

Structure of an Irreversibly Adsorbed Polymer Layer Immersed in a Solution of Mobile Chains

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Received March 21, 1994*

ABSTRACT: We discuss the structure of an irreversibly adsorbed layer made of neutral, flexible polymer chains (degree of polymerization N) exposed to a solution of mobile chains (degree of polymerization P). We assume that the mobile chains are chemically identical to the adsorbed chains and that their length is shorter (or comparable). According to the value of the bulk volume fraction, ϕ_b , the mobile chains may, or may not, penetrate into the layer and may, or may not, affect the layer conformation. Using scaling laws, we locate the domains of existence of these different regimes in terms of the variables ϕ_b , P , and N . In particular, we expect the mobile to penetrate into the layer if the bulk volume fraction ϕ_b is greater than a critical value ϕ_{bM} given by $\phi_{bM} \cong (P/N)^{4/7}$ for $P > N^{5/12}$ and by $\phi_{bM} \cong N^{-1/3}$ for $P < N^{5/12}$.

I. Introduction

Adsorption of linear, polymer chains at interfaces is of both practical and theoretical interest and has been the subject of many recent studies.¹ Most of the existing studies focus on the properties of reversibly adsorbed polymer layers.²⁻¹⁴ Much less is known about *irreversible* adsorbed layers.¹⁵⁻¹⁹ Recently, a very elegant scaling approach has been proposed by Guiselin¹⁹ who considered irreversible adsorption from a polymer melt (or from a semidilute solution) onto a planar surface assuming that the time necessary to saturate all the surface sites was small compared to that of chain diffusion in the bulk. The conformation of the chains is thus not modified during the adsorption process. Guiselin considered the following sequence of events: (i) The planar solid surface is put in contact with a polymer melt and all the monomers touching the surface adsorb instantaneously and irreversibly. (ii) The surface is then washed with pure solvent and only the initially adsorbed chains are retained onto the surface. The so-formed layer can be visualized as a succession of loops and tails. In Guiselin's approach, each loops made of $2n$ monomers is considered as two pseudotails of n monomers. The number (per unit area) of pseudotails made of more than n monomers is given by¹⁹

$$S(n) \cong a^{-2} n^{-1/2} \quad (1 < n < N) \quad (1)$$

where N is the degree of polymerization of the adsorbed chains and a the monomer size. Let us assume that the n th monomers of all pseudotail larger than n are located at the same distance z from the surface. We can then consider n as a function of z . At a distance z from the surface, the average distance between two pseudotails is given by $D(z) \cong [S(n(z))]^{-1/2}$. Using eq 1 we get

$$D(z) \cong a n(z)^{1/4} \quad (1 < n < N) \quad (2)$$

By analogy with the Alexander-de Gennes model for monodisperse polymer brushes,^{20,21} we expect that, locally, at a distance z from the surface, the layer can be visualized as a closely packed system of units of size $D(z)$. In order to determine the function $n(z)$, we consider the number $G(z)$ of monomers within a volume $[D(z)]^3$. The function $n(z)$ satisfies the differential equation

$$\frac{dn}{G(z)} \cong \frac{dz}{D(z)} \quad (3)$$

At a scale smaller than D , the chain behaves like a free chain and G is related to D by the relation $G \cong (D/a)^{5/3}$.^{22,23} Equation 3 then leads to $n(z) \cong (z/a)^{6/5}$. The volume fraction of monomers is given by $\phi(z) \cong (D(z)/a)^{-4/3} \cong (a/z)^{-2/5}$ and the total extension of the layer scales as $aN^{5/6}$.¹⁹

In the present paper we consider the situation where an irreversibly adsorbed layer is exposed to a solution (of volume fraction ϕ_b) containing some mobile polymer chains (P monomers per chain). Our discussion is restricted to the case where the mobile chains are chemically identical to the adsorbed chains and where their length is smaller or comparable ($P \leq N$). Our aim is to describe the progressive penetration of the mobile chains inside the layer as the bulk volume fraction ϕ_b increases. Our model is based on the behavior of monodisperse polymer brushes in the presence of a polymer solution. This problem was first considered by de Gennes.²⁰ In section II we first recall his main results. In section III, we consider the case of an irreversibly adsorbed layer which has been prepared from a melt. In the Appendix we extend our results to the case where the irreversibly adsorbed layer has been prepared from a semidilute solution. All our discussion is based on scaling laws, and all numerical coefficients will be omitted.

II. Case of a Polymer Brush: de Gennes Results

The behavior of a monodisperse polymer brush in the presence of a polymer solution of shorter, chemically identical chains was studied by de Gennes.^{20,24} We here recall his main results.

a. Consider polymer chains with degree of polymerization N terminally grafted onto a flat solid surface and exposed to a melt made of chemically identical chains with degree of polymerization P ($P < N$). The number of grafted chains per unit surface is $a^{-2}\sigma$. The average distance between two grafting sites is then $D \cong a\sigma^{-1/2}$. At sufficiently high coverage density σ , the grafted chains stretch away forming a polymer "brush" of extension L . In a Flory-type approach, the free energy per chain is given by

$$\frac{F_{\text{chain}}}{kT} \cong \frac{L^2}{Na^2} + \frac{1}{P} \frac{N^2 a^3}{LD^2} \quad (4)$$

* Abstract published in *Advance ACS Abstracts*, August 1, 1994.

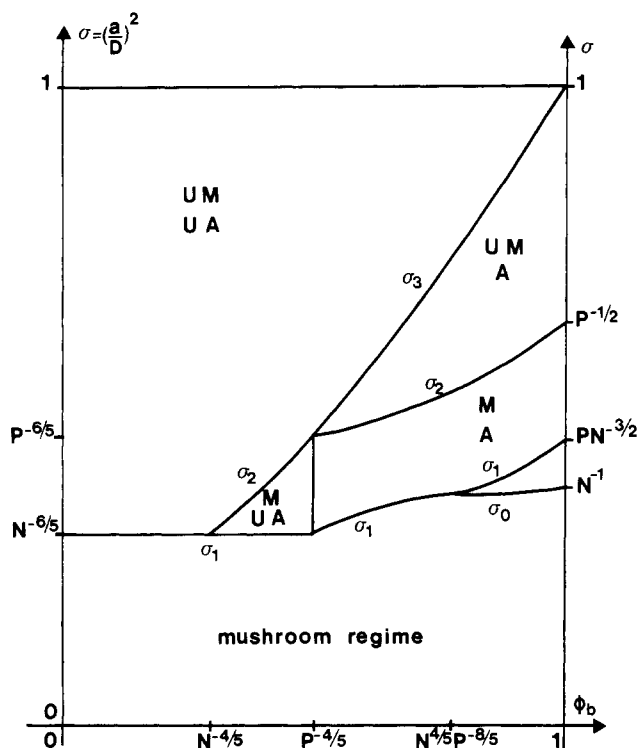


Figure 1. Various regimes for a monodisperse polymer brush (N monomers per chain) of grafting density σ exposed to a solution of shorter chains (P monomers per chain, volume fraction ϕ_b). Symbols are as follows: M, mixed; UM, unmixed; A, affected; UA, unaffected. Note that the intermediate regime localized in between $\sigma_0 \approx N^{-1}\phi_b^{1/4}$ and σ_1 disappears if $P < N^{1/2}$. (After de Gennes ref 20.)

The first term of eq 4 represents the elastic contribution. The second term corresponds to the effect of two-body interactions; the factor $1/P$ corresponds to the Edwards' screening of the excluded volume interactions.²⁵ Minimizing the free energy (eq 4), we get $L \approx aP^{-1/3}\sigma^{1/3}N$. A grafted chain may be subdivided into subunits of size D , each containing g monomers. Within one subunit, the chain behaves like a free chain leading to $D \approx aG^{3/5}P^{-1/5}$. Different subunits repel each other, and the brush is essentially a closely packed system of subunits. The N -monomer volume fraction ϕ_N is given by $\phi_N \approx G(a/D)^3 \approx P^{1/3}\sigma^{2/3}$. Since $L \approx (N/G)D$, a grafted chain can be viewed as a string of subunits of size D almost fully stretched along the normal to the wall.

As σ increases, the volume fraction $\phi_N \approx P^{1/3}\sigma^{2/3}$ increases and the free chains (of volume fraction $\phi_P = 1 - \phi_N$) are progressively expelled from the layer. The expulsion can be considered as total when $\phi_N \approx 1$, leading to a critical density $\sigma_2 \approx P^{-1/2}$. Above σ_2 , the volume fraction ϕ_N is of order unity and the layer extension scales as $L \approx aN\sigma$.

In writing eq 4 we have assumed that the grafted chains were stretched compared to their free size. This condition corresponds to $\sigma > \sigma_1$, where σ_1 is given by $\sigma_1 \approx PN^{-3/2}$ for $N < P^2$ and by $\sigma_1 \approx P^{2/5}N^{-6/5}$ for $N > P^2$. If σ is smaller than σ_1 , the extension of the layer remains equal to $aN^{1/2}$ for $N < P^2$ and to $aP^{-1/5}N^{3/5}$ for $N > P^2$. Note that the situation $\sigma < \sigma_1$ does not always correspond to the so-called "mushroom regime" where the grafted chains do not overlap. Indeed, if $N < P^2$, de Gennes showed that there exist an intermediate regime defined by $\sigma_1 > \sigma > \sigma_0 \approx N^{-1}$ where the grafted chains do overlap while the layer extension remains equal to $aN^{1/2}$ (see Figure 1).

b. The above discussion can be immediately transposed to the case where the brush is exposed to a semidilute

solution (of P chains). Indeed, a semidilute solution of volume fraction ϕ_b can be visualized as a melt of non-overlapping blobs of size $\xi_b \approx a\phi_b^{-3/4}$, each blob being made of $m \approx (\xi_b/a)^{5/3} \approx \phi_b^{-5/4}$ monomers.²² The results of the previous section can then be generalized providing that the substitutions $P \rightarrow P/m$, $N \rightarrow N/m$, $a \rightarrow a(\xi_b/a)$, and $\sigma \rightarrow \sigma(\xi_b/a)^2$ are used. The grafting density σ_1 , which characterizes the onset of stretching, is thus given by $\sigma_1 \approx \phi_b^{7/8}PN^{-3/2}$ for $\phi_b > (N/P^2)^{4/5}$ and by $\sigma_1 \approx \phi_b^{1/2}P^{2/5}N^{-6/5}$ for $\phi_b < (N/P^2)^{4/5}$. Note that the situation $\phi_b > (N/P^2)^{4/5}$ does not exist if $N > P^2$.

In the regime $\sigma_1 < \sigma < \sigma_2$, where now σ_2 is given by

$$\sigma_2 \approx \phi_b^{7/8}P^{-1/2} \quad (5)$$

a grafted chain can be viewed as a string of subunits of size D almost fully stretched along the normal to the wall. Each subunit contains G monomers with

$$G \approx \phi_b^{5/12}P^{1/3}(D/a)^{5/3} \quad (6)$$

and the layer extension scales as

$$L \approx a\phi_b^{-5/12}P^{-1/3}\sigma^{1/3}N \quad (7)$$

Above σ_2 , the mobile chains are no longer present in the brush. In the regime $\sigma_2 < \sigma < \sigma_3$ (where σ_3 is defined below) the osmotic pressure in the layer is imposed by the bulk solution and the layer can be viewed as a closely packed system of subunits of size ξ_b , each subunit containing $m \approx \phi_b^{-5/4}$ monomers. The number of monomers within a volume D^3 is thus given by

$$G \approx m(D/\xi_b)^3 \approx \phi_b(D/a)^3 \quad (8)$$

and the layer extension scales as $L \approx a\phi_b^{-1}\sigma N$.

The above results are valid as long as D is larger than ξ_b . This defines a critical value of the grafting density:

$$\sigma_3 \approx \phi_b^{3/2} \quad (9)$$

Above σ_3 , the osmotic pressure within the layer is larger than the bulk osmotic pressure and the structure of the layer is no longer affected by the solution. The layer behaves like an Alexander-de Gennes' polymer brush in an athermal solvent and the number G of monomers within a volume D^3 is thus given by

$$G \approx (D/a)^{5/3} \quad (10)$$

The layer extension scales as $L \approx a\sigma^{1/3}N$.

c. The discussion of section b is valid as long as the solution is in the semidilute regime, i.e. as long as $\phi_b > \phi_b^* \approx P^{-4/5}$. If $\phi_b < \phi_b^*$, the layer is not affected by the presence of the mobile chains. Above $\sigma_1 \approx N^{-6/5}$, the grafted chains overlap and form a brush. Inside this brush, the number G of monomers within a volume D^3 is given by eq 9. One can show that in the regime $\sigma_1 < \sigma < \sigma_2 \approx \phi_b^{3/2}$ the mobile chains penetrate into the brush;²⁶ the corresponding volume fraction is given by $\phi_P \approx \phi_b - \phi_N \approx \phi_b - \sigma^{2/3}$.

All these results are summarized in Figure 1 where the different regimes are represented as a function of σ and ϕ_b . Note that the part of Figure 1 corresponding to the dilute regime ($\phi_b < P^{-4/5}$) differs slightly from the σ - ϕ_b diagram proposed by de Gennes.²⁰ According to Figure 1, (a) there exists a regime where the mobile penetrate into the brush without affecting its conformations, and

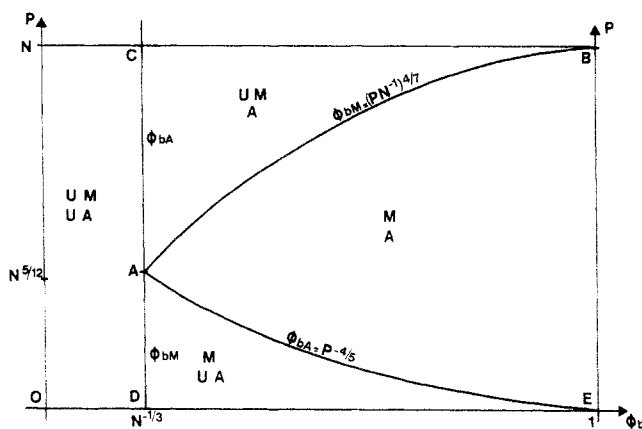


Figure 2. Various regimes for an irreversibly adsorbed layer exposed to a solution of shorter polymer chains (P monomers per chain, volume fraction ϕ_b). Symbols are as follows: M, mixed; UM, unmixed; A, affected; UA, unaffected.

(b) the layer extension $L(\sigma, \phi_b)$ does crossover at all the boundaries of the diagram.

III. Case of an Irreversibly Adsorbed Layer

Consider now the case of an irreversibly adsorbed layer exposed to a solution containing mobile P chains. The layer can be visualized as a very polydisperse polymer brush. The local grafting density is given by $a^2S(n(z))$ and decreases with z . Let us assume that locally, at a distance z from the surface, the irreversibly adsorbed layer behaves like a monodisperse brush of grafting density $a^2S(n(z))$. The structure of the layer can then be obtained by solving the differential equation 3 using the various scaling relations between G and D found in section II.

a. The "Mixed and Affected" Regime. This regime is defined by

$$\phi_b > P^{-4/5} \quad \text{if } P < N^{5/12} \quad (11)$$

$$\phi_b > (P/N)^{4/7} \quad \text{if } P > N^{5/12} \quad (12)$$

(these boundaries will be justified below) and corresponds to the zone ABE in the P - ϕ_b diagram of Figure 2. Near the surface, the layer is dense and $a^2S(n(z))$ is of order of unity. According to the discussion of section II (see Figure 1), the mobile chains are not present in the layer and the bulk solution does not affect the conformation of the adsorbed chains. By using eqs 2 and 10, eq 3 can be rewritten as $a \, dn/dz \cong n^{1/6}$ yielding

$$n(z) \cong (z/a)^{6/5} \quad (13)$$

The volume fraction $\phi_N(z)$ scales as $\phi_N(z) \cong (a/D(z))^{4/3}$. Using eqs 2 and 13 we obtain

$$\phi_N(z) \cong (z/a)^{-2/5} \quad (14a)$$

$$\phi_P(z) \cong 0 \quad (14b)$$

The results of eqs 13 and 14 are valid as long as we are in the "unmixed and unaffected regime" of the corresponding monodisperse brush (see Figure 1), i.e. as long as the inequality $a^2S(n(z)) > \sigma_3$ holds. The limit z_A (where the subscript A stands for *affected*) of this region is obtained by setting $a^2S(n(z_A)) = \sigma_3$ (see Figure 3). Combining eqs 1, 9, and 13, we get

$$z_A \cong a\phi_b^{-5/2} \quad (15)$$

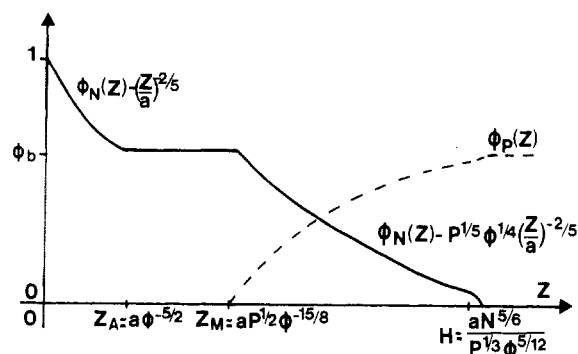


Figure 3. Volume fraction profiles for the grafted chains (full line) and for the mobile chains (dotted line) in the case where the mobile chains both penetrate into the layer and affect its conformation (zone ABE of Figure 2).

Further away from the surface ($z_M > z > z_A$, where z_M is defined below), the local grafting density $a^2S(n(z))$ satisfies the double inequality $\sigma_3 > a^2S(n(z)) > \sigma_2$. According to the discussion of section II, the mobile chains compress the layer but does not penetrate into it. The scaling relation between $G(z)$ and $D(z)$ is given by eq 8. The differential equation (eq 3) then leads to

$$n(z) \cong \phi_b^2(z/a)^2 \quad (16)$$

In this region the volume fraction $\phi_N(z)$ is independent of z and

$$\phi_N(z) \cong \phi_b \quad (17a)$$

$$\phi_P(z) \cong 0 \quad (17b)$$

The limit z_M of this region is obtained by setting $a^2S(n(z_M)) = \sigma_2$ (where the subscript M stands for *mixed*). Combining eqs 1, 5, and 16, we obtain

$$z_M \cong a\phi_b^{-15/8}P^{1/2} \quad (18)$$

Finally, at a distance z larger than z_M , the layer is characterized by the double inequality $\sigma_2 > a^2S(n(z)) > \sigma_1$. In this region, the scaling relation between $G(z)$ and $D(z)$ is given by eq 6, and the differential equation eq 3 then leads to

$$n(z) \cong \phi_b^{1/2}P^{2/5}(z/a)^{6/5} \quad (19)$$

This region is characterized by the fact that the mobile chains are present in the layer. The corresponding volume fractions are given by

$$\phi_N(z) \cong \phi_b^{1/4}P^{1/5}(z/a)^{-2/5} \quad (20a)$$

$$\phi_P(z) \cong \phi_b - \phi_b^{1/4}P^{1/5}(z/a)^{-2/5} \quad (20b)$$

Note that the smallest grafting density in the adsorbed layer is obtained for the largest pseudotails and is of the order of $a^2S(N) \cong N^{-1/2}$ (see eq 1). Since $a^2S(N) \cong N^{-1/2}$ is much larger than $\sigma_1 \cong \phi_b^{7/8}PN^{-3/2}$, one never reaches a region where the pseudotails are unstretched. The overall extension of the layer H is obtained by setting $n(z=H) = N$ in eq 19 leading to

$$H \cong a\phi_b^{-5/12}P^{-1/3}N^{5/6} \quad (21)$$

Note that H is comparable to the extension of a N -

monodisperse polymer brush of grafting density $N^{-1/2}$ immersed in a semidilute solution of P chains (see eq 7).

The regime described by eqs 11–21 corresponds to a situation where the mobile chains both penetrate into the layer and affect its structure (zone ABE of Figure 2). We now determine the boundaries (eqs 11 and 12) of this regime. Let us first consider the “penetration length” $H - z_M$ (see Figure 3). From eq 18 and 21, we have $H - z_M \cong a(P\phi_b^{5/4})^{-1/3}N^{5/6}\{1 - (N^{4/7}P^{-4/7}\phi_b)^{-35/24}\}$ which vanishes for a critical volume fraction $\phi_{bM} \cong (P/N)^{4/7}$. This volume fraction defines the line AB of Figure 3. One may also consider the quantity $z_M - z_A$ which corresponds to the extension of the region where the volume fraction $\phi_N(z)$ is independent of z [$\phi_N(z) \cong \phi_b$]. The quantity $z_M - z_A$ vanishes for the volume fraction $\phi_{bA} \cong P^{-4/5}$ (see eqs 15 and 18). This criteria corresponds to the line AE of Figure 2. The point A where the two boundaries (line AB and line AE) merge is defined by $\phi_b \cong N^{-1/3}$ and $P \cong N^{5/12}$.

b. The Other Regimes. Consider the zone ABC of the P – ϕ_b diagram of Figure 2. Since in this regime ϕ_b is smaller than $\phi_{bM} \cong (P/N)^{4/7}$, the mobile chains are not present inside the layer. The structure of the layer is characterized by eqs 13 and 14 if $z < z_A$, and by eqs 16 and 17 if $z > z_A$ (z_A still being given by eq 15). The total extension of the adsorbed layer H is now obtained by setting $n(z = H) = N$ in eq 16 yielding

$$H \cong a\phi_b^{-1}N^{1/2} \quad (22)$$

Combining eqs 15 and 22, we find $H - z_A \cong \phi_b^{-1}N^{1/2}\{1 - (N^{1/3}\phi_b)^{-3/2}\}$. By setting $H - z_A \cong 0$ one obtains the critical volume fraction ϕ_{bA} corresponding to the line AC of Figure 2:

$$\phi_{bA} \cong N^{-1/3} \quad (23)$$

Consider now the zone ADE of the P – ϕ_b diagram of Figure 2. In this regime some mobile chains penetrate into the adsorbed layer but they do not affect the layer conformation (remember that the bulk solution is in the dilute regime). The free chains are present in the region $z > z_M$ where z_M is obtained by setting $a^2S(n(z_M)) = \sigma_2$. Since σ_2 is now given by $\phi_b^{3/2}$ (see section II.c), we have

$$z_M \cong a\phi_b^{-5/2} \quad (24)$$

In the region $z_M < z < H \cong aN^{5/6}$, the volume fraction ϕ_P of the mobile chains is given by $\phi_P(z) \cong \phi_b - (z/a)^{-2/5}$. By setting $H \cong z_M$ one obtains the critical volume fraction ϕ_{bM} corresponding to the line AD of Figure 2:

$$\phi_{bM} \cong N^{-1/3} \quad (25)$$

Finally, in the regime $\phi_b < N^{-1/3}$ of Figure 2, the mobile chains do not penetrate into the layer and do not affect its structure. We thus recover the Guiselin's results described in section I: The volume fraction ϕ_N varies as $\phi_N(z) \cong (a/z)^{-2/5}$ and the extension H of the layer scales as $aN^{5/6}$.

III. Concluding Remarks

In this work we have examined the penetration of a polymer solution into an irreversibly adsorbed layer made of larger, chemically identical chains. All our discussion relies on the hypothesis that the local conformation of a polydisperse polymer brush (characterized by a local grafting density $\sigma = (a/D(z))^2$, where $D(z)$ is the average distance between two pseudotails) is similar to the bulk

structure of a monodisperse brush with the same grafting density σ . This hypothesis might not be too restrictive since the variations of the local grafting density are rather smooth. This point may be quantified by considering the parameter $x = D(z)/L(z)$, where $L(z)$ is the characteristic length over which the grafting density varies. Since $L(z)$ is of the order of $D(z)/D'(z)$ (where $D'(z)$ denotes the derivative of $D(z)$ with respect to z), one has $x \cong D'(z)$. This quantity may be readily evaluated by using eqs 2, 13, 16, and 19 which describe the generic “mixed and affected” regime of section II.a (see Figures 2 and 3). One has

$$x \cong (a/z)^{7/10} \quad a < z < a\phi_b^{-5/2} \quad (26a)$$

$$x \cong \phi_b^{1/2}(a/z)^{1/2} \quad a\phi_b^{-5/2} < z < a(P\phi_b^{5/4})^{1/2}\phi_b^{-5/2} \quad (26b)$$

$$x \cong (P\phi_b^{5/4})^{1/10}(a/z)^{7/10} \quad a(P\phi_b^{5/4})^{1/2}\phi_b^{-5/2} < z < a(P\phi_b^{5/4})^{-1/3}N^{5/6} \quad (26c)$$

Since $x \ll 1$ everywhere in the layer, the characteristic length over which the grafting density varies is indeed much larger than the average distance between two pseudotails.

Our predictions concerning the structure of the layer might be tested experimentally by using either neutron diffraction²⁸ or evanescent wave-induced fluorescence. By labeling the adsorbed chains, one has access to the extension H of the layer. According to our analysis, the layer extension is modified by the mobile chains if the volume fraction of the solution ϕ_b is larger than the critical value ϕ_{bA} given by $\phi_{bA} \cong N^{-1/3}$ for $P > N^{5/12}$ and by $\phi_{bA} \cong P^{-4/5}$ for $P < N^{5/12}$. If, on the other hand, one uses labeled mobile chains, one can measure the concentration profile of the mobile chains. According to our analysis, the mobile chains penetrate into the layer if ϕ_b is larger than the critical value ϕ_{bM} given by $\phi_{bM} \cong (P/N)^{4/7}$ for $P > N^{5/12}$ and by $\phi_{bM} \cong N^{-1/3}$ for $P < N^{5/12}$.²⁷ Current experiments at the Collège de France (C. Marzolin and L. Léger) and at Saclay (P. Auroy and L. Auvray) will allow a test of the predictions presented in this work.

A natural extension to our study would be to introduce a small chemical mismatch between the grafted chains and the mobile chains. Such an effect might be of some relevance in the interpretation of experiments using labeled chains (deuterated and protonated polystyrene chains, for example, are characterized by a small but nonzero value of the interaction parameter).^{29,31}

Acknowledgment. This problem has been suggested to us by P. G. de Gennes. We thank him as well as L. Léger, Y. Marciano, and C. Marzolin for very useful discussions.

Appendix: Case of an Irreversibly Adsorbed Layer Prepared from a Semidilute Solution

In this appendix we consider the case of an irreversible layer prepared by the adsorption of a semidilute solution of volume fraction ϕ_0 . For $\phi_0 > N^{-4/7}$, Guiselin proposed to replace eq 1 by

$$S(n) \cong \frac{1}{a^2n^{6/5}} \quad 1 < n < \phi_0^{-5/4} \quad (A1a)$$

$$\cong \frac{\phi_0^{7/8}}{a^2n^{1/2}} \quad \phi_0^{-5/4} < n < N \quad (A1b)$$

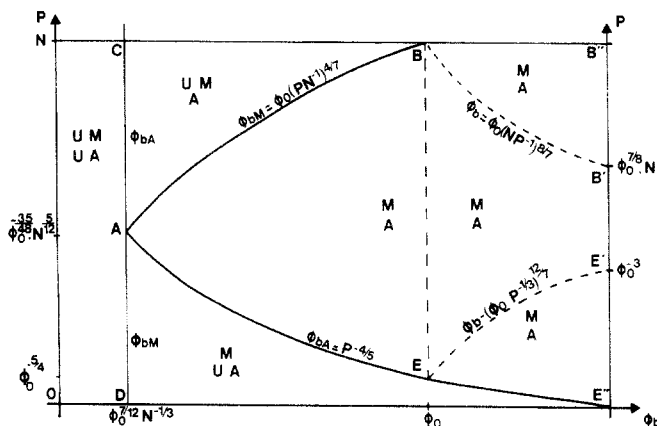


Figure 4. Various regimes for an adsorbed layer exposed to a solution of shorter polymer chains (P monomers per chain, volume fraction ϕ_b) in the case where the layer has been prepared by irreversible adsorption of a semidilute solution of volume fraction ϕ_0 .

Using this distribution law one can build the P - ϕ_b diagram represented in Figure 4:

(i) Let us first consider the zone $BB'E'E$ (defined by $\phi_b > \phi_0$ for $P > \phi_0^{-5/4}$ and by $\phi_b > P^{-4/5}$ for $P < \phi_0^{-5/4}$). This zone may itself be divided into three zones:

If $\phi_b > \phi_0 (N/P)^{8/7}$, that is in the zone $BB'B''$ of the diagram, the scaling laws for H and z_M are given by

$$z_M \cong 2a\phi_b^{-1}(\phi_b^{1/4} - \phi_0^{1/4}) + a\phi_0^{7/4}\phi_b^{-15/8}P^{1/2} \quad (A2)$$

$$H \cong a\phi_0^{7/4}\phi_b^{-15/8}P^{-2}N^{5/2} + a(N - \phi_0^{7/4}\phi_b^{-7/4}N^3P^{-2})^{1/2} \quad (A3)$$

In between the line BB' and the line EE' (this last line being defined by $\phi_b \cong (\phi_0 P^{-1/3})^{12/7}$) we have

$$z_M \cong 2a\phi_b^{-1}(\phi_b^{1/4} - \phi_0^{1/4}) + a\phi_0^{7/4}\phi_b^{-15/8}P^{1/2} \quad (A4)$$

$$H \cong a\phi_b^{-5/12}\phi_0^{7/24}P^{-1/3}N^{5/6} \quad (A5)$$

Finally, in the zone $EE'E''$ we have

$$z_M \cong 2a\phi_b^{-3/4} - a(P\phi_b^{41/4})^{-1/12} \quad (A6)$$

$$H \cong a\phi_b^{-5/12}\phi_0^{7/24}P^{-1/3}N^{5/6} \quad (A7)$$

Note that the results of eqs A2–A7 are valid as long as $\phi_0 > N^{-8/31}$.

(ii) In the other zones of the diagram, the scaling laws for H and z_M found in section II are still valid but the limits of the different regimes are now given by

$$\phi_{bM} \cong \phi_0^{7/12}N^{-1/3} \quad \text{if } P < \phi_0^{-35/48}N^{5/12} \quad (A8a)$$

$$\cong \phi_0(P/N)^{4/7} \quad \text{if } P > \phi_0^{-35/48}N^{5/12} \quad (A8b)$$

$$\phi_{bA} \cong P^{-4/5} \quad \text{if } P < \phi_0^{-35/48}N^{5/12} \quad (A9a)$$

$$\cong \phi_0^{7/12}N^{-1/3} \quad \text{if } P > \phi_0^{-35/48}N^{5/12} \quad (A9b)$$

References and Notes

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