Morphology of Steps in Terraced Block Copolymer Films

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Thin films of microphase separated symmetric diblock copolymers exhibit terraces. Atomic force microscopy is used to measure the free surface profile and transmission electron microscopy is used to elucidate the morphology within the film. Previous work has found the terraces to be composed of homeotropically aligned lamellae and has assumed the step between terraces to contain a dislocation. Our direct observations show that in ultrathin films steps contain homogeneously aligned lamellae. We suggest a minimal-surface model for the morphology of these steps. As the film thickness is increased, the lamellar alignment within steps displays a homogeneous-to-homeotropic transition.

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In their ground states, symmetric diblock copolymers and smectic-*A* liquid crystals both display a defect-free stacking of amorphous layers. This shared characteristic has motivated an analogy between the two systems [1–3]. Actual materials, however, contain a myriad of defects and through a taxonomy of these imperfections we can come to know how this analogy is limited. In liquid crystalline systems, where stiff molecules define the layer and the cost to compress or dilate a layer is high, surface defects are not seen. Defects, instead, appear as line singularities [4], i.e., focal conics. At the boundary between two highly tilted grains [5], the distortion can be accommodated through the inclusion of edge dislocations. In both cases, the defects exhibit the one-dimensional crystalline behavior that is the signature of the smectic-*A* state.

Symmetric diblock copolymer systems display these defects too. Yet copolymer systems also contain surface defects, and recent studies [6–8] on bulk systems have shown that such boundaries can adopt the structure of a minimal surface. These surfaces partly owe their existence to the flexibility of the copolymer chain. Indeed, it has been argued that the presence of constant mean curvature surfaces in copolymer systems reflects the drive to minimize interfacial area between opposing blocks over and above the need to minimize chain deformation [6].

In this Letter, we report a microscopic study of steps in thin films of microphase separated symmetric diblock copolymer. The films are terraced and within the terraces lamellae are found in the homeotropic orientation: The lamellar directors are aligned perpendicular to the substrate plane. The height difference between adjacent terraces has the dimension of a copolymer bilayer, *L*. Previous reports [1,9] have assumed the steps to contain an edge dislocation, much like one would find in a thin, terraced, homeotropic liquid crystalline film [10,11]. Since this analogy calls for the hypothetical dislocation to exist at the free surface, one expects a step width of size *L*, yet atomic force microscopy (AFM) measurements [1,2] show this width to be many times greater than *L*. This discrepancy could be explained [2,3] if the dislocation were buried; in this case, the lamellar displacement field above the dislocation core would be broadened. In fact, one recent transmission electron micrograph has shown a dislocation buried below the step of a terraced block copolymer film with a total thickness of 8*L* [2]. Our direct observations, however, show that in ultrathin films, between terraces, lamellae can align in the homogeneous orientation, with their directors parallel to the substrate. Since these lamellae must reorient at the lower and higher terraces, each step contains two twist boundaries. We suggest a minimal-surface model for the morphology of the step region.

The results reported here were obtained from a poly(sytrene)/poly(methylmethacrylate) (PS/PMMA) diblock copolymer with a total molecular weight of 108 000, a polydispersity of 1.10, and a PS volume fraction of approximately 0.5. We have also investigated terraced films of lamellar forming poly(styrene)/poly(butylmethacrylate) (PS/PBMA), poly(styrene)/poly(2–vinylpyridine) (PS/PVP), and poly(styrene)/poly(butadiene) (PS/PB) and have uncovered similar step morphologies. Films were made by depositing 10 μL of a dilute solution of the copolymer in its nonpreferential solvent (toluene) onto a carbon support. Samples were prepared on carbon coated silicon wafers for the AFM work. For the transmission electron microscopy (TEM) studies, carbon coated mica substrates were used; after evaporation of the solvent (30 sec), the film and its carbon support were floated off onto a pool of water and picked up with copper index grids. By varying the concentration of the polymer solution, either isolated droplets (0.5 mg/mL) or continuous films (10 mg/mL) could be produced within the deposition area (10 mm^2). The as-cast droplets were found to have a variety of thickness (<500 nm), while the central regions (1 mm^2) of the continuous films were close to a trilayer thick (60 nm). Spin coating is a useful means of producing thin, continuous copolymer films; we tried this approach but found it difficult to remove the film and its carbon support from the mica backing, even when a weak

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surfactant boundary layer was added between the carbon and mica.

Both the droplets and the continuous films display terraces, but only after a heat treatment above the glass transition temperature. In order to compare our results with previous work, we adopted an established protocol [12] and heated the films to $T = 175\,^{\circ}\mathrm{C}$ for 24 h in vacuum. Free surface profiles of the terraced films were obtained using a Nanoscope III AFM with a contact force less than 2×10^{-8} N. The morphology within the films was explored with bright field TEM using a Jeol 200CX operating at 100 kV. Instead of staining with a heavy atomic number species, we found that good contrast between the PS and PMMA blocks could be achieved with electron irradiation induced thinning of the PMMA domains [13]. Because both blocks remain glassy in the electron beam, the observed morphology is not caused by the irradiation and was not seen to change while the sample was exposed to the beam.

Figure 1 is an AFM topograph of representative terraced PS/PMMA droplets on a carbon film substrate. Four terraces are visible on the droplet at the left and five terraces can be seen at the right. The two droplets are connected and are part of a larger necklace of droplets that formed as the solvent evaporated. Optical microscopy and secondary ion mass spectrometry studies of similar annealed PS/PMMA copolymers deposited on SiO_2 have shown that within the terraces the lamellae exhibit homeotropic alignment and that the PS and PMMA components segregate to the free and SiO_2 surfaces, respectively [12]. Previous measurements [9] of a symmetric diblock PS/PMMA sample with total molecular weight 100 000 gave $L \simeq 40$ nm, so we expect a similar value here. In fact, cross-sectional AFM scans show the first terrace to increase in height from 14 to 20 nm as the film is traversed from the bare substrate; the height differences between the remaining terraces were found to have a constant value of 41 ± 2 nm. These values indicate that the first terrace consists of a copolymer monolayer, while the second and higher terraces consist of bilayers. When we couple this information with the knowledge that PS segregates to the free surface we can deduce that the PMMA component resides at the carbon substrate.

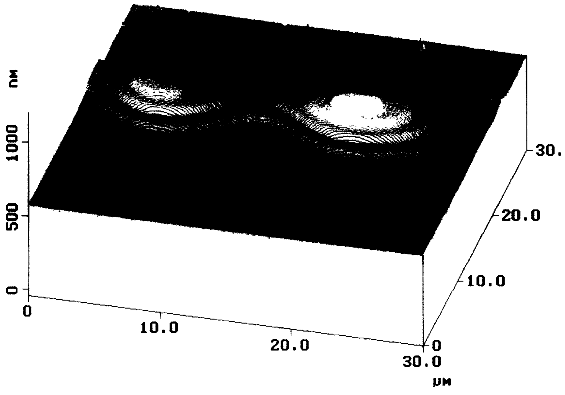

FIG. 1. AFM topograph of a pair of terraced block copolymer droplets.

Figure 2 is a TEM plan view of a section of a terraced droplet. The discrete contrast variations seen in the electron micrograph are indicative of step changes in film thickness and the lack of contrast within a terrace confirms a homeotropic alignment of lamellae. What is striking about the transmission electron micrograph is the presence of reoriented lamellae at the boundary between terraces. There, lamellae are found in a homogeneous orientation. Note that the PS phase (dark) appears thicker than the PMMA phase (light), even though the copolymer is symmetric by volume. Radiation induced thinning of the PMMA phase, which is the contrast mechanism in the electron microscope, explains this asymmetry. Figure 2 gives a representative view of the many edges that we have examined in thin copolymer droplets. At the step between the first and second terraces, the lamellae are aligned with a homogeneous orientation over an extent $\sim 3L$; they meander and exhibit edge dislocations and disclinations. At the higher steps, these lamellae are usually seen over a width closer to L and they are typically more ordered, although examples of meandering lamellae are still observed. The presence of homogeneously aligned lamellae is not influenced by the degree of step separation and they are seen when this separation is as

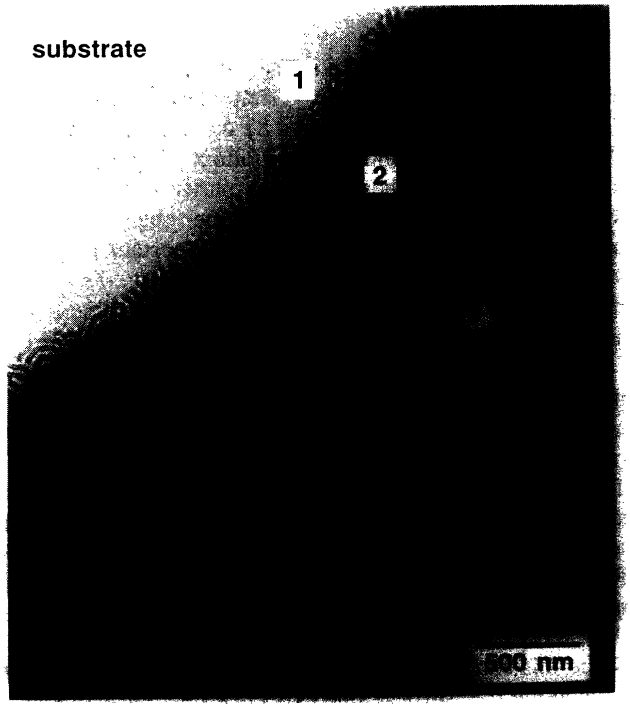

FIG. 2. TEM plan view of a section of a droplet exhibiting three terraces.

short as 200 nm and as long as several μm. Homogeneous alignment is always seen at the steps below the third terrace ($n = 3$) but is never observed above the eighth terrace ($n = 8$). This change presumably reflects a transition from homogeneous to homeotropic alignment within the steps.

We have also used AFM to probe the width of steps. By defining this width as the extent over which the free surface profile decreases in height by $0.9L$, we found step widths of ~500 nm. Another measure of the step width is the slope evaluated at the step's midpoint; step slopes of 0.13 were found. These values are comparable to previous results of PS/PBMA terraced films on SiO_2 [1,2], although one study [2] found the step widths to increase with n. For thin films ($n < 5$) of PS/PMMA on carbon, step widths and slopes did not vary with n. AFM can also be used to image the homogeneously aligned lamellae [14]. The lamellae appear as a 2 nm height oscillation with a period equal to L [15]. We located the homogeneously aligned lamellae with respect to the complete step profile and found them to reside at the region of steepest descent.

Homogeneous lamellae are also present at the edges of depressions [16] in otherwise continuous films. In Fig. 3, we present a transmission electron micrograph of depressions in a film three layers thick. The thickness of this region was deduced through (Nomarski) optical microscopy. The micrograph also shows what might be cylindrical PS channels at some steps. This channel structure is sometimes seen in steps on isolated droplets.

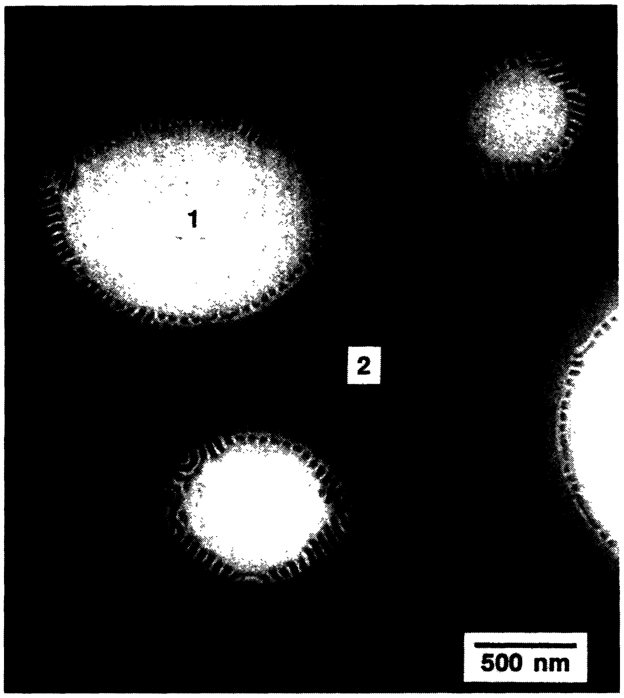

FIG. 3. TEM plan view of a terraced film with depressions.

Why the lamellae reorient within a step and why edge dislocations are not seen can be understood if we recall one basic difference between copolymers and liquid crystals. Whereas liquid crystalline layers are comprised of stiff molecules, the layers, themselves, can adopt high curvatures, provided they remain equidistant. Copolymer layers, however, contain flexible chains that seek to minimize interfacial area and, therefore, curvature between layers with opposing blocks. Hence, minimal surfaces and their constant mean curvature companions have been useful in describing the morphology [6] and energetics [17] of various block copolymer phases. One model that might describe the energetics of the observed step morphology is given in Fig. 4. In this model, the homogeneous lamellae extend from the free surface down to the carbon substrate. Whether or not the lamellae actually make this full excursion is not yet known. Cross-sectional TEM has, so far, proved difficult, but an examination of the TEM contrast in plan view shows the PS within the homogeneously aligned lamellae to be darker, and therefore thicker, than the stacks of PS in the adjacent terraces.

The main features of this model are the two lamellar twist boundaries that join the homogeneously and homeotropically aligned lamellae. In the bulk, high angle lamellar twist boundaries are seen to take the form of Scherk's (doubly periodic) surface [7], and so it is natural to consider this interface as a possible model of a thin film lamellar twist boundary. Because the Scherk surface is bicontinuous, it allows phase continuity of PS and PMMA across a step. If we define two principal curvatures c_1 and c_2, the Scherk surface has zero mean

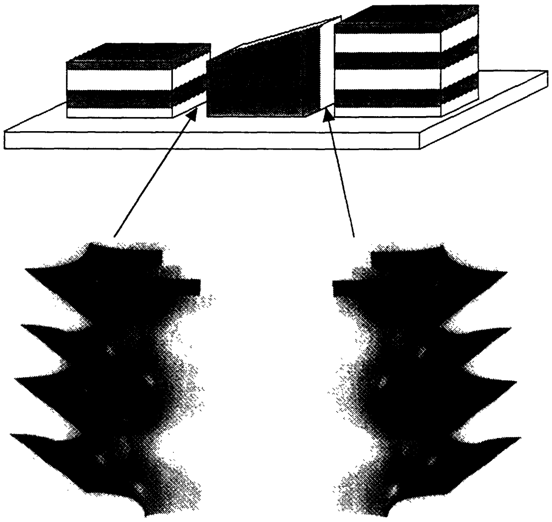

FIG. 4. Schematic of step morphology in thin block copolymer films. Scherk surfaces are present at the two lamellar twist boundaries [15].

curvature, $H = (c_1 + c_2)/2$, and a variable negative Gaussian curvature, $K = c_1 c_2$, along the various saddles, while an edge dislocation displays zero Gaussian curvature but nonzero mean curvature at its core. It is the null cost of zero mean curvature and the low cost of Gaussian curvature that drives the formation of the twist boundaries.

We can support this assertion by comparing the defect energy associated with an isolated edge dislocation to the energy of two Scherk surfaces. The curvature elastic free energy per unit area of a single interface is given by [17]

$$f = 2\kappa H^2 + \bar{\kappa} K, \tag{1}$$

where κ and $\bar{\kappa}$ account for energetic changes due to deviations from the spontaneous and Gaussian curvatures, respectively. Consider an edge dislocation. If we model the core's cross section as a semicircular cylinder with radius $L/4$ and length l, $H = 2/L$, $K = 0$, and at the core the free energy is given by $F_e = 2\pi\kappa l/L$. The actual dislocation energy will be larger and will depend on the depth of the dislocation and the mean curvature away from the core. Consider now two Scherk surfaces, each of length l. At the step between the nth and $(n + 1)$th terraces there are $4nl/L$ Scherk saddles, with each saddle contributing an energy $\bar{\kappa} \int K dA = -2\pi\bar{\kappa}$ for a total elastic free energy cost of $F_s = -8\pi\bar{\kappa} nl/L$. A comparison shows that $F_s/F_e = -4n\bar{\kappa}/\kappa$ $(\bar{\kappa}/\kappa < 0)$ and that as n increases the cost of two Scherk surfaces can become greater than the cost of a single edge dislocation. In fact, our step morphology observations indicate that a homogeneous-homeotropic transition occurs as the step number increases. While it is difficult to assign a precise number n_c for this transition, we find that it occurs between $3 \leq n_c \leq 8$. If we take $\bar{\kappa}/\kappa = -1/4n_c$, then $1/32 \leq |\bar{\kappa}/\kappa| \leq 1/12$. Measured values of $\bar{\kappa}$ and κ do not yet exist, but one theory [17] gives $\bar{\kappa}/\kappa = -4/15$. The agreement between this theoretical value and our estimates of $|\bar{\kappa}/\kappa|$ is not unreasonable, given the simplicity of our model.

This energy comparison ignores the small cost of having PMMA blocks at the free surface and PS blocks at the carbon substrate within the homogeneously aligned region. Let $\Delta\gamma_f$ and $\Delta\gamma_s$ be the differences in surface tensions between the PS and PMMA blocks at the free and substrate surfaces, respectively. Literature values [18] give $\Delta\gamma_f$ as a fraction of a dyn/cm; $\Delta\gamma_s$ is not now known for carbon substrates but we expect it to also be small. For the PS/PBMA system, $\Delta\gamma_f = 10$ dyn/cm yet, despite this large cost, homogeneous alignment is observed at steps in terraced, carbon-supported droplets.

In summary, it has been shown that the morphology of steps in terraced block copolymer films obeys many of the rules that govern bulk block copolymers. Homogeneously aligned lamellae are observed at the steps in ultrathin, terraced, block copolymer films. We have modeled the lamellar twist boundaries with minimal surfaces. As the film thickness and twist boundary areas increase, the homogeneous alignment disappears and is replaced by a homeotropic orientation. The presence of homogeneously aligned lamellae allows for chain migration through the film's thickness which should influence the coarsening dynamics of terraces [9,19].

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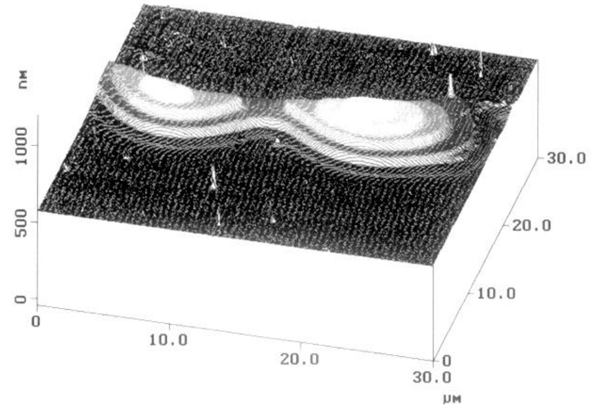

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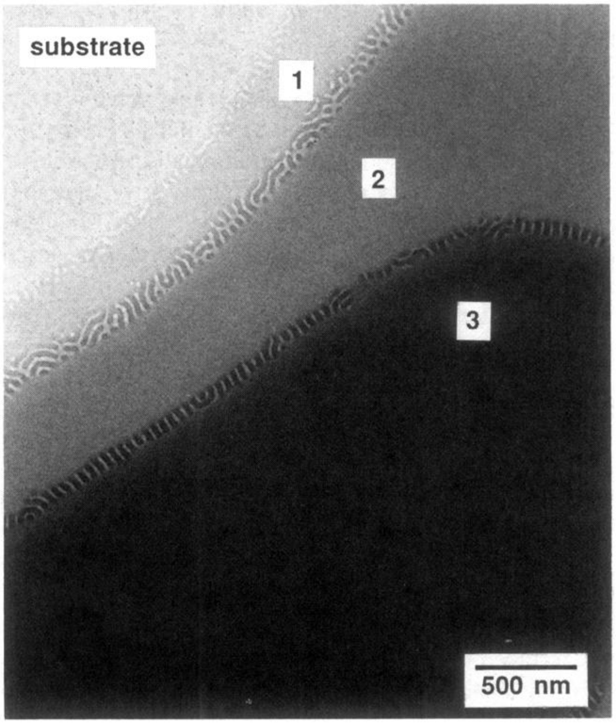

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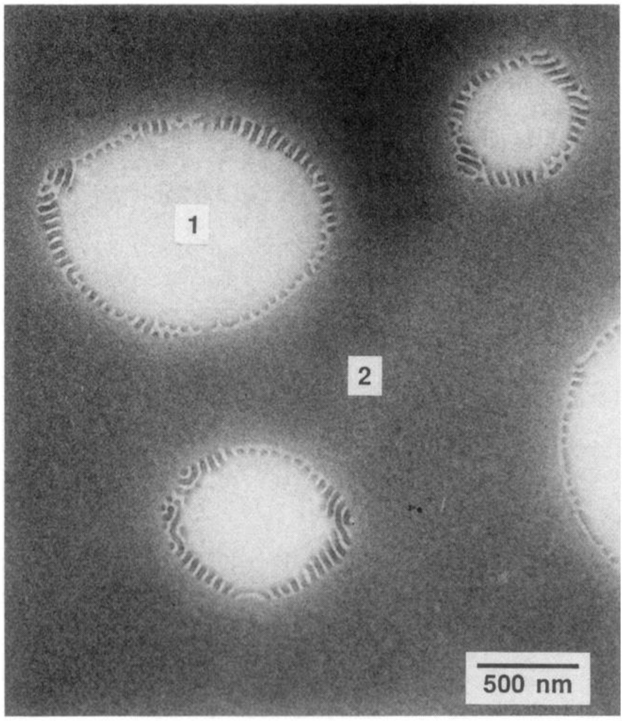

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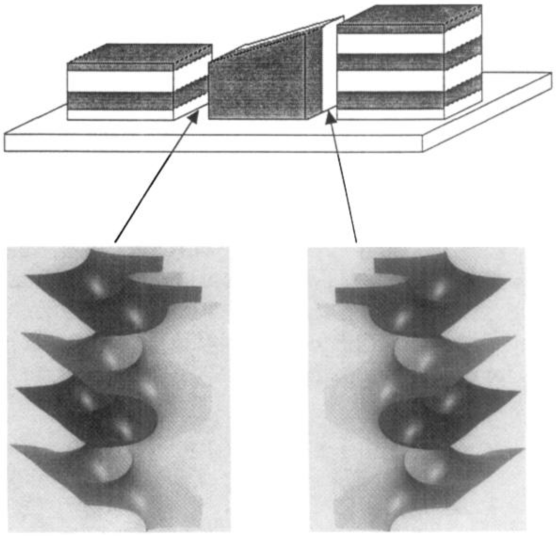

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