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Ordering of Copolymer Thin Films As Revealed by Atomic Force Microscopy

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Introduction. Block copolymers are increasingly being used as surfactants and thin-film adhesives in biomedical and microelectronics applications. Thus, a fundamental understanding of the behavior of copolymers at surfaces and interfaces is essential.[1]

Symmetric diblock copolymers, AB, are macromolecules composed of two unlike polymers of equal length linked together by a covalent bond. In general, the A and B blocks are incompatible for temperatures between the glass transition temperature T_g and the microphase separation temperature (MST). Thin films of symmetric diblock copolymers due to the specific interactions of the blocks with the air and substrate interfaces exhibit an orientation of the lamellar microdomain morphology parallel to the external surfaces.[2–7] The lamellar period L corresponds to the thickness of a –ABBA– (or a –BAAB–) bilayer. Minimization of interfacial energies dictates which block is present at the two interfaces (air/polymer and substrate/polymer). As-cast thin films, prepared by spin-coating a copolymer solution onto a substrate at $T < T_g$, are in a disordered state and their free surface is flat and smooth. The lamellar ordering can be induced by annealing these films at temperatures T between T_g and MST.

Interference microscopy[4,8] shows that, after ordering, the film thickness is quantized, i.e.

$$\begin{cases} e_{\mathrm{ord}} = (n+1)L & \text{if the same block is present at both interfaces} \\ e_{\mathrm{ord}} = \left(n+\frac{1}{2}\right)L & \text{otherwise} \end{cases}$$

where e_{ord} is the film thickness in the ordered state and n an integer ≥ 0. As a consequence, the morphology of the free surface of the ordered film depends on its initial thickness e in the disordered state. If e is equal to $(e_{\mathrm{ord}} + \epsilon)$ with $0 < \epsilon < L$, the free surface is covered either with islands ($0 < \epsilon < L/2$) or holes ($L/2 < \epsilon < L$) of height L. For very thin films, it has been shown[5] that the lamellar order starts at the silicon substrate and then propagates through the entire film thickness. Thus, the formation of islands or holes of height L should reflect the lamellar ordering and orientation process. The fraction x of the film surface occupied by the islands (or holes) in the ordered state is directly related to the initial film thickness because of the conservation of the total amount of copolymer.[9] Due to the resolution limit of "in situ" interference microscopy ($\simeq 1\ \mu$m), the growth of these defects can be visualized by this technique, but not their formation.[9] This can be achieved by atomic force microscopy (AFM) by imaging with high resolution the evolution of the free surface.[10]

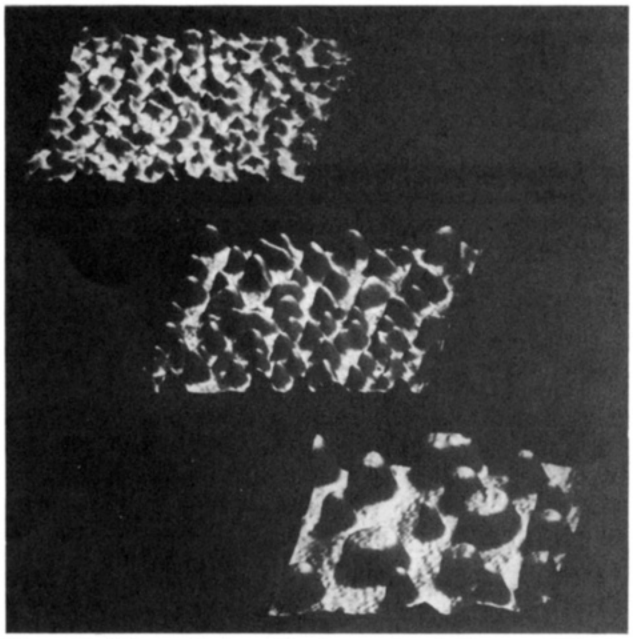

Figure 1. Time evolution of the free surface in the case of islands. The initial thickness of the film was equal to 2.25L. The annealing times are 8, 16, and 1080 min from top left to bottom right. The size of the images is (10 × 10) μm^2. The vertical scale is the same for the three pictures and is given by the height of the islands (300 Å) in the bottom right picture.

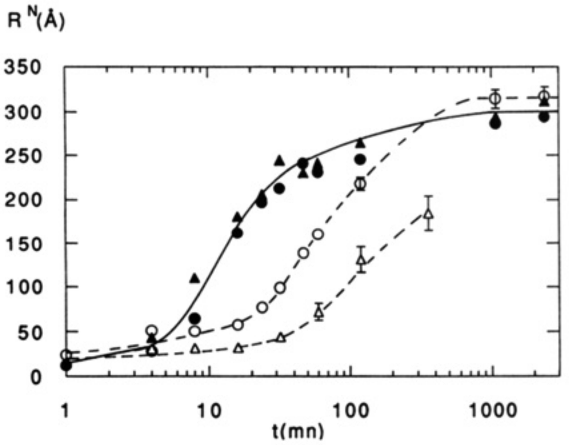

Figure 2. Evolution of the normalized root-mean-square roughness R^N with annealing time for different surface morphologies [(●) holes, x = 48%; (○) holes, x = 27%; (▲) islands, x = 25%; (△) islands, x = 17%]. The R^N values have been calculated from (50 × 50) μm^2 AFM images. The dashed and solid curves are only guides for the eye.

Experimental Section. The poly(styrene-*b*-*n*-butyl methacrylate) diblock copolymer, P(S-*b*-BMA), we used was synthesized by anionic polymerization. Its molecular weight is equal to M_W = 82 000, with a polydispersity of M_W/M_n = 1.05 and a weight fraction of PS of 0.527. Films were prepared by spin-coating toluene solutions of the copolymer onto a silicon substrate, previously cleaned by UV irradiation under oxygen flow. The specimens were annealed at 125 °C in a Mettler hot stage under nitrogen flow for the desired "annealing time" t. Interference microscopy[8] shows that the lamellar period of ordered films is $L \simeq 300$ Å and their thickness is $e_{\mathrm{ord}} = (n+1)L$. Since the surface energy of PBMA is lower than that of PS, PBMA is expected to be located at both interfaces.[11]

Images of the free surface were obtained with a Digital Nanoscope II atomic force microscope operated at room temperature, in air, in the force-constant mode ($F = 1.5 \times 10^{-8}$ N). No modification of the surface structures was observed even while scanning for a long time. For all

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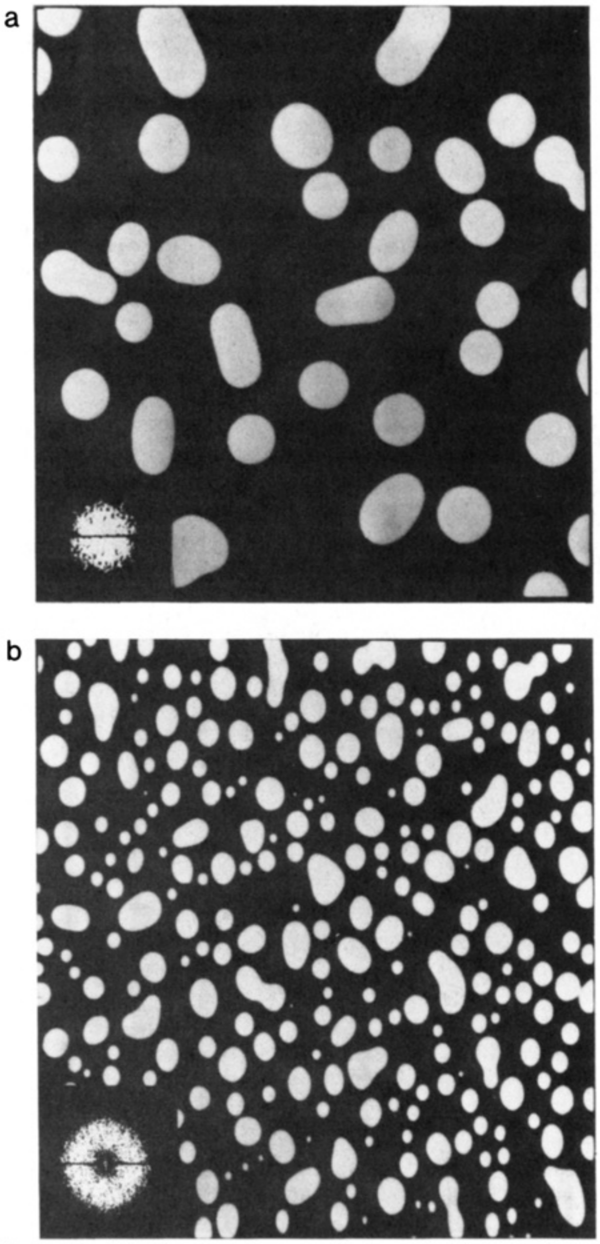

Figure 3. AFM images of two typical morphologies of islands at t = 2400 min: (a) x = 17%, (b) x = 25%. The size of the images is (50 × 50) μm^2. The insets are the corresponding two-dimensional Fourier transforms.

samples, the images presented here for successive annealing times correspond to different areas of the surface.

Results and Discussion. Varying the initial film thickness between $2L$ and $3L$, we investigated the formation of islands and holes, for two different values of x in each case. Those values were determined from height histograms of AFM pictures at long annealing times except in the case of islands when x = 17% because of the insufficient field of view of the AFM. For this sample, x was determined from optical micrographs at t = 2400 min. For the same reason, quantitative measurements on this sample were performed only up to t = 320 min.

Figure 1 shows the time evolution of the free surface in the case of islands when the initial thickness is equal to $2.25L$. In order to get quantitative information about the time evolution of the free surface, we have measured its root-mean-square (rms) roughness R. In the ordered state, the rms roughness is equal to $[x(1-x)]^{1/2}L$, and thus the value of the normalized roughness $R^N = R/[x(1-x)]^{1/2}$ is L. Hence, whatever the morphology of the free surface, a plot of R^N versus time should exhibit a plateau once the ordered state is reached. Figure 2 shows the R^N curves corresponding to the four different systems we have investigated. The three upper R^N curves tend to the same limit value 310 ± 15 Å after about the same annealing time t = 2400 min. Within the error bars, it corresponds to the lamellar period $L \simeq 300$ Å as measured by interference microscopy. For $t < 2400$ min, i.e., during the ordering process, the R^N curves exhibit different behaviors depending on the type of morphology. As shown in Figure 2, for the same value of x (25% for islands, 27% for holes), the R^N curves corresponding to either holes or islands differ. Besides, the two-dimensional Fourier transforms (2DFT), calculated from the AFM digitized images, corroborate this discrepancy in the ordering process. Figure 3 shows that, in the case of islands, the 2DFT exhibits a diffuse ring for a high enough value of x while, for a low value of x, there is only a central spot. This diffuse ring is visible even after 3 min of annealing. This allows us to define dilute (x = 17%) and concentrated (x = 25%) situations according to the evidence for spatial correlations. In the case of holes, the behavior is quite similar, but for different values of x the system is dilute for x = 27% and concentrated for x = 48%; in the latter case, the corresponding R^N curve is very close to that of the islands (x = 25%). Obviously, the existence or nonexistence of spatial correlations characterizes the ordering kinetics for both islands and holes; however, the limit between these regimes is not the same in the two cases. A qualitative analysis of the time evolution of the 2DFT's shows that, for both islands and holes, when correlations are present, the characteristic length l_c of the morphology and the maximum intensity of the isotropic ring increase with the annealing time. A more quantitative analysis of the data is currently under way.

Although previous optical microscopic observations[9] led us to suggest the difference in the way of formation of islands and holes, only atomic force microscopy allows us to prove this discrepancy quantitatively.

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