

CHARACTERIZATION OF SYMMETRIC DIBLOCK COPOLYMERS WITH HIGH THROUGHPUT TECHNIQUES

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Introduction

Thin films of symmetric diblock copolymers have been observed to form surface patterns of circular holes and island structures. Previous work¹⁻⁹ has shown that the holes and islands form when the total film thickness, h , deviates substantially from multiples of the bulk lamellar thickness, L_0 , of the bulk block copolymer material, $h \approx (m + \frac{1}{2})L_0$, m an integer. There has been relatively little study, however, of the factors that govern the size of these surface patterns at long times and there is no predictive theory of this novel surface pattern formation. Notably, these surface patterns can be remarkably large in size in comparison to L_0 , (or even h) and there has been no previous experimental study of the thickness range over which the block copolymer films remain smooth. In the present work, we develop a flow gradient technique to cast films having a continuous range of thickness and a range of molecular mass, M , to combinatorically study block copolymer films in order to identify aspects of this type of pattern formation.

Experimental

Near symmetric polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymers with $M_n = 26$ kg/mol, 51 kg/mol and 104 kg/mol and $M_w/M_n = 1.05$ were purchased from Polymer Source Inc. and used as received.^{10,11} Thickness gradients were prepared on Si wafers (10 cm diameter, Polishing Corporation of America) that were "piranha-etched"¹² 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. 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 thickness gradients in other polymer studies.^{13,14}

For the current experiment, up to four PS-*b*-PMMA film thickness 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 (OM, 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.^{2,3} This behavior produces smooth films for film thickness ranges near the characteristic values, $h_s \equiv (m + \frac{1}{2})L_0$, and hole and island patterns are found when the film thickness deviates substantially from h_s .⁴

Results and Discussion

An example of the morphological change in the block copolymer films as a function of h is shown in Fig. 1. This image shows optical micrographs of a 26k PS-*b*-PMMA continuous gradient film annealed at 170°C for 6 h. The figure spans a thickness range of ≈ 2 lamellae spacings. The film thickness h varies from ≈ 81 nm at the left of the image to ≈ 117 nm on the right. The labels denote the approximate locations of h_s for $m = 4, 5$ and 6. Several distinct morphological regions are observed in Fig. 1, including broad "bands" of h where the film surface is smooth and relatively narrow h ranges where the film pattern is labyrinthine ("spinodal"). The regions of hole and

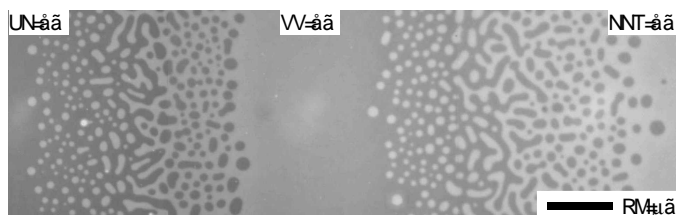


Figure 1. Optical micrograph of a 26k PS-*b*-PMMA film having a gradient in thickness from 81 nm ($m = 4$) to 117 nm ($m = 6$). The sample was annealed for 6 h at 170°C and two successive lamellae are shown.

Table 1. Measured and regressed parameters determined for each molecular mass sample. Errors are given as standard uncertainty.

island pattern formation (found on either side of the spinodal patterns) are consistent with

M_w (kg/mol)	L_0 calc. (nm)	L_0 meas. (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

previous observations in films of fixed thickness,^{1,4,8,15,16} but the smooth and spinodal morphology regions are apparently novel. We next study these films at higher magnifications using AFM.

Fig. 2 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 (2.5 to 3.5) L_0 . The film is smooth for $h \approx 72$ nm, but increasing h to 77 nm leads to formation of islands. As h increases further, the islands become larger and more irregular in shape ($h \approx 83$ nm), and eventually coalesce to form a bicontinuous morphology (see Fig. 3). For a greater h ($h \approx 90$ 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 decrease ($h \approx 94$ nm) and the number of holes to decrease ($h \approx 101$ nm), until a smooth film is reformed ($h \approx 104$ nm, not shown here). This morphological trend is observed for all M utilized here and for h up to 6.5 L_0 . Measurements of L_0 from AFM are shown in Table 1. These values agree well with the empirical relation³ $L_0 \sim M^{0.66}$ (see Table 1), corresponding to strong segregation chain stretching. This agreement with previous results provides an important validation on the continuous gradient method.

We next focus attention on the smooth regions between the island and hole surface patterns, as defined by the abrupt transitions separating areas where islands and holes exist. Notably, the smooth regions account for a large percentage of the gradient film area and thus correspond to a range of h deviating significantly from h_s . To quantify the thickness change across the smooth regions, we prepared and annealed gradients for 30 h at 170°C to obtain approximate "steady state" (or at least very slowly varying) film patterns. Positions of the interface between the holes and smooth areas as well as between the smooth region and islands were recorded. The unannealed h of these positions were then utilized to estimate the change in film thickness (Δh) across the entire smooth film region. The value of Δh obtained for each M investigated is shown in Table 1, along with the change in Δh relative to L_0 , $\delta h = \Delta h/L_0$. The data in Table 1 shows that δh is nearly an *invariant* within standard uncertainty for the films studied, regardless of the molecular mass of the block copolymer. Furthermore, no statistically significant variation in δh was found with increasing the total number of lamellae, up to films having a thickness $h \approx 6.5 L_0$. This observation indicates that the chain deformation is localized to the outermost surface lamella since the deformation of all lamellae would result in an h dependent value of δh . By considering this outer lamella as a brush-like chain layer, the Δh value can be explained as an increase in the surface chain density, resulting in the M independent value of Δh observed. We next consider how h and M influence the block copolymer surface patterns.

In Fig. 3, AFM micrographs at constant magnification of (a) 26k, (b) 51k and (c) 104k PS-*b*-PMMA samples annealed 30 h at 170°C are shown. The film thickness in each case is near the film h where the surface pattern is

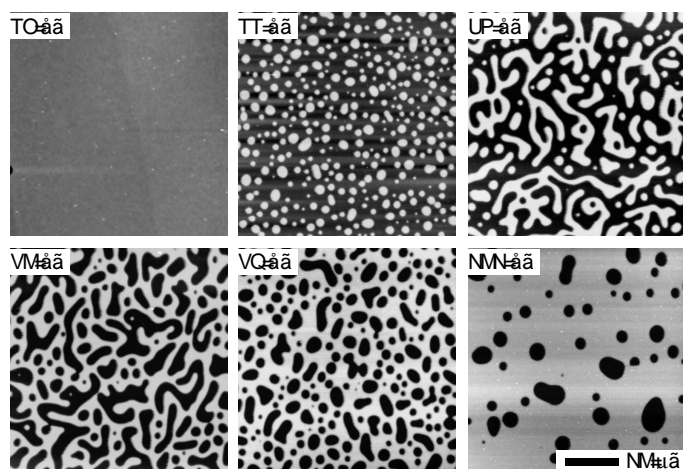


Figure 2. AFM micrographs (white corresponds to higher topography) of a 51k PS-*b*-PMMA gradient film annealed 6 h at 170 °C. Images show representative regions of the surface morphological evolution.

almost bicontinuous. It is apparent from this figure that the scale of the bicontinuous surface patterns decrease 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 wavevector (q^*) characteristic of the average pattern scale. The results of this analysis are shown in Table 1. Fig. 3d shows a plot of $\lambda \equiv (q^*)^{-1}$ versus L_o for samples annealed for 6 h and 30 h where a small evolution in the pattern scale with time is evident. A log-log plot indicates a good approximate scaling $\lambda(\mu\text{m}) \sim L_o^{-2.5}$ for both annealing times.¹⁷ Alternately, we find that λ scales with the molecular mass M according to the relation $\lambda(\mu\text{m}) \sim M^{-1.5}$. The hole and island patterns observed remain stable (or at least evolve very slowly), and the average size of these patterns also diminishes strongly with increasing M as in the spinodal regime. We attribute this effect to the increasingly viscoelastic nature of the outer block copolymer layer with increasing M . As the surface rigidity increases with increasing M , the ability of the chains to reorganize into large patterns decreases.

Conclusions

Our combinatorial method is found to be useful in identifying new features of pattern formation in block copolymer films. In particular, we find that the smooth film regions occur symmetrically about $h \approx (m + 1/2) L_o$ with m a positive integer for an h range that is nearly a constant fraction of L_o . This effect is attributed to an increase in the surface chain density in the outer copolymer layer with increasing h . Novel spinodal patterns are also observed for other characteristic thickness ranges. The average size λ of these patterns scales as an inverse power of L_o , $\lambda \sim L_o^{-2.5}$ (or equivalently $\lambda \sim M^{-1.5}$) and this effect is suggested to be caused by an increase in the film surface elasticity with increasing M . These observations would have been difficult in measurements performed on block copolymer films of fixed thickness because of the difficulty in controlling film thickness and show the value of the combinatorial measurement methods utilizing gradients in film thickness, and other parameters of primary physical importance.

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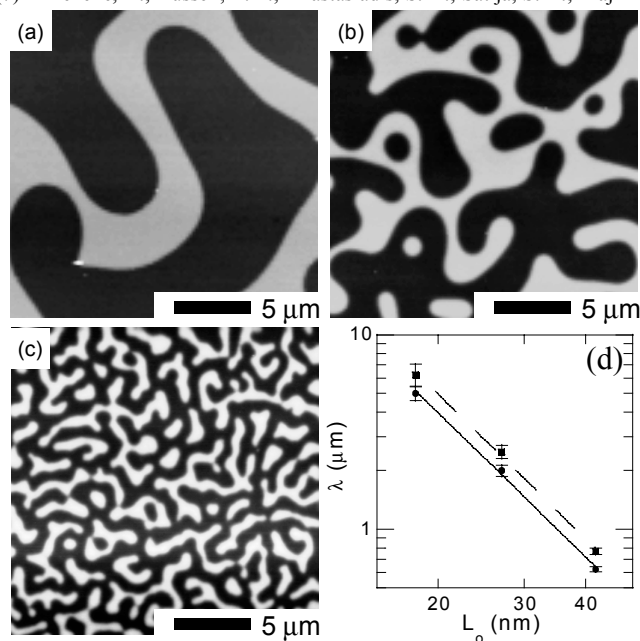


Figure 3. AFM micrographs (white corresponds to higher topography) obtained from (a) 26k, (b) 51k and (c) 104k PS-*b*-PMMA gradient films annealed for 30 h at 170 °C show the effect of M on the spinodal surface pattern formation. (d) λ vs L_o for samples annealed 6 h (●, solid line) and 30 h (■, dashed line) with standard uncertainties displayed. Lines are a power law fit of the data yielding $\lambda(\mu\text{m}) \approx 7200 L_o^{-2.5}$.

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