

Phase separation of ultrathin polymer-blend films on patterned substrates

A. Karim,¹ J. F. Douglas,^{1,2} B. P. Lee,^{1,2} S. C. Glotzer,^{1,2} J. A. Rogers,² R. J. Jackman,³ E. J. Amis,¹ and G. M. Whitesides³

¹Polymers Division, NIST, Gaithersburg, Maryland 20899

²Center for Theoretical and Computational Materials Science NIST, Gaithersburg, Maryland 20899

³Department of Chemistry and Department of Chemical Biology, Harvard University, Cambridge, Massachusetts 02138

(Received 6 February 1998)

The phase separation of ultrathin polymer-blend films of polystyrene and polybutadiene on microcontact printed alkanethiol patterns with hydrophobic and hydrophilic end groups ($-\text{CH}_3$ and $-\text{COOH}$) is investigated by atomic force microscopy. Simulations suggest that the phase-separation morphology can be controlled through patterns that modulate the polymer-surface interaction, and this concept is verified experimentally. Length scale pattern control is found to be limited to a scale on the order of a few micrometers. [S1063-651X(98)50406-0]

PACS number(s): 61.41.+e, 64.75.+g, 68.55.Jk

The growth of structures through phase separation and aggregation is commonly found to be sensitive to perturbations that break the isotropy of the bulk self-organization process. This sensitivity to perturbations inevitably leads to complexity in the growth morphology and in the theoretical description of this type of phenomenon, since small-scale details tend to be amplified in the ordering process. A diversity of morphologies then become possible through the adjustment of molecular geometry and the type of perturbing field. Many previous studies have considered the application of external fields (electric, flow, temperature, and gravity) to perturb phase separation and other self-organization processes, but the perturbing influence of modulated boundary surface interactions has received limited attention. Patterning on the solid substrate of phase-separating films offers a unique opportunity to study pattern selection in self-organization and, more practically, for controlling the phase-separation morphology of thin blend films spin cast on these substrates. In this paper, this concept is first demonstrated in a model Cahn-Hilliard simulation, and then verified experimentally using deuterated polystyrene (dPS) and polybutadiene (PB) blend films spun cast on self-assembled monolayer (SAM) substrates. The local surface interaction of these SAM layers are varied through microcontact (μCP) printing of hydrophobic and hydrophilic end-group alkanethiols to provide a modulation of the surface interaction as in the simulations. Control of the local boundary interaction with these patterned surfaces allows us to select the symmetry and scale of the resulting phase-separation morphology through templates which *direct* both in-plane and out-of-plane phase separation.

Simulation provides some important insights into this “pattern-directed spinodal decomposition,” which were helpful in the design of our measurements. We utilize a Cahn-Hilliard-Cook (CHC) model [1–3] of phase separation with modulated boundary interactions on the substrate surface [4]. Boundary-induced phase separation has been extensively studied theoretically [3], and experimentally [5], in the absence of surface interaction modulation, so our discussion here of the modeling is brief. The “free surface” (polymer-air interface) is taken to have neutral (nonselective) and mass conserving boundary conditions. The coordinate normal to the plane substrate defines the z axis, and x and y axes cor-

respond to the coordinates of the planar surface. The surface free energy of the substrate is then taken to have the form [4]

$$F_s/k_B T = \int \int dx dy [h_0 \sin(2\pi x/l_p) \phi(x, y) + (\frac{1}{2})g \phi^2(x, y)], \quad (1)$$

where h_0 is the magnitude of the chemical potential favoring a particular component at the substrate surface. In particular, this interaction is modulated in the x direction with a period l_p determining the stripe patterning length scale. The coupling constant g accounts for the change of the polymer-polymer short-range interactions near the boundary. We combine Eq. (1) with a Landau-Ginzburg-type bulk free energy, and utilize standard CHC dynamics [1–3]. The couplings h_0 and q are set to unity, corresponding to the standard CMC prescription for strong coupling regime [3].

Figure 1 shows cross-sections of the resulting phase-separation pattern for critical composition films where in Fig.



FIG. 1. Cross sections showing simulation of composition variations in phase-separating blend films on a patterned substrate. Simulations employ CHC dynamics with a modulated boundary interaction defined in Eq. (1). The surface pattern wavelength l_p is about twice the maximally unstable phase separation scale (“spinodal wavelength”) λ_0 in these simulations ($l_p \approx 2.2\lambda_0$). Variations in film height due to unequal surface and interfacial tensions, deformability of the polymer-air boundary, and hydrodynamic interactions are not treated in this simulation. (a) “Checkerboard” pattern in thicker film cross sections arising from surface-directed phase separation in combination with pattern-directed lateral phase separation. (b) Thinner films exhibit only pattern-directed lateral phase separation.

1(a) the film is thick enough for surface-directed waves to be well developed, and Fig. 1(b) shows a film thinner than the wavelength of the bulk phase-separation process. The inducement of composition waves, both in the plane and transverse to the solid substrate, leads to a “checkerboard” morphology in the thicker films [4]. These simulations indicate that composition waves normal to the solid substrate are suppressed in the thinner films, leading to better-resolved patterns in the plane of the blend films. Accordingly, we utilize “ultrathin” blend films (≈ 700 Å) in our initial studies of pattern-directed spinodal decomposition, as in our previous study of ultrathin blend film phase separation without surface patterns [6]. Krausch *et al.* [7] previously investigated thicker blend films (≈ 3000 Å) where surface-directed spinodal decomposition, normal to the surface, should accompany the in-plane segregation induced by the surface patterns (see Fig. 1).

The experimental probe used was atomic force microscopy (AFM) (Topometrix; see Ref. [8]) The films were mixtures of dPS ($M_w = 1000$ g/mol, $M_w/M_n = 1.13$) and PB ($M_w = 5300$ g/mol, $M_w/M_n = 1.07$) [8]. This blend exhibits a bulk upper critical solution temperature of 51 °C, and a critical PS composition (volume fraction) of 0.7 [6,9]. Blend mixtures of critical composition were dissolved in toluene and spin-cast [6] on silicon wafers coated with gold and patterned over areas approximately equal to 1 cm² with alkanethiols using μ CP. Our previous study on an unpatterned substrate (hydrogen passivated silicon) showed a suppression of surface-directed spinodal decomposition in films thinner than 2000 Å [6], and here we employ films (approximately 700 Å in thickness) that should be well within this ultrathin range. μ CP of alkanethiols on gold-coated (≈ 1000 Å thick) silicon wafers has also been discussed previously [10]. In brief, elastomeric stamps were formed by casting and curing PDMS against photolithographically patterned photoresist on silicon wafers. Stamps formed in this manner were used to print “ink,” consisting of hexadecanethiol [$\text{HS}(\text{CH}_2)_{15}\text{CH}_3$] in 1 μ mol ethanol solution onto a gold substrate. Washing the printed wafer with a 1 - μ mol ethanol solution of $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ formed carboxylic acid-terminated alkanethiols in regions of the surface not derivitized from methyl-terminated alkanethiols.

Several studies have characterized the topography and frictional properties of these model chemically patterned substrates [10,11]. Atomic force microscopy measurements indicated that our surface samples were very smooth (rms roughness ≤ 5 Å), so that the end functionalization of the alkanethiols does not appreciably affect the local film thickness. As in previous measurements, the chemical patterns are sharply defined by the frictional contrast between the hydrophobic and hydrophilic end groups in lateral force measurements. The μ CP stripe pattern utilized in our measurements on blend phase separation has a period of 4 μ m comprised of 1 μ m wide $-\text{COOH}$ -terminated stripes alternating with 3 μ m wide $-\text{CH}_3$ -terminated stripes.

Figure 2 shows topographic AFM images of a dPS-PB film undergoing phase separation on the μ CP patterned surface described above. These images were collected after a relatively short time (1.5 h) in the two-phase region at $T = 25$ °C. While there was no topographic structure in the bare μ CP patterned surface, the phase-separating blend

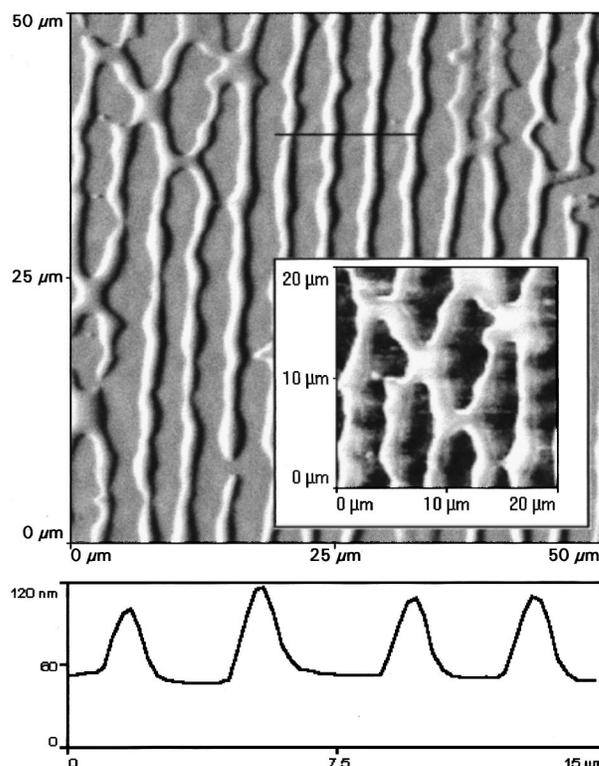


FIG. 2. Intermediate stage of dPS/PB blend film phase separation on a μ CP patterned surface. AFM image of topography with accompanying line profile (1.5 h at 25 °C). Solid line on figure denotes line profile position. Inset shows lateral force image (lighter PB-rich regions have higher friction) corresponding to the topography at the upper left-hand corner.

tracked the underlying pattern. Accompanying line profiles of the AFM images indicate that the narrower (≈ 1 - μ m-wide) and brighter stripes are higher. The topographical and lateral force images are similar, allowing us to determine whether the stripes were enriched in dPS or PB. We then find from the lateral force images (see inset) that the narrower, higher-friction, striped regions on top of the 1 μ m wide $-\text{COOH}$ SAM stripes are PB-rich regions. It is expected that the PB-rich regions are higher because they must occupy a smaller available surface area, but a quantitative prediction of this height asymmetry is complicated by a number of factors. An accurate description of the relative volume fractions of the coexisting phases requires further theoretical investigation and experiment on effects that occur in ultrathin films (e.g., changes of the coexistence curve shape, and the critical temperature, substrate-dependent tendency for segregation to occur normal to the solid substrate, and the deformability of the polymer-air boundary). The relative polymer volume fractions and relative surface pattern areas seem to be the primary parameters controlling the film height variation in the present study.

Figure 3 shows a profile lateral force image of the phase-separation morphology at a later time (6 h). The phase-separation pattern is well aligned with the μ CP pattern with sharp interfaces between the dPS- and PB-rich stripes. Topographical images (not shown) confirm the sharpness of these boundaries. The ridgelike PB-rich stripes flattened with time, and had greater height variations (“defects”) than the dPS-rich stripes [it is emphasized that the lower dPS-rich stripes

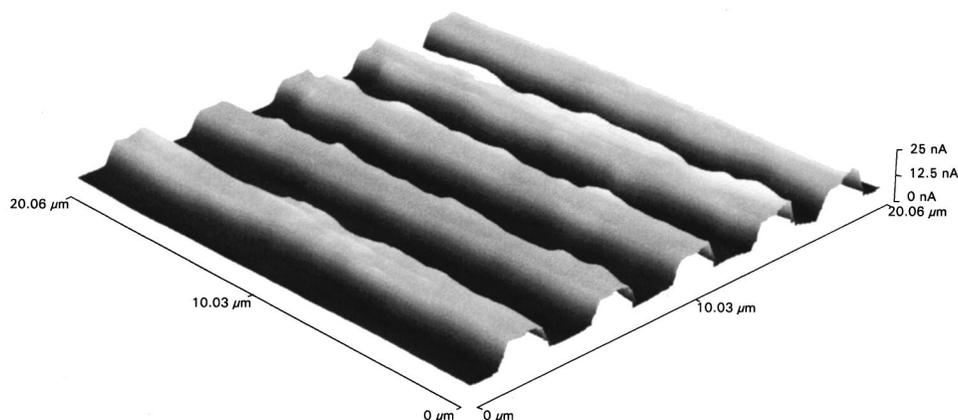


FIG. 3. Lateral force AFM image in profile view late stage of dPS-PB blend film phase separation on a μ CP patterned surface. Elevated regions correspond to PB-rich domains. The pattern is essentially unchanged after 24 h.

are significantly (≈ 50 nm) above the SAM surface]. We also noticed that imperfections in the μ CP pattern created some distortions in the initial blend pattern formation process, but these imperfections in the blend overlayer tended to “heal” at later times. After further periods of phase separation, the AFM and LFM patterns did not change in a detectable way and the film morphology was stable, at least for times on the order of days. These observations show the feasibility of using symmetry-breaking boundary perturbations to manipulate the local structure of phase-separating blend films.

As a control measurement, phase-separation experiments on ultrathin (≈ 700 Å) dPS-PB blend films on a gold surface *without* a μ CP pattern showed an isotropic spinodal decomposition-type pattern, consistent with our previous optical microscopy studies of dPS-PB phase separation on hydrogen-passivated silicon substrates [6]. The presence of a surface pattern clearly breaks the symmetry of the film phase separation, leading to a stable surface morphology having a prescribed pattern.

If the μ CP stripe pattern scale becomes too large compared to the natural scale of phase separation, then phase separation should occur within each stripe pattern as for a uniform surface. There is clearly some upper limit on the scale at which the surface patterning can be controlled. We then examined larger-scale chemical patterns while holding the film thickness constant (≈ 700 Å) to better understand this limitation. For a μ CP pattern with a $10\ \mu\text{m}$ period having equal width $-\text{COOH}$ and $-\text{CH}_3$ stripes, the phase separation proceeded to late-stage droplet formation on each stripe, similar to observations on unpatterned surfaces [6]. Thus, finite-size effects are indeed insufficient to stabilize the striped patterns when the pattern scale becomes too large. The scale at which our loss of pattern resolution occurred was comparable to the scale at which our bicontinuous phase-separation pattern broke up into droplets and became “pinned,” as in our previous measurements on unpatterned surfaces [6]. We also found that the polymers tended to dewet the $-\text{CH}_3$ pattern regions in even thinner films (≤ 300 Å), leading to a rather different film morphology. Thus, we must admit that the polymer-blend film patterning has some sensitivity to film thickness. It may be possible to eliminate

these dewetting complications by using $-\text{COOH}$ and $-\text{OH}$ end-group SAMs, which should have more favorable polymer-surface interactions for the dPS-PB blend.

This study has shown how the spinodal decomposition process can be manipulated using surface patterns created by microcontact printing μ CP of functionalized molecules on the solid substrate supporting the blends. In ultrathin blend films, blend components track the μ CP surface pattern and it seems likely from our simulations that more complicated three-dimensional structures can be formed in thicker films having modulated surface interactions (e.g., checkerboards). Blend films exhibiting stable and well-aligned stripes were formed on striped μ CP substrates when the film thickness was restricted to a range thin enough to suppress surface-directed spinodal decomposition, but thick enough to avoid dewetting phenomena. The upper scale of pattern control was set by a scale where the bicontinuous pattern breaks up on unpatterned surfaces (on the order of a few micrometers), and our preliminary experiments indicate that a film-thickness-dependent minimum length scale for pattern control also exists. The strategy of creating surface structure by nanofabricating surface template patterns should find increasing application in engineering [12], especially as fabrication of “master” surface patterns, and their impressions at smaller dimensions, become more routine.

Note added in proof: Since this work was submitted for publication we became aware of a related work [M. Böltan, S. Walheim, J. Mlynek, G. Krausch, and U. Steiner, *Nature* (London) **3391**, 877 (1998)] showing the control of structure of phase-separated blends through the use of SAM patterns on the solid substrate.

We thank Brett Ermi for investigations of film thickness effects on PS-PB film phase separation on patterned SAM substrates, and Steve Granick, LiPiin Sung, George Krausch, and Ulli Steiner for their many helpful comments. We thank Jimmy Mays for the polymers. Financial support of the research at Harvard was provided by the NSF Grant No. (Phy-9312572), DARPA, and ONR. J.A.R. and R.I.J. acknowledge funding from the Harvard Society of Fellows NSERC scholarship program, respectively.

- [1] J. D. Gunton, M. San Miguel, and P. Sahni, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8, p. 267, and references therein.
- [2] S. C. Glotzer, *Ann. Rev. Comp. Phys.* **2**, 1 (1995).
- [3] S. Puri and H. L. Frisch, *J. Phys.: Condens. Matter* **9**, 2109 (1997), and references therein.
- [4] B. P. Lee, J. F. Douglas, and S. C. Glotzer (unpublished).
- [5] R. A. Jones *et al.*, *Phys. Rev. Lett.* **66**, 1326 (1991); G. Krausch *et al.*, *Ber. Bunsenges. Phys. Chem.* **98**, 446 (1994).
- [6] L. Sung, *Phys. Rev. Lett.* **76**, 4368 (1996).
- [7] G. Krausch, *et al.* *Appl. Phys. Lett.* **64**, 2655 (1994). The surface patterning of this paper utilized an etching method where stripes of hydrogen-passivated silicon were created, separated by chromium spacer stripes. Local surface topography and chemistry are both changed in this type of solid substrate patterning. Experimental verification of the checkerboard composition modulations predicted in the thicker films [Fig. 1(a)] is difficult and is avoided in the present study.
- [8] The reference to commercial equipment does not imply its recommendation or endorsement by the NIST. According to ISO 31-8 the term “molecular weight” has been replaced by “relative molecular mass” M_r . The older, more conventional, notation for number and weight-average molecular weights is utilized here.
- [9] L. Sung and C. C. Han, *J. Polym. Sci., Polym. Phys. Ed.* **33**, 2405 (1995).
- [10] A. Kumar *et al.*, *Langmuir* **10**, 1498 (1994); C. D. Bain *et al.*, *JACS* **111**, 321 (1989); J. L. Wilber *et al.*, *Adv. Mater.* **6**, 600 (1994); A. Wilber, *Langmuir* **11**, 825 (1995); N. B. Larsen *et al.*, *J. Am. Chem. Soc.* **119**, 3017 (1997).
- [11] P. M. St. John and H. G. Craighead, *Appl. Phys. Lett.* **68**, 1002 (1996); P. C. Hidber *et al.*, *Langmuir* **12**, 1375 (1996).
- [12] R. P. Feynman, reprinted note in *J. Microelectromech. Syst.* **1**, 60 (1992).