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# Some views about the controversial dewetting morphology of polystyrene films

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**Abstract. PACS.** 47.20.Hw Morphological instability; phase changes – 68.15.+e Liquid thin films – 68.47.Pe Langmuir-Blodgett films on solids; polymers on surfaces; biological molecules on surfaces

It is well established that some polymer films supported by a substrate may rupture spontaneously by the spinodal mechanism [1–5]. The very criterion for this to happen is the free energy, $G(h)$, of the film as a function of film thickness, $h$, possesses a negative curvature at the starting thickness, $h_0$, i.e., $G''(h_0) < 0$. By using the mean field theory of Cahn [6] for spinodal decomposition of binary mixture, and assuming non-retarded Lifsitz-van der Waal's interactions for $G(h)$, i.e., $G(h) = -A/12\pi h^2$ (where $A$ is the Hamaker constant for polymer sandwiched between semi-infinite media of air and substrate) [7], it is straightforward to show that the initial dewetting morphology should display a characteristic length scale, $\lambda_m = (16\pi^3\gamma/A)^{1/2}h^2$ [8,9] where $\gamma$ is the surface tension of the polymer. Simulations based on linearized diffusion equations for the movements of the constituent molecules demonstrated that the spinodally destructing sample should develop the bicontinuous morphology [6]. While majority of studies of dewetting polymer films, encompassing a variety of polymer/substrate compositions, have found consistency with the $\lambda_m \sim h^2$ scaling [3,4,10,11] and hence supported the dewetting mechanism to be spinodal, many of these systems did not display the bicontinuous morphology but rather they showed isolated holes [5,10,11]. Jacob et al. [12] observed that the holes in some cases possessed no positional correlations, thus are unlikely results of spinodal dewetting. They proposed that the holes were due to heterogeneous nucleation. In principle, spinodal dewetting and heterogeneous nucleation can proceed in parallel [14,15], which largely weakens approaches that determine dewetting mechanisms by the film rupture morphology alone. Furthermore, it is recently recognized that scaling laws are generally unsuited for identifying spinodal dewetting since the dynamic range of $h$ over which the $\lambda_m \sim h^2$ scaling remains robust against corrections from retardation effects may be too small for the scaling law to be reliably checked [13]. As a result, the question of whether randomly distributed holes can be produced in polymer films dewet by the spinodal mechanism – notably polystyrene (PS) films with thicknesses $\geq 5$ nm – has been a much discussed issue. In this commentary, we examine whether randomly distributed holes can be produced in dewetting polymer films identified to be not dominated by heterogeneous nucleation based on a new method by us [13]. Then we discuss the evolution of dewetting morphology found in a 5.1 nm thick PS film that exhibited the said perplexing morphology. Based on these observations, we discuss the possible cause for the formation of the holes, and tentatively suggest a reason for why the controversy seems to be unique to PS films.

In the new method mentioned above [13], extrinsic defects were artificially introduced to the polymer film by rubbing the film surface with a piled fabric whereby the density of defects can be easily controlled by varying the number of rubbings. On the basis that the length scale of dewetting patterns dominated by heterogeneous nucleation should decrease with increasing density of the prescribed defects but that come from a spontaneous process should be relatively unaffected, we were able to unambiguously identify PS films ($M_w = 13.7$ kg/mol, $M_w/M_n = 1.1$) on oxide coated Si (where oxide thickness = 106 nm) with thickness, $h > \sim 13$ nm to be dominated by heterogeneous nucleation but those thinner than 13 nm are dominated by spinodal dewetting or a spontaneous mechanism.

We examine the dewetting morphologies that can arise in the thin film region ($h < 13$ nm). In Figure 1 is shown the time-series of atomic force microscopic (AFM) topographical images captured ex situ from two (unrubbed) films in this thickness range, one with $h = 3.2$ nm in the deep spinodal regime, and one with $h = 12.8$ nm close to the crossover thickness of 13 nm. In the $h = 3.2$ nm film, the evolution of morphology resembled that found

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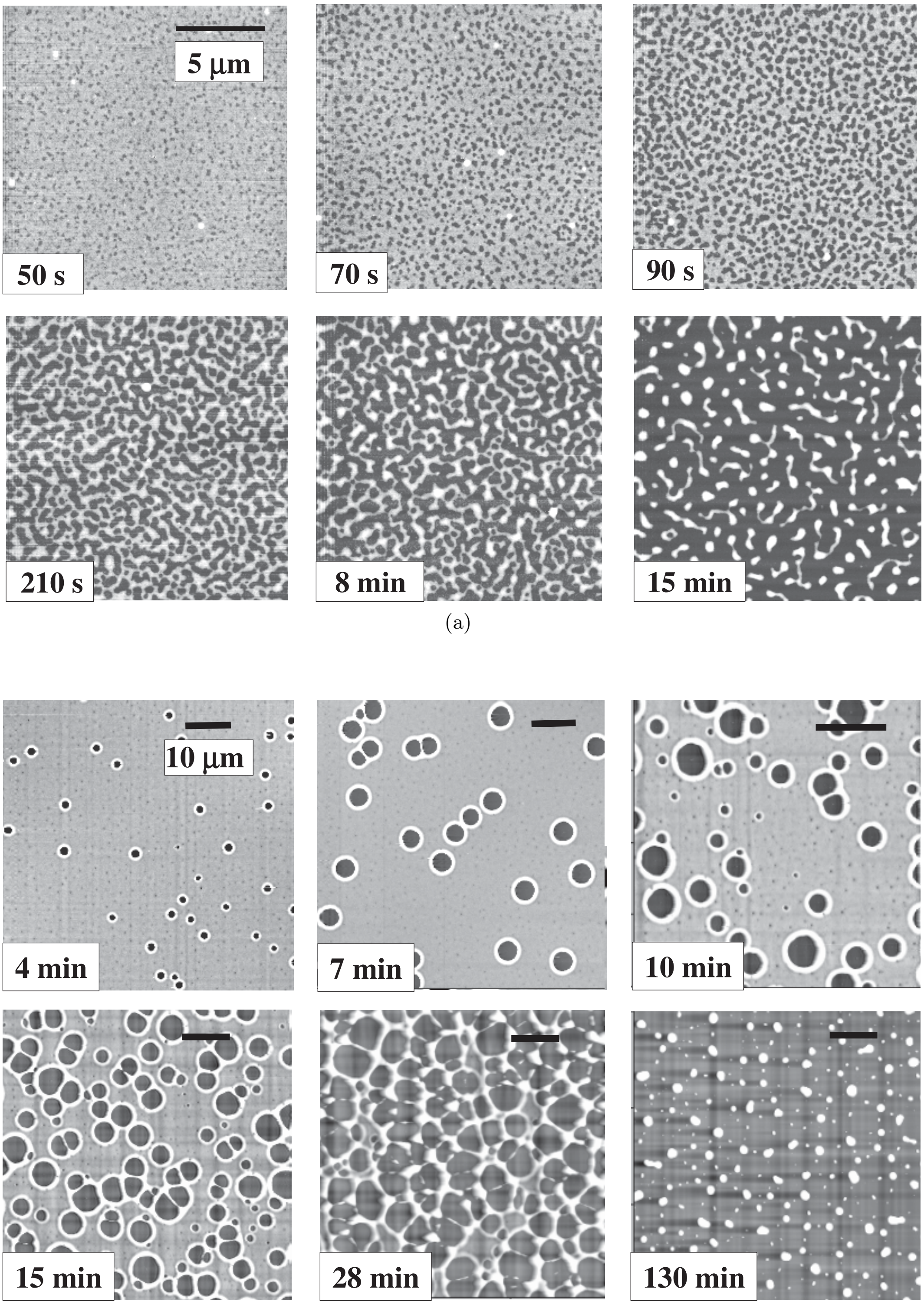
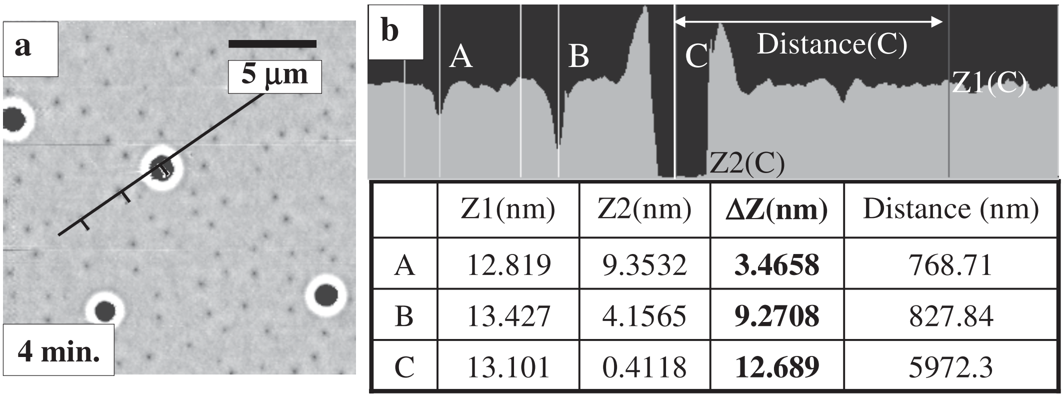


(a)

(b)

**Fig. 1.** Time-series of topographical images take from two dewetting PS films ($M_w = 13.7$ kg/mol) on silicon covered with 106 nm thick oxide with thicknesses (a) 3.2 nm and (b) 12.8 nm. Images were taken ex situ with a model SPA-300HV AFM from Seiko Instruments (Chiba, Japan). The 2.3 nm film was annealed at 180 °C in nitrogen while the 12.8 nm films were annealed at 145 °C in air. The different annealing temperatures and atmospheres had been found to have no effect on the dominating dewetting mechanism.



| | Z1(nm) | Z2(nm) | **ΔZ(nm)** | Distance (nm) |
|---|---|---|---|---|
| A | 12.819 | 9.3532 | **3.4658** | 768.71 |
| B | 13.427 | 4.1565 | **9.2708** | 827.84 |
| C | 13.101 | 0.4118 | **12.689** | 5972.3 |

**Fig. 2.** (a) AFM topographical image of a 12.8 nm thick PS film after annealing at 145 °C for 4 min in air. (b) Cross-sectional analysis of two indents (A and B) and a hole (C) in the film.

in Cahn's simulations, namely the bicontinuous dewetting structure appeared in the early stage [6]. In contrast, the $h = 12.8$ nm film undertook a pathway unconventional to spinodal self-destruction. The bicontinuous morphology never appeared but instead randomly distributed holes with different sizes surrounded by a rim emerged at the beginning. While the initial holes grew in size with time, new holes also emerged. Near time $t = 28$ min, all the holes touched each other whereupon the thin polymer ribbons connecting the holes broke up into droplets through the Rayleigh instability [16]. Data of Figure 1b allows us to conclude that polymer films dominated by a spontaneous rupturing process can be initiated by randomly distributed holes, and does not always produce the bicontinuous morphology.

From the images of Figure 1b taken within 15 min of dewetting, one may also notice small dimples densely dispersed between the much more visible holes. Cross-sectional analysis of Figure 2 reveals that the holes are of full-thickness while the dimples are indents at the surface with varying depths. It is apparent that the holes had developed from the dimples. Nonetheless, not all the dimples ultimately developed into full-thickness holes as evidenced from Figure 1b; most of them were consumed by the holes as the latter grew in size. Similar observation about the dimples was also made before [17]. However, the holes were attributed to heterogeneous nucleation by dust particles whereas the dimples were suggested to be result of spinodal growth of surface disturbances. It has not been established how the holes actually come into being, and whether the appearance and growth of the dimples corresponds to any known signatures of spinodal process. Clarifications on these issues may help shape how the controversy in the dewetting morphology of polymer films arises.

We study the evolution of dewetting in a film demonstrating the controversial dewetting morphology. In light of the high density of dimples revealed by Figure 1b, we found it necessary to carry out in situ measurements in order to accurately track down the development of individual holes. A 5.1 nm thick PS film with $M_w = 2.33$ kg/mol ($M_w/M_n = 1.07$, purchased from Scientific Polymer Products) deposited on the same kind of substrate as that in reference [13] was used. Although the crossover thickness for this $M_w$ had not been checked, previous study had found little effect of $M_w$ on the crossover thickness. One can moreover use the data produced by the film itself to self-consistently check if the spinodal mechanism indeed dominates the film rupture. In Figure 3, we display a time-sequence of AFM images taken in situ from the 5.1 nm thick PS film representative of its rupturing process at 60 °C. As seen, small amplitude surface fluctuations (recognizable by the graininess in the image) as well as randomly distributed holes and/or dimples occurred simultaneously at the beginning. But features of the former are largely overwhelmed by the latter. The holes, while coexisting with the surface fluctuations, widened in size as new holes emerged. This continued until all holes were touching each other whereupon the holes coalesced into bicontinuous ridges. We analyze the radial-averaged Fourier spectrum, $I(q)$, for all the images taken from the film throughout dewetting and display the result in Figure 4. Evidently, this new presentation provides a much clearer demonstration of the spinodal nature of the rupturing process. As is typical of a spinodal process, the spectra acquired in the initial stage are dominated by a peak at some wavevector, $q_{max}$, that remained constant for some time until coarsening took place whereupon $q_{max}$ continuously shifted to smaller values of $q$ with time. From the figure, $q_{max}/2\pi$ is $\sim 2.5$ $\mu\text{m}^{-1}$, leading to a value of the Hamaker constant, $A = 7.3 \times 10^{-20}$ J, which is in the same order of magnitude as those found in previous work [1,4]. It is interesting to note that the holes though were present throughout film rupturing, did not produce distinctive features in the curves. This is attributable to the wide distribution of holes sizes and the lack of positional order among the holes until a much later stage when the holes touched each other (Fig. 3).

We return to the AFM images shown in Figure 3 to analyze how the holes and/or dimples evolved. Seven holes were identified with number labels assigned as shown in Figure 3. The evolution of the holes is exemplified by the time-series of cross-sections taken from the #3 hole displayed in Figure 5. As seen, the #3 hole was a mere ∼1 nm

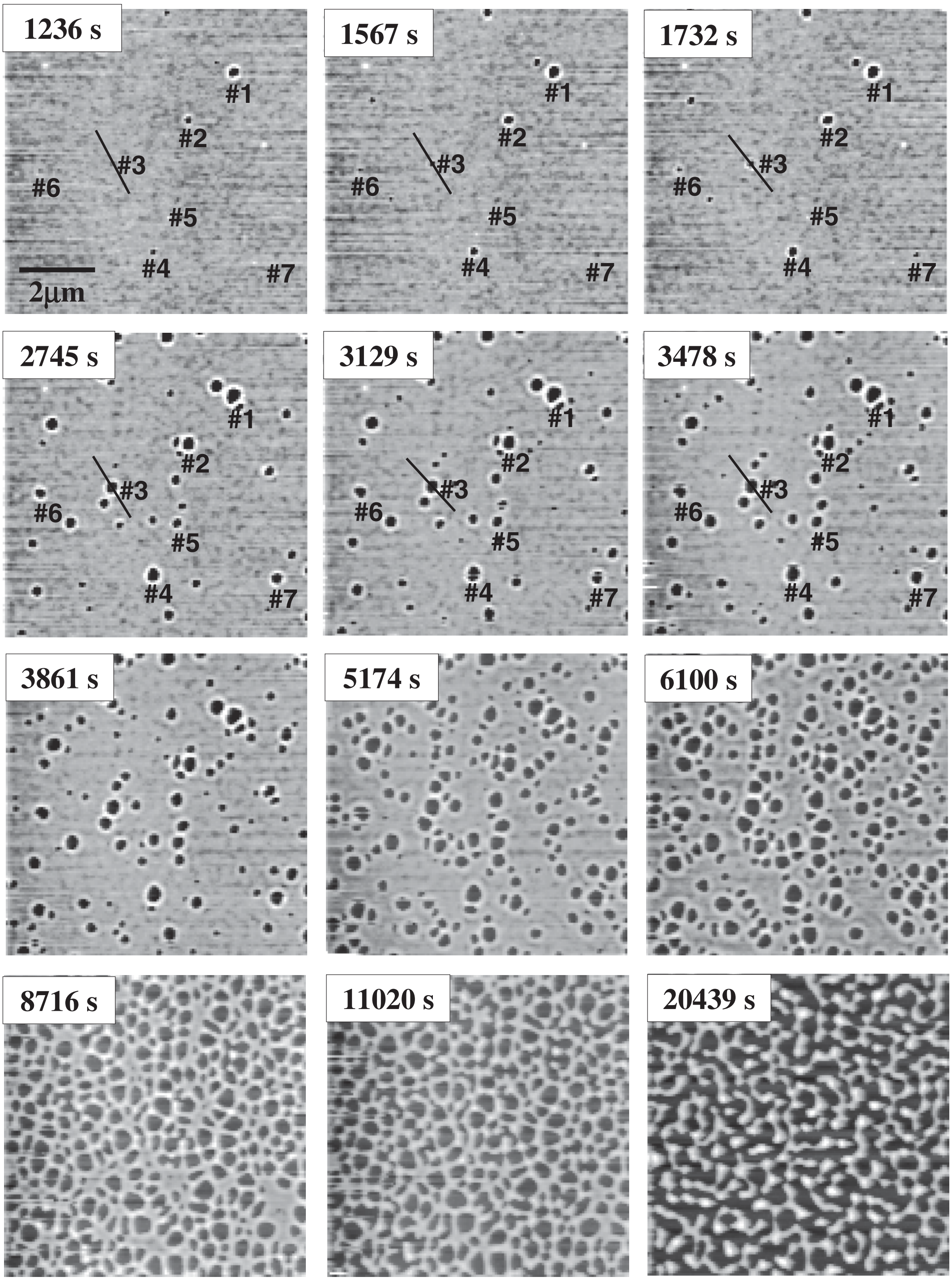


**Fig. 3.** A sequence of topographical images taken in situ at 60 °C from a dewetting 5.1 nm thick PS film ($M_w = 2.33$ kg/mol) on silicon covered with 106 nm thick oxide. Number labels #1 to #7 are markings to facilitate monitoring of the holes.

deep indent at $t = 1236$ s, but it continued to grow both in size and depth until $t \approx 2745$ s where it reached full-thickness. Thereafter, the hole only expanded laterally resulting in a rapid growth in the height of the surrounding culmination. In Figures 6a and 6b, we show, respectively, semi-log plots of holes depth, $d_h$, versus time and holes diameter, $2r_h$, versus time. Data for the temporal variation of $I(q_{max})$ was also shown in Figure 6a for comparison. As seen from Figure 6a, the initial growth of $d_h$ essentially followed that of $I(q_{max})$ until a sudden jump by 1 to 2 nm, which occurred at seemingly arbitrary times. Then the holes deepened quickly until $d_h$ ~3 nm whereupon the holes depth grew much more slowly to full-thickness. On the other hand, the holes diameter shows a comparatively steadier growth (Fig. 6b). Although some data seem to show a change in slope near the times when the

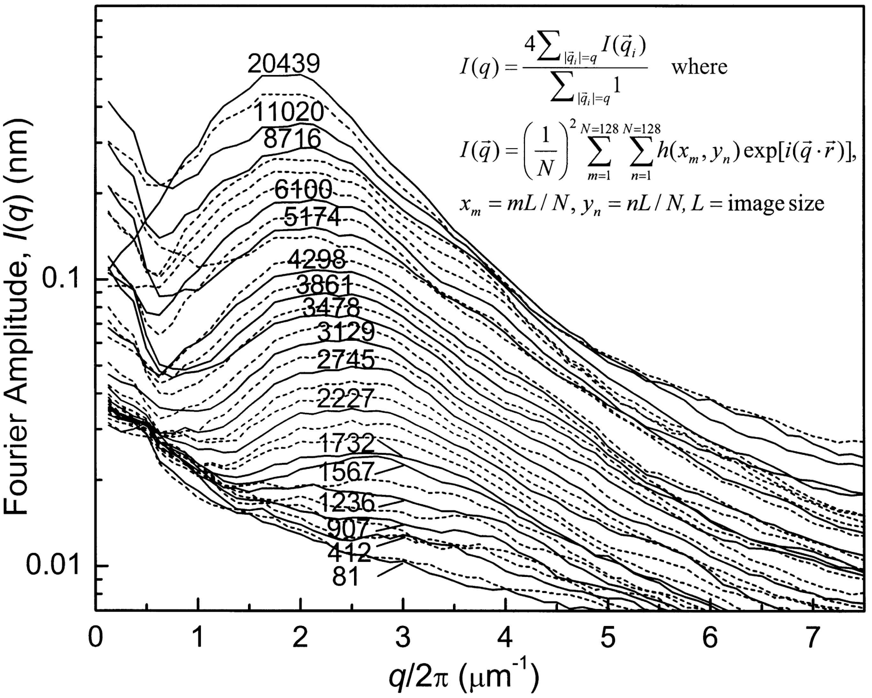


**Fig. 4.** Radial-averaged Fourier spectra deduced from a fuller set of images obtained from the dewetting film shown in Figure 3. The curves in solid lines are those with the image capture times (in seconds) indicated in the figure. The complete set of capture times is: 81, 247, 412, 576, 742, 907, 1071, 1236, 1402, 1567, 1732, 1898, 2062, 2227, 2393, 2568, 2745, 2921, 3129, 3303, 3478, 3656, 3861, 4065, 4298, 4524, 4753, 5174, 5614, 6100, 6578, 7283, 7990, 8716, 11020, 16250, 20439.

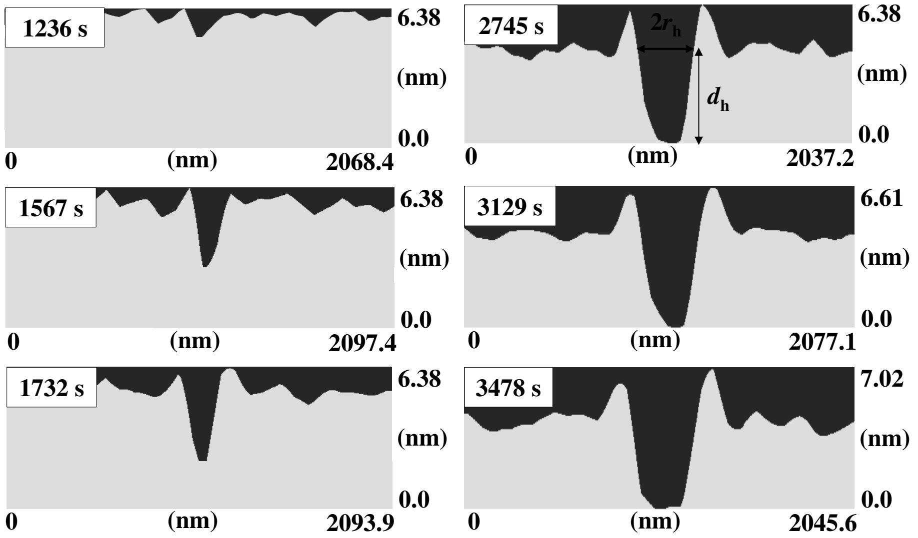
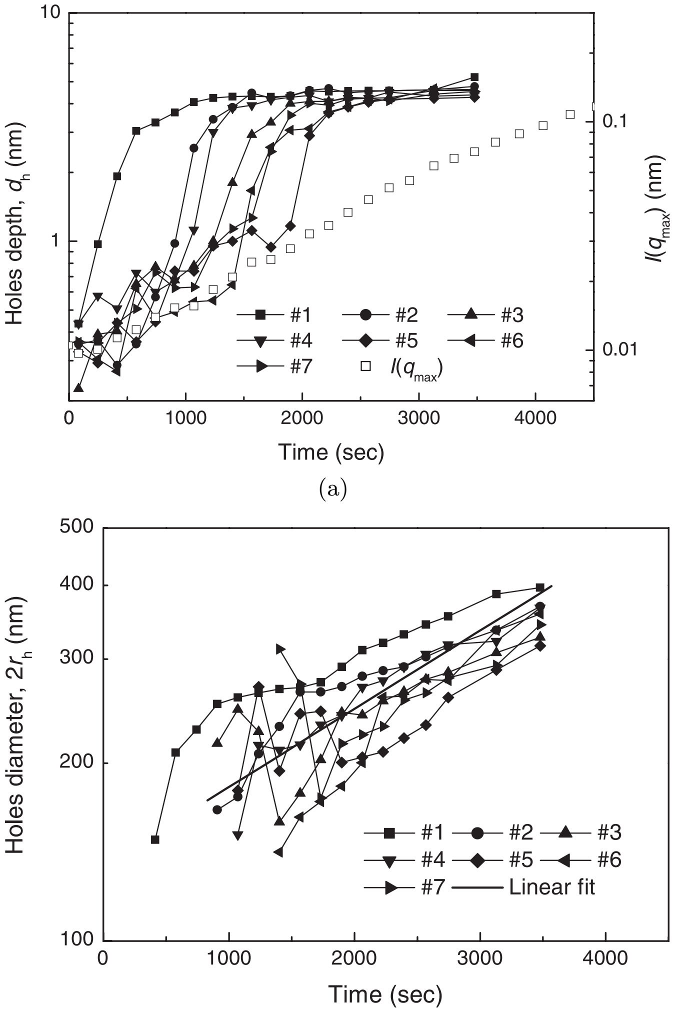


**Fig. 5.** Cross-sectional views of the #3 hole taken at different times as indicated.

corresponding hole demonstrated a jump in $d_h$, the features are much less prominent than that found in the change of $d_h$. The average rate $d(\log 2r_h)/dt$ is estimated to be $1.3 \times 10^{-4}$ nm/s (cf. $d(\log I(q_{max})/dt$ is $2.4 \times 10^{-4}$ nm/s in the initial stage). We do not see any length scales of the holes identifiable with $2\pi/q_{max}$. This, together with the vastly different evolution pathway assumed by the holes from that by $I(q_{max})$, makes the holes and the spinodal surface disturbances seem unrelated.

At a fundamental level, spinodal rupturing is a spontaneous self-destruction process wherein infinitesimal fluctuations of the system from homogeneity engenders an exponential growth of the starting fluctuations due to a lowering in the system free energy resulted from the growth. On the other hand, nucleation requires that an energy barrier be overcome either by thermal agitation or by taking a lower energy passage offered by some nucleation sites. One may thus gain some insight to the holes



(a)

(b)

**Fig. 6.** (a) Semi-log plot of holes depth vs. time. The Fourier amplitude of the fastest growing spinodal fluctuation mode, $I(q_{max})$ as a function of time is also shown (open squares). (b) Semi-log plot of holes diameter vs. time.

origin by examining the energy cost, $\delta W$, if any, required to form a hole. By assuming the free energy, $G(h)$, to be $-A/12\pi h^2$ and the holes circular, one can write

$$\delta W = 2\pi \int_0^{r_h} \left[ \frac{-A}{12\pi h(r)^2} - \frac{-A}{12\pi h_0^2} \right] r dr + \gamma \delta S, \quad (1)$$

where $h(r)$ is the hole-profile, $h_0$ is the starting film thickness = 5.1 nm, $A = 7.3 \times 10^{-20}$ J, $\gamma$ is the surface tension of polystyrene $\cong$ 35 mJ/m$^2$ [18], and $\delta S$ is the difference in surface area between the hole and the uniform film. Aiming only to obtain a rough estimate of $\delta W$, we further assume the holes to be circular cones with an opening angle, $\theta$ (see Fig. 7 for the definition). We may thus write

$$h(r) = h_0 - (r_h - r)/\tan\theta, \quad (2)$$

and

$$\delta S = \pi r_h \left(r_h^2 + d_h^2\right)^{1/2} - \pi r_h^2. \quad (3)$$

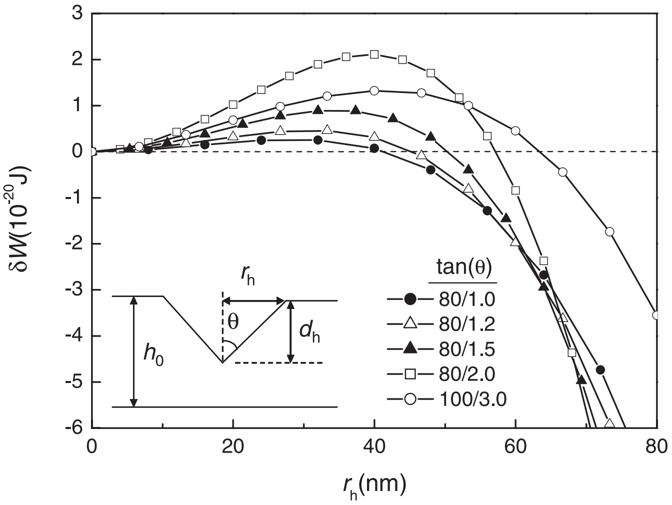


**Fig. 7.** Calculated energy cost, $\delta W$, for the formation of a hole plotted as a function of holes radius, $r_h$, for a set of opening angles, $\theta$, found in experiment. The calculation was based on equations (1–3). The inset illustrates the definition of various symbols used in the calculation.

From Figure 5, the first recognizable holes have average diameter 160 nm. This limit can be traced to the scanning condition = 8 $\mu$m scan size/128 pixels employed in the measurement. Since the AFM tip radius is 10 nm, the resolution of the holes depth should still be high. Figure 5a shows that the holes depth, $d_h$, immediately after the sudden jump lies between 1 nm and 3 nm. We calculate the energy pathway $\delta W(r_h)$ required to achieve the observed holes profile, i.e., $r_h = 80$ nm and depth $d_h$ (0.8 nm $\le d_h \le$ 2 nm) and $r_h = 100$ nm and $d_h = 3$ nm for fixed $\theta = \tan^{-1}(r_h/d_h)$. The result is shown in Figure 7. As shown, there is always an energy barrier in $\delta W(r_h)$ for all the observed holes indicating that they cannot be formed gradually from $r_h = 0$ as in a spinodal process through this route. However, the energy barriers varied between $0.27 \times 10^{-20}$ J and $2 \times 10^{-20}$ J are comparable to $k_B T \cong 0.46 \times 10^{-21}$ J. Hence, the holes can very well be produced via this pathway by thermal-induced nucleation. The fact that holes of different depths and opening angles bear energy barriers of different heights can immediately explain the randomness in their occurrence illustrated by Figure 6a. Nevertheless, the spinodal mechanism may not be ignored. Figure 8 shows that by increasing $d_h$ steadily from $d_h = 0$ with $r_h$ fixed at 80 nm, one can indeed make $\delta W$ increasingly negative as required in a spinodal process. Therefore, spinodal rupturing and thermal nucleation should be in competition. In the 5.1 nm PS film studied, both of them seem to be equally viable.

Based on the above, we tentatively suggest a reason to why spinodal rupturing with the formation of randomly distributed holes has seemed unique to PS films. From what we have gathered, the cases showing a clear bicontinuous dewetting pattern – notably poly(dimethylsiloxane) (PDMS) films [2,3,19] and very thin ($h \le 4$ nm) PS films [1,4,5] – usually have the bicontinuous structure developed within fairly short times (< 300 s to 1000 s).

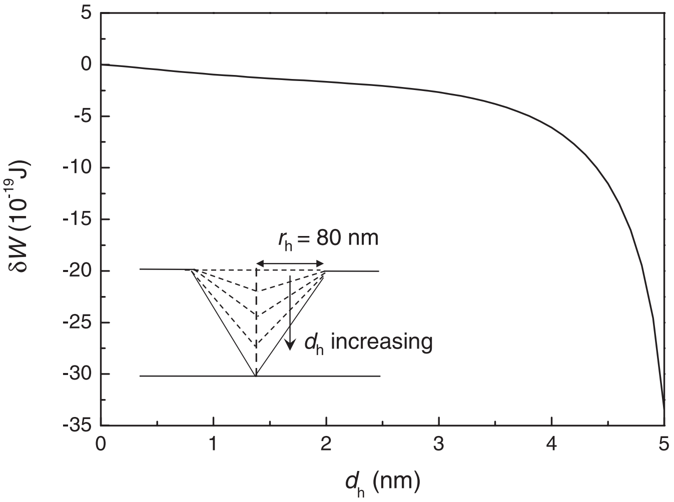


**Fig. 8.** Calculated energy cost, $\delta W$, for the formation of one hole with $r_h = 80$ nm plotted as a function of holes depth, $d_h$. The inset illustrates the holes growth process simulated by the calculation.

From Figure 6a, these times coincide with the nucleation time found in most of the holes studied. If the nucleation time did not increase rapidly with $h$ (which seems quite probable for the assumed form of $G(h)$, which has insofar been widely adopted), when the film thickness is increased above 5.1 nm, one expects the spinodal time (being $\sim h^5$) to quickly exceed the thermal nucleation time by large amounts, which may explain why holes become visibly dominant in the dewetting morphology as soon as the PS thickness goes beyond 5–6 nm [1,5,10]. The fact that the glass transition temperature of PS lies in a convenient temperature range (from about room temperature to 100 °C) and is variable through $M_w$, has given PS an obvious advantage for the study of thin film rupturing, namely it enables the experimenter to conveniently vary the rupture time by choice of $M_w$ and/or temperature. From the data presented here, the popular choice of experimental times – especially those for AFM evolution studies – i.e., a few minutes to several hours, intercepts with the noted nucleation time of holes (∼15 min) even at a moderate temperature of ∼60 °C. Since the nucleation barriers considered here have a magnitude comparable to $k_BT$, increasing the temperature will probably promote thermal nucleation more than spinodal growth of surface fluctuations. It follows that the kind of samples likely to exhibit clean spinodal dewetting morphology should be those with spinodal rupture times, $\tau_{sp} < \sim 15$ min at moderate temperatures. The commonly known cases of PDMS films and very thin PS films ($h \leq 4$ nm) fall into this category. One also expects thicker PS films but with $M_w$ low enough to bring $\tau_{sp}$ down to below ∼15 min should also constitute qualified examples. In search for reported cases as such, we came upon the work of Sehgal et al. [20] who demonstrated that a 12 nm thick PS film with $M_w = 760$ g/mol established the bicontinuous morphology within 2 min at 45 °C.

In this commentary, we have expressed some of our views about the controversy concerning the occurrence of randomly distributed holes in the dewetting morphology of polymer films conceded to be dominated by spinodal rupturing. Based on the results displayed above, we propose thermal nucleation as a viable mechanism for the formation of holes, rivaling spinodal growth of surface fluctuations. In addition, the relatively slow rupturing rate of PS films, which has been a desirable property for evolution studies, may also be the very reason for the films' long-discussed controversial dewetting morphology.

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# Discussion on contribution by O.K.C. Tsui et al.

### Question by the editor

Can you comment from you on the results of Becker et al. [Nature Materials **2**, 59 (2003)], in particular the example given there on the 4.9 nm thick film (Fig. 2a)?

### O.K.C. Tsui replies

There is similarity but also apparent difference between Becker et al.'s result (for a 4.9 nm thick film) and ours (for a 5.1 nm thick film). The two results are similar in the sense that both showed formation of distinctive holes in the films. But unlike what Becker et al. have emphasized in their observed morphology, majority of the holes we found did not accompany with satellite holes; far more new isolated holes emerged before satellite holes realized in our film (Fig. 3). I speculate the difference may be due to the difference in the holes nucleation rate relative to the satellite holes formation rate. One may notice that the annealing temperature adopted by Becker et al. was 70 °C, which is 10 °C higher than that by us. While the effect of this difference should have very little effect on the nucleation rate (since it is $\sim\exp(E_a/kT)$, $E_a$ = energy barrier for holes nucleation and $T$ in K), its effect may be large on the viscosity of the polymer considering that these temperatures are not much higher than the bulk $T_g$ of the polymer (~57 °C), thereby may dictate how oscillatory the hole rim profile should be (Herminghaus et al., Phys. Rev. Lett. **89**, 056101).

### Question by the editor

In that context, what is your opinion on the interpretations given by Thiele and by Sharma of Becker's results based on the process they call "nucleation in the spinodal regime" and "defect sensitive spinodal regime", respectively?

### O.K.C. Tsui replies

From Sharma [21], the different names refer to the same physical condition. According to Thiele et al. [22], it is a condition of an unstable film wherein the growth rate of a local disturbance ($\beta$) is greater than the growth rate of the dominant surface capillary wave ($\beta_m$). I think the two authors' interpretations for the formation process of the cascaded holes observed by Becker et al. are reasonable. However, I would also like to see discussions on additional related issues. For example, simulations for dewetting structures usually assume a starting disturbance. In reality, the disturbances (except for those intentionally introduced) should come from thermal excitations of surface capillary waves or incidental local indentations. Thiele et al. [22] calculated the spectrum of minimum amplitude for the starting disturbance below which the disturbance flattens. Subject to such minimum requirement of the disturbance amplitude and that $\beta > \beta_m$, the rate of formation for such disturbance may very well be the rate-determining step in the holes nucleation process. If so, it seems to me that whether the spinodal morphology can be seen in the "nucleation in the spinodal regime" or "defect sensitive spinodal regime" should depend on (1) how big the minimum required disturbance amplitude is, and (2) how $\beta_m$ compares with the rate of excitation of a local indentation by thermal agitation or defect induced excitation. My suggestion is in part due to the result we found of the 5.1 nm thick film in which signature of a spinodal process was apparent (from the time-evolution of Fourier spectra in Fig. 4), and that random surface fluctuations were apparent in areas between the holes (Fig. 3). We also note similar surface fluctuations in both experimental and simulation data of Becker et al. (Fig. 2a and 2b, respectively).

### Question by the editor

How is the approach used to calculate the energy barrier for nucleation (Eq. (1)) comparable with the concept of a critical radius?

### O.K.C. Tsui replies

The quantity involved in the calculation with equation (1) that may correspond to the prevailing concept of a critical radius would be the smallest value of $r_h$ above which $\delta W$ is $< 0$. But the smallest possible value of $r_h$ is in fact zero for the 5.1 nm thick PS film considered in the paper (Fig. 8 shows that a "critical hole" may have $r_h = 80$ nm and $d_h = 0$. But it is obvious that such hole has the same energy as one that has $r_h = 0$ and $d_h = 0$). In other words, the critical radius of this film is zero. But this is just a result of the fact that the film is in the spinodal regime.

### Comment by U. Steiner

It is suggested that for spinodal time larger than about 15 min, hole formation via thermal nucleation may dominate. I don't think, this can be stated in such a way. My guess is that this depends on all the parameters that govern the spinodal instability (Hamaker constant, surface tension, viscosity).

### O.K.C. Tsui replies

Fifteen min has been stated as the observed time for holes formation in the present system ($M_w = 2.3$ K Da PS on $\mathrm{SiO}_x$ covered Si). By no means is this same time meant to be applicable to all systems. But in predicting the criterion for the appearance of bicontinuous structure in the lower molecular weight PS ($M_w = 760$ Da), I did mean to use 15 min as the upper limit of the spinodal time since the nucleation time of the lower $M_w = 760$ Da PS can only be shorter than that of the $M_w = 2.3$ K Da PS because of the lower viscosity but similar surface tension and Hamaker constant.

## A. Sharma comments on the following statement

*"[in addition to spinodal dewetting] holes can very well be produced via the pathway of thermal-induced nucleation."*

Certainly. However, in the absence of any rigorous calculations thus far in the literature, I would guess that thermally-induced nucleation will remain effective only for the first few nanometers in the *metastable* regime, since both surface tension and disjoining pressure are stabilizing and the total amplitude of thermal capillary waves should be of the order of less than 0.5 nm or so.

For spinodally unstable films, "thermal nucleation" and "spinodal dewetting" are best viewed not as *separate* pathways, but thermal fluctuations provide a finite probability for the formation of increasingly higher amplitude "initial condition" for the spinodal process. It is doubtful that thermal fluctuations can provide more than a nanometer of depression on laboratory time scales, but this may be sufficient to greatly alter the spinodal kinetics, especially as the film gets thicker and enters the defect sensitive regime. It is worth noting that the amplitude of capillary waves (because of thermal excitations limited by surface tension) on thick films is not in much excess of about 0.2 nm. Thus spinodal effect would be needed to amplify such a disturbance.