The study of grafted polymer layers by neutron scattering

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Abstract. The structure of layers of poly(dimethylsiloxane) terminally grafted on silica has been studied by small angle neutron scattering. We have observed the influence of the polymer molecular weight, the grafting density and the solvent quality. At a high grafting density, in good and in bad solvents, the chains are stretched and the thickness of the layers is proportional to the polymer mass. In a good solvent the inner structure of the layers is similar to that of a semi-dilute solution of free polymer at the same local concentration, in agreement with the description of Alexander.

1. Introduction

Polymer chains can be attached to a solid surface by adsorption or by grafting. Adsorption [1] concerns all monomers, which are attracted to the wall by van der Waals or hydrogen interactions. Grafting is achieved in different ways: strong adsorption of a polar end group [2] or chemical reaction [3] of one functionalized end of the chains with reactive groups of the surface. If the grafting density is high so that the chains overlap and if the monomer adsorption is negligible, one expects to get a polymer brush of extended chains, first described by Alexander [4]. Both processes have important applications particularly in the stabilization of colloidal suspensions.

The structure of these diffuse interfacial polymer layers was first studied by spectroscopic and hydrodynamic techniques [1] yielding either local information (e.g. number of monomers in contact with the surface) or integrated information (adsorbed amount, hydrodynamic thickness of the layers). More recently techniques more sensitive to the details of the monomer density profile have been developed: direct force measurements [2], neutron reflectometry [5] and neutron small angle scattering [6, 7]. They have been mainly applied to adsorbed layers and in a few cases to grafted layers, but no complete picture has yet emerged.

One of us, P Auroy, has recently succeeded in grafting large molecular weight poly(dimethylsiloxane) (PDMS) chains on silica and in achieving a high surface density. We have performed a complete study of the structure of these layers in relation to the physicochemical aspects of the grafting reaction using neutron small angle scattering.

Detailed accounts of these results will be published elsewhere [8] but here we will focus on two points described a long time ago but never observed: the mass dependence of the layer thickness and the internal structure of the grafted layers in a good solvent.

2. Sample and experiments

Small angle scattering studies of interfacial layers require a sufficiently large amount of interface per unit volume. The solid substrate is a powder of porous silica such as that used in previous adsorption studies [7]. The nominal pore diameter is 3000 Å and the specific area is 2.5 m^2 cm^{-3}. The polymers are fractionated monodisperse PDMS chains terminated by silanol groups at both extremities. Typical polydispersity is 1.1 and the molecular weight ranges between 24 000 and 593 000.

The grafting reaction is a condensation reaction between a silanol group of the surface and a silanol end of a polymer chain. Unless otherwise stated, the reaction is performed in a concentrated solution of PDMS ($c = 0.15$ g ml^{-1}) in heptane under reflux for at least 24 h. For certain samples the silica has been pretreated by a grafting reaction with pentanol in order to diminish the spontaneous adsorption of PDMS onto silica. After reaction the silica is rinsed with pure dichloromethane, to remove the free polymer, and dried. Before the experiments the samples are reimbibed by solvents of chosen isotopic composition: a good solvent, dichloromethane, and bad solvents, acetone or methanol.

The neutron scattering experiments were carried out at Laboratoire Léon Brillouin on the spectrometer PACE. In most experiments the observed range of scattering vector was $10^{-2} \leqslant q \leqslant 10^{-1}$ Å^{-1} and when needed $3 \times 10^{-3} \leqslant q \leqslant 3 \times 10^{-2}$ Å^{-1}. In this range the scattering vector is still larger than the curvature of the pores; therefore the scattering intensity only depends on the specific area and on the interfacial structure. The corresponding formalism is described in [7]. Let us recall that our aim is to measure the two partial structure factors of the polymer layer: the polymer–polymer structure factor S_{pp} obtained by contrast matching between the solvent and the silica, and the polymer–solid cross-structure factor S_{pg} obtained from a complete contrast variation experiment. These structure factors are related to the profile of the polymer volume fraction $\Phi(z)$ and to the density–density correlation function in the polymer layer by the expressions:

$$S_{pp}(q) = \overline{S_{pp}}(q) + \widetilde{S_{pp}}(q) \tag{1}$$

$$\overline{S_{pp}}(q) = 2\pi(S/V)q^{-2} \left| \int_0^\infty \mathrm{d}z\, \Phi(z)\, \mathrm{e}^{\mathrm{i}qz} \right|^2 \tag{2}$$

$$\widetilde{S_{pp}}(q) = (S/V) \int \mathrm{d}z_1\, \mathrm{d}r_2\, \langle \delta\Phi(0, 0, z_1, \delta\Phi(r_2)\rangle \frac{\sin qr_{12}}{qr_{12}} \tag{3}$$

$$S_{pg}(q) = 2\pi(S/V)q^{-3} \int_0^\infty \mathrm{d}z\, \Phi(z) \sin qz. \tag{4}$$

3. Results and discussion

3.1. Measure of the grafted amount and layer thickness

Although this is probably not quite correct [9], we use the step profile originally introduced by Alexander to interpret our data at very small angles. Assuming that $\Phi(z)$ is a
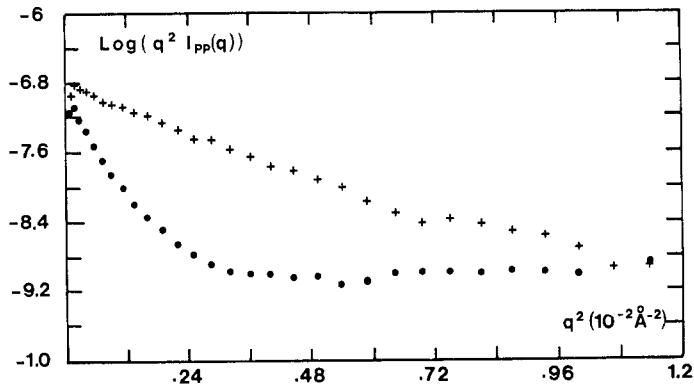
Figure 1. Scattering intensity under contrast match conditions in the form $\ln q^2 I(q)$ as a function of q^2. $M = 26\,000$; +, acetone; ●, dichloromethane; $\gamma = 52$ Å.

constant for z smaller than h, the thickness of the layer, and neglecting the contribution of the correlation term, expression (2) is reduced to the following formula, valid for $qh < 1$:

$$q^2 S_{pp}(q) = 2\pi(S/V)\gamma^2(1 - q^2h^2/12).\tag{5}$$

γ is the amount grafted in units of volume fraction.

On figure 1 we have plotted the intensity scattered under the contrast matching condition using $\ln q^2 I_{pp}(q)$ as a function of q^2. The data are obtained with a relatively low molecular weight polymer in good (dichloromethane) and bad (acetone) solvents. The linear behaviour of equation (5) is perfectly observed. Both curves extrapolate to the same point corresponding to the grafted amount γ. From γ we deduce the distance between the grafting points D because γ is proportional to the product D^2M. From the slope we measure the thickness of the layers, very different in good and bad solvents, the swelling effect of the good solvent being quite spectacular.

3.2. Variation of the layer thickness with molecular weight in a good solvent

In a good solvent as soon as the chains in the grafted layer overlap they repel each other by excluded volume interactions and adopt a stretched configuration, which has been described both by mean field [4, 9] and scaling [4] theories. The balance between the elastic energy of the chains and the excluded volume interactions leads to the following scaling relation between the layer thickness, h, the index of polymerization of the chains, N, and the distance between grafting points, D:

$$h \sim Na(a/D)^{2/3}.\tag{6}$$

a is a molecular length of the order of the monomer size.

We have thus plotted the experimental data h and D in the form $hD^{2/3}$ as a function of the molecular weight M (figure 2). We observe a proportionality which is in excellent agreement with the theoretical prediction. The fit yields: $hD^{2/3} = 0.045M$. Rewriting
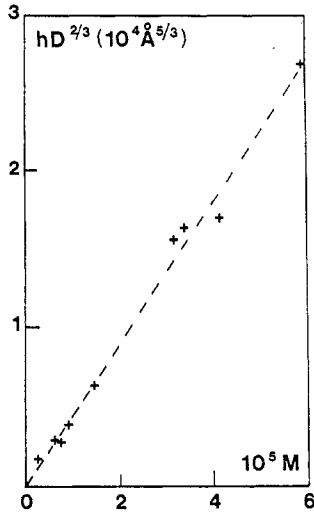
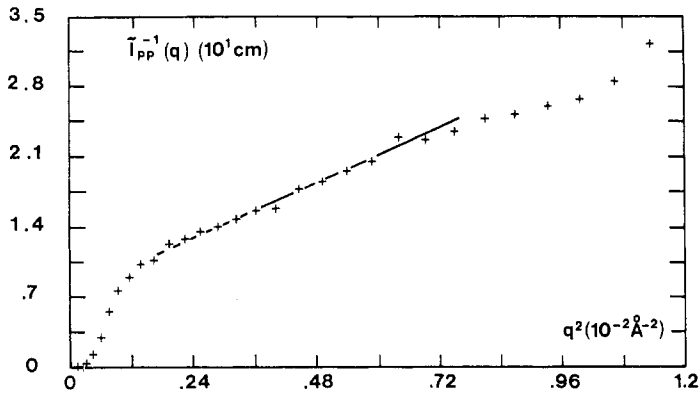**Figure 2.** Plot of $hD^{2/3}$ against M for grafted PDMS layers in a good solvent (dichloromethane).

Figure 3. Correlation term $\tilde{S}_{pp}(q)$ in the form $1/\tilde{I}$ as a function of q^2 ($M = 173\,000$, $\gamma = 65$ Å, $h = 290$ Å in dichloromethane).

this equality in terms of N as $hD^{2/3} = a^{5/3}N$, we obtain $a = 2.1$ Å, which is indeed of the same order of magnitude as a monomer size.

3.3. Correlations inside a layer

Finally we want to emphasize the fact that the concentration profile does not exhaust the description of polymer brushes. Returning to the picture of Alexander we expect that overlapping stretched chains can be considered as linear strings of blobs of size D, the distance between grafting points. Excluded volume correlations are important inside a blob, but totally screened at larger scales. Thus by analogy with bulk semi-dilute polymer solutions, the correlation term of the polymer structure factor $\tilde{S}_{pp}$ could be described by a Lorentzian contribution:

$$\tilde{S}_{pp}(q) \sim 1/(1 + q^2D^2).$$

We have plotted, on figure 3, the contribution of the correlation term $\tilde{S}_{pp}$ in the form

$1/\widetilde{S_{pp}}$ as a function of q^2. This term was obtained by subtracting the contribution of the average profile $\overline{S_{pp}}$ from the total measured structure factor S_{pp}. The former, for a thick layer, follows an asymptotic Porod behaviour in most of the observed range: $\overline{S_{pp}}(q) = 2\pi(S/V)\Phi_s^2 q^{-4}$, where Φ_s is the volume fraction of polymer at the surface. We know that $\overline{S_{pp}}$ follows this behaviour by observing the corresponding behaviour on the cross structure factor S_{pg}, $S_{pg}(q) = 2\pi(S/V)\Phi_s q^{-4}$ (not reported here). We thus also determine Φ_s, experimentally $\Phi_s = 0.33$, a rather large value indicating some additional adsorption of the polymer. The data are well fitted by a Lorentzian function

$$\widetilde{I_{pp}}(q) \propto \widetilde{S_{pp}}(q) \propto 1/(1 + q^2\xi^2)$$

with $q\xi < 1$ and $\xi = 17$ Å. This value of ξ corresponds to an equivalent volume fraction $\Phi = 0.17$ close to the original concentration of the reaction bath. We thus show that the grafted layer has locally the same structure as a semi-dilute solution of equivalent concentration.

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