Macromolecules **1997,** *30,* 5939−5943

Wetting of a Polymer Brush by a Chemically Identical Polymer Melt

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Received January 28, 1997; Revised Manuscript Received May 14, 1997[⊗]

ABSTRACT: We present a theoretical study of the conformations of a polymer brush (made of linear macromolecules chemically anchored to a flat, solid interface) when it is exposed to a molten, compatible polymer. At large brush grafting densities σ and melt molecular weights P, the melt only penetrates the brush over a distance λ that is small, compared to the brush thickness. For $P > N^{2/3}\sigma^{-2/3}$, the penetration length $\lambda \approx a\sigma^{-1/3}N^{1/3}$ (Leibler *et al.* Proceedings of the OUMS Conference, Osaka, Japan, June, 1993) is associated with partial wetting. For $P < N^{2/3}\sigma^{-2/3}$, although wetting is complete (as was predicted by Leibler *et al*), we find that penetration is still partial: $\lambda = a\sigma^{-1}NP^{-1}$. There should be implications in interfacial rheology and in wetting dynamics.

I. Introduction

Linear polymer molecules can be present at interfaces in various ways.[1] In particular, polymers at solid interfaces represent a field of considerable industrial stakes: polymer-stabilized colloidal suspensions are used in paints and inks; the presence of polymer chains on a flat, solid surface can also have wetting, rheological, or adhesion effects.[2] Such situations are achieved in different ways. The monomers can be attracted by the solid surface; the resulting adsorbed layer is greatly disordered. When the polymer does not adsorb on the surface (neutral or repulsive surface), chain ends can be forced onto the surface (chemical reaction, adsorbing copolymer block); the resulting structure is more ordered and is called a polymer brush. In the remainder of this article, we do not deal with adsorbed layers, but we focus on polymer brushes.

The structure of a polymer brush and the conformations of the grafted chains result from a balance between two effects. Osmotic effects account for monomer−monomer interactions between grafted chains and tend to swell the brush. The elasticity of the grafted chains, on the contrary, tends to diminish the brush extension. In good solvent conditions, increasing the grafting density progressively elongates the grafted chains and makes the brush denser;[3−5] ultimately, when the grafting density is maximum, the brush volume fraction is of order unity: it has expelled the solvent completely. This dry brush regime is reached only in the limit of maximum grafting. This regime is more extended, however, when a chemically identical solvent of high molecular weight, i.e., a compatible melt, is used (Figure 1).[4,6,7] More precisely, the solvent is expelled when the grafting density σ (average number of grafted chains per surface area a^2 of the solid substrate, where a is the monomer size) is high enough, depending on the polymerization index of grafted chains, N, and of free chains, P:

$$\sigma > P^{-1/2} \qquad (P < N) \tag{1}$$

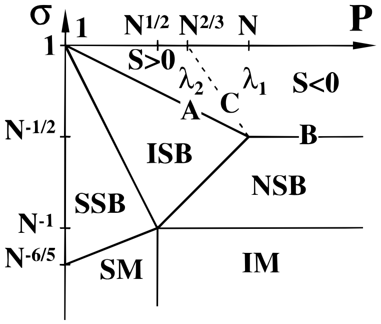

Figure 1. Different regimes for a brush of grafting density σ (chains N) facing a homopolymer (P) are presented. In the regimes of total penetration, symbols stand for swollen and ideal mushrooms (SM, IM), swollen and ideal stretched brush (SSB, ISB), and nonstretched brush (NSB) (see ref 6). The brush is only partially penetrated in the other two regimes, where the penetration lengths λ_1 and λ_2 are given by eqs 3 and 7.

for small free chains[4] (line A of Figure 1), and

$$\sigma > N^{-1/2} \qquad (P > N) \tag{2}$$

for long free chains[6] (line B of Figure 1). Within this regime, the conformations of the chains inside the brush should be essentially independent of the melt molecular weight P. In particular, the incompressibility of the grafted chains implies that the dry brush thickness is $h_0 = aN\sigma$. The interface between the brush and the melt, however, is not sharp; the melt penetrates over a distance λ inside the brush. This phenomenon arises as a balance between two effects. On the one hand, penetrating the brush is entropically favorable for the solvent; on the other hand, the melt penetration implies an extra stretching of the chains in the outer fringe of the brush and a subsequent cost in elastic free energy. The penetration length λ was calculated by Leibler, Ajdari, Mourran, Coulon, and Châtenay a few years ago[8,9] for a melt of long chains (sector BC of Figure 1):

$$\lambda = \lambda_1 \equiv a\sigma^{-1/3}N^{1/3} \; (P > P^* = N^{2/3}\sigma^{-2/3}) \tag{3}$$

In this regime, the melt wets the brush only partially (negative spreading parameter S). Expression 3 crosses over to complete penetration ($\lambda \sim h_0 = aN\sigma$) when $\sigma = N^{-1/2}$ (line B of Figure 1), as expected from the scaling

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1997.

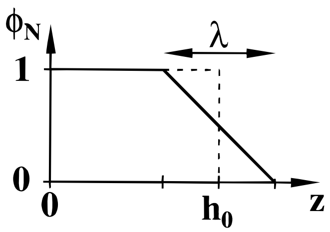

Figure 2. The concentration profile of a polymer brush facing a homopolymer melt is not steplike (dotted line). Instead, the interface is somewhat broader. For convenience, we assumed a linear profile of slope $1/\lambda$ (plain line).

theory[6] (eq 2). In the case of short melt molecules ($P < P^*$), Leibler *et al.* predict complete wetting[8] (positive spreading parameter). They do not mention any penetration length in this regime, however. In the present work, we investigate the penetration length in this small P regime and the corresponding wetting properties.

In Section II, we give the penetration length λ for short melt chains ($P < P^*$). A blob description of the interpenetrated region is given in Section III, along with additional remarks. Wetting consequences are briefly discussed in Section IV. Our approach neglects numerical factors.

II. Penetration Length for Short Melt Chains

Once the brush and the melt are in contact, they adjust the penetration length λ so as to minimize the overall interfacial free energy (In the present work, we take the simplest profile for an extended interface (Figure 2) and assume that more sophisticated (and real) forms only bring minor corrections to the free energy and to the equilibrium penetration length). The first contribution to the interfacial energy, F_{brush}, accounts for the extra stretching of the brush when the interface is broadened over the width λ. The other part of the free energy, F_{melt}, is discussed below. The elastic contribution to the free energy

$$F_{\mathrm{brush}} \cong kT\,\frac{\sigma\,\lambda^2}{Na^2a^2} \tag{4}$$

was calculated by Semenov[10] and by Leibler *et al.*[8] by identification to the work done by displacing the monomers of the brush fringe in the parabolic Milner–Witten–Cates (MWC) potential[11] $V(z)$, to obtain a broadened interface: $F_{\mathrm{brush}} = \int V(z)[\phi_0(z) - \phi_\lambda(z)]\,\mathrm{d}z$, where ϕ_0 is the steplike profile and ϕ_λ is a profile of width λ. In fact, the expression of F_{brush} can be obtained immediately by a simple convolution of the brush concentration profile with the elastic free energy $F_{\mathrm{el}}/kT \cong [\sigma(h)/a^2][h^2/Na^2] = [h/Na^3][h^2/Na^2]$ of a dry brush of height h (steplike profile):

$$F_{\mathrm{brush}} = \left\{\int -\frac{\mathrm{d}\phi_\lambda}{\mathrm{d}h}F_{\mathrm{el}}(h)\,\mathrm{d}h\right\} - F_{\mathrm{el}}(h_0) \tag{5}$$

This simple result reflects an intrinsic property of the chain conformations in the MWC brush description, which *rigorously* allows for such convolutions. Although expression 4 has already been established,[10,8] we present in detail this alternative derivation of it in the Appendix: the convolution property (eq 5) has broader implications by itself.

Using the sole expression of the elastic penalty for the brush, F_{brush} (eq 4), we can derive the melt component of the interfacial energy, F_{melt}, and the penetration length λ (eqs 3 and 7). We argue as follows:

(a) F_{melt} favors broader interfaces: it is a decreasing function of λ.

(b) Since we consider partial penetration ($\lambda \ll h_0$), F_{melt} should depend on the melt molecular weight P and on the concentration profile (i.e., on λ), but there is no reason why it should depend explicitly on the molecular weight N of the grafted chains.

(c) Total penetration ($\lambda \sim h_0 = aN\sigma$), according to the scaling result[4] mentioned in the Introduction, should occur for $\sigma = P^{-1/2}$ (line A of Figure 1, see eq 1).

Using the expression of F_{brush} given by eq 4, taking into account points (a, b, and c) above and assuming a scaling law for $F_{\mathrm{melt}}(\lambda,P)$, leads to the unique solution

$$F_{\mathrm{melt}} \simeq -\frac{\lambda}{Pa^3} \equiv F_{\mathrm{mix}} \tag{6}$$

$$\lambda = \lambda_2 \equiv a\sigma^{-1}\,NP^{-1}\,(P < P^* = N^{2/3}\,\sigma^{-2/3}) \tag{7}$$

which is valid for short matrix chains ($P < P^*$). Indeed, the interface is very smooth, the free chains can be considered as pointlike objects ($aP^{1/2} \ll \lambda$), and the contribution from the translational entropy of the solvent molecules reads:

$$\frac{F_{\mathrm{mix}}(\lambda)}{kT} = \frac{1}{a^2}\int\frac{\mathrm{d}z}{a}\left[\frac{\phi_P}{P}\log\phi_P\right] \simeq -\frac{\lambda}{Pa^3} + \mathrm{const}$$

where $\phi_P(z) = 1 - \phi_N(z)$ is the melt volume fraction.[12]

Note that the penetration length for a melt of longer chains ($P > P^*$, eq 3) can be recovered using the boundary condition that total penetration occurs[6] for $\sigma = N^{-1/2}$ (line B of Figure 1, see eq 2), instead of point (c) above. The resulting melt interfacial energy,

$$F_{\mathrm{melt}} \simeq F_{\mathrm{conf}} \equiv kT\int\frac{\mathrm{d}z}{a}\frac{(\nabla\theta)^2}{\phi(1-\phi)} \simeq \frac{kT}{\lambda a} \tag{8}$$

(see ref 8), accounts for the fact that when the interface width is smaller than the typical extension of the solvent molecules ($\lambda < aP^{1/2}$), many conformations of the free chains (those that would cross the interface) are forbidden near the interface: this loss of entropy itself is reduced by the interface broadening, so that F_{conf}, although positive, also favors larger penetration lengths λ.

III. Blob Description and Further Remarks

(i) Let us now work out the blob structure of the interface in the MWC picture. The blob size is the length scale at which the chains crossover from a random coil behavior (at smaller length scales) to a stretched behavior (at larger length scales). In the notations in the Appendix, the blob size Λ_{MWC} is defined by $\partial n_0/\partial z \equiv g/\Lambda_{\mathrm{MWC}}$, where g is the number of monomers per blob ($\Lambda_{\mathrm{MWC}} = ag^{1/2}$). Plugging $\rho \simeq h_0$ and $z \simeq \rho - \Lambda_{\mathrm{MWC}}$ into the MWC expression for n_0 (see Appendix), we get

$$\frac{\partial n_0}{\partial z} \simeq \frac{2N/\pi}{\sqrt{(2\rho\Lambda_{\mathrm{MWC}})}}$$

Omitting numerical factors: $\Lambda_{\mathrm{MWC}} \simeq aN^{1/3}\sigma^{-1/3}$. Thus, for $P > P^*$, the interface consists of just one layer of

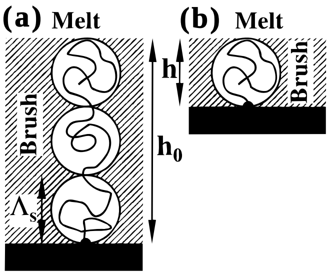

Figure 3. In the scaling picture of a dry brush, each grafted chain (N monomers) has the conformation of a string of blobs of size Λ_s, containing g monomers each (a). The conformation of the outer fringe is the same as that of a brush of shorter chains (b), since all chains behave alike at length scales larger than the blob size, Λ_s.

blobs ($\lambda_1 \simeq \Lambda_{MWC}$), whereas for small P, the interface resembles a brush with several blob layers ($\lambda_2 > \Lambda_{MWC}$).[13]

(ii) It is interesting, at this stage, to see what the interface would look like in the scaling picture. The scaling blob size, Λ_s, was calculated by Aubouy[6] *et al.* and can be recovered from the fact that the brush thickness is the length of a string of Gaussian blobs ($\Lambda_s = ag^{1/2}$): $h_0 = (N/g)\Lambda_s = aN\sigma$. Thus, $\Lambda_s = a\sigma^{-1}$. In the scaling picture, all chains behave alike at length scales larger than the blob size. Hence, the outer blob of each chain in the brush (Figure 3a) behaves as if all chains were only g monomers long (Figure 3b). Therefore, for the equivalent short brush (Figure 3b), $ag\sigma = h = \Lambda_s = a\sigma^{-1}$ and hence, $\sigma = g^{-1/2}$. Thus, it is (just) in the total penetration regime (see eq 2). In other words, the initial brush (Figure 3a) is penetrated over a distance corresponding to the size of the last blob: $\lambda_s = \Lambda_s = a\sigma^{-1}$.

(iii) Hence, for $P > P^*$, the interface is made of one blob layer ($\lambda_1 \simeq \Lambda_{MWC}$), as it would in the scaling picture ($\lambda_s \simeq \Lambda_s$), whereas each chain has several blobs in the interface for $P < P^*$ ($\lambda_2 > \Lambda_{MWC}$). But more interesting is the fact that the MWC penetration length values, λ_1 and λ_2, are larger than the scaling value, λ_s. Indeed, in the MWC picture, the chain strands located in the outer fringe of the brush are less stretched and can thus be penetrated more easily.

We now make further, more general remarks.

(iv) At very high grafting densities $\sigma \to 1$, the penetration length λ should reduce to a monomer size. Equations 3 and 7 do not account for this fact because the finite extensibility of the monomers is not included in the MWC approach. Shim and Cates give a better treatment of this point.[14]

(v) A satisfactory aspect of the result λ_2 is that it is a decreasing function of the solvent molecular weight P. This is qualitatively consistent with some poly(dimethylsiloxane) (PDMS) brush concentration profiles obtained by Marzolin[15] at moderate brush grafting densities (σ of order or smaller than $N^{-1/2}$) and with data by Liu[16] *et al.* on wetting properties of a polystyrene (PS) film on poly(vinylpyridine) (PVP)−PS block copolymer film surfaces.

(vi) Most formulas in the present work (especially the threshold $P^* = N^{2/3}\sigma^{-2/3}$) do not include possible numerical factors.

IV. Wetting Properties

In Section II, we evaluated the penetration length λ of a polymer melt inside a compatible polymer brush made of long molecules (eq 7). We now briefly address the consequent wetting properties of the system.

The wetting of the brush by the homopolymer melt is governed by the relative values of brush−air (γ_{Na}), melt−air (γ_{Pa}), and brush−melt (γ_{NP}) surface tensions. We here follow the argument of Leibler *et al.*[8] To a good approximation, γ_{Pa} can be assumed to be a melt interfacial energy (see eqs 6 and 8) with a very small penetration length (since air is a bad solvent for the polymer), $F_{\mathrm{melt}}(\lambda \approx a) = F_{\mathrm{mix}} + F_{\mathrm{conf}}$, hence reducing to F_{conf} ($\lambda \approx a$). The brush−air interface is assumed to have the same surface tension, except for a minor correction due to the brush stretching energy: $\gamma_{Na} = \gamma_{Pa} + F_{\mathrm{brush}}(\lambda \approx a)$, where F_{brush} is given by eq 4. The surface tension of the penetrated brush is $\gamma_{NP} = F_{\mathrm{melt}}(\lambda) + F_{\mathrm{brush}}(\lambda)$. Equation 3 yields a negative spreading parameter[8] $S \equiv \gamma_{Na} - \gamma_{NP} - \gamma_{Pa}$ (partial wetting, $P > P^* = N^{2/3}\sigma^{-2/3}$). For $P < \alpha P^*$, however, eq 7 implies that the spreading parameter S is positive (complete wetting). (The numerical factor α is a fraction of unity). Thus, in this small P regime, wetting is complete, although penetration inside the brush is only partial ($\lambda_2 < h_0$).

Dynamical wetting properties should be greatly influenced by the degree of interpenetration, characterized by λ. Indeed, various phenomena may arise. A melt of short molecules (small P) may develop a film inside the brush in the late stages of spreading.[17] For longer chains or on shorter time scales, friction at the interface may be a Rouse-type friction[18] (for nonentangled molecules, $P < N_e$) or may be significantly enhanced by entanglements[19] ($P > N_e$).

Acknowledgment. I gratefully acknowledge fruitful discussions with Armand Ajdari, Miguel Aubouy, Pierre-Gilles de Gennes, and Elie Raphaël.

Appendix: Elastic Energy of Penetrated Brush

Due to the incompressibility of the polymer melt, the penetration of the solvent inside the brush over a distance λ is associated with a corresponding extension of the concentration profile of the brush beyond its dry height h_0 (Figure 2). In this Appendix, we determine the free energy penalty for this extra brush stretching, in the MWC approach. Here, the result (eq 4) is less important than the method, presented below, which implies that a simple convolution (eqs 5 and A3) can be very easily used for a variety of situations, as pointed out at the end of the present Appendix.

Let us first consider a purely dry brush ($\lambda = 0$). The conformation of any chain whose free end is located at altitude ρ ($0 \le \rho \le h_0$) is described by a function $z(\rho,n)$, where n is the current monomer along the chain ($0 \le n \le N$, $n = 0$ at the grafting point and $n = N$ at the free end). In fact, z is an increasing function of n (since a nonmonotonous $z(\rho,n)$ could be substituted for a monotonous one that would contribute equally to the concentration profile but whose elastic cost would be smaller). Hence, we can invert $z(\rho,n)$ as $n(\rho,z)$, for future convenience. Let $\epsilon(\rho)\,\mathrm{d}\rho$ denote the grafting density of chains whose free end is between ρ and $\rho + \mathrm{d}\rho$ (hence, $\int_0{}^{h}-\ \epsilon(\rho)\,\mathrm{d}\rho = \sigma$). The more general program now amounts to minimizing the Flory elastic free energy of the chains,

$$\frac{F_{\mathrm{el}}}{kT} \equiv \int_0^{h_0} \frac{\mathrm{d}\rho\,\epsilon(\rho)}{a^2}\left\{\int_0^N \mathrm{d}n\,\frac{1}{2}\left(\frac{\partial z(\rho,\,n)}{a\,\partial n}\right)^2\right\} = \int_0^{h_0} \frac{\mathrm{d}\rho\,\epsilon(\rho)}{a^4}\left\{\int_0^{p} \mathrm{d}z\,\frac{1}{2}\left(\frac{\partial n(\rho,z)}{\partial z}\right)^{-1}\right\} \quad \text{(A1)}$$

under the condition of unity volume fraction $\phi_N(z) \equiv 1$ $(0 \leq z \leq h_0)$, where

$$\phi_N(z) \equiv \int_z^{h_0} \mathrm{d}\rho\epsilon(\rho)\,\frac{a\partial n(\rho,z)}{\partial z} \tag{A2}$$

The MWC scheme was developed not only for a brush in good solvent,[5] but also for a dry brush.[11] Their solution

$$\epsilon_0(\rho,h_0) = \frac{\rho}{Na\sqrt{h_0^2-\rho^2}}$$

and

$$n_0(\rho,z) = \frac{2N}{\pi}\arcsin\left(\frac{z}{\rho}\right)$$

satisfies $\phi_N(z) \equiv 1$ and minimizes eq A1, yielding

$$\frac{F_{\mathrm{el}}}{kT} = \frac{\pi^2}{24}\frac{N\sigma^3}{a^2}$$

as we now show. If we vary ϵ_0 and n_0 as $\epsilon(\rho) \equiv \epsilon_0(\rho) + \delta\epsilon(\rho)$ and $n(\rho,z) \equiv n_0(\rho,z) + \delta n(\rho,z)$ (with the boundary condition $\delta n(\rho,0) = \delta n(\rho,\rho) = 0$ for all ρ), then the resulting variations of the brush free energy (eq A1) and of the local volume fraction (eq A2) are linked through

$$\frac{\delta F_{\mathrm{el}}}{kT} = \int_0^h \frac{\mathrm{d}z}{a^5}\left[\frac{z^2\pi^2}{8N^2}\delta\phi_N(z)\right]$$

due to the form of n_0 and to the boundary conditions for δn (Second-order terms bring an additional positive, second term, proving that the solution indeed corresponds to a free energy minimum). Thus, the free energy is stationary for variations of ϵ and n that do not modify the concentration profile, independent of the initial free end distribution profile ϵ_0.[20] This feature proves that brush conformations obtained by convolution of the MWC free end distribution ϵ_0 with any (decreasing) brush profile $\phi_N(z)$ (keeping the chain conformations $n = n_0$ unaltered) also minimize the free energy (eq A1) for the corresponding brush concentration profiles. The free end distribution and the resulting free energy for an arbitrary profile are thus given by

$$\epsilon(\rho) \equiv \int_\rho^\infty -\frac{\mathrm{d}\phi(h)}{\mathrm{d}h}\,\epsilon_0(\rho,h)\,\mathrm{d}h$$

and

$$\frac{F_{\mathrm{el}}\{\phi_N(z)\}}{kT} = \int_0^\infty -\frac{\mathrm{d}\phi_N(z)}{\mathrm{d}z}\frac{\pi^2}{24}\frac{N[\sigma(z)]^3}{a^2}\,\mathrm{d}z$$

$$= \frac{\pi^2}{24N^2a^5}\int_0^\infty \mathrm{d}z\left\{-\frac{z^3\mathrm{d}\phi_N(z)}{\mathrm{d}z}\right\} \tag{A3}$$

where $\sigma(z)$ is defined by $z \equiv aN\sigma(z)$ (equivalent dry brush of height z). Using this convolution method, we work out the elastic free energy of a brush whose profile is that of Figure 2:

$$\frac{F_{\mathrm{el}}(\lambda)}{kT} = \mathrm{const} + \frac{\pi^2}{24}\frac{N\sigma^3}{a^2}\frac{\lambda^2}{h_0^2}$$

as announced at the beginning of Section II (eq 4).

A derivation of the parabolic profile in a good solvent can also be drawn at this point, using this simple convolution result (eq A3). The total free energy of a brush in a good solvent is given by

$$\frac{F_{\mathrm{tot}}}{kT} = \frac{\pi^2}{24N^2a^5}\int_0^h \mathrm{d}z\left\{-\frac{z^3\mathrm{d}\phi_N(z)}{\mathrm{d}z}\right\} + \int_0^\infty \frac{\mathrm{d}z}{a^3}\left\{\frac{{\phi_N}^2(z)}{2} - \phi_N(z)\right\} - \mu\int_0^\infty \phi_N(z)$$

where the first term is the elastic energy of the brush, the second one is the mixing free energy of the solvent in the low brush concentration limit, and μ is a Lagrange multiplier introduced to ensure the condition

$$\int_0^\infty \frac{\mathrm{d}z}{a}\phi_N(z) \equiv \sigma N$$

The result is

$$\frac{F_{\mathrm{tot}}}{kT} = \mathrm{const} + \int_0^h \frac{\mathrm{d}z}{2a^3}\left[\phi N(z) + \frac{\pi^2}{8N^2}\frac{z^2}{a^2} - 1 - \mu\right]^2$$

which yields the MWC parabolic profile after immediate minimization. This derivation is reminiscent of the argument by Pincus[21] in which a very simplified form of the free end distribution $\epsilon(z) \equiv \phi_N(z)/N$ and uniform elongation of each chain are assumed, leading to an elastic term of the form

$$\int_0^h \frac{\mathrm{d}z}{a^3}\left\{\frac{z^2}{2Na^2}\frac{\phi_N(z)}{N}\right\}$$

The elastic free energy contribution corresponding to any (decreasing) brush concentration profile can be immediately calculated, using this convolution method (eq A3).

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