type and thermal history effects.

The thermal characteristics of PAA(A) and PAA(S) appear to differ significantly with regard to the glass transition temperature (T_g) and thermal stability, i.e., the temperatures at which maximum water evolution (due to anhydride formation) and carbon dioxide evolution (due to anhydride decomposition) occur in the TG–MS experiment. These differences may be a direct consequence of tacticity or possibly an indirect effect due to enhanced hydrogen bonding in the syndiotactic polymer. In either case, variations in polymer tacticity may be the cause of a T_g discrepancy which appears in the literature regarding poly(acrylic acid).

Thermal characterization has also revealed three additional features of PAA: First, for certain combinations of sample type and thermal history, bound-water effects are noted in both tactic forms of the polymer; second, a weak transition, of undetermined origin, occurs in some PAA(S) polymers at a temperature similar to the T_g of PAA(A); third, a pronounced transition of unknown origin occurs at ~135 °C in atactic PAA. On the basis of studies of thermal history effects, this transition does not appear to involve intramolecular anhydride formation. Speculative proposals regarding its origin include some type of less reactive carboxyl groups or an as yet undetermined type of microstructure.

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Self-Similar Structure of an Adsorbed Polymer Layer: Comparison between Theory and Scattering Experiments

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ABSTRACT: We compare the predictions of the scaling theory of polymer adsorption to the neutron-scattering experiments that we have performed on a large molecular weight monodisperse poly(dimethylsiloxane) strongly adsorbed on mesoporous silica in the presence of pure cyclohexane. The contrast variations method has enabled us to isolate in the scattering vector range $10^{-2} < q < 10^{-1}$ Å^{-1}, chosen to probe the inner structure of the adsorbed layer, both the silica polymer cross-structure factor, $S_{pg}(q)$, related to the Sine–Fourier transform ϕ (q) of the polymer concentration profile $\phi(z)$, and the intrinsic structure factor of the layer, $S_{pp}(q)$. The prediction that the structure of the adsorbed layer is self-similar, with a concentration profile decreasing as $z^{-4/3}$, interprets the experimental observation that $\phi(q)$ increases as $q^{0.35\pm0.1}$ in the q range investigated. The contribution to $S_{pp}(q)$ of the fluctuation of polymer concentration in the layer, recently discussed, has, however, not been detected.

I. Introduction

One of the most beautiful predictions of the scaling theory of polymer adsorption[1] is that, in a good solvent, neutral linear long flexible chains strongly adsorbed on a solid wall build a self-similar diffuse layer (Figure 1). At a distance z from the solid, where the average polymer volume fraction is $\phi(z)$, the layer is assimilated to a semidilute solution of correlation length $\xi[\phi(z)]$, predicted to be simply equal to z. The relation $\xi(\phi) = a\phi^{-3/4}$, established for the bulk solutions,[2] then leads to a very singular polymer profile:

$$\phi(z) = (a/z)^{4/3} \qquad (a < z < R) \qquad (1)$$

a is a microscopic length comparable to the monomer size, and R is of the order of the Flory radius of the chains $R = aN^{3/5}$ (N, number of monomers per chain).

So far, this prediction has not been confronted directly by experiment because many techniques[3] used to study adsorbed layers such as spectroscopic techniques[4–6] (in-

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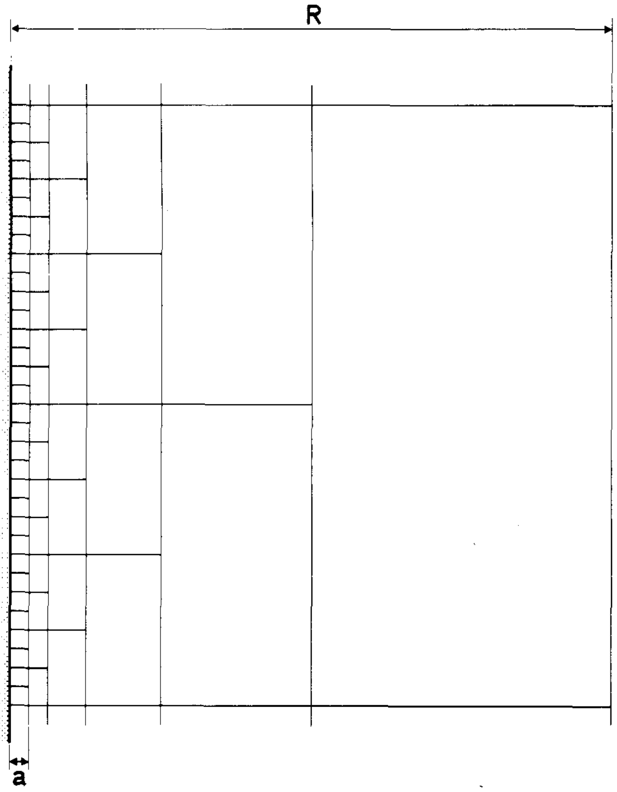

Figure 1. Sketch of the predicted self-similar structure of a layer of strongly adsorbed polymer chains in the presence of a good solvent. At a distance $z < R$ from the wall, the mesh size ξ of the random transient network of chains is of the order of z (after ref 1).

frared, NMR, EPR), hydrodynamic technique,[7,8] and even ellipsometry[9] have not the correct spatial resolution to probe the inner structure of the layers. This is not the case of the small-angle neutron scattering technique, and it was a great advance when the authors of the ref 10–13 showed that it was possible to use neutron scattering to observe adsorbed polymer layers coating colloidal grains. However, although a qualitative agreement with "tails-trains and loops" models[14] of adsorbed polymers was observed, no simple theoretical picture has emerged from the data, which were often taken at low molecular weight.

We present here a comparison between the predictions of the scaling theory of polymer adsorption and the neutron-scattering experiments that we have performed on a large molecular weight polymer adsorbed on mesoporous silica particles in the presence of a good solvent, varying the isotopic composition of the solvent in order to separate the different partial structure factors of the solid and of the adsorbed layer.

The polymer–solid cross-structure factor, which can only be measured in this way, is of particular interest because it is simply related to the Sine–Fourier transform of the polymer average concentration profile. This measurement thus complements the results of the Bristol group,[10–13] which were obtained at contrast matching between the solid and the solvent and which therefore concerned only the intrinsic structure factor of the layer. As explained recently,[15,16] this structure factor is a priori not simply related to the average polymer profile unless one assumes that the adsorbed layer is homogeneous; i.e., one neglects the possibly large concentration heterogeneities and transverse correlations in the adsorbed layer (cf. Figure 1). We thus test also this assumption.

We first recall in section II the general theory of the scattering by an adsorbed polymer layer, discussed and completed in ref 15, as well as the corresponding prediction of the scaling theory, stated in ref 16. The experimental procedure, the silica characterization, the data treatment, and the experimental uncertainties are discussed in detail in sections III, IV.A, and IV.B1. The main physical results on the polymer adsorption layers are presented in sections 2 and 3 of IV.B.

II. Scattering Theory

We consider the scattering by a polymer layer adsorbed on a solid surface (of a porous medium or colloidal grains) in the presence of pure solvent. We note n_p, n_g, and n_s, the scattering length densities of respectively the polymer, the solid, and the solvent. If we assume that the system is isotropic and globally incompressible, the coherent intensity $i(q)$ (in cm^{-1}) scattered per unit sample volume is written as the sum of three terms resulting from the interferences between the amplitudes scattered by the solid and by the polymer:

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

S_{gg}, S_{pg}, and S_{pp} (in cm^3) define the solid–solid, solid–polymer, and polymer–polymer partial structure factors (note the minus sign in front of S_{pg}).

If the inverse q^{-1} of the scattering vector q is small compared to the radius of curvature of the solid surface so that this surface can be considered as flat (but without specific orientation) at the scale q^{-1}, $i(q)$ depends only on the structure of the layer and on the specific area of the solid phase, S/V (S, area of the solid surface; V, sample volume). One then establishes the following expressions:[15]

$$S_{gg}(q) = 2\pi(S/V)q^{-4} \quad (3)$$

$$S_{pg}(q) = 2\pi(S/V)q^{-3}\int_0^\infty dz\ \langle\phi(z)\rangle \sin qz \quad (4)$$

$$S_{pp}(q) = \bar{S}_{pp}(q) + \tilde{S}_{pp}(q)$$

$$\bar{S}_{pp}(q) = 2\pi(S/V)q^{-2}\left|\int_0^\infty dz\ \langle\phi(z)\rangle e^{iqz}\right|^2 \quad (5)$$

$$\tilde{S}_{pp}(q) = 2\pi(S/V)\int_0^\infty \rho\ d\rho\ dz\ dz'\ \langle\delta\phi(0,z)\ \delta\phi(\rho,z')\rangle \times \frac{\sin(\rho^2 + (z - z')^2)^{1/2}}{q(\rho^2 + (z - z')^2)^{1/2}} \quad (6)$$

Each of these terms can be deduced from a series of contrast variation experiments (varying n_s at constant n_g and n_p). We note the following:

1. Equation 3 is independent of the presence of an adsorbed layer and expresses the famous Porod's law.[17]
2. Expression 4 of the cross-structure factor $S_{pg}(q)$ is particularly interesting because it shows that the Sine–Fourier transform of the average polymer profile $\langle\phi(z)\rangle$ is directly measurable.
3. Equations 5 and 6 separate into two terms the intrinsic structure factor of the layer, $S_{pp}(q)$, which is the only nonvanishing contribution to $i(q)$ at contrast matching ($n_s = n_g$). The first term $\bar{S}_{pp}(q)$ (expression 5) describes the contribution of the average polymer profile. The second term, $\tilde{S}_{pp}(q)$ (expression 6), neglected in the experiments performed so far, takes explicitly into account the local deviations of the polymer volume fraction from the average profile, $\delta\phi(\vec{r}) = \phi(\vec{r}) - \langle\phi(z)\rangle$; this last term thus vanishes for a homogeneous layer.

The evaluation of expressions 4–6 according to the scaling theory of polymer solutions has been carried out in ref 16 for the case of a layer of strongly adsorbed polymer in the presence of a good solvent. One separates the Fourier transform of the singular polymer profile (eq 1) into three convergent terms:

$$\int_0^\infty \mathrm{d}z\ \phi(z)e^{iqz} = \int_0^\infty \mathrm{d}z\ \phi(z) + \int_0^\infty \mathrm{d}z\ \phi(z)\ (\cos qz - 1) + i\int_0^\infty \mathrm{d}z\ \phi(z) \sin qz = \Gamma V_0 + a(qa)^{1/3}\Gamma_E(-1/3)e^{-i\pi/6}$$

Γ is the overall polymer surface excess (number of monomers adsorbed per square centimeter, and V_0 is the monomer molecular volume. Γ_E is the Euler Γ function; we will use $\Gamma_E(-1/3) = -4$.

In the range $a < q^{-1} < R$, one predicts

$$S_{pg}(q) = 2\pi(S/V)(2a^4(qa)^{-8/3}) \tag{7}$$

$$\bar{S}_{pp}(q) = 2\pi(S/V)(\Gamma V_0)^2q^{-2}(1 - f(3^{1/2})(qa)^{1/3} + f^2(qa)^{2/3}) \tag{8}$$

with $f = 4a/\Gamma V_0$.

The fluctuation structure factor $\tilde{S}_{pp}(q)$ is deduced from expression 6 by a scaling argument, which yields

$$\tilde{S}_{pp}(q) \sim (S/V)a^4(qa)^{-4/3} \tag{9}$$

According to these predictions, the intrinsic layer structure factor $S_{pp}(q)$ is dominated by a q^{-2} term independent of the inner structure of the layer. For $(qa) < 1$, this structure only appears in corrections, which are of the order of $(qa)^{1/3}$ and $(qa)^{2/3}$ when compared to q^{-2}. This gives an additional reason to perform the contrast variation experiments and to measure $S_{pg}(q)$.

III. Experimental Section

Chemicals. Adsorbent. Instead of using a dispersion of colloidal grains as in previous neutron-scattering studies, we used as solid support a powder made of mesoporous silica grains designed for high-performance liquid chromatography. This powder, whose trade name is Daltosil 3000, was purchased from SERVA. The mesh size of the grain is 0.1–0.2 mm, and the diameter of the pores is given to be 3000 Å. When the sedimentation of the powder in a wetting solvent is complete, the total fraction of space filled by the solvent in the porous medium so formed, determined by volume and weight measurements, is 80 ± 2%. Before any use, the silica was dried during 16 h at 110 °C under high vacuum in order to remove the physisorbed water; this silica (which we will call silica 1) was then conserved under vacuum over a silica gel.

Polymer. The polymer was a high molecular weight (M_w = 270 000), purified, monodisperse (M_w/M_n = 1.2) fraction of an industrial poly(dimethylsiloxane) (PDMS), kindly supplied by A. Lapp from the Centre de Recherches sur les Macromolécules (Strasbourg, France) and Laboratoire Léon Brillouin, who purified, fractionated, and characterized it. The radius of gyration of this polymer in toluene is 253 Å; it is thus much smaller than the pore diameter of the silica.

Solvent. The solvents were either hydrogenated cyclohexane (C_6H_{12}) (spectroscopy grade, Prolabo) or deuteriated cyclohexane (C_6D_{12}) (deuteriation > 99.7%, Service des Molécules Marquées, C.E.A.) or mixtures of both. They were used as received without supplementary drying. We used cyclohexane because it is a very good solvent of PDMS, which wets silica, and because we knew from published adsorption studies[18,19] that PDMS is strongly adsorbed on silica in the presence of similar solvents (hydrocarbons and especially hexane and heptane) and that this adsorption is not too sensitive to traces of moisture. We note x_s, the volume fraction of C_6D_{12} in the H–D mixture. We used seven different mixtures: x_s = 0.3, 0.45, 0.56, 0.65, 0.75, 0.9, and 1.

Sample Preparation. The preparation of the sample containing adsorbed polymer was made as follows: 2 g of dried silica was imbibed directly with 8.5 mL of a PDMS solution in deuteriated cyclohexane prepared at the onset of the semidilute[2] regime ($c = 3 \times 10^{-2}$ g/cm^3). The system was then equilibrated during 3 days with frequent agitation. After the supernatant was removed, the silica was separated in halves. For 3 days, the first half was rinsed with pure C_6H_{12}, while the second half was rinsed with pure C_6D_{12}. The first half was then dried again under vacuum at ambient temperature (silica 2), while the second was kept imbibed by C_6D_{12} (silica 3). We observed that the dried untreated silica (silica 1) was wettable by water, while this was no longer the case with silica 2; we thus are sure that in the treatment the silica has been coated by the polymer.

Finally, for each isotopic mixture, we prepared three samples directly in the quartz cells (2 mm thick) used for the neutron experiments. The first one (belonging to series 1) was a reference sample containing only the dried untreated silica (silica 1) imbibed by pure solvent. The second one (series 2) was made by reimbibing the polymer-coated dried silica (silica 2) by the pure solvent. The third one (series 3) was made in the following manner: 0.4 mL of silica 3, imbibed by C_6D_{12}, was first equilibrated with a given volume of C_6H_{12}, so that the resulting mixture of solvents had nearly the desired isotopic composition; this silica was then rinsed five times with the corresponding isotopic mixture. This procedure, contrarily to the preceding one, thus ensures that the adsorbed polymer layer remains unperturbed.

Neutron Experiments. The neutron experiments were done at Laboratoire Léon Brillouin ("ORPHEE" reactor, Saclay) on the spectrometer "PACE" equipped with an isotropic radial multidetector. The wavelength λ was 5.64 Å (resolution $\Delta\lambda/\lambda$ = 10%), the sample detector distance was 3.10 m, and the range of scattering vector was $0.011 < q < 0.11$ Å^{-1}. After subtraction of the electronic and ambient background noise, the neutron data are put on the absolute scale by using the incoherent scattering of hydrogenated cyclohexane. To study the reproducibility of silica sedimentation and samples filling, the spectra were recorded in multiple runs (two to four) of typically 2 h; the samples were shaken between runs. The scattering length densities are calculated from ref 20. We used the following values (in cm^{-2}): $n_{C_6H_{12}} = -0.279 \times 10^{10}$; $n_{C_6D_{12}} = 6.689 \times 10^{10}$; and $n_{PDMS} = 6 \times 10^8$. With these values, it is useful to express the contrasts in the following way: $n_s - n_g$ (cm^{-2}) $= 6.968 \times 10^{10} (x_s - x_g)$; $n_s - n_p = 6.968 \times 10^{10} (x_s - x_p)$. x_g and x_p are the isotopic compositions of the C_6H_{12}/C_6D_{12} mixture which match respectively the silica and the polymer; $x_p = 0.05$, and x_g will be determined experimentally.

IV. Results and Discussion

A. Characterization of the Solid Phase. The first step of the neutron experiments was to characterize the state of the adsorbent surface without polymer and particularly to determine the solid specific area and scattering length density; the weight density of the silica is between 2.2 and 2.3 g/cm^3,[21] so we expect that the contrast matching composition of the solvent (volume fraction of C_6D_{12}), $x_s = x_g$, will be between 0.54 and 0.56.

If nothing is adsorbed on the solid surface, the total (coherent and incoherent) intensity $i_g(q)$ scattered by the pure solid and solvent (of isotopic composition, x_s) is

$$i_g(q) = (n_g - n_s)^2S_{gg}(q) + B_{inc}(x_s)$$

$B_{inc}(x_s)$ is the isotropic incoherent background. At large angles, $S_{gg}(q)$ must obey Porod's law (eq 3), so that $S_{gg}(q) \sim q^{-4}$. However, we cannot exclude the possibility that there is a small quantity of water or other small impurities adsorbed on the surface or that the O–H surface groups of the silica contribute to the scattering, because they are not contrast matched to the bulk silica. In this case, it is well-known (cf. expression 4 and 5 or ref 22) that a thin surface layer gives a q^{-2} contribution to the scattered intensity. Then $i_g(q)$ has theoretically the general form

$$i_g(q) = A_4(x_s)q^{-4} + A_2(x_s)q^{-2} + B_{inc}(x_s) \tag{10}$$

with

$$A_4(x_s) = 2\pi(n_s - n_g)^2S/V \tag{11}$$

$$A_2(x_s) = 2\pi(S/V)(n_l - n_g)(n_l - n_s)d^2 \tag{12}$$

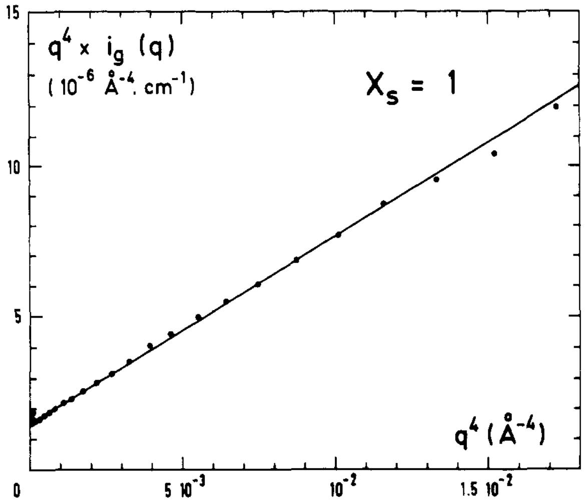

Figure 2. Total coherent and incoherent intensity scattered by the pure solvent and silica (without adsorbed polymers) at strong contrast ($x_s = 1$) in the representation $q^4 i_g(q)$ as a function of q^4.

n_l is the scattering length density of the thin surface layer, assumed to be homogeneous, and d is its thickness. We assume $qd < 1$.

We have fitted expression 10 to the experimental data of series 1 samples in the whole q range with a precision better than 1% (except for the first point), and we have deduced the coefficients A_4, A_2, and B_{inc} for each samples.

We observed that the q^{-2} contribution was completely negligible for the samples with a high silica solvent contrast (x_s = 0.3, 0.75, 0.9, and 1). In this case, $q^4 i(q)$ is theoretically and experimentally a linear function of q^4 (Figure 2). We then conclude that the silica surface is flat and well-defined at the scale 10–300 Å.

Knowing $B_{\text{inc}}(x_s)$ for each x_s, we have determined the scattering length density of the solid by plotting $A_4{}^{1/2}(x_s)$, the square root of Porod's coefficient, as a function of x_s. This quantity is theoretically and experimentally a linear function of x_s (Figure 3). The intercept with the x_s axis defines x_g, the isotropic composition of the solvent which matches the silica. Experimentally $x_g = 0.54 \pm 0.01$; this is the value corresponding to the lower silica density d = 2.2 g/cm^3.

Knowing x_g and n_g, we then deduced the silica specific area from the measurements of the coefficients $A_4(x_s)$ and we found

$$S/V = 2.5 \pm 0.2 \text{ m}^2/\text{cm}^3$$

We note that the length V/S = 4000 Å is of the same order of magnitude as the pore diameter given by the silica fabricant.

The q^{-2} contribution to $i_g(q)$ is definitely nonvanishing for the low-contrast samples (x_s = 0.45, 0.56, and 0.65). This term is experimentally the largest for the almost contrast-matched sample $x_s = 0.56$. One measures A_2 (x_s = 0.56) = 3×10^{11} cm^{-3}. There is thus a small contribution of a thin surface layer to the scattering. Comparing the experimental value of A_2 (0.56) with the theoretical expression 12 and assuming $n_l = 0$ (this surface layer scattering length density corresponds to a hydrogenated compound attached to the silica surface), we found $d \simeq 4$ Å. This thickness indeed corresponds to the width of either an adsorbed water molecule or an O–H silanol group.

The presence of this thin scattering layer, neglected in expressions 4–9, could in principle cause trouble in the interpretation of the scattering experiments on the adsorbed polymers. We will, however, neglect it in the following, checking that its contribution is much smaller than that of the polymer (see note 23).

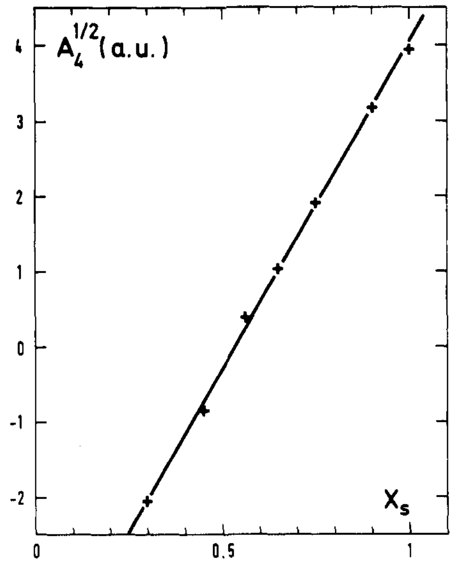

Figure 3. Plot of $A_4{}^{1/2}(x_s) = [2\pi(S/V)]^{1/2}(n_s - n_g)$, square root of the Porod's coefficient of series 1 samples, as a function of the isotopic composition of the solvent, x_s.

B. Scattering Study of the Adsorbed Polymer Layer. 1. Order of Magnitude. Data Treatment. Experimental Uncertainties. Recalling that the total coherent and incoherent scattered intensity of the porous polymer-coated silica (samples of series 2 and 3) is written

$$i_{\text{ads}}(q,x_s) = (n_g - n_s)^2 S_{gg}(q) - 2(n_p - n_s)(n_g - n_s)S_{pg}(q) + (n_p - n_s)^2 S_{pp}(q) + B_{\text{inc}}(x_s)$$

and that the intensity scattered by the pure solid and solvent (series 1 samples) is

$$i_g(q,x_s) = (n_g - n_s)^2 S_{gg}(q) + B_{\text{inc}}(x_s)$$

We find the simplest method of evaluating $S_{pg}(q)$ and $S_{pp}(q)$ is to form the difference $\Delta i(q,x_s) = i_{\text{ads}}(q,x_s) - i_g(q,x_s)$ and to solve for each q value a overdetermined system of n equations with two unknowns. This, however, assumes that the two areas S and S' of the silica in the two samples (and the two incoherent backgrounds, B_{inc} and B'_{inc}) are equal. If this is not the case then

$$\Delta i(q,x_s) = 2\pi V^{-1}(n_g - n_s)^2(S - S')q^{-4} - 2(n_p - n_s) \times (n_g - n_s)S_{pg}(q) + (n_p - n_s)^2 S_{pp}(q) + B_{\text{inc}}(x_s) - B'_{\text{inc}}(x_s)$$

The data treatment is meaningful only if the first and fourth terms are negligible relative to the second and third. In fact, observing the same samples shaken between runs, we noticed that the relative variations of the intensity scattered by the pure solid could be as large as 5%. These fluctuations of $i_g(q,x_s)$ are to be compared to the signal of the polymer.

We observed that, for $x_s < 0.75$, $\Delta i(q,x_s)$ was positive, while for $x_s \geq 0.75$, $\Delta i(q,x_s)$ was negative (Figure 4). This is in agreement with the theoretical predictions[16] concerning the sign of the effect of the adsorbed polymer: $S_{pp}(q)$ and $S_{pg}(q)$ are theoretically positive; for $n_s < n_g$ the cross term $-2(n_p - n_s)(n_g - n_s)S_{pg}(q)$ is negative and dominates at sufficiently large contrast.

Regarding the relative magnitude of $\Delta i(q,x_s)$ and $i_g(q,x_s)$, we observed the following: at strong contrast (x_s = 0.9 and 1), the value of the experimental ratio $|\Delta i(q,_s)|/i_g(q,x_s)$ is at most 10%; at medium contrast (x_s = 0.3 and 0.75), this value is at most 20%; and at small contrast (x_s = 0.45, 0.56, and 0.65), it is at most 50%. Thus a variation of 5% of the solid specific area leads to an uncertainty on $\Delta i(q,x_s)$

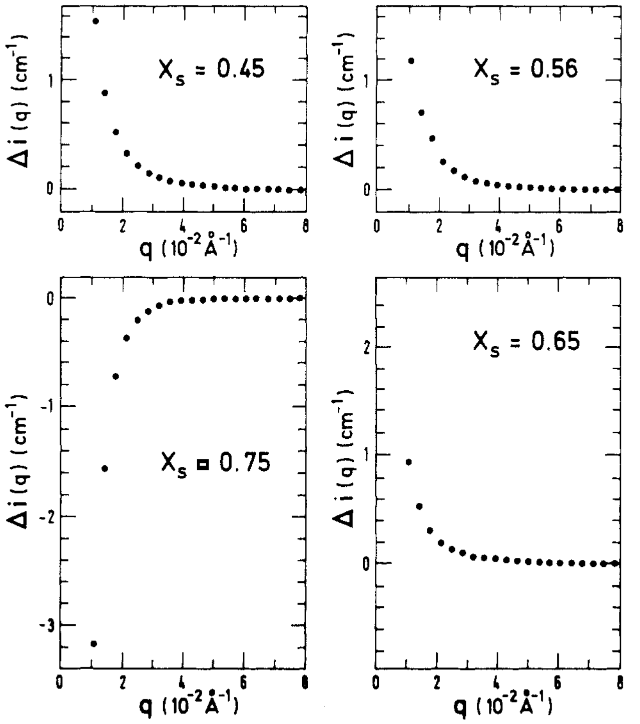

Figure 4. Difference, $\Delta i(q)$, between the intensity scattered by the polymer-coated silica and the intensity scattered by the silica without polymer, as a function of q, for four different contrasts corresponding to the solvent isotopic composition $x_s = 0.45$, 0.56, 0.65, and 0.75. Only the first 20 experimental points have been displayed.

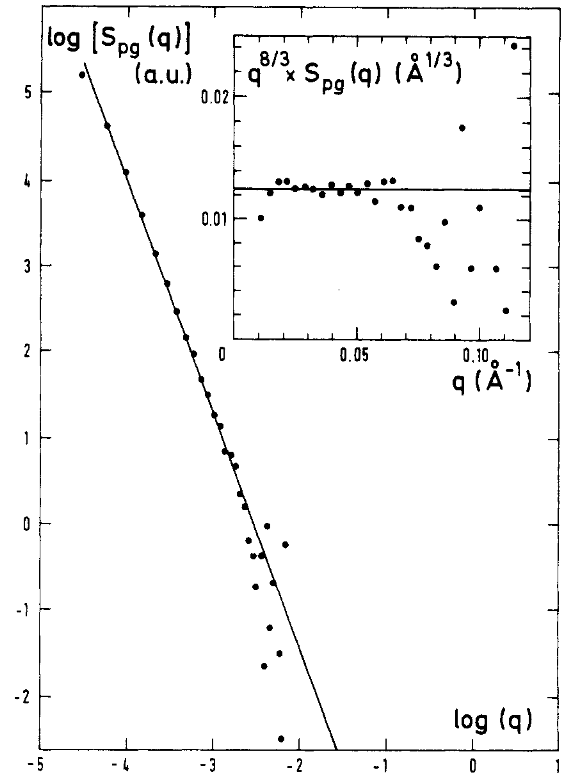

Figure 5. Logarithm of the polymer solid cross-structure factor $S_{pg}(q)$ as a function of the logarithm of the scattering vector. In the insert, $q^{8/3}S_{pg}(q)$ as a function of q.

that is 50% at strong contrast, 25% at medium contrast, and 10% at small contrast. Indeed we found a good reproducibility of the data only at small contrast. Contrary to what was believed in ref 16, it is not a good procedure with the present system to use the largest possible contrasts to measure the function $S_{pg}(q)$.

This opinion was reinforced by comparing the sample of series 2, where the polymer layer had been dried one time, to the samples of series 3, where the layer had remained unperturbed. The signal of corresponding samples with the same x_s in the two series was the same (within 5%) only for the lowest contrasts ($x_g = 0.45$, 0.56, and 0.65). This shows that the adsorbed layer in these samples is not destroyed by the operations of drying and rewetting and that its structure is not changed after the whole process.

As a consequence of all these observations, we have finally averaged the spectra of series 2 and 3 to diminish further the statistical uncertainty, and we have determined the two functions $S_{pg}(q)$ and $S_{pp}(q)$ by solving for each q with a least-squares method the overdetermined system of three equations with two unknowns provided by the experimental values of $\Delta i(q,x_s)$ for $x_s = 0.45$, 0.56, and 0.65.

We then have recalculated $\Delta i(q,x_s)$ from the determined values of $S_{pg}(q)$ and $S_{pp}(q)$. The relative deviations between the experimental and reconstructed $\Delta i(q,x_s)$ are better than 10% for $q < 0.08$ Å^{-1} (i.e., for the first 20 experimental points); for the last 10 points ($q > 0.08$ Å^{-1}), these relative deviations are between 10 and 100%.

Such a lack of precision is not astonishing because the coherent scattered intensity in the last 10 channels is smaller than 10^{-2} cm^{-1}, and the signal-to-noise ratio defined as the ratio of the coherent over the incoherent intensity is of order 10^{-2}. This is the present limit of sensitivity of the small-angle neutron scattering method.

2. Solid Polymer Cross-Structure Factor, $S_{pp}(q)$. The predictions of eq 7–9 of the scaling theory have been established by assuming that the scattering vector q is in the intermediate range, $qR \gg 1$, R being of the order of the radius of gyration of the dilute polymer chain in a pure (good) solvent. We first checked that this conditions was fulfilled experimentally by observing in an independent experiment the scattering of a dilute PDMS solution in C_6D_{12} ($c = 3 \times 10^{-3}$ g/cm^3). The well-known law $i(q) \sim q^{-5/3}$ ^{2} was verified in the range $0.014 < q < 0.11$ Å^{-1}. In this range, we thus explore the inner structure of the polymer chains.

Experimentally, $S_{pg}(q)$, determined as explained in the preceding paragraph, is a rapidly decreasing function of q. The experimental results are displayed on Figure 5 in a log–log representation. We observe that log $S_{pg}(q)$ is a linear function of log (q) in the domain $-4.5 < \log q < -2.5$, corresponding to the first 20 experimental points where the signal-to-noise ratio is sufficiently high. We thus write in this range

$$S_{pg}(q) = Cq^{-b}$$

Experimentally

$$b = 2.65 \pm 0.1$$

$$c = (1.25 \pm 0.1) \times 10^{-2} \text{ Å}^{1/3}$$

To estimate the uncertainties in the above results, we made all the possible determinations of $S_{pg}(q)$ by solving simply the different systems of two equations with two unknowns associated to the experimental values of $\Delta i(q,x_s)$ for three couples of samples: $x_s = 0.45$ and 0.56, 0.56 and 0.65, and 0.45 and 0.65. The announced uncertainties represent the dispersion observed in these different determinations of $S_{pg}(q)$.

Comparing the experimental results with the prediction of eq 7, $S_{pg}(q) = 2\pi(S/V)(2a^4)(qa)^{-8/3}$, we see that the agreement is excellent (cf. the insert of Figure 5, where the experimental quantity $q^{8/3}S_{pg}(q)$ is plotted as a function of q). Knowing experimentally S/V and the prefactor C

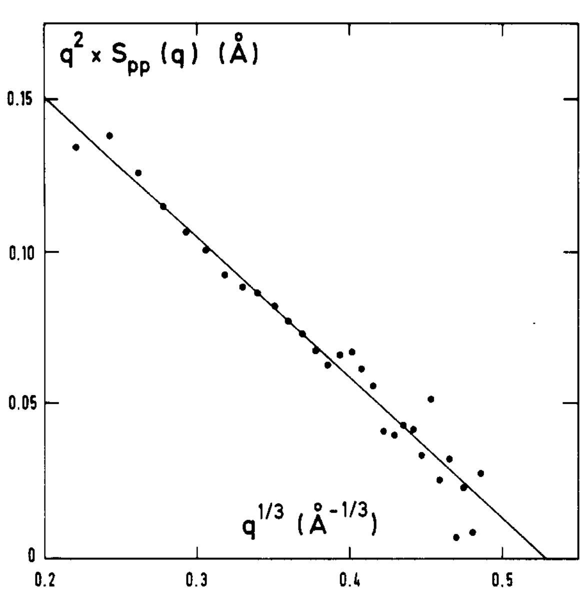

Figure 6. Intrinsic structure factor of the adsorbed layer $S_{pp}(q)$ in the representation $q^2S_{pp}(q)$ as a function of $q^{1/3}$.

$= 4\pi S/Va^{4/3}$, we deduce that the length a introduced as a lower cutoff in the theory has the experimental value

$$a = 3 \pm 1 \text{ Å}$$

As expected, a is a microscopic length of the order of the monomer dimension. We thus obtain the first evidence that PDMS is strongly adsorbed on silica, in the presence of cyclohexane, and that the scaling theory of the corresponding case correctly describes the structure of the adsorbed polymer layer. Experimentally, in the q range investigated the Sine–Fourier transform $\phi(q)$ of the polymer profile $\phi(z)$ obeys the law $\phi(q)\ \alpha\ q^3S_{pg}(q) \propto q^{0.35\pm0.1}$, in agreement with the prediction $\phi(z) \propto a^{-4/3}$ and $\phi(q) \propto q^{1/3}$.

3. Layer Intrinsic Structure Factor, $S_{pp}(q)$. Expressions 8 and 9 predict that the structure factor of the polymer layer $S_{pp}(q)$ is written

$$S_{pp}(q) = 2\pi(S/V)(\Gamma V_0)^2q^{-2}[1 - (4(3^{1/2})a/\Gamma V_0)(qa)^{1/3} + \lambda(qa)^{2/3}]$$

where λ is an unknown constant.

We thus have plotted on Figure 6 the experimental quantity $q^2S_{pp}(q)$ as a function of $q^{1/3}$. We observe a linear dependence

$$q^2S_{pp}(q) = Y(1 - Rq^{1/3})$$

with $Y = 0.24 \pm 0.02$ Å and $R = 1.9 \pm 0.2$.

Again, the theory correctly describes the experimental data.[23] We note, however, that we do not observe the term in $S_{pp}(q)$ which is predicted to vary as $q^{-4/3}$ and which is theoretically the sum of a contribution of the average profile and a contribution of the polymer concentration fluctuations in the adsorbed layer. In the q range observed, these fluctuations appear to be negligible. Clearly, other experiments with a wider q range and a lower signal-to-noise ratio at large angles are needed to study them.

Comparing the experimental values of the coefficients Y and R to their theoretical expressions and using $V_0 = 123$ Å as the PDMS monomer molecular volume, we obtain the total polymer coverage Γ and a new determination of the length a:

$$\Gamma = 0.1 \text{ monomer/Å}^2 = (1.2 \pm 0.1) \times 10^{-7} \text{ g/cm}^2$$

$$a = 2.5 \pm 1 \text{ Å}$$

This value of a is consistent with the precedent determination from $S_{pg}(q)$, and the value of Γ is of the same order of magnitude as those reported for the systems PDMS–glass–heptane[18] and PDMS–silica–hexane.[19]

Conclusion

The contrast variation experiments that we have performed show that large molecular weight chains of PDMS are strongly adsorbed on silica from cyclohexane solutions. In the observed range of scattering vectors, chosen to probe the inner structure of the adsorbed layer in the presence of pure solvent, the two scattering functions of the layer are well described by the scaling theory of polymer solutions and the resulting picture of a self-similar transient network of adsorbed chains. In particular, the Sine–Fourier transform of the average concentration profile of the layer has been measured directly for the first time and is found to increase as $q^{0.35\pm0.1}$, in agreement with the theory.

It must be the aim of future studies to investigate other systems, to increase the signal-to-noise ratio, and to widen the domain of scattering vectors in order to check the universality of the observed laws and to test the existence of concentration fluctuations in the adsorbed layer, which is predicted by the theory but not evidenced experimentally.

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(23) We remark that A, the coefficient of the q^{-2} contribution to the scattered intensity arising from $S_{pp}(q)$, $A = (n_s - n_p)^2Y$, has the value $A = 3 \times 10^{12}$ cm^{-3} for the sample $x_s = 0.56$. The q^{-2} contribution of the polymer to the scattered intensity is then 10 times larger than the contribution of the water or silanol surface layer of silica discussed in section IV.A; this justifies our use of only three partial structure factors.