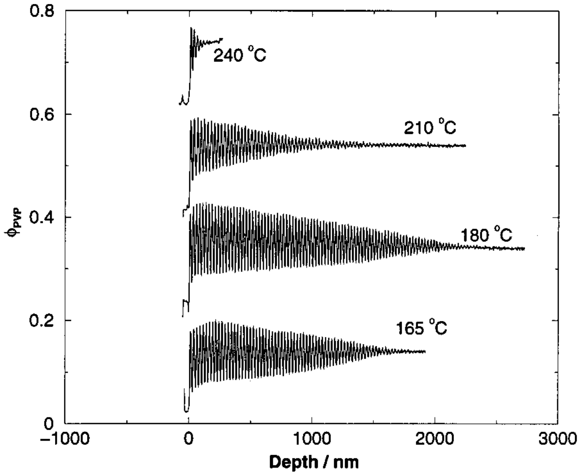

Figure 10. Temperature dependence of a layered structure of PS-PVP70 induced by a vacuum surface. The film was annealed at the temperatures indicated for 24 h and quenched to room temperature. ϕ_{PVP} is shifted vertically by 0.1 for easy comparison.

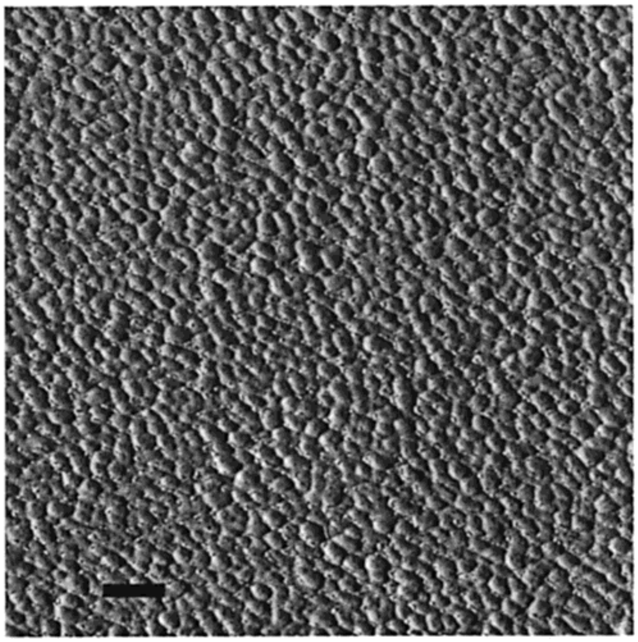

Figure 11. In-plane structure of the PS-PVP50 block copolymer in a thin film (annealed at 180 °C for 72 h) observed by SFM after RIE etching 20 nm from a vacuum surface. The solid line in the image indicates 100 nm.

ing that the layered structure is not kinetically trapped. We annealed thick films (several micrometers) of PS-PVP50 for 24 h at several different temperatures ranging from 135 to 240 °C. The observed depth profiles of the layered structures of the PS-PVP50 diblock copolymer induced by a vacuum surface are plotted in Figure 9. The lower the annealing temperature, the further from the surface the layered structure of spherical PVP domains of PS-PVP50 propagates. The temperature dependence further confirms that the layering of spherical PVP domains is governed by thermodynamics at this χN_{PVP}.

PS-PVP70 thick films were annealed for 72 h at different temperatures. We plot the observed PVP volume fraction from the PVP spherical domains as a function of the distance from the vacuum surface in Figure 10. There is an optimum annealing temperature (around 180 °C) at which the range of order of the layering of spherical PVP domains from the surface is a maximum after 72 h. We know the diffusion coefficients of the PS-PVP diblock copolymer in this χN_{PVP} range from the previous work.[17,27] The diffusion coefficients of the PS-PVP diblock copolymer decrease exponentially with χN_{PVP}, while the temperature-dependent monomeric friction coefficients of PS and PVP increase as T is decreased. One can easily imagine that the ordering process may be controlled by the slow diffusion of the diblock copolymer at low temperatures. It seems that a long-range ordering requires an optimum χN_{PVP} at a given annealing time that satisfies both the thermodynamic and kinetic requirements. Unfortunately, the region of optimum ordering is very narrow due to the exponential decrease of the diffusion of the diblock copolymer with χN_{PVP}.

In-Plane Structure and the Structure in the Bulk. The same RIE/SFM technique was also applied to PS-PVP50 and PS-PVP70 diblock copolymers to observe the in-plane structure of the near surface layers in these copolymers. The SFM amplitude image of the layered structure of PS-PVP50 (annealed at 180 °C for 72 h) at 20 nm from the vacuum surface is shown in Figure 11. The new surface created by RIE was exposed to methanol vapor prior to the SFM observation. Height images are also obtained simultaneously and show essentially the same pattern. As seen in Figure 11, small spherical domains are present similar to those in Figure 2 but with smaller sphere sizes and spacings. Although we find spherical domains, there is almost no ordered structure of the spheres. On the other hand, at a depth of 20 nm from the surface, SIMS depth profiling detects a peak of PVP volume fraction as shown in Figure 9. The vacuum surface seems to induce layering of spherical domains in the direction perpendicular to it, even though the in-plane structure of the spheres is barely ordered. Such ordering is similar to that of fluids near a surface.[25] If the PVP spherical domains in PS-PVP50 do not order but form a liquid-like packing in the bulk, the surface-induced layering at this copolymer may be explainable. We checked the bulk morphology of PS-PVP50 by small-angle X-ray scattering (SAXS) and TEM.

The SAXS result for PS-PVP50 is shown in Figure 12. The first-order peak (q^*) is found at both 135 and 180 °C. However, the characteristic peaks of the bcc structure ($(\sqrt{2})q^*$ and $(\sqrt{3})q^*$) are not present. Instead,

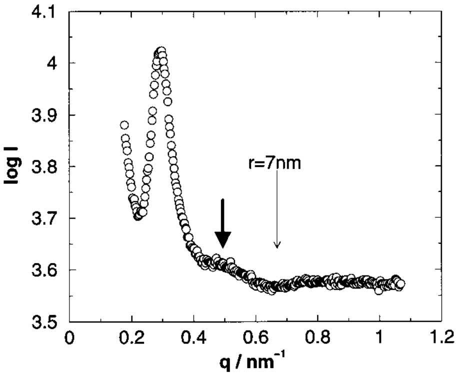

Figure 12. SAXS intensity versus wave vector q for the PS-PVP50 diblock copolymer. The radius of the PVP sphere, r, is estimated from the minimum of the scattering function fit by the structure factor of a sphere. Only a first-order peak at q^* and a broad shoulder at $(\sqrt{2})q^* \approx (\sqrt{3})q^*$ indicated by a dark arrow are observed.

a broad shoulder can be seen around the region where $(\sqrt{2})q^*$ and $(\sqrt{3})q^*$ peaks should be. The short-range correlation giving rise to the broad shoulder can be either a weak interparticle correlation (fluid-like packing) or an intraparticle correlation (from the structure factor of a spherical domain). In either case, the SAXS evidence suggests the presence of spherical domains without the formation of a bcc structure as discussed by Sakamoto et al.[3−5] and Schwab et al.[6] The radius of the PVP core spheres was determined to be approximately 7 nm by matching the first minimum of the structure factor of a sphere to the minimum in the SAXS indicated by the arrow in Figure 12.

The TEM of microtomed thin sections from bulk PS-PVP50 that was annealed at 180 °C for 72 h and quenched to room temperature reveals a fluid-like packing of spherical domains as seen in Figure 13. The dark cores of PVP are found everywhere in the specimen but have no lattice structure. The TEM micrograph in Figure 13 seems almost identical to that obtained by Sakamoto et al.[3−5] From both SAXS and TEM, it is reasonable to conclude that PS-PVP50 forms spherical domains with a fluid-like packing. The fluid-like packing of spheres is consistent with the damped oscillation of ϕ_{PVP} in Figure 9, which is similar to the density profile of a liquid near a solid wall. It should be noted, however, that the self-diffusion of PS-PVP50 is expected to be influenced little by the presence of the spherical domains seen in Figure 13. Such high diffusivity suggests that the diblock copolymer chains are not trapped in the spherical domains but frequently detach and hop. Therefore, it may be difficult to distinguish between the static fluid-like structure and fluctuations.

The thermodynamic parameter χN of PS-PVP50 is much closer to χN_{ODT}[28] than those of PS-PVP70 and PS-PVP97; therefore, the size of its spherical domains should fluctuate more than those of the other two diblock copolymers. Such fluctuations of spheres in size (aggregation number) may prevent ordering of the bcc domain structure in the bulk and the layering of spherical domains near the surface.

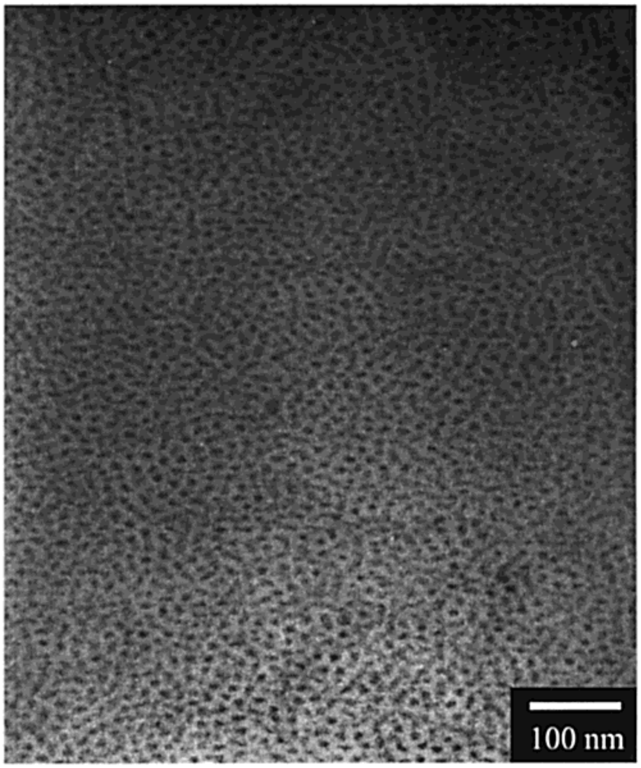

Figure 13. A TEM micrograph of the PS-PVP50 diblock copolymer annealed at 180 °C for 72 h and quenched to room temperature. The solid line in the micrograph indicates 100 nm. The dark regions are PVP domains stained by I_2.

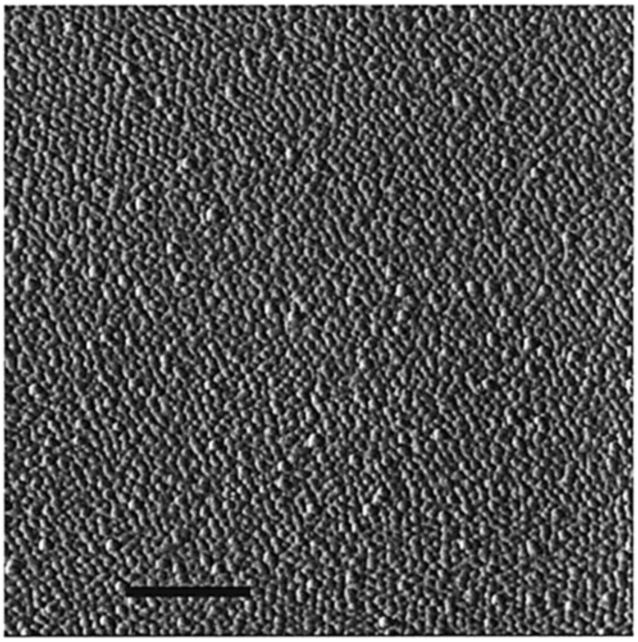

Figure 14. An in-plane structure of the PS-PVP70 block copolymer in a thin film (annealed at 180 °C for 72 h) observed by SFM after RIE etching 30 nm from a vacuum surface. The solid line in the image indicates 400 nm.

Similarly the SFM picture of the PS-PVP70 film (ordered by being annealed at 180 °C for 72 h) etched 30 nm from its surface by RIE is shown in Figure 14. In contrast to the structure of the PS-PVP50 film, the PS-PVP70 film is fairly well ordered. However, the grain size of the in-plane structure is not still comparable to the range of the ordering in the direction perpendicular to the surface as observed in the SIMS depth profile. The SAXS results for PS-PVP70 are shown in Figure 15, and a TEM micrograph of the PS-PVP70 bulk structure is shown in Figure 16. PS-PVP70 shows diffraction peaks at q^*, $(\sqrt{2})q^*$ and $(\sqrt{3})q^*$, peaks that are characteristic of a bcc lattice. The TEM reveals a polycrystalline bcc domain structure in a microtomed thin section of the bulk sample that was annealed at

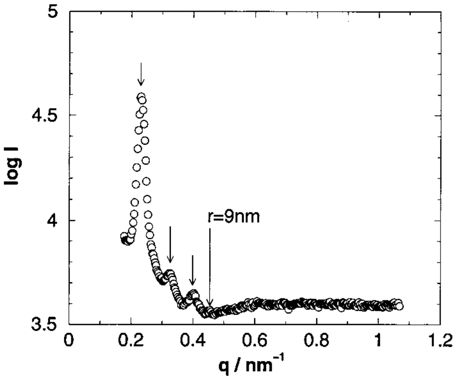

Figure 15. SAXS intensity versus wave vector *q* for the PS-PVP70 diblock copolymer. The radius of the PVP sphere, *r*, is estimated from the minimum of the scattering function fit by the structure factor of a sphere. q^*, $(\sqrt{2})q^*$, and $(\sqrt{3})q^*$, which are characteristic peaks for the bcc lattice, are indicated by arrows.

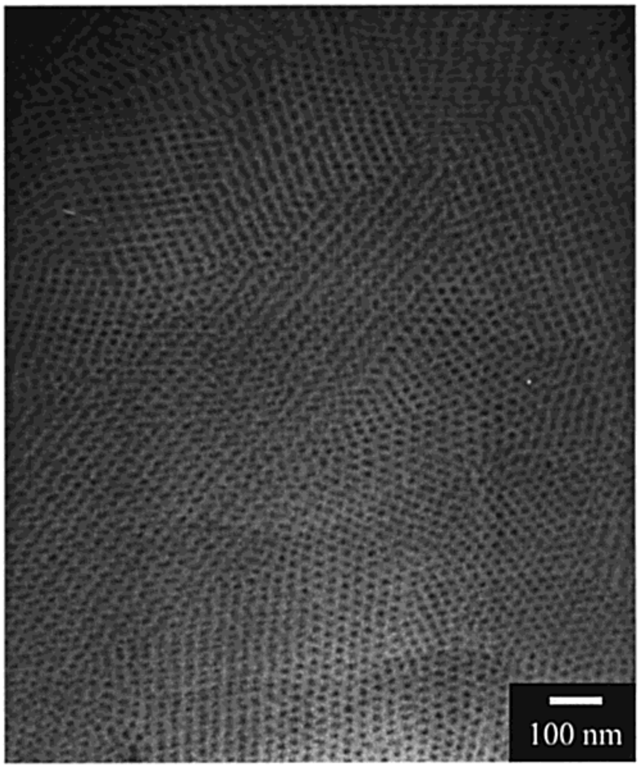

Figure 16. A TEM micrograph of the PS-PVP70 diblock copolymer annealed at 180 °C for 72 h and quenched to room temperature. The solid line in the micrograph indicates 100 nm. The dark regions are PVP domains stained by I_2.

180 °C for 72 h and quenched to room temperature. The grain size of the PS-PVP70 bcc structure is fairly large, giving clear higher order diffraction peaks in the SAXS pattern. It is clear that in the bulk each grain of the bcc structure is randomly oriented. That result can be established from the isotropic ring diffraction pattern in SAXS as well as the TEM micrographs. The presence of the surface induces layering in the direction perpendicular to it, but nevertheless, the structure within each plane is influenced very little by the order in the perpendicular direction. Although PS-PVP70 seems to have the longest range order of the copolymers in our experiment, the structure within each plane has about the same grain size as that in the bulk in contrast to the layering we observe extending over 2 μm in the direction perpendicular to the surface.

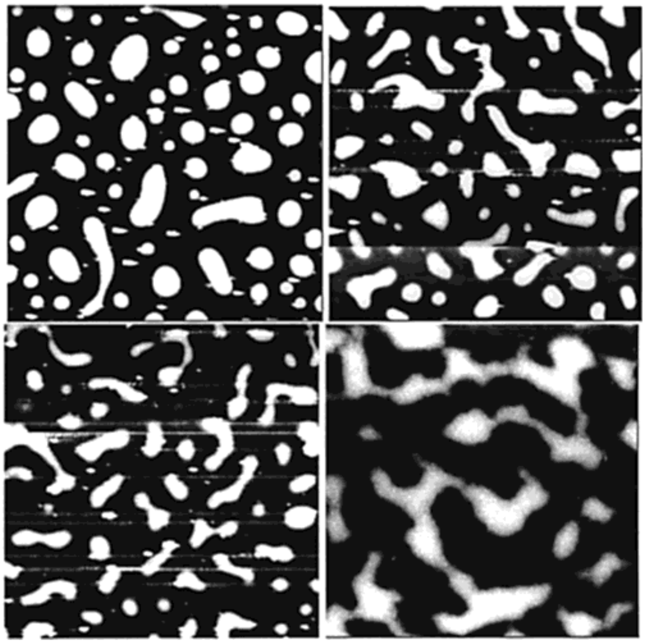

Figure 17. Island structures in thin films of the PS-PVP97 block copolymer. The islands correspond to the first layer of spheres on a brush (top left), the second layer of spheres from the brush (top right), the third layer of spheres (bottom left), and the sixth layer of spheres (bottom right). White regions are islands. The width and height of the images are 30 μm.

Island Formation in Thin Films. We have shown that a spherical domain block copolymer forms a layered structure from surfaces, similar to the layering observed for the lamellar block copolymers. This layered structure may lead to thickness quantization for the spherical domain block copolymer in thin films. To test this hypothesis, we prepared very thin films of PS-PVP97 with thicknesses between about 50 and 200 nm. These thicknesses range from about one layer to about six layers plus a brush. We find that islands and holes form after the films are annealed at 180 °C for 72 h when the initial film thickness does not match a natural thickness given approximately by

$$t = \alpha n + \beta \qquad (2)$$

where t is the natural thickness of the film, α is the thickness of a spherical domain layer, β is the thickness of the adsorbed brush of PS-PVP on the silicon oxide surface, and n is an integer. For PS-PVP97 used in this island/hole formation experiment, α is 30 nm and β is 25 nm. When the thickness of the film differs significantly from a natural thickness t, we find either islands or holes depending on the deviation of thickness from the natural thickness. The rule to determine whether islands or holes are formed is the same as that for the lamellar block copolymers. We show a series of island structures for films of different thicknesses in Figure 17. When the film thickness is very small, i.e., the islands are formed on the brush of PS-PVP, the islands are round and the boundary of an island is very sharp (boundary width ~0.5 μm). When the film becomes much thicker, the islands have a variety of shapes and the boundary of an island becomes diffuse (boundary width ~2 μm). Since the round shape of the islands for the thinnest film reflects a higher line tension, it is consistent with the sharp boundary observed for those islands. Typical height profiles of those island structures are plotted in Figure 18. The island boundary profile

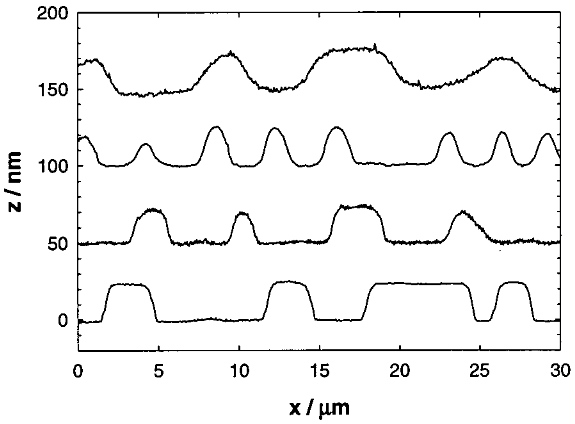

Figure 18. Height profile of the islands in Figure 17 versus distance along the film plane. The line of the profile was chosen such that the line crosses at the center of the islands.

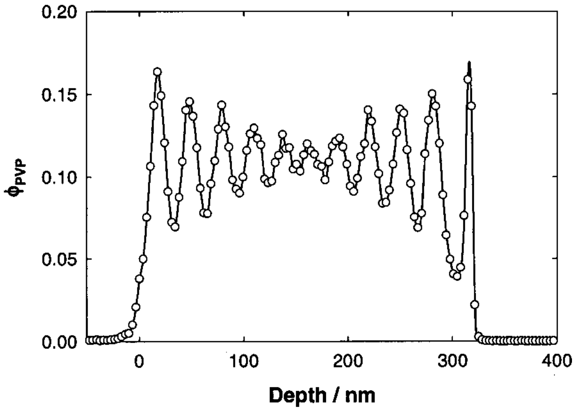

Figure 19. Internal structure of a frustrated film of PS-PVP97. The propagating oscillations of ϕ_{PVP} propagating from both the surface and the substrate interface destructively interferes in the middle of the thin film.

evolves from a step-like profile to a diffuse one as the film becomes thick. The diffuse profiles have less excess surface area (less total surface energy) than that of the step-like one. However, the diffuse profile must compress or stretch more spherical domains in the region where the local thickness is not the natural thickness. Apparently, the thicker film is softer and deforms more under the condition where the surface tension is constant irrespective of the film thickness. It could be that the deformation can be distributed to several layers of spheres for thicker films and thus cost much less energy than that for the thinner films.

When the film thickness becomes even thicker than six layers of spheres, islands and holes do not form. We prepared several films with a thickness around 300 nm, where we do not see the formation of islands and holes. These films range in thickness from nine to ten layers of spheres plus a brush. None of them show islands or holes. The SIMS depth profile shown in Figure 19 reveals the internal structure of such a film. The oscillations propagating from the vacuum and silicon oxide surfaces interfere with each other destructively. It is rare to see this kind of interference in our PS-PVP films. When the film thickness is smaller, islands or holes form to release the strain. On the other hand, when the film thickness is much larger than nine to ten layers, the strain per layer becomes smaller and we observe apparently perfect layering.

It is interesting that the disorder is confined to the middle of the layers of the film. At these thicknesses the strain "frustration" induced by film thickness departures from a natural thickness is apparently accommodated by adding defects in the layering to the middle layers of spheres, rather distributing these defects throughout the film. This fact suggests that such defects have a long-range displacement field that interacts with both the surface and the substrate that provide constraints enforcing the planar geometry.

Conclusions

We observe a strong effect of the surfaces in bcc block copolymer films that induces layering of the spherical domains. The layering propagates a surprisingly long distance perpendicular to a surface. The persistence length of such a layered structure from the surface is influenced by its bulk order and thermodynamics. When a fluid-like packing of spherical domains is observed in the bulk, the layering of spherical domains is limited to only a few layers just below the surface. On the other hand, when a well-ordered bcc structure is observed in the bulk, the layered structure propagates nearly 100 layers of spheres, over 2 μm from the surface. In the low molecular weight regime the layering is controlled by thermodynamics. Decreasing temperature and increasing χ increase the number of layers of spherical domains. However, at larger χN (further from the order–disorder transition temperature) the kinetics become very slow due to slow diffusion. In this regime the number of layers of spheres increases with increasing annealing time, and block copolymers with larger χN show a smaller number of layers of spheres at a given annealing time than those with smaller χN. For diblock copolymers to form a long-range-layered structure, the appropriate χN regime is very narrow, and a very fine-tuning of molecular architecture or use of solvents to adjust the effective χN is necessary.

In contrast to the strong effect of a surface on the layering in the direction perpendicular to the surface, the in-plane structure of the layers is not much different from the bulk structure. The surface does not very much influence the structure in the plane perpendicular to it.

Islands and holes consisting of layers of spherical domains of asymmetric diblock copolymers are observed, similar to the islands and holes observed for lamellar (symmetric) block copolymers. As the thickness of the film increases, the shape of the island becomes diffuse. With further increases in the thickness, no islands or holes are formed, but the layered structure in the film is distorted when the original film thickness is not a natural thickness of the diblock copolymer.

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