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STRUCTURES AND PHYSICOCHEMISTRY OF COVALENTLY GRAFTED LAYERS REVEALED BY SMALL ANGLE NEUTRON SCATTERING STUDIES

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ABSTRACT

Using small angle neutron scattering techniques, we have studied the structure and the physicochemistry of grafted layers. Various short chains and polydimethylsiloxane polymers have been attached onto a model porous silica. The effect of the solvent quality, of the grafting density, of the surface chemistry... have been observed.

1. INTRODUCTION

In the last ten years, two experimental techniques has been revealed as especially efficient in investigating interfaces: the surface force apparatus[1] and the small angle neutron scattering[2] (SANS) technique. The latter, though more indirect and sometimes less sensitive, does however allow to probe locally the inner structures of the interfaces without any external perturbation.

In this paper, we report some results we have obtained with the SANS technique on grafted layers. Our experimental system has allowed to do an exhaustive characterization of these interfaces. It will be described in section 2. In the **third** part, we present the results given by thin layers. The case of grafted polymer (thick) layer is more complicated. The grafting density, the solvent play an important role and induce completely different scattering laws (section 4). In the **fifth** part, we present results that stress the difference between adsorption and grafting and in the last section (6), some details of the physicochemistry of grafting will be discussed.

2. EXPERIMENTAL SECTION

The experimental system has been extensively described elsewhere[3-4]. The substrate was porous silica (Daltosil™ 3000 - Specific area: 2.5 m^2/cm^3. Mean diameter of the pores: 3000Å). In a few cases we have also used suspensions of silica particles synthetized following the method of Stöber and van Helden[5] (typical diameter: 2000Å. Polydispersity: less than 1.1). We have grafted onto the silica surface either small molecules (n-alcohols -pentanol, stearyl alcohol- trimethylchlorosilane, octadecylchlorosilane) or long polydimethylsiloxane (PDMS) chains (typical polydispersity: 1.1), carrying one or two -OH end-groups. The polymer naturally adsorbs onto the porous silica. Partial pretreatment using small molecules has been sometimes performed before the polymer grafting in order to prevent this adsorption. This will be further explained in section 5.

The grafting reaction are somewhat classical and the procedures have been already described[3-4].

The neutron scattering experiments have been carried out at the Laboratoire Léon Brillouin with the PACE spectrometer. We recall that the silica can be matched by a suitable isotopic mixture of various solvents. Under this latter condition (contrast matching), the scattering intensity comes only from the interface. Varying the contrast enables the determination of the cross term from which one gets complementary information about the interfacial density profile. For the data treatment, we have followed the general procedures described in reference 4.

3. THE SCATTERING FROM THIN LAYERS

We assume that the curvature of the interface is much smaller than the inverse of the scattering vector q^{-1} so that it can be considered as flat. If the layer is thin compared to q^{-1}, it has been shown[4] that the scattering intensity I(q), under contrast matching condition, is given by:

$$I(q) = \kappa^2 q^{-2} \Gamma^2 \left(1 - \frac{q^2h^2}{\alpha}\right) \qquad (1)$$

κ is a constant term related to the specific area of the sample and to the difference between the neutron refractive index of the solvent and of the grafted molecules. α is a geometrical coefficient related to the whole shape of the interfacial profile. In many cases, it is valid to assume that it is a step for which $\alpha=12$. Γ is the amount of attached material per unit area.

In figure 1, we have plotted $q^2I(q)$ vs q^2 for different thin grafted layers made with small molecules.

For every samples, the equation (1) is valid in the whole q-range and we can accurately determine both the grafting density and the thickness of the interface. For instance the ■ symbols correspond to a layer of octadecyl chains

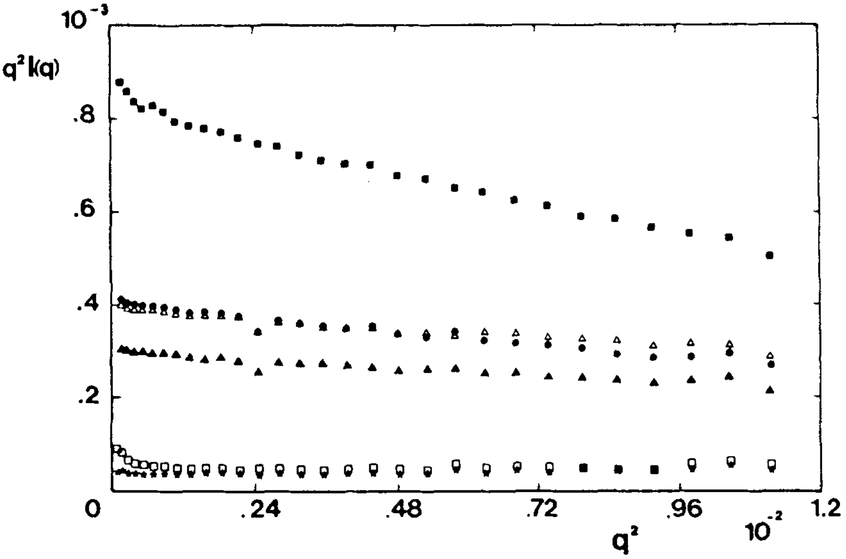

Figure 1 Plot of $q^2I(q)$ vs q^2 for thin layers immersed in dichloromethane. (Units: I in cm^{-1}, q in $Å^{-1}$)
★ : pentanol. □: trimethylsilane. ▲: stearyl alcohol (1h treatment). △: stearyl alcohol (2h treatment). ●: stearyl alcohol (24h treatment). ■: octadecylsilane.

obtained following the method of Silberzan et al[6]. From this spectrum one gets: Γ=1.9 mg/m^2 or Γ=21.1Å and h=22Å. These data are in good agreement with the picture of a dense monolayer of C_{18}-chains, stretched perpendicularly to the silica surface. However, it can be noticed that the data deviate slightly from the straight line in the very low q domain. This could be ascribed to some defects in this interface, namely to the presence of multilayered patches. Nevertheless they seem to be rather scarse and it can be concluded that this interface is seen by our SANS experiment as a nearly perfect monolayer of C_{18}-chains.

The three curves (▲, △ and ●) show the kinetics of grafting of stearyl alcohol and the last symbols (□ and ★) are related to very thin layers (a few Å) obtained with trimethylsilane and n-pentanol respectively. They stress roughly the lower limit of resolution of our experiments.

4. THE SCATTERING FROM POLYMER LAYERS

The main difference of the grafted polymer layers with the previous interface is that the solvent quality plays now an important role. In figure 2 we

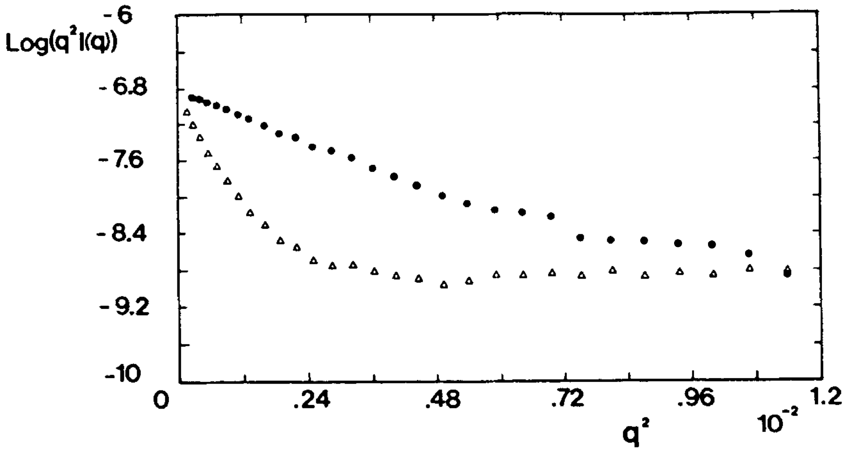

Figure 2 Plot of $Log(q^2I(q))$ vs q^2 for the same sample immersed in acetone (●) and in dichloromethane (△). Units: same as above. The PDMS has been grafted in a 15% solution in heptane. After grafting, all the chains which have not reacted have been washed out. The polymer had a molecular weight M_w = 34 500 and a polydispersity of 1.09 . From the spectra, one gets: $\Gamma=1.97$ mg/m^2 , thickness in acetone: $h_{acet.}=55Å$, thickness in dichlromethane: $h_{dichlo.}=128Å$

have reported the results given by the same PDMS grafted layer immersed in two different solvents: in acetone (●) and in dichloromethane (△) which are respectively a poor and a good solvent for PDMS.

It can be easily seen that both spectra extrapolate to the same point at $q \approx 0$ that is related to the amount of polymer per unit area Γ and is indeed independent of the solvent. But the slopes of the decay are very different: in good solvent, the interface is swollen and its thickness is more than two times greater than in poor solvent.

In the intermediate q-range (where equation **1** is no longer valid), we observe very different scattering laws depending on the solvent quality. In poor solvent, the interface is dense, homogeneous and the shape of its density profile is a step. This leads to interference phenomena, the neutrons being coherently scattered by two sharp boundaries: the solid-polymer and the polymer-solvent discontinuities. In good solvent, the scattering seems to be dominated by concentration fluctuations. As it can even be seen in figure 2, the scattering intensity decreases very slowly in the intermediate q-range. A more precise analysis[4] tells us that it follows a lorentzian law whose screening length is close to the average distance between grafting points, in agreement with the Alexander-de Gennes brush model[7]. The interfacial density profile is definitively not a step; the parabolic model, proposed by Milner et al.[8] provides a better agreement with the data.

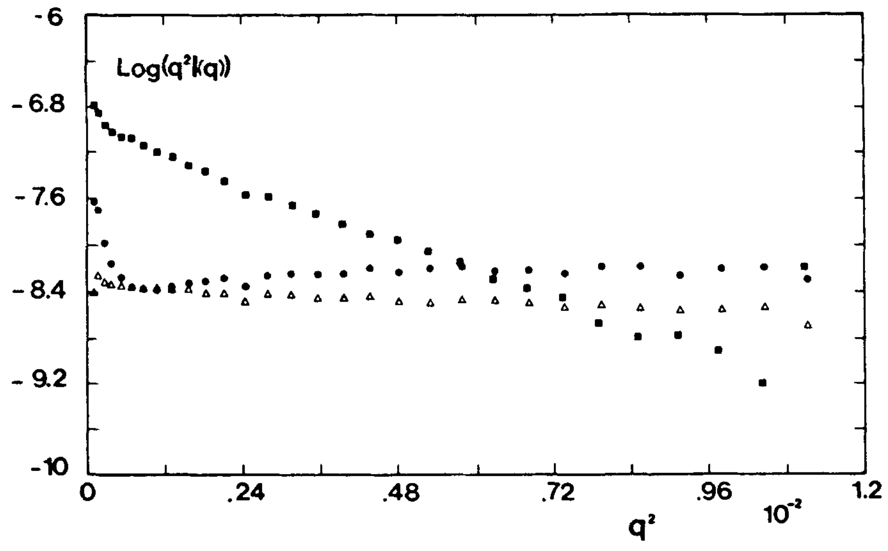

Figure 3 Plot of Log($q^2I(q)$) vs q^2. Same units as above. Initial substrate: 1-hour stearylated silica.

Δ : interface after "grafting" with a methyl-terminated polymer (immersed in dichloromethane). No polymer is detectable. ● and ■ : interface after grafting with a hydroxy-terminated polymer (observed in dichloromethane ●, and in acetone ■)

These local properties have their counterpart in terms of scaling laws between h, the thickness of the layer, D, the average distance between grafting sites and M, the molecular weight of the grafted chains. We have observed[3] that $hD^2 \approx M$ in poor solvent and $hD^{2/3} \approx M$ in good solvent, in accordance with the well-known predictions[7-9].

5. DISTINCTION BETWEEN ADSORPTION AND GRAFTING

Instead of hydroxy-terminated chains, one can use methyl-terminated PDMS and therefore make a comparison between adsorption and grafting. For that purpose, we have treated the bare silica with short chains (pentanol, stearyl alcohol or trimethylchlorosilane). Depending on the strength of this chemical pretreatment (i.e. on the grafting density of short chains), the "natural" adsorption can be reduced and eventually suppressed.

For instance, we have prepared two different silica samples: the first one has been esterified with stearyl alcohol for 1 hour (see figure 1, symbol ▲) and the second one for 2 hours (figure 1, symbol △) and we have used these modified silicas as substrates for the grafting of the PDMS. In figure 3 we have reported the data obtained with a -OH and a methyl-terminated polymer of the same molecular weight (140 000) which has been allowed to react with the 1-hour stearylated silica. Clearly, for the methyl-terminated PDMS case, we recover the initial pure stearyl layer (compare with figure 1). However, it can be noticed that the level of the scattering intensity is a little bit lower than for the initial protective layer. This is due to the fact that the stearyl layers are not very robuste and can be damaged by a thermal treatment. Nevertheless, without any ambiguity, the methyl-terminated chains do not adsorb onto the 1-hour stearylated silica.

In contrary, the hydroxy-terminated chains clearly have been grafted and a brush has been formed. (Γ=1.14 mg/m^2, thickness in dichloromethane: 172Å, thickness in acetone: 47Å)

If we repeat the same experiment with the 2-hours stearylated silica, we then obtain the results shown on figure 4. In this case, the PDMS does not adsorb nor can be grafted.

6. SOME DIFFERENCES BETWEEN PHYSICALLY END-ADSORBED AND CHEMICALLY GRAFTED LAYERS

We have carried out a few experiments with PDMS chains terminated by a NBD group (7-nitrobenzo-2-oxa-1,3-diazole). This fluorescent molecule adsorbs strongly at room temperature onto silica in hexane. We have used two silica substrates: suspensions of stearylated silica beads (synthetized following reference 3) and porous silica as previously.

The methyl- or hydroxy-terminated PDMS does not attach on to the silica beads in hexane. In contrary, the NBD-PDMS rushes towards these beads, even at low volume fraction of polymer. At very low volume fraction, this can induce an irreversible flocculation of the particules if one uses chains labelled with NBD at both ends. These simple experiments show that the NBD-PDMS is able to penetrate a steric barrier of around 15Å whereas the other chains are much more sensitive to the crowding of the surface.

More quantitatively, the NBD-PDMS chains exhibit a classical adsorption isotherm (figure 5) from which one can determine a sticking energy per anchor group of 11kT.

The OH-terminated chains have a complete different behaviour[11]. At low volume fraction, they can only form mushrooms. It is only above a critical concentration (of the order of a few %) in the reaction bath that they can be densely grafted. The osmotic pressure is in this case the driven force. We have observed that the adsorption isotherm obeys to the scaling law: $\Gamma \approx N^{1/2} c_b^{7/8}$ where N is the polymerization index of the grafted chains and c_b the volume fraction of polymer in the reaction bath. It can be interpreted by a simple argument: the concentration inside the interface is proportionnal to that of the bulk. Further work is necessary to understand more deeply these features.

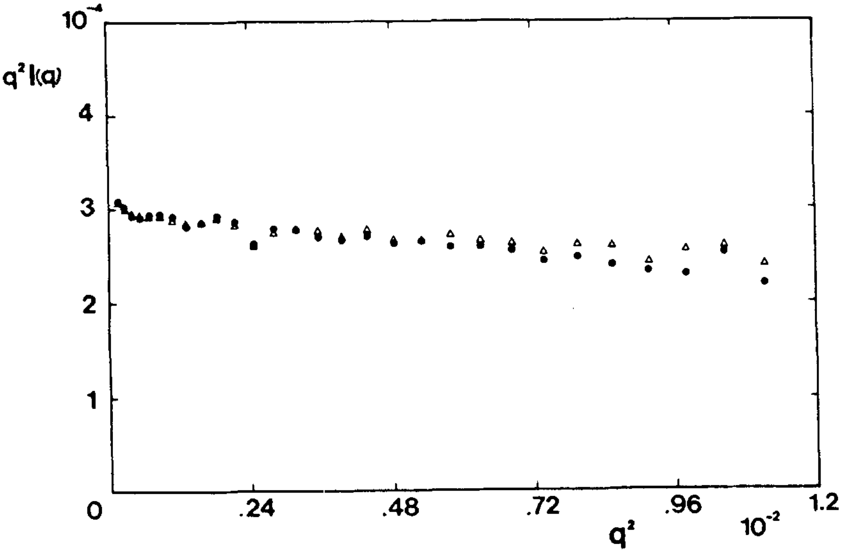

Figure 4 Plot of $q^2I(q)$ vs q^2. Same units as above. Initial substrate: 2-hours stearylated silica. Same polymers and same captions as for figure 3. No polymer is detectable.

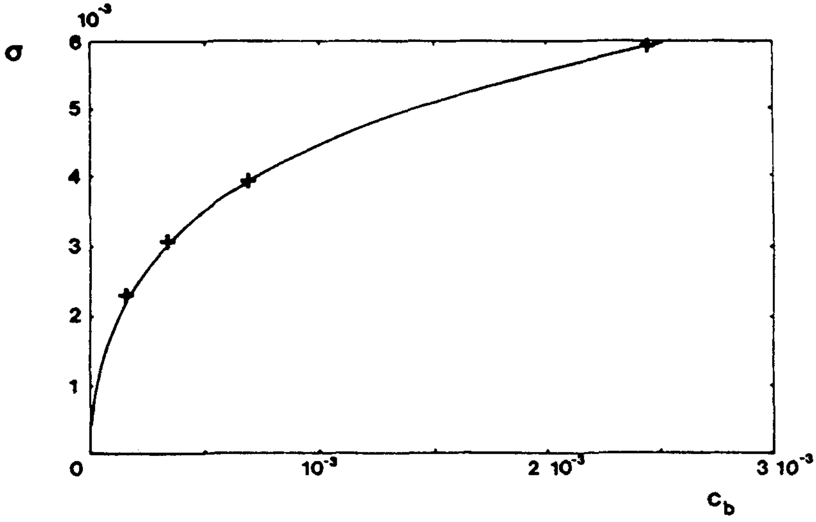

Figure 5 Adsorption isotherm of NDB-PDMS on porous silica (molecular weight of the polymer: 35 000, polydispersity: 1.3). σ is the grafting density and c_b the volume fraction of polymer in the bulk at equilibrium. The experimental data have been fitted by the theoretical prediction of Ligoure et al.[10]

CONCLUSION

Using small angle neutron scattering techniques, we have investigated the structures and the physicochemistry of grafted layers. Short chains yield thin layers that can be easily characterized in terms of grafting density and thickness. Long polymer chains provide a richer system: the grafting density and the solvent quality have a deep influence on the shape of the interface. The physicochemistry of the surface and of the anchor group modifies the building of these grafted layers.

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