Structure and Diffusion of Asymmetric Diblock Copolymers in Thin Films: A Dynamic Secondary Ion Mass Spectrometry Study

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ABSTRACT: The morphology and self-diffusion in thin films of asymmetric polystyrene-*b*-2-vinylpyridine (PS−PVP) diblock copolymers were investigated by secondary ion mass spectrometry (SIMS). An oscillatory depth profile of the PVP volume fraction is observed, implying a periodic arrangement of layers of PVP spherical domains organized parallel to the silicon substrate that persisted for films as thick as at least 200 nm (6 layers). The period of the PVP volume fraction oscillation is reasonably close to the (110) spacing of the body centered cubic (bcc) spherical domain structure in the bulk observed by small-angle X-ray scattering (SAXS). Into such films the (self) diffusion of a deuterium-labeled asymmetric diblock copolymer was followed by measuring the SIMS depth profile of ^{2}H(dPS−PVP). The resolution of SIMS is sufficient that the microscopic diffusion involving hopping of dPS−PVP from layer to layer in the microdomain structure can be seen. A very thin 20 nm layer of dPS−PVP was placed on a well-ordered PS−PVP film substrate and heated rapidly to the diffusion temperature. The dPS−PVP molecules diffuse rapidly into the first layer of the PS−PVP, but diffusion into the deeper layers of the PS−PVP is much slower. By measuring the ^{2}H depth profiles, we could determine the dPS−PVP content of each PS−PVP layer and thus a hopping frequency between layers. This hopping frequency could be converted into a diffusion coefficient which compares well to that determined from measurements of diffusion over much longer length scales.

Introduction

In thin films, the interaction with the interface and the surface play an important role in determining the domain morphology of diblock copolymers. Surface/interface-induced ordering of symmetric diblock copolymers, which form lamellar structures in bulk, has been quantitatively and extensively studied.[1−3] Typically one of the blocks is attracted to the substrate or surface to minimize the surface/interface energy, and lamellae are formed parallel to the surface/interface. The orientation of these lamellae persists over at least several lamellar periods. On the other hand, for asymmetric diblock copolymers with a cylindrical bulk morphology, the surface/interface-induced orientation does not persist for more than a few layers of cylinders.[4] Cross-sectional transmission electron microscopy (TEM) shows for thicker films that cylinders perpendicular to the substrate coexist with the cylinders parallel to the substrate. It seems impossible to convert this mixed orientation of cylinders to the parallel (presumably equilibrium) arrangement even after extremely long annealing times well above the glass transition temperature.

Asymmetric copolymers with a relatively low volume fraction of the short block are known to form a cubic ordered structure of spheres. The packing of these spheres in bulk is found to be body centered cubic (bcc).[5] However, very little is known about the packing of the spherical domains in a thin film. In contrast to the case of the diblock copolymers with lamellar or cylindrical morphologies, it is not obvious that the diblock copolymers with the spherical morphology will form an ordered layer structure on a flat substrate. One might expect a fine grained bcc polycrystalline arrangement by analogy to some of the structures observed in evaporated bcc metal films. Alternatively, again in analogy to known metal film structures, one might expect that a texture would be formed in which one plane, e.g., (110), of the bcc structure would be parallel to the interface with grains in the structure corresponding to different rotations about the ⟨110⟩ axis. In such a film, long-range periodicity of layers of spheres normal to the film plane would be expected.

In addition to these questions about the equilibrium film structure, how diffusion of asymmetric diblock copolymers occurs in such a film is important to understand the kinetics of microphase separation. In bulk melts the authors have measured self-diffusion of asymmetric poly(styrene-*b*-2-vinylpyridine) by forward recoil spectrometry and report an "activated hopping" diffusion mechanism, in which single copolymer chains hop from one spherical domain to another.[6] Films more than 1 μm thick were used in that study in order to obtain diffusion coefficients corresponding to the bulk.

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In the activated hopping mechanism the probability $\exp(-\alpha\chi N_{core})$ of the thermodynamically unfavorable state in which the short PVP block must diffuse from a PVP sphere until it is totally surrounded by PS block controls the diffusivity of the block copolymer. Here α is a constant, χ is the Flory–Huggins interaction parameter, and N_{core} is the number of segments of the PVP block that is in the core of spherical domain. Due to the limited resolution of FRES, typically 80 nm, we did not observe each step of the "activated hopping" diffusion, but rather only the statistically averaged bulk diffusion coefficient. On the contrary in this study, dynamic SIMS, a depth profiling technique with higher resolution (~15 nm) has the ability to reveal the local step-by-step diffusion of labeled diblock copolymer in an array of spherical domains with a spacing on the order of 30 nm. Besides detecting deuterium ions from the diffusing deuterium-labeled chains, SIMS can simultaneously detect CN^- ions from the PVP. This capability allows us to investigate simultaneously both the ordered structure of the asymmetric diblock copolymer in the thin film by measuring the PVP volume fraction and the diffusion of deuterated tracer chains in the ordered array of spheres by measuring the dPS volume fraction.

Experimental Section

1. Materials. Poly(deuterated styrene-*b*-2-vinylpyridine) (dPS–PVP) and poly(styrene-*b*-2-vinylpyridine) (PS–PVP) diblock copolymers were synthesized via sequential living anionic polymerization in which styrene was used as the first monomer and 2-vinylpyridine as the second monomer. The polymerization was carried out in tetrahydrofuran as solvent at −78 °C in an argon atmosphere. *sec*-Butyllithium was used as an initiator. Prior to the addition of the 2-vinylpyridine, a sample of the polystyrene precursor was taken to determine the molecular weight of the dPS or PS block. The molecular weight and molecular weight distribution of these block copolymers and PS precursors were measured by gel permeation chromatography (GPC) using polystyrene as a standard. The ratio of PVP to PS (or dPS) in each block copolymer was determined from the nitrogen content obtained from elemental analysis. The prefix "d" indicates a deuterated PS block while PS signifies a normal polystyrene. The PS–PVP has a number average molecular weight $M_n = 97\,000$ and a f_{PVP}, the volume fraction of PVP, of 0.11 while the dPS–PVP has $M_n = 114\,000$ and $f_{PVP} = 0.12$. Transmission electron microscopy confirms that the diblock copolymers form a spherical domain structure after annealing at 180 °C.

2. Sample Preparation. Diffusion couples consisting of a 20 nm top layer of dPS–PVP copolymer on a base layer of PS–PVP were prepared by the following steps. The base layer of PS–PVP was spun cast on the native oxide surface of silicon substrates from toluene solution. To achieve equilibrium ordering of the base layers, those films were annealed under vacuum at 180 °C for more than 3 days. The top layer of dPS–PVP was spun cast on glass plates, floated onto distilled water, and then picked up onto the preannealed base layer of PS–PVP. The couples were then annealed under vacuum and allowed to diffuse at 178 °C.

3. Dynamic SIMS Measurement. The samples were covered by a sacrificial thin (30 nm) film of polystyrene by floating it onto the diffused bilayer. This procedure ensured that steady-state sputtering conditions could be achieved before the sputtering crater reaches the original bilayer surface. The sputtering was performed on an Atomika 3000–30 ion microprobe using a 2 keV, 20 nA beam of Ar^+ ions directed at the surface at an angle of 30° from the normal. The beam is rastered over a 0.25 mm^2 region. Negative ions of C, D (D = ^{2}H), CN, CH, CD, O, and Si from the center region of the sputtered crater were monitored as a function of time. At a typical sputtering rate of 50 nm/h, a depth resolution of about 15 nm corresponding to the full width half-maximum of a Gaussian, is obtained.[7] Details of the experimental conditions for the SIMS depth profiling can be found elsewhere.[8] 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.

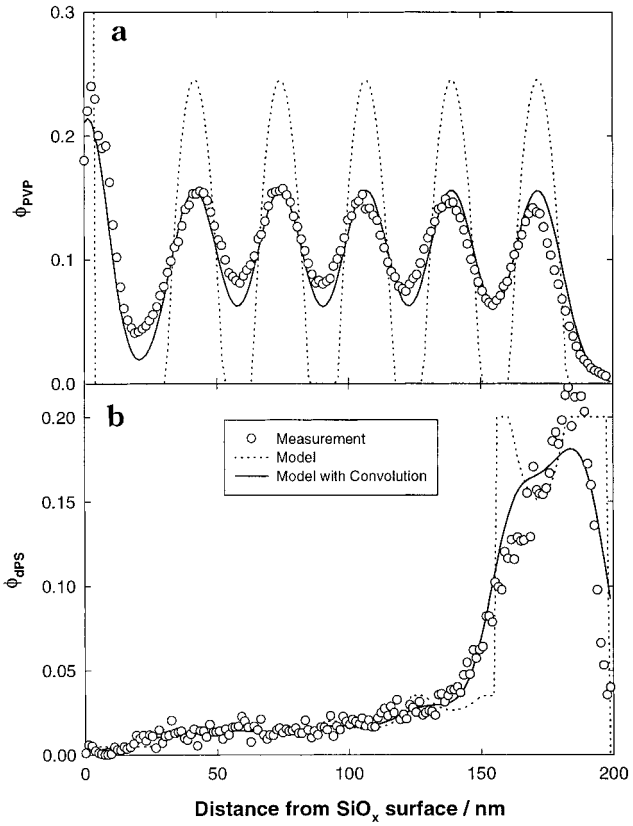

Figure 1. Volume fraction of PVP, ϕ_{PVP} (a), and volume fraction of deuterated PS, ϕ_{dPS} (b), plotted against distance from the silicon substrate after 7200 s of annealing at 178 °C. The symbols represent the measured volume fraction. In part a the dotted line is the calculated value from a model where the (110) plane of the bcc structure is parallel to the surface. In part b the dotted line is the diffusion histogram described in the text. In both parts a and b the solid line is calculated by convoluting the dotted line with the instrumental depth resolution.

Results and Discussion

A. Ordering of the Spherical Domain Structure in a Thin Film. The SIMS depth profile for a dPS–PVP film with a thickness of 200 nm is converted to volume fraction of PVP and plotted as circles in Figure 1a. The volume fraction of PVP (from the intensity of CN^- fragment signal) oscillates as a result of the ordering of the PVP spherical domain structure and indicates that the spherical domains pack and align in the layers on top of the silicon substrates. The amplitude of the oscillation is not as large as in the case of lamellar or cylindrical copolymer films reported previously,[2,4] but given the discontinuous nature of the PVP spherical domains in any plane of the domain structure, this observation is not surprising. Near the silicon surface, the PVP volume fraction, ϕ_{PVP}, has a global maximum while about 20 nm away from the silicon substrate in the ordered block copolymer ϕ_{PVP} has a global minimum. The extreme oscillation is due to an adsorbed brush of

diblock copolymers. This brush formation is to be expected due to the strong binding of PVP to silanol groups on the silicon oxide surface even though the diblock copolymer is very asymmetric. Asymmetric diblock copolymers with cylindrical morphology are also reported to form brushes on silicon oxide substrates.[4] Numerical self-consistent field calculations that show surface-induced morphology changes also support this identification of brush formation.[9] It should be also noted that we observed the formation of islands or holes near dust particles. Since the film thickness varies around such particles, the local film thickness may not match the thickness that corresponds to an integral number of layers of spherical domains so that in such regions islands or holes will form. The fact that we see islands or holes formation at certain values of film thickness suggests that surface of the film induce a strong layering similar to that observed in lamellar block copolymer films. The area of the film subjected to SIMS analysis fortunately was flat so that we could determine the depth profile of various species without confusion due to different film thicknesses in the area.

To understand the periodic PVP volume fraction profile perpendicular to the substrate, we fit the measured ϕ_{PVP} vs depth profile to a model consisting of a PS brush with a PVP anchor block against the silicon native oxide substrate followed by (110) planes of layers consisting of the bcc structure of PVP spheres in PS. This bcc structure is the equilibrium bulk structure. We ignore the finite interfacial thickness between the PS and PVP domains, while in any case is small (~2 nm)[10] relative to the depth resolution of SIMS (~15 nm in this case).

We introduce the three fitting parameters: (1) the periodicity of the layers of spheres, l_{BCC}, (2) the brush thickness, d, and (3) the depth resolution of the SIMS measurement. The PVP wetting layer thickness of the brush on SiO_x is then given by $f_{PVP}d$, and the sphere radius, r, is determined from l_{BCC} so that the volume fraction of the PVP spherical core in the BCC cubic lattice, $((4/3)\pi r^3 \times 2)/(\sqrt{2}l_{BCC})^3$, is equal to f_{PVP}. The lateral average of the model is calculated and then convoluted with the appropriate Gaussian SIMS depth resolution in order to compare it with the experimental depth profile.

In Figure 1a, we plot the experimental SIMS profile and compare it with the model profile based on stacking the (110) plane of bcc structure parallel to the substrate. The spacing of the (110) planes is found to be 33.0 nm, and the SIMS depth resolution is a Gaussian with a fwhm of 18 nm. That spacing is reasonably close to the spacing, 31.4 nm for the bulk block copolymer, measured by SAXS.[11] The depth resolution of 18 nm is a little larger than that we normally obtain for polymer films under the conditions described in the Experimental Section. This "resolution" includes the effects of our assumptions that the core PVP block sphere have sharp surfaces and are in exact registry with their layer.

On the other hand, if we assume that the (200) plane orients parallel to the substrate, the (110) spacing would be over 50 nm, which is not compatible with the results from SAXS.

It is quite remarkable that the (110) epitaxial orientation (to be sure, a fiber texture) persists to as many as five layers from the substrate to the surface. Since we are analyzing a film area that is approximately 100 μm × 100 μm laterally, the oscillation would be smeared out if there were a significant deviation from this fiber texture. We have evidently seen island and hole formation partly on the specimens that ensure a high degree of ordering induced by the interface/surface in the direction perpendicular to the substrates.

B. Diffusion of Deuterated PS−PVP. The high degree of orientation of the (110) planes in the film offers us a unique opportunity to observe the diffusion of a small amount of the dPS−PVP block copolymer from layer to layer in the epitaxially ordered PS−PVP film without disturbing the underlying structure. We make the assumption that such diffusion is by an "activated hopping" of individual block copolymer chains, whereby a chain must drag its PVP block through the PS matrix every time it moves from one (110) layer to the next in the film. While diffusion by an vacancy or interstitial mechanism can occur in atomic bcc structures, such diffusion should be glacially slow in block copolymers, being suppressed by the large free energy barrier for creating and moving "vacant" or "interstitial" PS−PVP melt micelles.[12]

The volume fraction vs depth of the deuterated polystyrene of the dPS−PVP diblock copolymer after annealing for 7200 s at 178 °C is plotted in Figure 1b as an example. To compare the diffusion profile with the domain layer structure, the PVP depth profile from the same sample is plotted in Figure 1a. The initial dPS profile before diffusion corresponds to a pure disordered layer of the dPS−PVP diblock copolymer 20 nm thick broadened by the 18 nm instrumental resolution. After the diffusion, as seen in Figure 1b, the dPS has penetrated well beyond the original dPS−PVP film thickness into the PS−PVP substrate. The most significant characteristic of the dPS profile is the step 45 nm from the surface, where the PVP volume fraction has its minimum. At any annealing time, t, there is a step at this depth which decreases in height as the annealing time t increases. This feature indicates that the deposited dPS−PVP diblock copolymer is absorbed into the top layer of spheres on the PS−PVP substrate and stays for a long time, resulting in a steplike volume fraction profile at the edge of the first layer even after long annealing. This absorption process into the top layer is quite fast. In 300 s, dPS blocks from diffusing dPS−PVP block copolymer surround the first layer of PVP cores giving a step at a position of 45 nm mid way between the first and second PVP core layers. After infiltration into the first layer of spheres, the dPS−PVP block copolymers are trapped in the spherical domains and the diffusion process slows dramatically. The profile of the volume fractions of PVP and dPS after 41 700 s of annealing at 178 °C are plotted in Figure 2. It should be noted that, even after 41 700 s, the concentration step, which represents the edge of the first layer of spheres, exists at the same position as seen in Figure 1. A smaller step just below the second layer of spheres is seen in Figure 2b near 80 nm from the surface.

Almost instantly, the labeled diblock copolymers were absorbed by the first layer, and then gradually moved to the second or deeper layers by overcoming the thermodynamic barrier with a probability proportional to $\exp(-\alpha\chi N_{core})$. In our previous FRES measurement, we observed statistically averaged diffusion over a rather large depth ≈500 nm and determined diffusion coefficients. In this study, however, we observe each layer of the ordered structure and the "activated hopping" diffusion process between layers by SIMS. Since

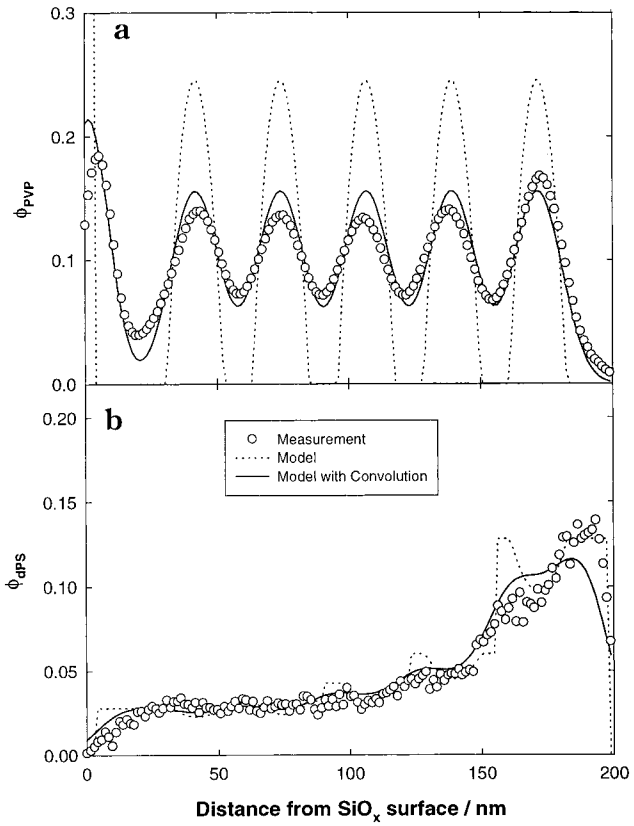

Figure 2. Volume fraction of PVP, ϕ_{PVP} (a), and volume fraction of deuterated PS, ϕ_{dPS} (b), plotted against distance from the silicon substrate after 41700 s of annealing at 178 °C. The symbols represent the measured volume fraction. In part a the dotted line is the calculated value from a model where the (110) plane of the bcc structure is parallel to the surface. In part b the dotted line is the diffusion histogram described in the text. In both parts a and b the solid line is calculated by convoluting the dotted line with the instrumental depth resolution.

the number of hops of each diblock copolymer from one layer of spheres to another in our experimental time scale is very small, the depth profile cannot be fit with solution of the standard (Fickian) diffusion equation that is derived microscopically by averaging a large number of hops. To extract a hopping frequency, the diffusion profile was modeled as resulting from a histogram with a centered volume fraction of dPS in layer 1, another volume fraction of dPS in layer 2, and so forth. This profile was convoluted with the instrumental resolution function and the values of ϕ_{dPS1}, ϕ_{dPS2}, etc. were adjusted to produce the best fit. The best fit of the model profiles before and after the convolution with a Gaussian are represented by the solid and dotted line in Figures 1b and 2b. The time dependence of the volume fraction of dPS at each layer was analyzed by the probability distribution of a random walk in discrete space with continuous time.

The exact probability distribution of the random walk with continuous time and discrete space can be found as a solution of the equation[13]

$$\frac{\partial}{\partial t}p_n = p_{n+1} + p_{n-1} - 2p_n \quad (-\infty < n < \infty) \qquad (1)$$

with the initial condition $p_n(0) = \delta_{n,0}$, where p_n is the probability at a discrete position n at time t, and $\delta_{n,0}$ is the delta function. The solution of eq 1 is

$$p_n(t) = e^{-2t/\tau}\sum_m \frac{(t/\tau)^{2m+n}}{(m+n)!m!} \qquad (2)$$

where $p_n(t)$ is the probability at position n, which is the number of planes from the surface plane, at time t and the sum extends over all integral values of m for which both m and $(m + n)$ are nonnegative, and t is the characteristic time of each step. For our particular sample geometry, we adopt a mirror boundary condition between the position $n = 0$ and -1 as the surface of the block copolymer film. Hence, for $n \geq 0$

$$p_n(t) = e^{-2t/\tau}\sum_{m=0}^{\infty}\left[\frac{(t/\tau)^{2m+n}}{(m+n)!m!} + \frac{(t/\tau)^{2m+n+l}}{(m+n+l)!m!}\right] \qquad (3)$$

The probability at position 0, $p_0(t)$ from eq 3, is compared with the experimentally obtained probability distribution of $p_0^*(t) = \phi_{dPS0}(t)/\phi_{dPS0}(300)$ where $\phi_{dPS0}(t)$ is the volume fraction of the top layer of spheres at time t and $\phi_{dPS0}(300)$ is that at 300 s found by fitting as shown in Figures 1b and 2b. We used $\phi_{dPS0}(300)$ instead of $\phi_{dPS0}(0)$ for normalizing the initial volume fraction to avoid any effect from the deposited nonequilibrium dPS−PVP layer, which may diffuse faster than such a layer at equilibrium. We know the deposited dPS−PVP thin layer penetrates into the PS−PVP substrate and absorbs into the first layer of spheres in less than 300 s. The characteristic time of hopping is found to be $(4.7 \pm 2.5) \times 10^4$ s from the best fit of $p_0(t)$ from eq 3 to the experimentally obtained $p_0^*(t)$.

The diffusion coefficient perpendicular to the substrate is calculated from $D = L^2/2\tau$, where L, the periodicity of the layered structure, is 33 nm found by measuring the periodicity of the PVP volume fraction. D was found to be $(1.4 \pm 0.6) \times 10^{-16}$ cm^2/s, which is smaller than the value determined by FRES, $(6 \pm 4) \times 10^{-16}$ cm^2/s. The diffusion coefficient in the thin film in the direction perpendicular to the layers of spheres is relatively close to that in the bulk.

Equation 3 allows us to predict the spatial dependence of the diffusion profile as well as the time dependence of the concentration at a given layer. The diffusion profile predicted from eq 3 using the characteristic time $\tau = 4.7 \times 10^4$ s obtained by fitting $p_0(t)$ with $p_0^*(t)$ is compared with the experimental profile at an annealing time $t = 4.17 \times 10^4$ s in Figure 3a. The dotted line represents the model profile while solid line represents the model profile convoluted with the Gaussian depth resolution. The theoretical distribution corresponding to a single jump time does not fit our experimental distribution well with any value of τ. The experimental distribution is much broader than the theoretical one. A similar deviation could be observed even for the FRES depth profile[6] and can be understood by the very strong dependence of the diffusion coefficient on N_{PVP}, i.e., $\exp(-\alpha\chi N_{PVP})$ where $\alpha \approx 1.2$. If $\langle N_{PVP}\rangle$ is 107, the standard deviation of N_{PVP} is expected to be 11 even for a perfect anionic polymerization. Thus about 30% of these ideal block copolymers will have a diffusion coefficient more than an order of magnitude faster than the $N_{PVP} = 107$ chain while about 30% will have a diffusion coefficient that is at least an order of magnitude less than this chain. The solution for the diffusion equation with a single diffusion coefficient, or equivalently a single hopping time τ, has no chance of fitting

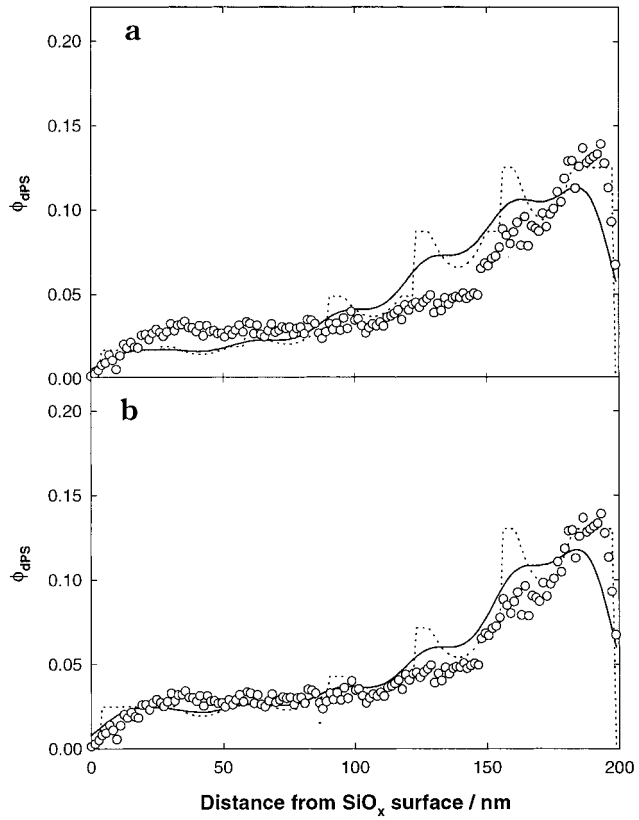

Figure 3. (a) Dashed diffusion profile computed from eq 3 assuming a single hopping time τ and a solid line, which is a convolution of that profile with the instrumental resolution function. The symbols are the experimental diffusion profile in Figure 2. (b) Dashed line computed from eq 3 allowing for the polydispersity of the N_{PVP} that gives a broad distribution of hopping times (see text) and a solid line which is a convolution of that profile with the instrumental resolution function. The symbols are the experimental data as in part a.

the diffusion profile of even this ideally polymerized block copolymer. The extreme sensitivity of D to N_{PVP} ensures that such a simple approach will not be adequate. We demonstrate the effect of the polydispersity of the PVP block assuming a Poisson distribution for N_{PVP}. The probability $P(N_{PVP})$ of the block length N_{PVP} is given by

$$P(N_{PVP}) = e^{-\langle N_{PVP}\rangle}\frac{\langle N_{PVP}\rangle^{N_{PVP}}}{N_{PVP}!} \quad (4)$$

where $\langle N_{PVP}\rangle$ is the mean block length. The characteristic time of a hop $\tau(N)$ is now a function of N and expected to have the form[6]

$$\tau(N_{PVP}) = \tau(\langle N_{PVP}\rangle)\exp\{\alpha\chi(N_{PVP} - \langle N_{PVP}\rangle)\} \quad (5)$$

where α is 1.19 and χ is 0.107 at 178 °C. Using eqs 3−5, one can predict the spatial probability distribution as a function of time for this "polydisperse" block copolymer. The prediction is compared with the experimental diffusion profile in Figure 3b. The volume fraction of 0.015 was used as a background that is determined from the diffusion profile after 5 min of annealing in order to avoid the influence of the nonequilibrium structure of the initial top layer deposited without preannealing. A mirror boundary condition at the silicon surface was also assumed. An appropriate normalization was done so that the integral of the volume fraction is equal to that of the experimental profile. The predicted profile is very close to the experimental one (a small additional polydispersity of PVP block may exist even for the copolymer made by the anionic polymerization). The good agreement indicates that the trivial statistical polydispersity ends up producing multiple characteristic times for hopping or equivalently a broad distribution of diffusion coefficients due to the strong exponential dependence of τ or D on the PVP block length.

Conclusions

Asymmetric block copolymer thin films organize themselves into layers of spherical domains parallel to the interfaces that persist to relatively large film thicknesses. The periodicity of the PVP volume fraction, which is equivalent to the distance between layers of spheres, is consistent with (110) spacing of the bcc structure obtained by SAXS. These layered films provide an interesting model system in which to study the diffusion of asymmetric diblock copolymers. The distribution of diffusing diblock copolymer in each layer can be observed and a characteristic time for hopping between layers can be extracted from this distribution. This microscopic hopping time can be compared with that determined from much longer range diffusion.

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