J. Phys.: Condens. Matter **9** (1997) 7753–7765. Printed in the UK PII: S0953-8984(97)80581-4

# Dewetting of solvated polymer brushes by thin liquid films

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Received 2 January 1997, in final form 18 April 1997

**Abstract.** Thin liquid oligostyrene films on top of a surface-anchored, polystyrene brush—solvated by the oligostyrene itself—roughen spontaneously. Using optical phase-interference microscopy and nuclear reaction analysis we have characterized the topography of such roughened films. We see that the undulations formed reach down at most to approximately the top of the solvated brush, but not to the underlying solid substrate on which the brush is anchored. Possible origins for this behaviour are discussed in terms of a picture wherein the solvated brush is regarded as a quasi-solid substrate for the liquid film on top.

## 1. Introduction

Thin films of a non-volatile liquid, which are forced to spread on a substrate which they do not wet, equilibrate by dewetting into a collection of droplets. Yet, for many of the technological applications of thin films, long-term stability of the film is crucial. It is known [1] that the stability of the films may be enhanced by coating the substrate with a monolayer of molecules of chemical structure similar to that of the liquid. An exceptional case, where chemical similarity is not a sufficient condition for wetting, was first observed by Hare and Zisman [2]. They found that a monomeric polar liquid would not spread on a monolayer formed by the same molecules. Recently, similar phenomena in non-volatile, polymeric liquids which show partial wetting on top of a dry polymer brush or block copolymer lamellae were described by theoretical models [3, 4] and observed experimentally [5–7]. A different aspect of partial wetting, driven by physical rather than chemical interactions, is presented in this paper.

Earlier we studied the behaviour of thin, low-molecular-weight, liquid films forced to spread on top of a long-chain polymer brush [8, 9]. We observed that the liquid solvates the brush, but that the thin film on top of the brush is not stable, and evolves spontaneously by roughening and pocking. It was noted that the roughening of non-wetting thin films on such a brush may be suppressed by adding small amounts of free polymers to the liquid. The free-polymer concentration necessary to achieve this depends on the chain length, and is within the semi-dilute regime [9].

Here we focus our attention on characterization of the steady state of the roughened liquid film formed on top of a solvated brush. Using interference microscopy we study the structures which form spontaneously at the liquid–air interface of the thin films. Depth–composition profiles of the films as measured by nuclear reaction analysis are presented as well. Finally, we discuss possible origins of the observed dewetting behaviour.

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0953-8984/97/377753+13$19.50

## 2. Experimental details

### *2.1. Materials*

Silicon wafers (p-type, (100), 0.5–1 Ω $\text{cm}^{-1}$, thickness of 406–470 $\mu$m, and p-type, (111), 6–13 Ω $\text{cm}^{-1}$, thickness of 380 mm) were purchased from Aurel GMBH (Germany) and from ITME (Warsaw, Poland). The mean surface roughness of these native oxidized silicon wafers (cleaned by the procedure described below) was measured by x-ray reflectometry [10] and found to be 1.7 nm ± 0.2 nm.

**Table 1.**

| Material | Weight-averaged molecular weight, $M_w$ (g $\text{mol}^{-1}$) | Designation | Poly-dispersity, $M_w/M_n$ | $R_F$ (nm) (swollen end-to-end dimension) |
|---|---|---|---|---|
| Polystyrene homopolymer (deuterated) | 10 500† | dPS–10.5 K | 1.02 | 7.2 |
| | 500 000† | dPS–500 K | 1.05 | 69.0 |
| End-functionalized polystyrene (deuterated) | 380 000‡ | dPSX–380 K | 1.05 | 58.8 |
| End-functionalized polystyrene (protonated) | 24 700‡ | hPSX–24.7 K | 1.02 | 11.9 |
| | 375 000‡ | hPSX–375 K | 1.03 | 57.5 |
| | 660 000‡ | hPSX–660 K | 1.02 | 80.1 |
| Diblock copolymer polystyrene (deuterated)–polyethylene oxide | 500 000† (dPS: 485 000 PEO: 15 000) | dPS–PEO | 1.18 | 67 |

† Purchased from Polymer Laboratories (UK). The characteristics of the polymers were determined by size-exclusion chromatography and provided by the suppliers.
‡ Synthesized by L J Fetters.

The toluene used was Frutarom analytical grade, or Sigma spectroscopic grade. Commercially available homopolymer polystyrenes, either protonated or fully deuterated, of various molecular weights were used. The characterization of the polymers is given in table 1. Polystyrenes end-functionalized with the zwitterionic group $-(CH_2)_3N^+(CH_3)_2(CH_2)_3SO_3^-$ (henceforth designated –X) were synthesized as described earlier [11] and kindly donated by L J Fetters. The end-functionalized polystyrene dPSX–380 K is fully deuterated.

A highly asymmetric diblock copolymer of polystyrene and polyethylene oxide (designated dPS–PEO) was synthesized by Polymer Laboratories (UK). The polystyrene moiety with dPS–PEO is fully deuterated. The PEO moiety, with $M_w = 15\,000$ g $\text{mol}^{-1}$, is very much shorter than the dPS ($M_w = 485\,000$ g $\text{mol}^{-1}$). Such diblocks are known to form brushes readily from solution on selective surfaces [11].

The non-volatile liquid used was a styrene oligomer, designated PS–0.58 K, with $M_w = 580$, and $M_w/M_n = 1.02$. This is a viscous liquid (glass transition temperature $T_g = -18$ °C, viscosity $\eta \approx 30$ P at 35 °C), and is a moderately good solvent for polystyrene [12]. Its refractive index was measured as $n(\text{PS–0.58 K}) = 1.571 \pm 0.003$ (Abbe refractometer, Fisher Scientific Model 6121).

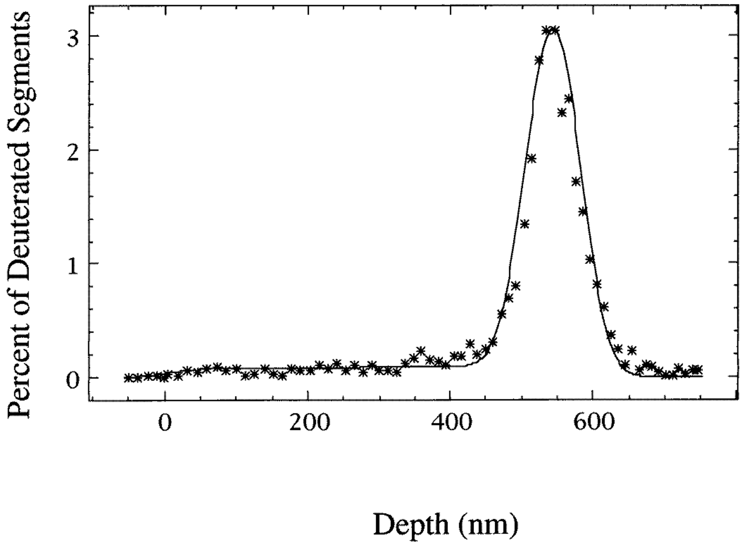

**Figure 1.** The concentration–depth profile $\phi(z)$ of dPSX–380 K within an oligostyrene film as determined by NRA. The polymer brush self-assembled from toluene as described in the text, following which a layer of PS–0.58 K was spin cast onto it. The film became rough and pocked with holes some hours after preparation (see e.g. figure 2(B)). The NRA profile of the film was measured two weeks after preparation. The roughening leads to a lower resolution of $\simeq$40 nm HWHM at the depth of 600 nm. From the $\phi(z)$ profile we determine the mean brush height and the surface excess $\Gamma$, per unit area: $\Gamma = \int^{\text{Film thickness}}[\phi(z) - \phi_b]\, dz$ where $\phi_b$ is the concentration in the bulk far from the interface. In the absence of deuterated chains in the bulk, as in the spectra presented here, $\phi_b = 0$. The inter-anchor spacing $s$ of the chains is obtained from $\Gamma$: $s = (\Gamma/M)^{-1/2}$.

### *2.2. Sample preparation*

Films in a thickness range of 100 to 600 nm, uniform to within 3–4 nm, were prepared by spin coating from solutions of PS–0.58 K in toluene, onto silicon wafers. Film thickness was controlled by means of the concentration of the solutions and the spin rate. Polished silicon wafers were cut by a diamond knife to dimensions $\simeq 1 \times 2.5$ cm$^2$, and cleaned by immersion in ethanol, followed by wiping (Kimwipes), and drying in a jet of filtered nitrogen. The dry wafers were washed in fresh toluene, and dried in a jet of nitrogen. Film thickness was correlated via nuclear reaction analysis and ellipsometry with the solution concentration. Spin coating (Headway Photoresist Spinner Model 1-PM101D-E790) was carried out in a regular hood. When polymer additives were used, they were pre-mixed to required concentrations with PS–0.58 K, dissolved in toluene, and the mixture was then spin coated as a homogeneous layer. For some of the studies we used brushes which were self-assembled from toluene solutions on the silicon. The exact procedure will be described in the relevant section. All of the samples were monitored visually while annealing at room temperature, $22 \pm 2.5$ °C.

### *2.3. Experimental methods*

Characterization of the topography of rough thin layers was carried by optical phase-interference microscopy (OPIM, Maxim 3D, manufactured by ZYGO Corporation, USA)

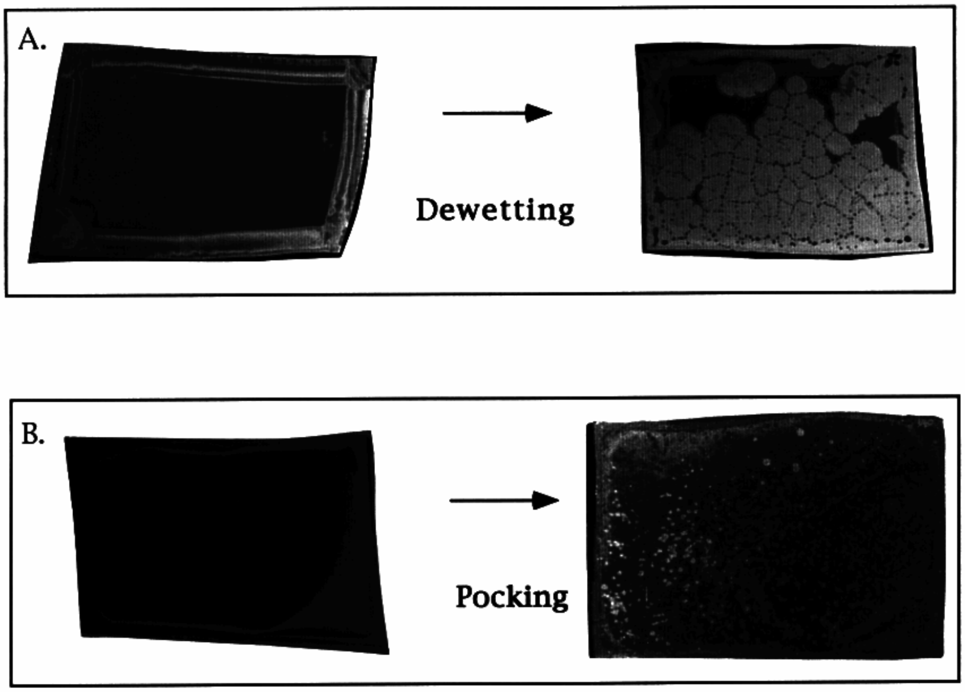

**Figure 2.** The initial and the steady-state appearance of oligostyrene films 400 nm thick. The films presented on the left are as cast, while those on the right are films which were annealed at room temperature for a few weeks. (A) Oligostyrene film spin-cast on bare silicon. (B) Oligostyrene film spin cast on a polystyrene brush. Films reach the pocked and roughened state (on the right) within several hours, and—within the limits of visual observation—do not appear to evolve further.

[13]. The method offers sub-nanometre resolution in the vertical direction, and a lateral spatial resolution better than a micron, without forming a mechanical contact with the sample. The high vertical resolution is obtained by measuring the amplitude and the phase of an interference pattern. With OPIM, sharp interference patterns are formed by low-contrast features, and the vertical resolution does not depend on the wavelength of the probing light. As the method only enables the measurement of relative heights in transparent thin films, the absolute mean thickness of the films was measured by ellipsometry (Olympus BO71). The composition ($\phi$)–depth $(z)$ profile normal to the silicon surface was measured by NRA on films which contain deuterium-labelled chains [14, 15]. In this method, a beam of $^3$He ions is incident on the film, and the exothermic nuclear reaction $^3\text{He} + {}^2\text{H} \rightarrow {}^4\text{He} + {}^1\text{H} + 18.3$ MeV takes place within the sample. The energy spectrum of the emitted $^4$He or $^1$H particles (normalized by the reaction cross section and the energy loss of the particles) yields the composition–depth $\phi(z)$ profile of deuterated segments. In this study we made use of both detection modes (alpha-NRA and proton-NRA) at different energies of the incident $^3$He particles (in the range 0.7–1.2 MeV) in order to optimize the resolution of the method for different sample thicknesses and roughnesses [16].

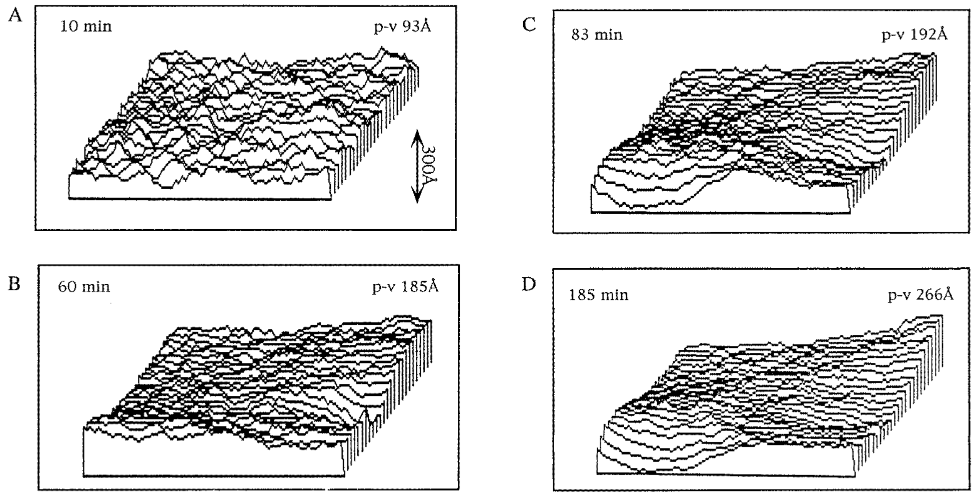

**Figure 3.** Phase-interference microscope images (OPIM) of a film of oligostyrene spin cast on top of a pre-assembled brush of dPS–PEO 500 K. The overall film thickness is $\simeq$400 nm. The same area in the sample was scanned repeatedly over a period of 185 minutes from the casting time, and characteristic images are shown. The area shown is $42 \times 42$ $\mu\mathrm{m}^2$, while the undulations (see the peak-to-valley values) are on a scale of a few hundred ångströms. Note the emerging valley on the lower LHS of the image.

## 3. Results

Two different routes were used for creating a polystyrene brush (composed of either hPSX, dPSX, or dPS–PEO) at the silicon substrate: either self-assembling from a toluene solution of the end-functionalized chains, followed by a thorough wash in pure toluene and drying, or spin coating from a toluene solution of end-activated polystyrene in oligostyrene. In the first case an oligomer film was subsequently spin cast on the assembled brush. The two routes gave equivalent results. The films were visually monitored and further analysed (by OPIM and NRA) after standing at room temperature (which is about 40 °C above $T_g$ for the oligomer) for periods of hours to months. Films which were formed on top of brush-bearing substrates were compared with films of similar thickness spin cast on bare silicon. We also studied the combined effect on the surface structure of a surface brush together with added non-functionalized long-chain polymers, which, as noted, have a marked stabilizing effect at sufficient free-chain concentrations [8, 9].

### *3.1. Characterization of the surface brush*

The surface excess of dried, collapsed brushes, which were created by self-assembly from toluene solution followed by washing and drying, were measured by x-ray reflectivity [10]. The measured overall film thickness was in the range $3 \pm 0.5$ nm for the PSX–380 K and dPS–PEO brushes. This corresponds to a surface excess of $3 \pm 0.5$ mg m$^{-2}$, consistent with earlier studies of similar brushes formed from a good solvent on mica surfaces [11]. The composition profile of the films was measured by NRA. In figure 1 we present the NRA spectra of an oligomer film spin cast onto a brush previously self-assembled from toluene. The measured profile of the film indicates that the brush is swollen by the oligomer, stretching to $100 \pm 20$ nm. The NRA-measured surface excess, at $2.5 \pm 0.2$ mg m$^{-2}$, is

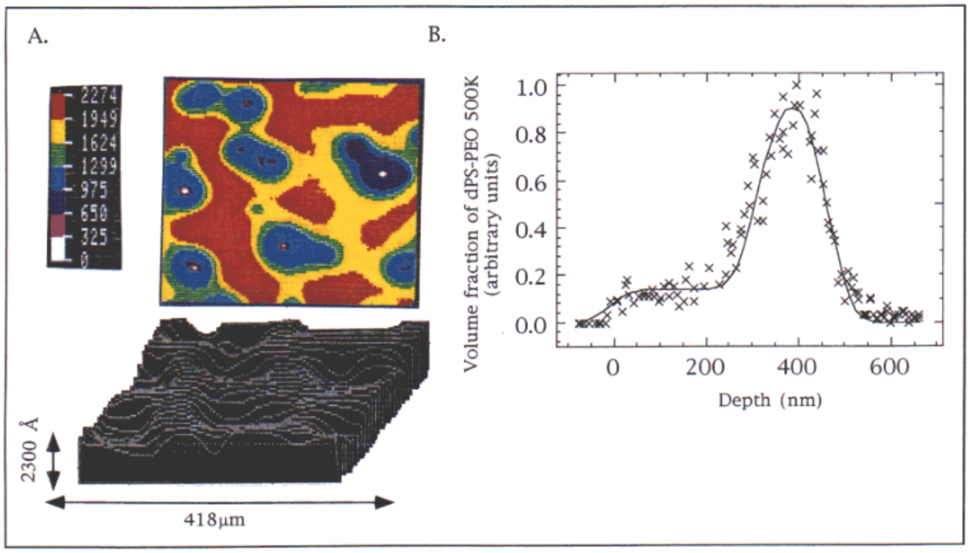

**Figure 4.** An oligostyrene film on top of a self-assembled brush of dPS–PEO 500 K. The film was observed visually to be ruptured and pocked. It was scanned by OPIM seven days after preparation, and measured by NRA two weeks later. (A) An OPIM image of the film. The lateral dimensions are 418 × 418 $\mu$m$^2$ and the vertical scale is 230 nm. The half-tone representation, top, shows a plan view of the undulations. (B) An NRA profile of the same film; the overall thickness is 470±40 nm. The profile shows excess of dPS–PEO at the film–silicon interface due to brush formation. The apparent thickness of the brush is about 150 ± 40 nm. The resolution of the NRA spectra is reduced due to the roughness of the sample.

within the scatter of the reflectometry value, and corresponds to an inter-anchor spacing of 18 ± 2 nm. This compares with a mean inter-anchor spacing of 14 nm for PSX–375 K brushes on mica from toluene [11].

### 3.2. Evolution with time of thin films

Films of polymer-free liquid oligostyrene which are spin cast on bare silicon wafers rupture within minutes from preparation. These films reach a final stage of disconnected droplets which form a polygonal droplet pattern within hours (figure 2(A)). The characteristic values of the contact angles (measured using an Olympus B071 TGHM goniometer) between residual droplets from thick films (0.6–1 $\mu$m) of the oligostyrene on native oxidized silicon wafer surfaces (from the two different manufacturers) are 22° ± 2°. The measured value is similar to that measured earlier for films of polystyrene on silicon wafers [9, 17, 18]. We recall that films which contain additives of non-functionalized polystyrene (up to 10% of polystyrene at varying molecular weights), and are more viscous, behave in a similar way but over longer times [9]. However, when the polymer-free oligomer layer is forced to spread on the surface brush (formed by any of the end-functionalized chains listed in table 1) rather than on the bare wafer, the resulting films become pocked and rough, as presented in figure 2(B).

### 3.3. *The topography of roughened films*

OPIM was used to follow the process of spontaneous roughening in thin films of oligostyrene coated on top of polystyrene brushes. Figure 3 presents four characteristic images out of a series taken during the initial stage of roughening (the first three hours). The steady state was reached within several hours [19], and did not appear to evolve further over a timescale of months. Figure 4 shows a roughened film on a coarser scale. The steady-state roughness in this section of the film is characterized by peak-to-valley height fluctuations of more than 120 nm. The transformation from a freshly cast smooth film to a pocked rough film may also be observed with the naked eye, as the appearance of many coloured contours instead of the bright uniform colour of the smooth samples. The images indicate that shallow undulations exist at the air–liquid interface, and we have carried out a more detailed analysis of these. Though the exact dimensions of the undulations depend on the thickness of the sample and on the concentration of added free polymer (if any), there exists a characteristic common trend in all samples. The peaks and valleys have lateral dimensions in the range of tens to hundreds of microns, and much smaller vertical dimensions covering a spectrum of sizes of tens to hundreds of nanometres. The mean slopes of the undulations are of order $10^{-2}$–$10^{-3}$ rad. As OPIM only enables the measurement of relative heights, we measured the total thickness of several of the samples by ellipsometry and by NRA, as in figure 4(B). Correlating the measured values of the film thickness with the OPIM images of a variety of samples indicates that, in all of the measured samples, the deepest valleys only penetrate at most to the top of the solvated brushes. This is deduced from the fact that the overall mean thickness of the layer is always about 100 to 150 nm larger than the depth of the deepest valleys, compared with a measured brush height of $100 \pm 20$ nm. That is, in all of the measured samples we find that apart from very few individual, randomly distributed defects, even the deepest valleys are not true holes in that they do not expose the bare surface of the silicon wafer.

### 3.4. *NRA of unstable films*

Composite films (liquid on top of a solvated brush) were profiled using NRA after different annealing periods. A typical profile following six weeks of annealing is shown in figure 5. The profiles indicate two main features: (1) roughening of the film does not lead, within our resolution, to an observable reduction in the swelling of the brush; and (2) there is little detectable free dPS within the film bulk. These observations suggest that the brush retains its structure and integrity even after the film as a whole roughens.

### 3.5. *OPIM characterization of stabilized films*

A picture of a stable film is presented in figure 6(A). In these films roughening is suppressed by the presence of high-molecular-weight polystyrene at sufficient concentration: they appear stable and unbroken when inspected visually after annealing for a few months at room temperature. A typical OPIM image of a stable film is presented in figure 6(B). These films are smooth: the RMS roughness is 1.2 nm, in contrast to the case for the pocked films where the deep valleys result in an RMS roughness of over 50 nm.

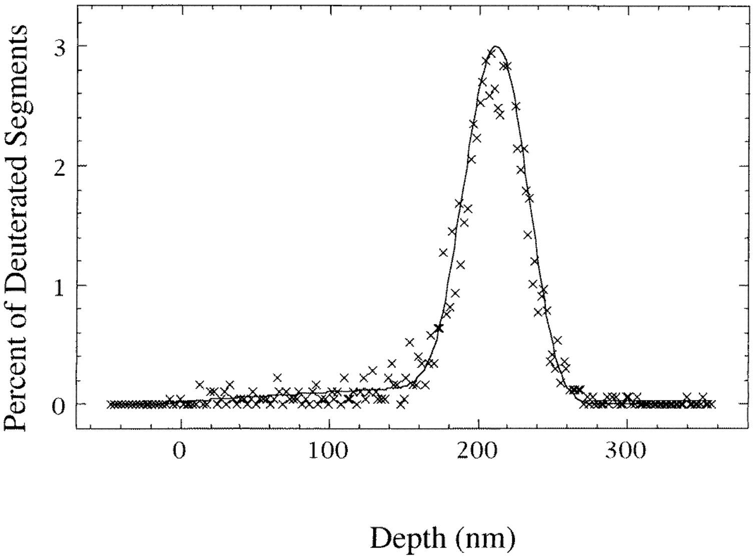

**Figure 5.** A NRA concentration–depth profile of a dPSX–380 K solvated brush covered by an oligostyrene film measured after six weeks of annealing at room temperature. The film was roughened and pocked. The mean thickness of the film is about 240 nm, and the brush height is about 100 nm.

## 4. Discussion

In this study we have focused on the structure of a film of liquid on top of a polymer brush (itself solvated by the liquid, which is a good solvent for the polymer). There have been several recent related theoretical discussions of wetting of surface-attached polymer layers [3, 4, 20, 22–24]. The wetting of dry polymer brushes by bulk polymer melts has been considered [3, 4], but the essential feature there (the entropy change due to free-chain penetration into the brush) is very different to the findings for our system.

The standard discussion of wetting of solid surfaces by liquid films [25] is in terms of an effective Hamaker constant $A$ related to the difference between the Hamaker constants of a liquid interacting with the solid, $A_{ls}$, and that of the free liquid film:

$$A = A_{ls} - A_{ll}. \tag{1}$$

The van der Waals interaction energy (which we assume to dominate other long-ranged interactions) of a liquid film of thickness $h$ is then given by

$$V(h) = A/12\pi h^2 \tag{2}$$

so at equilibrium ($V(h)$ a minimum), the liquid film tends to thin for $A < 0$ and thicken for $A > 0$.

The spreading coefficient $S$ for the liquid on the solid is the change in surface energy due to spreading of the liquid per unit area, and is given by

$$S = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \tag{3}$$

where $s, l$ and $v$ stand for solid, liquid and vapour, and $\gamma_{ij}$ is the surface tension between the $i$- and $j$-phases. These surface tensions may be controlled by shorter-ranged effects as well as by van der Waals forces. Brochard *et al* [26] have considered wetting of a surface by a

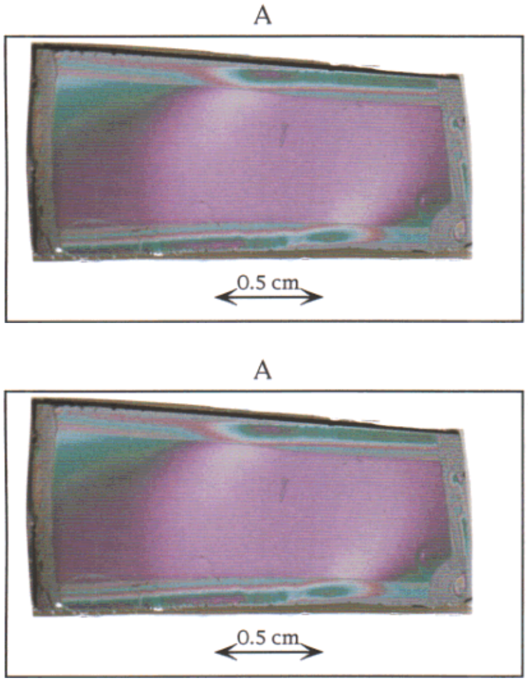

**Figure 6.** (A) An oligostyrene film containing 4.5% of dPS–500 K coated on top of a self-assembled brush of dPS–PEO (this concentration leaves sufficient free polymer in the film layer above the brush to stabilize it [9]). The picture was taken three months after spin casting, showing the film to be stable and smooth. (B) An OPIM scan of the film in (A) taken about two months after spin casting. The undulations are within the noise level (characteristic RMS roughness: 1.2 nm). Scanning revealed this structure to be uniform over the entire range of the film, with the exception of a small number of random defects.

non-volatile liquid for different combinations of values of $S$ and $A$. For the convenience of further discussion, we summarize these regimes in figure 7.

In the Brochard *et al* model [26] the free energy per unit area of the film of thickness $h$, $F(h)$, is given by

$$F(h) = \gamma_{sl} + \gamma_{lv} + V(h) \tag{4}$$

corresponding to different regimes as summarized in figure 7.

Consider first an oligostyrene film on the 'bare' silicon wafer. Since the dielectric constant of pure silicon is higher than that of the oligostyrene, we might expect the Hamaker constants to be similarly related [27], i.e. $A_{ll} < A_{ls}$, so we would have $A > 0$. In practice, the surface exposed by the wafer is not pure silicon, but is covered both by a native silicon oxide layer and by a layer of organic molecules adsorbed from the ambient atmosphere [28, 29]. The energies at the solid surface are then largely determined by these outermost layers. Moreover, the long-range interactions will be dominated by van der Waals fields of the surface layers if these are as little as a few nanometres thick [25]. In that case the value of $A$ depends on the relative dielectric constants of the silicon oxide/adsorbed organic layer combination and the oligostyrene liquid. We have not investigated this point in detail. The organic contamination from the atmosphere is likely to be of short alkyl chains [28], whose refractive index is $\simeq$1.4; in view of the relatively high refractive index (and thus dielectric

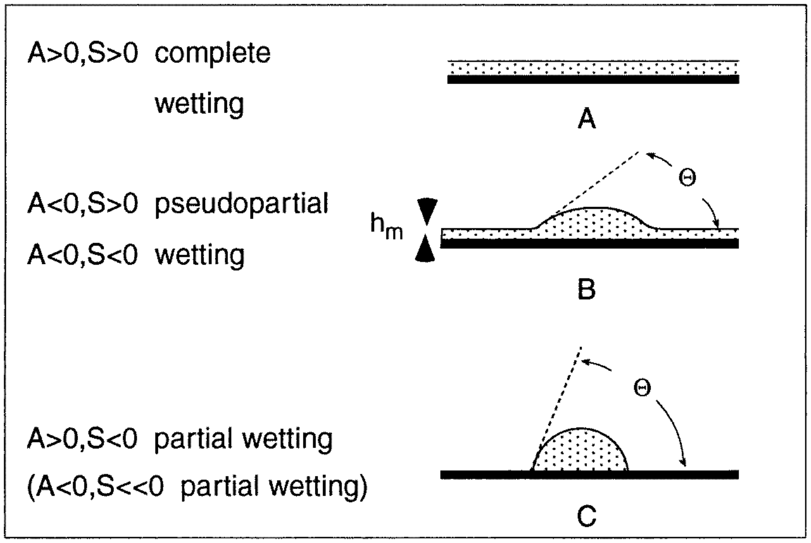

**Figure 7.** Illustrating the complete (A), pseudopartial (B), and partial (C) wetting regimes corresponding to different $A, S$ combinations (based on reference [26]).

constant) of the oligostyrene, we expect $A < 0$. By the same token, the spreading coefficient will be controlled by the short-ranged interactions at the solid surface, and where these are dominated by an adsorbed low-energy organic layer (i.e. low $\gamma_{sv}$) we expect $S < 0$; this is consistent with the dewetting behaviour observed (figure 2). From the above qualitative argument, the regime for oligostyrene on the bare wafer is then likely to be $A < 0, S < 0$, that is, the pseudopartial wetting regime of figure 7(B). If the conjecture regarding the sign of $A$ is not correct, i.e. $A > 0$ rather than $A < 0$, we would then expect the partial wetting regime of figure 7(C) $(A > 0, S < 0)$.

It is difficult, by visual observation alone, to distinguish experimentally between these two regimes of partial wetting of the silicon wafer surface by the oligostyrene. The thickness $h_m$ of the wetting film in the pseudopartial wetting case ($A < 0, S < 0$; figure 7(B)), is given by [26]

$$h_m = a[2(1 - \cos\Theta)]^{-1/2} \tag{5}$$

where $a$ is a microscopic length comparable with the size of a liquid molecule. For the large contact angles observed ($\Theta \approx 22°$), the wetting layer $h_m$ would be few nanometres at most: too thin to be visually distinguished from the underlying substrate. Thus for $S < 0$ (due to the organic layer adsorbed from the atmosphere) both $A > 0$ and $A < 0$ would result, for the oligostyrene on the solid substrate, in the droplet formation observed (figure 2).

The situation with a polymer brush which is anchored on the solid substrate and is solvated by the oligostyrene is very different, and is illustrated in figure 8. Rupture of the solvated brush is suppressed as a result of its finite shear modulus, an effect discussed at length earlier [9, 30]. The OPIM and NRA observations described in the previous section also suggest that the 'valleys' in the oligostyrene film on top of the brush extend down approximately to the brush tip. The situation is one where a substrate consisting of a solvated polymer brush is being partially wetted by the oligostyrene liquid. We may try to understand this in terms of $A$ and $S$ as for the liquid on the bare wafer surface, though we

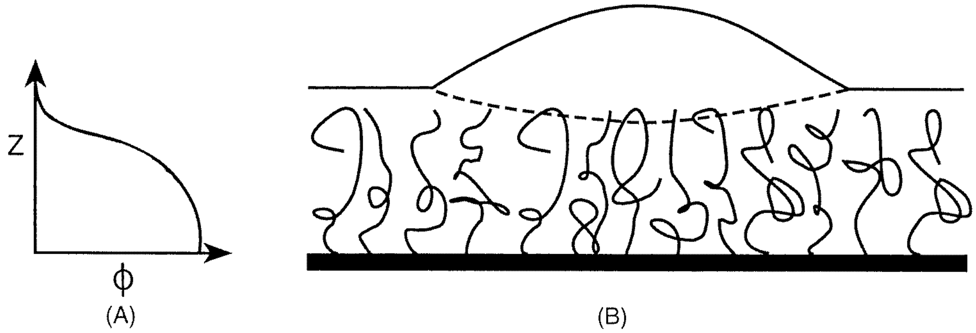

**Figure 8.** A schematic illustration of a liquid drop on top of a solvated brush. (A) The parabolic composition–depth segment profile decaying exponentially to pure liquid near the brush tip. (B) The broken curve indicates that the plane of the brush–drop interface is not sharply defined (see also the text).

should bear in mind that the solvated brush is rather different to a plane solid surface. The brush thickness is $\simeq 100 \pm 20$ nm, so the long-ranged interactions in the thin liquid film on top of the brush will be dominated by the brush layer itself, rather than by the underlying solid [27]. The relevant parameters are then $A' = A_{s'l} - A_{ll}$, where $A_{ll}$ is as before the Hamaker constant corresponding to a free oligostyrene film, but the 'solid' is now the brush layer; the prime on the subscript of $A_{s'l}$ is to remind us that we are not dealing with a well defined solid surface. Similarly we write $S' = \gamma_{s'v} - \gamma_{s'l} - \gamma_{lv}$. The value of $A'$ will depend on whether the Hamaker constant of the solvated brush is greater or smaller than that of the pure oligostyrene. Since the mean brush composition is $\simeq$97% oligostyrene and some 3% polystyrene, it is clear that $|A'|$ will in any case be very small. The refractive index measurements, which show that $n(\text{PS–0.58 K}) = 1.571$ is slightly smaller than the refractive index of polystyrene $n(\text{PS}) = 1.59$ [31], suggest that $A' < 0$ [32].

The value of $S' = \gamma_{s'v} - \gamma_{s'l} - \gamma_{lv}$ is open to conjecture. The concentration profile of the polymer segments within the brush decreases parabolically from the anchoring surface [33] (figure 8(A)), and detailed calculations indicate that it falls away exponentially to zero towards the brush tip [23, 24]. The composition at the very tip of the brush is thus essentially pure oligostyrene, so we expect the surface tensions at the brush–vapour interface and at the oligostyrene–vapour interface, determined by the short-ranged effects, to be essentially equal, $\gamma_{s'v} = \gamma_{lv}$. In that case $S' = -\gamma_{s'l}$, the surface tension between pure oligostyrene and the brush. While the interfaces between the brush tip and air, and the drop surface and air are sharp and well defined, this is not the case for the brush–drop interface. We indicate this lack of a sharp interface by the dashed line in figure 8(B). We are not aware of detailed calculations of $\gamma_{s'l}$—we would expect it to be roughly of order $(k_B T/\xi_{tip}^2)$, where $\xi_{tip}$ is the polymer segment correlation length close to the tip of the brush. In any case, $S'$ is clearly very small. The entire argument is somewhat qualitative, but it does suggest that—if it is appropriate to apply the Brochard model to the oligostyrene film on the brush—we may be in one of the two regimes corresponding to $S < 0$: either in the $A > 0, S < 0$ regime—partial wetting as in figure 7(C)—or in the $A < 0, S < 0$ regime—pseudopartial wetting as in figure 7(B). In either case we expect dewetting of the oligostyrene film to occur, consistent with our observations. We note that in the case of pseudopartial wetting, the thickness $h_m$ of the wetting film on the brush is given by $h_m$ of equation (5).

In conclusion, we have examined in detail the structure of a thin liquid film on top of a brush solvated by the same liquid. The behaviour observed experimentally is consistent with a simple picture of the solvated brush layer as a ‘solid’ substrate whose surface composition is essentially pure liquid, resulting in a negative spreading coefficient—and thus dewetting—of the overlying liquid film.

## Acknowledgments

We especially thank Sam Safran for enlightening discussions, and Lewis J Fetters for donation of the end-functionalized polystyrene. This work was supported by the Israel Science Foundation, the Minerva Foundation, the German Israel Foundation, the Ministry of Sciences and Arts, and the European Commission.

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