Structures of End-Grafted Polymer Layers: A Small-Angle Neutron Scattering Study

P. Auroy,*,† L. Auvray,† and L. Leger‡

Laboratoire Léon Brillouin, CEN Saclay, 91191 Gif-sur-Yvette Cedex, France, and Laboratoire de Physique de la Matière Condensée, Collège de France, 11 Place Marcelin Berthelot, 75231 Paris Cedex 05, France

Received May 23, 1990; Revised Manuscript Received November 13, 1990

ABSTRACT: The structures of grafted poly(dimethylsiloxane) layers at the solid–liquid interface, in the regime of high graft density, have been investigated in various solvents, using small-angle neutron scattering techniques. In a poor solvent, the grafted polymer layer is dense with two well-defined boundaries, leading to interference phenomena. In a good solvent, the chains are stretched and exhibit the same behavior as in semidilute solution. Although the average interfacial density profile is smoother than a step function, the "brush" model is in good agreement with our observations.

Owing to their physicochemical applications, grafted polymer layers have been the subject of several recent theoretical studies[1–4] and simulations,[5–7] since the brush model of Alexander and de Gennes.[8,9] Experimentally, there are two ways of determining the density profile of these interfacial layers. The first is a force balance technique[10,11] and the second is small-angle neutron scattering (SANS). The former gives precious information about the interactions between surfaces bearing grafted polymers. Moreover, the force law has been found to agree with theoretical predictions. Thus, it has been claimed that the grafted layer may have a parabolic profile in good solvent for sufficiently high graft density. Nevertheless, the force balance method does not directly probe the inner structure of the interfacial layers. The interpretation of these experiments is very dependent on theoretical models without which this method gives only qualitative information about the density profile.

The second experimental method, SANS, was first proposed in this context by Cosgrove et al.[12,13] They have investigated various systems such as grafted polystyrene on silica particles or adsorbed poly(vinyl alcohol) on polystyrene latex. Algorithms have been developed[14] to interpret the scattered intensity in terms of density profiles. However, this procedure requires a good estimation of the different sources of background, extrapolations of the scattered intensity both at low and high scattering vector, and smoothing of the data. None of which are in fact very easy. Nevertheless, important results have been already obtained and SANS is now recognized as the most efficient technique to characterize interfacial layers.

Using this experimental method, we have performed an extensive study[15] of grafted polymer layers. We have determined their conformation in various situations and examined some physicochemical aspects of the grafting reaction. In this paper, we present results obtained at high grafting density, which is the most important regime for many industrial applications. The system chosen for our study was poly(dimethylsiloxane) of narrow molecular weight fraction, grafted onto well-defined porous silica. This model system has many advantages. In particular, it is easy to use compared to small-particle dispersions, since there is no problem of stability. Thus, various solvents have been used, including poor solvents, which have allowed us to investigate the conformations of the grafted layers in very different environments.

In section I, the system and the details of the experimental procedures will be presented. The scattering theory will be briefly reviewed in section II. Particular emphasis will be given to the contribution of the concentration fluctuations and to the step function model, which will be very useful for taking a critical look at the data. In section III, the results will be presented and discussed, starting with the situation of the grafted layer in bad solvent, for which we can consistently analyze all our data in terms of a step density profile. This will allow us to move on to the question of the density profile of the grafted chains in good solvent, which will be much more complicated to reveal than in poor solvent due to strong concentration fluctuations.

I. Experimental Section

The solid was a porous silica (designed for liquid chromatography): Daltosil 3000, purchased from SERVA. Its characterization has been reported in an earlier paper.[16] The surface of this silica can be considered as flat and is well-defined on the scale 10–300 Å (specific area of 2.5 m^2/cm^3; diameter of the pores, 4000 Å). In some cases, we have modified the silica surface prior to performing the grafting reaction, in order to diminish the natural adsorption of the polymer: after reaction with a high-boiling alcohol (pentanol), most of the external hydroxyl groups were converted into $>SiOC_5H_{11}$ and the amount of polymer that could adsorb onto the silica was considerably reduced.

The polymer was poly(dimethylsiloxane). Narrow molecular weight samples were prepared by fractionation (nonsolvent/solvent mixtures procedure) of commercial grade PDMS. These polymers were cationically synthesized and carried a hydroxyl group at both ends. The characteristics of the polymer samples are reported in Table I.

The grafting procedure is simple. The silica particles were introduced in a PDMS solution in heptane. The sample was then refluxed for at least 24 h with constant agitation. During the reaction,[17] particular care was taken in maintaining the solution homogeneous and the polymer concentration rather constant. In most cases, the polymer volume fraction in the reaction bath was fixed at 0.15. After reaction, the particles were then rinsed several times with a great volume of dichloromethane in order to remove the free polymer.

The neutron experiments were carried out at Saclay on the PACE spectrometer. Two different wavelengths have been used: 6.7 and 16 Å. The data were put on the absolute scale by using the incoherent scattering of H_2O. All the samples were dried and degassed under vacuum at room temperature before the neutron experiments. The silica particles were introduced in a 2-mm quartz cell and then imbibed by the solvent. Bare silica

† Laboratoire Léon Brillouin.
‡ Collège de France.

0024-9297/91/2224-2523$02.50/0

Table I
Basic Parameters of the Samples

sample	M_w	polydispersity	Γ, mg/m^2	D, Å	surface
A	26 000	1.09	5.15	29	untreated
B	316 000	1.17	15.7	58	untreated
C	148 000	1.09	13.5	43	pretreated
D	37 000	1.08	7	30	untreated
E	282 000	1.13	18.7	50	untreated
F	172 500	1.09	6.5	67	untreated

(either chemically pretreated or not) was used as reference and its scattered intensity in the same conditions of solvent and of isotopic mixture was systematically substracted. After each experiment, the solvent has been removed by drying the sample and pumping over it. Thus, it could be used again with another solvent.

We used mixtures of fully protonated–fully deuterated solvents (dichloromethane, acetone, and methanol). We note x_D the volume fraction of the fully deuterated solvent. The contrast match between the solvent and the silica was achieved with x_D = 90% for dichloromethane, x_D = 63% for acetone, and x_D = 62.2% for methanol. For the contrast variation experiments, we also used mixtures of dichloromethane with x_D = 50% (x_D = 85% for acetone or methanol).

II. Scattering Theory

General Expressions. We note q the scattering vector. The scattered intensity I(q) of our three-component system has the general form

$$I(q) = I_{pp}(q) + I_{pg}(q) + I_{gg}(q)$$

where p is referred to polymer, g to solid grain. $I_{pp}(q)$ is the polymer–polymer form factor, $I_{pg}(q)$ the polymer–solid interference term, and I_{gg} the solid–solid form factor.

As soon as the scattering vector q is larger than the curvature of the pores, $I_{gg}(q)$ satisfies Porod's law:

$$I_{gg}(q) \approx 2\pi(S/V)(n_g - n_s)^2 q^{-4}$$

where n_g (n_s) is the scattering length density of the grains (solvent).

As pointed out by one of us,[18] two contributions could be important for the I_{pp} term: the first $\tilde{I}_{pp}$ comes from the scattering by the average profile and the second $\tilde{I}_{pp}$ is due to concentration fluctuations in the polymer layer. For a flat surface, $\tilde{I}_{pp}$ reduces to[12]

$$\tilde{I}_{pp}(q) = 2\pi(S/V)(n_g - n_s)^2 q^{-4} \left| \int e^{iqz} \langle \phi(z) \rangle \, dz \right|^2$$

where $\langle \phi(z) \rangle$ is the average polymer volume fraction, normal to the surface. In some cases, especially in good solvent for flexible neutral polymers, the contribution of the concentration fluctuations to the scattering intensity could be strong. If $\langle \phi(z) \rangle$ is not "too singular" near the wall, $\tilde{I}_{pp}$ should scale las q^{-4} at high q and could be dominated by the $\tilde{I}_{pp}$ term if $\tilde{I}_{pp}$ decreases more slowly.

Let us now examine the I_{pg} term. Since the polymer layer is globally invariant by translation parallel to the surface, the averaging of the scattered intensity over all the orientations of the grains reduces the contribution from the fluctuations in the I_{pg} term to zero; therefore

$$I_{pg}(q) = -4\pi(S/V)(n_p - n_s)(n_g - n_s)q^{-3} \, \mathrm{Im}\left(\int e^{iqz} \langle \phi(z) \rangle \, dz \right)$$

Obviously, for contrast matching condition, $I(q)$ reduces to the polymer–polymer form factor:

$$I(q) = I_0(q) = \tilde{I}_{pp}(q) + \tilde{I}_{pp}(q)$$

when

$$n_s = n_g$$

For the case where $\langle \phi(z) \rangle$ is a step function ($\langle \phi(z) \rangle = \phi$ for $0 < z < h$ and $\phi(z) = 0$ for $z > h$), we have

$$I_{pp}(q) = 2\pi(S/V)(n_p - n_s)^2 q^{-4} 2(1 - \cos qh)\phi^2$$

$$I_{pg}(q) = -4\pi(S/V)(n_p - n_s)(n_g - n_s)q^{-4}(1 - \cos qh)\phi \quad (1)$$

It is useful to consider the very small angle regime, where $qh \ll 1$. Then we have

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

$$q^2 I_{pg}(q) = -4\pi(S/V)(n_p - n_s)(n_g - n_s)^2 \frac{\gamma h}{2} \left[1 - \frac{q^2h^2}{12} \right] \quad (2)$$

where

$$\gamma = \int_0^h \phi(z) \, dz$$

Therefore, $\Gamma = 0.1\gamma d$ (Γ in mg/m^2, γ in Å, and d in g/cm^3) is the total amount of polymer in the layer per unit area. ($\gamma = \phi h$ for a step function; d is the polymer density. For the poly(dimethylsiloxane), $d \sim 0.98$ g/cm^3.)

We recall also, that, for a volume fraction profile that does not show any divergences or fluctuations, $q^4 I(q)$ must become constant at high q and follow a horizontal asymptote in the representation of $q^4 I(q)$ as a function of q.

To summarize, two representations of the scattered intensity are definitively more interesting: $q^2 I(q)$ as a function of q^2 (very small angle regime), from which we can determine the total amount of grafted polymer per unit area and the thickness of the layer, and $q^4 I(q)$ as a function of q, which emphasizes the local singularities and the (eventual) asymptotic behavior.

Case of Polymer Brushes. The introduction of a concentration profile does not exhaust the description of polymer brushes. If we follow the general pictures of Alexander and de Gennes,[8,9] the physical parameter relevant to this problem should be D, the average distance between grafted sites on the surface. When the chains are purely grafted (no adsorption), two different regimes could be distinguished in good solvent. In the low-density limit, the chains are separate and extend over a distance comparable to their radius of gyration. This situation will not be considered here. However, when the grafting density is very high, the coils overlap and could be considered as linear strings of blobs of size D. Excluded-volume correlations are important inside a blob but totally screened at larger scales. Thus we would obtain[19] for $\tilde{I}_{pp}$ when $qD < 1$

$$\tilde{I}_{pp} \approx \frac{1}{(1 + q^2D^2)}$$

Thus, the grafted chains should have the same local behavior as semidilute solutions of linear flexible polymer.[19]

III. Results and Discussion

Determination of the Grafted Polymer Amount. Since the data have been put on the absolute scale, it is possible to determine the surface coverage Γ from the extrapolated scattered intensity at $q \approx 0$. As shown in eq 2, $q^2 I(q)$ is linear in q^2 provide that q is sufficiently small. This means that q^{-1} must be greater than the typical thickness l[20] of the layer. Thus, if $ql \ll 1$, the extrapolated

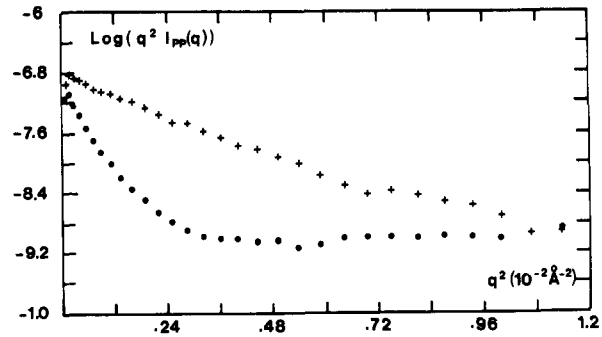

Figure 1. Sample A (M_w = 26 140). Scattered intensity in contrast match conditions (+, acetone; ●, dichloromethane) for a relatively low molecular weight polymer. Plots of the logarithm of $q^2I_{pp}(q)$ versus q^2.

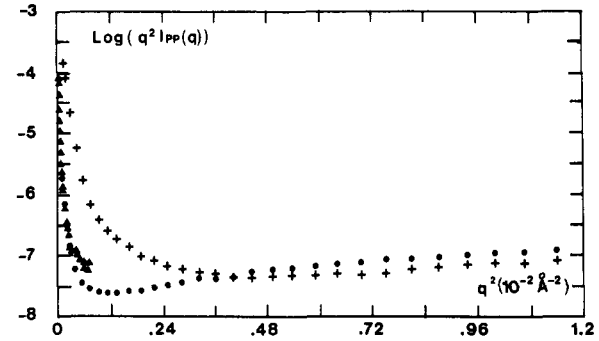

Figure 2. Sample B (M_w = 31 6000). Scattered intensity in contrast match conditions for two different neutron wavelengths (+, acetone, λ = 6.7 Å; ●, dichloromethane, λ = 6.7 Å; ▲, dichloromethane, λ = 16 Å). Plots of the logarithm of $q^2I_{pp}(q)$ versus q^2.

value $q^2I(q)|_0$ and the slope of the linear regime are related respectively to γ^2 and to l^2, in contrast match conditions. Therefore, since the q range is limited experimentally, the best conditions for an accurate estimation of γ will be in bad solvent, where the layer will be collapsed and l will be the smallest making the condition $ql \ll 1$ satisfied.

Figure 1 shows the scattered intensity plotted as log $[q^2I(q)]$ versus q^2 for a grafted layer obtained with a relatively low molecular weight polymer (Sample A, M_w = 26 140. See Table I.) The thickness is not very large, whatever the quality of the solvent is. The condition $ql \ll 1$ (here 10^{-2} Å$^{-1} < q < 10^{-1}$ Å^{-1}; the wavelength was 6.7 Å) is satisfied in acetone and in dichloromethane and the extrapolated value $q^2I|_0$ is the same in both solvents. Figure 2 shows the results given by a much longer polymer. To definitively prove the accuracy of our determination of Γ, we have also reported the data obtained in dichloromethane at a wavelength of 16 Å (where 2.5 10^{-3} Å$^{-1} < q < 2.7\,10^{-2}$ Å^{-1}). Both spectra overlap very well and reach the same limit at very low q.

We conclude that our procedure gives an accurate value of Γ, even for very high molecular weight polymers (Table I).

Grafted Layers in Methanol. Figure 3 shows the scattered intensity at contrast match for sample C in methanol plotted as $q^4I(q)$ versus q. The beautiful oscillations, which look like interference fringes, prove the existence of two well-defined boundaries: a solid–polymer and a polymer–solvent discontinuity. One can estimate the surface fraction (from the height of the first maximum—see eq 1) $\phi \approx 0.86$ very close to the mean volume fraction $\phi \cong \gamma/h$, and the mean concentration one can measure for bulk PDMS in methanol.

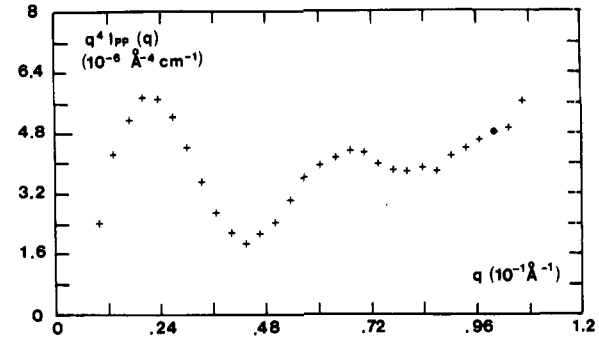

Figure 3. Sample C. Scattered intensity in contrast match conditions in methanol plotted as $q^4I_{pp}(q)$ versus q.

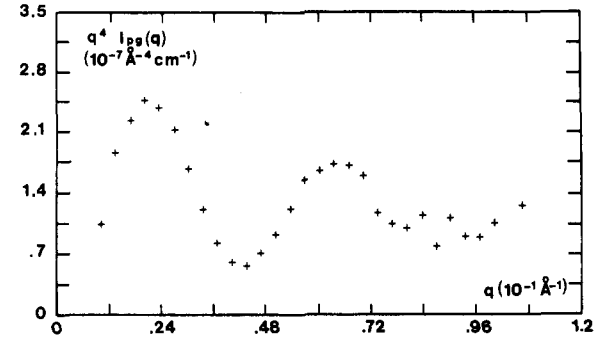

Figure 4. Sample C. Results of a contrast variation experiment in methanol. Plot of the polymer solid cross structure factor $I_{pg}(q)$ as $q^4I_{pg}(q)$ versus q.

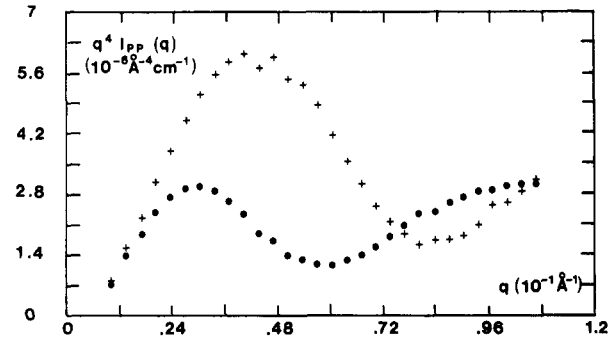

Figure 5. Sample D. Difference of the scattered intensity of the same grafted layer immersed in methanol (+) and in acetone (●) in contrast match conditions. Plots of $q^4I_{pp}(q)$ versus q.

Table II
Sample C (M_w = 148 000): Observations in Methanol

parameters	data from I_{pp}	data from I_{pg}
Γ, mg/m²	13.5	11.6
$h_{q\to0}$, Å	161	164
h_{osc}, Å	157	157
Φ_s	0.88	0.79
$\bar{\Phi}$	0.86	0.72

Such oscillations have never been observed up to now. They are closely related to the polymer polydispersity and to the grafting density.[21]

In Figure 4 we report our results for the same sample using the contrast variation method. The curve of the cross term $I_{pg}(q)$ has an identical shape with that obtained in contrast match conditions and the values of the characteristic parameters are in very good agreement with those determined above (Table II). The only slight difference is the behavior at very high angles, when the intensity weakly rises in contrast match conditions, while it drops for the cross term obtained with the contrast variation method. Since the volume fraction is not 100%, there is some solvent in the interfacial layer. This yields

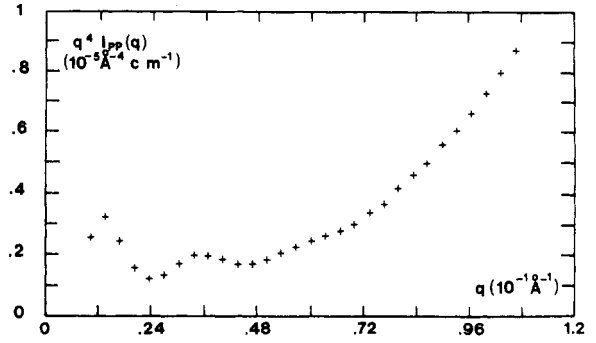

Figure 6. Sample E. Scattered intensity in contrast match condition in acetone plotted as $q^4I_{pp}(q)$ versus q. A weak background dominates at high q.

Table III
Sample D (M_w = 37 000): Comparison of the Observations in Acetone and Methanol

	methanol	acetone
Γ, mg/m^2	7.1	7
D, Å	30	30
$h_{q\to 0}$, Å	85	118
h_{osc}, Å	74	104
Φ_s	0.90	0.64
$\bar{\Phi}$	0.84	0.60

concentration irregularities and very local fluctuations, which may be responsible for an additional scattered intensity. Thus, in contrast match conditions, $I_{pp}(q)$ will be expressed as follows:

$$I_{pp}(q) = I_0(q) \cong q^{-4}(1 - \cos qh)\phi_s^2 + I_n$$

and

$$q^4I_0(q) \cong (1 - \cos qh)\phi_s^2 + q^4I_n \qquad (3)$$

where I_n is roughly constant.

As explained in ref 15, in principle, there is no contribution of concentration fluctuations in the cross term I_{pg}. Thus, the scattering due to the small irregularities is negligible in Figure 4, and it appears as a weak rise at very high q in Figure 5.

Therefore, it seems that we can well describe the density profile of grafted PDMS in methanol by a step function and we can neglect the concentration fluctuations in this solvent.

Acetone. We discuss now the results obtained in acetone, which is also a poor solvent for PDMS but which penetrates the polymer more than methanol does. This can be seen in Figure 5 where we show the scattered intensity times q^4 versus q for the same sample in both bad solvents. It is clear that, in acetone, the layer is less dense and extends from the surface up to a greater distance (Table III). However, the main conclusions about the volume fraction profile are the same, although the concentration irregularities become more significant as shown in Figure 6, which presents the data obtained with a grafted polymer of relatively high molecular weight. The scattered intensity has the same law as eq 3, but the constant term I_n is not negligible. It could be determined by a linear plot of $q^4I(q)$ as a function of q^4 (Figure 7) and substracted from the spectrum of Figure 6. One obtains thus Figure 8, where several oscillations appear very clearly.

As in methanol, the contrast variation experiments lead to identical spectra (with similar oscillations). This proves that the density profile is also a step function in acetone, although some deviations from this rough model are possible. Concentration irregularities are small but detectable.

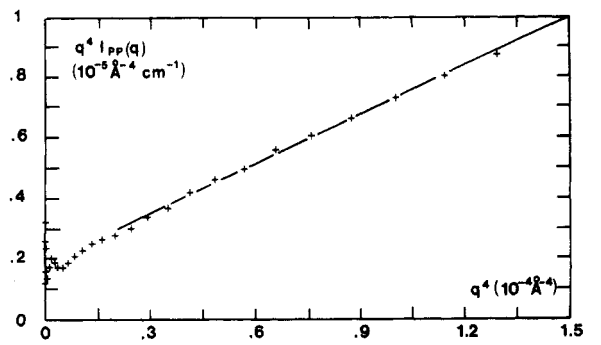

Figure 7. Sample E. Determination of the background in acetone, through a plot of $q^4I_{pp}(q)$ versus q^4.

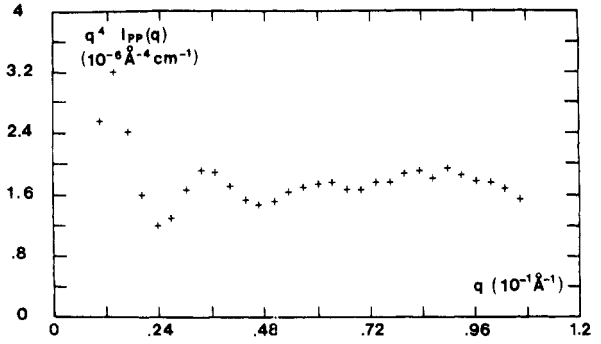

Figure 8. Sample E. Same as in Figure 6, but the weak background has been substracted. At least two oscillations are clearly visible.

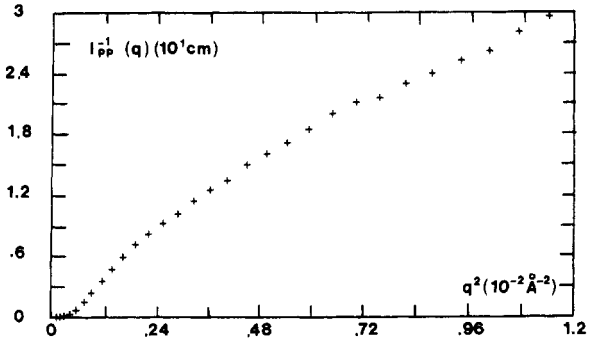

Figure 9. Sample F. Scattered intensity in contrast match condition in dichloromethane. Plot of $1/I(q)$ versus q^2.

Dichloromethane. Contrary to the previous solvent, dichloromethane is a good solvent for PDMS. As shown in Figure 1, the intensity decreases in CH_2Cl_2 much faster than in acetone. This indicates that the chains extend from the surface up to a much greater height in dichloromethane than in acetone. Obviously, as mentioned above, the extrapolated intensity at $q \approx 0$ is the same in both solvents, since it can be related to the amount of grafted polymer.

At high q, in contrast match conditions, the scattered intensity in CH_2Cl_2 decreases very slowly. A typical spectrum is shown in Figure 9 in the representation of $1/I(q)$ as a function of q^2. The data seem to be aligned for sufficiently high q (although some downward curvature should remain). This effect could be assigned to concentration fluctuations. In fact, the observation of the cross term, where the contribution of these fluctuations does not appear, gives completely different results, as shown in Figure 10 (same sample as above).

The scattered intensity exhibits a clear maximum in the representation of $q^4I(q)$ versus q in Figure 10. Then it reaches without further oscillations an horizontal asymptote, in agreement with the expected Porod be-

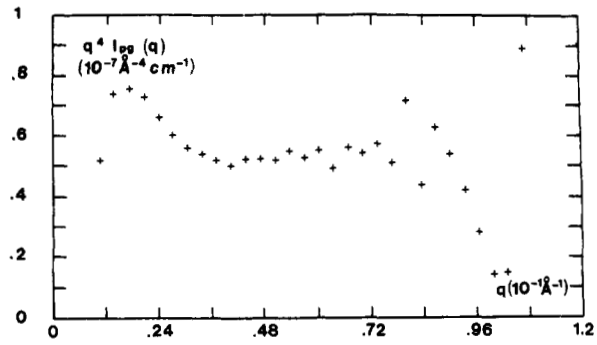

Figure 10. Sample F. Polymer solid cross structure factor in dichoromethane. Plot of $q^4I_{pg}(q)$ versus q.

Table IV
Sample F (M_w = 172 500): Observations in Dichloromethane

	step model		parabolic model	
	data from I_{pp}	data from I_{pg}	data from I_{pp}	data from I_{pg}
Γ, mg/m^2	6.6	5.1	6.6	5.5
$h_{q\to 0}$, Å	294	229	348	281
h_{osc}, Å		189		245
Φ_s		0.33		0.33
$\bar{\Phi}$	0.22	0.22	0.19	0.20
Φ_ξ	0.17		0.17	

havior:

$$I_{pg}(q) \cong -4\pi(S/V)(n_p - n_s)(n_g - n_s)\phi_s q^{-4}$$

This enables a determination of the surface fraction $\phi_s \approx 0.33$, which is much lower than in bad solvent.

It should be mentioned here that is has been necessary to substract from the spectrum of Figure 10 a weak background. The origin of this background is not clear. It could be due to experimental errors. In fact, the contrast variation method involves substraction of data obtained in different contrast conditions. This operation could introduce at high q some artificial noise. But the presence of this weak rise is reproducible and seems to be correlated to the grafting density and to the molecular weight of the polymer. Another explanation could be that the density profile slightly decreases from the surface. This would appear as a weak rise in the representation of $q^4I_{pg}(q)$ versus q. This description seems to be confirmed by the fact that if the silica surface is chemically treated in order to diminish the adsorption, then this surface contribution is less significant.[21]

By comparison with the spectra obtained in bad solvent, it seems that the density profile in good solvent is smoother than a step. In Figure 10, only one oscillation is remaining and the level of the horizontal asymptote is related to only one well-defined discontinuity. When we work out the physical parameters of the grafted layer using the step model, the values are not fully consistent. If we use the parabolic model, then the agreement is improved (Table IV). However, careful examination[15] of the data either in the limit regime of very small q (where we directly measure the four first moments of the density profile) or in the intermediate regime (where we can compare the dampening of the oscillations with theoretical calculations) leads to the conclusion that the density profile $\phi(z)$ of our brushes should decrease very slowly at large z, exhibiting definitively no singularities. This cannot be assigned to polydispersity or to finite length effects. We have no explanation for that. We are not yet able to determine exactly which density profile the grafted layer has.

Finally, using the estimation of ϕ_s obtained as explained above, we can return to the contrast matching experiment.

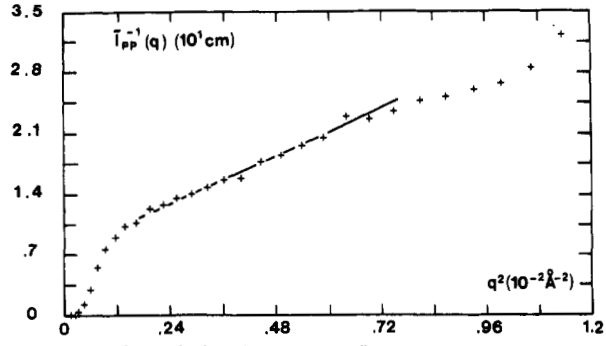

Figure 11. Sample F. Same as in Figure 9 but the scattered intensity of the average profile has been substracted.

The form factor $\bar{I}_{pp}(q)$ at zero contrast is also expected to follow asymptotically Porod's law:

$$\bar{I}_{pp}(q) \approx 2\pi(S/V)\Delta n_L^2 \phi_s^2 q^{-4} \quad (4)$$

This term is not sufficient to explain the slow decay of the scattered intensity at contrast matching. Therefore, it seems to be dominated by the fluctuation term at high q. But both are of the same order of magnitude for intermediate q range. Thus, if we return to the data of Figure 9, we can try to subtract from this spectrum the contribution of eq 4. The result is given in Figure 11. The data are now well fitted by a Lorentzian function:

$$I(q) \approx \frac{a}{(1 + q^2\xi^2)} \quad (5)$$

It is tempting to interpretate this screening length ξ as the typical range of excluded-volume interactions. Inside a blob of size ξ, these interactions are important but vanish at larger scale. For the example of Figure 11, the fit gives

$$\xi \approx 17 \text{ Å}$$

Reminding that the expression (5) for the scattered intensity of semidilute solutions holds if $q\xi \ll 1$, it may be remarked that this latter condition is roughly satisfied for the example of Figure 11 in the whole q range where the data are fitted by a Lorentzian function.

Furthermore, we can deduce from the measurement of ξ an estimation of the mean volume fraction ϕ inside the grafted layer. We have determined the scaling law between ξ and ϕ for semidilute PDMS solutions in dichloromethane[22]

$$\xi \approx 4.68\phi^{-0.74} \qquad \phi \approx 8.05\xi^{-1.35}$$

giving, for the example of Figure 11, $\phi \approx 0.17$. We note that this mean volume fraction is consistent with the original concentration $\phi_0 \approx 0.15$, in which we have performed the grafting reaction. It may be noticed also that it is lower than the surface fraction, estimated from the contrast variation method. This is not surprising, since the bare silica attracts the polymer in dichloromethane.

We remark also that the blob size[23] $\xi_b = 2.86\xi \approx 49$ Å is very close to the distance between grafting sites $D \approx 67$ Å. Thus, we obtain the important result that the grafted layer has almost everywhere a local behavior similar to that of a semidilute solution and the distance between anchored sites seems to be correlated to the concentration in which the grafting reaction has been performed.[24]

Conclusion

The structures of grafted PDMS in the regime of high graft density have been investigated in various solvents, using small-angle neutron scattering techniques. The contrast variation method and the contrast matching

experiments give complementary informations about the density profile and the local behavior of these interfacial layers. In addition to the characterization of the polymer brushes, our work demonstrates the efficiency of the SANS techniques in this particular context. None of the other experimental methods give simultaneously and independently of any model the grafting density, the thickness of the layer, and the surface fraction occupied by the polymer. With SANS, all these basic parameters are determined at least in two different ways and can be compared with each other. Furthermore, SANS provides a unique way for investigating the local structure of the brushes, which reveal a fundamental description of these interfacial layers.

In poor solvent, the data are in good agreement with the step function model. There are two well-defined boundaries that lead to interference phenomena. Concentration fluctuations are in most cases negligible, although some local inhomogeneities could appear.

In good solvent, we have observed that the grafted layer is much less dense and it extends from the surface up to a very great distance (compared to the radius of gyration of the free chains or to case of bad solvent). The surface–monomer attraction induces an accumulation of polymer just near the surface, but this effect seems to have only a slight influence on the brush conformations. Although we are not yet able to determine exactly the right density profile in good solvent, it has been clearly shown that it would be smoother than the step model.

Furthermore, the local behavior is similar to that of a semidilute solution, leading to analogous scattering laws. The measured blob size is very close to the distance between grafting sites D. This would imply a particular scaling law between h, D, and M_w.[25] We have also observed that the mean volume fraction inside the brush is related to the concentration of the solution in which the grafting reaction has been performed.

All these observations lead to a physicochemical description of the polymer brushes in good solvent, which is consistent with the overall picture of Alexander, although the density profile seems to be more complicated.

Acknowledgment. We thank P.-G. de Gennes and J.-P. Cotton for fruitful discussions. We are grateful to J. Dubois from the Centre de Recherches des Carrières (CRC Rhone-Poulenc Recherches, 69192 St. Fons Cedex, France) and to A. Lapp from the Laboratoire Léon Brillouin, who have performed the GPC characterizations. P.A. is especially grateful to Rhone-Poulenc for financial support. The Laboratoire Léon Brillouin is a "laboratoire commun CEA-CNRS" and the Laboratoire de Physique de la matière Condensée is a "unitée associée au CNRS" (URA 792).

References and Notes

(1) Milner, S.; Witten, T.; Cates, M. *Macromolecules* **1988**, *21*, 2160.
(2) Milner, S.; Witten, T.; Cates, M. *Europhys. Lett.* **1988**, *5*, 413.
(3) Muthukumar, M.; Ho, J. *Macromolecules* **1989**, *22*, 965.
(4) Shim, D.; Cates, M. *J. Phys. Fr.* **1989**, *50*, 3535.
(5) Cosgrove, T.; Heath, T.; van Lent, B.; Leermakers, F.; Scheutjens, J. *Macromolecules* **1987**, *20*, 1692.
(6) Murat, M.; Grest, G. *Macromolecules* **1989**, *22*, 4054.
(7) Chakrabarti, A.; Toral, R. *Macromolecules* **1990**, *23*, 2016.
(8) Alexander, S. *J. Phys. (Paris)* **1977**, *38*, 983.
(9) de Gennes, P.-G. *Macromolecules* **1980**, *13*, 1069.
(10) Hadziioannou, G.; Patel, S.; Grannick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.
(11) Taunton, H.; Toprakcioglu, C.; Fetters, L.; Klein, J. *Nature* **1988**, *332*, 712. Taunton, H.; Toprakcioglu, C.; Fetters, L.; Klein, J. *Macromolecules* **1990**, *23*, 571.
(12) Barnett, K.; Cosgrove, T.; Vincent, B.; Burgess, A.; Crowley, T.; King, T.; Turner, J.; Tadros, T. *Polymer* **1981**, *22*, 283.
(13) Cosgrove, T.; Heath, T.; Ryan, K.; Crowley, T. *Macromolecules* **1987**, *20*, 2879.
(14) Crowley, T. Ph.D. Thesis, Oxford, 1984.
(15) Auroy, P. Ph.D. Thesis, Orsay, 1990.
(16) Auvray, L.; Cotton, J. P. *Macromolecules* **1987**, *20*, 202.
(17) A question is the number of ends that are grafted. By comparison with monofunctional PDMS, we have checked that, in the moderate density regime, only one end is attached to the surface. Auroy, P.; Auvray, L.; Léger, L., unpublished results.
(18) Auvray, L. *C. R. Acad. Sci. (Paris), Série II* **1986**, *14*, 859.
(19) des Cloiseaux, J.; Jannink, G. *Les Polymères en solution: leur modélisation et leur structure*; Les Editions de Physique, Les Ulis, France, 1987.
(20) We note l the typical thickness of the grafted layer, obtained directly from the data in the very small angle domain, and h the thickness of the layer, deduced from l, if we assume a particular density profile. Then h is related to l through a numerical coefficient. For example, for a step profile, we have $h = 12^{1/2}l$ (see eq 2). For any other profiles, the numerical coefficient is greater than $12^{1/2}$.
(21) Auroy, P.; Auvray, L.; Léger, L., unpublished results.
(22) We have followed the method of Farnoux for determining this scaling law: Farnoux, B. *Ann. Fr. Phys.* **1976**, *1*, 73. See also ref 19. We note that it is very close to the theoretical prediction $\xi = a\phi^{-0.75}$ in good solvent (a is a monomer size).
(23) Lapp, A. Thèse de Doctorat d'Etat, Strasbourg 1984.
(24) More systematic results supporting this statement will be published in forthcoming papers. Auroy, P.; Auvray, L.; Léger, L. *Macromolecules*, in press.
(25) Auroy, P.; Auvray, L.; Léger, L. *Phys. Rev. Lett.* **1991**, *66*, 719.

Registry No. SiO_2, 7631-86-9.