Instabilities of Thin Polymer Films on Layers of Chemically Identical Grafted Molecules

Günter Reiter,*,† Philippe Auroy,‡ and Loïc Auvray

Laboratoire Léon Brillouin, CEN Saclay, F-91191 Gif-sur-Yvette Cedex, France

Received March 7, 1995; Revised Manuscript Received July 24, 1995⊗

ABSTRACT: We report autophobic behavior of end-functionalized polystyrene molecules. By grafting such molecules from a melt onto the surface of a silicon wafer these molecules formed a "brushlike" layer which entropically repelled the nongrafted but otherwise identical molecules. The brush became nonwettable by the same molecules. Thin polystyrene films on top of dense polystyrene brushes were unstable and ruptured as a consequence of long-range van der Waals interactions which tried to make the films thinner. The films dewetted the polymer brush by the growth of cylindrical holes. We investigated this dewetting process in detail as a function of grafting density, which was varied by annealing thin films of end-functionalized molecules for different times. The contact angle formed by the nongrafted molecules on top of the brush, and also the dewetting velocity, increased significantly with increasing grafting density. Neutron reflectometry results showed that the brush layer could be notably penetrated, regardless of the observed dewetting. Implications of these results to the success of block copolymers and end-functionalized molecules for improved adhesion or for stabilization of thin liquid films are discussed.

Introduction

The question of stability of thin liquid films on solid substrates is of great importance in many practical applications such as in microelectronics. A controlling parameter is wettability.[1] Films on nonwettable substrates are either metastable or unstable. Short-range interactions can easily be changed, e.g., by coating the substrate with an appropriate monolayer.[2] It is possible to modify a nonwettable surface so that a liquid will be able to spread on such a surface. The opposite is also possible. Coating a wettable surface with a monolayer may even lead to so-called, "autophobic" behavior; i.e., a liquid does not spread on its own monolayer.[3] There exist several possible origins for autophobicity. In ref 3 a few possibilities, probably occurring simultaneously, were proposed: packing or steric effects; orientation or dipolar effects. For small molecules it is difficult to distinguish and separate these contributions. Here, we will show that polymers enable us to investigate the origin of autophobicity, focusing on steric effects. Adding a monolayer usually does not much affect long-range interactions like van der Waals forces. Thus, although the liquid spreads on the substrate, a thin film of this liquid is still not stable and may roughen or even rupture.[1] To achieve long-range stabilization of such films, one may use long polymers anchored by one end to the substrate as was shown previously.[4] In those experiments, the grafting density was not very high and the grafted molecules did not yet experience significant stretching. Intuitively, such a stabilizing effect appears to be plausible. An open question is how many of these molecules are necessary to reach this goal. Does increasing the number of anchored molecules always improve stability?

A related problem is the improvement of adhesion between a polymer and a solid substrate or between incompatible polymers. Commonly, end-functionalized polymers or block copolymers are used to increase the region of interaction between the two bodies one wants to "glue" together.[5,6] Again, it is not yet answered experimentally whether an increasing number of such molecules at the interface between the two bodies would always improve adhesion.[7,8]

Anchoring chainlike molecules to a solid surface by one end may induce steric constraints causing stretching of the molecules.[9] Stretching, in turn, may result in entropic repulsion for nongrafted macromolecules. Grafting molecules onto a solid surface leads to the formation of a distinct interface between grafted and nongrafted molecules with a nonzero interfacial tension. Thus, such conditions can lead to the striking phenomenon that the melt does NOT wet a "brush" of molecules of its own kind. This was predicted theoretically first by Leibler et al.[10] and later by Shull.[11] The first experimental evidence of autophobic behavior for identical molecules of different molecular weight was observed by Mourran, Chatenay, and co-workers[12] and Liu et al.[13] Nonspreading drops or dewetting was found for systems where the melt on top of a chemically identical brush consisted of significantly longer molecules. In ref 13 films thinner than the radius of gyration were put on top of the grafted layers, so we cannot exclude that confinement effects as observed earlier[14] have at least partially caused dewetting.

The effect of steric repulsion preventing the penetration of a brush was observed directly[15] in a related experiment. However, in that case *two* layers of grafted polymers *in solution* were interacting. Here we will describe the consequences of increasing grafting density on the wettability of the brush. Entropic repulsion exerted by the molecules of the grafted layer reduces the interaction zone and consequently decreases both stability and adhesion once a certain grafting density is exceeded.

Experimental Section

Samples. We have studied the behavior of thin films (thickness (d) ∼100 nm) of molten polystyrene on layers of completely identical molecules end-attached onto silicon wafers. Two different molecular weights of deuterated polymers were synthesized in our laboratory by anionic polymerization, split into two batches, and terminated either by a methyl group or by a monochlorosilane group. The monochlorosilane end group could chemically react with hydroxyl groups. This

---

† Present address: Institut de Chimie des Surfaces et Interfaces, CNRS, 15, rue Jean Starcky, B.P. 2488, F-68057 Mulhouse Cedex, France.

‡ Present address: Section de Physique et Chimie, Institut Curie, URA 448 du CNRS, 11, rue Pierre et Marie Curie, 75231 Paris, Cedex 05, France

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1996.

0024-9297/96/2229-2150$12.00/0

Table 1. Molecular Characteristics of Polystyrenes Used[a]

sample	wt-av MW (g/mol)	M_w/M_n	radius of gyration (Å)	end group
PS-S-R	9 300	1.04	25	monochlorosilane
PS-S-N	9 300	1.04	25	methyl
PS-L-R	43 500	1.03	55	monochlorosilane
PS-L-N	43 500	1.03	55	methyl
PS-p1-N	43 000	1.09	56	methyl
PS-p2-N	1 120 000	1.25	288	methyl

[a] The first four samples are deuterated while the last two are protonated (indicated by p). The monochlorosilane end group is reactive while the methyl end group is nonreactive. The abbreviations have the following meaning: PS for polystyrene, S and L for short and long, respectively, and R and N for reactive and nonreactive end groups, respectively.

allowed the formation of a chemical bond between the polymer and the substrate. Methyl-terminated protonated polystyrene was also synthesized. The molecular characteristics of the polystyrenes we used are given in Table 1. The silicon wafers were irradiated by UV light in a water-saturated oxygen atmosphere (UV−ozone treatment). This treatment had two purposes: First, it oxidized organic molecules and therefore had a cleaning effect. Second, it led to the formation of hydroxyl groups on the surface necessary for the grafting of polystyrene onto this surface. The thin polymer films were prepared by diluting the polymer in toluene and spin-coating the solution directly onto the wafers.

Preparation of Polymer Brushes of Variable Grafting Density. We started by preparing thin films of reactive polymer which we annealed above the glass transition temperature (T_g) in order to enable the molecules to move around. To initiate the grafting reaction, the reactive end had to find an appropriate site at the surface of the substrate. We observed dewetting[1,16,17] i.e., the formation of cylindrical holes which grew upon annealing, for films of just end-functionalized polystyrene molecules. Similar results were also found for mixtures of nonreactive and end-functionalized molecules of identical length with a sufficient concentration of reactive molecules.[18] The nongrafted polymers were dewetting a brush formed by identical molecules. For the shorter molecules (PS-S-R) such autophobic behavior was already visible after 30 min of annealing at 160 °C. For the longer molecules (PS-L-R), however, we had to anneal more than 40 h at 160 °C in order to observe the first indications of dewetting.

For a systematic study of the dependence of dewetting on the grafting density of the brush, we had to separate between the processes of grafting and dewetting. The grafting density would become very inhomogeneous if dewetting set in before the grafting process was terminated. Grafting could continue in regions that were still covered with a polymer film while it could not in the already dewetted regions. As a consequence, the dewetting process would speed up with progressing time because of the increase of grafting density. Thus, we performed our experiment in two stages to separate the grafting kinetics process (step 1) from the dewetting dynamics process (step 2). First, we prepared a grafted layer, and second, we covered this layer with a thin film of *nonreactive* polymer by spin-coating a dilute polystyrene solution directly onto the brush. For the first film we spin-coated a ~100 nm thick film of end-functionalized polymers onto the UV-treated silicon substrates. After different times of annealing at temperatures well above T_g, the samples were put into a bath of toluene to wash off all nongrafted molecules. To avoid a significantly inhomogeneous grafting density, we stopped the grafting process usually before the holes became larger than 100 μm, i.e., less than 10% of the surface was dewetted.

The thicknesses of the remaining layers were determined by ellipsometry and X-ray reflectometry. In Figure 1 we have plotted the thicknesses of the brushes of PS-S-R and PS-L-R molecules after washing and drying vs the time of annealing at 160 °C. Some samples were annealed at lower or higher temperatures. The corresponding annealing times at 160 °C were calculated using the WLF equation.[19] It is quite obvious that the brush thickness increased rather fast at short times but then only very slowly at later times. Plots of the data on a logarithmic time scale suggested that the brush thickness increased with the logarithm of annealing time once the thickness is larger than ~2 times the radius of gyration (R_g = 25 Å for PS-S-R and 55 Å for PS-L-R). A similarly slow increase in the grafting density was expected theoretically.[20] It was attributed to difficulties for polymers to penetrate an already existing brush in order to reach the substrate for grafting. While our data are insufficient to be compared in detail with theoretical predictions, it is evident that we do NOT reach a saturation level for the grafting density.

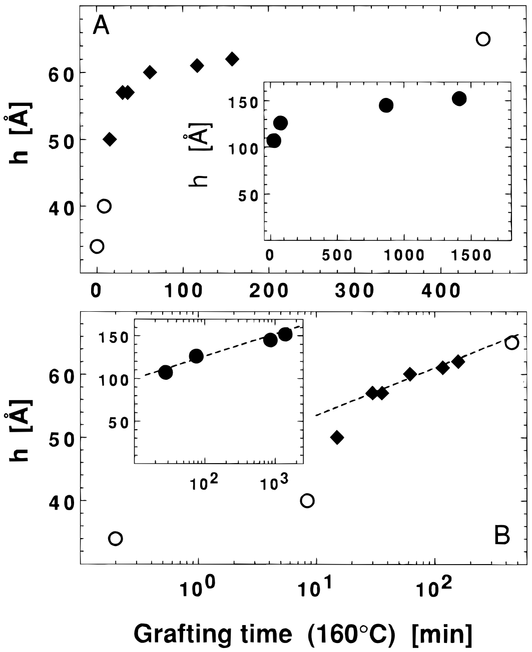

Figure 1. Thickness (h) of polystyrene brushes (PS-S-R; the insets show PS-L-R) after washing in toluene and drying as a function of time (t) allowed for grafting from the melt state at 160 °C. The open symbols represent data points obtained at different temperatures. The corresponding grafting time at 160 °C was calculated using the WLF equation. Plotting the data on a linear time scale (A) emphasizes the fast increase in brush thickness at short times. At later times, h increases very slowly, possibly logarithmically, as indicated by the dashed line on the semilogarithmic plot (B).

Table 2. Conditions of Preparation and Results for Bimodal Brushes[a]

name	% of long molecules	grafting time (min)	h_0 (Å)	h_{core} (Å)	contact angle (deg)	av veloc (μm/min)
A	15	1080	72 ± 1	60 ± 2	~5	not meas
B	3.5	315	74 ± 1	68 ± 2	7 ± 0.5	0.2 ± 0.1
C	12	870	78 ± 1	69 ± 2	8 ± 0.3	0.5 ± 0.1
D	28	5650	76 ± 1	66 ± 2	6.5 ± 0.7	0.35 ± 0.1

[a] Contact angles and averaged veolocity were determined for a polystyrene film (PS-p1-N, ~900 Å thick) on top of the resulting brushes for an annealing temperature of 160 °C. The brush thickness h_0 was determined by neutron reflectometry measurements of the washed and dried brushes before coating. h_{core} reflects only the thickness of the inner part of the bimodal brush consisting mainly of short molecules as determined from the midpoint of the steep region of the density profile seen by neutron reflectometry.

Preparation of Bimodal Brushes. In order to get an idea about the effect of polydispersity, we prepared brushes from mixtures of short and long *reactive* molecules (PS-S-R and PS-L-R).[21] The concentration of the long molecules was varied. The samples were annealed at 160 °C until small holes became visible. While under the same conditions we needed only a few minutes to create holes in a sample of just small reactive molecules (PS-S-R), we had to anneal for more than 1 day to see the first indications of dewetting for a sample containing ~25% long molecules. The bimodal brushes were then washed and coated with a film of PS-p1-N molecules. Neutron reflectometry was used to determine the interface of such bimodal brushes in contact with a polymer melt. Conditions of preparation and some results are given in Table 2.

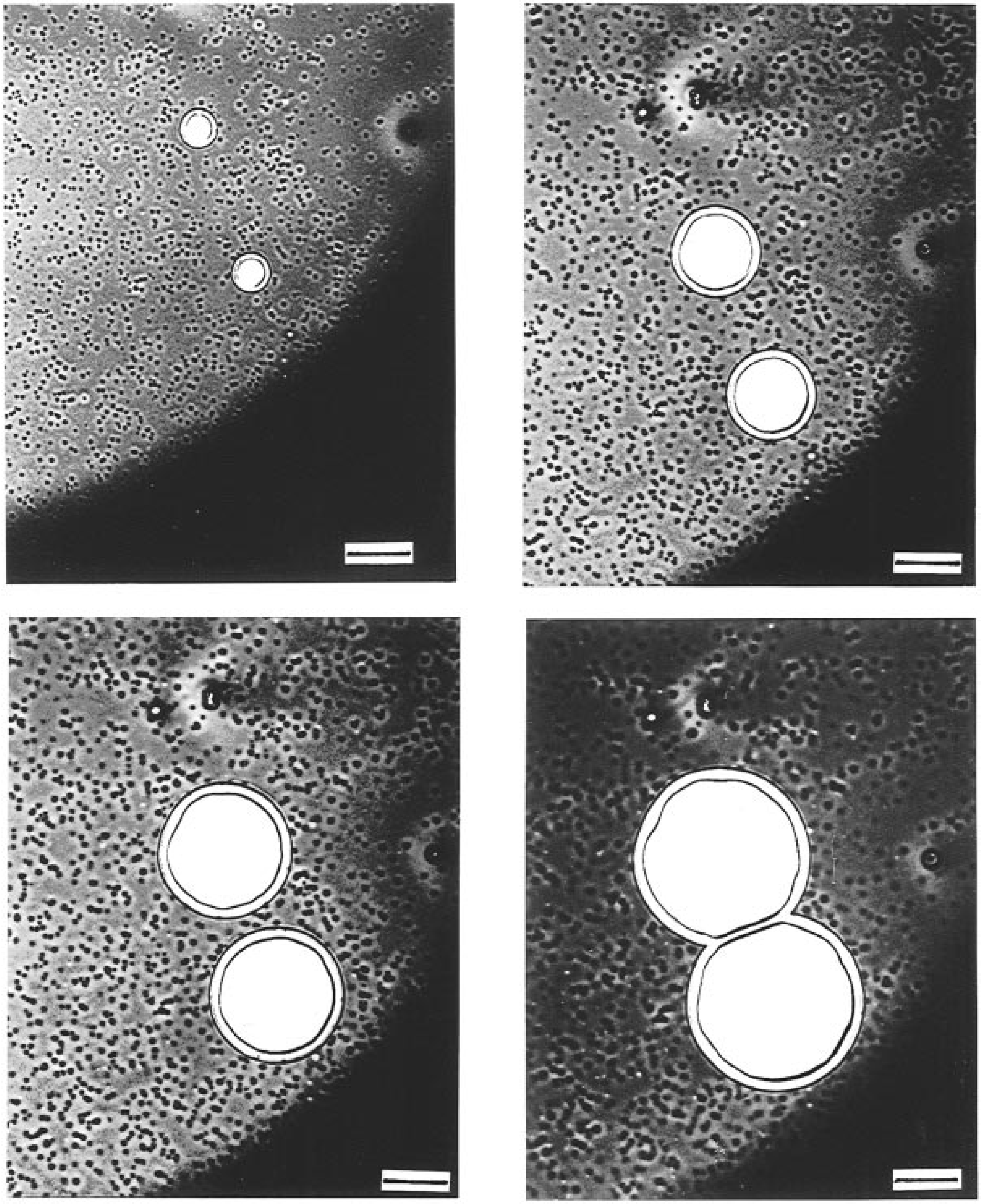

Figure 2. Optical micrographs (using white light) showing the growth of two typical cylindrical holes in a 900 Å thick polystyrene film (PS-p1-N) on a 66 Å thick polystyrene brush (PS-S-R) after (a, top left) 8, (b, top right) 38, (c, bottom left) 68, and (d, bottom right) 103 min of annealing at 175 °C. The black dots originate from a roughening of the film during the first minutes of annealing. Note that no holes are nucleated by the dust particle visible on the micrographs. The length of the bar is 100 μm.

Results

Dynamics of Dewetting: Hole Growth. Wafers covered with a brush were coated again, but this time with nonreactive polymer (~100 nm thick films of PS-S-N, PS-L-N, PS-p1-N, or PS-p2-N). The samples were progressively annealed above T_g for various times. Annealing was done in an external oven and the samples were successively checked by optical microscopy after quenching to room temperature. Alternatively, real-time experiments were performed with a hot stage directly under the microscope. Only samples with densely grafted layers showed dewetting.

In Figure 2 one can see micrographs of the growth of two typical holes for a ~900 Å thick PS-p1-N film on a 72 Å thick brush of PS-S-R molecules. The increase of their diameter with time (t) is shown in Figure 3. The data seem to fall quite nicely onto a straight line implying linear growth. However, such a representation would yield the inexplicable observation that the holes already had a diameter of ~30 μm at $t = 0$.

A closer look at the data revealed that hole growth slowed down with progressing time. Brochard-Wyart et al.[22] proposed a different time dependence for the growth of holes for the case where the liquid slips over the substrate. Assuming for the moment that we have indeed observed slippage, we plotted the same data vs the predicted $t^{2/3}$ dependence. The data could be approximated better by a straight line and the holes

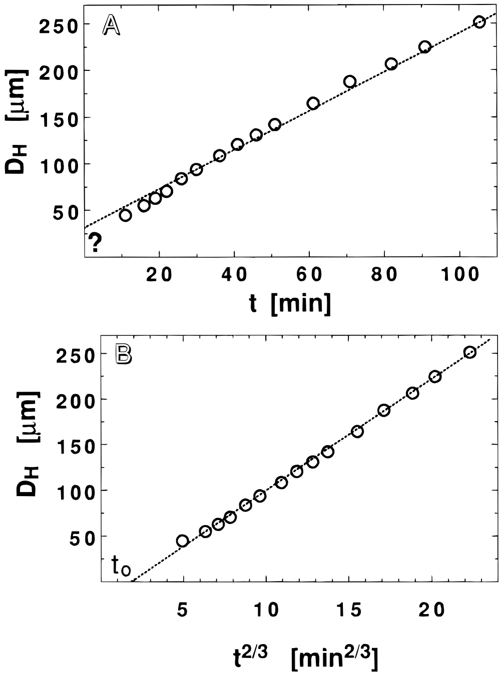

Figure 3. (A) The diameter (D_H) of the holes seen in Figure 2 as a function of annealing time (t) at 175 °C. The dotted line is a guide for the eye. Note that this straight line does not go through the origin (see question mark). The data seem to show a slight curvature, indicating that the growth rate (dewetting velocity) decreases with time. (B) The same data plotted vs $t^{2/3}$. The dotted line is a guide for the eye. Note that the data points fall quite nicely onto this line, indicating that the holes grow with t^{β} with $\beta \sim 2/3$. In addition, this line yields $D_H = 0$ at $t = t_0 > 0$.

started to grow at $t = t_0 > 0$. It is not expected that the holes start to grow at $t = 0$ as the hole has to be created first, a process that needs time.[1,17] In addition, due to experimental uncertainties (mainly due to a finite heating rate), t_0 could only be determined with an accuracy of ~1 min.

In ref 22, it was also predicted that in the case of slippage the shape of the rim should become asymmetric. A blowup of a hole focusing on the interference pattern of a rim showed that in our case the shape of the rim was indeed not symmetric. (see Figure 4) The steepness of the rim on the side toward the hole was significantly larger (the spacing between two successive fringes was smaller) compared to the side toward the unperturbed film. It has to be mentioned that it is rather surprising that the results (nonlinear time dependence of the hole growth and the asymmetric shape of the profile of the rims surrounding the holes) suggest that the free polymers slipped over the brush as this would imply rather weak interactions between brush and film molecules. An alternative possibility to interpret our observations was offered by Leibler,[23] based on viscoelastic effects due to the interaction between brush and melt.

We have also compared the dewetting behavior of the same molecules on top of the brush (PS-S-N on top of a PS-S-R brush) with the system mentioned above (PS-p1-N on a PS-S-R brush). For a 54 Å thick brush, the holes grew slightly faster in the film of the smaller molecules than in a film of longer molecules. (see Figure 5). Assuming linear growth of these holes resulted again in the unphysical consequence of a finite hole diameter at $t = 0$. A comparison of the difference in the hole growth velocities (a factor of ~1.5) with the difference in viscosity of the two polymers (a factor of ~5) made it quite obvious that this growth rate was not linearly dependent on the reciprocal viscosity.[24]

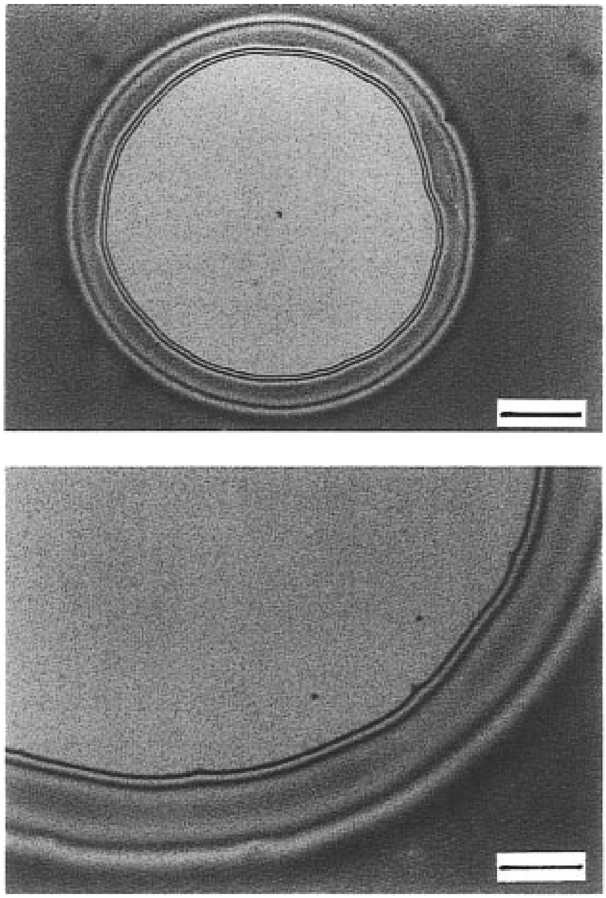

Figure 4. (a, top) Optical micrograph (using white light) of a typical hole in a ~900 Å thick polystyrene film (PS-p1-N) on a 63 Å thick polystyrene brush (PS-S-R). The length of the bar is 25 μm. Due to mass conservation, one can calculate a contact angle (θ) from measures of the diameter of the hole (bright circle) and the diameter of the rim (see text for details). We obtained $\theta = 7°$ using eq 1 and $\theta = 2.5°$ using eq 2. (b, bottom) Magnification of a portion of the hole in (a) indicating the asymmetric shape of the rim. The length of the bar is 10 μm. Although this micrograph was obtained by using white light, a check with a monochromatic light source showed qualitatively the same behavior. The spacing between two consecutive dark fringes (representing a change in height proportional to half a wavelength) is much smaller on the side toward the hole compared to the side facing the unperturbed film. From this inner and outer fringe spacing we obtained $\theta \sim 10°$ and $\theta \sim 4°$, respectively. However, the uncertainties of determining θ from the fringe spacing are quite large.

The time (t_R) necessary for rupture is expected to depend dramatically on molecular weight.[26] For the smaller molecules in films thinner than ~100 nm, t_R was always of the order of the time needed for growing a hole large enough to be visible by light microscopy. For the long PS-p2-N molecules, however, t_R could be even longer than the time the whole dewetting process needed as indicated in Figures 6 and 7. Films of long molecules are thus apparently stable for reasonably long times. This effect can be attributed to entanglements between the molecules.[26]

Penetration Depth of Free Polymers in Brushes of Chemically Identical Molecules. To determine whether nongrafted molecules can penetrate the brush all the way to the substrate, we prepared two similar brushes (PS-S-R, thickness after washing ~60 Å) and coated them with an ~800 Å thick film of longer molecules (PS-L-N and PS-L-R). One sample was coated with the reactive and the other with the nonre-

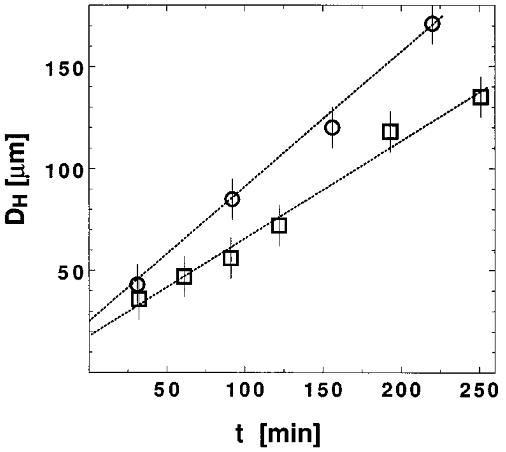

Figure 5. Diameter of the holes (D_H) as a function of annealing time (*t*) at 160 °C for a ~900 Å thick polystyrene film (circles PS-S-N; squares PS-p1-N) on a 54 Å thick polystyrene brush (PS-S-R). The dotted lines are guides for the eye. These data points were obtained by successive annealing and quenching. The values represent averages over several holes.

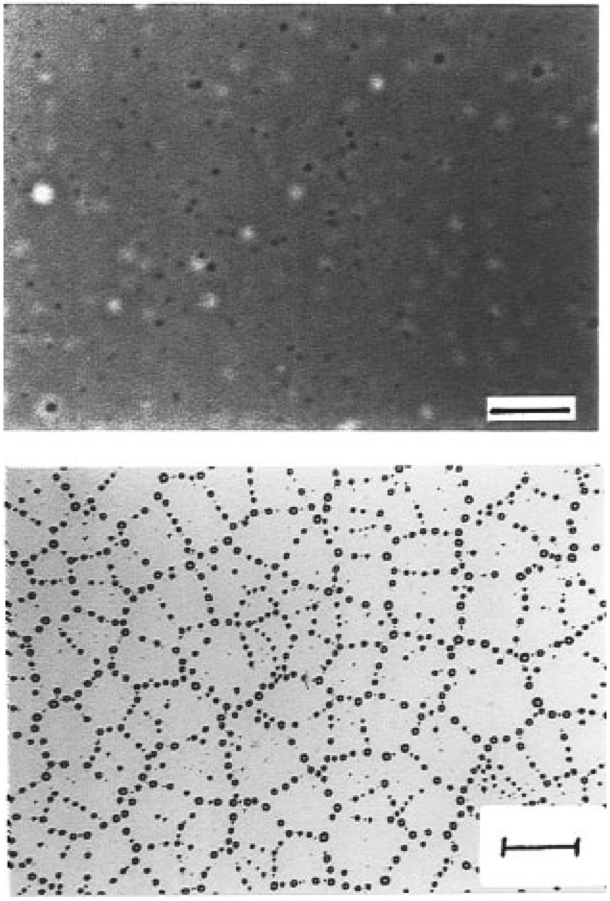

Figure 6. Optical micrograph (using white light) of a ~600 Å thick polystyrene film (PS-p2-N) on a 60 Å thick polystyrene brush (PS-S-R): (a, top) after annealing for 25 h at 180 °C. The length of the bar is 25 μm. (b, bottom) After annealing the same sample for additional 40 h at 180 °C. The length of the bar is 200 μm.

active version. Annealing both samples (for ~200 min at 160 °C) resulted in dewetting of the nonreactive polymer while the reactive polymer did NOT show any signs of hole formation, even after annealing for a few days at 180 °C. This clearly indicated that the PS-S-R brush was dense enough to be nonwettable by PS-L-N. Nonetheless, it still could be significantly penetrated by these longer molecules on top, allowing for grafting of the molecules of the reactive version. The underlying brush prohibited, however, the formation of a second dense brush of the longer molecules on top of the first one of smaller molecules, and thus no dewetting was observed. The result can be compared with a PS-L-R brush of low grafting density in contact with a melt of

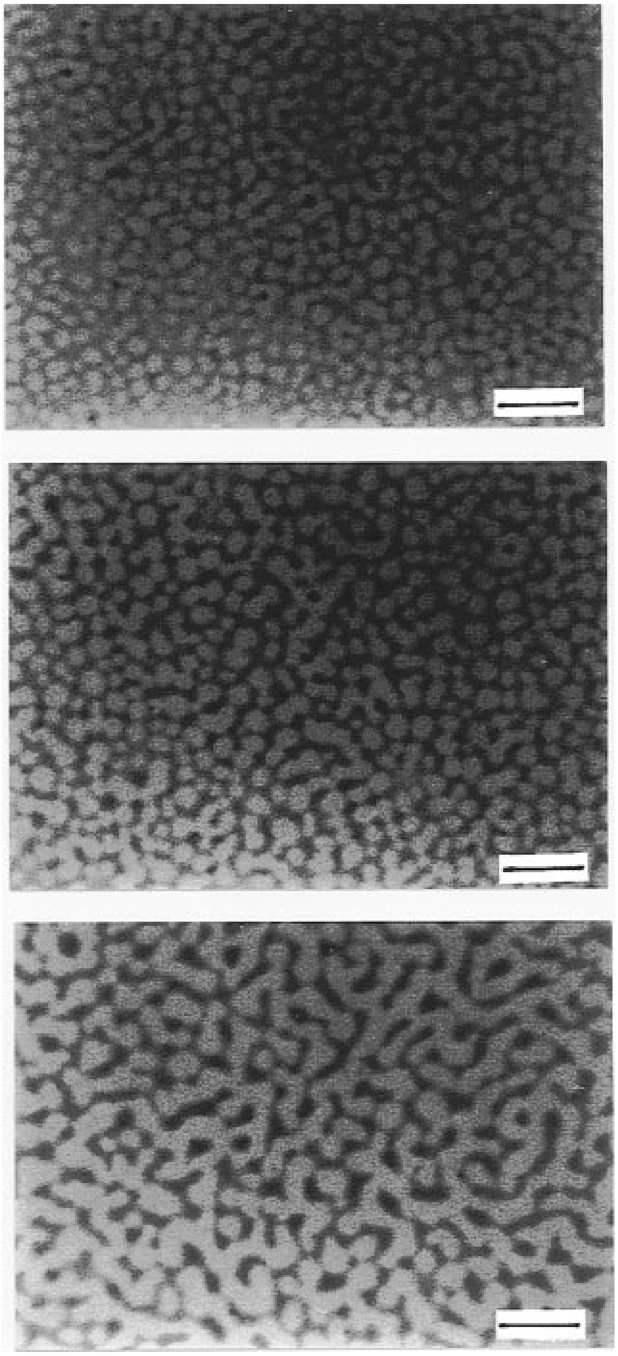

Figure 7. Optical micrograph (using white light) of a ~200 Å thick polystyrene film (PS-p2-N) on a 125 Å thick polystyrene brush (PS-L-R): (a, top) after annealing for 28 h at 170 °C. (b, middle) after annealing for an additional 2.5 h at 170 °C, and (c, bottom) after annealing for an additional 6 h at 170 °C. (After further annealing the structure seen in micrograph c transforms into many isolated droplets). The length of the bar is 10 μm. Note that the holes grew by a factor of ~2 during the last 8 h of annealing, implying that rupture occurred after ~20 h of annealing at 170 °C. Although the sample of Figure 6 was annealed at a higher temperature and the film was deposited onto a less wettable brush of shorter molecules, there were no indications of real rupture even after 25 h. This hints that thicker films need longer times for rupturing. Note also that the final polygons of Figure 6b are significantly larger than the structure visible in Figure 7c.

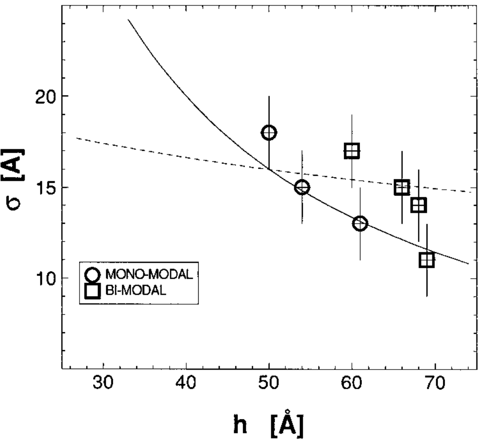

Figure 8. Interfacial width (penetration depth) as determined from the standard deviation σ of an error function profile for the interface between a polystyrene film (PS-p1-N, ~900 Å) and a polystyrene brush (monomodal PS-S-R; bimodal PS-S-R/PS-L-R mixtures—see Table 2 for details) as a function of the thickness (h) of the brush. The values were obtained from fits to neutron reflectivity curves. The thicknesses of the bimodal brushes were determined from the midpoint of the steep part of the interface between brush and melt. This thickness accounts mostly for the layer of the shorter molecules. The dashed line describes the expected values of λ given by eq 3 taking into account a factor of $^1/_2$ for the ratio of σ/λ. The solid line represents the following relation: $\sigma = 800/h$.

PS-L-N molecules. The number of grafted PS-S-R molecules, however, is large enough to build up a resisting force higher than the driving capillary force exerted by the underlying brush of short molecules.

For a few samples we used neutron reflectometry[27] to determine in a quantitative way the penetration of free polystyrene molecules into the brush. For a 900 Å thick film of PS-p1-N on a PS-S-R brush, we found that the width of the interface as approximated by an error function varied between $\sigma = 12 \pm 2$ Å and $\sigma = 18 \pm 2$ Å for brush thicknesses between 63 and 50 Å, respectively. This means that significant penetration occurred only at the outer part of the brushes and only very few molecules could reach the substrate. In Figure 8 we plotted the σ values vs the thickness of the washed brushes. The interfacial profile for bimodal brushes consisted of two parts corresponding to a layer of short grafted molecules with an overlayer of long molecules (see ref 21 for a schematic drawing). We consider this system as a brush of short molecules with a few embedded long "connector" molecules. Consequently, we plotted the width of the interface between the brush of short molecules and the film of free molecules including the penetrating connectors. Details about these neutron reflectometry studies will be published elsewhere.

Dependence of Contact Angle and Dewetting Velocity on Grafting Density. Contact angles (θ) have been determined from balancing the volume of a hole of diameter D_H (for D_H of the order of 100 μm) and a depth equal to the initial film thickness (d) with the volume of the rim of diameter D_R using the following equation[22] predicted for slippage of a polymer on a solid substrate:

$$\theta = (D_H d)/(4{D_R}^2 s) \qquad (1)$$

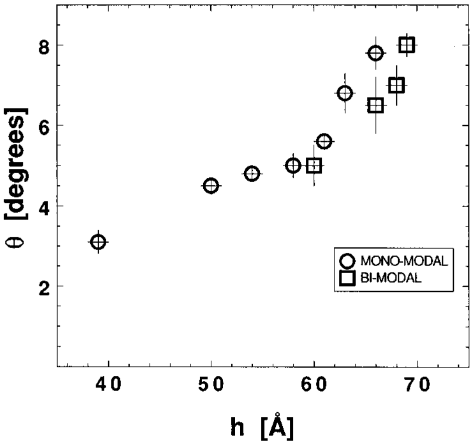

Figure 9. Contact angles (θ) as determined from the diameters of the holes and the surrounding rims using eq 1 as a function of the thickness (h) of the brush after washing and drying for the system described in Figure 8. The samples were annealed at 160 °C and quenched to room temperature. The diameter of the holes was ~100 μm on the average. The thickness of the bimodal brushes has the same meaning as in Figure 8.

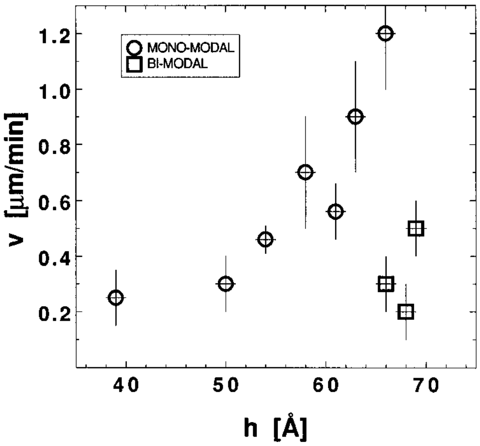

Figure 10. Averaged velocity (v) as a function of the thickness (h) of the brush after washing and drying for the system described in Figure 8. The samples were annealed at 160 °C. The thickness of the bimodal brushes has the same meaning as in Figure 8.

The parameter s takes into account that the shape of the rim is asymmetric. s has a value of ~0.1. If the shape of the rim is symmetric, the equation for the equilibrium contact angle reads

$$\theta = \sqrt{2}({D_H}^2 d)/({D_R}^3 + D_H {D_R}^2) \approx \sqrt{2}(D_H d)/{D_R}^2 \qquad (2)$$

The approximation is valid if D_H is much larger than D_R. For large holes, eqs 1 and 2 differ only by a constant factor of ~1.8. In the case of very thick rims, we could determine the contact angles directly from the interference fringes. The results compared better with the values obtained from eq 1. In Figure 9 we plotted θ as a function of brush thickness for monomodal and bimodal brushes. θ was determined by using eq 1.

The higher the grafting density, the larger was θ formed by polystyrene melt on top of a polystyrene brush. In correlation with θ, the dewetting velocity also increased with grafting density. This is shown in Figure 10 in a quantitative way for PS-p1-N films (~900 Å thick) on PS-S-R brushes of different grafting densities. We showed earlier that the dewetting velocity was not constant (see Figure 3). The values in Figure 10 are therefore averages over approximately the first 100 μm of hole growth. Plotting this averaged velocity (v) as a function of contact angle (see Figure 11) shows that v increased with θ. This increase was faster than linear,

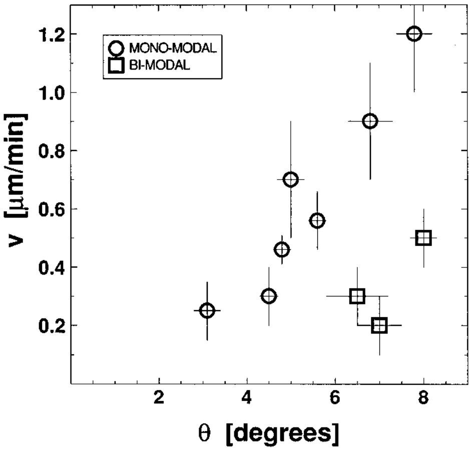

Figure 11. Averaged velocity (v) as a function of the contact angle (θ) for the same data as in Figures 9 and 10.

but significantly slower than the θ^3 dependence (Tanner's law) of the dewetting velocity on ideal solid surfaces.[17,25]

Molecular Weight Effects. Experiments with longer molecules (PS-L-R) exhibited qualitatively the same behavior. However, in order to observe dewetting of the same molecules on their own brush, we had to anneal the samples for much longer times (days rather than hours[28]). Several reasons may have been responsible for this change in rate. The formation of brushes of high enough grafting density was kinetically slowed down. The thickness of the layer at the onset of stretching of the brush molecules is proportional to $N^{1/2}$, N being the degree of polymerization of the molecules in the brush. Additional molecules have to travel through this layer in order to be able to graft onto the substrate. The dewetting velocity was reduced as a consequence of the increased viscosity of the longer molecules. In order to create holes large enough to be visible under a light microscope they have to be larger than ~1 μm. Consequently, for higher viscosities one has to wait longer until the holes become observable.

Covering layers of grafted molecules with nonreactive polymer of much higher molecular weight favored dewetting as was expected from theory[10,11] and already shown experimentally.[13] We also performed a brief study. PS-L-R brushes with a thickness of 80, 100, and 125 Å, respectively, showed no signs of dewetting when coated with PS-L-N. However, when coated with the much longer molecules of PS-p2-N all, except the sample with the 80 Å brush, showed the formation of holes, indicating that these brushes could not be wetted by the longer molecules.

Discussion and Conclusions

Although one purpose of these experiments was to prevent dewetting by using end-functionalized molecules, we failed to stabilize the system in most cases. It is certainly not at all obvious that the observed dewetting behavior of our brush/melt system should be similar to the behavior of a simple polymer film on a nonwettable solid substrate. In a qualitative sense, however, concerning rupture the behavior of the two cases did not differ. Preliminary tests showed that the average distance between holes decreased significantly with decreasing film thickness.[30] As all molecules, both in the brush and in the film, were polystyrene molecules it seems reasonable to assume that the brush layer has no (significant) effect on the long-range van der Waals forces acting on the surface of the polymer film. Quantitatively, we expect, however, that the influence of the brush layer should affect the thickness dependence of the average distance between initial holes and the related size of the final droplets.

Autophobic behavior for a melt of infinitely long molecules on top of a brush was predicted theoretically.[10] The effect was attributed to entropic repulsion exerted by the brush molecules. Free molecules that penetrate a brush cause stretching of the brush molecules. Therefore penetration is unfavorable.[31] Although our free molecules were of finite length, we nonetheless compared our results with the theoretical prediction for the penetration depth (λ) or the contact angle (θ). λ and θ should vary according to the following relations

$$\lambda \cong (12/\pi^4)^{1/3}(Na\Sigma)^{1/3} \tag{3}$$

and

$$\theta \cong (3kT/2\lambda a\gamma)^{1/2} = (3kT/2a\gamma)^{1/2}(\pi^4 h/12N^2a^4)^{1/6} \tag{4}$$

where we used $\Sigma = Na^3/h$, with N the degree of polymerization of the grafted molecules, a the statistical segment length, Σ the area per grafted molecule, γ the "chemical" surface tension of the brush/air interface, and h the thickness of the grafted layer. It is easily seen that for increasing N the degree of stretching (defined as $h/N^{1/2}a$) has to increase with $N^{3/2}$ in order to obtain the same contact angle. In other words, the contact angle depends only on the *absolute* penetration depth. For the short and long reactive molecules in our experiments, this means that the longer molecules have to be ~10 times more stretched than the shorter ones. This could explain why it is more difficult to observe dewetting for long grafted molecules.

We observed the predicted trends of eqs 3 and 4 only in an very qualitative way. A quantitative comparison revealed severe discrepancies. In particular, according to eq 4 θ should not vary much with brush thickness, while experimentally a strong increase of θ with brush thickness was observed. However, one has to note that our experimental conditions deviate from the assumptions made by theory. First, the length of the brush molecules was rather small and thus we may not be in a regime for which the theory is applicable. Second, our free molecules were not infinitely long. At present, it is not exactly known what would happen if both, the grafted and the free molecules, have the same molecular weight.

As shown by the neutron reflectometry measurements, there is still measurable interpenetration between the free molecules and the brush. It may be helpful to divide the brush into two regions, an outer and an inner part. The outer region of thickness λ can be represented as a layer where the molecules (their segments) experience little constraints. The inner region is almost impenetrable as the cost for stretching the molecules is always higher than a gain in translational entropy. Obviously, there is only a diffuse border between the inner and outer regions. We may identify this border as a virtual interface at which dewetting can occur. Such splitting of the brush layer makes two effects visible: first, entropic repulsion of the free molecules by the inner region of the brush molecules. However, that does not mean that we automatically will be able to observe dewetting. As a second process we have to account for the interaction between the outer layer and the free molecules. If this outer layer is reasonably thick, we speculate that this interaction may play a dominant role in the sense that it can prevent dewetting even on a nonwettable virtual interface. We assume that the parts of the grafted molecules situated in the outer region may act as "connectors" between the free molecules and the virtual interface. The length of these connectors depends on the position of the virtual interface (the penetration depth λ).[32] In order to have dewetting, these connectors have to be pulled out of the melt of free molecules. This pull-out force[33] has to be at least compensated by the driving Young's force, the balance of the interfacial forces at the three-phase contact line.

Our experiments with bimodal brushes seem to support this concept. The dewetting velocity depends sensitively on the number of long molecules embedded in a brush of shorter ones. For the same contact angle, i.e., the same driving force, we observed a significantly lower dewetting velocity in the case of bimodal brushes (see Figure 11).

On the basis of these considerations, it becomes clear that the dynamics of dewetting for the brush/melt system have to be different compared to dewetting on an ideal solid. The interaction of the outer brush region with the melt of nongrafted molecules may be responsible for the observed relatively weak dependence of the dewetting velocity on contact angle. Furthermore, it might be possible that these brush/melt interactions can account for the asymmetric shape of the rim profile and the nonlinear growth of the cylindrical holes. Attribution of these effects to properties of the brush is more appealing than interpreting them in terms of slippage.

It is not yet understood how the penetration of nongrafted molecules into the brush affects the rupture of the films. The possibility of penetrating the brush may shorten the rupture time due to an additional amplification of fluctuations of the film surface. Viscoelastic losses, on the other hand, may lead to a damping of such fluctuations.

These investigations are relevant also for brush/elastomer systems. Grafted molecules are used to improve adhesion of the elastomer to a solid. To find the optimal grafting density for maximum adhesion is a matter of current investigations.[7,8] Interaction between the brush and the elastomer may be limited by the necessary swelling of the elastomer in order to allow penetration by the brush molecules. Our results indicate a second limiting constraint. It is difficult to penetrate brushes of high grafting density with non-cross-linked polymers. One can imagine that it will be even more difficult for an elastomer. We therefore conclude that brushes with very high grafting density are never useful for the purpose of improving adhesion.

This study indicates that it is preferable to use rather long molecules for the grafted layer in order to stabilize liquid films or to improve adhesion for at least two reasons. First, the formation of a brush of high grafting density is extremely slow for long polymers. Second, the degree of stretching has to be larger for longer molecules in order to obtain the same autophobic behavior. However, even for long polymers, for high enough energy gain by grafting and after enough time for the grafting process, a brush may be formed with a grafting density high enough to repel even identical molecules, as we have shown in this study for comparatively short polystyrene molecules.

Acknowledgment. This work would not have been possible without the help of P. Bassereau, A. Menelle, and P. Silberzan. Very helpful and inspiring discussions with M. Aubouy, F. Brochard-Wyart, D. Chatenay, L. Leibler, A. Mourran, and E. Raphaël are gratefully acknowledged.

References and Notes

(1) Sharma, A. *Langmuir* **1993**, *9*, 861.
(2) Langmuir, I. *Trans. Faraday Soc.* **1920**, *15*, 62.
(3) Hare, E. F.; Zisman, W. A. *J. Phys. Chem.* **1955**, *59*, 335; **1955**, *59*, 1097.
(4) Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J. *Science* **1994**, *263*, 793.
(5) Creton, C.; Brown, H. R.; Deline, V. R. *Macromolecules* **1994**, *27*, 1774.
(6) Washiyama, J.; Kramer, E. J. Creton, C. F.; Hui, C.-Y. *Macromolecules* **1994**, *27*, 4382.
(7) Brochard-Wyart, F.; de Gennes, P. G. *J. Adhes.*, in press.
(8) Deruelle, M.; Tirrell, M.; Marciano, Y.; Hervet, H.; Leger, L. *Faraday Discuss.* **1994**, *98*, 55.
(9) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(10) Leibler, L.; Ajdari, A.; Mourran, A.; Coulon, G.; Chatenay, D. In *Ordering in Macromolecular Systems*; Teramoto, A.; Kobayashi, M., Norisuje, T., Eds.; Springer-Verlag: Berlin, 1994; pp 301−311.
(11) Shull, K. *Faraday Discuss.* **1994**, *98*, 203.
(12) Partly in ref 10 and Chatenay, D., Mourran, A., private communication.
(13) Liu, Y.; et al. *Phys. Rev. Lett.* **1994**, *73*, 440.
(14) Zhao, W.; et al. *Phys. Rev. Lett.* **1993**, *70*, 1453.
(15) Klein, J.; Perahia, D.; Warburg, S. *Nature* **1991**, *352*, 143.
(16) Reiter, G. *Phys. Rev. Lett.* **1992**, *68*, 75; *Langmuir* **1993**, *9*, 1344.
(17) Brochard-Wyart, F., Daillant, J. *Can. J. Phys.* **1990**, *68*, 1084.
(18) Reiter, G.; Auroy, P.; Auvray, L. *Macromolecules*, submitted.
(19) Tassin, J. F.; Monnerie, L.; Fetters, L. J. *Macromolecules* **1988**, *21*, 2404.
(20) Ligoure, C.; Leibler, L. *J. Phys. (Fr.)* **1990**, *51*, 1313; and private communication.
(21) Dan N.; Tirrell, M. *Macromolecules* **1993**, *26*, 6467.
(22) Brochard-Wyart, F.; de Gennes, P.-G.; Hervet, H.; Redon, C. *Langmuir* **1994**, *10*, 1566.
(23) Leibler, L., private communication.
(24) A linear relation between velocity and inverse viscosity is expected for dewetting on a perfect solid surface as shown experimentally.[25]
(25) Redon, C.; Brochard-Wyart, F.; Rondelez, F. *Phys. Rev. Lett.* **1991**, *66*, 715.
(26) Safran, S. A.; Klein, J. *J. Phys. II (Fr.)* **1993**, *3*, 749.
(27) See, e.g.: Russell, T. P. *Mater. Sci. Rep.* **1990**, *5*, 171.
(28) For a 90 nm thick film of PS-L-R autophobic behavior (signs of hole formation) was observed only after annealing the sample for 48 h at 160 °C.
(29) Auroy, P.; Auvray, L.; Léger, L. *Macromolecules* **1991**, *24*, 5158.
(30) This can be inferred, for example, from a comparison of Figures 6 and 7. A quantitative study will be performed in the future.
(31) Witten, T. A.; Leibler, L.; Pincus, P. A. *Macromolecules* **1990**, *23*, 824.
(32) This concept of inner and outer regions may also hold for layers of adsorbed polymers. We expect that dewetting will be observed for systems where an inner repulsive region exerts a larger driving force than the resisting force due to tails and loops embedded in the melt of nonadsorbed molecules. This might be the case for a layer of irreversibly and strongly adsorbed short polymers coated by a layer of much larger polymers.
(33) We assume that there exists a threshold force for pull-out similar to what was predicted for the case of adhesion. See: Raphaël, E.; de Gennes, P.-G. *J. Phys. Chem.* **1992**, *96*, 4002.

MA950297Z