

Influence of Dendrimer Additives on the Dewetting of Thin Polystyrene Films

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A small mass concentration of poly(benzyl ether) dendrimer added to a low molecular mass polystyrene is found to inhibit the dewetting of a thin (≈ 50 nm) polystyrene film from an acid-etched silicon substrate. The inhibition effect is found to depend on generation number where the lowest generation ($G = 3$) tested was the most effective. Our findings are qualitatively similar to previous observations by Barnes et al. [*Macromolecules* **2000**, *33*, 4177–4185.] where the addition of fullerenes (“buckyballs”, C_{60}) similarly inhibited the dewetting of thin polystyrene and polybutadiene films. Thus, dewetting inhibition by nanoparticles appears to be a general effect, although certain conditions apparently need to be met for its occurrence. Specifically, a general tendency for the particles to segregate to the solid substrate seems to be required and the interaction between the particles and polymer must not be too unfavorable. The phase boundaries of the dendrimer–polymer mixtures depend on the generation, the higher generation being more miscible in terms of mass fraction. This suggests that the driving force for the dendrimer to segregate to the boundary is varied by changing the generation number, thus giving rise to a dendrimer generational effect on dewetting suppression.

Introduction

Synthetic polymer films often dewet from inorganic substrates, but stable continuous films are required for numerous technological and biological applications where dewetting can compromise the effectiveness of these coatings. This fundamental problem motivates the development of strategies for stabilizing thin polymer films against dewetting, and the present paper pursues the recent finding¹ that nanoparticles can be useful in achieving this type of film stabilization. In particular, we consider the use of dendrimer additives as agents to inhibit the dewetting of synthetic polymer films.

The usual approaches to stabilize films naturally involve a modification of the polymer–surface interaction to promote wetting through grafting chains onto the surface,^{2,3} sulfonation and metal complexation of the polymer,⁴

the introduction of specialized end groups onto the polymer with a high affinity for the inorganic substrate,⁵ or modification of the substrate roughness or chemistry by irradiation or other means.⁶ Kinetic stabilization over appreciable time scales can often be achieved by spin-coating very high molecular mass, glassy or entangled, polymer films which can be trapped in a nonequilibrium state upon solvent evaporation. As a final resort, it is sometimes possible to irradiate a film (converting it into a solid) to stabilize the film against dewetting.⁷ Much work has been performed to determine the fundamental mechanisms of film dewetting, motivated in part by the desire to avoid this often undesirable process.

Pioneering studies of dewetting by Reiter^{8,9} focused on the dynamics of hole growth in thin polymer films and the

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(1) Barnes, K. A.; Karim, A.; Douglas, J. F.; Nakatani, A. I.; Gruell, H.; Amis, E. J. *Macromolecules* **2000**, *33*, 4177.

(2) Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J. *Science* **1994**, *263*, 793.

(3) Kerle, T.; Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J. *Europhys. Lett.* **1998**, *44*, 484.

(4) Feng, Y.; Karim, A.; Weiss, R. A.; Douglas, J. F.; Han, C. C. *Macromolecules* **1998**, *31*, 484.

(5) Henn, G.; Bucknall, D. G.; Stamm, M.; Vanhoorne, P.; Jerome, P. *Macromolecules* **1996**, *29*, 4305.

(6) Kerle, T.; Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J. *Europhys. Lett.* **1997**, *38*, 207.

(7) Paek, U. C. *J. Heat Transfer* **1999**, *121*, 774.

(8) Reiter, G. *Phys. Rev. Lett.* **1992**, *68*, 75.

(9) Reiter, G. *Macromolecules* **1994**, *27*, 3046.

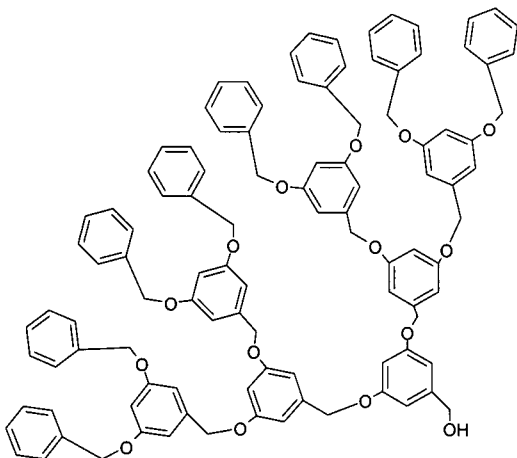


Figure 1. Molecular structure of the generation 3 (G3) poly-(benzyl ether) dendrimer with an hydroxyl focal point.

Table 1. Glass Transition Temperatures of PS13K, Various Generation Dendrimers, and Their Blends as a Function of Weight or Mole %^a

system	wt % dendrimer	mol % dendrimer	$T_g-1/^\circ\text{C}$	$T_g-2/^\circ\text{C}$	$T_g\text{-calc}/^\circ\text{C}$
PS13K	0	0		97	
PS13K + G3	1	8		95	96
	5	30		93	93
	10	48		90	89
	20	67	32	87	82
	30	78	32	83	75
	50	89	29	79	61
	100	100	32 (32, ^b 34 ^c)		
PS13K + G4	5	17		90	94
	10	31		88	90
	20	50		88	84
	30	63	41	84	77
	50	80	40	88	66
	100	100	41 (39, ^b 41 ^c)		
PS13K + G5	5	9		93	94
	10	18		91	91
	20	33		91	85
	30	45		89	79
	40	56	42	85	73
	50	66	43	91	68
	100	100	43 (42, ^b 44 ^c)		
G6		100	(43, ^b 45 ^c)		

^a The columns headed T_g-1 and T_g-2 are the glass transition temperatures for the phase near that for the pure dendritic and linear polymer, respectively. The column headed $T_g\text{-calc}$ is the mixture glass transition temperature calculated according to eq 1. The error in the glass transition temperatures is $\pm 1^\circ\text{C}$. ^b Values from Wooley et al. (ref 32). ^c Values from Mackay et al. (ref 25).

interpretation of these results using the capillary wave instability model of Vrij^{10,11} and Brochard and Daillant.¹² It was later found that the classic spinodal dewetting mechanism, giving rise to surface patterns similar to near-critical phase separation patterns, is observed in polymer films having a thickness on the order of nanometers.¹³ Recent theoretical^{14,15} and experimental work^{16,17} has clarified that a nonmonatomic surface potential is required to understand the transition from spinodal dewetting to

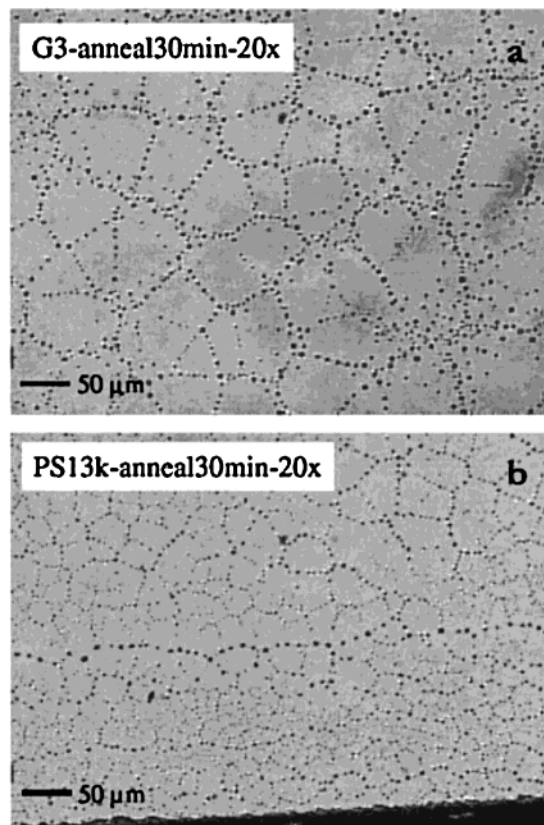


Figure 2. Dewetting of (a) the G3 poly(benzyl ether) dendrimer and (b) 13 kDa polystyrene on silicon wafers at 170 °C for 30 min. Note that the edge of the wafer is visible in (b). These pictures were taken using reflection OM.

dewetting through the homogeneous nucleation of holes. Kargupta and Sharma¹⁸ have also made theoretical advances in the modeling of dewetting on nonhomogeneous substrates and have indicated the important role that *gradients* in the substrate surface energy can have on film stability.

Although the fundamental mechanism of thin film dewetting is beginning to be understood, a simple method is still desired to *inhibit* it. Recently, Barnes et al.¹ discovered a novel stabilizing method through addition of nanoparticles. The effectiveness of this method is striking in comparison to the normal effect of large particles and other film heterogeneities to cause film dewetting.¹⁹ Thus, this nanosize of the particles seems to be essential to the nature of this inhibited dewetting phenomenon.

Barnes et al.¹ used fullerene nanoparticles (“buckyballs”, C₆₀) that were found to segregate to the solid substrate of spin-coated polystyrene (PS) or polybutadiene films. Furthermore, they formed a diffuse layer near the solid substrate that was apparently essential to the film stabilization effect. No stabilization effect was observed for other alkane thiol coated nanoparticles that did not segregate to the boundary.²⁰ The dewetting inhibition mechanism was hypothesized to be the result of two concerted effects: (1) the irregular (probably fractal-like) structures at the substrate pin contact lines of holes formed by dewetting and (2) the polymer–surface interaction energy is modified by the surface roughness.²¹ Spin-coating

- (10) Vrij, A. *Discuss. Faraday Soc.* **1966**, *42*, 23.
 (11) Vrij, A.; Overbeek, J. Th. G. *J. Am. Chem. Soc.* **1968**, *90*, 3074.
 (12) Brochard, F.; Daillant, J. *Can. J. Phys.* **1990**, *68*, 1084.
 (13) Xie, R.; Karim, A.; Douglas, J. F.; Han, C. C.; Weiss, R. A. *Phys. Rev. Lett.* **1998**, *81*, 1251.
 (14) Sharma, S.; Khanna, K. *Phys. Rev. Lett.* **1998**, *81*, 3486.
 (15) Konnur, R.; Kargupta, K.; Sharma, A. *Phys. Rev. Lett.* **2000**, *84*, 931.
 (16) Herminghaus, S.; Jacobs, K.; Mecke, K.; Bischof, J.; Fery, A.; Ibn-Elhaj, M.; Schlagowski, S. *Science* **1998**, *282*, 916.
 (17) Seeman, R.; Herminghaus, S.; Jacobs, K. *Phys. Rev. Lett.* **2001**, *86*, 5534.

- (18) Kargupta, K.; Sharma, A. *Phys. Rev. Lett.* **2001**, *86*, 4536.
 (19) Stange, T. G.; Evans, D. F.; Hendrickson, W. A. *Langmuir* **1997**, *13*, 4459.
 (20) Cole, D. H.; Shull, K. R.; Baldo, P.; Rehn, L. *Macromolecules* **1991**, *32*, 771.
 (21) Douglas, J. F. *Macromolecules* **1989**, *22*, 3707.

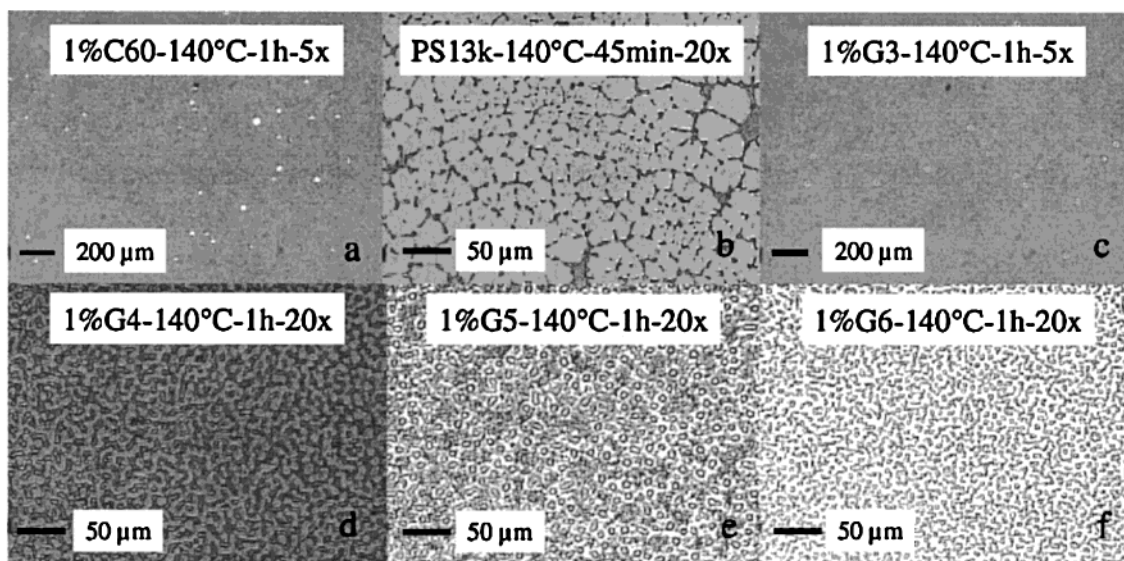


Figure 3. Dewetting patterns for various thin polymer films aged for 1 h at 140 °C unless otherwise noted. The base polymer for all blends is PS13K. (a) 1 wt % fullerenes; (b) pure PS13K aged for 45 min; (c) 1 wt % G3; (d) 1 wt % G4; (e) 1 wt % G5; (f) 1 wt % G6. These pictures were taken using reflection OM.

of fullerenes followed by spin-coating of a PS layer onto a wafer did not inhibit dewetting, so the presence of a diffuse segregation layer seems to be essential to the effect.

In the present work, we show that dendrimers also give rise to dewetting inhibition. Dendrimers are highly branched polymers that can be synthesized from a variety of multifunctional monomers; we use benzyl ether with a functionality of three and a synthesis technique that leads to extraordinary control in the molecular architecture.^{22,23} Despite their highly branched structure, these molecules can readily swell and contract similar to linear polymers.²⁴ In fact, a molecular mass independent intrinsic viscosity can be obtained in certain solvents when the dendrimer is collapsed suggesting particle-like behavior. Furthermore, under these conditions, the measured individual molecular density is quite close to the bulk²⁵ suggesting that intermolecular interpenetration is quite small. This may explain the unusual rheological properties of dendrimers such as a linear scaling of viscosity with molecular mass.^{26,27} Despite this relatively high individual molecule density, even when expanded, dendrimers can change shape, and recent studies have shown unique surface properties of these polymers in monolayers because of this capability.^{28,29}

Here, we find that dendrimers behave similarly to a nanoparticle, fullerene, in stabilizing polymer films against dewetting. For reference, fullerenes have a diameter of ca. 1 nm, while dendrimers are on the order

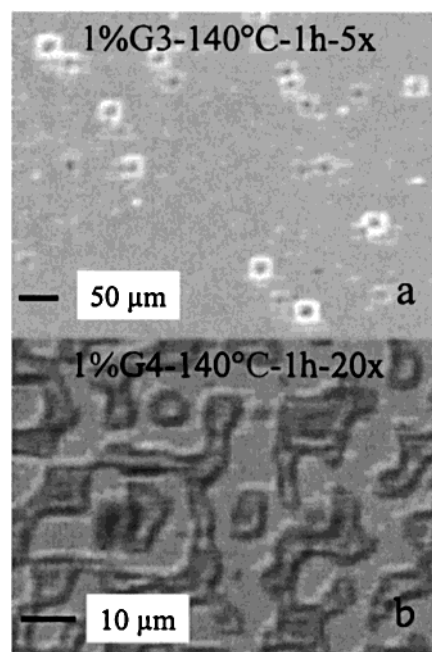


Figure 4. Dewetting patterns for thin polymer films containing G3 and G4 dendrimers aged for 1 h at 140 °C; these are the same images in Figure 3c,d with a larger magnification. (a) 1 wt % G3; (b) 1 wt % G4.

of 1.5–4.5 nm in size depending on molecular mass (generation) and solvent conditions. Interestingly, the least soluble dendrimer (lowest generation) produces the greatest effect. The lower generation's decreased solubility leads to a greater tendency toward surface segregation that in turn enhances the dewetting suppression.

Materials and Experiment

Materials. Poly(benzyl ether) dendrimers were made as previously reported²² with a molecular structure representation for the third generation (G3) dendrimer given in Figure 1. The molecular mass (M) for this molecule is 1592 Da and is essentially monodisperse in mass. Generations 4 (G4), 5 (G5), and 6 (G6) are much larger molecules with the mass approximately doubling at

(22) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

(23) Hawker, C. J.; Malmstrom, E. E.; Frank, C. W.; Kampf, J. P. *J. Am. Chem. Soc.* **1997**, *119*, 9903.

(24) Jeong, M.; Mackay, M. E.; Hawker, C. J.; Vestberg, R. *Macromolecules* **2001**, *34*, 4927.

(25) Mackay, M. E.; Hay, G.; Hawker, C. J. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1766.

(26) Hawker, C. J.; Farrington, P. J.; Mackay, M. E.; Wooley, K. L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1995**, *117*, 4409.

(27) Farrington, P. J.; Hawker, C. J.; Fréchet, J. M. J.; Mackay, M. E. *Macromolecules* **1998**, *31*, 5043.

(28) Kampf, J. P.; Frank, C. W.; Malmström, E. E.; Hawker, C. J. *Langmuir* **1999**, *15*, 227.

(29) Kampf, J. P.; Frank, C. W.; Malmström, E. E.; Hawker, C. J. *Science* **1999**, *283*, 1730.

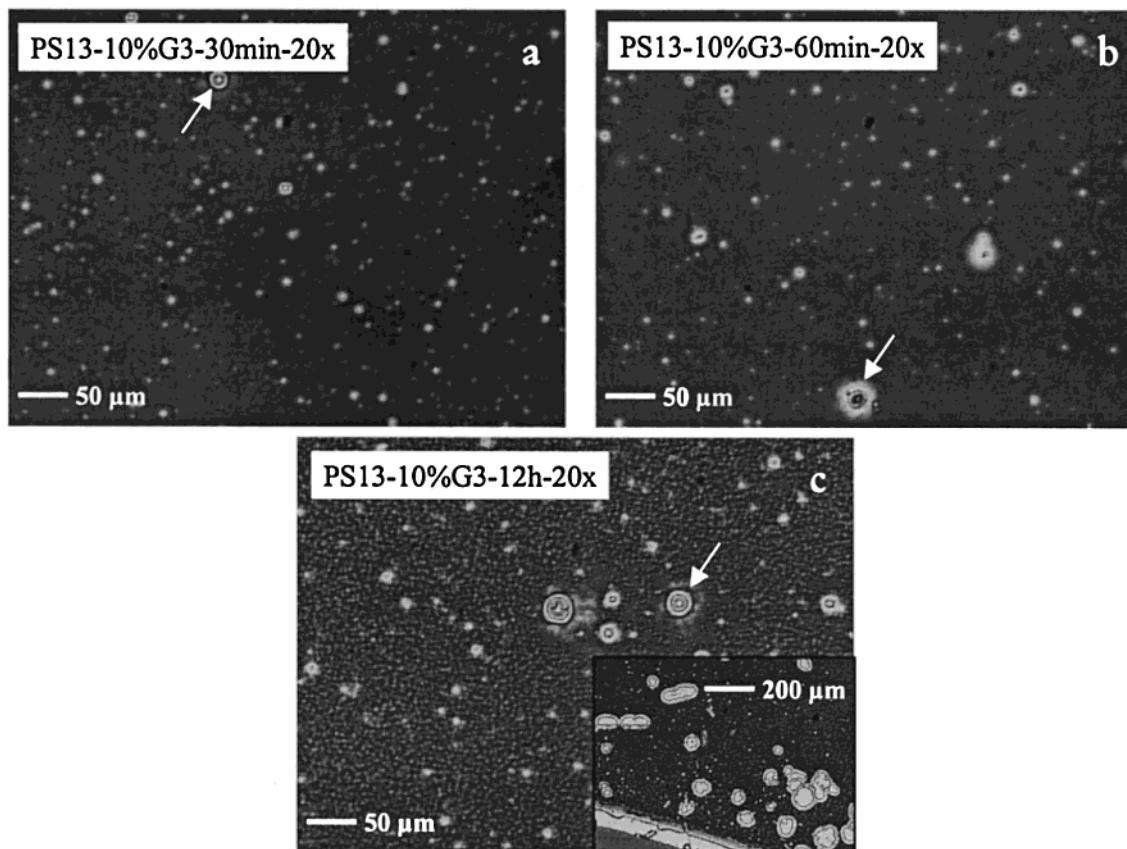


Figure 5. Addition of 10% G3 dendrimer to PS13K shows no macroscopic dewetting after 12 h of aging: 30 min (a), 60 min (b), and 12 h (c) of aging at 170 °C. The large objects are dust particles as shown by the arrows. The inset in (c) is an optical micrograph taken near the wafer edge after 12 h of aging to show minimal dewetting. These pictures were taken using reflection OM.

each generation³⁰ (G4, $M = 3288$ Da; G5, $M = 6680$ Da; G6, $M = 13\,479$ Da). A polystyrene standard was obtained from Scientific Polymer Products Inc. and had a low polydispersity index (PS13K: $M_w = 13\,200$ Da, PDI = 1.06; M_w is the weight-average molecular mass and PDI is the polydispersity index expressed as the ratio of weight- to number-average molecular mass; both M_w and PDI were supplied by the manufacturer).³¹ Fullerenes (predominantly C₆₀) were purchased from Aldrich Chemicals. All silicon wafers were cleaned in a 70/30 volume ratio solution of concentrated H₂SO₄ (98% by mass) and H₂O₂ (30% by mass) overnight, rinsed in deionized water for 1 h, and then oven-dried under nitrogen immediately before spin-coating.

Preparation of Dendrimer Filled Films and Evaluation of Film Morphology. Mixtures of dendrimer and polystyrene with specific compositions were dissolved in benzene (2% w/w), filtered using 0.45 μm poly(tetrafluoroethylene) (PTFE) filters, and spin-coated onto the treated silicon wafer at 4000 rpm for 60 s. The resulting films had an approximate thickness of 40 nm. The coated substrates were then annealed at 140–170 °C under nitrogen for different time intervals. To avoid problems associated with cooling and reheating one sample,¹⁹ different samples were used for each annealing time. The morphology of the films was investigated after annealing using reflection optical microscopy (OM) and atomic force microscopy (AFM, Digital Instruments NanoScope) in both height and phase modes.

Bulk Miscibility of Polystyrene and Dendrimers. Mixtures of PS13K with various generation dendrimers were prepared by dissolution in benzene and evaporation of the solvent under vacuum. This produced a homogeneous blend which was similar to that produced by other means such as freeze-drying.

(30) Mourey, T. H.; Turner, S. R.; Rubenstein, M.; Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **1992**, *25*, 2401.

(31) Certain commercial materials and instruments are identified in this article to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST nor does it imply that materials or equipment identified are necessarily the best available for the purpose.

The glass transition temperature (T_g) was determined for each blend with a Perkin-Elmer DSC 7 after the third heat cycle from –20 to 200 °C at 10 °C/min.

The measured T_g 's are given in Table 1 for all the blends; note the agreement of pure component T_g 's found in this work and the studies of Wooley et al.³² and Mackay et al.²⁵ For the PS13K–G3 blends, the T_g results indicate that a pure dendrimer phase coexists with a phase that contains approximately 10–20 wt % G3 when the concentration is above 10–20 wt %. The higher generation dendrimers are miscible to greater levels, and dendrimer solubility limits are approximately as follows: G3, 15 wt %; G4, 25 wt %; G5, 35 wt %. The solubility limits correspond to concentrations where the dendrimer mole fraction is $1/2$.

The mixture T_g was estimated using the Fox rule³³

$$T_g^{-1} = \sum w_i T_{gi}^{-1} \quad (1)$$

as shown in Table 1. The sum over each component i in the block copolymer is performed with w_i representing the mass fraction of that component in the blend. This rule shows a consistent trend with the data for mixtures that do not exhibit phase separation.

Results and Discussion

Dewetting of Pure Dendrimers and Linear Polystyrene. The dewetting patterns of the pure G3 dendrimer and PS13K after elevated temperature aging are shown in Figure 2. The familiar pattern of Voronoi dewetting patterns is observed corresponding to the dewetting of a Newtonian fluid. Other generation dendrimers cast onto silicon substrates dewetted in a similar manner. A further

(32) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Fréchet, J. M. J. *Macromolecules* **1993**, *26*, 1514.

(33) Utracki, L. A. *Polymer Alloys and Blends*; Hanser Publishers: New York, 1990.

experiment was conducted with a thin film of PS13K floated onto a wafer having a spin-coated layer of G3 on its surface. Upon heating to 170 °C, we observed the film to dewet.

To understand these dewetting observations of poly-(benzyl ether) dendrimers, preliminary measurements of the dendrimer melt surface tensions (γ_L) were obtained³⁴ by the micro-Wilhelmy fiber technique.^{35,36} To an accuracy of ± 1 mN/m, the melt surface tensions of the G3 and G4 dendrimers at 140 °C are 26 and 31 mN/m, respectively, which can be compared to that of linear polystyrene with a value of 31.5 mN/m for the molecular mass used in our work.³⁷ The dispersive surface energy (γ_S^d) for a cleaned, hydrated silicon wafer surface, similar to those used in this study, is approximately 36.5 mN/m at room temperature.³⁸ This was determined through the method described by Fowkes, where liquids that interact only via dispersive forces were used.³⁹ Should the wafer be prepared by another manner, not involving hydration, then γ_S^d was found to be 44.7 mN/m.³⁸ Water has a dispersive surface energy component of 21.8 ± 0.7 mN/m which no doubt contributes to the lower value. Assuming the dendrimer and polystyrene liquids interact through dispersive forces, it can be concluded that γ_S^d has decreased at the elevated temperature to at least 26 mN/m at 140 °C. The wafers' dispersive surface energy (tension) component can be roughly estimated by assuming that it scales with the fourth power of the (bulk water) density⁴⁰ to determine if this value is realistic. This yields a value of 25 mN/m for γ_S^d at 140 °C which is near the above value ($\gamma_S^d \sim \rho^4 \sim \exp(4\alpha[T - T_0])$; ρ is the bulk density, α is the thermal expansivity (8×10^{-4} °C⁻¹, near water's normal boiling point), T is temperature, and T_0 is a reference temperature).

On the basis of these values of the surface and interfacial tension, the observed dewetting of the thin dendrimer films can be described by the spreading coefficient, S , defined as the work of adhesion between the liquid and solid less the liquid work of cohesion. Since the wafer (dispersive) surface energy is lower than the dendrimer's, S is negative and dewetting occurs. Thus, despite their predominantly spherical molecular architecture, dendrimers display surface behavior similar to that of simple or polymeric liquids.

Dewetting of Dendrimer–Linear Polystyrene Blends. Barnes et al.¹ found that fullerenes can inhibit dewetting at bulk volume fractions as low as ≈ 0.01 . Consistent with the observations of Barnes et al., we find a marked suppression of dewetting for PS13K with the dendrimer additive. Figure 3b shows, for comparison, pure PS13K film after heating to 140 °C for 45 min where dewetting is evident. Only small holes ≈ 10 μ m in diameter are present when 1 wt % of C₆₀ is added and large-scale dewetting is arrested (Figure 3a).

Experiments were performed using various generation dendrimers where the smallest generation (G3) significantly affects the results at constant mass fraction, 1 wt %. In this case (Figure 3c), similar behavior to that of the fullerenes at 1 wt % composition is seen. In the dendrimer

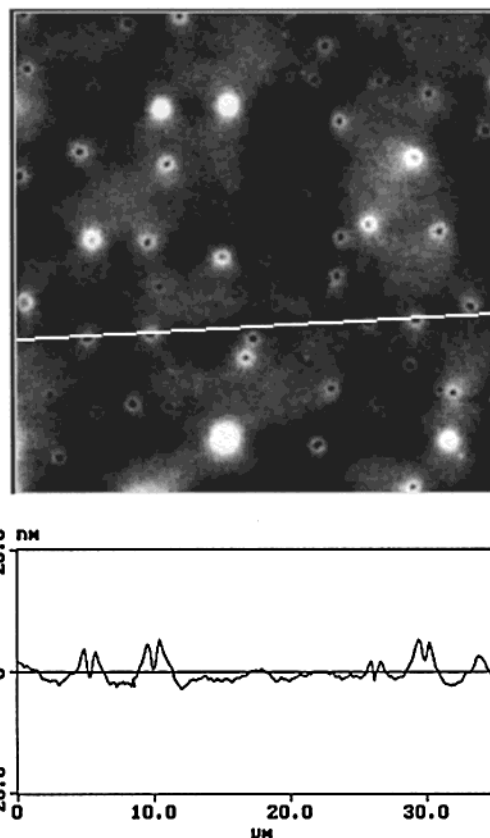


Figure 6. (top) AFM image (height) of 10% G3 dendrimer blended with PS13K after 12 h of aging at 170 °C. The image is 30 μ m \times 30 μ m. (bottom) Line profile across the upper image. Mesa-like structures 5–7 nm high are present on an otherwise flat film.

case, however, a droplet of polymer is found in the center of each dewetting hole (Figure 4a). This suggests that droplets rich in dendrimer are forming within the film so the tendency for surface segregation is weaker than in C₆₀-containing films. The stabilization effect is nevertheless observed.

The film morphology changes dramatically with increasing dendrimer generation (molecular mass) after high-temperature aging. As seen in Figure 3d–f, a pattern resembling phase separation is observed and the scale of the pattern increases with generation. A greater magnification comparing G3 to G4 is given in Figure 4 to highlight the difference when dewetting occurs.

We noted above that spin-coating a layer of G3 onto the wafer followed by floating a PS layer onto it did not inhibit dewetting. Thus, a sandwichlike structure of silicon wafer–dendrimer–polymer is not essential for wetting. Also, G3 is the least soluble, in terms of mass fraction (see Table 1), and so this generation dendrimer is closest to the phase envelope at 1 wt % bulk concentration. The formation of a diffuse layer, rich in dendrimer, near the wafer surface is postulated to be the main mechanism for dewetting inhibition, similar in effect to that observed for the fullerenes. This possibility will be checked by neutron reflection measurements.

Higher Dendrimer Concentrations. Addition of 5–10 wt % G3 dendrimer creates a system where dewetting is retarded to a greater extent as seen in Figure 5. Even after 12 h of aging at 170 °C, the 10 wt % G3 system does not exhibit gross dewetting. Close inspection of the wafer edges reveals a slight amount of local dewetting that does not propagate into the central wafer

(34) Sauer, B. B. Personal communication to M. E. Mackay, 2001.

(35) Sauer, B. B.; Dipaolo, N. V. *Colloid Interface Sci.* **1991**, *144*, 527.

(36) Mackay, M. E.; Carmezini, G.; Sauer, B. B.; Kampert, W. *Langmuir* **2001**, *17*, 1708.

(37) Dee, G. T.; Sauer, B. B. *Colloid Interface Sci.* **1992**, *152*, 85.

(38) Zhao, W.; Rafailovich, M. H.; Sokolov, J.; Fetters, L. J.; Plano, R.; Sanyal, M. K.; Sinha, S. K.; Sauer, B. B. *Phys. Rev. Lett.* **1993**, *70*, 1453.

(39) Fowkes, F. M. *Ind. Eng. Chem.* **1964**, *56*, 40. Fowkes, F. M.; McCarthy, D. C.; Mostafa, M. A. *J. Colloid Interface Sci.* **1980**, *78*, 200.

(40) Dee, G. T.; Sauer, B. B. *Adv. Phys.* **1998**, *47*, 161.

region as shown in the inset in Figure 5c. Even dust particles do not nucleate dewetting as seen in the figure. However, coarsening of a structure within the film is present with aging time. This may be dendrimer phase separation within the film.

Although the films are nearly smooth on a large scale, there are small-scale irregularities apparent on the scale of AFM observation. An AFM (height) image along with a line profile is shown in Figure 6 to demonstrate this. Circles of material create a mesa-like structure approximately 800 nm in diameter with 5–7 nm high walls that does not appear to expose the wafer surface in the center (note the scale change in the vertical and horizontal axes). The mesas are located approximately 5 μm apart (center-to-center) which agrees with the optical micrograph shown in Figure 5c. The size of the G3 dendrimer ($2R_g$, R_g is the radius of gyration) varies between 2.0 and 2.6 nm, depending on the solvent,⁴¹ while $2R_g$ for the polystyrene molecules is 6.2 nm (see Cotton et al.,⁴² $R_g(\text{nm}) = 0.87M(\text{kDa})^{1/2}$). Thus, the mesa walls could be two dendrimer molecules or one polystyrene molecule high. More sophisticated analytic techniques must be applied to determine the walls' chemical composition although we hypothesize that this unique observation may be related to the dendrimer phase separation mentioned above.

(41) Tande, B. M.; Wagner, N. J.; Mackay, M. E.; Hawker, C. J.; Vestberg, R.; Jeong, M. *Macromolecules* **2001**, *34*, 8580.

(42) Cotton, J. P.; Decker, D.; Benolt, H.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C.; desCloizeaux, J. *Macromolecules* **1974**, *7*, 863.

Conclusion

It has been shown that the addition of a low concentration of dendrimer to a polymer film can cause a retardation of dewetting. While the smallest generation dendrimer (G3) behaves similarly to fullerenes, a different mechanism seems to be operative as the generation number increases. Future work will focus on determining the origin of this behavior. Increasing the concentration for G3 dendrimer leads to full arrest of dewetting, which is coupled with the formation of ≈ 5 nm elevated ("mesa-like") structures that we associate with phase separation of the film into dropletlike regions rich in dendrimer. The exact mechanism of dewetting retardation is unknown in the present study although the results for G3 dendrimer are consistent with those of Barnes et al.¹ Surface segregation of dendrimers by phase separation seems to be an important factor in the observed film stabilization effect.

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