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Phase-Separation-Induced Surface Patterns in Thin Polymer Blend Films

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Received May 16, 1997; Revised Manuscript Received October 13, 1997

ABSTRACT: Atomic force microscopy (AFM), neutron reflection (NR) and secondary ion mass spectroscopy (SIMS) are used to examine phase separation in symmetrically segregating thin polymer blend films (≤ 1000 Å). Phase separation in the film leads to undulations of the liquid–air interface, provided the film is sufficiently thin to suppress surface-directed spinodal decomposition waves. Flattened droplets are formed at a very late stage of phase separation, and the aspect ratio of these droplets can be rationalized by an interfacial free energy minimization argument.

1. Introduction

The study of liquid–liquid phase separation in thin films confined between two impenetrable plates has been the focus of much current research.^{1–3} Recent studies have also focused on the corresponding phenomena for polymer thin film coatings with a deformable polymer–air interface,^{4–9} where surface tension has a strong influence on the boundary shape. The inherent flexibility of this interface can cause the film surface to form unique patterns which track the underlying phase separation process within the film. As summarized in the next paragraph, most previous measurements consider the case where the blend components segregate asymmetrically to the two interfaces (“asymmetric surface segregation”), which induces the blend to stratify into a bilayer when phase separation occurs. In contrast, the present work emphasizes *symmetrically surface segregating* thin blend films, where the same blend component is preferred at both interfaces, and is applicable only for films thin enough to suppress the development of surface-directed spinodal decomposition waves.^{9,10} Under these circumstances, we observe that the blend phase separation within the film is accompanied by undulations of the free boundary height.

Previously, Kajiyama et al. measured the local viscoelastic properties of ultrathin phase separated polystyrene (PS)/poly(vinyl methyl) ether (PVME) blend films cast on hydrophilic silicon at ambient temperature using atomic force microscopy (AFM).⁶ They reported that for films thinner than twice the radius of gyration of the unperturbed chains, dewetted PVME droplets formed on top of a layered PS phase at the Si surface (“asymmetric” segregation). Klein et al.⁷ observed a transient “roughening” of the air–film boundary in thicker films [i.e., $D/R_g > 20$] of asymmetrically segre-

gating polyolefin blend films due to an initial unfavorable placement of polymer components at the air and silicon boundary, but the final state of the film was a bilayer having a smooth surface. Straub et al.⁵ briefly report observing a film thickness dependence of this “roughening” phenomena.

In contrast to these earlier measurements, here we focus on symmetrically surface segregating blend films undergoing phase separation.^{10,11} The results of the present paper stimulated our earlier studies reported in refs 10 and 11. Previously,¹⁰ an optical microscopy study emphasizing the kinetics of phase separation in thin films was presented for a symmetrically segregating blend system, polystyrene and polybutadiene on a hydrophobic silicon substrate. It was found that films less than ≈ 2500 Å were thin enough to suppress the development of surface-directed spinodal decomposition waves.^{9,10} The present paper provides strong evidence that the optical measurements (in films¹⁰ as thin as 200 Å) were made possible primarily by optical path length variations introduced as a result of undulations of the phase separating film surface rather than refractive index contrast between coexisting phases inside the film. AFM images of typical quenched film surface patterns showing an evolution to an intermediate–late stage of phase separation are presented. These observations are consistent with simulations of surface pattern formation in thin film phase separation.¹¹ An estimate of the late-stage pattern size based on an interfacial free energy minimization scheme is also presented.

2. Experimental Section

Measurements are reported here on two symmetrically segregating blend systems.

The first is dPS ($M_w = 443\,000$, $M_w/M_n = 1.05$, $T_g = 105$ °C)/PVME ($M_w = 84\,000$, $M_w/M_n = 1.40$, $T_g = -40$ °C) films, which exhibit a lower critical solution temperature (LCST ≈ 140 °C) in the bulk.¹² The films were cast on a hydrophobic, HF-etched silicon substrate.

The second is Poly(ethylenepropylene), PEP ($M_w = 290\,000$, $M_w/M_n = 1.02$, $T_g = -40$ °C)/deuterated polyethylenepropylene,

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dPEP ($M_w = 374\,000$, $M_w/M_n = 1.02$, $T_g = -40\text{ }^\circ\text{C}$), films which have an upper critical solution temperature (UCST $\approx 241\text{ }^\circ\text{C}$) in the bulk.¹³ Films were cast on a hydrophilic silicon oxide surface.

Films of dPS/PVME mixtures (5–70 mass % dPS; 200–2500 Å thick), which were carefully dried before dissolving in toluene, were spin coated onto HF-etched Si substrates.¹⁴ Film thickness could be controlled by solution concentration and spin speed, e.g., a 2 mass % dPS/PVME polymer solution spun at 3000 rpm produced a blend film of thickness of approximately 850 Å. Neutron reflection (NR) measurements on as-cast blend films indicate that the average film composition is indistinguishable from the solution composition. Phase separation was achieved by annealing at elevated temperatures in the two-phase region under high vacuum ($\approx 10^{-6}$ Pa) to prevent oxidative degradation of the polymers and dewetting due to hydration of the substrate.¹⁴ Films of PEP/dPEP mixtures (50% by mass) were spin coated from toluene solutions onto Si substrates, which had been cleaned in an oxidizing mixture of sulfuric acid/hydrogen peroxide (7:3 by volume) at 80 °C for 120 min to ensure that the Si surface was hydrophilic. The films were then annealed deep in the bulk two-phase region at 90 °C.¹³

The surface topography of both blend systems was characterized by AFM. In addition, simultaneous friction and elastic compliance measurements using a Topometrix¹⁵ atomic force microscope permitted the evaluation of the areal distribution of the two polymers in the dPS/PVME case¹⁶ since the dPS is glassy at room temperature, whereas the PVME is liquidlike. However, no such contrast is available for the PEP/dPEP system. The samples were scanned at a rate of 1 Hz using a Si_3N_4 cantilever tip with a force of 10 nN, modulated at 2 kHz with a vertical rms amplitude of 200 Å.

NR measurements^{17a} presented here were performed at the NG7 reflectometer at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. Briefly, the technique at NIST consists of reflecting a well-collimated beam of neutrons of fixed wavelength (4.7 Å) from the sample surface and varying the neutron momentum by varying the angle of incidence on the sample surface, typically between 0 and 3°. The reflected beam is picked up by a neutron detector at a reflection angle that is same as the angle of incidence, and the incident, reflected, and film normal are in one plane (specular reflectivity). NR measurements were conducted in-situ in a vacuum chamber on-line at elevated temperatures, while all other instrumental measurements were performed at room temperature within 8 h of quenching the sample to room temperature.¹⁸ The reflectivity data were fit by using a standard multilayer fitting routine for scattering length densities described in ref 17a.

Static and dynamic secondary ions mass spectrometry (SIMS) measurements of surface and depth profile analysis were carried out on an Atomika 6000 SIMS instrument¹⁵ equipped with a negative Argon ion beam rastering the sample surface at an operating voltage of 2 kV and a base pressure of 1.3×10^{-6} Pa. A more detailed description of the technique as applied to polymer depth profiling, surface analysis and mass assignments can be found in ref 17b.

3. Results and Discussion

Neutron reflectivity (NR) measurements were made on an 850 Å thick dPS/PVME film of composition $\phi_{\text{dPS}} = 0.30$ at several annealing temperatures between 100 and 180 °C, i.e., over a temperature range covering the single- and two-phase region of the bulk phase diagram (Note that the bulk binodal at $\phi_{\text{dPS}} = 0.30$ is estimated to be $\approx 150\text{ }^\circ\text{C}$).¹² Parts a and b of Figure 1 show representative NR data obtained on this sample after it was heated under vacuum for 120 min each, in the single-phase region at $T = 110\text{ }^\circ\text{C}$ and subsequently in two-phase region at $T = 170\text{ }^\circ\text{C}$.¹⁹ The NR profile at $T = 110\text{ }^\circ\text{C}$ stopped evolving after 120 min of annealing,

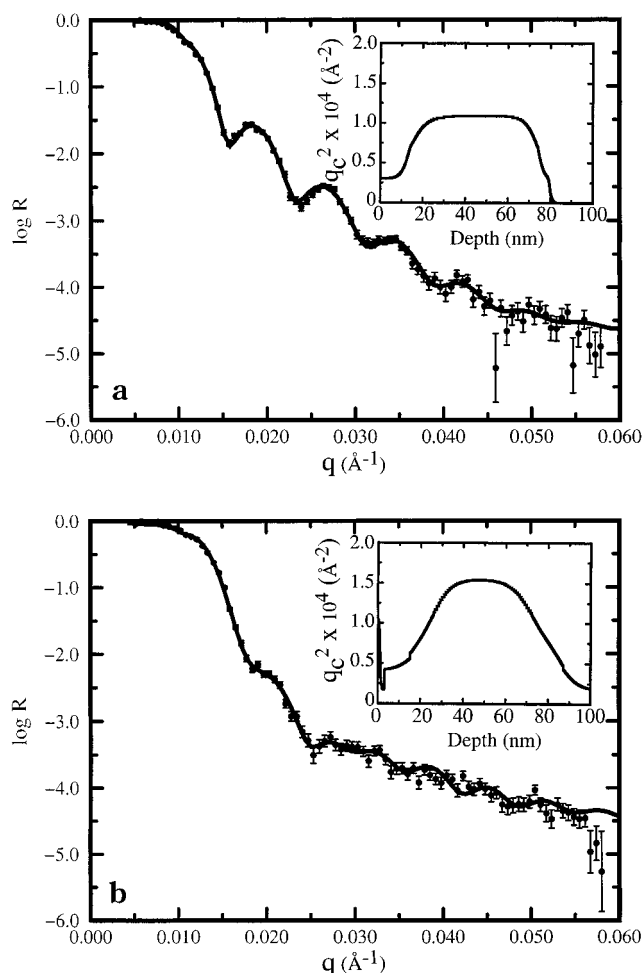


Figure 1. (a) NR spectrum from an 850 Å thick spin-coated dPS/PVME ($\phi_{\text{dPS}} = 0.30$) film annealed for 120 min (profile does not evolve for longer times) in a vacuum at 110 °C. The insert shows the volume fraction profile corresponding to the fit to the reflectivity data. A relative decrease of scattering length density at the air surface ($z = 0$ nm) and at the HF etched silicon surface ($z = 85$ nm) indicates a qualitatively symmetric surface segregation of excess PVME. (b) NR spectrum from the same film after annealing for 120 min. (profile continues to evolve with time) in a vacuum at 170 °C shown for qualitative comparative purposes only. The volume fraction profile insert illustrates that the segregation of PVME to the two boundaries is heightened due to phase separation. Additionally, the apparent film thickness increases due to undulations of the air–film boundary (see Figure 4b).

while it continued to change with time at $T = 170\text{ }^\circ\text{C}$, consistent with the notion that these two temperatures correspond to the single- and two-phase region of the phase diagram, respectively. (An estimate of the binodal temperature for the thin film and the temperature dependence of the concentration profile is out of the scope of the present paper, and this will be reported separately.) It should be appreciated that the NR profile at $T = 170\text{ }^\circ\text{C}$ was taken while the structure was slowly changing and is only shown for qualitative comparative purposes.

The composition profile shown in the insets to Figure 1a,b demonstrates an enrichment of lower scattering length density PVME ($q_c^2 \approx 0.18 \times 10^{-4}\text{ Å}^{-2}$) over dPS ($q_c^2 \approx 3.14 \times 10^{-4}\text{ Å}^{-2}$), to both the vacuum and HF etched silicon interfaces at the two temperatures. Likewise, Figure 2 shows a dynamic SIMS²⁰ depth profile obtained on an annealed (in the two-phase region) 1700 Å thick dPEP/PEP blend film with com-

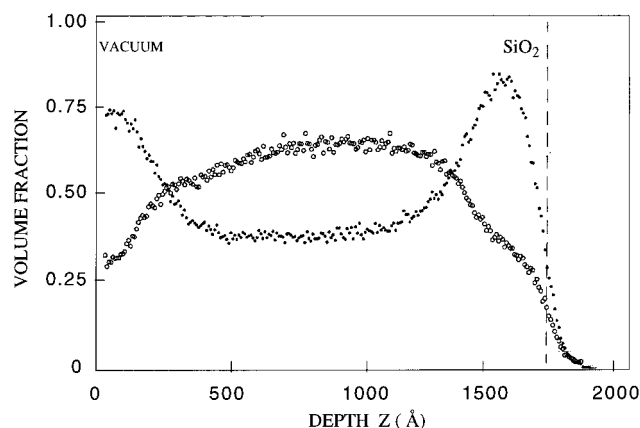


Figure 2. Dynamic SIMS depth profile of an ~ 1700 Å thick dPEP/PEP blend film with composition $\phi_{\text{dPEP}} = 0.5$, quenched into the bulk two-phase region at 90°C for ~ 2 h (solid circles = dPEP; open circles = PEP). The development of surface topology with phase separation in these thicker films is significantly suppressed,¹⁰ so that the concentration profile obtained is a semiquantitative indication of the average local concentration depth profile.

position $\phi_{\text{dPEP}} = 0.5$, which confirms the preference of dPEP over the nondeuterated PEP phase at both interfaces (similar to observations by Krausch et al.⁹ for methyl-terminated organic monolayer on Si only).

Thus, both blend systems discussed above are in the category of symmetrically surface segregating films.

In fact, static SIMS measurements (see Figure 3) on identically prepared and treated dPS/PVME films (quenched to ambient temperature and measured within a few hours¹⁸) confirm that a pure layer of PVME is present for at least the top 5 Å of the outer surface of the film, regardless of whether it was annealed at 110 or 170°C . This result is a consequence of the lower surface tension of PVME and is consistent with measurements in bulk samples of PS/PVME by Dee et al.,²¹ which show that the surface tension above and below the binodal approaches that of pure PVME, even when the PVME composition was only $\sim 18\%$. Such a thin layer of pure PVME is undetectable by NR due to its very low scattering length density and limits of depth resolution of NR (~ 10 Å under ideal conditions).

The inset profiles of Figure 1 shows that the film thickness has seemingly increased from 850 Å at 110°C to above 1000 Å at 170°C . This apparent paradox is resolved by AFM measurements of the surface topography at different temperatures. The AFM image of an 850 Å thick dPS/PVME blend film ($\phi_{\text{dPS}} = 0.30$) annealed in the one-phase region at 130°C (a similar result is obtained at 110°C) and quenched to room temperature exhibited a smooth surface with a root-mean-squared surface roughness of about 6 – 10 Å

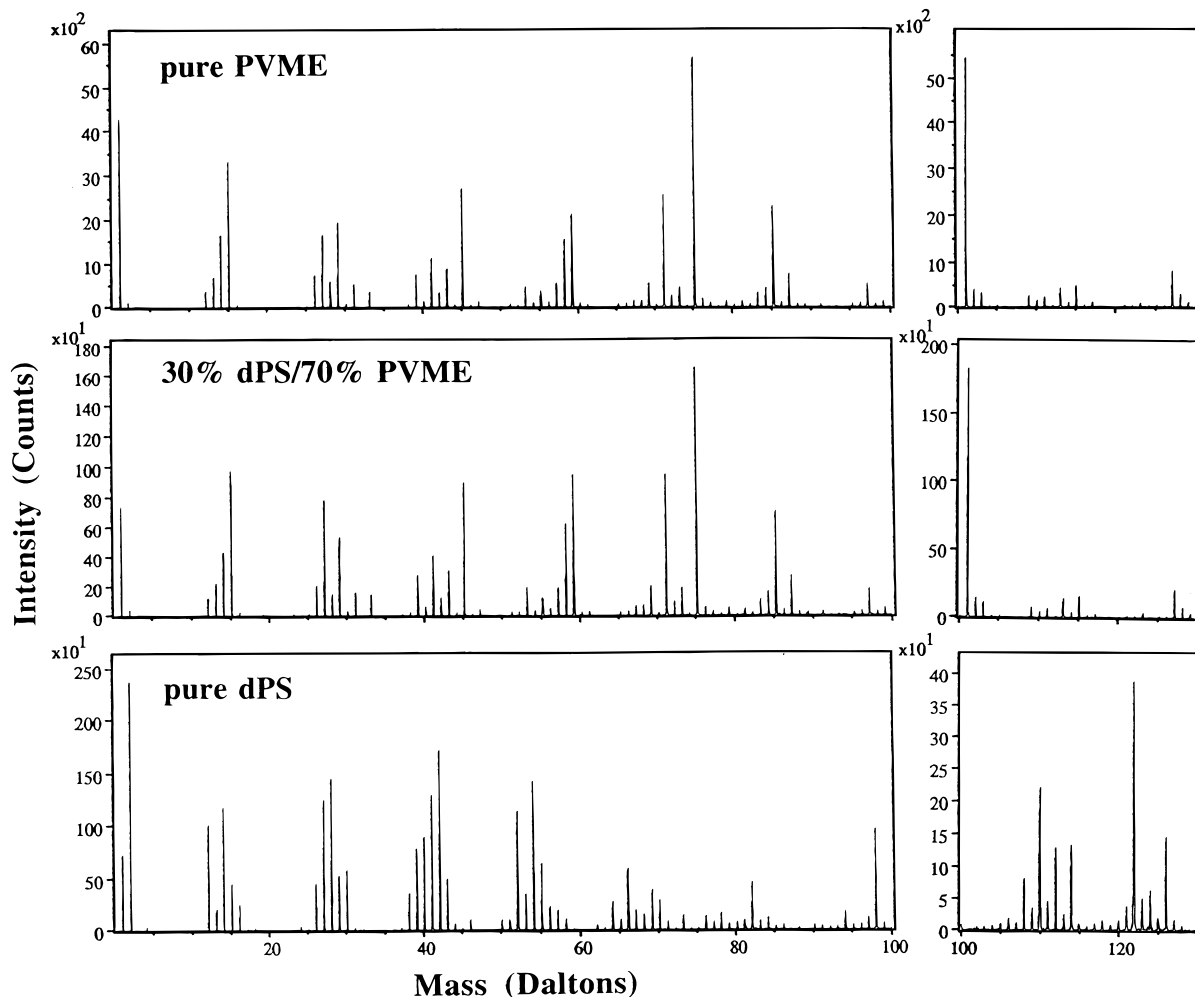


Figure 3. Static SIMS from a dPS (30%)/PVME (70%) blend film (middle spectrum) annealed at 170°C . The blends spectrum is almost identical with that of pure PVME (top spectrum) but quite different from that of pure dPS (bottom spectrum). The x -range is split to accommodate changes in y -scale intensity counts that are individually adjusted in each plot for maximum counts display.

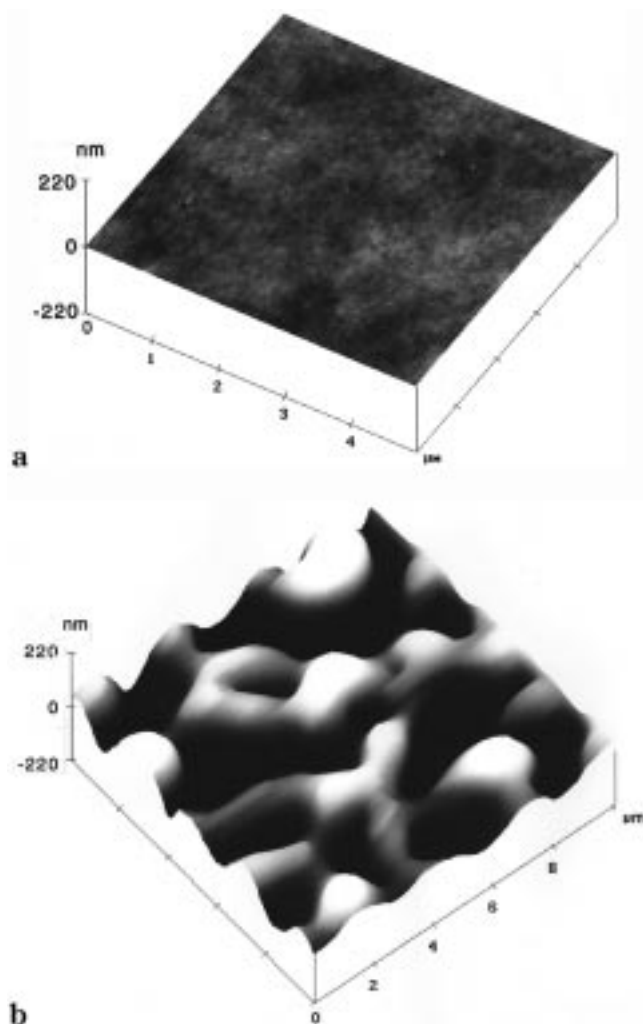


Figure 4. Three-dimensional AFM topographical image of an 850 Å thick dPS/PVME ($\phi_{\text{dPS}} = 0.30$) film after annealing under vacuum for 120 min at (a) 130 °C and (b) 170 °C. The samples were measured after quenching to room temperature. The undulations of the film surface in part b are apparently caused by variations of the interfacial tension within the plane of the film arising from phase separation.

(Figure 4a). In contrast, the surface topography of the film changed dramatically when heated to $T = 170$ °C (bulk two-phase region) for 120 min (see Figure 4b). The surface is now undulating with features on the surface protruding approximately 2500 Å above the base level. While it is not possible to definitely state the origin of the surface roughening from our NR or AFM data, the image certainly has the appearance of a pattern obtained from a blend undergoing spinodal decomposition in the bulk. Our previous optical microscopy study¹⁰ of phase separation kinetics in another symmetrically segregating blend is in agreement with this interpretation.

If the topographical features occur as a result of lateral phase separation within the film at $T = 170$ °C, then the regions rich in dPS should have a very different mechanical response from the rubbery PVME-rich areas. These expectations are indeed verified from the AFM measurements shown in Figure 5. Figure 5a shows the surface topography of a sample prepared in a similar manner at $T = 170$ °C, while parts b and c of Figure 5 show the corresponding friction and compliance images.¹⁶ The frictional response of the flat regions is approximately four times greater than that of the higher

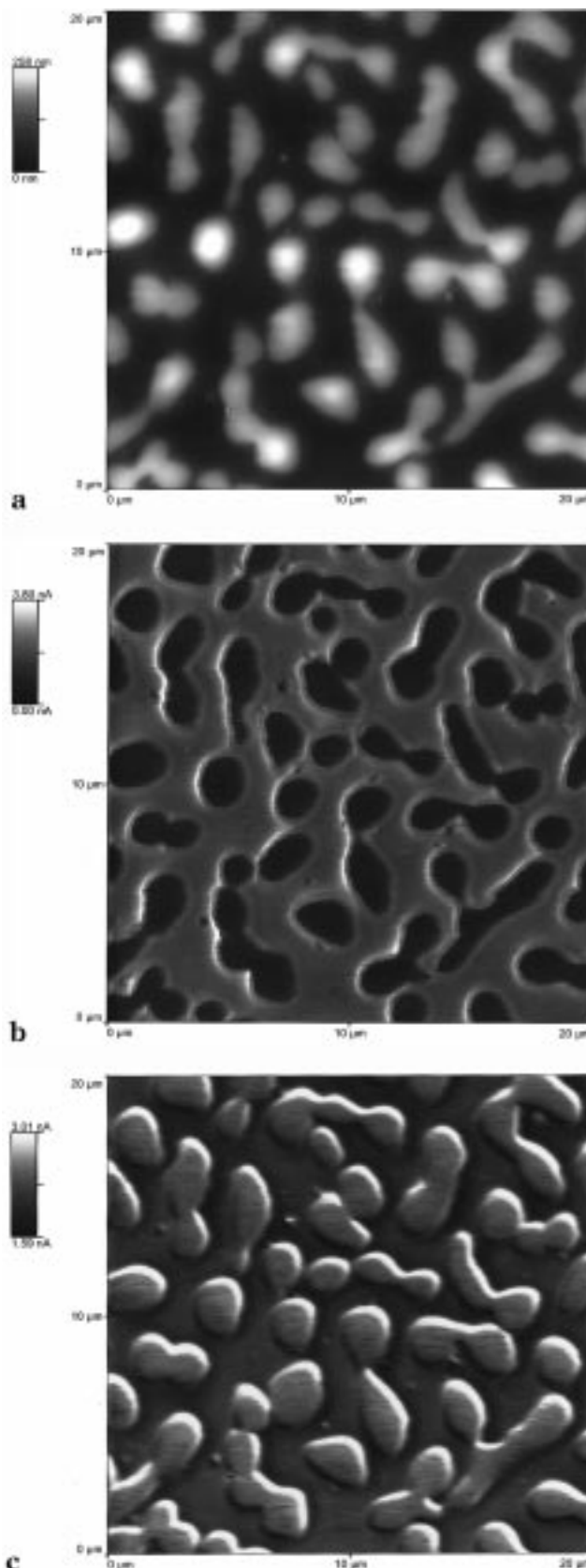


Figure 5. AFM measurements of (a) topography, (b) friction, and (c) compliance, recorded for the same area of a phase-separated film of dPS/PVME ($\phi_{\text{dPS}} = 0.30$) annealed at 170 °C.

protrusions.²² This is supported by the compliance measurements which show that the protrusions are much stiffer than the surrounding shallow sections. Local, low frequency measurements at 100 Hz show a

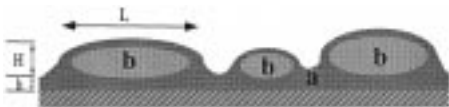


Figure 6. Schematic cross section of the phase-separated layer where a and b depict the coexisting dPS- and PVME-rich phases, respectively. The degree of connectivity within the plane depends on the stage of phase separation. At late stage, these form pinched-off "pancake-shaped" droplets with average dimensions L and height H ($H/L \ll 1$).

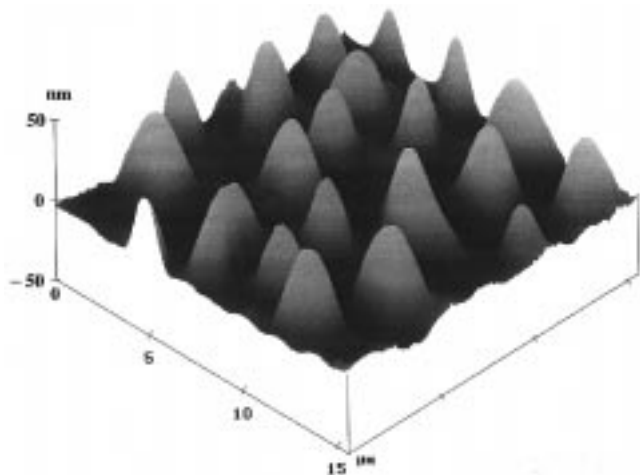


Figure 7. AFM image of an 800 Å thick dPEP/PEP film ($\phi_{\text{dPEP}} = 0.5$). The sample was quenched into the two-phase region at 90 °C for ~48 h. These images are similar to optical micrographs of late-stage phase separation for another symmetrically segregating blend in ref 10, where the size of the "pancake-shaped" droplets increased with film thickness.

decrease in the storage modulus by a factor of ≈ 5 on the flat areas relative to the protruding sections. From these results we can conclude that the elevated regions are behaving like a glassy or very viscous polymer liquid while the flatter and lower regions are less viscous.²³ As mentioned before, the static SIMS measurements (Figure 1c) confirms presence of pure PVME at the top ≈ 5 Å of the film surface, which supports the conclusion that the protrusions are the dPS-rich phase encapsulated by a thin layer of PVME, presumably due to its higher mobility and lower surface tension. Unlike the work of Marti et al.,¹⁶ the cover PVME layer is liquid-like and much thinner in our case, and consequently the subsurface nanomechanical contrast between phase-separated PS- and PVME-rich regions is detectable. Therefore, the surface roughening is interpreted as resulting from lateral phase separation of the mixture within encapsulating PVME layers. This is illustrated schematically in cross section in Figure 6. Continuity of the phases within the layer no doubt depends on the degree to which the spinodal decomposition process has developed.¹⁰

To indicate the generality of the phenomena, we briefly describe the phase separation-induced pattern formation for yet another symmetrically segregating blend film, PEP/dPEP. This system has a UCST, rather than LCST, type phase separation so that the bulk phase diagram is "inverted" in temperature as compared to dPS/PVME. The film thickness is kept very similar to the dPS/PVME case to minimize complications arising from finite size effects. Figure 7 is an AFM image of an 800 Å thick PEP/dPEP film (50% composition by volume), annealed at 90 °C for 48 h. The AFM image shows isolated droplets that are ≈ 250 Å in height and

2–3 μm in diameter, arranged in an arraylike fashion. This image is very similar to what was observed through optical microscopy in another symmetrically segregating UCST blend system in the *very late stages* of phase separation.¹⁰ This result is expected to be due to the large quench depth ($\Delta T \approx 151$ °C) in the present measurements, which results in faster kinetics. Additionally, the annealing time was longer in comparison to the dPS/PVME measurements. Thus, we believe that the phenomena of phase-separation-induced surface pattern formation is generic to symmetrically surface segregating thin blend films.

The spreading coefficient, $S_{b,a}$ provides a criterion²⁴ for the encapsulation of one coexisting phase (b) by another (a). Specifically, $S_{b,a} = (\gamma_{b,s} - \gamma_{a,s}) - \gamma_p$, must satisfy the inequality, $S_{b,a} > 0$ at *both* the air and the substrate surfaces (s). Here, $\gamma_{b,s}$ and $\gamma_{a,s}$ are the surface tensions of the two phases and γ_p is the polymer–polymer interfacial tension arising from phase separation. This inequality is apparently satisfied for the dPS[~phase(b)]/PVME[~phase(a)] case based on our estimates of the surface and interfacial tensions,²⁵ but this could not be verified for the PEP/dPEP case.

The morphology of the films at late-stage evolve to a dropletlike form (see Figure 7 and ref 10), where the b phase (see Figure 6) has pinched off from the bicontinuous structure formed at an earlier stage of phase separation. These droplets evidently have an anisotropic "pancake-like" form so that the aspect ratio, α , the ratio of the height H to diameter L of the droplets, is small ($\alpha = H/L \ll 1$). We can obtain a theoretical estimate of α by minimizing the free energy for a flattened pancake droplet. For simplicity, we take the droplet to be rectangular in cross section which yields a simple scaling relation between α and the polymer–polymer interfacial and polymer–air surface energies, $\alpha \approx \gamma_p / \gamma_{b,s}$. Utilizing $\gamma_p \approx 1$ mN/m for dPS/PVME mixtures at $T = 170$ °C and $\gamma_p \approx 0.2$ mN/m for the dPEP/PEP blend at $T = 90$ °C²⁵ gives an order of magnitude difference in value of the aspect ratio, $\alpha \approx 1/30$ and $1/100$, respectively. The experimental value of α corresponding to the dPEP/PEP case can be estimated from Figure 7 where $H \approx 0.03$ μm and $L \approx 3$ μm , so that $\alpha \approx 1/100$, consistent with our theoretical order of magnitude estimate. Although this type of argument is not strictly applicable to the dPS/PVME structures shown in Figure 4b where the pancake droplets have not fully formed,¹⁰ we can nonetheless estimate the flattening of the surface features at an order of magnitude level. From the extremal height ($H \approx 0.2$ μm) and the average cross section width of the surface features ($L \approx 3$ μm) we estimate that $\alpha \approx 1/15$. The argumentation is rough in this case, but again the right order of magnitude is found.

In summary, we have observed a distinct surface patterning in thin films of phase separating binary polymer blends in which surface directed spinodal waves are suppressed. This phenomenon, which apparently reflects local variations of surface tension within the plane of the film, was observed in systems where the same component segregated to the vacuum and the substrate interfaces. A transition from asymmetric (most previous studies) to symmetric segregation can often be induced by simply tuning the polymer/substrate interaction through chemical modification of the substrate. The present work shows that this strategy not only alters the morphology of the film but also affects the character of phase separation in thin blend films

due to a coupling between the boundary segregation and finite size effects. The magnitude of the interfacial tension relative to the surface tension is shown to set the aspect ratio of the surface features in the limit of long times.

Acknowledgment. Partial financial support was provided by NSF [Penn State: DMR-9024234, CTS-931915. SUNY at Stony Brook: DMR-9316157], DOE [SUNY at Stony Brook: DE-FG02-93ER45481. T.P.R.: DE-FG03-88ER45375]. We thank Rick Goyette, and Gian Felcher for the NR studies, Steve Schwarz for the dynamic SIMS data, Barry Bauer for the PVME, Lewis Fetters for the PEP samples, and Y. Cohen and S. Reich for useful discussions. The NR work at Argonne National Laboratory was supported by DOE, BES-Materials Sciences, under Contract W-31-109-Eng-30.

References and Notes

- (1) Tanaka, H. *Europhys. Lett.* **1993**, *24*, 665 and references therein.
- (2) Liu, A. J.; Durian, D. J.; Herbolzheimer, E.; Safran, S. A. *Phys. Rev. Lett.* **1990**, *65*, 1897.
- (3) Reich, S.; Cohen, Y. *J. Polym. Sci. Polymer Phys. Ed.* **1981**, *19*, 1255.
- (4) Jones, R. A. L.; Norton, L. J.; Kramer, E. J.; Bates, F. S.; Wiltzius, P. *Phys. Rev. Lett.* **1991**, *66*, 1326.
- (5) Bruder, F.; Brenn, R. *Phys. Rev. Lett.* **1992**, *69*, 624. Straub, W.; Bruder, F.; Brenn, R.; Krausch, G.; Bielefeldt, H.; Kirsch, A.; Marti, O.; Mlyner, J.; Marko, J. F. *Europhys. Lett.* **1995**, *29*, 353.
- (6) Kajiyama, T.; Tanaka, K.; Ohki, I.; Ge, S.; Yoon, J.; Takahara, A. *Macromolecules* **1994**, *27*, 7932. Tanaka, K.; Yoon, J.; Takahara, A.; Kajiyama, T. *Macromolecules* **1995**, *28*, 934. Their observations of phase separation in PS/PVME on hydrophilic Si at ambient temperature (compare to $T_{c, bulk} \sim 150^\circ\text{C}$) was attributed to a large shift (destabilization) in the phase boundary due to finite size effects.
- (7) Steiner, U.; Klein, J.; Fetters, L. J. *Phys. Rev. Lett.* **1994**, *72*, 1498. Kramer, E. J. Personal communication.
- (8) Katzen, D.; Reich, S. *Europhys. Lett.* **1993**, *21*, 55.
- (9) Krausch, G.; Dai, C. A.; Kramer, E. J.; Marko, J. F.; Bates, F. S. *Macromolecules* **1993**, *26*, 5566. Krausch, G.; et al. *Ber. Bungen-Ges. Phys. Chem.* **1994**, *98*, 446.
- (10) Sung, L.; Karim, A.; Douglas, J. F.; Han, C. C. *Phys. Rev. Lett.* **1996**, *76*, 4368. Karim, A.; Douglas, J. F.; Sung, L.; Ermi, B. *Physics News in 1996* American Institute of Physics: New York, 1996; *APS News* **1997**, *6*, 25. Karim, A.; Satija, S. K.; Han, C. C.; Slawacki, T. M.; Kumar, S. K.; Russell, T. P. *ACS PMSE* **1994**, *71*, 280. Ermi, B.; Karim, A.; Douglas, J. F. *J. Polym. Phys.* **1998**, *36*, 191. Ermi et al. show that the structures which form in ultrathin films through phase separation dissolve when the film is reintroduced in the one phase region.
- (11) Keblinski, P.; Kumar, S. K.; Maritan, A.; Koplik, J.; Banavar, J. R. *Phys. Rev. Lett.* **1996**, *76*, 1106.
- (12) Han, C. C.; Bauer, B. J.; Clark, J. C.; Muroga, Y.; Matsushita, Y.; Okada, M.; Tran-Cong, Q.; Chang, T.; Sanchez, I. C. *Polymer* **1988**, *29*, 202. Hashimoto, T.; Kumaski, J.; Kawai, H. *Macromolecules* **1983**, *16*, 641.
- (13) Bates, F. S.; Rosedale, J. H.; Bair, H. E.; Russell, T. P. *Macromolecules* **1989**, *22*, 2557.
- (14) Our dPS/PVME blend films were observed to dewet either when cast on unetched hydrophilic Si or when the blend film (moisture sensitive PVME) was exposed to air for several days.
- (15) The reference to commercial equipment does not imply its recommendation or endorsement by the National Institute of Standards and Technology. 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-average (M_n) and weight-average (M_w) molecular weights is utilized in the present paper.
- (16) Marti, O.; Colchero, J.; Mlynek, J. *Nanotechnology* **1990**, *1*, 141. Krausch, G.; Hipp, M.; Boltau, M.; Marti, O.; Mlynek, J. *Macromolecules* **1995**, *28*, 260. Meter, G.; Amer, N. M. *Appl. Phys. Lett.* **1990**, *56*, 2100. Overney, R. M.; Meyer, E.; Frommer, J.; Brodbeck, D.; Luethi, R.; Howald, L.; Guentherodt, H. J.; Fujihura, M.; Takano, H.; Gotoh, Y. *Nature* **1992**, *359*, 133.
- (17) (a) Russell, T. P. *Mater. Sci. Rep.* **1990**, *5*, 171. (b) Schwarz, S. A.; Wilkins, B. J.; Pudensi, M. A. A.; Rafailovich, M. H.; Sokolov, J.; Zhao, X.; Zhao W.; Zheng, X.; Russell, T. P.; Jones, R. A. L. *Mol. Phys.* **1992**, *76*, 937. Sikka, M.; Singh, N.; Bates, F. S.; Karim, A.; Satija, S. K.; Majkrzak, C. F. *J. Phys. II (Fr.)* **1994**, *4*, 2231. Brant, P.; Karim, A.; Douglas, J. F.; Bates, F. S. *Macromolecules* **1996**, *29*, 5628. For mass assignments, see: *Static SIMS handbook of Polymer Analysis*; Hohlt, T. A., Ed.; Perkin-Elmer Corp.: Eden Prairie, MN, 1991.
- (18) Due to the glassy nature of dPS, the rate of remixing at room temperature is extremely slow and does not significantly affect our AFM measurements.
- (19) Significant off-specular scattering was only observed after several hours of annealing at 170°C . See Slawacki, T. M., PhD. Thesis, Penn State University, 1995. Thus we believe our NR results provide a reliable estimate of surface segregation. A more detailed study on the temperature and composition dependence of the NR data will be reported separately.
- (20) Coulon, G.; Russell, T. P.; Deline, V. R.; Green, P. F. *Macromolecules* **1989**, *22*, 2581.
- (21) Dee, G. T.; Sauer, B. B. *Macromolecules* **1993**, *26*, 2771.
- (22) Calibration measurements on thick liquid polymer films and pure polystyrene films show that the friction on the shallow flat regions is almost the same as that of pure liquid PVME while that on the protrusions is a factor of ~ 3 higher than that of pure PS.
- (23) Since the viscous penetration depth is on the order of centimeters, these measurements probe the full depth of the film.
- (24) Hobbs, S. Y.; Dekkers, M. E. J.; Watkins, V. H. *Polymer* **1988**, *29*, 1598. Aussere, D.; Raghunathan, V. A.; Maaloum, M. M. *J. Phys. II* **1993**, *3*, 1485.
- (25) Dee, G. T.; Sauer, B. B. *Macromolecules* **1993**, *26*, 2771. Bhatia, Q. S.; Pan, D. H.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2166. Sauer, B.; Rafailovich, M. H. Unpublished results.

MA970687G