# Topological Coarsening of Symmetric Diblock Copolymer Films: Model 2D Systems

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Films of diblock copolymers with thicknesses less than a lamellar period on a noninteracting surface were found to be model systems for studying the late stages of two dimensional phase separation. It was found under conditions of constant surface coverage that the average particle size $\langle R(t) \rangle$, the inverse of the total number of particles $N(t)^{-1}$, and the correlation length $\xi(t)$ varied as $t^\alpha$, $t^{2\alpha}$, and $t^\alpha$, respectively, where $\alpha = 0.23 \pm 0.03$.

Thin films of symmetric diblock copolymers can be used as model systems for studying the kinetics of phase separation in two dimensions. The effect of reduced dimensions on phase transitions has been studied theoretically [1-5] and by simulation [6-10]. However, there is little experimental data which clearly test current theories [11]. Also, the results of some simulations disagree with theory [7]. Here we present optical microscopic studies on the coarsening of the surface topology of thin films of symmetric diblock copolymers where the fractional coverage of the surface topography is conserved. These provide a direct experimental test of theoretical predictions. Our results contradict these predictions but are in agreement with simulations.

Symmetric diblock copolymers are polymer chains comprised of two chemically distinct polymers which are covalently linked to one another. In this study we used a symmetric diblock copolymer of polystyrene, PS, and polymethylmethacrylate, PMMA, denoted P(S-b-MMA). The weight average molecular weight of this copolymer was $9.1 \times 10^4$ daltons with a polydispersity of 1.05. The volume fraction of PS in the copolymer was 0.5. PS homopolymer impurity was removed from the copolymer by extraction with cyclohexane. Solutions of the copolymer in toluene were spin coated to produce films 114 and 280 Å thick, corresponding to $0.3L$ or $0.7L$, respectively, where $L$ is the period of the lamellar microdomain morphology in the bulk. For this copolymer $L = 400$ Å [12]. The copolymer films were heated at 170 °C under vacuum for a desired time and quenched to room temperature.

A key element in this study was the use of a Si wafer coated with a chemically attached layer of PS as a substrate. Because of the unfavorable interactions of the PMMA block with the PS and the packing constraints in the chemically attached PS layer, the diblock copolymer does not substantially penetrate into the brush. In contrast to islands on the surface of a copolymer multilayer, the PS brush forms, effectively, an impenetrable substrate where only lateral diffusion of chains is permitted.

The specific interactions of the different blocks with the substrate and the surface energies of the two components induce the formation of a multilayered structure comprised of alternating layers of the two blocks [13]. The layered structure forces the film thickness at any point to be quantized according to the repeat period $L$. Thus, if PMMA interacts favorably with the substrate, as in the case of $SiO_2$, and since PS has a lower surface energy than PMMA, then the film thickness at any point is given by $(n + \frac{1}{2})L$, when $n$ is an integer. In this study PS is preferentially located at both the substrate (chemically attached PS layer) and the air interface, and the thickness at any point is given by $nL$. When the initial film thickness $T$ does not conform to $nL$, the ordered copolymer relieves this constraint by the formation of a quantized surface topography. In the case where there is no strong interaction between the substrate and the two components of the block copolymer, for thin copolymer films $(T < L/2)$, islands are formed on the surface, whereas isolated holes form on the surface if $L/2 < T < L$ [14-17]. The step height in each case is $L$. The samples here consist either of isolated islands of height $L$ or a continuous film of thickness $L$ with holes penetrating to the underlying PS substrate. This is confirmed by the uniform interference color across the island and the correspondence of the thickness to the period of the lamellar repeat period. In addition, as discussed later, x-ray photoelectron spectroscopy studies showed that the surface was essentially pure PS. Since the lateral dimensions of the islands or holes are on the micron size scale and the step height is only 400 Å, the islands or holes can be viewed as two-dimensional objects. The reduced dimensionality of the copolymer surface was recognized in previous studies [14-17]. However, these studies were performed on films which formed multilayers. Because of peculiarities in the thermal expansion of confined multilayer films and the ability of the copolymer molecules to diffuse through the layers, time dependent variations of the surface topologies of multilayered samples have several origins. These complications are eliminated here.

Typically, the islands or holes on the surface are of the micron size scale. Under an interference microscope (Leitz Ergolux) using white light, each discrete thickness produces a distinct interference color. For the specimens discussed herein, only two colors were observed in the images. The colors corresponded to the thickness of the PS brush on the Si or to the well-defined thickness of a copolymer bilayer. Via image processing, these images can

be reduced to binary, black, and white images from which the average number, size, and surface coverage can be obtained directly as a function of the time allowed for the coarsening of the surface topology. In this study, we focus only on the later stages of the coarsening process, when the step height of all surface features is constant and when the fractional coverage of the surface with the islands or holes is conserved.

Shown in Figs. 1(a)–1(d) are a series of optical micrographs of the $0.3L$ copolymer film on the chemically attached PS layer after annealing the sample for 13.5 h (a); 37 h (b); 131.5 h (c); and 322 h (d) at 170°C. The magnitude of the area studied digitally was kept fixed throughout this study. The white regions indicate islands or elevated surface areas. Results similar to those in Fig. 1 are found for the case of holes. The magnification is indicated in the figure. These micrographs are digitized continuous tone images of the original micrographs. Arbitrarily setting a cutoff gray level converted these to binary images which were then processed numerically. Because of the finite optical resolution of the microscope, the cutoff level will slightly affect the overall sizes of the islands or holes and, consequently, the surface coverage. At most, an error of $\pm 5\%$ is introduced by this resolution limitation. In all cases the level was kept fixed which yielded a constant surface coverage throughout the study.

It can be seen that, as time progresses, the average size of the islands increases as would be expected. It should be noted that the average shape of the domains is circular which indicates that the growth of the island size does not
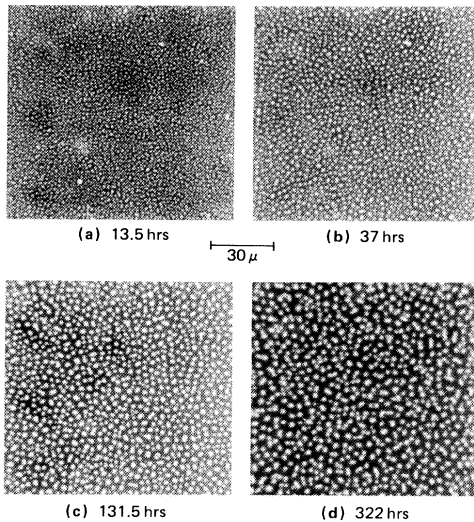
occur by a coalescence mechanism. In fact, the spatial position of the islands does not change with time. This was also found previously in the multilayer case [16,17]. Consequently, in this study, the size of the islands can change only by diffusion of copolymer chains across the surface from smaller islands to larger ones. X-ray photoelectron spectroscopy studies indicate that there is at most ~5% of PMMA on the surface. While this sets up an upper limit on the number of P(S-b-MMA) chains diffusing on the PS brush, translating this number into a concentration is most difficult due to the PMMA signal that would be observable from the edges of the islands or holes.

The total number of islands (or holes), $N(t)$, on the surface as a function of time, $t$, is given by

$$N(t) = \int_0^\infty \left[\frac{dn}{dS}\right] dS , \qquad (1)$$

where $(dn/dS)dS$ is the number of islands with a surface area between $S$ and $S+dS$. From this quantity the total average surface of the islands $\langle S(t)\rangle$ can be obtained by

$$\langle S(t)\rangle = \frac{\int_0^\infty S[(dn/dS)(S,t)]dS}{N(t)} . \qquad (2)$$

Assuming that the average shape of the islands is circular, then the average radius of an island, $\langle R(t)\rangle$, at time $t$ is given by

$$\langle R(t)\rangle = \langle S(t)/\pi\rangle^{1/2} . \qquad (3)$$

A normalized distribution of hole or island sizes can be defined by the quantity $f$:

$$f(S,t) = \left[\frac{dn}{dS}\right] \frac{\langle S(t)\rangle}{N(t)} . \qquad (4)$$

As shown in Fig. 2, where $f(S,t)$ is plotted as a function of the reduced area, $S/\langle S(t)\rangle$, the normalized particle



FIG. 1. Digitized optical micrographs of a $0.3L$ thick film of P(S-b-MMA) on a chemically grafted PS substrate after annealing at 170°C for 13.5 h (a); 37 h (b); 131.5 h (c); and 322 h (d). The circular white features are 400 Å elevations or islands comprised of a microphase separated morphology oriented parallel to the surface. The dark areas are the exposed, chemically grafted PS substrate.
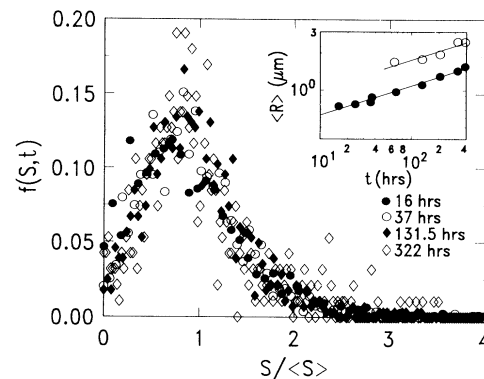


FIG. 2. Normalized distribution of the island size $f(S,t)$ as a function of reduced island area $S/\langle S\rangle$ for samples annealed at 170°C for 16 h ($\bullet$); 37 h (O); 131.5 h ($\blacktriangle$); and 322 h ($\triangle$). In the inset the average size of the islands ($\bullet$) and holes (O) is shown as a function of time.

size distribution over the time scale studied is invariant. For the $0.7L$ sample, i.e., on $L$ thick sample with holes, $f(S_i,t)$ for the holes was also invariant with time as a function of $S/\langle S(t) \rangle$ and, to within experimental errors, is identical to that obtained for the islands.

The self-similar behavior of $f(S,t)$ is a critical prediction in theories dealing with coarsening processes. In addition the shape of $f(S,t)$ should depend only upon the fractional surface coverage. This is consistent with the results found here since the two cases studied are complimentary. Theoretically, the kinetics of the late stages of phase separation are characterized by a universal scaling for the time evolution of the average particle size, i.e., $R(t)=kt^{\alpha}$ where $k$ is a constant. For both two- and three-dimensional processes, taking into account interactions between domains, $\alpha=\frac{1}{3}$. Most simulations [6–10] yield $0.2 < \alpha < 0.29$, slightly less than the theoretical value. This discrepancy has been attributed to diffusion effects at an interface, the inadequacy of mean field descriptions for the systems, or to insufficiently long simulation times.

The time evolution of $\langle R(t) \rangle$ for islands and holes is shown in the inset of Fig. 2. Over the time range studied, unlike previous measurements of islands or holes on the surface of a multilayer [16], the same exponent is found for both topologies, i.e., $\alpha=0.24 \pm 0.02$ (islands) and $\alpha=0.23 \pm 0.02$ (holes). This result is consistent with a common driving force for coarsening, i.e., the line tension, but with a different growth mechanism.

Since the total area covered by the topology is conserved, then it follows directly that the total number of particles, $N(t)$, scales as $-2\alpha$, i.e.,

$$N(t)=k't^{-2\alpha}, \tag{5}$$

where $k'$ is an arbitrary constant. $N(t)$ for the $0.3L$ (islands) and $0.7L$ (holes) samples as a function of time are shown in Fig. 3. As can be seen both topologies behave
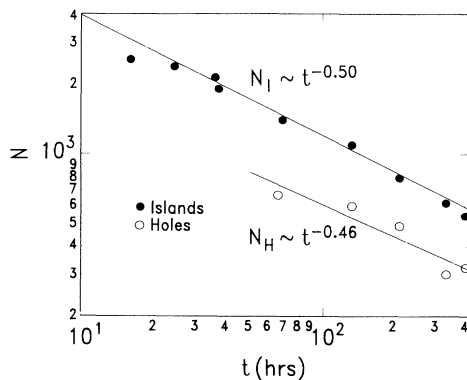
identically yielding $\alpha=0.23 \pm 0.02$. The result is consistent with the exponent determined from $\langle R(t) \rangle$.

The two-dimensional autocorrelation function can be determined by image analysis of the optical micrographs. Since the surface topology is isotropic, radial averaging of the data markedly improves the accuracy of the correlation function. The correlation function for the islands and for holes has a value of $\phi(1-\phi)$ at $r=0$, where $\phi$ is the fractional coverage of the surface, and decays to zero with increasing $r$. Oscillations in the correlation function about zero characterize the spatial distribution of the topological features on the surface. The correlation length $\xi(t)$, determined from the position of the first maximum in the correlation function, characterizes the average center-to-center distance between adjacent islands or holes. Theoretically, $\xi(t) \propto t^{\alpha}$. The experimental variation of $\xi(t)$ as a function of time is shown in Fig. 4 for holes (O) and islands (●). To within experimental uncertainty, $\alpha=0.23 \pm 0.03$ for both cases.

Therefore, $R(t)$, $N(t)$, and $\xi(t)$ exhibit a power law behavior but the exponent is less than the theoretical predictions. In fact, our observations are more consistent with simulations and are virtually identical with the Langevin dynamics simulations of Abraham and co-workers [7]. There are, however, several features of the coarsening behavior on a molecular level that warrant further attention. While $\langle R(t) \rangle \propto t^{1/4}$ for both islands and holes, the absolute growth rate of holes is nearly twice that of the islands. $\langle R(t) \rangle$ will depend upon $(DC)^{\alpha}$ where $D$ is the diffusion coefficient of the molecules on the surface and $C$ is the concentration of the diffusion species on the surface surrounding the islands or holes. From x-ray photoemission spectroscopy (XPS) measurements we can estimate $C \lesssim 0.05$ for the island case which leads to the result that the diffusion in the case of islands is up to an order of magnitude greater than that for holes. This difference may reflect the mobility of isolated co-
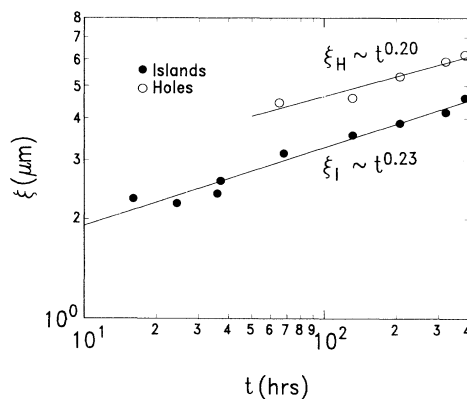


FIG. 3. The total number of islands (●) and holes (O) as a function of time for P(S-b-MMA) films with initial thicknesses of $0.3L$ and $0.7L$, respectively, upon annealing at 170°C under vacuum.



FIG. 4. The correlation length $\xi(t)$ as a function of time in the case of islands (●) and holes (O) for P(S-b-MMA) films with initial thicknesses of $0.3L$ and $0.7L$, respectively.

polymer molecules on the surface in comparison to a lateral diffusion of the chains in a copolymer microdomain. It could also result from a difference in the concentration of copolymer chain, i.e., self versus mutual diffusion. An interesting point that requires further attention is the geometry of the islands or holes and the role this geometry plays in the coarsening process. As Coulon *et al.* [14] have shown by atomic force microscopy studies of islands or holes on the surface of a multilayer, the edge profiles of the surface feature are not step functions. Rather the angle with respect to the surface is only 6°. Since the difference in elevation is only 400 Å, under an optical microscope this gentle slope appears as a step. However, the edges of the islands (holes) extend over many molecular diameters and the characteristics of the microphase separated or multilayered morphology in this region must be different than that at the center of the island (or hole). It is for this reason that XPS measurements cannot yield an absolute measure of the concentration of free copolymer chains on the surface. The morphology of the edges of the islands is currently under study. In conclusion, the results shown in this study demonstrate that thin copolymer films constitute model systems to study two-dimensional coarsening behavior without the complication of possible exchange between an underlying multilayer film. The data shown exhibit significant deviations from theoretical predictions but do conform to simulations.

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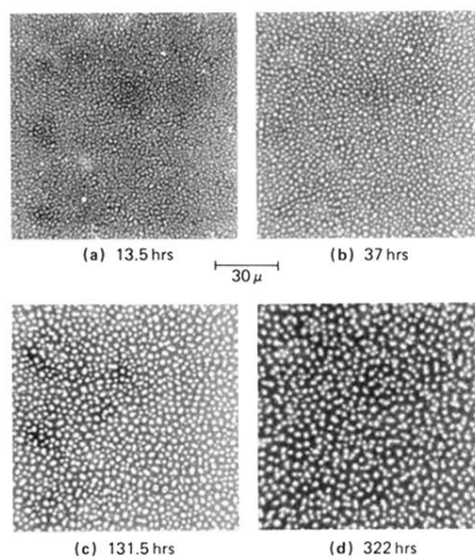[17] D. Aussere, D. Chatenay, G. Coulon, and B. Collin, J. Phys. (Paris) **51**, 2571 (1990).

(a) 13.5 hrs    30 μ    (b) 37 hrs

(c) 131.5 hrs    (d) 322 hrs

FIG. 1. Digitized optical micrographs of a $0.3L$ thick film of P(S-b-MMA) on a chemically grafted PS substrate after annealing at 170 °C for 13.5 h (a); 37 h (b); 131.5 h (c); and 322 h (d). The circular white features are 400 Å elevations or islands comprised of a microphase separated morphology oriented parallel to the surface. The dark areas are the exposed, chemically grafted PS substrate.