Stabilization of Nonwetting Thin Liquid Films on a Solid Substrate by Polymeric Additives

Rachel Yerushalmi-Rozen and Jacob Klein*

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

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Thin films of a low molecular weight, nonvolatile liquid which are forced to spread on silicon wafers, rupture within minutes and dewet. Addition of long polystyrene chains (for which the liquid is a good solvent) up to a concentration of 10% does not change this behavior qualitatively. In contrast we find that the unbroken uniformity of the films may be preserved for many months or longer by a polystyrene brush attached to the silicon, together with some unattached polystyrene in the liquid. By varying the molecular weights and concentrations of the unattached chains within the film, we were able to establish a stability diagram in this system which shows that suppression of rupture is only observed at free-polymer concentrations which exceed the overlap concentration. This suggests that the effect may arise from the formation of an entanglement network between the free chains (within the liquid film) and the surface-tethered brush molecules.

I. Introduction

A thin film of a liquid may be forced to spread on a substrate which it does not wet. When the liquid is nonvolatile the system will tend to minimize the solid–liquid contact area by spontaneously dewetting into droplets. Applications for thin uniform films on solid substrates are found in a variety of technological fields, as in lithography in the microelectronics industry. These thin films are often applied mechanically, by spin-coating. Thin films may be used for coating optical devices, while the paint, food, and cosmetics industries also utilize thin film coatings. The resulting thin layer (of thickness ranging from a few nanometers to microns) may be stable or unstable, according to the wetting properties of the solid–liquid pair. The stability of the thin films is practically important in all those applications, and its understanding presents a challenge from a fundamental point of view.

The question of wetting of solids by liquids is classic.[1] More recently, Brochard et al.[2] discussed the wetting criteria for pairs of a solid and a nonvolatile liquid. They showed that two parameters are important when the liquid is dominated by van der Waals interactions: The Hamaker constant, A, which describes the long range interactions, and the spreading coefficient, S, which is a measure of the short range surface interactions.

The free energy, U, per unit area of a liquid film with thickness h_0, due to the van der Waals interactions is given by[3]

$$U(h_0) = -\frac{A}{12\pi h_0^{\,2}} \tag{1}$$

Where $A = A_{ll} - A_{sl}$ is the difference between the liquid–liquid and solid–liquid Hamaker constants. If A is positive, van der Waals interactions tend to thin the film. The spreading coefficient is defined as

$$S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}) \tag{2}$$

with γ_{sv}, γ_{sl}, and γ_{lv} being the solid–vapor, solid–liquid, and liquid–vapor surface tensions. A negative value of S indicates that the surface is not wetted by the liquid. A solid–liquid pair with positive A and negative S is classified as a case of *partial wetting*. Starting from a thin film of thickness h_0, the film will eventually breakup into droplets. Dewetting of a film involves two steps, the formation of holes and their subsequent growth.[1] Theoretical models[4–6] which describe the dewetting process predict that thin nonwetting films are unstable and that holes in them are expected to evolve by spontaneous amplification of thermal fluctuations. Recent experimental observations[7] suggest that hole formation may be the result of a more complicated mechanism. Holes which are formed in the first stage of the dewetting process may expose a dry patch of the substrate. The interfacial rim energy of the liquid surrounding the hole then increases linearly with the radius, R, of the growing hole, but the van der Waals energy reduces with the exposure of solid area, which is proportional to R^2. Once formed the hole will grow if the total free energy is negative and that happens at a critical radius,[5] while holes of a smaller diameter heal. The second step of dewetting (hole growth) has also been extensively studied.[6,8,9]

Static features of the dewetted state and the mechanism of the dewetting process were investigated in ultrathin (h_0 < 100 nm) films of polystyrene.[10] In this study it was found that the film breaks into holes with a mean spacing d, $d \approx h_0^2$, the area of a hole $R^2 \approx h_0^4$, and the size distribution of holes at a given time is narrow. These findings agree well with the theoretical model which assumes that the film ruptures due to amplification of thermal fluctuations.[4–6] The absolute values observed for the rupture time however, were very much shorter than predicted by theory.

We describe here a new approach for suppressing the rapid breakup of thin (h_0 = 100–600 nm) nonvolatile liquid films of oligostyrene, spread on a smooth solid substrate which they do not wet. We find that the films may be

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Table 1

material	weight averaged molecular weight, M_w (g/mol)	designation	polydispersity, M_w/M_n	R_F[a] (nm)[17]
polystyrene homopolymer (protonated)	30 300	PS-30.3K	1.03	13.4
	330 000	PS-330K	1.04	54.1
	550 000	PS-550K	1.04	72.9
	710 000	PS-710K	1.05	84.7
	1 930 000	PS-1930K	1.06	152.1
	7 100 000	PS-7100K	1.11	325.9
polystyrene homopolymer (deuterated	10 500	dPS-10.5K	1.02	7.2
	500,000	dPS-500K	1.05	69.0
end-functionalized polystyrene[b] (deuterated)	380 000	dPSX-380K	1.05	58.8
end-functionalized polystyrene (protonated)	24 700	hPSX-24.7K	1.02	11.9

[a] Swollen end-to-end dimension. [b] The end-group, designated-X, is the zwitterion $(CH_2)_3N^+(CH_3)_2(CH_2)_3SO_3$. a

stabilized against rupture by the presence of a polymer amphiphile which end-attaches to the silicon, together with small amounts of free polymers in the liquid. The stabilized films remain smooth and uniform for many months. In contrast, similar films to which polymers have not been added in the appropriate combination rupture within minutes from spreading. A brief account of some of these findings has recently appeared.[13] The present paper describes a more extensive study. In sections II and III we describe the materials and the experimental procedures used and present our findings. In section IV we discuss the results and propose some possible mechanisms which might be responsible for the stabilization effect.

II. Experimental Section

I. Materials. Silicon wafers (3″ P(100) 0.5−1 Ω/cm 406−470 m pol/etch) were purchased from Aurel GMBH. Such wafers are covered by a thin silicon oxide layer.[12,14]

The toluene used was Frutarom analytical grade or Sigma spectroscopic grade. Polystyrenes, either protonated or fully deuterated, of various molecular weights (M) were purchased from Polymer Laboratories. Characteristics of the polymers were determined by size-exclusion chromatography (SEC) and provided by the suppliers. Polystyrenes end-functionalized with the zwiterionic group $(CH_2)_3N^+(CH_3)_2(CH_2)_3SO_3^-$ (henceforth designated X) were prepared as described earlier.[15] The end-functionalized polystyrene dPSX-380K is fully deuterated. The nonvolatile liquid used was a styrene oligomer, designated PS-0.58K, with $M_w = 580$, $M_w/M_n = 1.02$. This is a viscous liquid (glass transition temperature $T_g = -18$ °C, viscosity $\eta \approx 30$ P at 35 °C) and is expected to be a moderately good solvent for the long PS and PSX chains.[16]

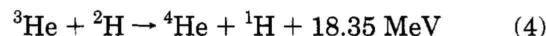
The characteristics of all polymers used are given in Table 1.

2. Sample Preparation. Films in a thickness range of 100−600 nm were prepared by spin coating from solutions of PS-0.58K in toluene and mixtures of PS-0.58K with additives, onto silicon wafers. Film thickness was controlled by the concentration of the solutions and the spin rate.

Polished silicon wafers were cut by a diamond knife to dimensions of ca. 1 × 2.5 cm, and cleaned by immersion in ethanol, followed by wiping (Kimwipes) and drying in a jet of filtered nitrogen. The dry wafers were immersed in toluene, and immediately before coating, were washed in fresh toluene and dried in a jet of nitrogen. Film thickness was correlated experimentally (Nuclear Reaction Analysis and ellipsometry) with the solution concentration: For example, a thickness of 400 nm was obtained from solutions of 70 mg/mL (PS-0.58K in toluene) spin cast at 2800 rpm (Headway photoresist spinner model 1-PM101D-E790). Spin coating was carried out in a regular hood. When additives were used, they were premixed to required concentrations with PS-0.58K dissolved in toluene, and the mixture was then spin coated as a homogeneous layer. For some of the studies we used monolayers which were self-assembled on the silicon. The exact procedure will be described in the relevant section. All samples were monitored visually while annealing at room temperature, 22 ± 2 °C.

Atomic force microscopy (AFM) was used to study the quality and surface topography of the spin-coated films. Images were obtained using a Digital Instruments Nanoscope II scanning probe microscope with a 140 μm scan head and SiN tip with a spring constant of 0.38 N/m. For this study we used an oligostyrene analogous to the PS-0.58K but of higher molecular weight (3000 g/mol), which is glassy at room temperature and thus does not dewet in the course of the measurement. The measurements were performed in air (at room temperature), following annealing of the films at 82 °C (well above their glass transition temperature of 66 °C) for 55 min. Imaging was conducted in the height mode. A typical measured root mean square roughness of less than 4 nm was found.[18] We believe that the surface characteristics of these layers following their annealing (and rapid quenching) are similar to those of the PS-0.58K liquid.

3. Nuclear Reaction Analysis. Depth distribution of deuterated polymers in a matrix of protonated polystyrene and the overall thickness of the samples were measured by nuclear reaction analysis:[19,20] In this method a beam of ^{3}He ions is incident on the film and the reaction



$$^3He + ^2H \rightarrow ^4He + ^1H + 18.35\ MeV \qquad (4)$$

takes place within the sample. From the energy spectrum of the emitted ^{4}He particles and the known energy losses and reaction cross section, the concentration depth profile $\phi(z)$ of the deuterated segments is directly measured, as a function of depth. A helium beam with kinetic energy

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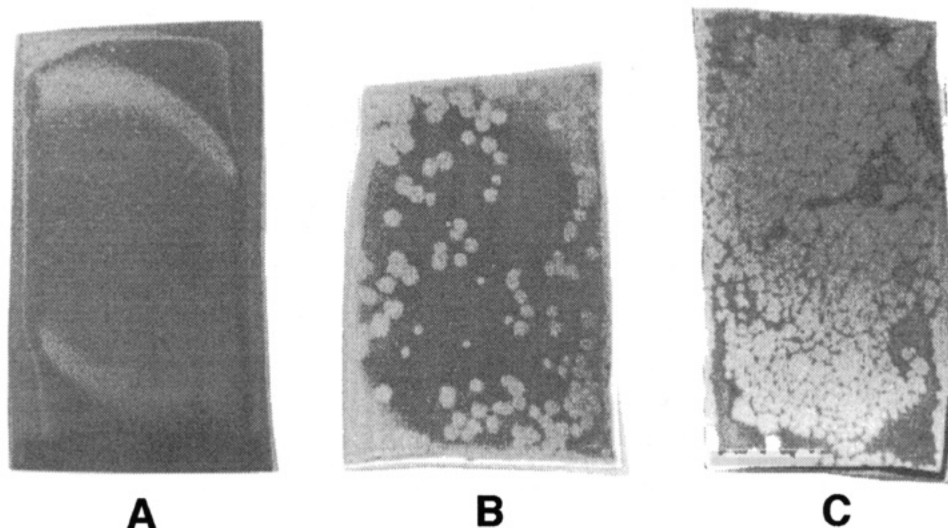

Figure 1. Evolution of dewetting from a uniform film spread on a silicon surface to a totally dewetted layer is presented in three stages. In all cases, the size of the silicon wafers shown is ca. 1 × 2 cm^2. (A) A layer of pure oligostyrene PS-0.58K immediately after spin casting on a silicon wafer. The film is smooth and uniform (to within ±5 nm from the uniformity of the interference colors); its thickness is 400 ± 20 nm. (B) A different spin-cast film of PS-0.58K, of thickness ca. 180 ± 20 nm, about 10 min after spin casting. Holes begin to form and grow. (C) A film of pure PS-0.58K on a silicon wafer 24 h after it was cast, showing clearly the dewetting into a polygonal pattern. Similar droplet patterns were obtained in films containing up to 10% of unfunctionalized PS. The area of the polygons and the diameter of the droplets depend on the film thickness.

of 900 keV leads to a straggling-limited resolution of 10 nm HWHM at the air interface and ca. 20 nm HWHM through the depth range of 400 nm.[20] From the $\phi(z)$ profile we determine the mean brush height and the surface excess, Γ, per unit area (for the case where there is polymer aggregation at the silicon surface):

$$\Gamma = \int^{\text{film thickness}} [\phi(z) - \phi_b]\, dz \qquad (5)$$

where ϕ_b is the concentration in the bulk far from the interface.[21] In the absence of deuterated chains in the bulk, for example when only a monolayer of deuterated amphiphiles is anchored at the silicon–liquid interface, ϕ_b reduces to zero. The interanchor spacing of the chain, s, is obtained from Γ:

$$s = \left(\frac{\Gamma}{M}\right)^{-1/2} \qquad (6)$$

III. Results

There are several regimes under which the thin films of the PS-0.58K have been observed. For clarity we describe these under separate numbered headings.

1. Polymer-Free Thin Liquid Films. *1.1. The Dewetting Process.* The oligostyrene PS-0.58K is a viscous (Newtonian) liquid at room temperature. Thin uniform films of PS-0.58K were formed on silicon wafers by spin coating from toluene solutions. These films which are 100–600 nm thick show bright interference colors, resulting from interference between the reflection of light from the two sides of the polymer film lying on the reflecting surface of the polished silicon. Color fluctuations in the films indicate an optical path difference, i.e., change in the thickness. Uniformity of color across large areas in typical samples indicates that possible fluctuations in the thickness are smaller than a few nanometers.[22]

A freshly formed, smooth and unbroken film of the pure oligomer begins to dewet spontaneously. In films which are in a thickness range of ca. 300–500 nm, holes appear within a few minutes from spin coating and grow as described below. The final stage of dewetting is reached at room temperature (22 ± 2 °C) within a time interval of 8–15 h from film formation. Films at different stages are presented in Figure 1. As the dewetting proceeds, the rim breaks into droplets. Initially, the drops are still connected by the thinning rim. As the diameter of the hole grows, more liquid is collected in the drops, and the circular shape of the rim develops spontaneously into a polygonal form. Finally, the rim breaks into disconnected drops which form the edges of a polygon, as presented in Figure 1C. These qualitative observations agree well with those reported ealier by Reiter.[10] Contact angles of 22 ± 2° were measured (by a goniometer Olympus B071 TGHM) in residual drops of thick films (0.6–1 μm) of PS-0.58K which dewetted on silicon surfaces.

1.2. Film Thickness. Preliminary observations of the effect of film thickness on the rupturing process indicate that features of the ruptured films depend strongly on the initial thickness, h_0. Though in this study we did not investigate the thickness dependence in a quantitative manner, it was clear that, in thicker films, the density of holes was much lower than in the thinner ones. Also, the final size of the droplets and the area of the polygons was larger for thicker films. We also observed that longer time intervals pass before holes first form in thicker films. For example, holes were first observed ($2R = 0.1$ mm) in a 1 μm thick film of the pure oligostyrene about 5 days after preparation as compared with less than 10 min in a 350 nm film. A picture of a typical hole is presented in Figure 2. The hole is composed of an exposed silicon patch surrounded by a round-contoured rim. In many of the holes we observed that the central part, that is, the exposed silicon, is not empty, but rather a dust particle or debris left over from the retracting film is located on it. The mechanism of hole formation, and in particular the nucleation of holes by dust particles or other species, is currently being studied by us, and is discussed at greater length later.

2. Films Which Contain Polymeric Additives. The effectiveness of various polymer additives in suppressing rupture and dewetting was studied. The experiments are summarized in Tables 2 and 3. Over the experimental time scale (minutes to months) three different types of

(21) It should be noted that the presence of free deuterated chains can mask the true concentration profile of the brush. Therefore brush features are always determined from profiles which contain small concentrations only of free deuterated chains.
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Table 2

variation no.	% dPSX-380K[a]	% homopolymer	layer state
1	none	none	ruptures and dewets (Figure 3a)
2	none	3–12% PS-30.3K 5–8% PS-330K 5.7% PS-550K 2–8% PS-710K 2–5% PS-1000K 5% PS-1930K	All the combinations described for no. 2 lead to formation of films that rupture and dewet
3	monolayer	none	ruptures (Figure 3b)
4	1–4%	none	ruptures
5	>4.6%	none	stable
6	monolayer or 1%	≤5% PS-330K	ruptures
7	monolayer or 1%	7% PS-330K	stable
8	monolayer or 1%	≤5% PS-330K	ruptures
9	monolayer or 1%	7% PS-550K	stable
10	monolayer or 1%	<5% PS-710K	ruptures
11	monolayer or 1%	≥5% PS-710K	stable
12	monolayer or 1%	2.5% PS-1000K	stable
13	1–5%	1–5% PS-710K	stable[b]
14	monolayer or 1%	1.6% PS-1930K	ruptures
15	monolayer or 1%	2.5% PS-1930K	stable
16	monolayer or 1%	2% PS-7100K	stable

[a] Monolayer denotes brush formation from solution followed by washing and subsequent casting of the oligostyrene film. The percentages denote the amount of amphiphile that was incorporated in the oligostyrene prior to casting. [b] In combinations with total polymer concentration ⩾5%.

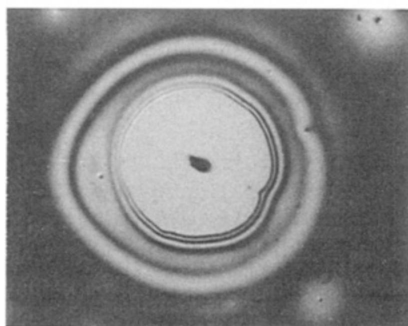

Figure 2. A dry patch formed in the dewetting process. The picture was taken with a light microscope. The central part of the hole is an exposed silicon surface (the dark spot at the center may be debris associated with nucleation by a dust particle, see the text). The diameter of the hole is about 0.15 mm.

film evolution were observed (Figure 3): (1) hole formation followed by rupturing and dewetting to the characteristic polygonal droplet pattern (Figure 3A), (2) roughening of the film surface and formation of holes (Figure 3B), and (3) full suppression of the formation of inhomogeneities and holes leading to films which are unbroken, uniform, and stable for many months (Figure 3C).

2.1. Films Which Rupture and Dewet (Type 1). Films of oligostyrene which contain unfunctionalized PS molecules in the bulk of the film at a range of concentrations and molecular weights (summarized in Table 2) were observed to dewet. The high molecular weight PS additives are expected to influence both equilibrium and dynamic properties of the oligomer films (via changes in T_g, viscosity, and surface tension[11]) and thus to affect the time evolution of the films as later discussed. We found that the formation of holes and subsequent rupture and dewetting of the films was not suppressed by addition of the PS chains up to ca. 10% (see Table 2), though at higher polymer concentrations the formation rate of holes (i.e. the time for their first appearance) was significantly slower. Typical polygonal droplet patterns as presented in Figure 3A are formed within 2 days or so.

NRA spectra of thin layers of oligostyrene which contain added dPS chains are presented in Figure 4. Within the resolution of our method the dPS chains appear to be homogeneously distributed and there is no evidence of excess dPS or depletion at either the air or silicon interfaces.

2.2. Films Which Roughen and Rupture (type 2). 2.2.1. Films Which Contain Low Concentrations of dPSX-380K. We studied the time evolution of films of the oligostyrene spread onto a silicon wafer covered by a self-assembled monolayer of dPSX-380K (category 3 of Table 2). Such monolayers were formed by overnight incubation of the silicon wafer in a solution of toluene (concentration 1 mg/mL), followed by immersion and a rinse in pure toluene. The procedure yields monolayers of end-attached polymers as shown by NRA (Figure 5). NRA spectra of such a film reveal the formation of a layer of mean thickness of 100 ± 20 nm end-attached (but otherwise nonadsorbing) PSX chains at the silicon interface. Adsorbance values of 2.4 ± 0.2 mg/m^2, determined from the NRA profile, yield a mean interanchor spacing $s = 17 \pm 2$ nm, which is about one-third of the swollen end-to-end dimension R_F of the free chains (for dPSX-380K in toluene, $R_F = 58$ nm). This spacing compares with $s \cong 14$ nm reported for the same amphiphile anchored onto mica from toluene[15] and indicates the formation of an appreciably overlapping polymer brush. It compares with the brush height of ca. 100 nm, indicating significant swelling as expected in a good solvent. These films lost their uniformity and became ruptured or pocked. It should be noted that holes formed in these layers, which contain an insufficient amount of polymer, do not expose the silicon surface. Preliminary measurements using phase contrast interference microscopy show that the holes extend down to the brush tip (i.e. ca. 100 nm from the silicon surface). The pocked films (Figure 3B) did not further evolve for many months and specifically did not dewet into droplets.

Preliminary AFM measurements of pocked rough layers[23] indicate that, in contrast to the characteristic smooth surface of the spin coated films (RMS of about 4 nm), large scale roughness (mean diameter of 20 μm and mean height 1 μm) develops in the roughened films.

As these films roughened and ruptured (to the brush tip) but did not dewet into droplets, we studied the effect of increasingly higher amounts of the functionalized PSX-

(23) AFM measurements of unstable films were performed in a cell containing a solution of 50% glycerol and 50% water at room temperature and atmospheric pressure. Imaging was conducted in the height mode.

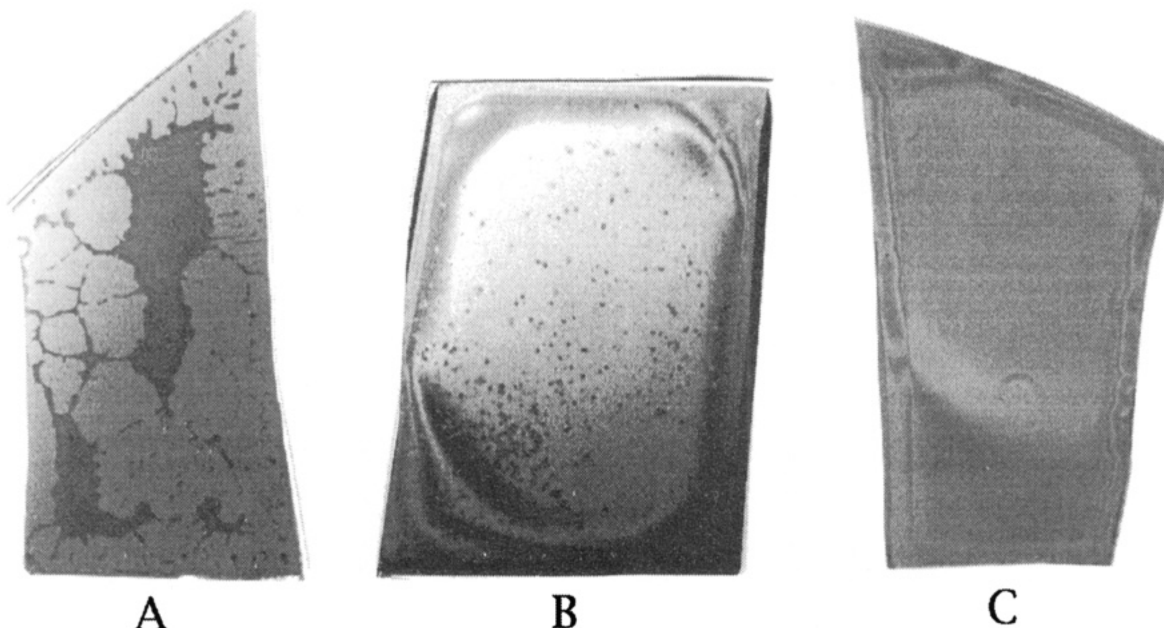

Figure 3. Films of oligostyrene which were prepared by spin casting from a toluene solution onto silicon wafers to an initial thickness (h_0) of 400 ± 20 nm. The films retained a uniform unbroken appearance for a characteristic time (described in the text) after which film A ruptured and dewetted (as in Figure 1C), film B ruptured, and film C retained its uniform unruptured form. The films are shown after they have evolved to a characteristic steady state: (A) A film of PS-0.58K containing 5% of PS-1930K 48 h after it was prepared. The droplet pattern is typical for dewetting films of type 1. (B) A film of PS-0.58K containing 2% of the amphiphile dPSX-380K, about 5 h after it was prepared. The pocked surface is typical for a ruptured film (type 2). (C) A film of PS-0.58K containing a monolayer of dPSX-380K and 2.5% of PS-1930K 4 months after it was prepared. The uniform smooth appearance is typical for stabilized films (type 3).

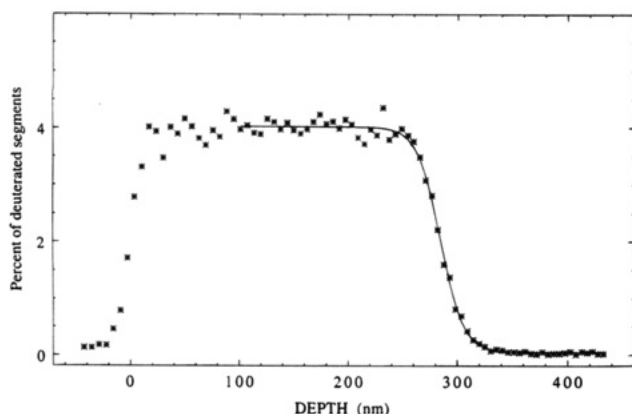

Figure 4. Concentration–depth profiles of deuterated PS within oligostyrene determined by NRA. The zero depth of the profile is the liquid–air interface, and the cutoff at 280 nm is the liquid–solid interface. The mean concentration of dPS-500K is 4%, and (within our resolution) the chains are uniformly distributed throughout the film. The film was measured less than 1 h after it was prepared and it dewetted some hours later.

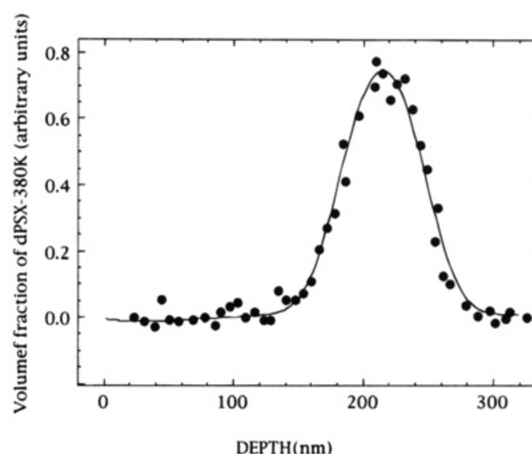

Figure 5. Concentration–depth profiles of a dPSX-380K monolayer within an oligostyrene film of thickness 280 ± 20 nm. The monolayer was assembled by the procedure described in the text. This film ruptured and roughened within minutes from preparation, leading to a lower resolution in the measured NRA spectra. The ruptured films (resembling Figure 3B) did not further evolve.

380K (nos. 4 and 5 of Table 2). We recall that some of the added amphiphile forms the brush, while the rest remains as unattached chains in the bulk of the film above the brush. Stability was first reached at films made of a mixture which contained about 4.5% of dPSX-380K (see section 2.3).

2.2.2. Films Which Contain a Short Amphiphile, hPSX-24.7K. In a different series of experiments (summarized in Table 3) we examined the specific role of the polymeric amphiphile in modifying the surface. Thin layers were formed from mixtures which contained a shorter amphiphile, PSX-24.7K. Such amphiphiles form thinner brushes (height ca. 250 Å[24]) and end-attach to the substrate at a much higher surface density ($s \cong 4.5$ nm). The motivation here was to investigate not only a different brush but whether a much increased concentration of zwitterionic end-groups attached to the silicon surface plays a role. In particular, whether this would modify the surface chemistry to the extent of changing the sign of A (eq 1) and thereby making the substrate wettable by the liquid. Concentrations of PSX-24.7K in PS-0.58K up to 8% as a sole additive, and also when combined with longer chain homopolymers, did not prevent the roughening and rupture (down to the brush tip) of the layers

Table 3

variation no.	% hPSX-24.7K	% homopolymer	layer state
1	1–8%[a]	none	ruptures
2	monolayer	7% PS-330K	ruptures
3	monolayer	6% PS-710K	ruptures
4	2%	6% PS-710K	ruptures

[a] A variety of concentrations within these limits were tested, each in a different experiment. All yielded layers which roughened within a few hours.

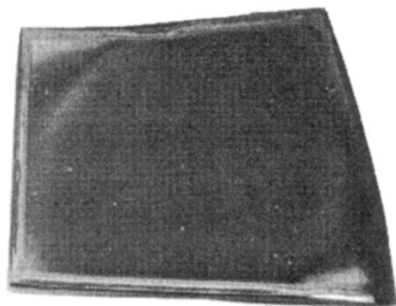

Figure 6. A film of PS-0.58K containing 5% of dPSX-380K spin cast on a silicon wafer. The picture, showing that the as-cast film retained its uniformity and smoothness, was taken 8 months after the film was cast.

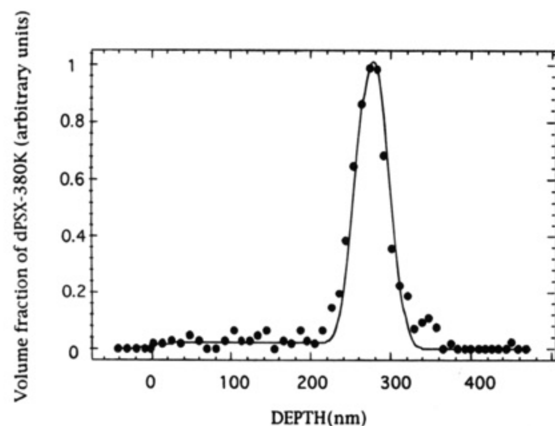

Figure 7. NRA concentration depth profile of a monolayer of dPSX-380K in PS-0.58K. The film also contains 4.3% of PS-710K. The film (thickness 320 ± 20 nm) was stable for several months.

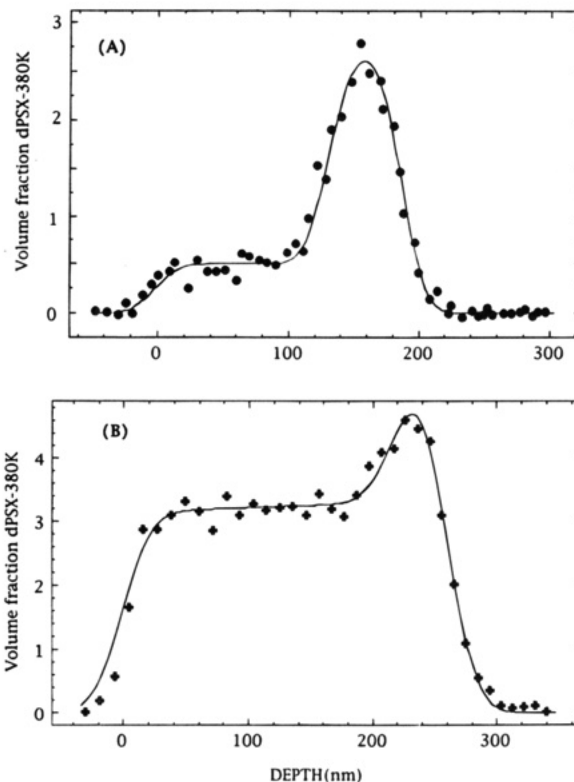

Figure 8. Depth concentration profiles of dPSX-380K within films of PS-0.58K. The spectra show an excess of the amphiphile at the oligostyrene–silicon surface. (A) 1.2% dPSX-380K in PS-0.58K. The film contains also 2% of PS-710K and is severely ruptured. The profile were measured 14 days after the film was prepared. (B) dPSX-380K incorporated to a mean concentration of 3.4%. This film also ruptured as in Figure 3B.

(though the dewetting into droplets did not occur). Initially smooth films pocked within some hours, reaching a typical ruptured state as shown in Figure 3B. The pattern was preserved for a few months without significant change.

2.3. Stable Films (Type 3). The last group of experiments includes films which contain the surface active dPSX-380K together with non-end-functionalized polystyrene. We studied the stabilizing effect of various molecular weights and bulk concentration (nos. 6–16 of Table 2). We found that rupture is suppressed in liquid films which contain a sufficient concentration of long enough unattached free chains, in addition to the surface attached layer of the polymeric amphiphile dPSX-380K. These films remain unbroken and smooth for many months. Figure 6 shows a typical film 8 months after it was first cast.

We studied separately the effect of the amphiphile and the free polymer on the stability of the films.

2.3.1 The Concentration of Polymeric Amphiphile. NRA was used for profiling the composition as a function of depth within both stable and unstable layers in which the bulk concentrations of the amphiphile dPSX-380K was varied. Figure 7 presents an NRA profile of a nonruptured, stable film containing a monolayer of dPSX-380K formed by the procedure described in section 2.2.1 and addition of 4.3% of PS-710K. Parts A and B of Figure 8 respectively show a composition profile of films which contain 1.2% and 3.4% of dPSX-380K. Both films (8A and 8B) rupture. The NRA profiles of the three samples (Figures 7 and 8) reveal similar brush features (height of 80 ± 20 nm, interanchor spacing $s = 18 \pm 2$ nm). This is consistent with the trend expected from earlier studies of the isotherms of tethered polymeric amphiphiles[25,15] which show that brushes reach their limiting saturated structures already at low bulk concentrations. The profiles also indicate that the features of the brush do not depend on the procedure by which it was assembled. Comparing the stability of the films presented in Figures 7 and 8, we observe that although all three films contain a saturated surface brush, only the film (Figure 7) which contains an additional amount of free polymer is stable. We may therefore conclude that the presence of a saturated surface brush alone is not sufficient for preventing the rupture of the oligostyrene film.

2.3.2. Stabilizing Concentrations of Different Molecular Weight PS Chains. In this series we studied films spread on silicon wafers covered by a preformed brush of dPSX-380K. Additional nonfunctionalized PS chains were premixed to the required concentration with PS-0.58K and the mixture was spin coated as a thin film on silicon wafers. In Figure 9 we show results (summarized in Table 2) in the form of a stability phase diagram. "Ruptured" or unstable films are those in which holes appear within up to a day from preparation. "Stable" films are those which remain unbroken for at least 1 month at room temperature. It is of particular interest that the transition between a stable film where the rupture is suppressed (solid circles in Figure 9) and a film which roughens (open circles in Figure 9) is rather sharp. For example, we observed that films which contained a brush of dPSX-380K and additional (4.5%) PS-710K were stable for many months. On the other hand, films which contained 3.5%

(24) Klein, J.; Kamiyama, Y.; Yoshizawa, H.; Israelachvili, J. N.; Fetters, L. J.; Pincus, P. *Macromolecules* **1992**, *25*, 2062.

(25) Green, P. F.; Russell, T. P. *Macromolecules* **1992**, *25*, 783. See also the review: Halperin, A.; Tirrel, M.; and Lodge, T. *Adv. Polym. Sci.* **1991**, *100*, 31.

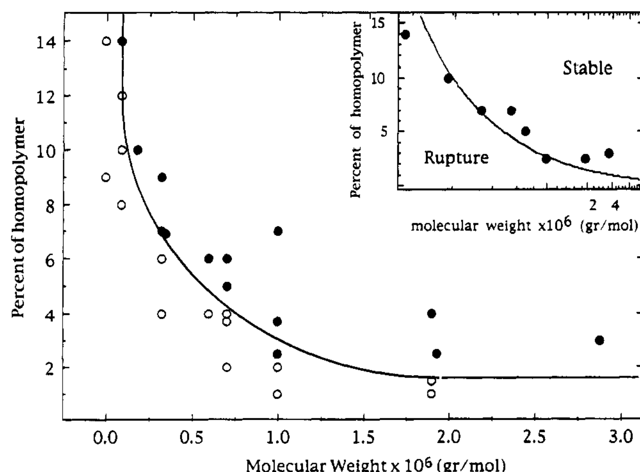

Figure 9. A diagram showing the effect of adding free (unattached) polymer chain of different molecular weight and at different concentrations on the stability of films which contain a monolayer of dPSX-380K self-assembled from solution: (○) films which rupture in times $t < 0$ (hours), (●) films which remain smooth and uniform for times $t > 0$ (months). The solid curve separating the two regimes is a guide to the eye. Inset: data on a semilogarithmic scale (showing only the lowest concentrations required for suppression of rupture). All films were in the thickness range 350 ± 70 nm.

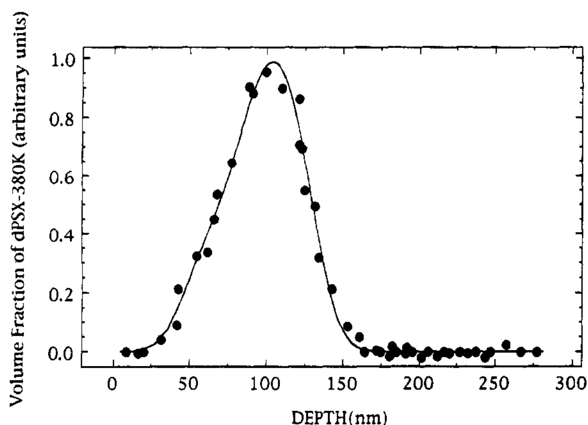

Figure 10. Concentration-depth profile of 1.17% dPSX-380K in a *thin* layer (ca. 130 nm) of PS-0.58K. The profile was measured 32 days after the thin film was prepared. This sample remained uniform and unbroken for several months.

of PS-710K, in addition to a surface brush, pocked and roughened within 5 h at room temperature.

2.3.3. Very Thin Films Stabilized by a Surface Brush. As was reported in section 2.1, films of the pure oligostyrene, up to a thickness of 1 μm, dewet spontaneously. In general, we found that thicker films dewet more slowly than thinner ones. In contrast, we find that very thin films (<150 nm) which contain even small amounts of the brush-forming polymer are stable. A minute amount of dPSX-380, which is not sufficient for preventing rupture of thicker films, prevents the rupture of a thin enough film. The NRA profile of Figure 10 shows the distribution of 1.17% of dPSX-380K in a film of oligostyrene PS-0.58K and reveals that in a film of this thickness the brush occupies practically the whole thickness of the layer. The film corresponding to the profile of Figure 10 remained stable for many months. These observations are considered in more detail in section IV.

IV. Discussion

Our main finding is that thin liquid films, forced to spread on a surface which they do not wet, can be stabilized against rupture and dewetting by the presence of a sufficiently long polymer brush attached to the solid surface together with a small amount of sufficiently long, unattached polymer in the bulk of the film. Before discussing possible reasons for this, it will be useful to consider the behavior of the nonstabilized films.

1. Hole Formation in Films of Simple Liquids. The stability of thin films of nonvolatile, van der Waals liquids was analyzed by a linear model developed by Vrij, Ruckenstein, and others,[4,5] and extended by Brochard et al.[6] The model assumes that roughness in a thin film evolves by amplification of thermal fluctuations, which are caused by capillary waves

$$|h(x,t) - h_0| \propto \exp(\omega t + iqx) \tag{7}$$

where ω is the growth rate of the disturbance, t is the time, q is the wave vector of the fluctuation, and x is a coordinate in the plane of the surface. Small disturbances grow if $\omega > 0$ and decay if $\omega < 0$. The value of $\omega(q)$ is given by

$$\omega = -\frac{h_0^{\,3}}{3\eta}\left(\gamma q^4 - \frac{3Aq^2}{6\pi h^4}\right) \tag{8}$$

where η is the viscosity of the liquid and γ is the liquid–vapor surface tension. For systems with a positive value of the constant A (and thus with a tendency to thin), there exists a critical value $q = q_c$ below which ω becomes positive and the van der Waals interactions dominate the surface tension, leading to rupture when the amplitude of the fluctuations equals the film thickness. This is given by

$$q_c = \left(\frac{A}{2\pi h_0^{\,4}\gamma}\right)^{1/2} \tag{9}$$

From eq 8 the frequency ω_m associated with the most rapidly growing fluctuations may be evaluated (these occur at $q^2 = q_m^{\,2} = q_c^{\,2}/2$), to yield an upper limit for the characteristic time for hole formation (rupture time) $\tau_m = 1/\omega_m$, given by

$$\tau_m = 48\pi^2\gamma\eta h_0^{\,5}\frac{1}{|A|^2} \tag{10}$$

The effect of nonlinearities, which are relevant at the limit of rupture, is to accelerate the rupture process. Williams and Davis[26] found that the characteristic rupture time may be as much as 5–10 times smaller than the time predicted by the linear theories.

For PS-0.58K the viscosity η is on the order of 100 P at room temperature, the surface tension $\gamma \approx 32$ (dyn/cm) and $A \approx 10 \times 10^{-19}$ J.[11] For films of thickness $h_0 = 400$ nm, eq 10 then leads to characteristic rupture times on the order of 1 year or more, and the nonlinear model to a characteristic time on the order of months. Since we observe hole formation on a time scale of a few minutes for the polymer-free liquid, it is clear that, in the system observed by us, eq 10 is not adequate. There are indications (reported in detail elsewhere[7]) that the discrepancy is due to local changes in the film thickness induced by the presence of dust particles on the substrate surface. We believe that holes in the films do form due to amplification of thermal surface fluctuations; the much-shorter-than-predicted rupture times, however, arise because the effective film thickness that should enter eq 10 is not the mean film thickness h_0 but a much smaller value. As demonstrated in the Results section, addition to the oligostyrene liquid of PS chains, by themselves,

(26) Williams, M. B.; Davis, S. H. *J. Colloid Interface Sci.* **1982**, *90*, 220.

does not prevent rupturing and subsequent dewetting of the thin films. Within their resolution, the NRA spectra of films containing polystyrene additives indicate that the additives are uniformly distributed in the layer and are not adsorbed to excess at either of the interfaces.[27]

The effect of free polymer chains on the formation of holes in the films must then result from a modification of those parameters of the oligostyrene layer relevant to the dewetting process. These are the surface tension, γ, and the viscosity, η (the value of A is essentially unchanged since we are dealing with chemically identical species). We estimated the change in the value of each of these properties for 8% of PS-1930K: At this concentration, with the PS-0.58K acting as a good solvent, PS-1930K forms a semidilute solution. The change in γ is expected to be around 1%, little change is expected in the value of the Hamaker constant, and the largest change is a 30-fold increase in the viscosity η. Indeed, the time for hole appearance in the latter case (8% of PS-1930K in the PS-0.58K) was on the order of some hours compared with a few minutes for the additive-free liquid, and also the dewetting rate was lower.

2. Stability of a Solvated Brush. The changes expected—and observed—in the oligostyrene films due to addition of unattached polymer, as discussed above, are relatively small and very different from the striking suppression of hole formation possible once brushes have formed. Qualitatively, we may conclude that the effect of the brushes is not due to chemical changes in the silicon surface induced by the attachment of the zwitterions; this is because for PSX-24K brushes, where the density of zwitterions on the surface is about 10 times higher than with the dPSX-380K brushes, no stabilization is achieved (see Table 3). The stabilizing effect must therefore be due to some coupling of the free chains with the surface-attached brush, effective for the longer brushes but not for the shorter ones.

A recent theoretical analysis by Safran and Klein[28] addresses the question of hole formation in thin films of elastic and viscoelastic materials, and we may get some insight into the behavior in our system from the results of that treatment. In our stabilized films, we have typically a 400 nm thick liquid film (containing the unattached polymer) on top of the PSX-380K brush-covered silicon substrate; the brush is solvated (the volume fraction of polymer in the brush is ca. 2.5%) and, being of height ca. 100 nm, pervades only a fraction of the overall film thickness. This is a complex structure, and to make contact with existing models we consider first the case of a solvated brush layer alone.

In the present study we have examined a number of such layers: Figure 10 shows the brush profile in a very thin liquid film with no added unattached polymer. The profile shows the brush to extend more or less throughout the film thickness: i.e. the film is just a solvated brush with no "free" liquid on top. This film remained stable and unbroken for many months, despite the fact that from eq 10 one might expect it, being thinner than other films studied (and consisting of 98% or so liquid), to rupture rapidly. The case of hole formation in solvated polymer brushes has been analyzed explicitly:[28] Rupture is strongly suppressed in such films—even when the polymer is reversibly tethered to the surface, so that holes can in principle form—because the brush has a shear elastic modulus $E = E_b$, associated with it (a simple model gives $E_b = (3k_BT/s^3)$, where s as before is the mean interanchor spacing). The existence of such a finite shear modulus clearly makes it more difficult for surface instabilities to grow and can change the sign of the growth rate ω appearing in eqs 7 and 8. Thus, for the case of a simple (Newtonian) fluid such as the oligostyrene, one may write the viscosity η as

$$\eta = G\tau_0 \tag{11}$$

where G is the (infinite-frequency) modulus of the liquid (typically k_BT per unit molecular volume) and τ_0 is a molecular relaxation time. The fastest growing mode ω_m ($=1/\tau_m$) deduced from eq 8 can then be written (substituting for η) as

$$\omega_m\tau_0 = \beta_A \equiv \frac{\gamma h_0^3 q_c^4}{12G} \approx (a/h_0)^5 \tag{12}$$

where a is a molecular length scale, typically a monomer size[28] (the approximate equality is obtained by setting all energy scales to k_BT per monomer unit). For the case where a finite shear elastic modulus E_b is associated with the film—as for the solvated brush—it can be shown[28] that the effect this has on the fastest growing mode is to modify eq 12 to

$$\omega_m\tau_0 = \beta_A - \beta_E \tag{13}$$

where $\beta_E = E/G$, the ratio of the elastic shear modulus to the viscosity modulus. Clearly, as soon as β_E exceeds β_A, ω_m becomes negative and the film is stable to surface undulations. In the present case we expect $\beta_E = E_b/G \approx (3k_BT/s^3)/(k_BT/a^3) = 3(a/s)^3$, while $\beta_A \approx (a/h_0)^5$. Taking $s = 17$ nm, $a = 1$ nm, and $h_0 = 100$ nm for the solvated PSX-380K brush, we see at once that $\beta_E \gg \beta_A$, so that $\omega_m < 0$ and the layer is quite stable to surface fluctuations, in line with our observations.

3. Thin Films on a Brush-Covered Substrate. The case of a solvated brush of thickness h_b with a liquid film of thickness $h_f = (h_0 - h_b)$ on top is more complicated. In view of the stability to undulations of the solvated brush layer itself, we may consider separately the processes occurring in the liquid film of thickness h_f between the brush tip and the air interface. Here we might expect holes—reaching from the liquid–air interface down to the top of the solvated brush—to form in accordance with eq 10, and indeed we observe such holes to form when no free polymer is added to the oligostyrene (Table 2, variation no. 3). Stabilization of this top layer to undulations is seen to occur when there is a sufficient concentration of long enough unattached polymer in the top liquid layer. As noted in section 1 above, the effect of the added polymer even in extreme cases (5% of PS-1930K) should not increase the expectation time for hole formation τ_m in eq 10 by more than a factor 30 or so. Yet we observe that hole formation is in fact suppressed from minutes to many months or more.

A clue to this behavior is provided by Figure 11: here we reproduce schematically the stability phase diagram suggested by the data in Figure 9. This shows also the calculated value of c^*, the overlap concentration of the added free chains in the oligostyrene,[29] taken as $c^* = M/((4/3)\pi R_{F,g}{}^3 N_A)$, where M is the polystyrene molecular weight, N_A is Avogadro's number, and $R_{F,g}$ is the Flory radius of gyration taken from the data for polystyrene in toluene.[30] Within the range of our parameters, the stability line is seen to be somewhat above c^* (approximately $5c^*$) but to follow it closely; i.e. the minimal concentration of the polymer additive which is necessary for suppressing the rupture of the liquid film above the brush is always above

(27) The opposite case, of a nonadsorbing polymer added to a wetting film ($S > 0$) was discussed: Boudoussier, M. *J. Phys.* **1987**, *48*, 445.
(28) Safran, S. A.; Klein, J. *J. Phys. II Fr.* **1993**, *3*, 749.
(29) de-Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca; 1985.
(30) $R_{F,g} = 0.408R_F$, where for polystyrene in toluene[15] $R_F = 0.32M^{0.588}$.

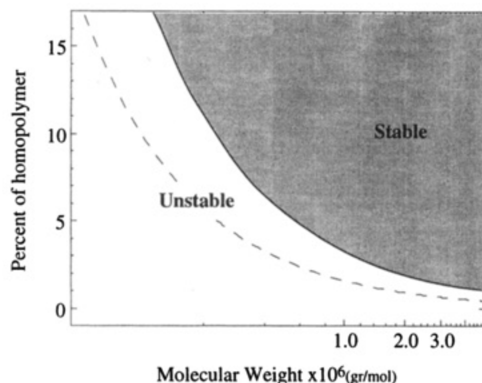

Figure 11. A semilog representation of the stable–unstable "phase diagram" in the concentration–molecular weight plane derived from the experimental results of Figure 9 (where the phase boundary corresponds to the curve in the inset of Figure 9). The broken line is proportional to the overlap concentration c^*, presented in weight percent, calculated from the relation[16] $c^* = (3/4\pi N_A)/(M/R_F^3)$.

the overlap concentration. This suggests that the stabilization (in the presence of a brush) may be related to the formation of an overlapping (semidilute) or entangled solution of the free chains within the liquid film. We note that entangled behavior in overlapping polymer solutions often occurs at[31] $c \approx (5-8)c^*$. Such solutions display viscoelastic behavior,[32] and a relaxation time, τ_r, separates the intermediate-time elastic response (with a plateau modulus E) from the long-time viscous behavior. For films of such liquids the characteristic time for rupture, $\tau_{m,v}$, is predicted to be much longer than its value τ_m for the case of simple (non-viscoelastic) liquids, τ_m, (eqn 10), for a given γ, A, and film thickness, h_0:

$$\tau_{m,v}/\tau_m \approx (\tau_r/\tau_0)(E/G) \tag{14}$$

Since the zero-shear rate viscosity η_0 of a viscoelastic solution is $\eta_0 = E\tau_r$,[33] eq 14 simply says that the ratio of the characteristic times for hole formation in films of simple and of viscoelastic liquids should vary as the ratio of their respective viscosities. This alone—as discussed in subsection 1 above—cannot account for the sharpness of the transition between rupturing and nonrupturing behavior summarized in Figure 9 (and Figure 11). Rather, the explanation may be as follows.

When the free polymer in the liquid layer above the brush is dilute (nonoverlapped) it does not penetrate into the solvated brush and there is little entanglement coupling: the liquid layer continues to behave like a simple fluid, obeying eq 10. The situation is shown schematically in Figure 12A. Once overlap occurs so that the chains are in the semidilute regime, the situation changes in two respects. Firstly, one expects[34] appreciable interpenetration of free chains into the brush for $c > c^*$; secondly, the free chains are now entangled with each other and with the brush layer. When fluctuations in the liquid film height become large, the entanglement coupling of the solution with the brush (which is immobilized by the surface) provides an additional brake on the flow of liquid in the region of greatest thinning. This is shown schematically in Figure 12B. We believe this additional dissipative effect due to the entanglement coupling may lead to an "effective" viscosity in the thinned region which is much higher than that of the bulk semidilute polymer solution and thereby prevent hole formation in the times observed.[35]

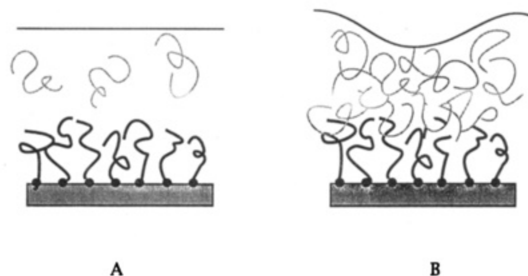

Figure 12. A schematic picture showing a thin film which contains a long chain brush at the silicon–liquid interface. (A) The film also contains a low concentration of free long-chain polymer. (B) The thin layer contains a high concentration (above the overlap threshold) of free long-chain polymer.

To summarize, thin films of an oligostyrene liquid which are forced on a nonwetted silicon surface rupture within a few minutes. These films may be stabilized and rupture-inhibited for many months by the presence of a polymer brush on the silicon surface, together with some free polymer in the liquid. The presence of both the brush and a sufficient amount of the free long-chain polymer are necessary for the prevention of rupture. A possible mechanism is entanglement coupling between the brush and the free polymer.

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(34) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(35) There is one other possibility which we offer tentatively. The transition from unstable to stable behavior as the concentration of unattached polymer increases beyond c^* is rather sharp (we recall for example that 3.5% of PS-710K in the film resulted the appearance of pocking after about 5 h, while with 4.5% the film on the brush layer was stable for several months or more). This suggests a thermodynamic rather than a kinetic origin for the stabilization. It may be that the interpenetration of the free chains into the solvated brush at $c > c^*$, together with their repulsion from the liquid–air interface, results in a composition gradient of free chains in the liquid layer, decreasing from the brush tip toward the air interface. Such a gradient would have the effect[36] of causing a repulsion between the brush and the liquid–air interface, which may offset the tendency—indicated in eq 1—of the film to thin. We have not analyzed in detail the relative contributions of the dynamic and the thermodynamic effects.
(36) Safran, S. A. *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes*; Addison-Wasley Publishing Co.: New York, 1994.