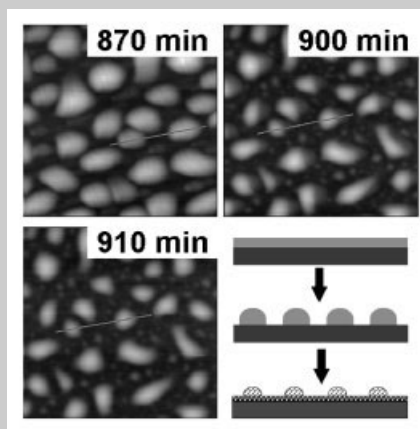


Summary: Dynamics of dewetting and phase separation in ultrathin films (thickness is ca. one radius of gyration, $\approx 1 R_g$) of poly(methyl methacrylate) (PMMA) and poly(styrene-*ran*-acrylonitrile) (SAN) blends on Si substrate has been studied by in situ atomic force microscopy (AFM). In the miscible region, a “spinodal-like” dewetting driven by a composition fluctuation recently predicted by Wensink and Jérôme (*Langmuir* **2002**, *18*, 413) occurs. In the two-phase region, the dewetting of the whole film is followed by phase separation in the droplets, coupling with the wetting of the substrate by the PMMA extracted by the strong attractive interaction between them.



Dewetting and Phase Behaviors for Ultrathin Films of Polymer Blend^a

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Introduction

The stability of polymer films is important for industrial applications ranging from coatings and soft lithography to biophysics, and for fundamental understanding of mean field theories of wetting.^[1] The polymers have been used to study the dewetting because of their two outstanding advantages.^[2] One is the mass conservation due to the very low vapor pressure; the other is the time resolution for the low mobility of polymer chains. There are many reports on dewetting of polymer films. However, most of them focused on single-component polymer films on different substrates, such as on silicon wafer, glass slide, and mica,^[2,3] on self-assembly monolayers or grafted substrate,^[4] on patterned substrate,^[5] or one component on top of another.^[6] In the

phase-separated regions, some thin blend films, such as poly(*p*-methylstyrene) and deuterated polystyrene,^[7] deuterated oligomeric styrene and oligomeric ethylene-propylene (OEP),^[8] OEP and hydrogenated oligomeric styrene,^[8] poly(vinyl methyl ether) and polystyrene,^[9] have been investigated, and the results suggest the formation of bilayer via phase separation, followed by the dewetting of the upper layer (the former of the blend) relative to another (the latter), which we call “phase separation/bilayer-dewetting” mechanism. When an ultrathin blend film of poly(styrene-*ran*-acrylonitrile) (SAN) and deuterated poly(methyl methacrylate) (dPMMA) ($\approx 3/4$ radius of gyration, R_g) was quenched into the two-phase region, according to the experimental data obtained by ex situ atomic force microscope (AFM), it was supposed that the dPMMA instantaneously wetted the silicon oxide substrate for their strong attractive interaction, and then the SAN molecules aggregated into SAN-rich droplets on the top of the sub- R_g layer of dPMMA.^[10] Recently, it was predicted that a film of a binary miscible polymer blend can dewet on a solid substrate, which

^a Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mrc-journal.de>, or from the author.

attracts one component preferentially.^[11] Under ambient conditions, a homogeneous thin or ultrathin film of a miscible polymer blend can be obtained by spin-coating since the solvent evaporates too fast for the polymer chains to reconstruct.^[11a] If one of the components interacts more favorably with the substrate than the other, it would diffuse to the substrate so as to create a composition gradient across the film when the film is heated to above its glass transition temperature (T_g). Since this diffusion cannot take place precisely in the same way over the whole film, this is likely to create composition fluctuations in the mixture along the surface. When the amplitude of this fluctuation is large enough, the free surface is eventually destabilized, i.e., the dewetting of this ultrathin film happens.^[11a] Unfortunately, there is no experimental evidence yet.

In this work, we present first direct experimental observations of this dewetting dynamics, driven by a composition fluctuation, of ultrathin films of PMMA/SAN blend in miscible region by in situ AFM,^[12] and then the dynamics of the complicated dewetting and phase behavior of this ultrathin film in two-phase region, which is not the phase separation/bilayer-dewetting mechanism,^[7–10] but the dewetting of the film is followed by the phase separation in the droplets, coupling with the wetting of the substrate by the PMMA extracted by the strong attractive interaction between PMMA and the substrate, which we call “dewetting-phase separation/wetting” mechanism.

Experimental Part

Materials

Poly(methyl methacrylate) ($\bar{M}_w = 387 \text{ kg} \cdot \text{mol}^{-1}$, PD = 3.72) and SAN (30% AN by mass, $\bar{M}_w = 149 \text{ kg} \cdot \text{mol}^{-1}$, PD = 2.66) were used without any further purification after purchased from Across and Aldrich, respectively. The glass transition temperatures of PMMA and SAN were 128.7 and 112.0 °C, respectively. This blend exhibits lower critical solution behavior with a critical temperature and composition of $\approx 165 \text{ °C}$ and ≈ 0.5 , respectively.^[12,13]

Sample Preparation

Silicon wafers were boiled in a bath of 100 mL of 80% H_2SO_4 , 35 mL of H_2O_2 , and 15 mL of deionized water for 15 min and rinsed in deionized water, and then blown dry with compressed nitrogen.^[12] Ultrathin blend films of PMMA/SAN with $90 \pm 2 \text{ \AA}$ ($\approx R_g$) were prepared by spin-coating a $1.0 \text{ g} \cdot \text{L}^{-1}$ 1,2-dichloroethane solution of the blend (50:50 wt.-%) onto the silicon wafer.

Characterization

The thickness of all films was measured by a Bruker D8 Discover X-ray reflectometer. The in situ topography and phase images were obtained simultaneously using an SPA-

300HV AFM (Seiko Instruments Inc., Japan) driven in tapping mode at high temperatures under ultrahigh vacuum ($< 10^{-4}$ Pa). A silicon tip (Budget Sensors, Bulgaria) with a spring constant of $40 \text{ N} \cdot \text{m}^{-1}$ was used. To ensure the steadiness of the contrast in the height and phase images and to minimize the influence of height variations on the phase images, the set-point ratio under ultrahigh vacuum was set at 0.96 ± 0.01 . The data of root-mean-square surface smoothness of height (RMS_h) and of phase (RMS_p) were directly obtained from topography and phase images of a $2 \times 2 \text{ }\mu\text{m}^2$ area using the commercial software bundled with the AFM, and the data of characteristic wave numbers, q^* , were computed from the topography image of a $2 \times 2 \text{ }\mu\text{m}^2$ area, where a further spherical average was performed after the routine 2D Fourier transforms (FT).^[12]

Results and Discussion

In our case, on a silicon wafer,^[12] although an ultrathin film of either pure PMMA or pure SAN (thickness $\approx R_g$) does not show any dewetting behavior after being annealed for 36 h under vacuum at 175 °C (cf. *Supporting Information*), well above their T_g 's, interestingly, an ultrathin film of their blend (50:50 wt.-%) with a similar thickness exhibits obvious dewetting behavior at 155 °C (Figure 1). The morphology features were flat [Figure 1(A)], pinhole [Figure 1(B)], bi-continuous [Figure 1(C)], and insular [Figure 1(D)], sequentially. Because this system completely matches the conditions of the composition fluctuation theory,^[11a] this may be the first example of the dewetting of polymer blends driven by this mechanism. PMMA/SAN is a typical system with lower critical solution temperature (LCST), which is miscible under ambient conditions, and the attractive interaction between the Si substrate and PMMA is stronger than that for SAN.^[10] The dewetting kinetics were followed by the power law of $q^* \approx t^{-n}$ (Figure 2), where q^* denotes the characteristic wave number of the topography images and t the annealing time. Based on the dependence of the exponent n on the annealing time, the dewetting of the

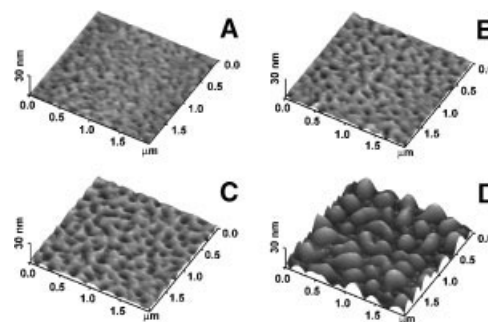


Figure 1. Snapshot images of the three-dimensional topography for an ultrathin film of PMMA/SAN blend (50:50 wt.-%) onto a silicon wafer, heated at 155 °C for 4 min (A), 31 min (B), 60 min (C), and 4015 min (D). The dimensions and the z -axes values are $2 \times 2 \text{ }\mu\text{m}^2$ and 30 nm, respectively.

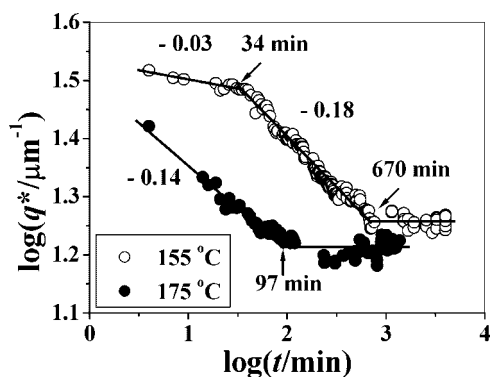


Figure 2. Characteristic wave number (q^*) computed from the topography images of a $2 \times 2 \mu\text{m}^2$ area for films annealed at 155°C (open circles) and 175°C (solid circles) vs. annealing time on a log-log scale.

ultrathin film follows spinodal-like mechanism. Initially, q^* is almost independent of the annealing time ($n \approx 0$). Then, $n \approx 0.18$, which is different from $1/3$ controlled by diffusion and 0.43 for polystyrene ($\approx 3 R_g$) on a silicon substrate.^[3a] Finally, q^* is almost independent of the annealing time again ($n \approx 0$). There are two crossovers (q^*), $30.55 \mu\text{m}^{-1}$ at 34 min and $18.09 \mu\text{m}^{-1}$ at 670 min .

However, when an ultrathin blend film is abruptly quenched into the two-phase region, combining the phase separation and the dewetting processes, there may be two types of behavior: (1) The film first phase separates into a bilayer, and then the upper layer dewets on the film of the other,^[7–10] namely, the phase separation/bilayer-dewetting mechanism. Even if the thickness was less than R_g (i.e., $\approx 3/4 R_g$), on the substrate, a sub- R_g layer of one component was supposed to completely wet the substrate once the film was quenched into the two-phase region.^[10] (2) The whole film first dewets the substrate and then phase separation occurs in the droplets, coupling with the wetting of the substrate by one component extracted by the strong attractive interaction between them, which we call dewetting-phase separation/wetting mechanism. All experimental results reported to date support the former, and there is no direct experimental observation of the latter case. We investigated the behavior of an ultrathin film of PMMA/SAN (50:50 wt.-%) ($\approx R_g$) on Si substrate after it was heated to 175°C , at which the blend was in two-phase region.^[10,12] First, a dewetting behavior similar to that observed at 155°C occurred with the power exponent $n = 0.14$ during the early time and $n \approx 0$ at the late stage (Figure 2). The first stage with $n \approx 0$ was not observed, and the crossover ($16.35 \mu\text{m}^{-1}$ at 97 min) between the power law growth of $t^{-0.14}$ in the early time and $t^{\approx 0}$ in the later time is much earlier than the second crossover ($18.09 \mu\text{m}^{-1}$ at 670 min) at 155°C presumably because the high temperature accelerated the dewetting dynamics. A detailed dewetting and phase separation process of this ultrathin film was monitored by in situ AFM (Figure 3). At 14 min , the phase contrast was more than 110° [Figure 3(b)].

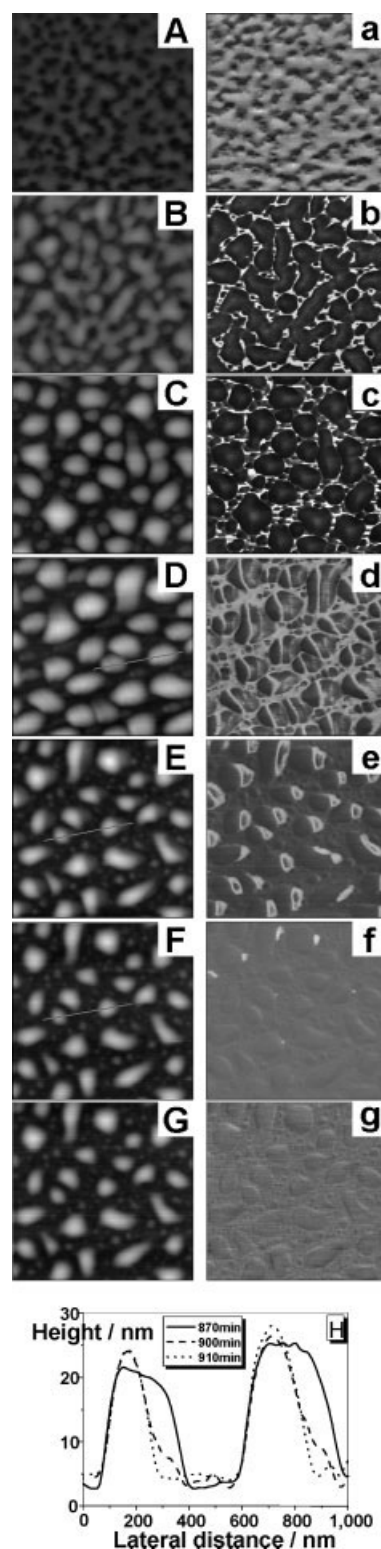


Figure 3. Topography (left) and phase (right) images for an ultrathin blend film annealed at 175°C for 4 min (A, a), 14 min (B, b), 182 min (C, c), 870 min (D, d), 900 min (E, e), 910 min (F, f), and 914 min (G, g). The z -axis values for the topography and the phase images are 35 nm , 23.0° for (a) and (g), and 110.0° for (b)–(f), respectively. The edge length of all images is $2 \mu\text{m}$. (H) is the sectional view along the lines in (D), (E), and (F).

Based on our previous work,^[12] the phase contrast between PMMA and SAN is much smaller at $\approx 10^\circ$ at this temperature because both of them are fluids with similar viscoelastic properties. Although a phase contrast depends on many factors, such as parameters that control the cantilever movement in the tapping mode, ambient conditions, in this case, a phase contrast of this magnitude should be mainly from the tip-sample interaction, the very hard substrate (solid), and the much softer polymer fluids, which has been verified by an elemental analysis method (cf. *Supporting Information*). This indicates that the film broke up and the Si substrate was exposed. This result is very different from dewetting behavior reported in the literature,^[7–10] namely, the film does not form bilayer first but wholly dewets. From 14 min [Figure 3(B)] to 182 min [Figure 3(C)], the continuous long ridges decayed into droplets, and the droplets became rounder and rounder. From ≈ 120 to 300 min, although the root-mean-square of height (RMS_h) increased gently with time, the root-mean-square of phase (RMS_p) decreased sharply (Figure 4). These results indicate that in this time period the droplets must be on a different substrate other than the *naked* Si. As mentioned earlier, at the experimental temperature (175 °C) at this composition, this polymer blend would phase separate. Since the attractive interaction between the Si substrate and PMMA is more favorable than that for SAN, this attraction is strong enough to compensate the loss of conformational entropy of the PMMA.^[10] Therefore, what happened was that PMMA separated from the fluid blend droplets spread onto the Si substrate, leading to decrease of RMS_p with time. However, RMS_h increased slightly with time, which implies that the coalescence of the droplets did not reach equilibrium. After ≈ 300 min, RMS_h remained almost constant with time, implying that coalescence of the droplets was approaching. The RMS_p , however, after slow decrease from ≈ 300 to 800 min, dropped sharply to $\approx 1.0^\circ$ and stayed there for the rest of the time. Under the experimental conditions, PMMA separates from the droplets and wets the Si substrate. The spread of the PMMA on the Si substrate slows down when the *naked* Si is covered completely. With the phase

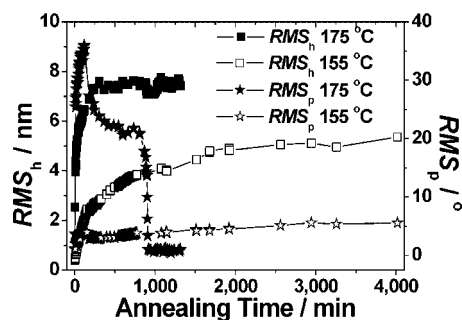


Figure 4. Time dependence of the root-mean-square of height (RMS_h) and the root-mean-square of phase (RMS_p) of a $2 \times 2 \mu\text{m}^2$ image at 155 and 175 °C.

separation continuing, steadily and slowly, more PMMA spread on the substrate, gradually thickening the PMMA layer, which damps the AFM tip, resulting in the slow decrease of the RMS_p . When this PMMA layer reaches a critical thickness, however, the AFM tip can no longer “feel” the hard Si substrate, and all it sees are soft SAN-rich droplets and soft PMMA liquid layer; the phase contrast between them is very small, and remains almost a constant. Additionally, the droplet size decreases with time. The mean diameters of the droplets are 246 nm [Figure 3(D)], 204 nm [Figure 3(E)], and 193 nm [Figure 3(F)]; and the height barely varies [Figure 3(H)]. Although the topography is almost constant after 910 min, the phase contrast becomes less and less. The obvious much lighter regions in Figure 3(f) disappear in Figure 3(g). Finally, at the very late stage [i.e., after 914 min in Figure 3(H)], the system almost reaches equilibrium, where the mean volume of the SAN-rich domains is about 62% of that of the blend droplets, and both RMS_h and RMS_p vary little with time. Furthermore, the phase images obtained at the very long annealing time provide evidence for the identification of the different domains. The liquid droplets are a little lighter than the valleys, and the phase contrasts are only $\approx 10^\circ$. According to our previous work,^[12] SAN domains are slightly lighter than PMMA domains. Therefore, these phase images prove that the droplets are SAN-rich, while the valleys are PMMA separated from the blend droplets spreading on the Si substrate. Additional experiments were carried out to provide further evidence (cf. *Supporting Information*). Furthermore, the SAN-rich domains cannot wet the ultrathin PMMA film.

From the above results, the complicated dynamic behavior of the ultrathin film in two-phase region can be interpreted as follows: first, the ultrathin film undergoes a spinodal-like dewetting process, driven by a composition fluctuation, which increases the conformational entropy; then the polymer blend fluid droplets experience phase separation coupled with the wetting of the Si substrate by the PMMA extracted by the strong attractive interaction between them; finally a stable structure forms of SAN domains dewetting the PMMA layer underneath which wets the Si substrate. Namely, here the complicated dynamic behavior does not follow phase separation/bilayer-dewetting mechanism but dewetting-phase separation/dewetting mechanism.

Conclusion

The dynamics of dewetting and phase separation in ultrathin films (thickness $\approx R_g$) of PMMA/SAN blends on Si substrate has been studied by in situ AFM. In the miscible region, a spinodal-like dewetting occurs, which is the first experimental evidence of dewetting induced by a composition fluctuation. In two-phase region, the dewetting of the whole film is followed by phase separation in the droplets, coupling with the wetting of the substrate by the PMMA

extracted by the strong attractive interaction between them. This dynamics in the two-phase region is dewetting-phase separation/wetting, which, to our knowledge, is also observed for the first time. In fact, this in situ AFM technique has indeed provided more information than ex situ AFM for our *ultrathin* polymer blend films, so it helps us reveal the complicated behavior of ultrathin blend films. However, further investigations, including quantitative or semi-quantitative studies of substrate-polymer and polymer-polymer interactions and the composition gradient effect are necessary to better understand such complicated processes.

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