

## Characterization of the Brush Regime for Grafted Polymer Layers at the Solid-Liquid Interface

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Using small-angle neutron-scattering techniques, the scaling laws between the thickness of a grafted polymer layer  $h$ , its graft density  $\sigma$ , and the molecular weight of the grafted chains  $M$  have been determined for polydimethylsiloxane chains end grafted on porous silica. The observed laws  $h \approx M\sigma$  in bad solvent and  $h \approx M\sigma^{1/3}$  in good solvent provide the first experimental evidence of the "brush" regime, where the grafted chains, confined by their neighbors, are stretched normal to the surface.

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It is commonly admitted that polymer chains should provide efficient interfacial layers for the so-called steric stabilization of colloidal suspensions.<sup>1</sup> Because of this potential practical importance, strong efforts have been devoted to the understanding of the structure of such layers, both experimentally and theoretically. Surprisingly enough, the experimental efforts have been centered either on adsorbed layers in which the polymer chains can interact with the solid surface by any of their monomers or on layers formed with end-grafted short chains which are not very different from surfactants.

More than ten years, ago, however, Alexander<sup>2</sup> underlined that long grafted polymers may extend very far from the surface and be stretched. This is quite different from what is known about adsorbed layers.<sup>3</sup> Since this original paper, several other theoretical works or simulations<sup>4-7</sup> have completed the description of Alexander or taken issue over it. Nevertheless, it is commonly admitted that in the so-called moderate-density (or brush) regime in which the chains strongly interact with their neighbors, the thickness of the brush would be related to the grafting density  $\sigma$  and to the chain length  $N$  through the following scaling laws:

$$h \approx N\sigma^{1/3} \text{ in good solvent,} \quad (1)$$

$$h \approx N\sigma \text{ in poor solvent.} \quad (2)$$

Experimental studies of the grafted layers<sup>8-12</sup> appear rather scarce, certainly due to strong difficulties in the control of the grafting procedure with long polymer chains and in independently determining  $h$  and  $\sigma$ . A clever way of avoiding the chemical difficulties has been to use polymers with an anchoring head which strongly adsorbs on a surface. Interfacial layers formed with such systems have been investigated using the force-balance technique,<sup>10-12</sup> which provides, however, only a global characterization of the layers. It has been found<sup>12</sup> that the force-versus-distance law in good solvent agrees with the scaling description, but instead of (1), the thickness of the layer seems to vary like  $h \approx N^{0.6}$ . This non-

linear dependence of  $h$  with  $N$  has been recently interpreted<sup>13</sup> taking into account the possibility of exchanges between the so-called anchored chains and the free polymers, which can definitively not be described by scaling.

Other information about the grafted layers has been obtained with small-angle neutron-scattering (SANS) experiments.<sup>8,9</sup> Several studies, carried out with dispersions of particles bearing grafted polymers, have yielded some important results and it is now widely recognized that SANS is the most efficient experimental way to probe the inner structure of the interfacial layers.

But the fundamental laws like (1) have never been checked, because of the serious difficulties in independently determining  $h$ ,  $N$ , and  $\sigma$  and in obtaining grafted layers with high-molecular-weight chains. We have carried out an extensive study on polymer brushes. SANS experiments have been performed on polydimethylsiloxane (PDMS) covalently end bonded on porous silica. They have led to a straight and global characterization of the brush regime and to a description of the inner structures of these interfacial layers,<sup>14</sup> which are closely related. The aim of this Letter is to present the former results.

The system and the experimental procedures will be given elsewhere<sup>14</sup> in more detail. The characteristics of the solid substrate have been previously reported.<sup>15</sup> It is a porous silica, with a flat and well-defined surface at a scale 10–300 Å (specific area, 2.5 m<sup>2</sup>/cm<sup>3</sup>; diameter of the pores, 4000 Å). It is sometimes chemically pretreated by an esterification with pentanol in order to diminish the natural adsorption of the polymer on the bare silica.

Fractionated PDMS have been used. Their molecular weight ranged from 24000 to 593000 [determination by gel permeation chromatography (GPC)] and their polydispersity was typically 1.1. They carried at both ends a hydroxyl group which can undergo a condensation reaction with the silanols of the silica surface. We point out that in the brush regime, we have checked that the chains are attached to the surface by only one end.<sup>16</sup> The grafting procedure is as follows: The silica was in-

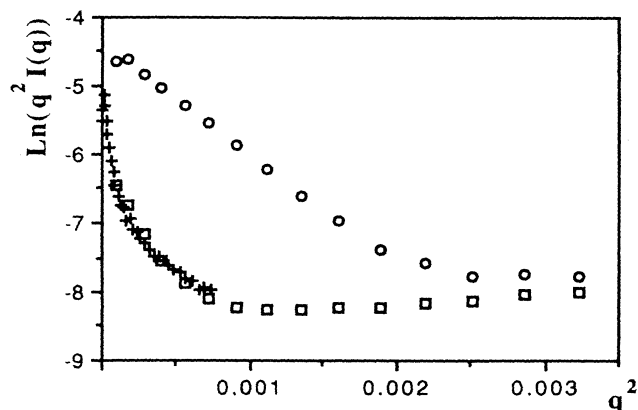


FIG. 1. Plot of the scattering intensity as  $\ln[q^2 I(q)]$  vs  $q^2$  for a typical grafted layer immersed in acetone (O) (poor solvent) or in dichloromethane (+, □) (good solvent) under contrast-matching conditions. For the latter observation, two  $q$  ranges have been used. Molecular weight of the polymer, 145 000; polydispersity, 1.09;  $\Gamma = 8.4 \text{ mg/m}^2$ .

troduced in a PDMS solution in heptane, whose concentration in most cases was fixed at 15%. The samples were then heated at  $100^\circ\text{C}$  under a controlled atmosphere for typically 24 h, and after the reaction, rinsed several times with a great volume of dichloromethane.

The amount of grafted polymer  $\Gamma$  and the thickness of the layer  $h$  were determined from the scattered intensity  $I(q)$  at very low scattering vector  $q$ , which can be expressed under the contrast-matching condition (when the neutron refractive index of the solid has been matched by that of the solvent) as

$$q^2 I(q) = 2\pi(S/V)(n_p - n_s)^2 \Gamma^2 (1 - q^2 h^2 / \alpha). \quad (3)$$

$S/V$  is the specific surface area and  $n_p$  ( $n_s$ ) is the scattering length density of the polymer (solvent).  $\alpha$  is a numerical factor, depending only on the shape of the density profile  $\phi(z)$ . We have made the assumption of a step function for  $\phi(z)$ , leading to  $\alpha = 12$ . This restriction is not too dramatic since the "exact"  $h$  would differ from our estimation by only a numerical factor greater than 1.

A typical plot of  $\ln[q^2 I(q)]$  vs  $q^2$  for a grafted layer, observed either in poor or in good solvent, is reported in Fig. 1. According to (3), both spectra have the same extrapolation at  $q \approx 0$ , while the slope of the linear decrease in good solvent is much greater than in poor solvent. Therefore, we emphasize that our experiments give an accurate and absolute determination of  $\Gamma$  and at the same time, but independently, the thickness of the layer.<sup>17</sup>

One can deduce from  $\Gamma$  (in  $\text{mg/m}^2$ ) the average distance between grafting sites  $D$  (in  $\text{\AA}$ ) as follows:  $D = (6.023\Gamma/M)^{-1/2}$ . We also have  $\sigma = (a/D)^2$ , where  $a$  is the monomer size.

Figure 2 shows  $h$  times  $D^2$  vs  $M$  in a linear representation for samples in acetone (a poor solvent for the

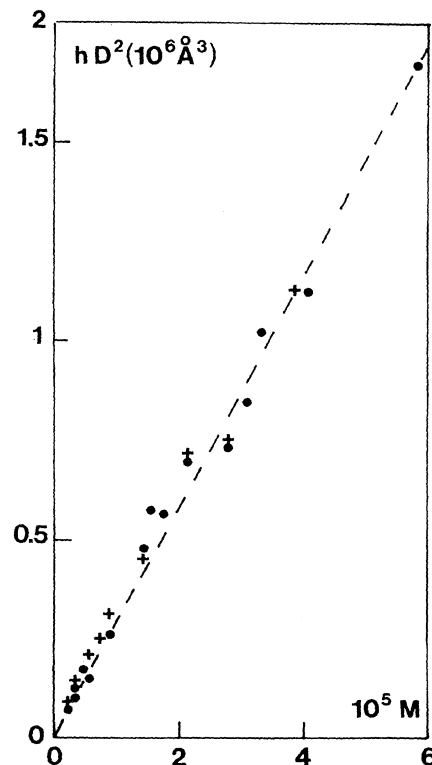


FIG. 2. Plot of  $hD^2$  vs  $M$  for grafted layers in poor solvent (acetone). (+) bare silica surface; (●) chemically pretreated silica surface.

PDMS).  $D$  ranges from 28 to 73  $\text{\AA}$ . The data show clearly that

$$hD^2 \approx M, \quad (4)$$

whether the surface is modified or not, in agreement with (2). The linear fit gives

$$hD^2 = 2.93(\pm 0.1)M + V_0,$$

whether the silica is pretreated or not.

We can deduce from the slope of this relation an estimation of the mean volume fraction of polymer  $\Phi$  inside the layer:  $\Phi \approx 60\%$ . This value is very close to the mean concentration one can measure separately for each sample.<sup>14</sup> The constant factor  $V_0$  is low and corresponds to a thin depletion layer, whose thickness would be about 15  $\text{\AA}$ . A careful examination of the data shows that this depleted zone seems to be a little bit thicker for the pretreated surface than for the bare one.<sup>18</sup>

The conclusion is, however, that this regime near the surface has no influence on the whole structure of the grafted layer in poor solvent. The general scaling law (4) could be interpreted as a close packing of monomers whose density  $\Phi$  is fixed by the solvent-polymer interaction. ( $\Phi \approx 60\%$  for acetone, and about 90% for methanol.) It contains further nontrivial information:

Although the chains are almost fully collapsed, the thickness of the grafted layer increases linearly with  $M$ . The chains tend to be stretched and to have an anisotropic configuration. This was theoretically derived by Halperin a few years ago.<sup>7</sup>

Figure 3 shows the results obtained in dichloromethane, which is a good solvent for the PDMS. The silica surface was not treated before the grafting reaction. For these samples,  $D$  ranges from 28 to 113 Å and  $h$  from 196 to 1160 Å. We have plotted the data as  $hD^{2/3}$  vs  $M$  in a linear representation. The results are in excellent agreement with the theoretical prediction. The fit gives

$$hD^{2/3} = 0.0453M - 16. \quad (5)$$

The constant is very low and has no particular significance. Rewriting (5) in terms of the number of monomers, we obtain

$$hD^{2/3} = a^{5/3}N,$$

where  $a = 2.1$  Å is of the same order of magnitude as the monomer size.

This is the first time, to our knowledge, that this important scaling law, which was predicted more than ten years ago, has been experimentally checked.

In comparison with the relation in poor solvent, the thickness of the grafted layer varies with the grafting density to the power of one-third, rather than linearly. This is the effect of the solvent quality; in good solvent, the repulsive monomer-monomer interactions make the density of the interfacial layer much weaker than in poor solvent. But the thickness is still a linear function of the molecular weight: This is the signature of the chain grafting in the brush regime, where the lateral interchain stresses force the polymer to stretch in the solvent, perpendicularly to the surface, whatever the solvent quality is.

These results may have some important technological applications. Grafted polymers are used<sup>1</sup> to prevent colloidal particles from aggregating, which occurs in organic media or when the surface charge effects are screened out. The protective layer has to be thicker than the typical range of the van der Waals interparticle attraction: about 100 Å. In good solvent, this will be achieved more easily<sup>19</sup> with long polymers than with short chains, which should be very densely grafted, since the relation (5) indicates that the thickness of the grafted layer varies linearly with the molecular weight of the chains, but with the third power of the graft density.

In the absence of any solvent, the relation (2) still holds. Thus, it may be possible to make thick polymer interfacial layers (up to 200 Å) using grafted chains on various solid surfaces. This layer would have the following noteworthy features: It is homogeneous, without defects, and its thickness is well defined (see Ref. 14). It is also chemically resistant.<sup>16</sup> All these properties could be

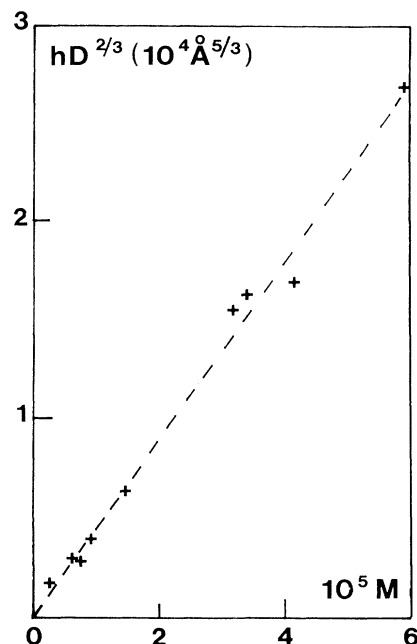


FIG. 3. Plot of  $hD^{2/3}$  vs  $M$  for grafted layers in good solvent (dichloromethane).

important for technological applications like lubrication, antioating, wetting, etc.

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der of 1%. But, because of normalization or GPC measurement uncertainties, the precision of the parameters of this paper can be estimated to 10%.

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<sup>19</sup>An example of steric stabilization due to long grafted chains will soon be published [P. Auroy, L. Auvray, and L. Léger (to be published)].