Combinatorial Study of Surface Pattern Formation in Thin Block Copolymer Films

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(Received 20 October 2000; published 18 June 2001)

Surface pattern formation in diblock copolymer films is investigated as a function of film thickness h and molecular mass M. Smooth films are observed for certain h ranges centered about multiples of the lamellar thickness L_0, and we attribute this effect to an increase in the surface chain density with h in the outer brushlike copolymer layer. We also observe apparently stable labyrinthine surface patterns for other h ranges, and the average size of these patterns is found to scale as $\lambda \sim L_0^{-2.5}$. Hole and island patterns occur for h ranges between those of the labyrinthine patterns and the smooth regions, and their size similarly decreases with L_0 and M.

DOI: 10.1103/PhysRevLett.87.015503 PACS numbers: 61.41.+e, 68.35.Bs, 68.55.Jk

Although there have been many previous studies of surface pattern formation in block copolymer films [1–7], there is no predictive theory of this type of pattern formation and many questions remain about basic phenomenology. For instance, the factors governing the size of the ubiquitous island and hole patterns (e.g., molecular mass M and temperature T dependence) in these films are not well understood. Notably, the size of these patterns is often large in comparison to the lamella spacing L_0 (or even the film thickness h) so that the molecular interpretation of these patterns is subtler than ordering in bulk block copolymer materials. The precise h ranges in which the films remain smooth is another basic film property that requires further investigation. Since these film properties are crucial for the development of a theoretical description of this type of pattern formation, we have combinatorially investigated pattern formation in block copolymer films using a flow-gradient technique to create films having a range of h and M.

Near symmetric poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymers with $M_n = 26$ kg/mol (48.5% PS), 51 kg/mol (49.4% PS), and 104 kg/mol (48.1% PS) and $M_w/M_n = 1.05$ [8] with less than 4% PS homopolymer contamination were purchased from Polymer Source Inc. [9] and used as received. Thickness gradients were prepared on Si wafers (10 cm diameter, Polishing Corporation of America) that were "piranha-etched" [10] to form a native SiO_x surface layer. The cleaned wafer was placed on a robotic stage and secured, and a 3 cm wide knife-edge, angled at approximately 5°, was placed 0.3 mm above the surface. Approximately 50 μL of solution with mass fraction (2 to 5)% PS-*b*-PMMA in toluene was placed under the knife-edge and the stage driven at constant acceleration to spread the solution, producing a film thickness gradient that varied with the spreading velocity. Control of initial thickness and slope was achieved by modifying the solution concentration, stage acceleration, and maximum velocity [11]. The resultant films have thickness variations of about 40 nm over a length of (20 to 35) mm. We characterize the film thickness using an automated 0.5 mm diameter UV-visible interferometry (with standard uncertainty ± 1 nm at 500 nm film thickness) every 2.5 mm across the gradient sample. This technique has been previously utilized to produce h gradients in other polymer studies [11].

For the current experiment, up to four PS-*b*-PMMA h gradients were placed on the same wafer. After characterization of the film thicknesses, the films were annealed at 170 °C under vacuum for up to 30 h. Optical microscopy (Nikon Optiphot 2) and atomic force microscopy (AFM, Digital Nanoscope Dimension 3100) were utilized to characterize the surface morphology produced upon annealing under conditions of variable h and M. Previous studies have shown that when PS-*b*-PMMA is cast and annealed on a Si substrate with a SiO_x surface layer, the PMMA preferentially segregates to the substrate while the PS segregates to the air interface [1,2]. This behavior produces smooth films for film thickness ranges near the characteristic values, $h_s \equiv (m + \frac{1}{2})L_0$ (m an integer) [4], and hole and island patterns are found when the film thickness deviates substantially from h_s.

An example of the morphological change in the block copolymer films as a function of h is shown in Fig. 1(a). This image shows optical micrographs of a 26k PS-*b*-PMMA continuous gradient film annealed at 170 °C for 6 h. A thickness range of ≈4 lamellae spacings is covered in the figure. The h varies from ≈45 nm at the top of the image to ≈117 nm on the bottom with an h variation that is nonlinear [12]. The labels denote the approximate locations of h_s for $m = 2$, 3, 4, 5, and 6. Distinct morphological regions are observed in Fig. 1(a), including broad "bands" where the film surface is smooth and relatively narrow ranges where the film pattern is labyrinthine (we term these "spinodal patterns" by analogy with phase separation). The regions of hole and island pattern formation (found on either side of the spinodal patterns) are consistent with previous observations on films of fixed thickness [3,4], but the observation of broad smooth regions and the spinodal morphology are apparently novel. (The spinodal patterns observed at long times are permanent features and should not be confused with transient

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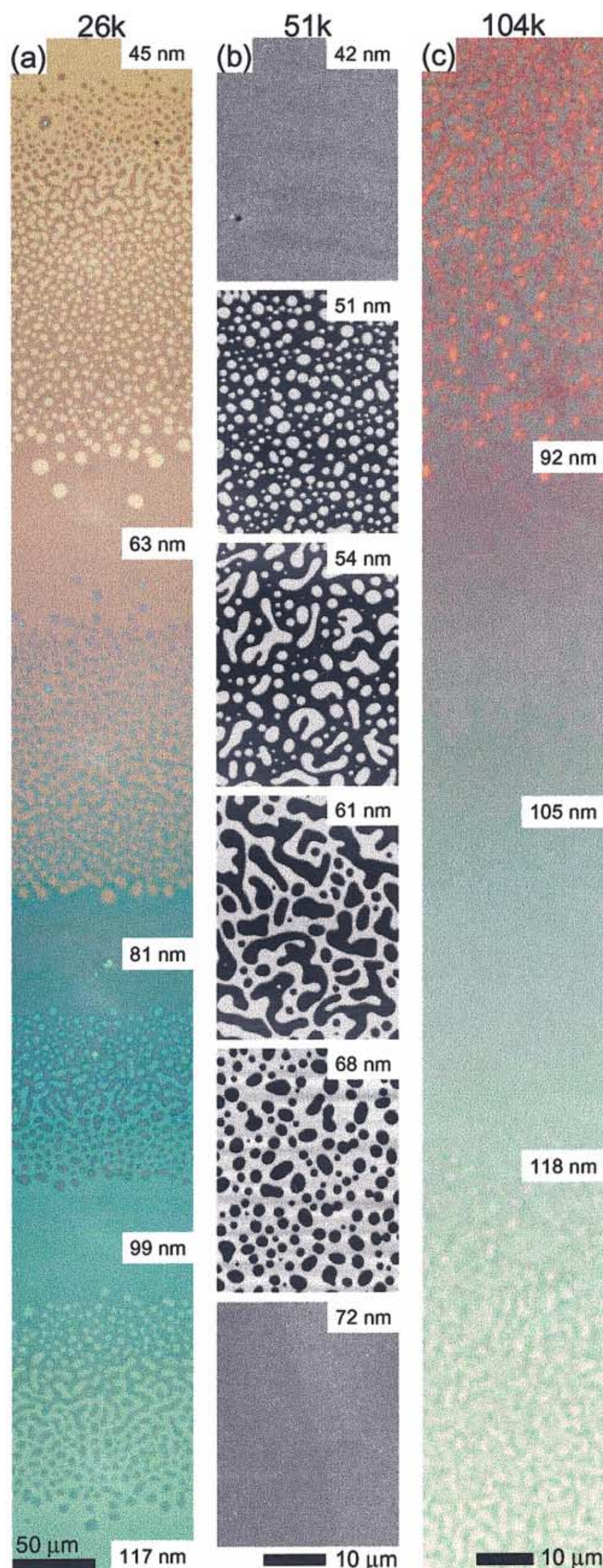

FIG. 1 (color). Gradient block copolymer films. (a) True color optical micrographs of a 26k PS-*b*-PMMA film having a gradient in thickness from 45 nm ($m = 2$) to 117 nm ($m = 6$) [12]. The sample was annealed for 6 h at 170 °C and four successive lamellae are shown. (b) AFM micrographs (white corresponds to higher topography) of a 51k PS-*b*-PMMA gradient film annealed 6 h at 170 °C. Images show representative regions of the surface morphological evolution. (c) True color optical micrograph of a 104k PS-*b*-PMMA gradient film annealed 22 h at 170 °C showing a smooth region between the cessation of holes (orange, top) and the initiation of islands (green/yellow, bottom). The smooth region changes in color from purple to blue/green, indicating a change in thickness of approximately 25 nm.

labyrinthine patterns sometimes observed at short times which later evolve into islands or holes [5].) We next study these films at higher magnifications using AFM.

Figure 1(b) shows AFM micrographs of a 51k PS-*b*-PMMA gradient film at selected locations. The average h, determined by interferometry, is indicated in each micrograph. The sample was annealed at 170 °C for 6 h and the thickness range corresponds to $(1.5-2.5)L_0$. The film is smooth for $h \approx 42$ nm, but increasing h to 51 nm leads to formation of islands. As h increases further, the islands become larger and more irregular in shape ($h \approx 54$ nm), and eventually coalesce to form a spinodal pattern (see Fig. 2). For a greater h ($h \approx 61$ nm), a continuous lamella with holes extending down to the underlying lamella "substrate" forms. A further increase in h causes the average hole size to initially decrease ($h \approx 68$ nm) followed by an increase in size and a decrease in the number of holes. The holes finally disappear ($h \approx 72$ nm) and a smooth film forms. This morphological trend is observed for all M utilized here and for a thickness range up to $6.5L_0$. Measurements of L_0 from AFM agree well with values calculated from the empirical relation $L_0 \sim M^{0.66}$ [2] (see Table I) corresponding to chain stretching by strong segregation. This agreement with previous results provides a validation of the continuous gradient method. The smooth regions between the island and hole surface patterns, as defined by the abrupt transitions separating areas where islands and holes exist, account for a significant portion of the gradient film area and correspond to a range of h deviating significantly from h_s.

Previous studies on the formation of polymer brush layers grafted in a poor solvent and dried in air have indicated a progression between island, spinodal, hole surface patterns, and finally smooth polymer "brush-type" films with an increase in the surface density σ of the grafted polymer chains [13]. The *outer layer* of block copolymer films exposed to air can be likened to a brushlike layer with variable σ. For films with $h < h_s$, the outer block copolymer layer forms a smooth continuous layer with a σ that is smaller than that found in a "complete" lamella ($h = h_s$). We define the thickness of the outer layer as h_l. The chain deficiency in this layer regime should lead to weak interchain interactions and thus to chain conformations similar to block copolymers under weak segregation

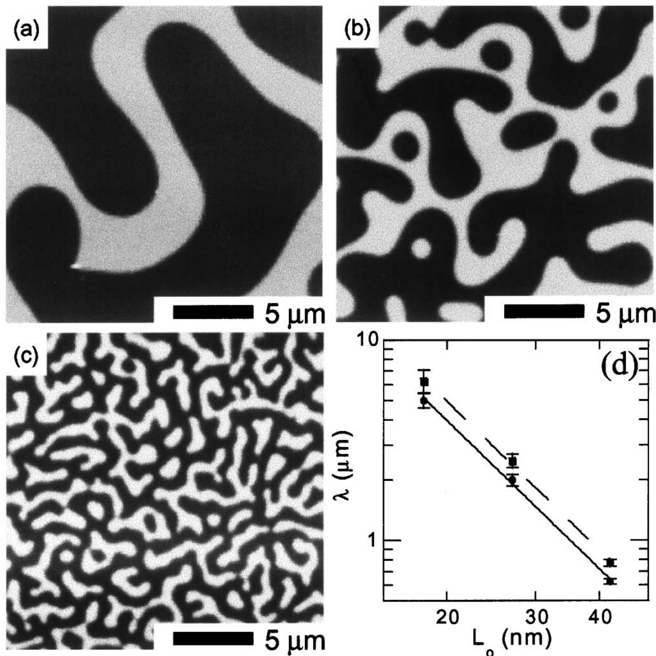

FIG. 2. M dependence of the scale of spinodal surface pattern formation in block copolymer films. AFM micrographs (white corresponds to higher topography) obtained from (a) 26k, (b) 51k, and (c) 104k PS-b-PMMA gradient films annealed for 30 h at 170 °C show the effect of M on the spinodal surface pattern formation. (d) λ vs L_0 for samples annealed 6 h (●, solid line) and 30 h (■, dashed line) with standard uncertainties displayed. Lines are a power law fit to the data yielding $\lambda(\mu\mathrm{m}) \approx 7200 L_0^{-2.5}$.

conditions. For $h > h_s$, σ should be larger than for complete lamella, leading to a stretching of the outer chain layer into an extended "brushlike" form. We then expect the layer height scaling of the outer block copolymer to correspond to the strong segregation limit ($h_l \sim \alpha M^{2/3}$) layer for $h > h_s$, but with a prefactor α different from the scaling relation for $L_0 \sim \alpha_e M^{0.66}$ for a complete layer in the bulk. [Russell *et al.* [6] made the important observation of a significant swelling in the outer block copolymer layer based on a (single) neutron reflection measurement on a film of constant thickness ($h > h_s$).] The stretching of the outer block copolymer layer between h_s ($h_l = L_0$ for $h = h_s$) and the swollen edge of the smooth band equals $(\alpha - \alpha_e)L_0$, and this stretching in comparison to L_0 should be *constant* $(\alpha - \alpha_e)/\alpha_e$ in a fully developed scaling limit ($h_l \sim \alpha M^{0.66}$) where α is M independent [14]. We then expect the height change of the extended smooth region relative to their width to be insensitive to M.

The hypothesis of chain deformation in the outer block copolymer surface layer across the smooth bands can be observed directly using the continuous h-gradient technique. Figure 1(c) shows a true color optical micrograph of the edge a 104k PS-b-PMMA gradient film annealed for 22 h at 170 °C across a smooth region [12]. The orange features on the top of Fig. 1(c) are holes while the green/yellow features at the bottom are islands, and both lack definition since their size is at the resolution limit of optical microscopy. The color of the smooth region between the holes and islands varies from purple to blue/green due to the interference changes caused by changes in h. This color change indicates a smooth h variation of ≈25 nm, centered about h_s for $m = 2$. This micrograph is representative of the h variation of the smooth bands observed across much larger distances in the gradient film center.

To quantify this thickness change across the smooth regions, gradients were annealed for 30 h at 170 °C to obtain stationary (or at least very slowly varying) film patterns. The h of the smooth region interfaces as determined by interferometry were then used to estimate the change in h across the entire smooth film region Δh and the change in Δh relative to L_0, $\delta h = \Delta h/L_0$. These data are given in Table I and show that δh is an *invariant* with M for the films studied, in accord with the scaling arguments above [14]. No statistically significant variation in δh was found with increasing the total number of lamellae up to films having $h \approx 6.5L_0$, supporting the further hypothesis that chain deformation is localized to the outermost surface lamella (since the deformation of all lamellae would result in an h dependent value of δh).

Lastly, we consider how M influences the block copolymer surface patterns. A number of authors have suggested that the ordering of block copolymer films can be described by two-dimensional "phase separation" [4,15,16] based on a phenomenological similarity of the surface pattern growth in the block copolymer films to phase separation in fluid mixtures. Although this model is conjectural, it does have implications relevant to our measurements. In this model the film height relative to a critical value defines an order parameter for the phase transition and implies the formation of "spinodal" patterns for h near some critical height and holes and islands structures for h greater or less than this critical height [15]. (The holes and islands correspond to droplet formation in off-critical fluid mixtures.) This predicted behavior is remarkably consistent with our observations where h_c (the film thickness where the spinodal patterns form) is identified with the critical height in the phase transition model. In the present measurements, we find $h_c = (m + [0.91 \pm 0.03])L_0$.

TABLE I. Measured and regressed parameters determined for each molecular mass sample. Errors are given as standard uncertainty.

M_w (kg/mol)	L_0 calc. [2] (nm)	L_0 measured (nm)	Δh (nm)	$\delta h = \Delta h/L_0$	q^* (30 h) (μm^{-1})
26	17.1	17.8 ± 0.8	4.1 ± 1.4	0.23 ± 0.068	0.16 ± 0.02
51	26.8	30.2 ± 0.8	8.4 ± 1.0	0.278 ± 0.026	0.40 ± 0.03
104	42.4	42.3 ± 1.4	11.6 ± 1.6	0.274 ± 0.028	1.31 ± 0.05

Surface elasticity has been suggested to play a large role in determining the scale and form of surface pattern formation in phase separating thin films, and this type of model (phase separation plus surface elasticity) has been invoked to rationalize pattern formation in the lipid bilayer films arising in cell membranes [17,18]. A preliminary calculation of phase separation with surface elasticity was performed based on a Cahn-Hillard model of phase separation and the Helfrich model of surface elasticity [19]. This calculation indicates that the presence of a surface curvature elasticity κ can "pin" the scale of the phase separation over appreciable time scales. Apparently this type of elasticity inhibits long wavelength phase separation much like the presence of a chemical junction in block copolymers that leads to an elastic restoring force acting against macroscopic phase separation. This elastic effect could potentially cause the formation of equilibrium mesophases in phase separating fluid films.

Theoretical estimates of κ for block copolymers and surfactant layers indicate that κ increases strongly with M ($\kappa \sim M^3$) [20], and we propose that the decrease in the average pattern size λ with an increase in M arises from the increasing energetic cost of the surface deformation that accompanies pattern formation. This leads us to expect that λ should scale as an inverse power of κ, $\lambda \sim \kappa^{-\beta}$, where $0 < \beta < 1$ so that the patterns become large in low M films where κ is small. In Fig. 2, we show AFM micrographs at constant magnification of (a) 26k, (b) 51k, and (c) 104k PS-*b*-PMMA samples near $h = h_c$ annealed 30 h ($T = 170\,^\circ\mathrm{C}$). Kinetic studies of the growth of these patterns [21] show that their scale "pins" at long times and the images in Fig. 2 correspond to a time regime where there is little further evolution of the surface patterns [5]. It is apparent from this figure that the scale of the patterns decreases with an increase in M. To quantify this behavior, we obtain a 2D fast-Fourier transform of the images and circularly average the transform to obtain a peak wave vector (q^*) characteristic of the average pattern scale (Table I). Figure 2(d) shows a plot of $\lambda \equiv (q^*)^{-1}$ versus L_0 for samples annealed for 6 and 30 h where a small evolution in the pattern scale with time is evident. A log-log plot yields a scaling $\lambda(\mu\mathrm{m}) \sim L_0^{-2.5}$ for both annealing times [parallel lines in Fig. 2(d)] [22]. The relation $L_0 \sim M^{0.66}$ then implies $\lambda \sim M^{-1.65}$ so that the exponent β proposed above is near $\frac{1}{2}$ (i.e., $\lambda \sim \kappa^{-0.55}$) [23]. The hole and island patterns that form for $h > h_c$ and $h < h_c$ remain stable (or at least evolve very slowly), and their average size also diminishes strongly with increasing M.

Our combinatorial approach is found to be useful in discovering and characterizing new features of pattern formation in block copolymer films. Specifically, smooth films are observed for a symmetric range of h about the characteristic values $h_s \approx (m + \frac{1}{2})L_0$. The height variations across these regions are found to be a constant fraction of L_0 nearly independent of m and M. This effect is attributed to an increase in the surface chain density in the outer copolymer layer with increasing h, as in polymer brushes. Spinodal patterns are also observed having an average size that scales as an inverse power of L_0, $\lambda \sim L_0^{-2.5}$. We suggest that the increase in surface curvature elasticity κ with M and the increased energetic cost of surface deformation accompanying pattern formation are responsible for this effect. The present measurements would have been difficult in block copolymer films of fixed thickness because of the difficulty in reproducibly controlling film thickness to high accuracy, and demonstrate the value of combinatorial methods for thin polymer film characterization.

We thank Dr. Mark VanLandingham for assistance with AFM. We also acknowledge helpful discussions with Dr. Peter Green and Dr. Igel Szleifer.

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