Influence of a Polymer Solution on a Polymer Interface

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ABSTRACT: We have investigated the influence of a solution of mobile polymer chains on a polymer interfacial layer. The mobile chains were synthesized to be invisible during the scattering experiment. We show how the interfacial density profile is modified as a function of concentration of mobile chains, polymer grafting density, and compatibility of the two polymeric species. We use these results to discuss the penetration of mobile polymer chains into immobilized polymer chains.

The question whether a polymer interface can be penetrated by free polymer segments is of great technological importance. For example, the degree of penetration can have a strong effect on the adhesive properties of two polymer blocks. This effect is well-known by industrial researchers, and the phenomenon is well understood and characterized from a scientific point of view.[1] The issue of interpenetration becomes more delicate when the chains of one polymer are in solution. de Gennes[2] has provided a theoretical "phase" diagram for the case of a grafted layer (grafting density σ, chain length N) in the presence of a homopolymer solution (chemically identical, concentration ϕ_b, chain length P). Various regimes have been described, which depend on all these parameters. For instance, it has been shown that at "high" grafting density, in the brush regime, the interface evolves as the concentration ϕ_b increases. It goes from a strongly stretched configuration without penetration to a weakly stretched configuration with penetration (if $P > N^{1/2}$). Observing polymer penetration has remained an experimental challenge for scientists. Most of the techniques[3] that have been used for studying the influence of a polymer matrix are not applicable to the study of the influence of a polymer solution because the solution flows or because the solvent evaporates or degrades easily or because the solvent would dominate the signal, etc. Thus, to the best of our knowledge, no experimental results have been obtained on the influence of a polymer solution on a polymer interface.

We have solved the above difficulties by using the small-angle neutron scattering (SANS) techniques.[4] In the past, SANS has allowed us to determine the density profile of various polymer interfaces in a pure solvent or more generally in a simple liquid.[5,6] This was achieved by using different isotopic compositions (H/D) for the solvent. Modifying the isotopic composition varies the contrast of the samples without introducing significant perturbations to the system. For instance, a solvent made using 90% CD_2Cl_2 and 10% CH_2Cl_2 allowed us to show that polymer brushes have a parabolic density profile in a good solvent.[5a] When a polymer soluion replaces the solvent, the experiment becomes far more difficult. Indeed, the polymer in solution gives a coherent scattering signal which dominates the contribution from the interfacial layer. Due to chain correlations, this problem persists even when H-polymer chains and D-polymer chains are mixed to have the same average scattering length density as the solvent (henceforth referred to as n_s). The only way to avoid this problem is to use a statistical polymer of H-monomer and D-monomer whose composition exactly matches n_s at any concentration. Under this condition, the free polymer in solution (henceforth referred to as the "stealth" polymer) is invisible to the neutrons and the scattering signal is due solely to the polymer interface.

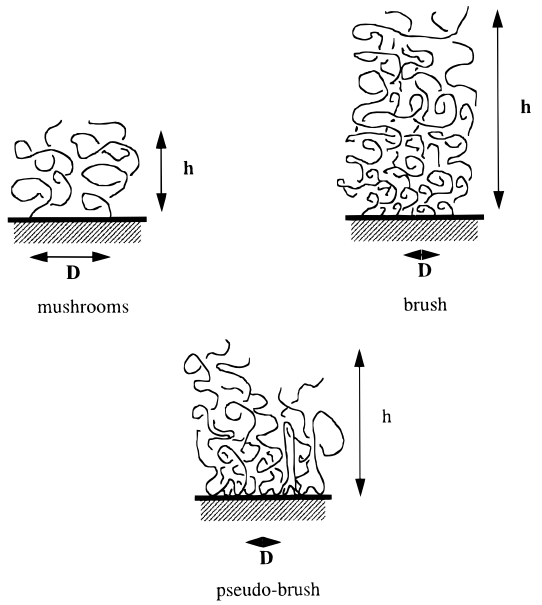

Figure 1. Schematic representation of the three types of interface we treat in this article, in good solvent.

This contrast-matching technique has allowed us to determine how the shape of the density profile of a polymer interface changes as the concentration of the free polymer solution, ϕ_b, is increased. Three types of interface were studied: (i) a high grafting density polystyrene (PS) brush, (ii) a low grafting density polystyrene layer in the slightly overlapping mushroom regime, and (iii) a polydimethylsiloxane (PDMS) pseudo-brush, consisting of a layer of irreversibly adsorbed PDMS (cf. Figure 1). These samples will be described in detail in the first section. For all three layers, the structure of the interface in pure good solvent has been extensively discussed in previous reports.[5] In this paper, we will limit ourselves to a brief description of the experimental method. In the second section, we will

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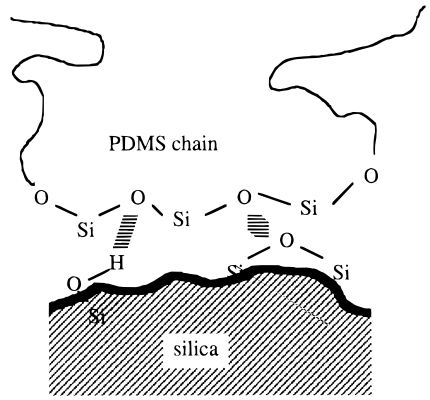

Figure 2. Irreversible adsorption of PDMS on silica, via H-bonds involving silanol groups or strained siloxane bonds.

present the density profile of the grafted layer. From this density profile, we deduce the mean interfacial concentration, the surface excess, and the thickness. Their variation with the bulk concentration, ϕ_b, is examined. The final part of the second section will be devoted to answering the question: does the free polymer penetrate into the interface?

Experimental Section

1. Sample Characteristics and SANS Experiments. All of the interfaces of this paper are solid−liquid interfaces where the solid substrate is a porous silica. Its main characteristics are as follows: scattering length density, $n_s = 3.484\ 10^{-10}$ cm^{-2}; specific surface area, 2.5 m^2/cm^3; average pore diameter, 3000 Å.

Two PS grafted layers have been prepared on this silica. The PS (fully deuterated, $n_s = 6.543\ 10^{-10}$ cm^{-2}, molecular weight = 69 000 or 75 000, and polydispersity index = 1.1) has been anionically synthesized and terminated by an excess of dichlorodimethylsilane. This leads to a monofunctional polymer, terminated by a chlorodimethylsilyl end-group which binds covalently to the silica. The grafting reaction is performed as described in ref 5b. The polymer is dissolved at a fixed concentration c_b in carefully dried benzene. We recall that the surface coverage is fixed by the polymer concentration of the reaction bath c_b: the grafting density increases roughly linearly with concentration in the reaction bath. The PS mushrooms were obtained using $c_b = 5\%$, while the PS brushes were obtained using $c_b = 60\%$. The samples were thoroughly rinsed after the grafting reaction to eliminate all the ungrafted chains. We have checked by using nonreactive polymer that the natural adsorption of the PS, under these conditions, is negligible. The amount of grafted polymer per unit area γ was measured in poor solvent:[5d] $\gamma = 11.1$ mg/m^2 for the dense brush, and $\gamma = 2.0$ mg/m^2 for the sample in the mushroom regime. This corresponds to an average distances, D, between anchoring points of 32 and 79 Å for the brush and mushroom samples, respectively. (The radius of gyration of the corresponding free PS, in good solvent, is 94 Å.)

The PDMS pseudobrush has been obtained as described in ref 5c. The PDMS has a molecular weight of 170 000 and a polydispersity index of 1.2. It has been obtained by the fractionation of a commercial polydisperse polymer. It is terminated at both ends by a trimethylsilyl end-group that cannot form a chemical bond with the surface. However, the PDMS is able to strongly adsorb onto the silica surface via H-bonds (Figure 2). This adsorption can be considered as irreversible, since no significant amount of polymer is removed after several days of immersion in a good solvent. The amount of adsorbed PDMS is again controlled by the bulk concentration. For the sample used in this study, we used a pure melt of PDMS at room temperature. The amount of polymer per unit area was measured after all the free chains were washed out: we obtain $\gamma = 21.0$ mg/m^2, which corresponds to $D = 37$ Å.

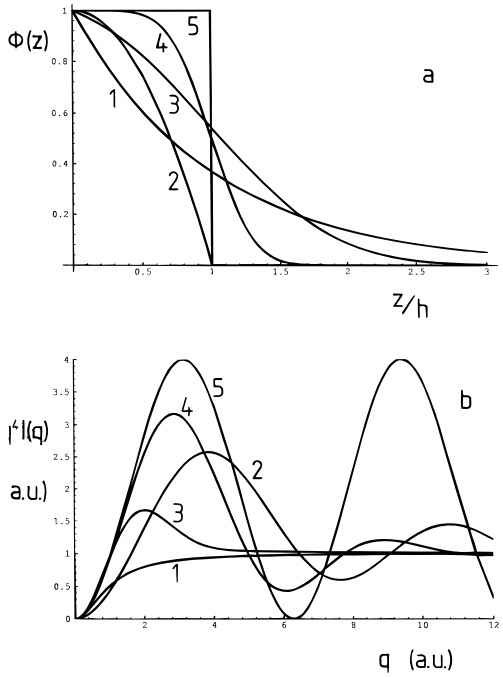

Figure 3. (a) Models of density profile. The variation with z has been normalized with respect to the thickness of the interface, h:1, exponential; 2, parabolic; 3, generalized error function with $m = 1$; 4, generalized error function with $m = 3$; and 5, step function. See text for the mathematical expression for these profiles. (b) The corresponding calculated scattering intensity.

The dichloromethane solvent used in this study is a good solvent for PS and PDMS. The free polymer is a statistical copolymer of H-styrene and D-styrene (molecular weight = 160 000, polydispersity index = 1.1). Its scattering length density perfectly matches the solid substrate (volume fraction of D-styrene = 40.4%). The solvent (dichloromethane) is a mixture of 90% of CD_2Cl_2 and 10% of CH_2Cl_2. Its scattering length density also matches the substrate.[7] The free polymer solution only gives rise to an incoherent scattering signal at all values of ϕ_b studied and over the whole q-range probed. This signal is negligible when compared to the coherent scattering signal from the interface. The experimental setup and procedures used to obtain the $I(q)$ spectra are described in ref 4.

2. Interpretation of the Data. A. Dense Interfaces (PS Brush and PDMS Pseudobrush). As explained in ref 4, the scattering intensity from any kind of (polymer) interface follows the general Porod law

$$I(q) \approx q^{-4} f(qh) \tag{1}$$

where h is the typical thickness of the interface and $f(qh)$ is a weakly q-dependent function, characteristic of the exact shape of the density profile, $\phi(z)$. z is the coordinate normal to the interface. More precisely, it can be shown that

$$f(qh) = |q \int_0^{+\infty} \phi(z)\, e^{iqz}\, dz|^2 \tag{2}$$

provided that the concentration fluctuations can be neglected. This is applicable to our study, because the fluctuations only become significant at q-values higher than those probed. Therefore, an appropriate plot which emphasizes the changes in the shape of the density profile is $q^4 I(q)$ versus q (Porod plot). We use this plot in Figure 3 to show a few examples of the calculated scattering intensity for different types of density profiles, $\phi(z)$.

Observing the data (Figures 4 and 5), we see, especially in Figure 5, that the spectra change significantly as the bulk polymer concentration increases. How can we interpret this in terms of a density profile? Our approach is to fit the data

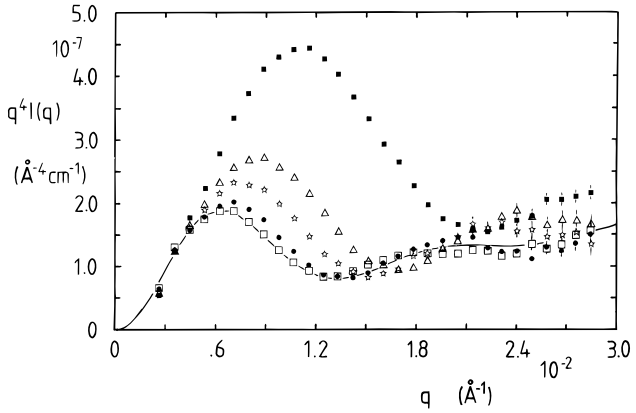

Figure 4. Porod plot of the scattering intensity for the PS brush. □, ●, ★, △, and ■ correspond to $\phi_b = 0$, 0.1, 0.15, 0.2, and 0.3, respectively.

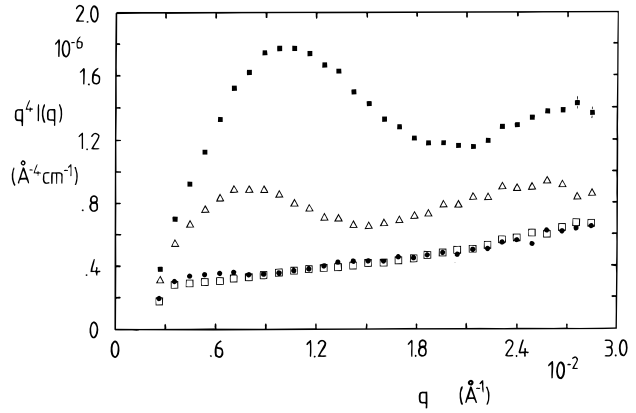

Figure 5. Porod plot of the scattering intensity for the PDMS pseudobrush. □, ●, △, and ■ correspond to $\phi_b = 0$, 0.1, 0.2, and 0.3, respectively.

with a model for $\phi(z)$ which depends on a reduced number of parameters (four). To account for the strong changes in the spectra as ϕ_b increases, we need to use a general model which can describe density profiles with strongly differing shapes. This is achieved by the generalized error function $H_m(z)$ defined as

$$H_m(z) = \phi_s \frac{1 - \mathrm{erf}\left[m\left(\frac{z}{h} - 1\right)\right]}{1 + \mathrm{erf}[m]} + d\delta(z) \qquad (3)$$

Depending on m, as shown by Figure 3, the first term in $H_m(z)$ can vary from gently sloped (a Gaussian with a single, dampled bump in the $q^4I(q)$ vs q plot) to infinitely steep (a step function with undamped oscillations). The addition term $d\delta(z)$ has been introduced to account for deviations in the experimental data from the Porod law at high q. These deviations can be due to several phenomena: concentration fluctuations, thin layer of unmatched species at the surface, residual multiple scattering, etc. However, the most likely source for a deviation from the Porod law is the presence of a thin depletion or adsorption layer of the polymer.

This heuristic model provides an excellent fit of the data for all ϕ_b (see Figures 7 and 8, below), except for the PDMS pseudobrush at low bulk polymer concentration ($\phi_b = 0$ and $\phi_b = 10\%$). In these last two cases, the density profile appears to be so gently sloped that it cannot be reproduced by the generalized error function. A far more suitable model is the exponential form, which appears to be in good agreement with the data.

For an easier theoretical comparison, we also fit the data with the so-called parabolic model,[5a] modified by an exponential tail. We note that this model was not necessary to interpret the data, since its shape can be reproduced by the

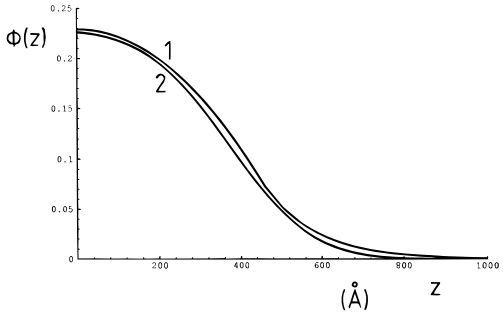

Figure 6. Comparison between a parabolic model (1) and a generalized error function (2) for the interpretation of the spectrum obtained for the PS brush in good solvent.

generalized error function. A fit to the data for the PS brush in pure dichloromethane using the parabola and generalized error function models is shown on Figure 6. The two density profiles are very similar and cannot be distinguished experimentally.

Finally, we summarize the mathematical expressions corresponding to the three types of $\phi(z)$ used in this article.

exponential

$$\phi(z) = \phi_s \exp(-z/h) + d\delta(z) \qquad (4)$$

parabolic

$$\phi(z) = \phi_s\left(1 - z^2\frac{u^2}{h^2}\right) + d\delta(z) \quad \text{for } z \le h \qquad (5)$$

$$\phi(z) = \phi_s(1 - u^2)\exp\left(-\frac{2u^2(z - h)}{h(1 - u^2)}\right) \quad \text{for } z > h$$

generalized error function

$$H_m(z) = \phi_s \frac{1 - \mathrm{erf}\left[m\left(\frac{z}{h} - 1\right)\right]}{1 + \mathrm{erf}[m]} + d\delta(z) \qquad (6)$$

B. PS Mushrooms. The scattering signal from this interface is weak, due to the small amount of polymer per unit area, rendering the above data analysis by density profiles unfeasible. Nevertheless, we can still take advantage of the SANS technique because it allows us to measure the thickness of the interface in the Guinier regime. This measurement does not require a precise knowledge of the interfacial profile. Indeed, when $qh < 1$ (h is the typical thickness of the interface, as before), it can be shown[4] that the scattering intensity $I(q)$ is given by

$$I(q) \approx q^{-2}\gamma^2\left(1 - \frac{q^2h^2}{\alpha}\right) \qquad (7)$$

where γ is the amount of polymer per unit area and α is a numerical constant. The precise value of α depends on the shape of the interfacial density profile. However, it varies little between interfacial shapes. Therefore, given the accuracy of these experiments, we can take $\alpha = 12$, which corresponds to a step function. This will give us an estimate of the thickness of the interface.

C. Error Bars. The fits give parameter error bars of the order of 1%. However, this is not really meaningful. The main source of errors comes from the experiment itself and not from the analysis of the data. On average, the experiment has a reproducibility of 10%. This means that if we repeat exactly the same experiment with a different sample (prepared in the

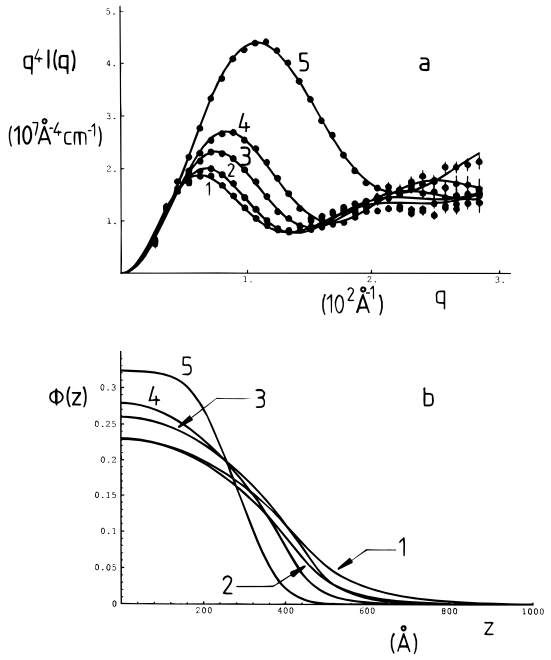

Figure 7. Density profile as a function of ϕ_b for the PS brush: (a) fit to the data; (b) plot of $\phi(z)$. Curves 1, 2, 3, 4, and 5 correspond to $\phi_b = 0$, 0.1, 0.15, 0.2 and 0.3, respectively.

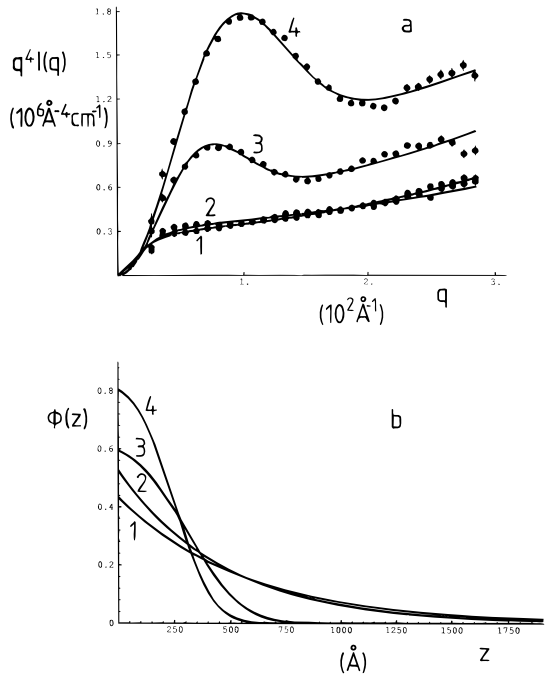

Figure 8. Density profile as a function of ϕ_b for the PDMS pseudobrush: (a) fit to the data; (b) plot of $\phi(z)$. Curves 1, 2, 3, and 4 correspond to $\phi_b = 0$, 0.1, 0.2, and 0.3, respectively.

same conditions), we find the same results within a margin of error of 10%. This is also applicable to the PS mushrooms.

Results

Spectra and their corresponding density profiles, obtained at the different bulk concentrations, are shown in Figure 7 for the PS brush and Figure 8 for the PDMS pseudobrush. For both samples, we observe the same trend as ϕ_b increases, the interface becomes thinner and steeper. However, this evolution is much more dramatic for the case of the PDMS interface. This is especially pronounced when we compare the surface fraction occupied by the polymer $\phi(z=0)$: it goes from 0.43 to

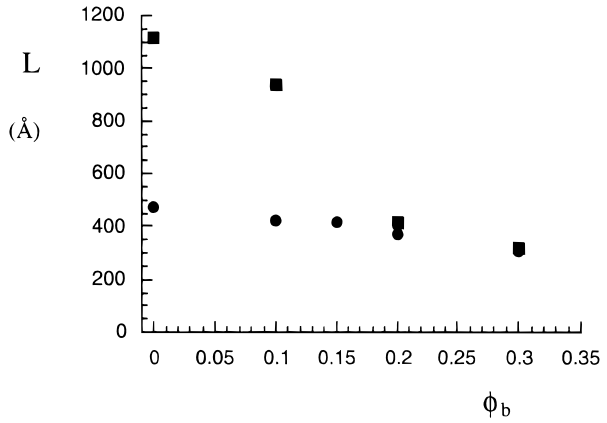

Figure 9. Variation of the mean thickness of the two dense interfaces as a function of ϕ_b. ■, PDMS pseudobrush; ●, PS-brush.

0.80 for the PDMS pseudobrush, whereas it varies only from 0.22 to 0.32 for the PS brush. If we now plot the mean thickness L, defined as $L = 2\int z\phi(z)\,dz/\int\phi(z)\,dz$ (cf. Figure 9), we observe that the thickness is always a decreasing function of ϕ_b (even for the PS mushrooms).[8] However, for the PDMS interface it varies rapidly with ϕ_b (between 0.1 and 0.2) whereas for the two PS interfaces the variation with ϕ_b is much weaker.

If we look at the exact shape of the two dense interfaces, we find that the PS brush has a parabolic form corrected by an exponential tail for almost all values of ϕ_b. However, we notice that the relative importance of the tail diminishes as ϕ_b increases. At $\phi_b = 0.3$, the spectrum is no longer fitted by this parabola. However, the generalized error function gives a good fit with a fairly high value of m ($m = 2.46$, cf eq 3).[9] This is a direct quantitative proof that the density profile has become steeper. All these results are in agreement with the predictions of Zhulina et al.[10] These changes are even more spectacular for the PDMS pseudobrush. Indeed, at low ϕ_b, the density profile is very gently sloped and extends very far from the surface. We find a good agreement with an exponential decay. However, we point out that we do not have the appropriate resolution (the interface is too thick compared to the q-range we have used, which is about the smallest we can reach) to distinguish between an exponential and a power law functional form (for example, $z^{-0.4}$, as predicted by Guiselin).[11] Nevertheless, we know from other studies[12] that a PDMS pseudobrush is indeed more gently sloped than the corresponding brush on a nonadsorbing surface. This might lead one to believe that such a loose interface would be more easily penetrated than the PS brush. However, as we shall see later, this is not the case because the free chains (PS) and the PDMS are incompatible. As ϕ_b exceeds 0.2, the bump which appears in the Porod plot [$q^4I(q)$ vs q] provides a clue that the interface becomes steeper. To get clearer picture of this new shape, we use the generalized error function, yielding an excellent fit. The rather small value of m, $m = 1.17$ for $\phi_b = 0.2$ and $m = 1.33$ and $\phi_b = 0.3$, indicates that the interface is still gently sloped. The spectrum for $\phi_b = 0.2$ cannot be satisfactorily fit by a parabola. Nevertheless, since m increases, we have a quantitative criterion that tells us that the density profile becomes steeper as ϕ_b increases.

In order to distinguish between the different possible forces responsible for the shrinkage of the interface, we need to rule out a trivial explanation. Indeed, we could imagine that the solvent quality changes due to its

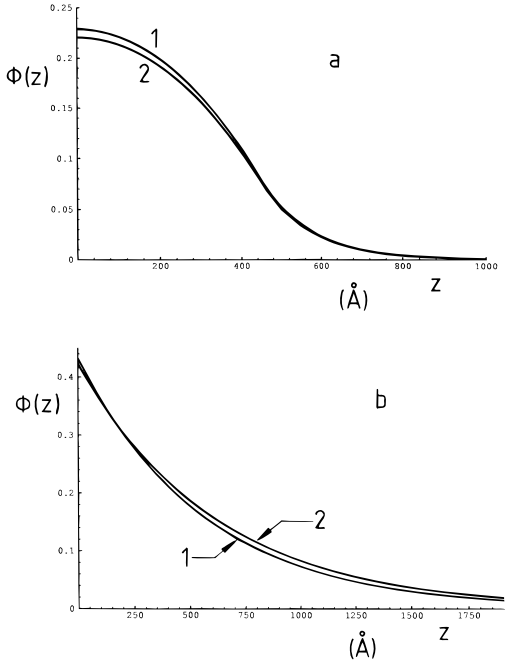

Figure 10. Comparison of the density profile for (a) the PS-brush and (b) the PDMS pseudobrush immersed in pure dichloromethane (1) or in a mixture of 70% dichloromethane and 30% styrene (2).

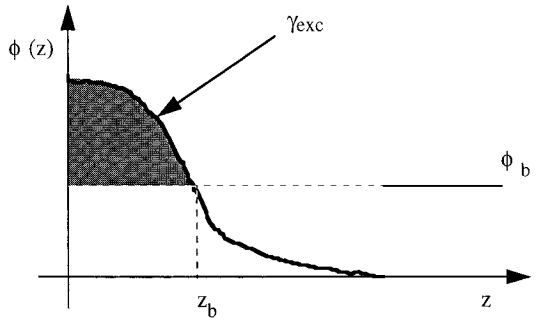

Figure 11. The surface excess γ_{exc} corresponds to the shadowed area.

change in composition. This is, a priori, not completely meaningless, since it is known that PDMS has a Θ temperature in styrene (monomer) around 30 °C. To check this, we put the same interfaces as above in a mixture of 70% of dichloromethane and 30% of styrene (monomer), using the same contrast matching condition. The result is shown on Figure 10. We plot the density profile for this mixture and, for comparison, $\phi(z)$ in pure dichloromethane. No difference can be found; the chains remain strongly stretched. Therefore, it is not because we simply replace three molecules of CH_2Cl_2 out of 10 by three molecules of styrene that the interfaces shrink. What we have observed and describe above can only be attributed to a polymer effect.

In the case of the PS brush, since the interfacial and the bulk chains are almost identical (omitting the H/D substitution), we can conclude that it is the increasing osmotic pressure of the reservoir solution which forces the interface to shrink. The effect of this osmotic stress is balanced by the elastic energy of the grafted chains. For the PDMS pseudo-brush, since the two polymers are incompatible, an additional entropic effect comes into play. Both the osmotic stress and the incompatibility act to give the same trend: they force the chains to shrink. However, the effect is far more spectacular than in the simple PS brush.

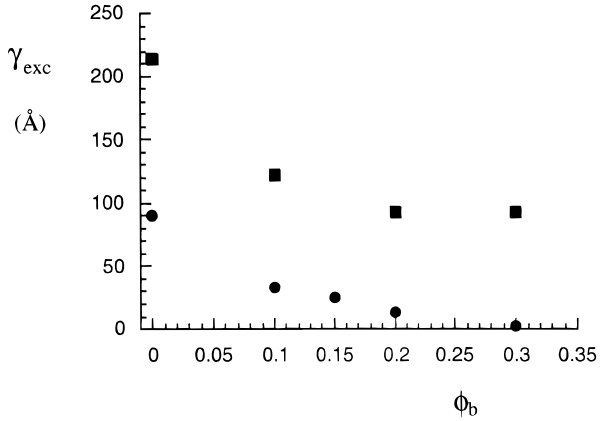

Figure 12. Variation of the surface excess γ_{exc} as a function of ϕ_b for the PDMS pseudobrush (■) and the PS brush (●).

How deeply are the different interfaces penetrated by the bulk polymer? We can now give a partial answer to this question. Let us call $\phi_{fc}(z)$ the local concentration of mobile chains at the distance z from the surface [$\phi_{fc}(z{=}\infty) = \phi_b$]. We first assume that the sum of $\phi(z)$ and $\phi_{fc}(z)$ must be at least equal to ϕ_b for all values of z. (This assumption is certainly valid since we do not have any sharp interfaces.) Thus, where $\phi(z) < \phi_b$, we have some mobile chains penetrating the interface. If we now compare $\phi(z)$ with ϕ_b, it is clear that as ϕ_b increases, the PS brush is penetrated more deeply by the free chains. The behavior of the PDMS pseudobrush is quite different. To illustrate this point, we define the surface excess, γ_{exc}, as follows:

$$\gamma_{exc} = \int_0^{z_b} [\phi(z) - \phi_b]\, dz \qquad (9)$$

where z_b is the root of the equation $\phi(z) = \phi_b$. γ_{exc} corresponds to the excess of polymer attached to the solid surface, as compared to the bulk (see Figure 11). We calculate γ_{exc} for the PS brush and the PDMS pseudobrush. This result as a function of ϕ_b is shown in Figure 12. For the PDMS pseudobrush, γ_{exc} does not go to zero as ϕ_b increases, in contrast with the PS brush. Further, it seems to level off at a finite value which is of the order of 43% of the total amount of adsorbed polymer γ_{PDMS}. If we calculate $\int_0^{z_b}\phi(z)\,dz$ for the PDMS pseudobrush, we obtain something that is never less than 80% of γ_{PDMS}. This is a strong argument which tends to prove that there is little interpenetration in the case of the PDMS pseudobrush. This should be attributed to the incompatibility of the two polymers. Indeed, with such a gently sloped interface we would have expected to see a weaker resistance to the penetration of the free chains. This should be easily verified if we use PDMS solutions instead of PS.[13] However, the fact that the chains do not like each other easily overcomes the entropy of mixing. Despite this effect, it should be noticed that there is always a tail at the outer edge of the interface, where free chains penetrate and mix with the attached polymers.

For the PS mushrooms, although we do not know the whole shape of the density profile, we can calculate the mean interfacial concentration $\bar{\phi}$ (refer to note 8). It is clear that the PS mushrooms are completely penetrated by the free chains, even at $\phi_b = 0.1$, because $\bar{\phi} \ll \phi_b$. $\bar{\phi}$ is almost insensitive to the presence of the bulk polymer. We can barely see an increase in $\bar{\phi}$. This loose interface offers a very weak resistance to the penetration of the mobile PS chains.

Conclusion

We have seen the influence of free polymer chains on a polymer interface in solutions with increasing concentration. For a brush of the same kind of polymer as the free chains, we have observed a shrinkage of the interface due to the increasing osmotic pressure. Nevertheless, at $\phi_b \approx 0.3$, we end up with an almost fully penetrated layer. For a pseudobrush made with a polymer that is incompatible with the free chains, while the interfacial profile is gently sloped in a pure solvent, the penetration seems to be much weaker. The shrinkage of the chains is spectacular and the density profile becomes relatively steep. This is due to the incompatibility between the two species. In the mushroom regime, almost no change is detected. Penetration occurs at nearly all concentrations of the polymer solution.

It would be interesting to extend this study. As we point out, the use of an H/D statistical PDMS copolymer would allow us to make a clear distinction between the effect of penetration on a brush and on a pseudobrush. Further, we could extend the range of variation of ϕ_b, since PDMS is never glassy. It would also be important to vary in a more systematic way the length, P, of the free chains. In this study, we have only two values for P: $P = 1$ and $P \approx N$, where N is the number of monomers of the attached chains. We have seen a clear difference, since at $P = 1$ no shrinkage is observed. However, the interesting question remains of what happens at intermediate values of P. This has been already considered by de Gennes,[2] and we are presently performing the experiments.

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References and Notes

(1) Kausch, H. H. *Polymer Fracture*, 2nd ed.; Springer-Verlag: Berlin, 1987.
(2) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(3) Jones, R. A. L.; Norton, L. J.; Shull, K. R.; Kramer, E. J.; Felcher, G. F.; Karim, A.; Fetters, L. J. *Macromolecules* **1992**, *25*, 2359. Budkowski, A.; Steiner, U.; Klein, J.; Fetters, L. J. *Europhys. Lett.* **1992**, *20*, 499.
(4) Auvray, L.; Auroy, P. In *Neutron, X-Ray, and Light Scattering*; Lindner, P., Zemb, Th., Eds.; Elsevier Science Publishers B.V.: Amsterdam, 1991; 199.
(5) (a) Auroy, P.; Mir, Y.; Auvray, L. *Phys. Rev. Lett.* **1992**, *69*, 93. (b) Auroy, P.; Auvray, L. *J. Phys. II* **1993**, *3*, 227. (c) Auvray, L.; Cruz, M.; Auroy, P. *J. Phys. II* **1992**, *2*, 1133.
(6) Auroy, P.; Auvray, L. *Langmuir* **1994**, *10*, 225.
(7) Since the dichloromethane solutions have a high Cl content, they adsorb neutrons more than the corresponding methanol solutions (62.2% of CD_3OD). However, their smaller incoherent scattering cross section reduces the multiple scattering. All of these effects are taken into account by the classical methods explained in ref 4.
(8) We cannot directly compare the data of the PS mushrooms with that from the other two interfaces. This is because the PS mushroom data were obtained from the Guinier regime (cf. eq 7), while L is calculated from $\phi(z)$ for the other two (dense) interfaces. Nevertheless, using the data obtained in the Guinier regime, we find that the thickness of the mushroom layer varies approximately linearly with ϕ_b. This leads to a linear variation of the mean interfacial concentration $\bar{\phi} = \gamma/L$ (γ is the amount of polymer per unit area) with ϕ_b. Experimentally, we find $\bar{\phi} = 0.042 + 0.046\phi_b$.
(9) Empirically, a parabolic profile modified by an exponential tail can always be fitted by a generalized error function, provided that the exponential tail is not important ($u > 0.7$, which is always the case in the present study, cf. eq 5). Under this condition, m varies between 1.2 and 2.1 for this particular type of profile.
(10) Zhulina, E. B.; Borisov, O. V.; Brombacher, L. *Macromolecules* **1991**, *24*, 4679.
(11) Guiselin, O. *Europhys. Lett.* **1992**, *17*, 223.
(12) P. Auroy, to be published.
(13) However, it is quite difficult (though not unfeasible) to synthesize a statistical H/D PDMS copolymer.

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