



HAL
open science

Structure of polymer layers adsorbed from concentrated solutions

Loïc Auvray, Philippe Auroy, Margarida Cruz

► **To cite this version:**

Loïc Auvray, Philippe Auroy, Margarida Cruz. Structure of polymer layers adsorbed from concentrated solutions. *Journal de Physique I*, 1992, 2 (6), pp.943-954. 10.1051/jp1:1992106 . jpa-00246613

HAL Id: jpa-00246613

<https://hal.science/jpa-00246613>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

61.25H — 68.45D — 82.70D

Structure of polymer layers adsorbed from concentrated solutions

Loïc Auvray ⁽¹⁾, Philippe Auroy ⁽¹⁾ and Margarida Cruz ⁽²⁾⁽¹⁾ Laboratoire Léon Brillouin (*), CEN Saclay, 91191 Gif-sur-Yvette, France⁽²⁾ Departamento de Fisica, Universidade de Lisboa Campo Grande, 1700 Lisboa, Portugal*(Received 27 January 1992, accepted in final form 12 March 1992)*

Résumé. — Nous étudions par diffusion de neutrons la structure interfaciale de couches de poly(diméthylsiloxane) irréversiblement adsorbées sur de la silice à partir de solutions semi-diluées et de fondus. Nous mesurons d'abord l'épaisseur h des couches gonflées par un bon solvant en fonction du degré de polymérisation des chaînes N et de la fraction volumique dans la solution initiale Φ . La relation $h \approx N^{0.8} \Phi^{0.3}$ récemment prédite à partir de l'analogie entre couches irréversiblement adsorbées et brosses de polymères greffés décrit bien nos résultats. Nous en déduisons qu'il existe au moins une grande boucle d'environ N monomères par chaîne adsorbée. Nous étudions aussi la forme du profil de concentration en polymère près de la paroi en mesurant sur deux échantillons le facteur de structure partiel polymère-solide qui est proportionnel à la transformée de Fourier du profil. Le modèle de pseudo-brosse prévoit une décroissance de la concentration avec la distance à la paroi z en $z^{-2.5}$. Ce profil en loi de puissance rend quantitativement compte de la dépendance angulaire du facteur de structure croisé polymère-solide, mais il est difficile de le distinguer sans ambiguïté de profils moins singuliers. Il implique que l'adsorption du PDMS sur la silice est suffisamment forte et rapide pour geler complètement la structure des boucles dans la couche adsorbée initiale.

Abstract. — We study by neutron scattering the interfacial structure of poly(dimethylsiloxane) layers irreversibly adsorbed from concentrated solutions or melts. We first measure the thickness h of the layers swollen by a good solvent as a function of the chain polymerisation index N and of the polymer volume fraction in the initial solution Φ . The relation $h \approx N^{0.8} \Phi^{0.3}$, recently predicted from an analogy between irreversibly adsorbed layers and grafted polymer brushes, describes well our results. We can therefore deduce that there is at least one large loop of about N monomers per adsorbed chain. We also study the shape of the polymer concentration profile in the layers by measuring on two samples the polymer-solid partial structure factor, that is proportional to the Fourier transform of the profile. The model of pseudobrushes predicts a concentration decay varying with the distance to the wall z as $z^{-2.5}$. This power law profile accounts quantitatively for the angular variation of the polymer-solid cross structure factor but it is difficult to distinguish it without ambiguity from less singular profiles. It implies that the adsorption of PDMS onto silica is sufficiently strong and fast to quench completely the loop distribution in the initial layer.

(*) Laboratoire commun C.E.A.-C.N.R.S.

1. Introduction.

The structure of a polymer layer adsorbed from a dilute solution has been known theoretically [1] and experimentally [2, 3] for a long time. The adsorbed chains build a self-similar diffuse structure with a singular $z^{-4/3}$ concentration profile, z being the distance to the adsorbing wall. The layer extends up to the radius of gyration of the chains and may be rather thick. The situation is more complex and less wellknown when the adsorbing wall is in contact with a semi-dilute polymer solution. Because of the screening of the excluded volume interactions, the self similar structure is cut off at the bulk correlation length ξ while the adsorbed chains develop large loops into the solution. The size of these loops has been discussed recently [4-7], it is of the same order of magnitude as the radius of gyration of the free chains in the semi-dilute solution if the polymer volume fraction is larger than the crossover value $N^{-4/7}$, N being the polymerization index. The main consequence is that the adsorbed chains are entangled with the free chains. This may modify strongly the rheological and mechanical properties of the solution near the surface and play an important role in many adhesion processes, particularly in the spreading of polymer films and in the reinforcement of rubber by mineral fillers.

In order to understand this role precisely, it is necessary to know the structure of the interfacial layer of bound chains. In principle this is difficult experimentally, because the structure of the bound chains is not directly related to a measurable gradient of concentration. One may however overcome this difficulty partially if the monomer adsorption is irreversible. In this case, it is possible to rinse the free chains with pure solvent without removing the adsorbed chains and one can observe the structure of the final layer by ellipsometry, small-angle scattering, neutron reflectometry or surface force measurements. As shown recently by Guiselin [5], this is particularly interesting because one can directly relate the thickness and concentration profile measurements to the loop and tail distribution in the layer structure. As Guiselin also calculates the loop distribution in the initial semi-dilute solution near the adsorbing wall as a function of the polymer molecular weight and volume fraction, a precise comparison with theory can be made, if adsorption in the initial solution is sufficiently strong and rapid to quench the loop structure. Deviations from the initial loop distribution can in principle also be detected and may inform about the kinetics of formation of the layer and on its eventual evolution.

The experimental studies of polymer layers irreversibly adsorbed from concentrated solutions are rather scarce. In fact, most of the studies of polymer adsorption have been restricted to the particular case of dilute solutions. The only exceptions concern elastomers because of the problems of rubber reinforcement by fillers. Very spectacular observations have been made recently by Cohen-Addad and coworkers on PDMS (poly(dimethylsiloxane), a silicone elastomer) adsorbed onto silica from the melt [8-10]. The authors observe that the adsorbed amounts of polymer are very large, much larger than the few milligrams per square meter measured usually after adsorption from dilute polymer solutions, and increases as the square root of the polymer molecular weight [10]. Note that the PDMS chains are strongly bound to silica by hydrogen interactions between the silanol groups of the silica surface and the oxygen atom of the PDMS backbone and that the adsorption is certainly irreversible.

A year and a half ago, we also started to study these layers of PDMS on silica by using the small angle neutron scattering technique [11]. We were interested in comparing the irreversible adsorption of polymers and the chemical grafting of chains on a surface, which we had studied previously [12-14] on almost the same system silica-PDMS, the PDMS chains being terminated by hydroxyl groups to react with the silanol groups of the silica surface. The first measurements that we have performed, were adsorbance measurements, which already give much information about the layer formation. Varying not only the polymer molecular

weight but also the polymer volume fraction in the initial solution, we confirm the last observations of Cohen-Addad and find that our results can be interpreted by the assumption of irreversible adsorption and a former prediction of Joanny and Marquès [4] :

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

This formula expresses that the total amount of polymer bound to a surface in a semi-dilute solution is simply proportional to the product of the size of the chains in the solution $R(\Phi) \approx aN^{1/2} \Phi^{-1/8}$ by the bulk volume fraction Φ . a is a monomer length.

We have since developed a complete study of the structure of the layers in good solvent using all the possibilities of the neutron scattering technique, which is by now one of the most simple, direct and powerful methods for investigating interfacial polymer structures [15]. We report here our results and compare them with the theory of Guiselin [5], which will be exposed in the progress of the discussion. We first present the measurements of the layer thickness as a function of the polymer molecular weight and volume fraction in the initial solution and then discuss the shape of the concentration profile.

2. Samples.

The preparation of the sample has already been described in reference [11]. The solid substrate is a powder of porous silica such as that used in our previous studies of PDMS adsorption [2] and grafting [12-14]. The nominal pore diameter is 3 000 Å and the specific area measured by neutron scattering is 2.5 m²/cm³. 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 [16]. The polymers are the same as in our previous study, these are fractionated PDMS chains (polydispersity 1.2) terminated by inert methyl groups. We have prepared eight different samples with six different molecular weights between 27 000 and 230 000 (the largest molecular weight that does not lead to an observable confinement effect on the adsorption) [11] with, depending on case, three different volume fractions in the initial solutions ($\Phi = 1, 0.5, 0.2$) (cf. Tab. I).

Table I. — *Characteristics of the samples and results of the measurements of adsorbed amounts and layer thicknesses. M : polymer molecular weight (by weight average), Φ : polymer volume fraction in the initial solution, γ , adsorbed amount per unit area expressed in terms of volume fraction, h : layer thickness in dichloromethane assuming a step profile.*

M	27 000	63 000	96 700			134 000	170 000			230 000	
Φ	1	1	0.2	0.5	1	1	0.5	1	0.2	0.5	1
γ (Å)	102	140	43	112	174	211	145	258	95	174	300
h (Å)	250	440	300	590	745	990	975	1 180	840	1 050	1 260

The samples are made 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 is ten days for the sample made from the melts and three days for the others. After imbibition, silica is rinsed by dichloromethane to remove the free polymer. Rinsing is repeated at least ten times during 10 days. The samples are dried after rinsing and reimbibed just before the experiments. We have compared equivalent samples made at one

year of interval, under slightly different conditions (different adsorption and rinsing time), the adsorbed amount and the spectra in good and poor solvent are the same within the experimental error.

3. Neutron scattering experiments.

The neutron scattering experiments are carried out at the Laboratoire Léon Brillouin on the spectrometer PACE. In most experiments, the observed range of scattering vector is $10^{-2} < q < 10^{-1} \text{ \AA}^{-1}$ and, when one needs to observe very thick layers, $3 \times 10^{-3} < q < 3 \times 10^{-2} \text{ \AA}^{-1}$. The data are put on the absolute scale by using the incoherent scattering of water.

The total coherent scattering intensity per unit volume of a given sample is written :

$$I(q) = (n_g - n_s)^2 S_{gg}(q) + (n_g - n_s)^2 S_{pp}(q) - 2(n_g - n_s)(n_g - n_p) S_{pg}(q)$$

where n_p , n_g and n_s are the respective scattering length densities of the silica grains (g), polymer (p) and solvent (s). $S_{ij}(q)$ are the partial structure factors defined as

$$S_{ij}(q) = \int d^3r \langle \delta \Phi_i(0) \delta \Phi_j(\mathbf{r}) \rangle e^{i\mathbf{q} \cdot \mathbf{r}}$$

There are two interesting partial structure factors : the polymer-polymer structure factors measured at contrast matching between the solvent and the silica ($n_g = n_s$) and the polymer-solid cross structure factor deduced from a complete series of contrast variation experiments. The direct contributions of the solid and the incoherent background are measured together for each contrast on a reference silica-solvent sample without polymer. They are then subtracted from the data.

In the range of observation, the scattering vectors q are much larger than the curvature of the pores, the interfaces appear flat at the scale q^{-1} . Then the scattering intensity only depends on the specific area and on the structure of the interfacial layers. This is Porod's regime. In this regime the two polymer partial structure factors are written :

$$S_{pp}(q) = 2 \pi \frac{S}{V} q^{-2} \left| \int_0^\infty dz \phi(z) e^{iqz} \right|^2 + \tilde{S}_{pp}(q) \tag{2}$$

$$S_{pg}(q) = 2 \pi \frac{S}{V} q^{-3} \int_0^\infty dz \phi(z) \sin qz. \tag{3}$$

Note that $S_{pp}(q)$ is the sum of the contribution of the average polymer profile and of the contribution of the concentration correlations in the layer $\tilde{S}_{pp}(q)$, which we do not need to detail here.

In the two ranges where the reciprocal of the scattering vector is either much larger or much smaller than the thickness h of the interfacial layer, the intensity has a simple and general behaviour that we will use to obtain — as far as we can — model independent information on the concentration profile.

In the range of small scattering vectors, qh much smaller than 1 (but q still in Porod's range), the scattering is only sensitive to the global characteristic of the layer structure :

— adsorbed amount (expressed in volume fraction), $\gamma = \int_0^\infty dz \phi(z)$,

— thickness or more precisely first moments of the concentration profile $\langle z^n \rangle = \gamma^{-1} \int_0^\infty dz z^n \phi(z)$.

By expanding the exponentials of expression (2) in series one obtains :

$$q^2 S_{pp}(q) = 2 \pi \frac{S}{V} \gamma^2 (1 - q^2 (\langle z^2 \rangle - \langle z \rangle^2)) + q^2 \tilde{S}_{pp}(0) + o(q^4). \quad (4)$$

By assuming a step profile of thickness h and neglecting the concentration fluctuations which are small for thick and dense layers we obtain the expression that we have used to analyse the data :

$$q^2 S_{pp}(q) = 2 \pi \frac{S}{V} \gamma^2 \left(1 - q^2 \frac{h^2}{12} \right) \approx 2 \pi \frac{S}{V} \gamma^2 e^{-q^2 \frac{h^2}{12}}. \quad (5)$$

This is the surface analog of the famous Guinier law. We obtain directly γ and the equivalent layer thickness h by plotting $q^2 \ln S_{pp}(q)$ vs. q^2 . Note that γ (in Å) can easily be converted into the adsorbance Γ (in mg/m²): $\Gamma = 0.1 \gamma d$, where d is the density of the polymer, $d \approx 1$ g/cm³ for PDMS.

At very large angles ($qh \gg 1$), the profile contribution to the scattering is dominated by the density discontinuity at the solid wall if the profile is not singular. By integrating expressions (2) and (3) by part, one obtains an asymptotic expression of the scattering intensity, which is very useful. One recognizes a strict analog to the wellknown Porod's law :

$$S_{pp}(q) = 2 \pi \frac{S}{V} \phi_s^2 \frac{1}{q^4} + \tilde{S}_{pp}(q) \quad (6)$$

$$S_{pg}(q) = 2 \pi \frac{S}{V} \phi_s \frac{1}{q^4} \quad (7)$$

where ϕ_s is the volume fraction of polymer right at the interface.

4. Results and discussions.

4.1 THICKNESS OF THE ADSORBED LAYER IN GOOD SOLVENT. — O. Guiselin proposes a simple calculation of the thickness of a polymer layer irreversibly adsorbed from a polymer solution based on the analogy with a grafted polymer layer :

If one admits with Joanny and Marquès that the extension of the bound chains in the initial polymer solution is of the same order of magnitude as the radius of the free chains $R(\Phi)$, the largest loop or tail of each chain contains a number of monomers of order N . If the adsorbance given by [1] is sufficiently large, these loops overlap and are stretched by the excluded volume interactions. The phenomena are exactly the same as in a polymer brush. The size of the large loops determines the thickness of the layer. Applying to this case the de Gennes-Alexander expression [17, 18] :

$$h \approx aN \left(\frac{a^2}{\Sigma} \right)^{1/3} \quad (8)$$

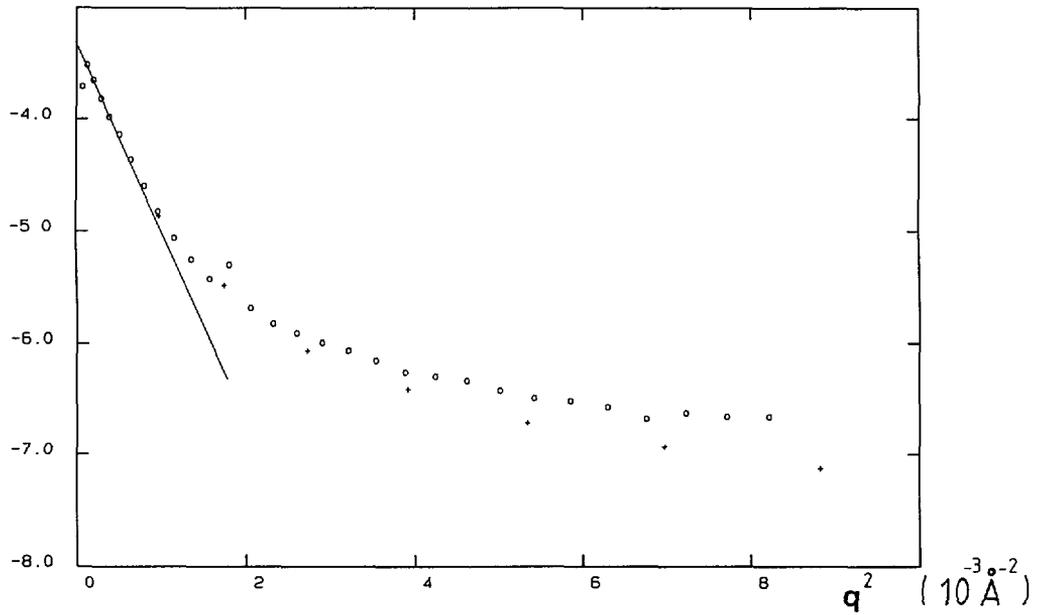
and expressing Σ , the effective area per chain, as a function of the known adsorbance γ :

$$\Sigma = \frac{Na^3}{\gamma} \approx a^2 N^{1/2} \Phi^{-7/8}, \quad (9)$$

one obtains

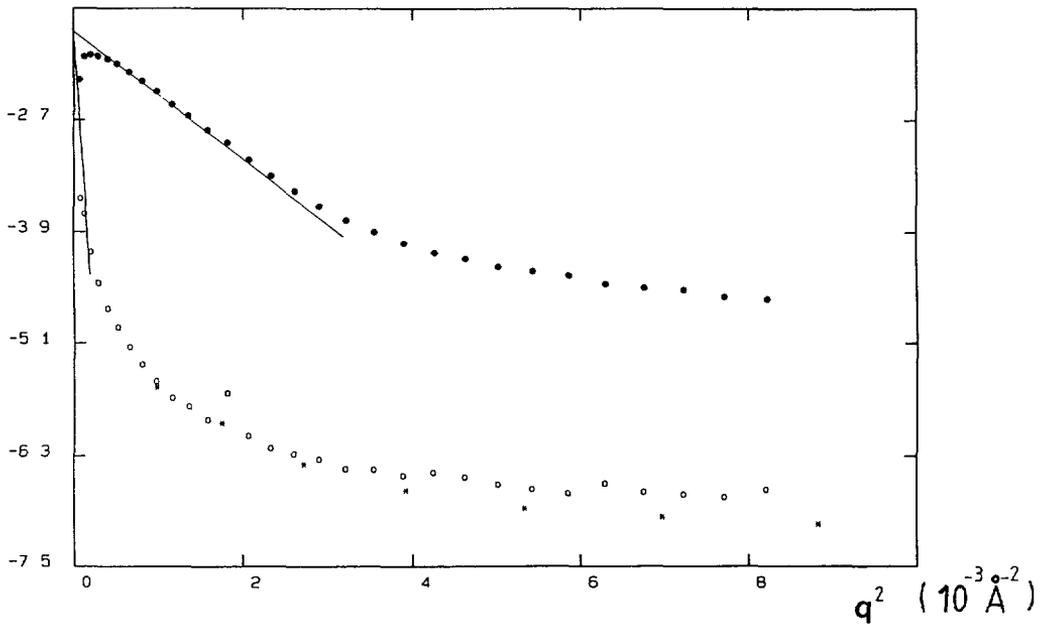
$$h \approx aN^{5/6} \Phi^{7/24} \quad (10)$$

$\ln q^2 I$



a)

$\ln q^2 I$



b)

Fig. 1. — Surface Guinier plots ($q^2 \ln S_{pp}(q)$ vs. q^2) of different samples observed at contrast matching condition between solid and solvent. (a) $M = 60\ 000$, $\Phi = 1$, solvent: dichloromethane. (b) $M = 230\ 000$, $\Phi = 1$, (O) solvent: dichloromethane; (●) solvent: acetone.

To illustrate the measurements of the layer thickness we present the surface Guinier plots of the intensity scattered by two different samples at contrast matching between the silica and the solvent (Fig. 1). The first plot (Fig. 1a) corresponds to a polymer of small molecular weight ($M = 60\,000$) in dichloromethane. The Guinier regime is easily observable at small q . From the slope and the intercept at the origin, one measures the adsorbance, $\gamma = 140 \text{ \AA}$ or $\Gamma = 14 \text{ mg/m}^2$ and the thickness, $h = 410 \text{ \AA}$. The average volume fraction in the layer $\Phi = \gamma/h$ is then about 30 %.

The two plots of figure 1b concern a polymer of large molecular weight ($M = 230\,000$). A well defined Guinier range is apparent only when the sample is observed in poor solvent, i.e. when the layer is collapsed and its thickness sufficiently small. The observation in poor solvent (here acetone) determines the adsorbed amount and fixes the reference value of $\ln q^2 I(q)$ at vanishing angle. If we now return to the sample in good solvent (dichloromethane) we interpolate by a surface Guinier law between this reference point and the first value of the intensity. In this way we measure a layer thickness of the order of $1\,000 \text{ \AA}$, with a relative uncertainty of about 20 %.

The variation of the thickness of the polymer layer as a function of the polymerization index when the chains are adsorbed from the melt ($\Phi = 1$) is represented in logarithmic coordinates (Fig. 2). A straight line fits the data correctly. The best fit corresponds to the relation

$$h = 2.1 N^{0.81} \text{ \AA}.$$

This relation is in very good agreement with the theoretical prediction [10] ($h \approx N^{5/6} \approx N^{0.83}$).

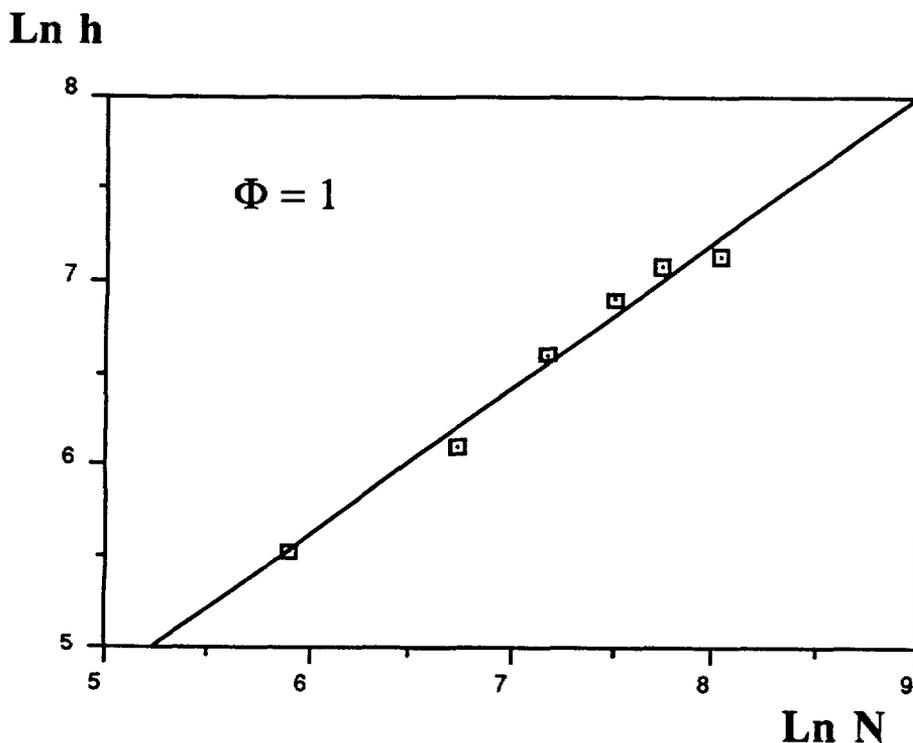


Fig. 2. — Dependence of the layer thickness h on the polymerization index N in dichloromethane. $\ln(h)$ vs. $\ln(N)$ at constant volume fraction $\Phi = 1$.

We have studied in less detail the dependence of h with the polymer volume fraction in the initial solution. Φ takes only three values : 0.2, 0.5 and 1. The data h vs. Φ at constant $M = 230\,000$ are plotted in figure 3. A power law variation $h \approx \Phi^y$ is compatible with the data. One measures $y = 0.3 \pm 0.1$. Again this is in agreement with [10].

Gathering the results, we plot the whole set of measured thicknesses against the quantity $N^{5/6} \Phi^{7/24}$ (Fig. 4). The data are more dispersed than on each individual plots, but the linear dependence between the coordinates appears clearly. We obtain the prefactor of the scaling law [10], $a = 1.9 \pm 0.3 \text{ \AA}$, indeed a molecular length.

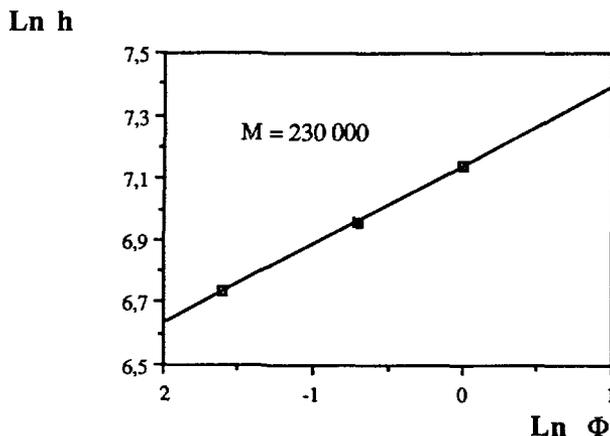


Fig. 3. — Dependence of the layer thickness h on the volume fraction Φ in the initial solution. $\text{Ln}(h)$ vs. $\text{Ln}(\Phi)$ at constant molecular weight $M = 230\,000$.

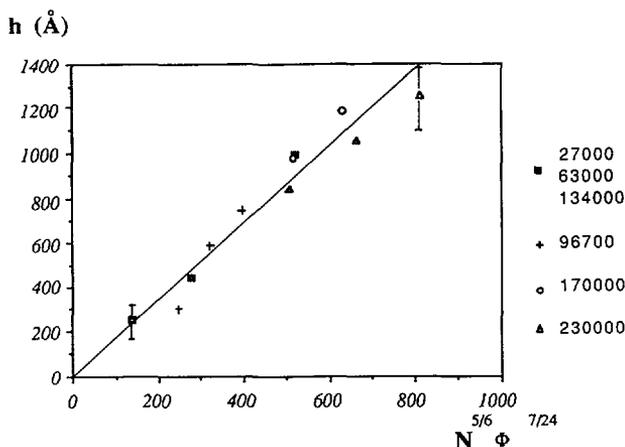


Fig. 4. — Master curve of the layer thickness measurements in good solvent : h vs. $N^{5/6} \Phi^{7/24}$

4.2 CONCENTRATION PROFILE. — The relation between the thickness of the adsorbed layer, the polymer molecular weight and the volume fraction in the initial solution is relatively independent of the detailed form of the actual concentration profile in the layer, provided that there are long tails or large loops. In order to obtain information about the profile we have to observe the inner structure of the layer and more particularly measure the polymer-

solid cross structure factor in the range $qh > 1$ (cf. expression (3)). Remember that for $qh > 1$, the polymer-polymer structure used precedently to determine the layer thickness does not inform about the profile but rather about the internal correlations in the layer. The observations, which will not be discussed in detail here, are not very different from what we observe on grafted layers [12]: the intensity is Lorentzian at large angles, indicating an analogy between the local structure of the layers and that of a semi-dilute solution of equivalent concentration.

Because the measurement of a cross structure factor requires a contrast variation experiment consuming more beam time than the observations at contrast matching, up to now we have performed the measurements on only two samples ($M = 27\ 000$ and $M = 170\ 000$, both adsorbed from the melt). As the layers are very thick, even for the smallest chains, most of the scattering data are recorded in the angular range $qh \gg 1$. The scattering intensity then depends essentially on the variations of the concentration profile near the solid wall and it is necessary to distinguish two kinds of profiles: regular profiles without singularity at the origin and singular profiles decaying as a power law.

We have first been inspired by the picture of a polydisperse polymer brush where the concentration profile is smooth and regular near the solid wall. According to expression [7], the cross structure factor decays then as $\Phi_s q^{-4}$, where Φ_s is the polymer volume fraction at the surface of the substrate.

In figure 5 we have plotted the product $q^4 S_{pg}(q)$ against q for a rather small polymer ($M = 27\ 000$) adsorbed from the melt. A plateau is not strictly reached but the deviation from the q^{-4} law, visible at the largest angles, is small and might be explained by the contribution of a small background noise. Neglecting for the moment this deviation, we take the value 10^{-3} \AA^{-1} as an asymptotic limit of the product $q^4 S_{pg}$. By comparison with expression [7], this leads to $\Phi_s = 60\%$. This value is about two times larger than the average volume fraction in the layer $\Phi = 30\%$. It is thus certain that a single step-function is not sufficient to describe the polymer concentration profile. As one could expect, the polymer adsorption imposes a volume fraction higher close to the surface than elsewhere within the adsorbed layer.

The hypothesis of a regular profile as encountered for polymer brushes seems to be the most natural, but it may not be the correct one.

Assuming that a layer of polydisperse interacting loops attached to a wall is locally analogous to a layer of interacting grafted chains, Guiselin establishes a general relation between the loop distribution, local stretching and local volume fraction of the chains [5]. In our case, if the adsorption of monomers is irreversible, the distribution of loops in the swollen layer after rinsing by pure solvent remains the same as in the initial semi-dilute solution and can be derived by scaling arguments. Because the loops are very polydisperse, the final concentration profile is, in a remarkable way, singular (although weakly singular):

$$\Phi(z) \approx \Phi^{7/10} \left(\frac{a}{z} \right)^{2/5} \quad (11)$$

z , the distance to the wall, is larger than the bulk correlation length, $\xi \approx a\Phi^{-3/4}$ and smaller than the overall layer thickness h discussed above. Note that the decay is slower and the singularity less pronounced than for a self similar layer at equilibrium.

The Fourier transform of this profile also decays as a power law in the range $qh \gg 1$, $q\xi < 1$: if, assuming $\Phi = 1$, one takes by definition of the length a , $\Phi(z) = (a/z)^{2/5}$, the sine Fourier transform of $\Phi(z)$ is

$$\Phi(q) \approx \frac{1.205}{q} (qa)^{2/5} \quad (12)$$

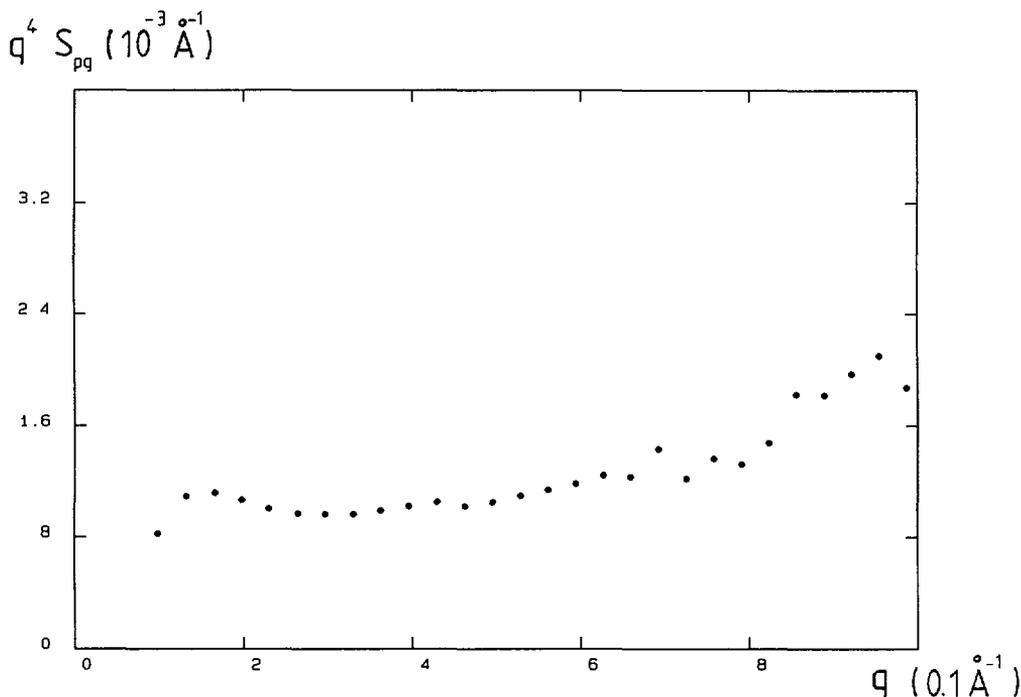


Fig. 5. — Porod's plot of the polymer-solid cross structure factor: $q^4 S_{pg}(q)$ ($M = 27\,000$, $\Phi = 1$, solvent: dichloromethane).

This decay explains the deviation from Porod's law previously observed (Fig. 5). When one plots $S_{pg}(q)$ in logarithmic coordinates, there is a well defined slope, whose value is -3.65 ± 0.1 , in agreement with Guiselin's prediction.

From the measurements at the absolute scale, we deduce the value of the length a by comparison with expression [12]. We obtain $a = 5.2 \text{ \AA}$, which is a reasonable value.

Although the agreement with the theory is very good for this sample, a definite conclusion cannot yet be drawn if we consider now the result obtained with the second sample made with a polymer of larger molecular weight, $M = 170\,000$. There is also a deviation from Porod's law but the apparent slope in a log-log plot is -3.8 (Fig. 7), a slightly larger (absolute) value than expected. Also one observes a strong deviation from the linearity at the largest angle, that we cannot explain but might be due to a badly subtracted background noise. If one does not take this noise into account the observed behaviour is close to Porod's law with a surface volume fraction $\Phi_s \approx 0.4$.

One of the advantages of the $z^{-2/5}$ profile with respect to the non-singular profiles is that the predicted value of the polymer volume fraction at the surface is $\Phi_s = 1$ in agreement with what is known about the adsorption from dilute solutions and with what is expected for a strong adsorption. The value $\Phi_s = 0.6$ or $\Phi_s = 0.4$ deduced from the hypothesis of a non-singular profile may be too small to be correct. On the other hand, one cannot exclude that a few loops unfasten from the surface. In this case according to reference [5] the surface volume fraction decreases and the concentration profile becomes flat near the wall without changing at large distance. One could thus observe a q^{-4} behaviour with a value of Φ_s smaller than 1. But it would remain to explain the origin of the small but systematic background noise. Only more precise and more sensitive experiments also probing the Φ dependence of the prefactor in

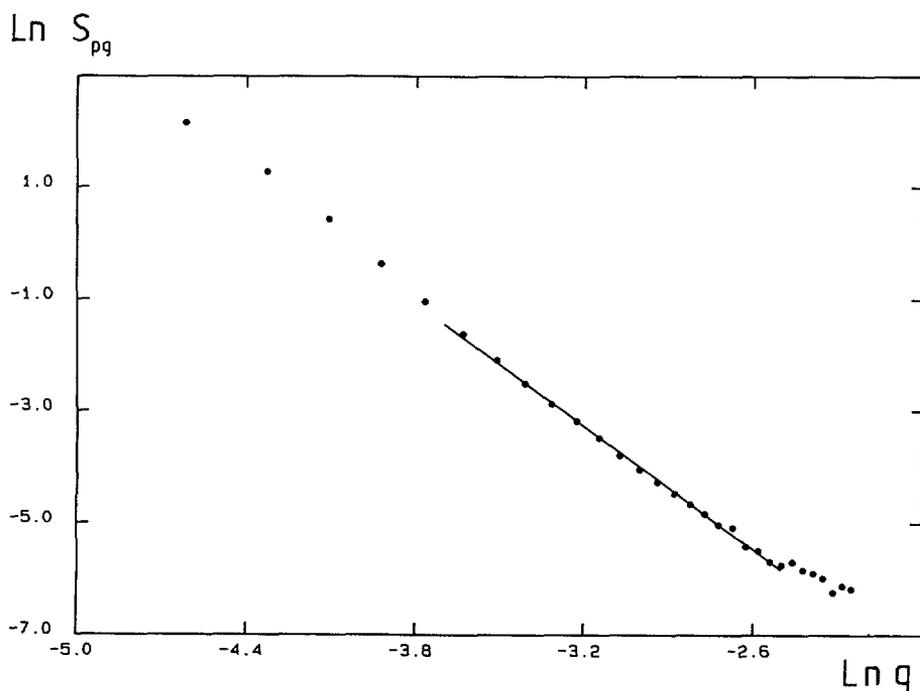


Fig. 6. — $\text{Ln } (S_{pg}(q))$ vs. $\text{Ln } (q)$ ($M = 27\,000$, $\Phi = 1$, solvent : dichloromethane). The slope of the straight line is -3.65 ± 0.1 .

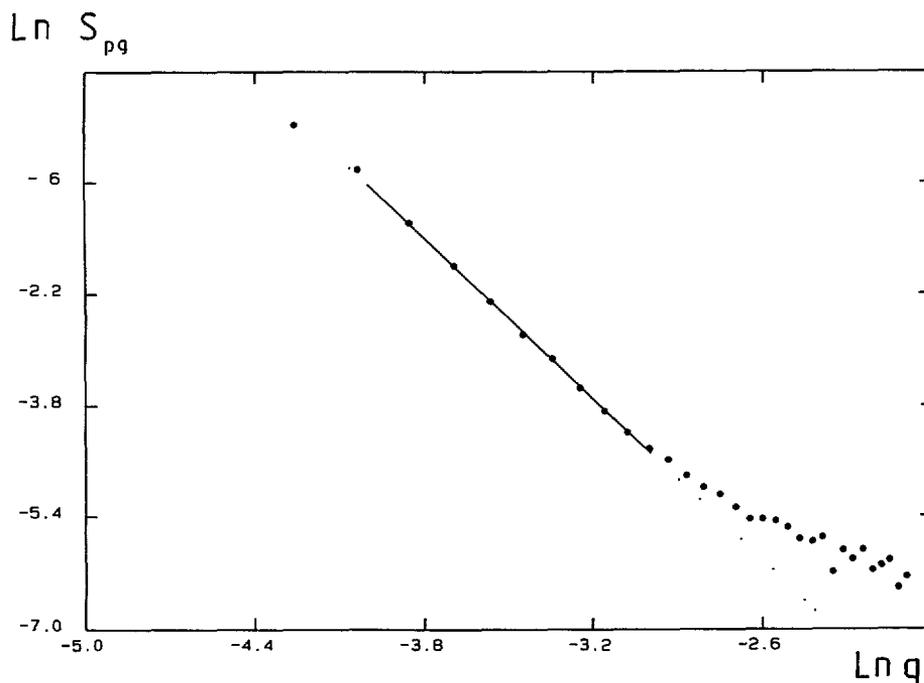


Fig. 7. — $\text{Ln } (S_{pg}(q))$ vs. $\text{Ln } (q)$ ($M = 170\,000$, $\Phi = 1$, solvent : dichloromethane). The slope of the straight line is -3.8 ± 0.1 .

[11] can establish the reality of the $z^{-2/5}$ profile more definitely and firmly than we have done yet.

5. Conclusions.

Our neutron scattering studies of PDMS layers irreversibly adsorbed from concentrated polymer solutions yield a precise picture of their structure in good solvent. They also inform a lot about the layer formation and structure in the initial semi-dilute solution, where the adsorbed chains are not observable directly.

There is at least one large loop or tail per chain, which contains a number of monomers proportional to that of the chain itself. This first determines the adsorbed amount, as thought by Marquès and Joanny and as we have observed previously. This also imposes the thickness of the layers h . The variation of h with the polymerization index N and the volume fraction in the initial solution Φ , $h \approx aN^{0.8} \Phi^{0.3}$ shows that adjacent loops interact strongly and are stretched as in a grafted polymer brush, in agreement with the theory of Guiselin.

The polymer concentration profile in good solvent is rather smooth. We obtain some indications that it might decrease as a power law, the exponent α being however small, so that it is difficult to distinguish between a singular and a non-singular profile. Two different values of α have been measured on two different samples, $\alpha = 0.35$ and $\alpha = 0.2$; the first value, $\alpha = 0.35$, is close to Guiselin's prediction $\alpha = 2/5$. This observation, if confirmed, would imply that the adsorption of PDMS onto silica is sufficiently strong and rapid to freeze completely the initial loop structure of the adsorbed layer.

Acknowledgments.

We thank O. Guiselin for numerous discussions.

References

- [1] DE GENNES P. G., *Macromolecules* **14** (1981) 1637.
- [2] AUVRAY L., COTTON J. P., *Macromolecules* **20** (1987) 202.
- [3] LEE L. T., GUISELIN O., FARNOUX B., LAPP A., *Macromolecules* **24** (1991) 2518.
- [4] MARQUES C. M., JOANNY J. F., *J. Phys. France* **49** (1988) 1103.
- [5] GUISELIN O., *Europhys. Lett.* **17** (1992) 225.
- [6] GUISELIN O., submitted to *J. Phys. France*.
- [7] DAUD M., JANNINK G., *J. Phys. II France* **1** (1991) 1483.
- [8] COHEN-ADDAD J. P., ROBY C., SAUVIAT M., *Polymer* **26** (1985) 1231.
- [9] VIALLAT A., COHEN-ADDAD J. P., POUCHOLON A., *Polymer* **27** (1986) 843.
- [10] COHEN-ADDAD J. P., *Polymer* **30** (1989) 1821.
- [11] AUVRAY L., CRUZ M., AUROY P., to appear in *J. Phys. II France*.
- [12] AUROY P., AUVRAY L., LÉGER L., *Macromolecules* **24** (1991) 2523.
- [13] AUROY P., AUVRAY L., LÉGER L., *Phys. Rev. Lett.* **66** (1991) 719.
- [14] AUROY P., AUVRAY L., LÉGER L., *Macromolecules* **24** (1991) 5158.
- [15] AUVRAY L., AUROY P., Neutron, X-ray and Light Scattering, P. Lindner and T. Zemb Eds. (Elsevier, 1991).
- [16] Analysis of « Laboratoire Central des Ponts et Chaussées », M. Buil, private communication.
- [17] DE GENNES P. G., *Rep. Prog. Phys.* **32** (1969) 187.
- [18] ALEXANDER S., *J. Phys. France* **38** (1977) 983.