Building of a Grafted Layer. 1. Role of the Concentration of Free Polymers in the Reaction Bath

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ABSTRACT: Using small angle neutron scattering techniques, we have studied the formation of layers of poly(dimethylsiloxane) chains grafted on nonadsorbing silica. The grafting density is uniquely determined by the concentration of free polymers in the reaction bath c_b and it increases like $c_b^{7/8}$ provided that c_b is greater than the overlap threshold. When the grafted layers are immersed in pure solvents, they exhibit different conformations, driven by the solvent quality and the grafting density. In poor solvent, at wide spacing D, the chains spread on the silica surface, forming two-dimensional films. When D becomes smaller, the grafted layer becomes thicker and more regular. In good solvent, at large D, the chains form juxtaposed mushrooms, without interactions. Below a threshold D^*, they stretch themself, yielding polymer brushes. At very high grafting density, saturation of the stretching occurs, which could be due to curvature effect or to the finite extensibility of the chains.

Introduction

Changing the wettability of a glass surface, preventing pigment grains from aggregation, enhancing the reinforcement of a rubber by a mineral charge, ... may be achieved by grafting suitable molecules, which would modify the interfacial properties of the considered materials. In most of the industrial applications, short chains are used and numerous theoretical and experimental works have been devoted to the physicochemistry of the grafting of small molecules. One of the required features of these interfacial layers is to be sufficiently dense. Otherwise, the surface modifications induced by the grafted molecules might be not efficient. If holes appear in the layer, these defects may promote a chemical contamination[1] or they may be potential sites of bridging[2] (Figure 1). However, even if the grafting density is high, the interfacial properties induced by short grafted molecules are nonuniversal: for instance, in the case of colloidal suspensions,[3] the stability of a dispersion of grains protected by a thin grafted layer depends strongly on the nature of the grains, on their radius, on the dispersion medium (its polarity, surface tension, etc.), on the particle concentration, and also on the temperature. Actually, if the thickness of the interfacial layer is of the same order of magnitude as the range of the van der Waals interaction (10 nm, typically)—or of the electrostatic force—the net result for the interparticle potential is not easy to predict and may be strongly affected by a slight variation of the experimental conditions. Nevertheless, if the grafted chains are long enough, all these considerations become irrelevant and it has been recently observed[4] that the thermodynamic properties of a suspension of particles grafted with long polymers are determined by the interfacial layer, provide that it is dense enough.

But the main difficulty is now to reach a sufficiently high grafting density. Indeed, as soon as the chains overlap at the interface, they are forced to stretch perpendicularly to the surface[5] (Figure 2), which is energetically very unfavorable compared to the "free" situation for long polymer chains. Thus as the layer becomes denser and the chains more stretched, the difficulty of approaching the surface for free chains greatly increases. Therefore, the strategy for building a dense grafted layer has to overcome this steric hindrance and the anchoring must be tight enough to balance the stretching energy.

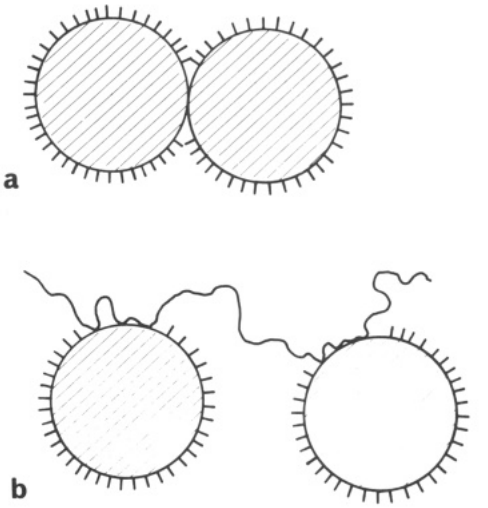

Figure 1. Bridging between unperfectly protected particles (a) directly via uncovered spots and (b) via adsorbing polymers.

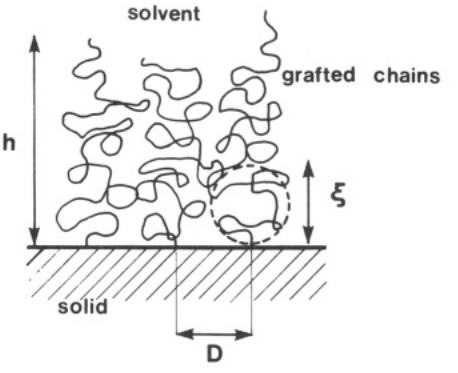

Figure 2. Polymer brush. Note that $h \gg D$ and $\xi \approx D$.

Schematically, two basic ways of building a grafted layer can be distinguished: the first[6] involves a polymerization, starting from initiators attached to the surface, and the second polymers with particular end groups (specially synthetized), which are used as anchors onto the surface. The

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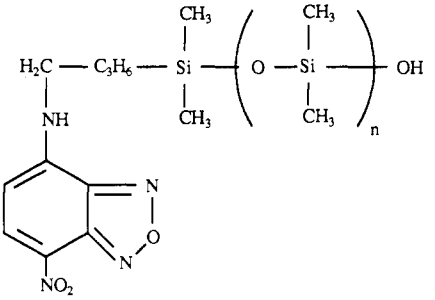

Figure 3. End-functionalized PDMS. The end/group strongly adsorbs on silica, yielding physigrafted layers.

former will be not discussed there. The latter itself could be subdivided in two, depending on the type of anchoring, which can by physical or chemical. For instance, one of us[7] has obtained grafted layers with poly(dimethylsiloxane) chains whose ends carried polar groups (Figure 3) that have a great affinity for the silica surface. In an earlier and more extensive study,[8] polystyrene chains have been used, one of whose extremities was a zwitterionic group that adsorbs strongly on mica sheets. However, as pointed our recently,[9] not many parameters can influence the building of these "physigrafted" layers. Furthermore, it is not clear if these interfacial layers have reached their equilibrium conformation after finite time and slow rearrangement processes could be very important. A last example of physical grafting is provided by block copolymers, one part of which strongly adsorbs on the substrate while the other moiety is repelled and plays the role of a buoy. These block copolymers are widely used in industrial applications and also in fundamental studies.[10] By comparison with the previous example, they provide more facilities, since the strength of the bonding may be adjusted by changing the length of the anchor moiety. However, using theoretical arguments, it can be shown[11,12] that, even in this case, the grafting density is practically limited (and is not very high for long polymers). Moreover, the variation of the grafting density σ is dependent on very delicate syntheses, since each value of σ corresponds to one particular block copolymer. It may be also noticed that up to now there is almost no kinetic control of the building of these physigrafted layers. And last, the use of these physically grafted molecules is restricted to dilute solutions, since above a critical concentration, they form micelles that impose the chemical potential and dominate every other phenomenon.[12]

The chemical grafting precludes most of these inconveniences thanks to the strength of the single bond, which may be of several 100 kT. Therefore, the range in which the grafting density may vary (at fixed molecular weight) is very wide, allowing a precise investigation of the influence of σ either on the structures of the grafted layers or on the stabilization properties. But the grafting density is not a priori the single parameter that could be determinant. The surface attractivity, the length of the polymer, the concentration of the reaction bath, ... might play also an important role. These are some of the parameters whose influence has been determined. We have used, for this purpose, porous silica as substrate and poly(dimethylsiloxane) chains with reactive end groups. This system was particularly convenient for our study for many reasons. The polymer is very flexible, with a low T_g, which provides favorable conditions for obtaining high grafting densities and for rearrangement processes. What is perhaps more important is that the substrate avoids any problems of stability that occur systematically with colloidal suspensions. The stability requirement is actually very restrictive, making the grafting on colloidal particles specific and fraught with difficulty. With porous media, all physicochemical conditions of grafting (and of observation) are available, allowing a wide investigation of their influence and the optimization of the building of grafted layers. These results have allowed us to extend our know-how to colloidal particles and to prepare model hairly grains.[4]

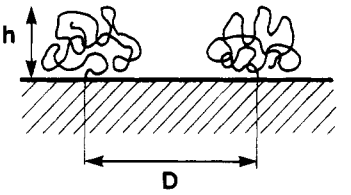

Figure 4. Mushroom structure (in good solvent). Note that $h < D$.

In this paper, we will focus on the role of the polymer concentration in the reaction bath c_b, which has been revealed as the most important parameter for the building of grafted layers, determining to a great extend their structures. In an earlier paper,[13] we have shown that, in the so-called moderate density regime,[14] the grafted chains form a brush (cf. Figure 2). This regime is characterized by scaling laws, which involve σ, the thickness of the layer h, and the molecular weight of the polymer M_w. We have observed that $h \approx M_w\sigma$ in poor solvent and $h \approx M_w\sigma^{1/3}$ in good solvent, or if we express σ as $\sigma = (a/D)^2$ where D is the average distance between grafting sites (a is a molecular size) $hD^2 \approx M_w$ in poor solvent and $hD^{2/3} \approx M_w$ in good solvent. These laws tell us that, in the brush regime, the thickness of the layer, at fixed molecular weight and solvent condition, is imposed by the grafting density. We have also proved[15] that the local structures of these interfacial layers are similar to that of a semidilute polymer solution. They are characterized by a screening length ξ, which is experimentally close to D. This result is in agreement with the theoretical description of Alexander.[5] Moreover, ξ can be related to a local concentration, which has been found equal to the polymer concentration c_b of the solution in which the grafting reaction has been performed (c_b was typically 0.15).

Furthermore, we have also obtained a few data concerning the so-called mushrooms regime[16,18] (Figure 4). The samples were characterized by a very small amount of grafted polymer per unit area. It has been found also that the chains extend up to a distance comparable to their radius of gyration and would exhibit concentration fluctuations analogous to those of dilute polymers solutions. But more important for our purpose is that the concentration c_b at which these latter samples have been prepared was very low, typically 0.05%.

Therefore, it turns out that c_b has a great influence on the structures of the grafted layers. To confirm further this result, we have extended our investigations to a broader c_b range. The key experiment of this paper is the following: we have prepared six samples under identical conditions (same polymer, same silica, same time or temperature of reaction), except that c_b has been changed. It ranged between 0.05 and 100%. These samples were then characterized by small-angle neutron scattering (SANS) experiments.

In section I, the preparation of the samples will be described in more detail and the basic tools for interpreting the results of scattering experiments will be briefly reviewed. In section II, we will focus on the fundamental result: the grafting density σ (or equivalently the amount of grafted polymer per unit area Γ) is imposed by c_b. In

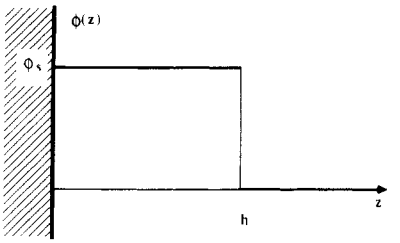

Figure 5. Step function model. For $z \leq h$, $\phi(z) = \phi_s$. For $z > h$, $\phi(z) = 0$.

the last two sections, the influence of σ on the structures on the grafted layers will be discussed, when they are immersed either in poor (part III) or in good solvent (part IV).

I. Experimental Section

I.1. Samples Preparation. The system we have used and the grafting procedure have been described in earlier papers[13,15] in great detail. We recall only that the substrate was porous silica (designed for liquid chromatography), with a diameter of pores equal to 4000 Å (or equivalently with a specific surface of 2.5 m^2/cm^3). The surface of this silica is flat and well defined—at least on the scale 10–300 Å. This silica naturally adsorbs strongly PDMS through hydrogen bonding between surface silanol groups and oxygen atoms of the siloxane backbone.[17] In order to avoid this undesirable phenomenon, the surface of the silica has been modified prior the grafting reaction thanks to an esterification with pentanol. This latter reaction has been performed for 24 h. After this treatment, about 3 chains of OC_5H_{11}/nm^2 have been grafted (estimation by SANS). If we assume that there are on the bare silica surface 5 OH/nm^2, this means that about 60% of these hydroxyl groups have been converted in alkyl chains, which is in agreement with the maximal value one can find in ref 1. It has been checked that this esterification prevent any adsorption of PDMS.[18]

The polymer that has been grafted was poly(dimethylsiloxane) or narrow molecular weight distribution (M_w = 145 000; polydispersity, 1.09). The chain was terminated by an OH group at both extremities. It is assumed that only one end per grafted chain has reacted. This has been proved[7] in the moderate-density regime (for $c3b \approx 0.15$) by comparison with monofunctional polymers. For higher grafting density, it is reasonable to consider this assumption still true. For weak density, it may fail. But this would not affect our conclusions.

We have prepared six samples at six different concentrations of polymer: $c_b = 5 \times 10^{-4}$, 5×10^{-3}, 5×10^{-2}, 1.5×10^{-1}, 5×10^{-1}, and 1 (volume fraction). Except for $c_b = 1$, the polymer was in solution in heptane. For every sample, the amount of silica that was introduced as 0.4 g, which corresponds to 2.3 m^2. The grafting reaction has been performed at 100 °C for 72 h in sealed flasks, which were periodically agitated. After reaction, the silica has been rinsed at least seven times by a great volume of dichloromethane, waiting for 24 h between each washing. It has been checked that this procedure ensures that no free chains remain.

I.2. SANS Experiments. The SANS theory, the experimental procedures, and the analysis of the data have been described in great detail.[15] For the purpose of this paper, we need only to recall a few basic points.

By using a suitable isotopic mixture of fully hydrogenated–fully deuteriated solvent, it is possible to match the "neutral refractive index" of the silica. Under that condition, the scattering intensity comes only from the grafted layer. (Actually, since the contrast matching is never perfect, we have substracted the residual contribution of the solid, which has been recorded in a separate experiment.) The six samples were characterized following the same procedure, under contrast-matching condition, in two different solvents: acetone (poor solvent of PDMS) and dichloromethane (good solvent).

As explained in ref 15, instead of inverting the data, we prefer to analyze directly the spectra in the reciprocal space (as they were obtained). For that purpose, we use a step function model (Figure 5) for the interfacial density profile $\phi(z)$, which is not an a priori assumption for the shape of $\phi(z)$ but rather provides a useful tool for comparing the data. The scattering intensity of this step is, at contrast matching

$$I(q) = 2\pi\frac{S}{V}(n_p - n_s)^2 q^{-4} 2(1 - \cos qh)\phi_s^2 \quad (1)$$

where q is the scattering vector, S/V the specific surface, n_p (n_s) the scattering length density of the polymer (solvent), h the thickness of the layer (cf. Figure 5), and ϕ_s the fraction of the surface occupied by the polymer. (1) could be rewritten as

$$q^4 I(q) = 2\pi\frac{S}{V}(n_p - n_s)^2 2(1 - \cos qh)\phi_s^2 \quad (2)$$

which is a purely oscillating term. A Taylor expansion of (1) leads to

$$q^2 I(q) = 2\pi\frac{S}{V}(n_p - n_s)^2 \gamma^2\left[1 - \frac{q^2h^2}{12}\right] \quad (3)$$

for very small q, where $\gamma = \int_0^h \phi(z)\,dz$ (in Å). We point out that γ is determined independently of any model for $\phi(z)$. γ can be easily converted into the amount of polymer per unit area Γ (in mg/m^2): $\Gamma = 0.1\gamma d$, where d is the density of the polymer (in g/cm^3). $d \approx 0.98$ g/cm^3 for PDMS. Knowing the molecular weight of the polymer M_w, one can deduce from Γ the average distance between grafting sites D and the grafting density σ as follows

$$D = \left(\frac{6.023\Gamma}{M_w}\right)^{-1/2} \text{Å} \quad \text{and} \quad \sigma = (a/D)^2 = a^2\frac{6.023\Gamma}{M_w}$$

a is a monomer size. In our analysis, we have arbitrarily used a = 2.1 Å, according to our previous studies.[13,15]

Therefore, two plots are definitively useful: $q^4I(q)$ versus q, which emphasizes the possible discontinuities of the density profile—the solid–polymer and the polymer–solvent boundaries—and $q^2I(q)$ versus q^2, which allows the determination of two basic parameters: Γ and h.

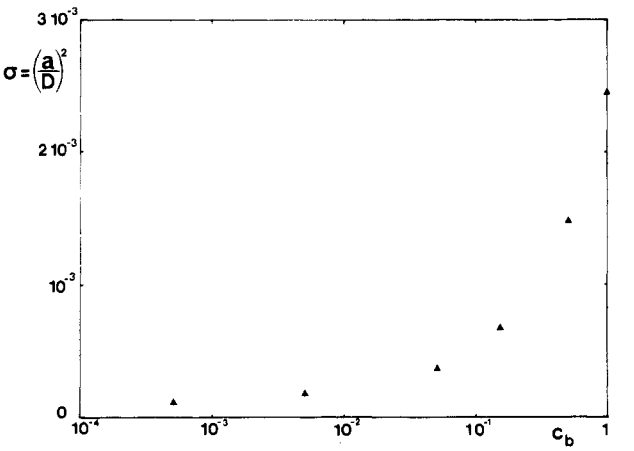

Figure 6. Semilog plot of the grafting density versus c_b.

II. Relation between σ and c_b

II.1. Results. On Figure 6, we have reported the grafting density versus c_b in a semilog plot. (All the data of this article are listed in Table I.) Before trying to interpret this curve, one has to answer to the fundamental question: are those samples at equilibrium? Or, in other words, are the grafted layers, in the chosen experimental conditions, saturated? We have performed a few kinetics experiments[19] on grafted layers in the moderate-density regime (c_b = 0.15). We have observed that when the polymer does not adsorb onto the silica surface, the layers are saturated after a typical time of 2 h. For the most dilute grafted layers, although we have not made systematical studies, we have several data that lead to the same conclusion. Therefore, for the four samples obtained at $c_b \leq 0.15$, we believe that the grafted layers are saturated.

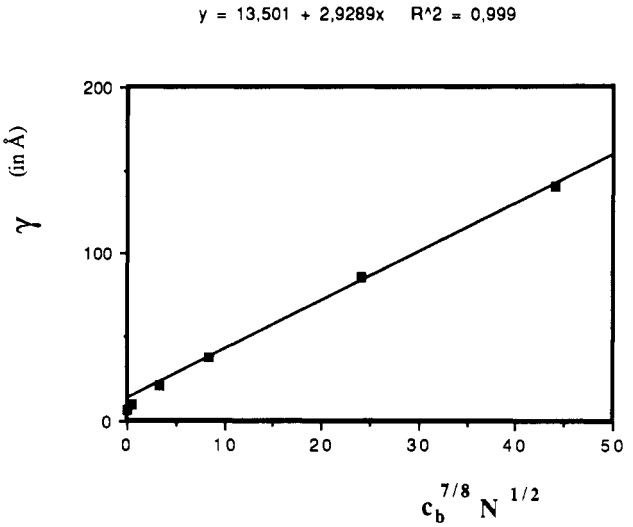

Figure 7. Plot of γ (in Å) versus $c_b^{7/8}N^{1/2}$.

Table I
Values of the Different Parameters of This Paper

					h, Å	
c_b	Γ, mg/m²	D, Å	$N^{1/2}c_b^{7/8}$	γ, Å	acetone	dichloro
5×10^{-4}	0.69	187	0.06	7.05	40	240
5×10^{-3}	1.00	155	0.4	10.2	47	251
5×10^{-2}	2.13	106	3.2	21.73	64	246
1.5×10^{-1}	3.73	80	8.37	38.06	87	279
5×10^{-1}	8.43	53	23.99	86.02	143	921
1	13.84	42	44	141.22	228	1037

For the two most concentrated samples, we can only assume this. However, we point out that the condition of no adsorption ensures fast grafting reaction kinetics, compared to the case when adsorption occurs.[18] The pure grafting process seems not to be limited by diffusion and rearrangement phenomena. Therefore, the 3 days that the layers have been allowed to build make the assumption of equilibrium reasonable for every sample. However, we cannot rule out any long-time process such as a logarithmic increase of σ.[9]

Figure 6 shows that there is a unique relation between σ and c_b. $\sigma(c_b)$ is a strictly increasing function. This is the basic result of our experiment.

II.2. Discussion. We can go further in the interpretation of the relationship $\sigma(c_b)$. In Figure 8, we have plotted γ (in Å) versus $c_b^{7/8}N^{1/2}$. (The factor $N^{1/2}$ is constant in this experiment but it will make the interpretation easier.) We obtain a nice straight line, well fitted linearly for the four most dense layers:

$$\gamma = 2.93c_b^{7/8}N^{1/2} + 13.5 \quad (4)$$

The slope of this fit (2.93 Å) is again of the same order of magnitude as a monomer size. For the two most dilute layers, the agreement is not so good.

This dependence of γ with c_b can be understood with simple arguments, suggested by de Gennes[16] and by Marques in another context.[20] When the reaction is started at $t = 0$, the chains are homogeneously distributed in the semidilute solution, their radius of gyration being $R_F(c_b) \approx aN^{1/2}c_b^{-1/8}$. None of them are grafted: $\sigma(t = 0) = 0$. At $t \approx \tau$, the grafting process has gone to completion; the solution is still homogeneous because of the osmotic pressure imposed by the free chains. However, all the chains in the vicinity of the solid surface have been grafted; therefore, all the monomers in a layer of thickness $R_F(c_b)$ close to the surface are irreversibly attached to the surface (Figure 8) and the amount of grafted polymer per unit

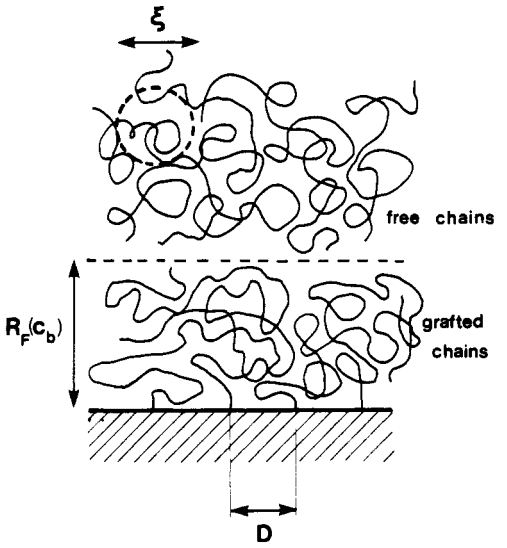

Figure 8. Final stage of the grafting process. All the chains in a layer of thickness $R_F(c_b)$ close to the surface have been irreversibly grafted. Free and grafted chains are strongly segregated.

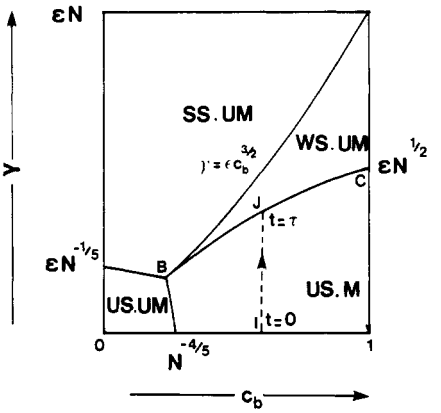

Figure 9. Phase diagram of grafted chains facing solutions of free polymers of the same length (cf. ref 16). WS = weakly stretched; SS = strongly stretched; US = unstretched; M = mixed; UM = unmixed. Dashed line: grafting process as a function of time t. (Start at point $I - t = 0$, end at point $J - t = \tau$.) Line BC: $\gamma = \epsilon c_b^{7/8}N^{1/2}$. ϵ has the dimensions of length.

area is equal to $c_bR_F(c_b) \approx ac_b^{7/8}N^{1/2}$. Using the "phase diagram" proposed by de Gennes[16] (Figure 9), the grafting process would be described by the dashed line. At $t = 0$, $\gamma(t=0) = 0$. At $t \approx \tau$, the grafted chains and the free polymers are segregated: the grafting process is effectively finished. Nevertheless, at this point, the grafted chains are either weakly stretched or unstretched. We point out that in this scheme, the end of the building would not correspond to a true equilibrium but rather to a very slow (logarithmic) stage of the process,[21] which would be unobservable experimentally.

Our analysis is consistent only if we assume that there are always a large fraction of free reactive sites on the surface. We have seen that the chemical pretreatment converts about 60% of the silanol groups into $SiOC_5H_{11}$. Therefore, assuming an initial density of 5 OH/nm², the surface area per OH group before the grafting reaction is 50 Å², which is much smaller than the smallest area per grafted chain (1740 Å²). Therefore, less than 3% of the available reactive surface groups are involved in the grafting reaction.

Moreover, it is important to check that the volume fraction of the free chains remains constant during the whole grafting process. Indeed, this is true as indicated

Table II
Ratio ρ between the Amount of Polymer That Has Been Grafted and the Total Amount of PDMS Introduced in the Reaction Flask

c_b	ρ, %	c_b	ρ, %
5×10^{-4}	30	1.5×10^{-1}	2.3
5×10^{-3}	7	5×10^{-1}	1.5
5×10^{-2}	2.5	1	1.6

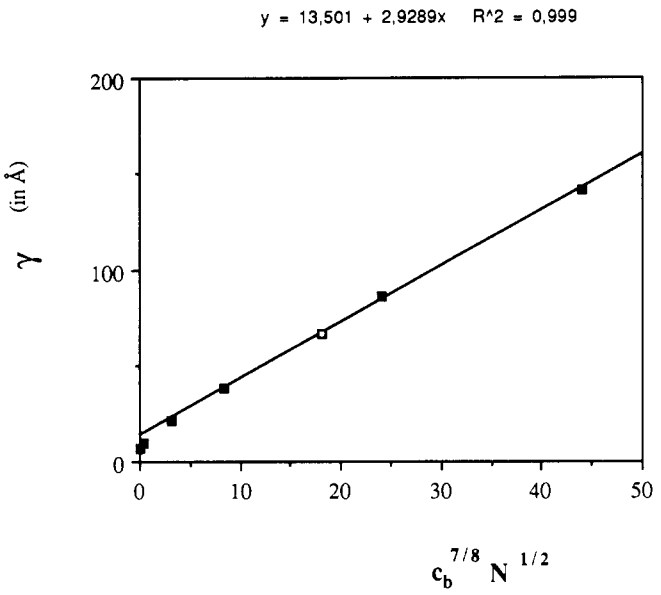

Figure 10. Influence of the molecular weight. Plot of γ (in Å) versus $c_b^{7/8}N^{1/2}$. ■: same as for Figure 7. □: $M_w = 24\,400$, $c_b = 1$, $\gamma = 66.2$.

by Table II, where we have reported the amount of grafted polymer compared to the total amount of PDMS introduced in the reaction bath. We also point out that the two samples obtained at very low concentration may be included to our scheme: they correspond to nonoverlapping coils ($c_b \leq c^*_b \approx N^{-4/5}$; region US. UM of Figure 9).

II.3. Consequences. It would be very interesting to investigate the influence of the molecular weight of the chains on the relationship $\gamma(N,c_b)$. In Figure 10, we have added to the previous data the result (□) obtained with a polymer of lower molecular weight, grafted on an identical surface at $c_b = 1$ ($M_w = 24\,400$, $p = 1.09$, $\gamma = 66.2$). The agreement with the previous experiment is remarkable. However, more systematic investigations are necessary, and it would be especially interesting to extend our observations to the grafting of chains of length N immersed in a semidilute solution of chains of length P ($N^{1/2} < P < N$) since theoretical predictions[16] tell us that γ would scale as $NP^{-1/2}c_b^{7/8} \gg c_b^{7/8}N^{1/2}$. This is currently in progress.

The relationship (4) implies a dependence of D on c_b and also on N. Neglecting the constant term in (4), we have

$$D = a' c_b^{-7/16} N^{1/4}$$

and therefore, in good solvent, following the picture of Alexander,[5] if we note ϕ, the average volume fraction inside the layer, we obtain

$$\phi = \chi c_b^{7/12} N^{-1/3} \quad (5)$$

where χ is a numerical coefficient (actually, greater than 1). Therefore, there is no naive correspondence between c_b and ϕ and ϕ is a weakly decreasing function of N. The fact that we have found in a previous study[15] $\phi \approx c_b$ would be somewhat fortuitous and result from numerical compensations in eq 5. Theoretically, taking $\chi = 1$, we have

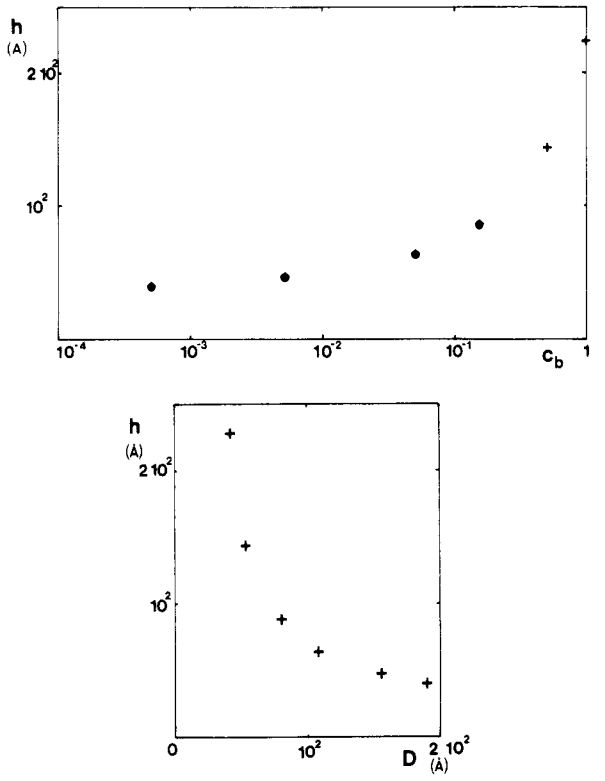

Figure 11. Variation of the thickness h of the layers immersed in acetone (poor solvent) versus c_b (a, top) or D (b, bottom).

$\phi = c_b^{7/12}N^{-1/3} < c_b$, since the grafted layer has been built in a semidilute solution for which $c_b > N^{-4/5}$.

III. Influence of σ on the Structures in Poor Solvent

First, we remind the reader that the values of the thicknesses are deduced from the spectra in the very low q range using a step model for the interfacial density profile. This is a crude assumption but it is useful for comparing the different samples. The validity of this model will be discussed in due course.

III.1. High-σ Regime. In Figure 11, the thickness h of the six samples, immersed in acetone, has been plotted versus c_b (Figure 11a) or equivalently versus D (Figure 11b). (The data are listed in Table I.) h is a strictly increasing function of c_b, all the more strongly if c_b is greater. Comparing h to D, one can see that for $c_b < 0.05$, $D \geq 2h$ and the chains would not overlap, while, for $c_b \geq 0.05$, the mutual interactions become important and would force ultimately the polymers to stretch themself perpendicularly to the surface.

This seems to be confirmed by Figure 12, for which we have used the plot hD^2 versus c_b suggested by our previous studies.[13] At c_b sufficiently high (or D sufficiently small), hD^2 is constant: we recover the brush regime. Contrary to earlier results, the sample obtained at $c_b \approx 0.15$ seems to be a little bit out of this regime. This is probably the influence of the strong surface modification before the grafting, which tends to diminish the grafting density. From the level of the horizontal regime ($hD^2 \approx 4.1 \times 10^5$), one can obtain an estimation of the average density of the interface: $\Phi^* = 0.6$, which is comparable to the ratio $\Phi = \gamma/h$ computed separately for each sample (Figure 13) and to the mean concentration for bulk PDMS saturated with acetone. (We have measured 0.66.) The property $hD^2 \approx$ constant expresses that the monomers form a close packing in the interfacial layer, whose compacity is fixed by the solvent–polymer interaction.

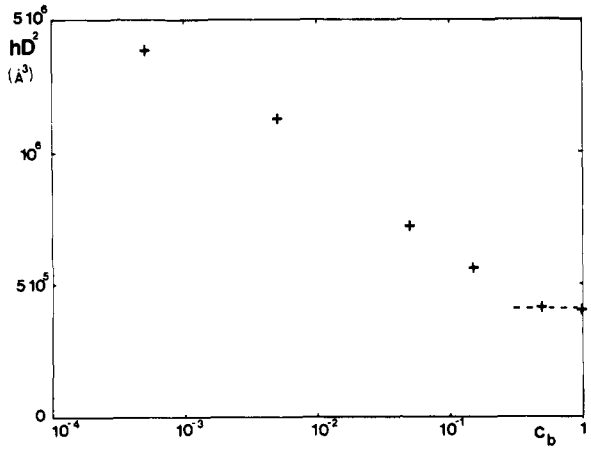

Figure 12. Plot of hD^2 versus c_b, in acetone. Dashed line: brush regime, $hD^2 \approx$ constant.

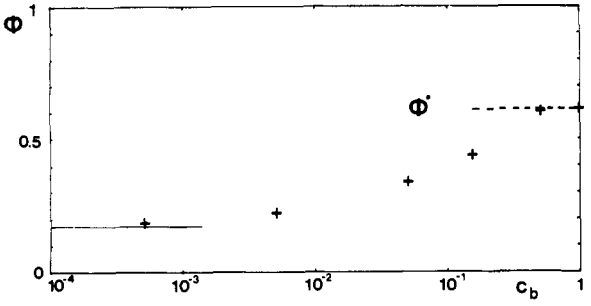

Figure 13. Plot of $\gamma/h = \Phi$ versus c_b. Dashed line: brush regime, $\Phi \approx 0.6$.

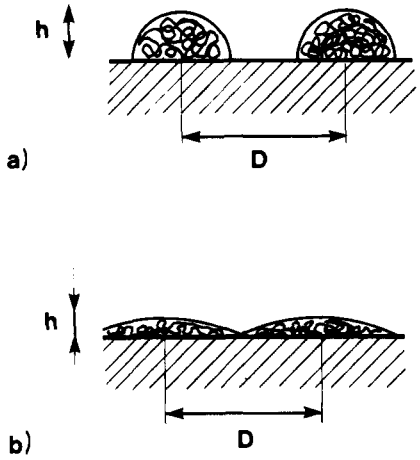

Figure 14. Conformations at wide spacing: (a) hemispherses; (b) juxtaposed spherical cuts.

III.2. Low-σ Regime. From Figure 13, one can also obtain information about the low-density regime for which $D > 2h$ and the chains do not overlap. If one assumes that they form small homogeneous hemispheres, widely spaced (Figure 14a), one obtains for the average density profile, $\Phi(z)$, normal to the surface

$$\Phi(z) = 4\pi\frac{h^2 - z^2}{D^2}\Phi^*$$

with $\Phi^* = 0.6$ as seen above. One can then compute the average density

$$\Phi = \frac{8\pi}{3}\left(\frac{h}{D}\right)^2\Phi^*$$

which does not agree with the curves of Figures 13 and 15.

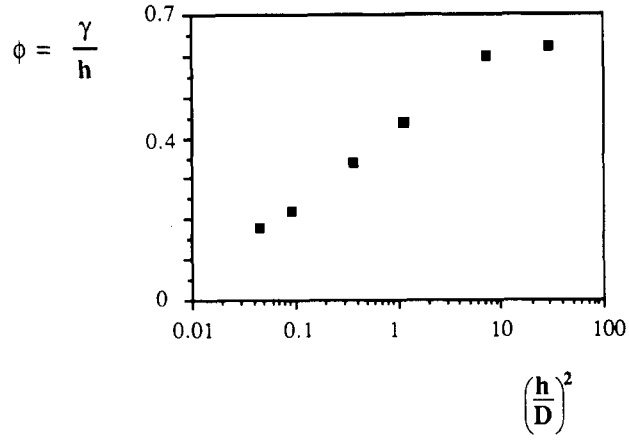

Figure 15. Plot of $\gamma/h = \Phi$ versus $(h/D)^2$.

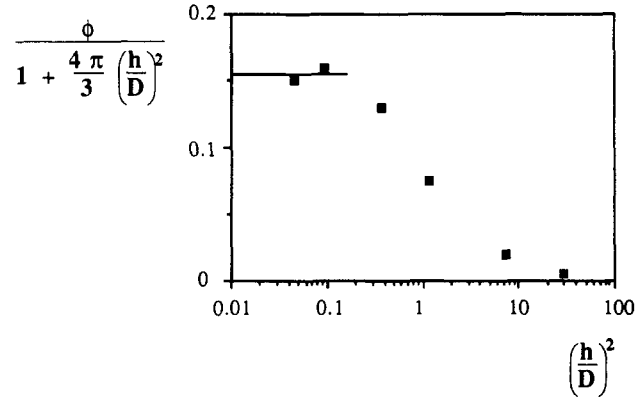

Figure 16. Plot of $\Phi/[1 + (4\pi/3)(h/D)^2]$ versus $(h/D)^2$.

One can make another hypothesis for the conformation of the chains in the low-density regime: one can assume that they form juxtaposed spherical cuts (Figure 14b). One gets, taking $D^2 = 4\pi\delta^2$

$$\Phi(z) = \frac{4\pi}{D^2}\left(\delta^2 - z\frac{(\delta^2 - h^2)}{h} - z^2\right)\Phi^* \qquad (5)$$

and for Φ

$$\Phi = \frac{\Phi^*}{2}\left(1 + \frac{4\pi}{3}\left(\frac{h}{D}\right)^2\right) \qquad (6)$$

(6) agrees well, at least qualitatively, with our data (see Figure 16) but the asymptotic value at very wide spacing is lower than $\Phi^*/2$. This may be due to our crude initial model for $\Phi(z)$, which was a step and which has allowed us to determine h. (But it did not give D, because it is independent of any model.) We should have to work out h from the spectra self-consistently, assuming for $\Phi(z)$ the polynomial form (5). This can be done only numerically, but it is easy to compute the "first-order" modification: the "exact" thickness would be greater than that obtained with the step model by a factor of $(3/2^{1/2} \approx 1.225$, which would not modify greatly Figure 16 in the wide spacing domain. Therefore, this is not sufficient to account for the discrepancy between the horizontal level at wide spacing and $\Phi^*/2$. Another possible explanation would be that, in thin layers, the equilibrium value of the polymer concentration would be lower than in bulk and actually, from our data, this would be $0.3\Phi^*$. This is very similar to what is usually observed with thin wetting films.[22]

Therefore, it turns out that the PDMS chains tend to spread on the silica surface at wide spacing, forming $2d$ films. This can be understood in terms of interfacial tension: the surface tension of the modified silica surface

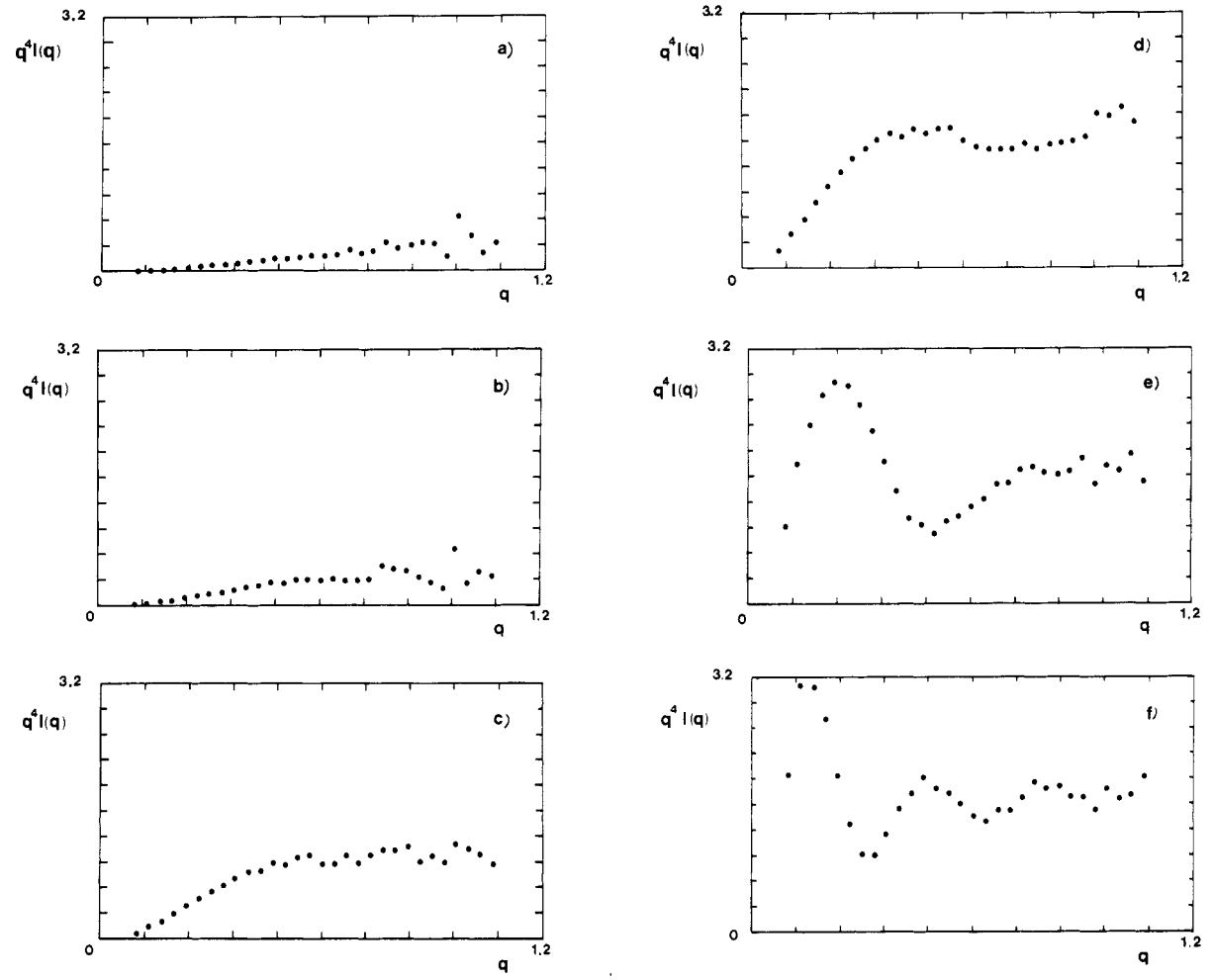

Figure 17. Scattering intensity of the six samples in acetone under contrast-matching conditions as $q^4I(q)$ versus q. The same scale has been used. Units: horizontal axis, 10^{-1} Å^{-1}; vertical axis, 10^{-6} Å^{-4} cm^{-1}. (a) $c_b = 0.05\%$; (b) $c_b = 0.5\%$; (c) $c_b = 5\%$; (d) $c_b = 15\%$; (e) $c_b = 50\%$; (f) $c_b = 100\%$.

(in the presence of acetone) would be greater than that of PDMS. A confirmation would be to use another surface pretreatment, which would prevent the silica to be wet by PDMS (in presence of acetone). We would then obtain an interfacial layer as described in Figure 11a rather than that in Figure 11b.

III.3. Detailed Characterization. We have reported in Figure 17 the spectra of the scattering intensity for the six samples, plotted as $q^4I(q)$ versus q, keeping the same scales in order to compare them with each other.

Clearly, the level of the horizontal asymptote at high q increases with c_b. This is not surprising since it is proportional to Φ_s^2 (see eq 3) and corroborates our previous observations. For the two most concentrated samples, this horizontal asymptote is at the same level, from which one obtains $\Phi_s \approx 0.68$, very close to the $\Phi = \gamma/h$ values derived above.

One can observe also that, for $c_b \geq 0.15$, oscillations appear, indicating that the interface becomes more and more well-defined. The threshold $c_b \geq 0.15$ for oscillations coincides roughly with $2h \geq D$. The periodicity of the oscillations decreases as c_b increases, which is related to increasing thicknesses. The values of h deduced from the position of the arches are very close to those obtained from the very low q domain. Thus, it turns out that the interface obtained at high c_b is well described by a step model (for which $\Phi_s = \Phi = \Phi^*$). At low c_b (or wide spacing), the oscillations are fully dampened, which is the counterpart of a "smoother" interface with a fluctuating thickness, in agreement with our spherical cut model.

Therefore, our observations are strikingly consistent. In poor solvent, at low grafting density, the chains have a flat conformation, spreading onto the surface. As the spacing between anchor points becomes sharper, the thickness of the interface increases, owing to mutual interchain interactions. At high grafting density, the layer is homogeneous, of well-defined thickness and consistently described by a step model. This scheme can be illustrated by Figure 18. It can be noticed that our results are, at least qualitatively, in agreement with theoretical calculations[23] of the effects of σ on the structures of grafted layers.

IV. Influence of σ on the Structures in Good Solvent

In this section, the same six samples as before have imbibed dichloromethane, which is a good solvent for PDMS, and their scattering intensity has been recorded under contrast-matching conditions.

On Figure 19, we have reported h versus c_b (Figure 19a) or versus D (Figure 19b). The difference from the results obtained in acetone is striking (compare with Figure 11). For $c_t \leq 0.05$, h is remarkably constant (we note h_0 is the thickness at low grafting density), as the spacing varies considerably but remains smaller than h. The value of $h_0 \approx 240$ Å is comparable to the radius of gyration that the same free polymer would have in dilute solution in dichloromethane. The $R_F(M_w)$ law is not precisely known in CH_2Cl_2, but in toluene we would have $R_F \approx 135$ Å.[24] Since dichloromethane is a better solvent than toluene, we should

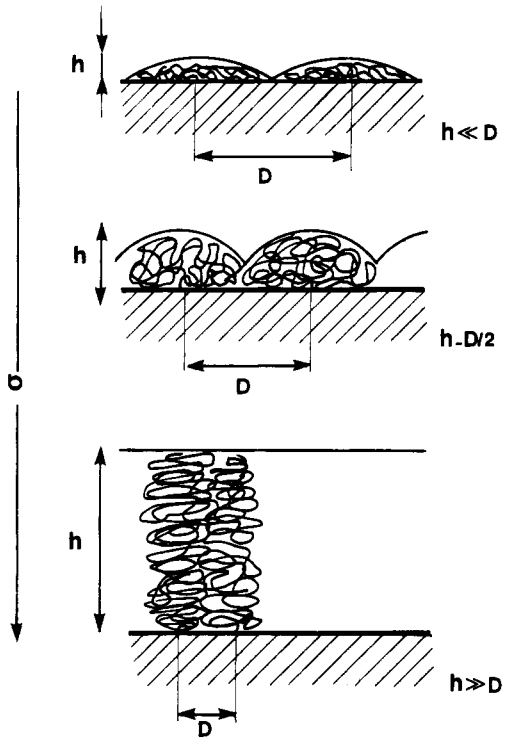

Figure 18. Scheme of the conformations of the grafted chains in poor solvent at different spacings between anchor sites.

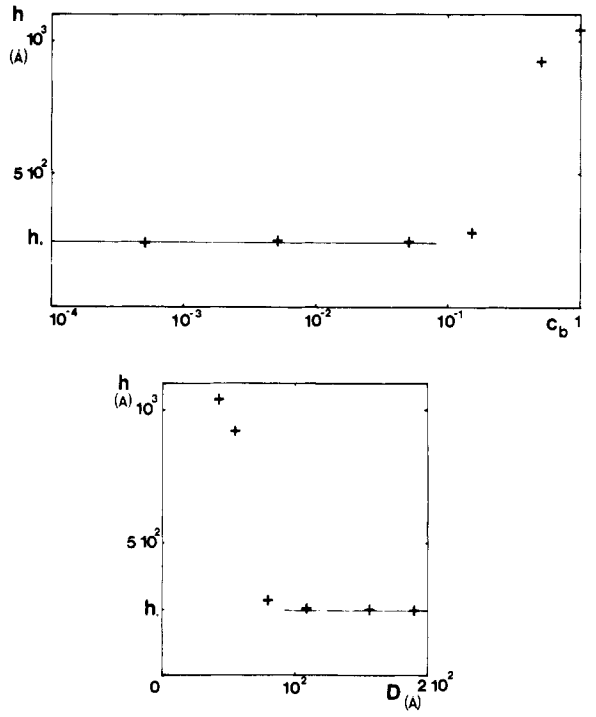

Figure 19. Variation of the thickness h of the layers immersed in dichloromethane (good solvent) versus c_b (a, top) or D (b, bottom). Solid line: mushrooms regime.

obtain a value a little bit greater.

The fact that at low-density grafting the layer has a constant thickness, which is comparable to the radius of gyration of free chains, could be interpreted by using the "mushroom" structure (see Figure 4). However, we have also observed that $h > D$ in this regime, which is in contradiction to this picture. Actually, just as the cross over between dilute and semidilute solutions is usually soft and occurs at greater concentration than the theoretical prediction $N^{-4/5}$, in our experiments, it seems that the mutual interchain interactions become important in dichloromethane for a spacing D^* smaller than h_0. One would have $h_0/2 < D^* < h_0/3$.

When $D < D^*$ (or $c_b > c^*_b = 0.05$), the mutual interactions force the chains to stretch themselves perpendicularly to the surface. However, there is a difference with the results obtained in acetone, at small D: when c_b is very high (0.5 or 1), h increases much slower than for moderate concentrations. This can be due to the finite extensibility of the chains[23] (for $c_b = 1$, their extension is greater than a fourth of the geometrical length of a rod of same molecular weight) or to the size of the pores, which could also limit the stretching of the chains. It can be noticed that the sample $c_b = 0.15$ belongs to the brush regime, in agreement with our previous study.[25] However, to interpret further the curve h versus c_b, more data are required.

Unfortunately, we cannot discuss the whole shape of the scattering intensity spectra, as we have done for acetone, because we have not made the contrast-variation experiments, which are actually the only way to get informations about the density profile in good solvent.[15] These complementary details will be derived from further experiments.

Conclusion

We have shown that the grafting density is uniquely determined by the concentration of free polymer in the reaction bath c_b. The building of a grafted layer ends when all the chains in the vicinity of the surface have been grafted, which leads to the increase of the amount of grafted polymer per unit area γ with c_b: $\gamma \approx c_b^{7/8} N^{1/2}$.

When the grafted layers are immersed in pure solvents, they exhibit different conformations and structures, which depend mainly on the grafting density. In poor solvent, at wide spacing, we have observed that PDMS forms very thin films, spreading on the silica surface, and when the spacing is sharper the interface becomes thicker and more regular. In good solvent, at wide spacing, the polymers are juxtaposed, swollen by the solvent but without noticeable interactions. When the spacing becomes smaller than a threshold value D^*, the chains stretch themself, forming brushes. But at very high grafting density, saturation of the stretching occurs and other effects have to be taken into account.

These results are in good agreement with a quite different work,[4] in which the effects of grafted polymers on the dispersion properties of colloidal particles were investigated.

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