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## Classification

Physics Abstracts

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## Irreversible adsorption from concentrated polymer solutions

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**Résumé.** — Nous étudions l'adsorption de solutions concentrées de Poly(diméthylsiloxane) (PDMS) dans le chlorure de méthylène sur de la silice poreuse. Nous varions le degré de polymérisation  $N$  et la fraction volumique  $\Phi$  des chaînes depuis la concentration de recouvrement jusqu'au fondu. L'adsorption du PDMS sur la silice par liaison hydrogène est très forte et une grande quantité de polymère reste liée à la surface après lavage de la silice par du bon solvant. Nous mesurons cette quantité  $\Gamma$  par diffusion centrale des neutrons. S'il n'y a pas eu désorption des chaînes,  $\Gamma$  représente le poids de polymère attaché au solide dans la solution initiale qui varie selon une prédiction récente comme le produit  $N^{1/2} \Phi^{7/8}$ . Cette relation de proportionnalité rend effectivement compte de nos résultats. Quand la taille des chaînes est du même ordre de grandeur que le diamètre des pores (qui prend les valeurs 500, 1 200 et 3 000 Å selon les échantillons), nous observons des effets de confinement abaissant la quantité adsorbée.

**Abstract.** — We study the adsorption of concentrated Poly(dimethylsiloxane) (PDMS) solutions in Dichloromethane on porous silica. We vary the polymerization index  $N$  and the chain volume fraction  $\Phi$  from the overlap concentration to the melt. The adsorption of PDMS on silica by hydrogen bonding is very strong and a large amount of polymer remains bound to the surface after the washing of the silica with a good solvent of the chains. We measure this quantity  $\Gamma$  by small angle neutron scattering. If there is no chain desorption,  $\Gamma$  represents the weight of polymer attached to the solid in the initial solution, which varies as the product  $N^{1/2} \Phi^{7/8}$  according to a recent prediction. This relation of proportionality indeed interprets our experimental results. When the size of the chains is comparable to the pore diameter (either 500, 1 200 or 3 000 Å depending on the samples) we observe confinement effects which lower the adsorbed amount.

### 1. Introduction.

Most of the studies of the adsorption of polymers on solid surfaces are made in the very particular situation, where the substrate is in contact with a dilute solution [1]. The adsorption is very often irreversible. The adsorbed amount never exceeds a few milligrams per square meter, this corresponds approximately to one monolayer of monomers. Still the polymer adsorption from concentrated solutions or even melts is also interesting: it plays a very important role in many adhesion processes, spreading of polymer films or reinforcement of

rubber by mineral fillers [2] and leads to new behaviours. Very spectacular observations have thus been made recently by Cohen-Addad and coworkers [3, 4, 5].

Microscopic silica particles are incorporated mechanically in poly(dimethylsiloxane) (PDMS) melts and the authors measure after abundant rinsing with a good solvent the amount of polymer which remains attached to the particles (known in the reinforcement literature as the « bound rubber »). In the case of PDMS, the adsorption is due to the setting up of hydrogen bonds between the oxygen of the siloxane bridge and the silanol groups of the silica surface and is particularly strong. The striking result of the experiments is that the adsorbed amounts are very large, much larger than the values obtained by absorption from dilute solution [6]. The experiments also show that the adsorbed amounts depend strongly on the polymer molecular weight and probably also on the polymer polydispersity and particle size. Different results have been obtained on different series of samples : in the first series [3, 4] the amount of bound PDMS is proportional to the chain molecular weight, in the last one [5], it varies as the square root of the molecular weight.

If one assumes that the adsorption of the PDMS chains onto silica is completely irreversible, i.e. that there is no desorption during the rinsing process, the latter result is easy to interpret [5] and has been discussed by Marques and Joanny in the general case of a semi-dilute polymer solution in contact with a fractal surface [7]. In absence of desorption, the adsorbed amount (per unit area) after rinsing is equal to the adsorbance of the polymer in the semi-dilute solution, i.e. the total amount of polymer bound to the surface. Let us call  $R(\Phi)$  the radius of the polymer chains in the bulk solution at a volume fraction  $\Phi$  and let us assume that a finite fraction of the chains in the boundary layer of thickness  $R(\Phi)$  is adsorbed on the surface, then the adsorbance  $\gamma$  scales as  $R(\Phi)\Phi$ . As  $R(\Phi)$  is proportional to  $aN^{1/2}\Phi^{-1/8}$  [8], one gets

$$\gamma \approx aN^{1/2}\Phi^{7/8} + \gamma_0 \quad (1)$$

$a$  is the monomer length,  $\gamma_0$  represents the adsorbed amount at infinite dilution, about one monomer of volume  $a^3$  per area  $a^2$  [9], thus  $\gamma_0 \approx a$ .

In melts,  $\Phi = 1$  and equation (1) accounts for the observations of reference [5].

There are several common features between the irreversible adsorption of polymer considered above and the chemical end grafting of chains on a surface that we have studied recently on the system silica-hydroxyl terminated PDMS [10-12] : qualitatively the amount of polymer irreversibly bound to the surface is very large in both processes and this could lead to similar structures ; quantitatively equation (1) might also control the amount of polymer that can be grafted on a solid surface in semi-dilute solutions, if for kinetic reasons, the grafting reaction stops at the point where the grafted chains begin to be stretched and segregated [13, 12]. Furthermore, these two modes of fixations may be in competition in the same system as is precisely the case for silica and hydroxyl terminated PDMS, if the silica surface is not specially treated [10].

In order to investigate the resemblances and differences between adsorption and grafting, we have begun to study the adsorption of monodisperse non reacting (methyl terminated) PDMS on silica from semi-dilute solutions as a function of the polymer molecular weight and volume fraction, trying first to test completely equation (1). We describe our results below.

## 2. Samples and experiments.

The solid substrate is a powder of porous silica such as the one used in our previous studies of PDMS adsorption [14] and grafting [10-12]. The nominal pore diameter is 3 000 Å and the specific area measured by neutron scattering is 2.5 m<sup>2</sup>/cm<sup>3</sup>. Mercury porosimetry shows that

the size distribution of the pores is narrow around the nominal value and that in particular there are no small pores [15]. A few samples have also been prepared with silica of nominal pore diameter of 500 and 1 200 Å (their specific area determined by neutron scattering being respectively 14.5 and 7.7 m<sup>2</sup>/cm<sup>3</sup>). The polymers are fractionated PDMS chains (polydispersity 1.2) terminated by inert methyl groups. The molecular weight varies between 27 000 and 470 000 and the volume fraction varies between 5 and 100 % (see Tab. I).

Table I. — Characteristics of the samples and experimental results, *d* : pore diameter, *M* : polymer molecular weight (weight average),  $\Phi$  : polymer volume fraction in the initial solution,  $\gamma$  : adsorbed amount per unit area in unit of volume fraction. Different values (*M* = 96 700) correspond to different determinations on different samples.

<i>d</i> (Å)	3 000					3 000			1 200	500	3 000			3 000					3 000			3 000					
<i>M</i>	470 000					230 000						170 000			96 700					63 000			27 000				
$\phi$	0.50	0.35	0.20	0.10	0.05	1.00	0.50	0.20	1.00	1.00	1.00	0.50	1.00	0.50	0.20	0.10	0.05	1.00	1.00	0.20	0.10	0.05	1.00	1.00	0.20	0.10	0.05
$\gamma$ (Å)	143	97	57	39	17	283	165	91	163	82	254	137	219/166	117	44	23	15	168	102	18	14	10					

The samples are prepared by immersing 1 g of silica in a given solution of PDMS in dichloromethane (a good solvent) or directly in the melt at ambient temperature. The time of complete immersion varies between 24 h and 3 days depending on the sample viscosity. Test experiments on samples which have incubated a longer time exhibit no difference in the amount of adsorbed polymer. After imbibition the silica is rinsed by dichloromethane to remove the free polymer. The rinsing is repeated at least ten times during at least 24 h. The samples are dried after rinsing and reimpregnated just before the experiments.

The amount of bound polymer per unit area  $\gamma$  is measured by neutron scattering, which is a very sensitive non perturbing method. The application of small angle neutron scattering to the study of the structure of polymers at interfaces is explained with much detail in references [14, 10]. At vanishing scattering vector *q*, in the limit where  $q^{-1}$  is larger than the thickness of the layer but still smaller than the pore diameter,  $I_{pp}(q)$ , the scattering intensity (in cm<sup>-1</sup>) obtained at contrast matching between the solvent and the silica, is related to  $\gamma$  by

$$\lim (q \rightarrow 0) q^2 I_{pp}(q) = 2 \pi \frac{S}{V} \gamma^2 (n_p - n_s)^2 \tag{2}$$

*S/V* is the area per unit volume of the sample,  $\gamma$  is the adsorbed amount in unit of volume fraction, so that  $\gamma$  has the dimension of a length,  $n_p$  and  $n_s$  are respectively the scattering length densities of the polymer and of the solvent (in cm<sup>-2</sup>).

The neutron scattering experiments were carried out at L.L.B. on the spectrometers PACE and PAXE. The data were put on the absolute scale using the incoherent scattering of water. The polymer layers are observed in methanol, which is a very bad solvent of PDMS, thus the layers are almost dense [10]. More precisely we use a mixture of hydrogenated and deuteriated methanol, which has the same scattering length density as silica : this is achieved if the mixture contains 62.2 % of deuteriated methanol. The uncertainty on  $\gamma$  (about 10 %) arises from the errors on the absolute scale determination and also from the fact that in some cases the layers remain very thick even in methanol so that only a few points are within the scattering vector range, where expression [2] can be used.

### 3. Results.

The first result of our experiments is that, as observed by Cohen-Addad, the PDMS appears to be very strongly fixed to the silica surface, although no chemical bond is involved. The adsorbed amounts or adsorbances are very large, much larger than the values obtained from dilute solutions, and are not changed by repeated rinsing. They depend on the polymer molecular weight  $M$  and the polymer volume fraction in the initial solution,  $\Phi$  (cf. Tab. I).

In figure 1 we first plot in logarithmic coordinates different subsets of data, which show that the variations of the adsorbed amount  $\gamma$  with the polymer molecular weight  $M$  at constant volume fraction ( $\Phi = 1$ , Fig. 1a) and with the volume fraction  $\Phi$  at constant molecular weight ( $M = 470\,000$  (Fig. 1b) and  $M = 96\,700$  (Fig. 1c)) can be well described by power laws. From the slope measurements we obtain that at constant  $\Phi$  ( $\Phi = 1$ ),  $\gamma$  is proportional to  $M^x$ , with  $x = 0.45 \pm 0.1$  (the best fit for  $\Phi = 1$  is  $x = 0.47$ ), and that at constant  $M$ ,  $\gamma$  is proportional to  $\Phi^y$ , with  $y$  between 0.8 (best fit for  $M = 470\,000$ ) and 1 (best fit for  $M = 96\,700$ ). We note that the values of  $x$  and  $y$  are compatible with the predictions of Marques and Joanny leading to equation (1), where  $x = 0.5$  and  $y = 7/8 = 0.875$ .

Thus in a second step we plot in figure 2 the whole set of values of the adsorbed amount per unit area  $\gamma$  (in  $\text{\AA}$ ) as a function of the quantity  $N^{1/2} \Phi^{7/8}$  so that a direct comparison with equation (1) is possible. We see that the agreement between the data obtained with the  $3\,000 \text{\AA}$  pore diameter silica and the theory is very good. The only apparent problem is that we obtain two straight lines with different slopes. The first one through the asterisks corresponds to the polymer of largest mass,  $470\,000$  and the second one to the other samples of smaller mass.

We will first discuss the case of the smallest chains in pores of diameter  $3\,000 \text{\AA}$ . By fitting the data (Fig. 2, dashed line) with equality [1],  $\gamma = aN^{1/2} \Phi^{7/8} + \gamma_0$ , which defines precisely  $a$  and  $\gamma_0$ , we obtain the experimental values

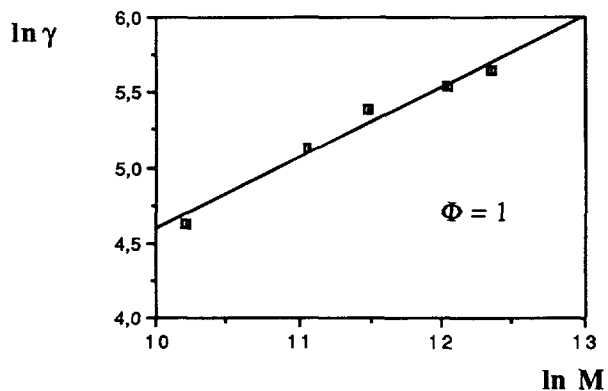
$$a = 4.9 \text{\AA} \quad \text{and} \quad \gamma_0 = 13 \text{\AA}.$$

As expected,  $a$  is of the order of a monomer length and  $\gamma_0$  corresponds to the observed values of the adsorbance in the dilute regime [6, 14]. ( $\gamma_0 = 13 \text{\AA}$  expressed in unit of weight corresponds to an adsorbed amount  $\Gamma_0 = 1.3 \text{ mg/m}^2$ , because the density of PDMS is  $1 \text{ g/cm}^3$ ).

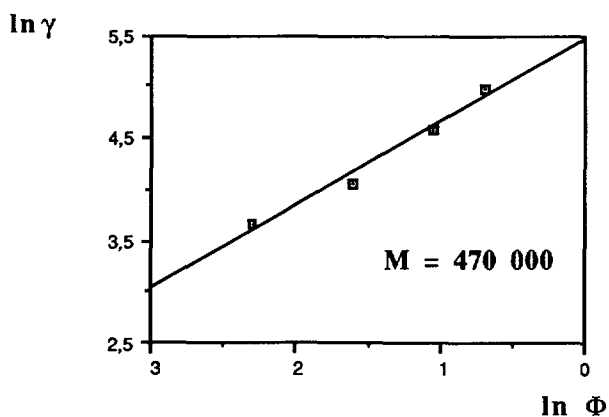
We can therefore conclude that the measured adsorbances are determined by the geometry of the chains in the initial bulk solutions.

It remains to understand why the values concerning the polymer of molecular weight  $470\,000$  deviate so strongly from the preceding observations. Because the size of the chains,  $R \approx 400 \text{\AA}$ , is not small compared to the diameter of the pores,  $d \approx 3\,000 \text{\AA}$ , we have looked for a possible origin of the observed difference in the confinement of polymer coils. In order to investigate the influence of the pore size on the polymer adsorption, we thus have made a few experiments on other silica samples with smaller, but still well-defined, pore diameters:  $1\,200$  and  $500 \text{\AA}$ . The chosen polymer had a molecular weight of  $230\,000$  dalton, in order to imbibe the porous silica relatively rapidly.

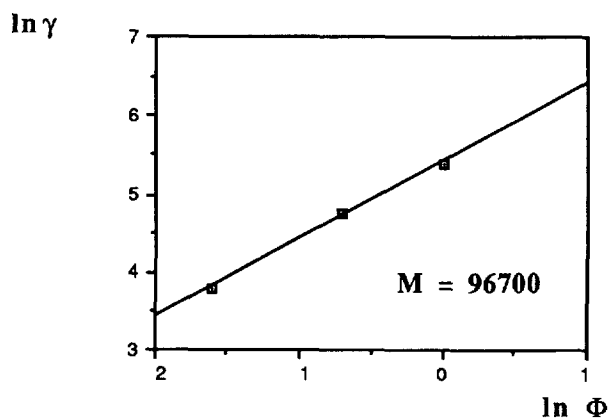
In figure 2 we can see that the reduction of the pore diameter at constant polymer molecular weight diminishes strongly the adsorbance. One could first think that the adsorption is smaller because the chains cannot enter easily the pores, but this would not be true. Because the initial polymer solutions are very concentrated, their correlation lengths are always much smaller than the diameter of the pores, and there should be no steric hindrance to the penetration of the chains in the silica samples [16]. So there must be a direct effect of the pore geometry on the amount of bound chains.



a)



b)



c)

Fig. 1. — a) Logarithm of the adsorbed amount *versus* logarithm of the molecular weight at constant polymer volume fraction in the initial solution,  $\Phi = 1$ ; the slope of the best fit is  $x = 0.47$ . b) and c) Logarithm of the adsorbed amount *versus* logarithm of the volume fraction at constant molecular weight; b)  $M = 470\,000$ , the slope of the best fit is  $y = 0.81$ ; c)  $M = 96\,000$ , the slope of the best fit is  $y = 1$ .

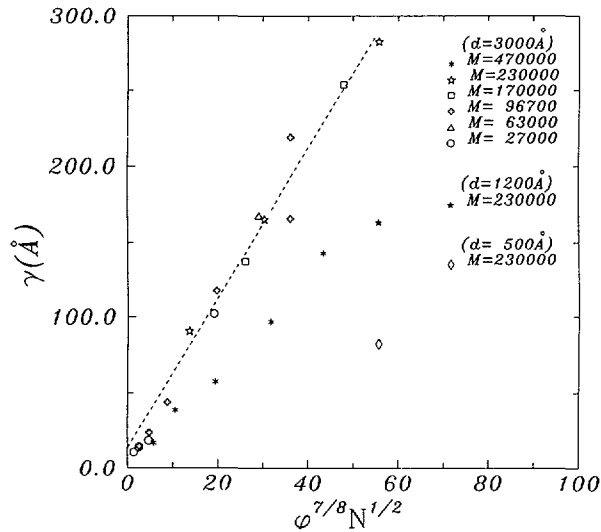


Fig. 2. — Plot of the amount of PDMS adsorbed onto silica,  $\gamma$  (in Å), versus  $N^{1/2} \Phi^{7/8}$  ( $N$ , polymerization index,  $\Phi$ , volume fraction of the initial polymer solution).

Let us assume as a crude model that the initial solution is confined in cylindrical pores of diameter  $d$  and that the chains bound to the solid are uniformly distributed in a layer of thickness  $e$  smaller than  $d$ , the adsorbance is then simply :

$$\gamma \approx \Phi e \left(1 - \frac{e}{d}\right). \quad (3)$$

The adsorbance must decrease as the pore diameter decreases. If the thickness of the layer of bound polymer is only slightly perturbed by the curvature of the pores,  $e \approx R(\Phi) \approx aN^{1/2} \Phi^{-1/8}$ . This suggests to plot the ratio  $\gamma/aN^{1/2} \Phi^{7/8}$ , evaluated for each sample, versus the dimensionless variable,  $aN^{1/2} \Phi^{-1/8}/d$  (Fig. 3). We have taken the value  $a = 4.9 \text{ Å}$  obtained from figure 1. We observe that all the data, including those concerning the polymer of mass 470 000, stand roughly on a master curve. There is a large uncertainty due to the dispersion of the data, but  $\gamma/aN^{1/2} \Phi^{7/8}$  appears to vary linearly with the ratio  $aN^{1/2} \Phi^{-1/8}/d$  when the latter is smaller than 0.2, we measure  $\gamma/aN^{1/2} \Phi^{7/8} \cong 1.4 (1 - 3 aN^{1/2} \Phi^{-1/8}/d)$ , this form, with its numerical coefficients of order unity, is not very far from expression [3]. This shows that the systems and phenomena of irreversible adsorption and confinement that we observe are relatively clear and well-defined, in any case less complicated than one might expect. Here again, we observe that in the regime investigated, the geometry of the chains in the bulk determines the adsorption behaviour.

#### 4. Conclusion.

We confirm that PDMS molecules adsorb strongly, irreversibly and in large amount on silica surfaces from concentrated solutions. The adsorbed layers can be observed in the presence of pure solvent. The adsorbed amount  $\gamma$  depends strongly on the chain molecular weight and on the polymer volume fraction in the initial solution in contact with the silica. Our data are well interpreted by the prediction of Marques and Joanny  $\gamma = aN^{1/2} \Phi^{7/8} + \gamma_0$  with  $a = 4.9 \text{ Å}$ .

The adsorbed amount is much larger than the amount  $\gamma_0$  adsorbed from dilute solution and

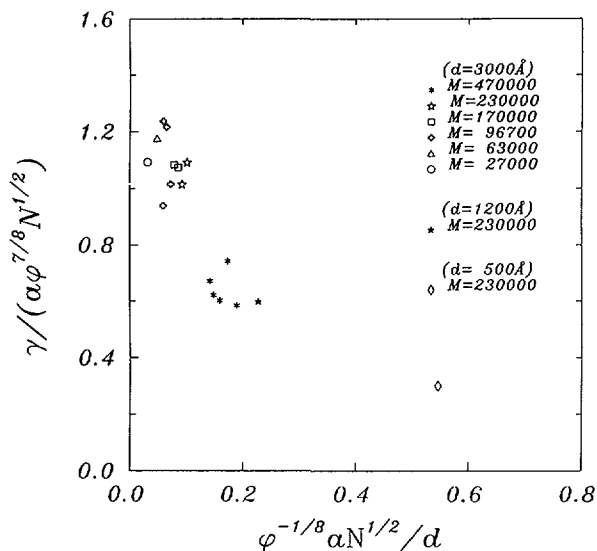


Fig. 3. — Effect of confinement. Plot of  $\gamma/\alpha\phi^{7/8}N^{1/2}$  versus  $\alpha N^{1/2}\phi^{-1/8}/d$ ,  $d$  pore diameter (for the smallest masses, only the values of  $\gamma$  much larger than  $\gamma_0$  have been represented,  $M = 27\,000$ ,  $\Phi = 1$  and  $M = 96\,700$ ,  $\Phi \geq 0.1$ ).

thus the structure of the layers must differ very much from the self-similar grid predicted theoretically [9] and observed experimentally [14]. Rather one might expect that in good solvent the layers resemble brushes of grafted chains. The study of their structure has been undertaken theoretically [17] and experimentally.

When the size of the polymer chains is comparable to the pore diameter, we observe that confinement effects lower strongly the adsorbed amount; of course it will be also interesting to study the regime of strong confinement, when the chains are much larger than the pores.

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