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When Tethered Chains Meet Free Ones; The Stability of Polymer Wetting Films on Polymer Brushes

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Summary:
We present a combined experimental and theoretical self-consistent field (SCF) investigation of the wetting behavior of a polystyrene melt (composed of chains with degree of polymerization P) on top of a polystyrene brush (composed of chains with length N) grafted onto a silica surface. The control variables are the grafting density σ of the brush chains and the length of mobile chains P. Experiments show in agreement with the theory that there is a window of complete wetting. Both at very low and at high grafting densities the system remains partial wet. At large degree of polymerization P, there is a difference between the experimental and theoretical results. Theory predicts partial wetting only, whereas the window of complete wetting persists in the experiments even when $P \gg N$. This difference is attributed to the double-well structure of the disjoining pressure as revealed by the SCF theory. With this type of disjoining pressure it is conceivable that a metastable zero contact angle remains present for very long times.

Keywords: interfaces; thin films; melt; computer modeling; atomic force microscopy

Introduction

When a polymer melt is brought into contact with a hard wall that neither attracts nor repels the monomers (an *indifferent* surface), the interface carries a small but significant latent entropy per unit area due to the entropic restrictions of chains confined to a half space. The same kind of restriction occurs when two polymer surfaces are pushed together but the chains have not yet crossed the interface between them. As a result, a thin film of a polymer melt on such a surface is expected to be unstable: it will break up into droplets with a contact angle which might be (depending on temperature) of order a few to a few tens of degrees. This typical polymer effect, deriving entirely from the large number of internal degrees of freedom of such molecules, is well known and usually referred to as ‘autophobicity’, that is, the polymer seems to ‘dislike’ itself.

A different case would be if we bring the polymer into contact with the surface of a different material. Depending on the chemical nature of this material, the lowering of the interfacial

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free energy may sometimes be enough to drive the formation of a totally stable film (this is called *complete wetting*). However, if this is not the case, we have again a situation where the polymer melt forms droplets (this is called *partial wetting*). Now, it is the unfavorable contact between the polymer and a 'foreign' substrate that causes the partial wetting; an appropriate term for this is 'allophobicity'. The macroscopic quantity that characterizes a wetting situation is the *spreading parameter* S defined as the following combination of interfacial tensions $S = \gamma_{\mathrm{sg}} - (\gamma_{\mathrm{sl}} + \gamma_{\mathrm{lg}})$, where the subscripts *s, l,* and *g* refer to the substrate, polymer melt, and gas phase (vacuum), respectively. Partial wetting occurs whenever $-2\gamma_{\mathrm{lg}} < S < 0$ and the corresponding contact angle is given by Young's law: $\cos\theta = (\gamma_{\mathrm{sg}} - \gamma_{\mathrm{sl}})/\gamma_{\mathrm{lg}}$.

Complete wetting is achieved as soon as S becomes equal to zero and the contact angle vanishes. When this happens, one usually calls this a *wetting transition.*

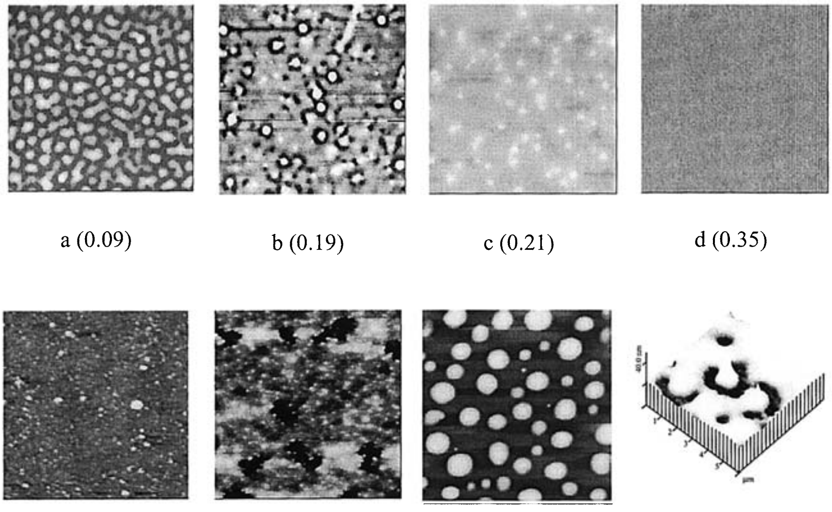
In many practical cases, it is important to have complete wetting, as this avoids trapping of gas bubbles at interfaces, improves adhesion, and is expected to stabilize particle dispersion in melts. We therefore wondered whether it is possible to remedy a case of allophobicity by introducing end-attached chains that would be chemically identical to those of the melt. Such chains might mix with those of the melt and thus suppress the allophobic effect to some extent, thereby stabilizing the film. Such effects have indeed been reported.[1-3] The stronger the allophobic effect, the more attached polymers would seem to be needed. However, if the density of attached chains becomes too high, it is conceivable that one eventually produces an almost indifferent surface, which displays autophobicity. What grafting density should be chosen? The purpose of the present study was to elucidate the effects of density of the grafted chains and length of chains in the melt on the wetting behavior of an experimental model system (allophobic substrate, end-attached polystyrene chains, and polystyrene melt). Alongside, we performed numerical calculations based on self-consistent field (SCF) theory to establish a link with theoretical models.

Experimental

As the allophobic substrate we selected silicon wafers. The length of end-attached chains was kept approximately constant at about 200 polystyrene (PS) monomers per chain. The length of the free chains P was varied between 10 and 10^4 monomers. The remaining control parameter is then the number of attached chains per unit area, the grafting density σ. Controlling and varying this parameter over a wide range (0.01-1.0 per nm^2) is not trivial. Two methods were found to work well.[3,4]

For low grafting densities we used wafers with a thin oxide film onto which we spin-cast films of polyvinylpyridine (PVP)-PS diblock copolymers with varying PVP block lengths. This serves to vary σ: Short PVP blocks give high grafting densities and long PVP blocks give a wide spacing between grafted chains. The films were dried and annealed at 120°C for 1h, after which they were thoroughly rinsed with a non-selective solvent (chloroform). This treatment removes all polymers that do not have their PVP block on the substrate, and leaves a surface covered with a thin film of PVP from which PS 'hairs' emerge. The amount of polymer per unit area was measured in the dry state by means of ellipsometry and from this, the grafting density could be calculated. With this method we could vary σ in the range 0 – 0.3 nm^{-2}.

In order to achieve higher densities we employed a chemical grafting method.[4] The silicon wafers were treated with dilute HF which etches away the oxide layer and produces a surface layer of hydrogenated silicon. Vinyl-terminated polystyrene of the appropriate chain length (Polymer Source) was dissolved in toluene and spin coated onto the hydrogenated silicon. After drying, the sample was heated at 140°C during 2h. The vinyl group reacts with the



a (0.09) b (0.19) c (0.21) d (0.35)

e (0.5) f (0.52) g (0.95) h = 3D of b (0.19)

Figure 1. AFM images of a PS melt (M_n = 183 kg/mole) onto a PS brush. Image 10x10 μm^2 maximum height difference between the dark depressed regions and the elevated bright patches 30 nm. (a) partial wetting, (b) 'holes + hills', (c) 'hills', (d) complete wetting, (e) 'hills', (f) 'holes + hills', (g) dewetting. From a-g, σ increases as indicated: σ = 0.09 (a), 0.19 (b), 0.21 (c), 0.35 (d), 0.50 (e), 0.52 (f), 0.95 (g) nm^{-2}. In (h) a 3D image of a 6x6 μm part of panel (b) is given.

silicon surface, forming a very stable Si-C bond. The grafting density could be varied by employing mixtures of long (200 monomers) and very short (20 monomers) vinyl-terminated PS. The short PS occupies a certain fraction of the reactive surface sites and thus dilutes the long chains. Using this method, we could achieve grafting densities up to almost 1 nm^{-2}.Thin films (about 10 nm) of monodisperse PS, varying in MW from about 600 to 1000,000 g/mol, were prepared on the substrates by spin coating from toluene. At room temperature, these films are stable because PS is in a glass state. The stability of the films was subsequently tested, by storing them at 140°C for 12 days. It was important to do that not in air but in nitrogen atmosphere because oxygen was found to attack the polymer and lead to irreproducible results. After the thermal treatment, the samples were rapidly cooled to room temperature and analyzed by contact mode AFM.

Experimental results

Many samples were prepared, varying the density σ of grafted chains as well as the length P of free PS. Together, the samples span a parameter plane (σ, P) ranging from (0, 10) up to about (0.95 nm^{-2}, 10^4 monomers). In the AFM analysis of all these samples, various kinds of surface patterns were found. Examples of these are given in figure 1 that shows a series of patterns found upon increasing σ, at fixed P. Two kinds of patterns were very common. The first case is that of smooth films without any features as fig. 1d; these were classified as stable films. The second is that of films which had either developed a number of holes, or had broken up entirely into droplets or islands of irregular form (figs. 1a, 1g). These films were classified as unstable.

In addition, we found more complicated cases in small areas of the parameter surface. Examples of these are in figs. 1b, 1c, 1e, and 1f. In all these cases we see not only macroscopic liquid in the form of (small) droplets, but also some other kind of structure. Often one observes a mesoscopic thin film of about 5 nm thick together with something else. In fig. 1b we see droplets (white) surrounded by a circular depression (black), and the remaining surface is covered with a thin film (gray). In fig 1c the depressions have disappeared but the thin film is still there. In fig. 1e the droplets appear again together with thin film, and in fig. 1f there are droplets and dry surface, but also irregular patches of mesoscopic film.

Using such kinds of data, we constructed the diagram figure 2 which divides the (σ, P)-plane into three main regions and four minor regions. At zero or low σ we always find unstable films. Apparently, the grafted chains are not yet able to suppress the PS-repelling character of

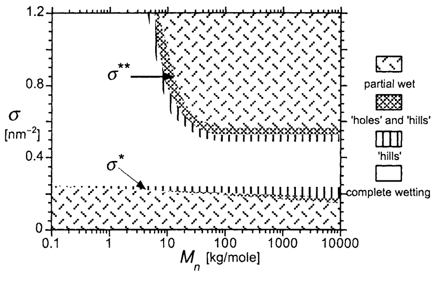


Figure 2. Wetting phase diagram of a PS melt of varying M_n onto a PS brush of varying grafting density σ after annealing 12 days at 145°C under reduced pressure. The initial film thickness in all experiments is 5 nm ± 0.1 nm.

the substrate. This is the *allophobic* region where the film has too many unfavorable contacts with the substrate to be stable. At somewhat higher σ, stable films appear. This could be the region of complete wetting that we were aiming for. At still higher σ, one finally enters a second region of unstable films. Clearly, this is the *autophobic* partial wetting region mentioned in the introduction. As can be seen, the minor regions always occur in narrow bands around the transitions between partial and complete wetting, suggesting that the brush/melt interactions in that area are of a complicated nature.

Theoretical analysis

In this section we attempt to substantiate the very preliminary conclusions on the basis of a theoretical analysis.

Let us first consider some simple scaling arguments. The bare substrate, on which PS has a finite contact angle θ_0, is characterized by a negative value of the spreading parameter S_0. Using the Young equation, we have the following relation between S_0 and θ_0: $S_0 = \gamma_{lg}(\cos\theta_0 - 1)$.

Attached chains will modify the properties of the surface and, hence change the value of the spreading parameter to S. The change $S - S_0$ is equal to the change in Gibbs energy per unit area due to the grafting. If we express the change in Gibbs energy per grafted chain, and denote this quantity as ΔG, we have as a criterion for the wetting transition occurring at σ^*:

$$S = S_0 - \sigma^* \Delta G = 0 \qquad (1)$$

As long as the density of attached chains is low (i.e., in the so-called 'mushroom' regime), we can neglect any interactions between them and ΔG will be independent of σ. In the absence of the melt, that is, when the surface is dry, grafted chains will assume the form of collapsed globules of size $R \sim N^{1/3}$. Upon being immersed in a melt of chains, two things will happen simultaneously: (a) the chains will swell, and (b) they will mix with the free chains. Both effects contribute to a lowering of the free energy with respect to the bare-wall case. The Gibbs energy contributed by each grafted chain thus has two terms, one for the swelling, and one for the mixing. The entropy loss associated with the collapse of a chain can be expressed by the Flory expansion coefficient α defined by $\alpha^2 = R^2 / R_0^2$, where R_0 is the radius of the unperturbed coil, characterized by $R_0^2 \sim N$. The Gibbs energy of a collapsed coil is given by kT/α^2. Upon swelling, this is the Gibbs energy recovered. The (ideal) mixing contribution is easily shown to be given by $-kTN/P$. Hence, we arrive at:

$$\frac{\Delta G}{kT} = -\left(\frac{N}{P} + N^{1/3}\right) \tag{2}$$

and using our wetting transition criterion, we find for the transition between the allophobic and the stable region:

$$\sigma^* = \gamma_{\mathrm{lg}}\left(1 - \cos\theta_0\right) / \left(kT\left(\frac{N}{P} + N^{1/3}\right)\right) \tag{3}$$

The surface tension, γ_{lg} of the melt generally increases somewhat with molar mass, i.e., with chain length P. However, this variation rarely amounts to more than a few percent and occurs mainly at low values of P. Because we will primarily deal with large values of P, we ignore the effect in the present scaling approach. Then, N/P is small as compared to $N^{1/3}$. In any case, σ^* *increases* with P but over most of the experimental range, the increase is very minor. In the limit of small P, σ^* becomes very small.

As we increase the grafting density further, we eventually reach interacting grafted chains, a structure commonly known as a *brush*. The swelling of a brush in a liquid (e.g., a solvent, or a polymer melt) to a thickness H depends on the balance between the osmotic interaction between the segments, which tends to enhance the swelling, and the stretching entropy which tends to reduce it. The difference with the brush in a low molecular weight solvent is that the osmotic term is smaller by a factor of order $1/P$:

$$\frac{G}{kT} = \frac{H^2}{N} + \frac{N^2\sigma}{PH} \tag{4}$$

Minimization of this Gibbs energy with respect to H gives for the equilibrium height: $H \cong NP^{-1/3}\sigma^{2/3}$.

In a 'melt' of monomers ($P = 1$), such a brush may be strongly swollen, but upon increasing P, the brush contracts and it may eventually collapse entirely to a segment volume fraction of order unity (a 'dry' brush). The collapse would thus be expected to occur when, $\langle\varphi\rangle = N\sigma / H$ becomes of order unity, that is when

$$\sigma^{**} \cong P^{-1/2} \tag{5}$$

It is likely that the separation between brush chains and free chains is a rather gradual process, driven by increasing entropic restrictions. It need not give a very sharp point where the brush switches between swollen and dry. A precise criterion where the spreading parameter becomes zero is therefore not so easily given. A more detailed calculation by Leibler *et al.*[5,6] considers the interpenetration between brush and melt, and concludes that a transition should be expected for $\sigma^{**} \sim P^{-2/3}$. More precise numerical calculations may possibly shed light on this point. We can conclude with certainty, however, that the transition σ^{**} will *decrease* with increasing P. Because we concluded above that σ^* *increases*, it seems that we cannot avoid that the two transitions meet at some value of P.

Numerical SCF calculations

The basic concepts of the numerical SCF theory have been extensively described elsewhere.[7] We therefore just briefly outline the procedure to obtain wetting data. The system chosen consists of grafted chains, each N = 200 segments long and with grafting density σ (per surface lattice site), and free chains of varying length P. Free volume is taken into account as a separate component ('vacancies') so that the polymer is compressible. Flory-Huggins χ parameters are introduced for the pair wise interactions between polymer segments (p),

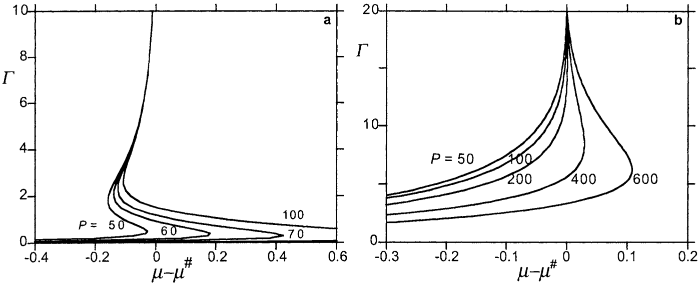


Figure 3. Adsorption isotherms for polymer melt chains (with length P, as indicated) on a polymer brush with length $N = 200$. The grafting density is $\sigma = 0.005$ (a) and 0.025 (b). In the left diagram the isotherm is plotted up to Γ = 10; the curves continue as in figure 3 and approach $\mu = \mu^{\#}$ from below saturation (first-order wetting transition). In right diagram the isotherms approach the binodal from the supersaturated side (second order wetting transition).

surface (s), and vacancies (v) with the following values: $\chi_{sv} = 0$, $\chi_{ps} = -1$ and $\chi_{pv} = 1$. For each value of σ, *P* and the chemical potential μ of the free polymer the equilibrium amount of free polymer on the surface was calculated. Plotting this amount of free polymer as a function of its chemical potential gives the adsorption isotherm.

Sets of isotherms are given in figure 3 a,b. Fig. 3a is for a low grafting density ($\sigma = 0.005$) and shows that there is a small loop in the isotherm that is obtained for $P = 50$ which develops to a large loop as *P* increases to 100. Clearly, there is a value of *P* between 50 and 100 where the step in the isotherm occurs below bulk saturation ($\mu < \mu^{\#}$), (complete wetting for low values of *P*) to the situation that the equal area construction does not work any longer (partial wetting, large values of *P*). This means that there is a wetting transition. As this transition occurs in a discontinuous manner, it can be classified as first order. The isotherms of fig. 3b for $\sigma = 0.025$ are of a different shape. Here, for $P = 50$ a monotonic curve is found, which is followed by the development of a loop. The loop does not develop from a small part of the curve (as in fig. 3a), but involves the entire curve. As a result, a film of finite thickness coexisting with the macroscopic liquid polymer develops gradually in the sense that the thickness of this film decreases gradually from infinity to lower and lower values. The corresponding contact angle also appears and increases in a very gradual manner. There is no discontinuity here; this wetting transition is of second order.

Figure 4 summarizes the (σ, *P*) points where wetting transitions occur. As expected, there are two lines at low *P*, which we label σ^* and σ^{**}. Below σ^* we have allophobic behavior, between σ^* and σ^{**}, there is complete wetting and above σ^{**} we have autophobic behavior. The σ^* transition is of first order, and the σ^{**} transition is of second order. As *P* increases, an interesting situation arises. The two transitions approach each other; the complete wetting gap closes. This was anticipated on the basis of our very simple scaling analysis and seems to be confirmed here: there is a finite value P^* beyond which there is only partial wetting. Yet, in the experimental data (figure 2), the gap does *not* seem to close. What is the situation at $P > P^*$?

In order to get an idea about this, we plot in fig. 5 the contact angle as a function of σ, for various values of *P*. Clearly, for low values of *P*, and in the direction of increasing σ, the contact angle first drops steeply, and becomes zero at σ^*. Then, at σ^{**}, a finite contact angle reappears, but in a very gradual manner. Thus, we have two wetting transitions, a first-order and a second-order one, separated by a region of complete wetting. As *P* increases, little

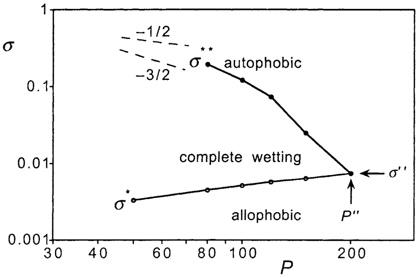


Figure 4. Theoretical phase diagram in terms of the grafting density σ and the length melt chains P, for $N = 200$. The parameter σ^* (open symbols) represents the first-order wetting transition at low grafting densities, whereas σ^{**} (filled symbols) corresponds to the second-order transition at high grafting densities. The allophobic, complete wetting and autophobic regimes are indicated. The two crossover σ^* and σ^{**} meet at $P = P''$, $\sigma = \sigma''$. Two short dashed lines at the top of the graph indicate the –3/2 slope (Leibler[5]) and the –1/2 slope (eqn. 5).

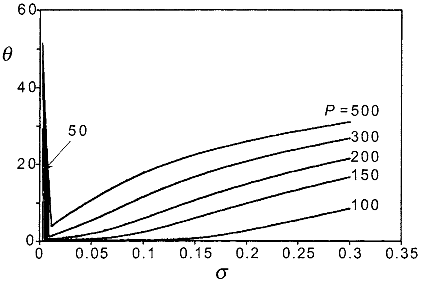


Figure 5. Calculated contact angle θ (in degrees) for different values of the length of the melt chains P as a function of the grafting density, $N = 200$.

changes at low σ, but the contact angles at higher σ increase and, along with this, the transition σ^{**} shifts to a lower value. Eventually, the entire curve detaches from the zero-angle axis. However, it still has a minimum at $\sigma_{\min}$ and, more importantly, there is a sharp break in the curve precisely at this minimum.

Evidently, the contact angle does not change in a gradual manner, and we must conclude that there is some sort of transition at $\sigma_{\min}$. One may wonder what kind of transition this is. It occurs at finite contact angle and involves bulk liquid and two values of the thickness of the mesoscopic film. In the conventional language of wetting, the term ‘wetting transition‘ is reserved for those cases where at coexistence a mesoscopic film disappears in favor of a macroscopic film at $\theta = 0$. The term ‘prewetting‘ refers to coexisting mesoscopic films that are *off*-coexistence. Here we have coexisting thin films, but *at* coexistence. It seems to us that there is no adequate terminology to deal with this case; we propose the term ‘wetting transition at finite contact angle‘.

Concluding discussion

Clearly, the interaction of free and tethered molecules leads to a complicated scenario. The SCF calculations show that regions of partial and complete wetting must be expected at low

P; this is in full agreement with the observations. The calculations also show that at higher *P* complete wetting is no more possible, but there is a point at finite contact angle where bulk liquid, a mesoscopic film, and 'dry' surface coexist. This seems to be contradicting the experimental results that always had a window of stable films at intermediate σ, whatever the length of the free chains. Now, the intersection of σ^* and σ^{**} implies that the isotherm has essentially *two* loops, and this has also other consequences. One such consequence is that films may be *metastable* at a certain thickness; this is easily seen by considering the disjoining pressure (= the 'rotated' curve) which has two minima separated by a maximum. If the barrier is too high to be easily crossed, a metastable film will be sufficiently long-lived to be experimentally undistinguishable from a true stable film. Since we did not deliberately induce destabilization (e.g., by nucleating holes) we tentatively conclude that experimentally we are dealing with metastable rather than with true stable films at high *P*.

Another consequence is that whenever an unstable film begins to develop towards its thermodynamic equilibrium, it forms correlated transient structures. The evolution of such structures has been theoretically investigated by Sharma *et al.*,[8.9] and what these authors obtain bears striking resemblance with the sequence of structures that we report in figs. 1 b,c,e, and f. By way of example, we replot data from Fig 1b in a 3D representation in Fig 1h. This is the first pattern one gets when, coming from the allophobic region, σ is increased. One can distinguish places where the original film has disproportionated into bulk liquid droplets (white) surrounded by dry surface (black), but also areas where the original film has not changed, presumably because it is metastable. In fig. 1c, the dry surface has disappeared and one observes just droplets on top of a mesoscopic film; this seems to 'announce' the appearance of the stable film (fig. 1d). In our opinion, the very fact that such structures appear supports our numerical calculations, where we found free energy curves with double minima. This then makes it all the more likely, that the discrepancy between our experimental 'phase diagram' (fig. 2) and its theoretically expected counterpart is due to metastability.

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