Synthesis of Poly(styrene sulfonate) Brushes

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Abstract: Dense poly(styrene sulfonate sodium salt) brushes were prepared on silicone wafers using a two-step procedure: polystyrene (PS) chains, terminated by a reactive trichlorosilane group, were first covalently grafted, and then the PS brush was converted to a poly(styrene sulfonate) brush by a soft sulfonation reaction. Ellipsometry and infrared spectroscopy in ATR were used to characterize the samples and to optimize the procedure: in particular, the sulfonation was shown to be homogeneous along the chain backbone and the neutralization complete. In some cases, the polymer layer revealed to be quite fragile: the chains were pulled out of the brush. A consolidation treatment which consisted in grafting oligomers inbetween the long PS chains significantly increased the robustness of the layer. This might be relevant for industrial applications.

Introduction

When polymer chains are attached to a surface by one end, they can stretch perpendicularly to the surface to form a so-called brush. This occurs when the grafting density is high enough and the net monomer−monomer interaction repulsive.[1] The case where the grafted chain backbones carry electrostatic charges has received particular attention; indeed, these poly-electrolyte brushes would combine interesting properties, as emphasized by several recent theoretical papers:[2−7] they are water-soluble; the chain stretching would be very strong in salt free solutions; at high grafting density, they would be insensitive to the addition of salt, whereas at low grafting density, under certain conditions, they would exhibit a sharp response to a change of ionic strength or temperature. These properties could be used in various applications: polyelectrolyte brushes could help in stabilizing aqueous suspensions, in preventing surfaces from being colonized by microorganisms, in improving the biocompatibility of some plastics, or in preparing new drug delivery- or other controlled-release systems. All of these appealing features should have stimulated the synthesis and the study of real polyelectrolyte brushes.

However, up to very recently, there have been very few experimental works on such polymer interfaces because their synthesis or preparation appears very difficult to control. Diblock copolymers can be used to form polyelectrolyte brushes:[8−10] one block which is hydrophobic acts as an anchor, while the other, carrying the ionizable groups, can stretch in water. The adsorption of such ampholytic copolymers is, however, strongly dependent on the ionic strength and pH. Therefore, they are prone to be quite easily displaced, for instance if counterions are exchanged or if other adsorbing species are used in solution. In addition, Kelley et al. have observed in these systems inhomogeneities in the lateral direction at a length scale of the order of 100 nm.[9] But the main advantage of this approach is the relative simplicity of the brush preparation. Recently, Biesalski et al. reported results on tethered quaternized poly-(4-vinylpyridine):[11] the polymer chains were generated in situ from a radical immobilized on the solid surface. This seems to be promising, but further work is needed to explain why the amount of attached polymer is 3 orders of magnitude larger than what was found earlier with a similar approach.[12] Mir et al. used another method: they first attached poly(styrene) chains terminated by a reactive chlorosilane group on silica and converted the brush to a grafted poly(styrene sulfonate) layer by a sulfonation reaction.[13] They were able to study by small-angle neutron scattering the structure of the water soluble polymer layer and showed, among other results, the effect of the ionic strength on the polymer interfacial density profile and the monomer−monomer correlations at fixed grafting density. However, their preparation method was not sufficiently well-controlled to allow a systematic investigation. For better reproducibility, we decided to change both the sulfonation method and the substrate. Instead of a porous silica, we used silicon wafers, whose surface can be easily characterized by combining ellipsometry and infrared in attenuated total reflection (IR-ATR) techniques. This permitted finding the optimal conditions for the brush synthesis and preparing well-defined samples in a very reproducible way. Neutron reflectivity was finally used to determine the interfacial polymer concentration profile, the distribution of counterions, etc., but these results are presented in another publication.[14] In this paper, we focus on the polyelectrolyte brush synthesis.

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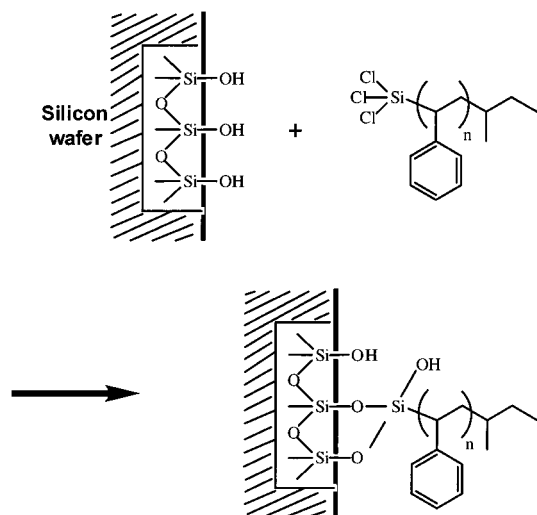
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Figure 1. Scheme of the grafting reaction. The PS chain is linked to the surface by only two siloxane bonds. The third function did not condense after hydrolysis. The two other cases (a single- or three-chain surface bonds) are also possible.

Table 1. Main Characteristics of the PS Chains

| molecular weight, M_w (g/mol)	polymerization index, N	polydispersity
6550	63	1.16
12550	121	1.08
33550	300	1.03
32250	310	1.04
114020	1100	1.03
194970	1875	1.03

In the first part, we describe the grafting and sulfonation procedures. The methodology to analyze and characterize the interfaces is also explained. Two important features have received particular attention: the neutralization yield is shown to be 100%, and the sulfonation reaction is proved to be homogeneous along the chain backbone. Special care has been taken to make the samples as robust as possible; we found that a consolidation treatment, which consists of grafting very short oligomers in between the long PS chains, remarkably improves the resistance of the layer to the subsequent sulfonation.

These results are discussed in the second part and put back in the context of both a rapidly growing academic interest in polymer brush synthesis and a fast-developing industrial use of thin organic layers to modify surface properties.

Results

Polystyrene Grafting. The polystyrene macromolecules were synthesized by anionic polymerization. For each sample, we prepared reactive chains, terminated by a trichlorosilane end-groups (PS$-$SiCl$_3$), which are able to form covalent bonds with the silanol Si$-$OH surface groups of the silicon substrates (Figure 1), and nonreactive polymers (PS$-$H) of exactly the same molecular weight. The characteristics of the different PS used in this study are summarized in Table 1.

The silicon blocks we used as substrates were carefully cleaned before the grafting reaction. Their oxide surfaces were rendered completely hydrophilic. The grafting procedure itself is quite simple: a thin film of reactive PS was spin-coated on the silicon block at room temperature (typical concentration of the spin-coating solution: 2%$-$see Experimental Section below). The chains were then allowed to react in a vacuum oven by raising the temperature up to 160 °C for typically 24 h. After
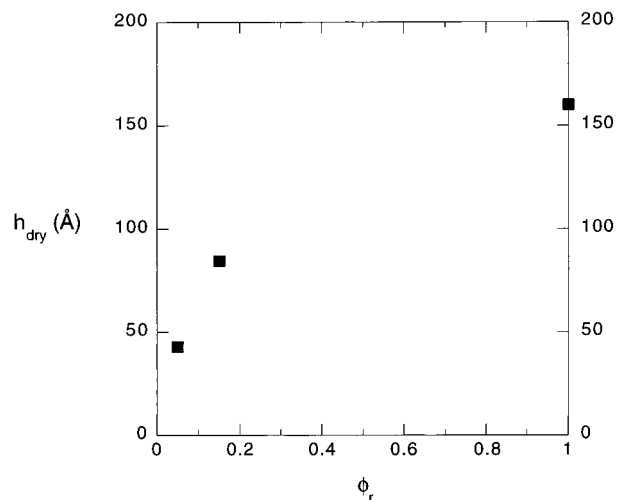
Figure 2. Variation of the amount of grafted PS h_{dry} (in Å) as a function of the volume fraction of reactive chains ϕ_r in the spin-coated film. The data were obtained with $N = 310$.

being washed, the silicon wafer was covered by a dry PS brush whose thickness h_{dry} was measured by ellipsometry. h_{dry} is also the amount of PS per unit area and is directly related to σ_{PS}, the grafting density (see below).

σ_{PS} was maximum when all of the PS chains of the film deposited onto the silicon block were reactive. To decrease σ_{PS}, the reactive chains were diluted with nonreactive PS of the same molecular weight. Indeed, for a given reaction time, h_{dry} is an increasing function of ϕ_r, the volume fraction of reactive chains in the film, as shown by Figure 2.

Brush Sulfonation. We have adapted the sulfonation method described in ref 15 to our grafted PS layers. We used an "acetyl sulfate" solution in 1,2-dichloroethane to convert the grafted PS chains to poly(styrene sulfonic acid) and eventually to poly-(styrene sulfonate sodium salt), after neutralization (see Figure 3).

A complete characterization of the PSS brushes requires the determination of their grafting density and sulfonated fraction. Both were obtained by combining ellipsometry and IR-ATR measurements (see below). As explained above, the grafting density σ_{PS} (or, equivalently, the average distance between grafting points D_{PS}) of the PS brush before sulfonation, was determined by measuring the thickness of the dry grafted layer by ellipsometry. The samples were also characterized by IR-ATR before sulfonation. A typical spectrum is shown in Figure 4a. Two absorption bands were used for a quantitative analysis: 2924 cm^{-1} characteristic of the $-$CH$_2-$ group and 3026 cm^{-1} characteristic of the monosubstituted phenyl ring. A series of PS brushes (of different grafting density) allowed us to calibrate these measurements. A typical calibration curve is shown in Figure 5 which reports the height of the absorption band at 2924 cm^{-1} h_{CH_2} versus σ_{PS} (measured by ellipsometry). It can be noticed that this calibration curve is a straight line: the IR-ATR signal is proportional to the number of absorbing species. This is always the case for all of the IR-ATR measurements reported in this paper. Other calibration curves were also obtained, following the same method; for instance, the absorption band at 2195 cm^{-1}, characteristic of the $-$CD$_2-$ group, was used to analyze samples prepared with deuterated PS.

Figure 4b shows the IR-ATR spectrum of the same sample as in Figure 4a, but after sulfonation. It can be noticed that the

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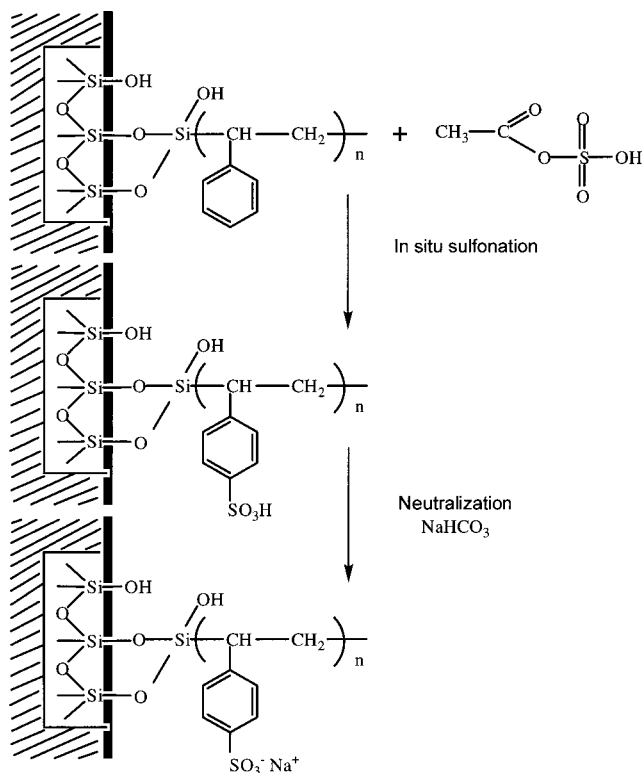
Figure 3. Sulfonation and neutralization of the PS brush.
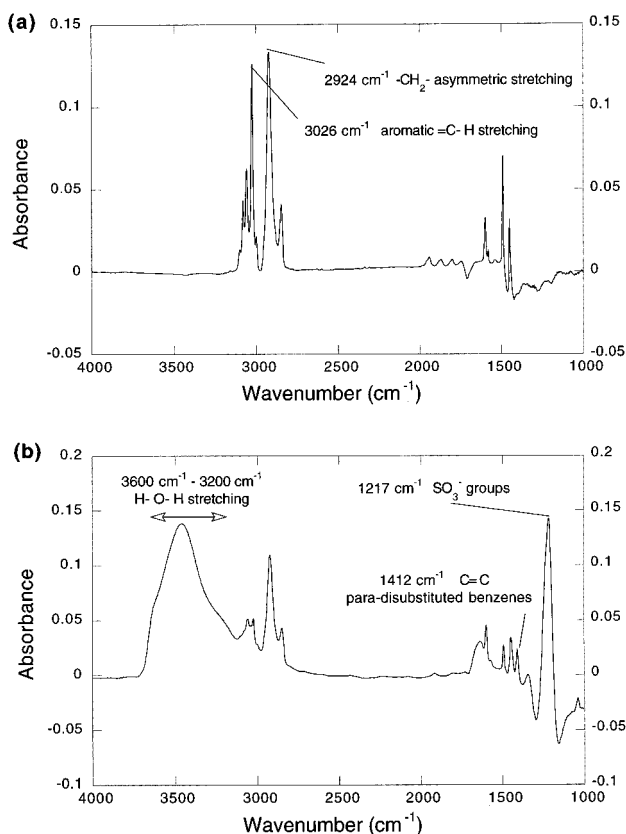
Figure 4. (a) IR-ATR spectrum of a PS brush ($N = 310$, $D = 17.8$ Å). (b) IR-ATR spectrum of the same brush as in (a) but after sulfonation and neutralization. The absorption bands at 2924 and 3026 cm^{-1} were used to determine the grafting density and the sulfonated fraction.

height of the two bands (at 2924 cm^{-1} and at 3026 cm^{-1}) has changed. In the first case (band at 2924 cm^{-1}), this is due to some degrafting. One can define the strongly bound fraction δ
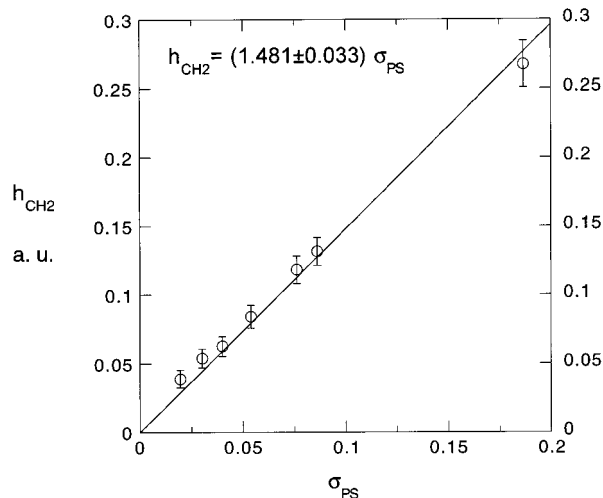

Figure 5. Calibration curve of the absorbance at 2924 cm^{-1}.

as the ratio of the height of this 2924 cm^{-1} absorption band before and after sulfonation $\delta = h_{CH_2}(PSSNa)/h_{CH_2}(PS)$. The grafting density of the PSS brush can thus be calculated: $\sigma_{PSSNa} = \delta\sigma_{PS}$ or $D_{PSSNa} = D_{PS}/\sqrt{\delta}$, where D_{PSSNa} is the distance between grafting points of the PSSNa brush. The 3026 cm^{-1} absorption band on the other hand, can be used to determine the sulfonated fraction α, since it is characteristic of a mono-substitution of the phenyl ring. α is given by: $\alpha = 1 - h_{CH}(PSSNa)/h_{CH}(PS)\delta$ (h_{CH} is the height of this 3026 cm^{-1} absorption band). For the sample of Figure 4, we found $\delta = 0.65 \pm 0.06$ and $\alpha = 0.62 \pm 0.08$.

Other features can also be noticed in Figure 4b: an intense absorption band which is the signature of the sulfonate group has appeared at 1217 cm^{-1}; a less intense band at 1412 cm^{-1} can also be observed. It is characteristic of a *para*-disubstitution of benzene. These two bands cannot be used for a quantitative analysis because they are located in the spectral domain where the silicon is (slightly) absorbent. Finally, a broad band between 3200 and 3600 cm^{-1} can also be observed: it is due to the presence of water.

The sulfonation reaction conditions were adjusted to maximize the strongly bound and the sulfonated fractions. The influence of the reaction time and the molarity of the sulfonation reagent was investigated using PS brushes of identical characteristics: $N = 310$, $D_{PS} = 17.8$ Å. The sulfonated fraction (respectively the strongly bound fraction) increases (respectively decreases) with the reaction time to reach a plateau after 5 h: δ and α amounts respectively to 65 and 62% (see Figure 6a). This value, $\alpha = 62\%$, was also measured for free PS chains sulfonated in solution. For a given reaction time, δ and α remain constant for acetyl sulfate molarities between 0.1 mol/L and 1 mol/L; Figure 6b displays the results obtained after 5 h of reaction, but the same behavior has been observed for 1 h. Thus, 5 h of sulfonation and 1 mol/L of acetyl sulfate solution seem to be a good compromise; the sulfonation yield is maximum and the degrafting remain within acceptable limits. The PSS$^-$Na$^+$ brush obtained under these conditions has the following characteristics: $N = 310$, $D_{PSSNa} = 22.0$ Å ($\delta = 0.65 \pm 0.06$) and $\alpha = 0.62 \pm 0.08$ (D_{PS} of the initial PS brush was 17.8 Å). Moreover, the sulfonated fraction can be adjusted by varying the reaction time. However, we did not go below $\alpha = 30\%$, because the poly(styrene sulfonate sodium salt) becomes insoluble in water, and not above $\alpha = 62\%$ because this is the maximum sulfonation yield allowed by the method we have chosen.
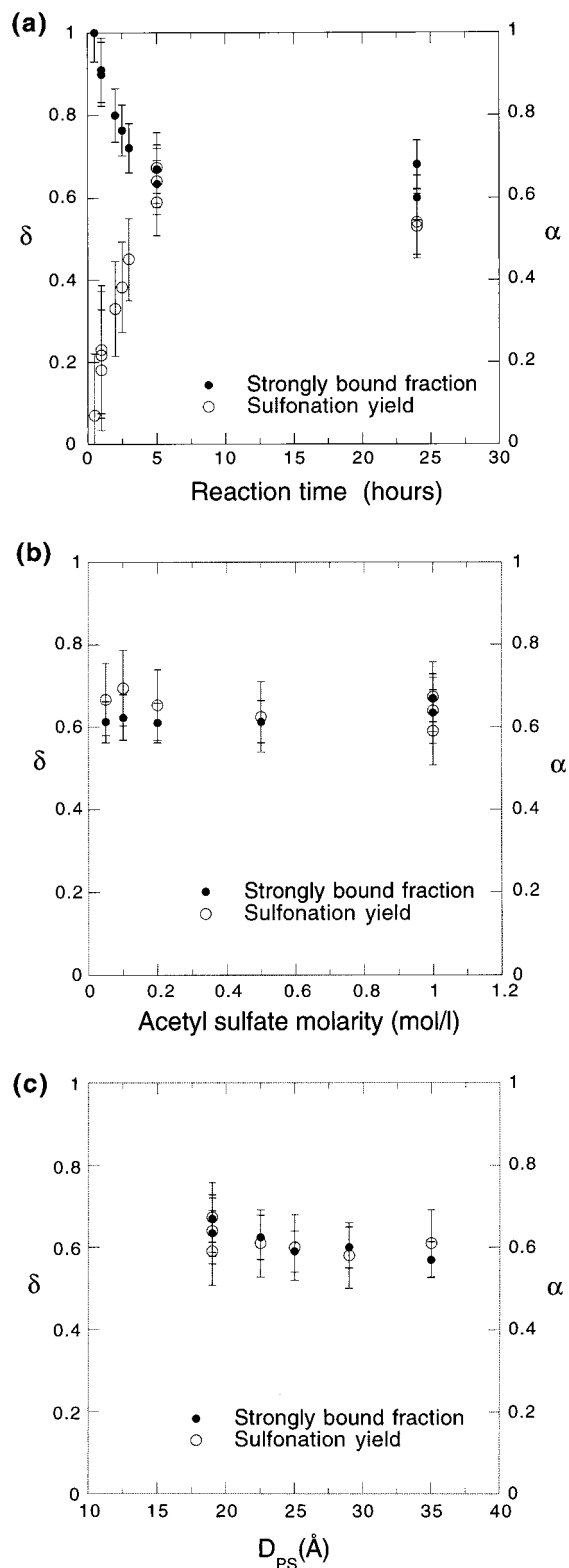
Figure 6. (a) Variation of the strongly bound fraction δ and the sulfonated fraction α as a function of the sulfonation reaction time. The acetyl sulfate molarity was 1 mol/L. The reaction was performed on a standard PS brush ($N = 310$, $D = 17.8$ Å). (b) Same as for (a), but the variable is the acetyl sulfate molarity (reaction time = 5 h) c) Variation of δ and α as a function of D_{PS} (in Å). The brushes were sulfonated for 5 h with 1 mol/L of acetyl sulfate.

The influence of the grafting density and the PS molecular weight on the results of the sulfonation reaction was also investigated. Indeed it was important for our structural studies[16] to be able to control and to vary the different molecular

parameters: N, D and α. Figure 6c shows that δ and α are constant when the distance between grafted PS chains ($N = 310$) increases from 17.8 to 35.0 Å. For chains of polymerization index $N \geq 310$, the maximum sulfonated fraction α is 62% (δ is about 65%), it is obtained after 5 h of sulfonation reaction, and it does not depend on the grafting density. However, for shorter chains ($N = 120$ and $N = 63$), we were not able to increase α above 45%, even after 20 h of sulfonation reaction (δ was 77% for $N = 120$ and 91% for $N = 63$). We did not investigate this point thoroughly, but we believe that this limit is due to the very high grafting density obtained with these short chains. D_{PS} was 13.7 Å for $N = 120$ and 12.4 Å for $N = 63$.

Finally, we observed an unexpected effect of the hydrogen/ deuterium substitution. The use of deuterated monomers allowed us to focus on one particular component of the interface with both the IR-ATR and the neutron reflectivity techniques. For a deuterated PSd brush (characteristics: $N = 300 -$ polydispersity index $= 1.031$, $D = 19.0$ Å), very similar to (hydrogenated) PSh brushes used in the previous paragraphs, the standard sulfonation conditions (5 h of reaction time, 1 mol/L of acetyl sulfate solution) yielded $\delta = 0.75 \pm 0.06$ and $\alpha = 0.40 \pm 0.10$. These values were determined by following the same procedure as for protonated samples, using the absorption band of the $-CD_2-$ group (respectively of the aromatic $C{=}C{-}D$ group) at 2195 cm^{-1} (respectively at 2274 cm^{-1}).[17] This sulfonated fraction of about 40% is maximum, and it corresponds also to what was measured (by acid/base titration and elemental analysis) for free deuterated PSd chains, sulfonated in solution. Thus, it turns out that deuterated PSd chains can be less sulfonated than hydrogenated samples, and accordingly, their strongly bound fraction is higher.

Neutralization Fraction. It was important to check that in the sulfonated brush, all of the sulfonic acid groups were efficiently converted to salt after neutralization with a base. Indeed, it is known that polystyrene sulfonic acid groups can cross-link to form sulfone bonds, if they are not rapidly neutralized. Moreover, for all of the experiments which required counterion exchanges,[14] it was preferable to be sure that a single type of counterion was involved. The neutralization fraction was calculated by determining the number of counterions per unit area in the polyelectrolyte brush with IR-ATR and comparing it with the number of grafted sulfonates per unit area. For that purpose, Na$^+$ cannot be used because it has no visible signature in the IR domain that we could investigate. Unlike Na$^+$, $(C_2H_5)_4N^+$ can be observed, provided its absorption bands do not overlap with those due to the grafted chains. This is the case if the brush is made of deuterated PS. Therefore, we prepared poly(styrene-d sulfonate tetraethylammonium salt) $(PSdSO_3^-(C_2H_5)_4N^+)$ brushes by neutralizing deuterated poly-(styrene sulfonic acid) PSdSO$_3$H with tetraethylammonium hydroxide $(C_2H_5)_4$NOH. The absorption band of $(C_2H_5)_4N^+$ at 3010 cm^{-1} can thus be used for a quantitative analysis. However, to infer from the height of this band the number of counterions per unit area, a calibration curve has to be established.

The calibration was obtained by using films made of free PSdSO$_3^-(C_2H_5)_4N^+$ chains, prepared in solution. We checked that each SO$_3$H group of the free PSdSO$_3$H chains was neutralized by one $(C_2H_5)_4$NOH molecule. First, one-half of a PSdSO$_3$H sample (synthesized following the same method as explained above) was titrated with 0.01 M NaOH to determine the sulfonated fraction: we found $\alpha = 37\%$. Then, the other

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(17) The frequency ν_d of the CD absorption bands is shifted with respect to the frequency ν_h of the corresponding CH bands according to: $\nu_d = 0.734 \nu_h$.
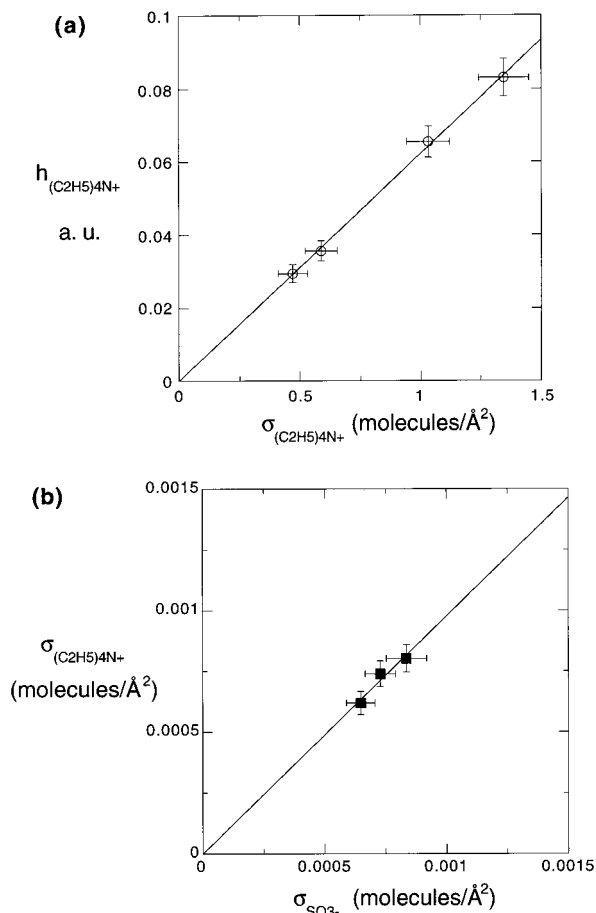
Figure 7. (a) Calibration curve of the height of the 3010 cm^{-1} absorption band characteristic of $-CH_2-N^+$ as a function of the number of $(C_2H_5)_4N^+$ per unit area $\sigma_{(C_2H_5)_4N^+}$. (b) Variation of $\sigma_{(C_2H_5)_4N^+}$ as a function of $\sigma_{SO_3^-}$ in poly(styrene sulfonate) brushes of same molecular weight ($N = 310$).

half was titrated with a 0.01 M $(C_2H_5)_4NOH$ solution and we obtained the same result. Therefore, each sulfonate group of the free chains is associated with one tetraethylammonium counterion. Then, $PSdSO_3^-(C_2H_5)_4N^+$ films of different thicknesses were prepared on IR-ATR prisms by spin coating. The height of the 2195 cm^{-1} band, characteristic of the $-CD_2-$ group, allowed us to determine the average number of monomers (styrene and styrene sulfonate) per unit area, thanks to a calibration curve previously established as explained above. And since the sulfonation yield was known ($\alpha = 37\%$), the number of sulfonates per unit area $\sigma_{SO_3^-}$ was obtained. Since it was known that for these free chains, each sulfonate group was associated with one tetraethylammonium, the number of $(C_2H_5)_4N^+$ per unit area $\sigma_{(C_2H_5)_4N^+}$ had to be equal to $\sigma_{SO_3^-}$. Finally, the height of the absorption band of $-CH_2-N^+$ at 3010 cm^{-1} was plotted versus $\sigma_{(C_2H_5)_4N^+}$ (Figure 7a). This gave us the calibration curve needed to estimate the neutralization rate of the brushes.

On three different $PSdSO_3^-(C_2H_5)_4N^+$ brushes (prepared with the same PS $-$ N $= 300$, but with three different grafting densities), the number of sulfonate groups per unit area $\sigma_{SO_3^-}$ was determined by measuring the height of two absorption bands: one at 2195 cm^{-1} due to the $-CD_2-$ group (which gives the amount of styrene and styrene sulfonate per unit area) and the other at 2274 cm^{-1} due to the aromatic $C=C-D$ group (which gives the sulfonated fraction). The combination of these two measurements gave us $\sigma_{SO_3^-}$. In addition, the height of the 3010 cm^{-1} band characteristic of $-CH_2-N^+$ was measured as
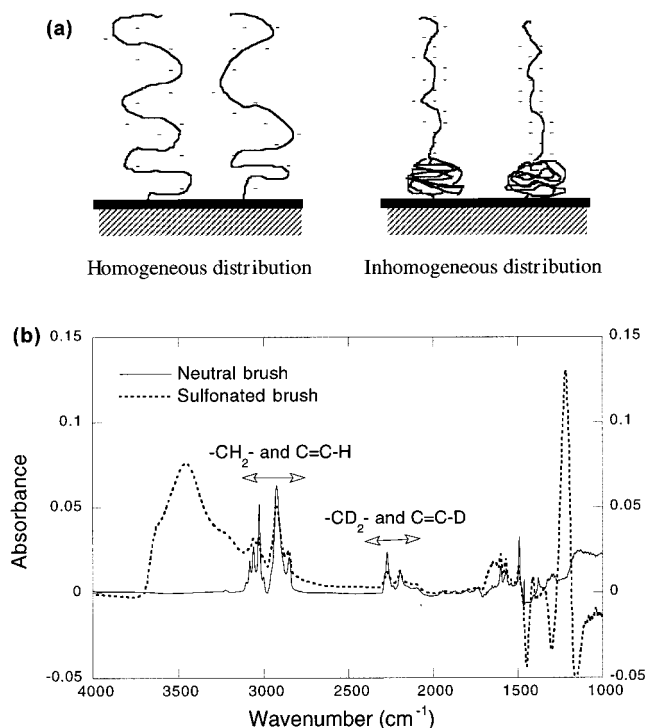

Figure 8. (a) Two types of charge distribution along the chain backbones. (b) IR-ATR spectra of the D/H diblock polystyrene brush before and after sulfonation.

in the previous paragraph, and the amount of $(C_2H_5)_4N^+$ per unit area $\sigma_{(C_2H_5)_4N^+}$ was deduced from the calibration curve shown in Figure 7a. Finally, for these three samples, $\sigma_{(C_2H_5)_4N^+}$ was reported versus $\sigma_{SO_3^-}$, as shown in Figure 7b. It can be clearly seen that $\sigma_{(C_2H_5)_4N^+}$ is proportional to $\sigma_{SO_3^-}$. A linear fit gives $\sigma_{(C_2H_5)_4N^+} = (0.98 \pm 0.02) \sigma_{SO_3^-}$ which means that the neutralization fraction of the brushes is about 100%.

Homogeneity of the Brushes along the Chains. As seen above, the maximal sulfonation yield we can achieve with our "soft" sulfonation method is about 62% for protonated brushes and 40% for deuterated brushes. Since all monomers are not substituted, the question of the homogeneity can be raised. Two extreme cases may be considered (Figure 8a): in the first situation, the sulfonates are distributed regularly along the backbone; in the second case, the sulfonated chain resembles a diblock copolymer: all of the sulfonated monomers are concentrated near the free end of the chains, the rest, close to the grafting point, remaining neutral.

To settle this question, it was necessary to distinguish the monomers along the chain. This was achieved with a diblock polystyrene $PSd-PSh-SiCl_3$. The deuterated part had about the same number of monomers as the protonated one ($N_d = 156$, $N_h = 131$). This diblock was grafted and sulfonated following the same method as for the homopolymers. Since IR-ATR spectroscopy is sensitive to the H/D substitution, it was possible to determine the strongly bound fraction and the sulfonated fraction for each block of the grafted chains. If the sulfonation reaction was completely inhomogeneous as drawn in Figure 8a (right), we should find a sulfonation fraction of $\alpha_d \approx 0.40$ for the deuterated monomers and $\alpha_h \approx 0$ for the protonated ones. On the contrary, a completely homogeneous reaction would yield sulfonated fractions similar to those found for homopolymers, namely $\alpha_h \approx 0.60$ and $\alpha_d \approx 0.40$. A similar reasoning applies for the strongly bound fraction δ. Figure 8b displays the spectra of the diblock brush before and after sulfonation. The bands due to $-CH_2-$ and $C=C-H$ (respectively $-CD_2-$
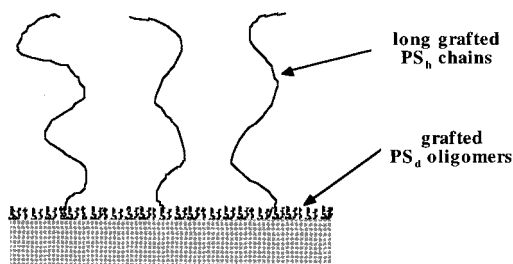
Figure 9. Schematic representation of a consolidated PS brush.

and C=C−D) were used to characterize the protonated (respectively deuterated) block, as above. The strongly bound fraction was found almost the same for both blocks ($\delta_h = 0.69$ and $\delta_d = 0.72$), and it means that the decrease of the amount of polymer per unit area is due to degrafting and not to random chain scission; this result will be very helpful when we will discuss the mean to consolidate these grafted layers. Besides, we measured $\alpha_h = 0.57 \pm 0.08$ and $\alpha_d = 0.42 \pm 0.10$ which are similar to the sulfonated fractions found for the corresponding homopolymer brushes. Therefore, it can be concluded that the sulfonation reaction took place regularly along the chain.

Consolidation of the Grafted Layers. In some cases (long chains or weak grafting density), the degrafting was a serious difficulty which prevented any further structural investigation. This degrafting occurred either right after the sulfonation or progressively when the polyelectrolyte brush was immersed in water. The presence of NaCl in solution worsened this degradation. To solve this problem, we consolidated the PS brushes by "protecting" the anchoring point with a dense layer of (very) short deuterated chains (Figure 9). These oligomers (PSd−SiCl₃) had the following characteristics: $N = 37$, polydispersity index = 1.322. IR-ATR is a very powerfull technique to analyze the consolidated brushes because it can distinguish between the oligomers and the long chains. In addition, for neutron reflectivity, the deuterated oligomers are "invisible" because they are contrast matched with D_2O; they do not contribute to the reflectivity signal. The deuterated oligomers were grafted according to the following procedure: on a PSh brush prepared with long (protonated) chains and already characterized, an oligomer solution (1% in dried toluene) was spin-coated. The resulting film was heated at 150 °C under vacuum for 24 h, and the excess of short chains were washed off. The consolidated brush was analyzed with IR-ATR before and after sulfonation. Only a few oligomers were degrafted ($\delta \approx 95\%$); their sulfonated fraction was about 40%. On the other hand, we measured for the long grafted (protonated) chains the same sulfonated fraction (∼60%) as the one found without consolidation.

The consolidation treatment appeared to be very efficient to prevent the chains from degrafting. Figure 10 shows the results obtained with brushes made of the same polymer ($N = 310$) but of various grafting density: the lower the grafting density, the more efficient the consolidation. For the least dense brush, the effect of the oligomers is spectacular: $\delta = 95\%$ after consolidation whereas it is only 55% without it. Moreover, the consolidated PSS^-Na^+ brushes appeared to be very robust: no chain degrafting was observed after long immersion in pure water or even in a 5 M NaCl solution.

Consequences of the Consolidation on the Interfacial Structure. The consolidation treatment allowed us to prepare polyelectrolyte brushes with a broad range of grafting density and chain molecular weight. However, it was necessary to investigate whether this oligomer layer could modify the density profile of the long grafted chains. This was achieved, to some
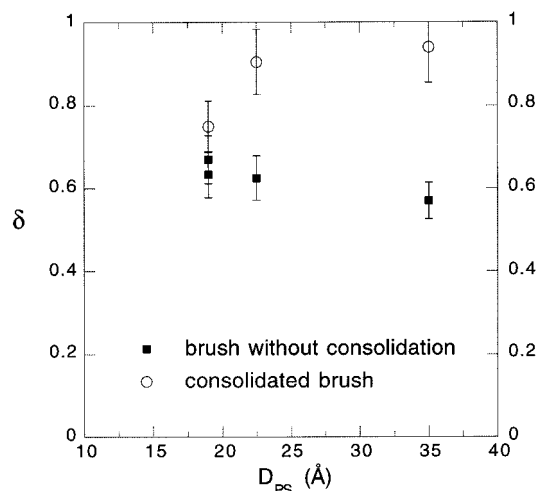

Figure 10. Effect of the consolidation treatment on the strongly bound fraction δ as a function of the grafting density.
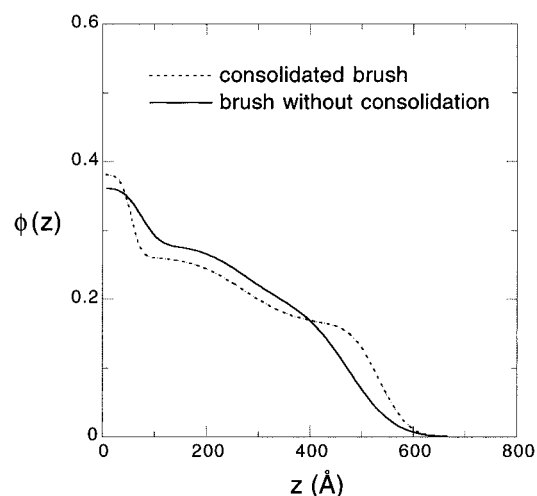

Figure 11. Effect of the consolidation treatment on the interfacial volume fraction profile of a PSS^-Na^+ brush, determined by neutron reflectivity.

extent, by comparing the structure determined by NR of a brush with or without the protective oligomers. This was possible only with a few samples, which were already stable without consolidation. We remind the reader that the oligomers were contrast-matched with D_2O and did not contribute to the NR. In Figure 11, we can observe that the concentration profile of the consolidated brush ($N = 310$, $D = 21.2$ Å, $\alpha = 0.60 \pm 0.08$) is similar to that of the brush without consolidation ($N = 310$, $D = 22.0$ Å, $\alpha = 0.62 \pm 0.08$). The only region of the interface where there might be a significant effect of the oligomers is close to the silicon surface; this perturbation is located in a thin layer of about 60 Å which corresponds to the thickness of the sulfonated oligomer layer in pure water.

Thus, the consolidation treatment opened the possibility to investigate the influence of the molecular weight and the grafting density on the structure of polyelectrolyte brushes, without introducing any significant bias. As an example, we present in Figure 12 the density profile determined by NR, as a function of the molecular weight. The brush made with the longest chains ($N = 1100$) could not be studied without consolidation. We can observe that in this polyelectrolyte brush, the chains can be stretched up to about 2500 Å from the solid surface. The detailed analysis of the structure of these charged brushes is described in another paper.[16]
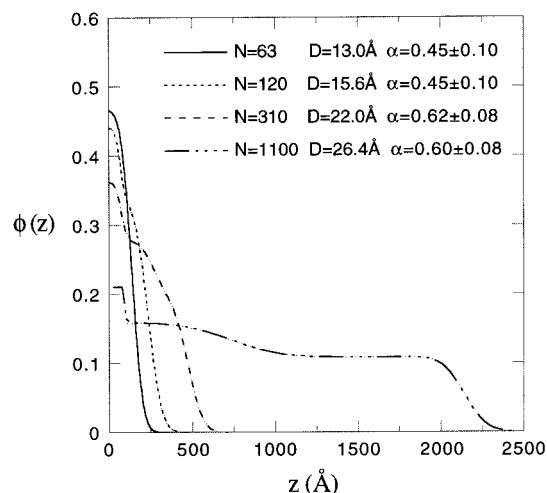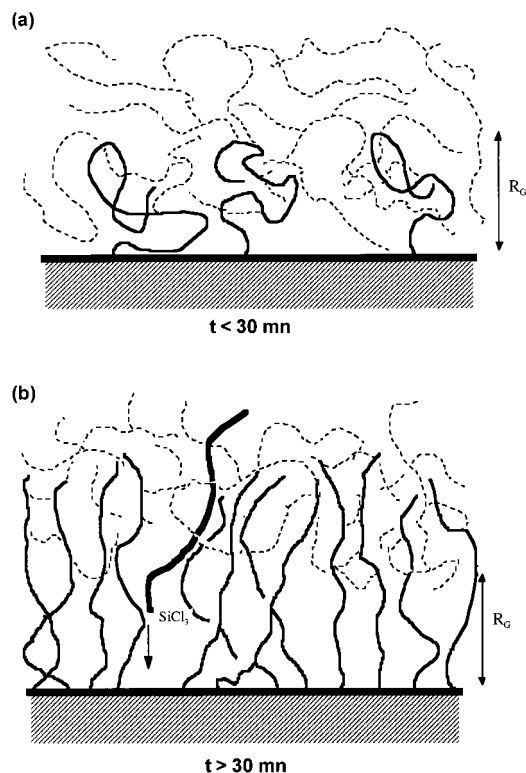
Figure 12. Volume fraction profile of PSS⁻Na⁺ brushes prepared with chains of increasing length.
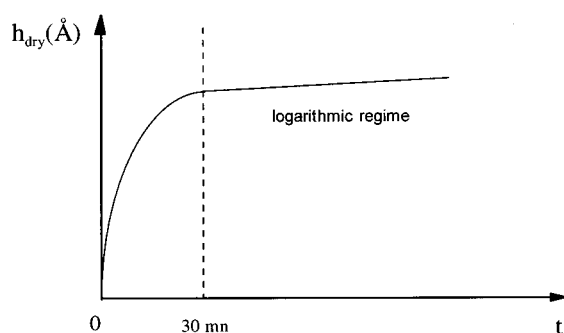
Figure 13. Schematic representation of the PS grafting reaction kinetics.

Discussion

Grafting Kinetics and Control of the Grafting Density. It has been shown[18] that two different regimes can be distinguished in the kinetics of the PS−SiCl$_3$ grafting reaction we use in this study (see Figure 13); at short time (grafting reaction time t typically less than 30 min), the amount of grafted polymer h_{dry} increases rapidly with t. At longer time, h_{dry} increases much more slowly, roughly logarithmically. The existence of these two regimes can be understood with simple arguments: at short time, the chains which are in close vicinity of the surface have a strong probability to form a bond between their reactive ends and the surface. The kinetics, in this regime, is controlled by the grafting reaction itself and by "free" diffusion processes. This holds as long as all of the chains, within a layer of thickness roughly equal to R_G (the radius of unperturbed chain), have not reacted. When this threshold is attained, the chains which would like to graft, must stretch themselves and the already attached polymers to reach the surface (cf Figure 14). This is still possible, but strongly slowed by the energy barrier (of entropic origin) to overcome. This corresponds to the second regime when the amount of grafted polymer increases logarithmically. This scenario accounts for several observations, in addition to the shape of the kinetics; it has been shown that h_{dry} increases indeed with the square root of the molecular weight,[19] the kinetics does not depend, to a large extent, on the end functionality,[20] and the threshold already mentioned corresponds

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(20) Reiter, G.; Sharma, A.; Casoli, A.; David, M.-O.; Khanna, R.; Auroy, P. *Langmuir* **1999**, *15*, 2551.

Figure 14. (a) For a grafting reaction time t < 30 min, all the chains in a close vicinity of the solid surface can easily graft. (b) At longer time, a chain which would "like" to attach to the surface, must stretch itself and the already grafted chains to reach the surface.

also to the onset of the autophobic behavior, observed with thin films.[18]

This scenario was helpful to find the appropriate way to vary the grafting density σ_{PS}. The challenge was to decrease σ_{PS}; indeed, by spin-coating films of molten reactive PS chains as explained above, we sought to achieve the highest grafting density. A priori, there were two equivalent possibilities to diminish σ_{PS}: to perform the grafting reaction in solution or to reduce the grafting time. Although the first method was efficient, the brushes prepared in this way revealed to be very fragile: they did not resist enough to the subsequent sulfonation. The reason for this fragility is not clear; it might be due to a less good condensation of the reactive chain ends with the surface silanol groups.[21] The second method did not allow to vary σ_{PS} in a very reproducible way because the reaction kinetics is initially too fast (first regime) compared to other characteristic times (temperature equilibration). In particular, it was not possible to reduce σ_{PS} to sufficiently small values. Thus, it was necessary to find an alternative method. Using the scenario explained above as a guide line, we tried to slow the initial step of the grafting by diluting the reactive chains in a nonreactive matrix of the same molecular weight. In this way, we did not change the chemistry involved in the binding of the PS chains; we just modified the diffusion process. It was therefore possible to stop the grafting reaction after a few hours but still in the first regime of the kinetics (i.e., well before the onset of stretching). σ_{PS} could even be limited by the total amount of reactive chains in the spin-coated film. The grafted layers obtained in this way were not dramatically fragile; after consolidation (as explained above), they exhibited an excellent resistance to the sulfonation (δ = 95%, typically).

(21) For this attempt of grafting in solution, we used (carefully dried) toluene as solvent, a temperature of 120 °C, and a reaction time of 24 h.

Similar kinetics was also observed in the case of block copolymer adsorption.[8a] However, the interpretation of the slow increase regime might be different, because the bulk concentration did not play the same role as in our experiments. It might be due to slow reorganization of the already adsorbed chains.

It has been argued[11] that "grafting on" techniques would be intrinsically limited; the grafting density of the brushes prepared in this way could not be as high as for those obtained with "grafting from" techniques. As shown by this study, this is not the case; similar results are obtained in comparable reaction times.[22] However, a fair comparison between both approaches would require an exhaustive study, beyond the scope of this paper. The main advantage of the "grafting on" techniques is their relative simplicity, whereas the "grafting from" techniques open the possibility of preparing more sophisticated grafted layers. Besides, it is far from being obvious that the real challenge is to attain extremely high grafting density. On the contrary, it appears that many physical interfacial phenomena, like adhesion, friction, contact angle hysteresis, or liquid-crystal anchoring, for which grafted chains can play a role, are sensitive to the presence of a very few of these chains, and nothing is really improved if the grafting density is high.[23] In most cases, especially for applications, the real issue is the durability of the interfacial layer.

Sulfonation. There are several methods to sulfonate polystyrene. A few examples are given by refs 15, 24−25. Mir et al.[13] have chosen the 1.5/1 complex of sulfur trioxide/triethyl phosphate [SO_3:TEP] to prepare their PSSNa brushes.[24b] Although this method was relatively mild and the conditions were optimized, the synthesis was not reproducible enough for a systematic investigation. This motivated us to use a different approach, allowing a better control of the interface chemistry and to change the sulfonation method. The one described in ref 15 had a priori two advantages: it seemed to be relatively mild and free of side reactions (like cross linking or chain scission), and it proceeds homogeneously in dichloroethane which is a good solvent for PS. This should promote an homogeneous substitution along the chain backbone since all of the monomers would be accessible whatever its position from the grafting point and also in the plane, since there would be no macroscopic phase separation. The block copolymer experiment proves that the sulfonation yield is indeed the same for the chain half close to the anchoring point as for the "free" half. However, it should be recalled that this result corresponds to an average over many grafted chains. In the lateral directions, we have much less information. AFM studies (we used a Nanoscope 3 from Digital Instruments, in taping mode) were performed on dry PS layers and did not reveal any inhomogeneities. The AFM revealed a very smooth surface (with a roughness of less than 5 Å); very few holes, corresponding to ungrafted spots (on the whole wafer), were detected, which allowed us to check the measurement of the PS brush thickness obtained by ellipsometry. On the poly(styrene sufonate) brushes, the resolution of our experiments is poor; the most precise result was gained with ellipsometry: we did not observed variations of the layer thickness after sulfonation greater than 5%, from one illuminated

spot to one another. The size of the spot was 10 μm × 30 μm; this tells us that, at least at this scale, the sulfonation was also homogeneous in the directions parallel to the solid surface.

It appears that our sulfonation procedure was very reproducible; by varying the reaction time, we could control the degree of substitution α. There were, however, two puzzling observations: α was limited to 45% for deuterated PS (whereas it could reach 69% for protonated chains), and it seemed to increase with the molecular weight of the grafted chains. We do not have any explanation for the first result, but it might be related to the sulfonation mechanism itself.[25] The second one might be interpreted by a grafting density effect; for $N = 300$, we did not observe any influence of the grafting density on the sulfonation yield. It was the same as for free chains, sulfonated in dilute solution. However, the grafting density of the brushes prepared with the shortest chains ($N = 63$ and $N = 120$) was significantly higher; thus, we believe that the steric hindrance (and not directly the molecular weight) is at the origin of the low α values found with very short chains.

Comparison with Grafted Layers Obtained with Low-Molecular Weight Molecules. The grafting of low-molecular weight molecules (on glass and silicon oxide surfaces) has been the subject of numerous studies, and a vaste literature is devoted to this topic. Depending on the end function of the molecules, the surface, the grafting procedure, and the grafting conditions (solvent, amount of water, time of reaction, etc.), the resulting grafted layer can exhibit very different microscopic structures. Two main cases can be distinguished according to the surface coverage γ. If it exceeds γ_0 corresponding to the 2-dimensional close packing of the molecules, then it can be concluded without further investigation that the grafted layer presents a certain degree of 3d-cross-linking. For example, trialkoxysilanes (among them (aminopropyl)triethoxysilane is the most widely used) can easily form relatively thick layers on glass substrates when they are deposited in solution.[26] Although this kind of layer is not clean from an academic point of view, it allows one to obtain an interface (or interphase) highly functional and well-suited to various applications (for the adhesion of polymer matrixes to glass fibers, for the binding of proteins in biological assays, etc.). If γ is less than γ_0, the grafted molecules can form a submonolayer. This is usually the case when the molecule to be grafted has a single reactive end function (provided that there are no parasitic side reactions). For molecules carrying a multifunctional end group, submonolayers can also be obtained under specific conditions which are optimized to prevent the formation of 3d agregates.[27] AFM can be used to check the absence of such cross-linked aggregates.[28] This technique is also very useful to reveal the in-plane structure of these monolayers, especially its evolution as a function of the reaction time (which controls the surface coverage).[29] In general, monolayers corresponding to the close packing of the (grafted) molecules ($\gamma = \gamma_0$) are obtained solely with trifunctional molecules; indeed, the pattern of surface reactive groups usually does not match the close packing density required by the molecules to be grafted. This mismatch can be overcome by trifunctional molecules

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because they can form a self-assembled 2d-network which is attached only by a few points to the surface.

The PS brushes of this paper cannot perfectly fit with the above-described general framework despite some analogies. Indeed, the limit corresponding to the close packing of the PS chains cannot be reached for entropic reasons; it would exceed the chemical energy of the grafting point (whatever the chemistry involved in this bond). Thus, the comparison with this limit is not relevant. However, there is still a possibility that the PS chains form 3d-aggregates because they carry a trifunctional end group (but the surface coverage would remain below the close-packing limit—at least on average). The AFM studies we performed on dry PS brushes rule out this possibility; indeed, as mentioned above, they reveal a very flat and smooth surface (with a roughness of less than 5 Å). Moreover, if porous silica (with a specific surface area of 2.5 m^2/cm^3) is used as substrate instead of silicon wafers, it is possible to analyze by GPC the molecular weight distribution of the ungrafted chains (as above, a large excess of PS was used) after the grafting reaction. No significant broadening was observed which proves that the polymer does not cross-link in bulk, under the conditions we have used.

Strength of the Anchoring. The observation that the layer thickness did not increase after sulfonation according to what would be expected raised the following question: Where did the chain break? Anywhere along the backbone or at the anchoring point? A series of arguments are in favor of the second answer.

It was observed that the PS chains are more strongly attached to the silicon oxide surface when a trifunctional end-group, SiCl$_3$, is used instead of a monofunctional dimethylsilicon-chloride termination. This is probably due to the possibility of forming more than one bond per chain, either with the silanol surface groups (Figure 15a) or with other PS chains, by partial hydrolysis and condensation of the end groups (Figure 15b). In addition, this trifunctional end-group may still keep some reactivity after the grafting which can be used to consolidate the grafted polymer layer by the posttreatment as explained above.

Non reactive PS chains, of very high molecular weight (M_w > 10^5 g/mol), slightly adsorbed on the clean silicon wafers, that is, they could not be removed by rinsing the substrates (either with toluene or THF). But after sulfonation, they were completely washed off. IR-ATR and ellipsometry revealed that the superficial oxide layer was completely free of any polymer chains.

Mir et al. also observed that some of the grafted PS chains were removed after sulfonation.[13] Because they were using as substrate a porous medium of relatively high specific surface, they could analyze the released polymers. They found that these (water soluble) chains had the same narrow molecular weight distribution as the initial polystyrenes. In our case, it was not possible to do the same analysis because the amount of matter was too small. But the block copolymer experiment described above has shown that the remaining chains were intact: they kept the same length.

Finally, we also observed that for a given grafting density, the longer the chains, the more fragile the brush. For the longest chains, the samples were so fragile that they could not be immersed in pure water for a long period (>8 h) whatever their grafting density.

All of these observations led us to conclude that the chain breaking caused by the sulfonation occurs at the anchoring point. This was the weak point of the grafted layer. Therefore, when
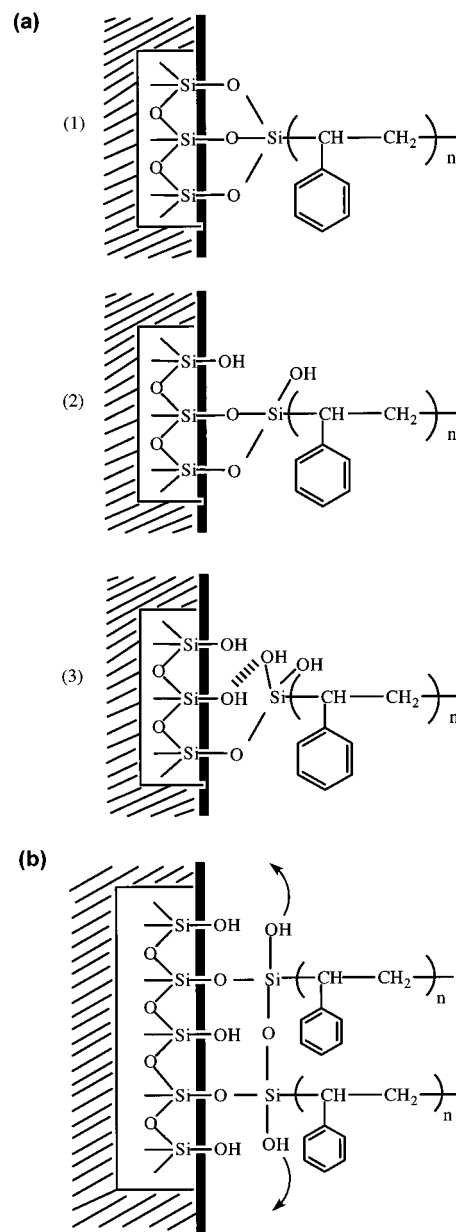
Figure 15. (a) A single PS chain grafted to the superficial silicon oxide layer via different siloxane bridge or H-bond combinations. (b) Two grafted PS chains connected by a siloxane bond.

we were seeking to settle the problem of degrafting, we focused on a mean to protect and to strengthen the bond between the polymer chain and the solid surface. We noticed that the brush made with the shortest chains ($N = 67$) was especially robust ($\delta \approx 95\%$). This result suggested the use of oligomers to fill the holes inbetween the grafted long chains, and indeed this worked remarkably well. It has to be mentioned that the conditions for the consolidation posttreatment reported above (24 h in a vacuum oven at 150 °C) were optimized; a shorter reaction time reduced the efficiency of the posttreatment, while a longer time led to a (slight) degrafting of the long chains, increasing with time.

The mechanism responsible for the consolidation is likely 2-fold: the dense oligomer layer would prevent the sulfonation agent and the sodium ions (known to weaken the siloxane bonds) from approaching the anchoring points of the long grafted chains, and the oligomers could also form a self-assembled network which would include the long grafted chains via their uncompletely condensed end functions (cf. Figure 15b).

This consolidation process could be interesting for many applications; indeed, a crucial issue of all organic thin layers used to modify the properties of various surfaces in industrial applications (for instance, glass windshields) is their durability. They must be resistant to chemical attack, mechanical abrasion, UV exposure, in some cases for years. The mechanisms of degradation are far from being completely understood; they are complex and probably numerous. Nevertheless our study shows that the anchoring bond can be the weak point of these organic layers, and it suggests a means to strengthen it: the use of very short molecules which have the ability to form a network connecting the surface and all of the anchoring points together and to protect the base of the layer.

Conclusions

Dense poly(styrene sulfonate) brushes have been prepared on silicon wafers according to a two-step procedure: first, poly-(styrene) chains, terminated by a silicon trichloride group, were grafted in melt, and second, they were converted to poly(styrene sulfonate) by sulfonation with acetyl sulfate and neutralization. Ellipsometry and IR-ATR, used as complementary techniques, allowed a full characterization of the formed polyelectrolyte brushes; in particular, they have shown that the substitution is homogeneous along the chain backbone. The sulfonation induced in some cases a substantial degradation of the initial PS brush; the chains were pulled up from the surface (and not randomly cut). This degrafting was significantly reduced after consolidation of the PS brush with a dense layer of oligomers.

Experimental Section[30]

Solvents and Other Chemicals. Benzene, sulfuric acid, 1,2-dichloroethane, and tetrahydrofuran were from SDS. Hydrogen peroxide solution (30% v/v), sodium hydrogen carbonate were from Prolabo. The other chemicals were from Aldrich. Unless specified, all of these solvents and chemicals were of analytical grade. 1,2-Dichloroethane was dried over molecular sieves; toluene was dried over calcium hydride; these solvents were distilled just before use. Benzene (of HPLC grade) was first dried over calcium hydride, distilled using a vacuum line over red oligostyryllithium, and finally distilled into the polymerization flask. Styrene (+99%) (to which a small amount of tetrahydrofuran corresponding to 2−3 mol of initiator has been added) was first dried over calcium hydride, distilled over fluorenyllithium, and finally distilled into the polymerization flask. Deuterated styrene was purchased from CEA; its initial deuteration rate was 98%. A very small amount of regular styrene was added to lower this deuteration rate to 96%, to contrast match the PS chains made from this monomer with D_2O (from CEA, 99.9% deuterated). The initiator for the anionic polymerization of styrene was a *sec*-butyllithium solution in cyclohexane, from Fluka.

Silicon Wafers. The polymers were grafted onto polished silicon blocks. Before grafting, the solid substrate was immersed for 20 min in a hot mixture (7:3 v/v) of concentrated sulfuric acid and aqueous hydrogen peroxide. The silicon wafer was then thoroughly rinsed with deionized water (of 18 MΩ cm resistivity) and dried under an argon stream. Ellipsometry and IR-ATR were used to check that the wafer surface has been cleared of all organic molecules (either adsorbed or grafted). If some contaminants were still detected, the oxidizing treatment was repeated. After this treatment, the silicon block surface was free of all organic molecules, completely hydrophilic. In addition, this procedure allowed the wafer to be recycled without altering the quality of its surfaces. Just prior to the grafting, the silicon block was ultimately cleaned by a UV/ozone treatment for 30 min.

Polystyrene Synthesis. The polystyrene macromolecules were synthesized by anionic polymerization in carefully dried benzene using *sec*-butyllithium as initiator, at room temperature. The monomer being completely consumed after a few hours (depending on the desired

(30) Tran, Y. Ph.D. Thesis, Université Paris, June, 1998.

molecular weight), the living polymer was divided into two parts and terminated either with a few drops of methanol or with a 50-fold excess of silicon tetrachloride $SiCl_4$. The polymer was finally recovered by lyophilization, directly from its benzene solution and stored under vacuum. For each of the polystyrene samples, we had therefore reactive chains, terminated by trichlorosilane end-groups (PS−$SiCl_3$) which were able to form a covalent bond with the silanol Si−OH surface groups and nonreactive polymers (PS−H), of exactly the same molecular weight (M_w). M_w was determined by gel permeation chromatography (see Table 1).

The co-polystyrene PSd−PSh−$SiCl_3$ was synthesized, following the same method as for the homopolymers: the deuterated monomer was polymerized first, and after 3 h, an aliquot was withdrawn and quenched with a drop of methanol. Then, the second monomer (protonated styrene) was introduced and allowed to polymerize again for 3 h. The termination was the same as for the homopolymers. The number of deuterated (respectively, protonated) monomers of this diblock was N_d = 156 (respectively N_h = 131), with in both cases, a polydispersity index of 1.03.

Grafting Procedure. The PS was dissolved in carefully dried toluene. The solution (of typically 2% volume fraction) was then spin-coated or evaporated onto the clean silicon block. This resulted in the formation of a thin, dry PS film. The silicon block was immediately put in a vacuum oven, and the grafting reaction was performed at 160 °C, under vacuum, for typically 24 h. Finally, the wafer was rinsed with toluene (using an ultasonic bath) to remove all of the chains which had not reacted, and the wafer was dried under an argon stream.

Sulfonation. "Acetyl sulfate" was prepared in a dried glass apparatus by adding concentrated sulfuric acid to a solution of acetic anhydride in freshly distilled 1,2-dichloroethane. This solution was prepared by mixing 49.8 mL of dichloroethane and 10.2 mL (11.04 g, 0.108 mol) of acetic anhydride and cooled in an ice bath. Sulfuric acid (3.6 mL, 6.29 g, 0.064 mol, 95%) was then slowly added. A clear solution of acetyl sulfate (molarity = 1.008mol/L) resulted. Since the sulfonation reagent is not very stable, it was prepared just before use. The sulfonation reaction was performed in an airtight Teflon reactor, especially designed to fit the silicon block size. The acetyl sulfate solution was poured onto the PS brush, and the reactor was hermetically closed and heated at 60 °C for typically 5 h (see the effect of the reaction time in the next part). The reaction was stopped by rinsing the surface with methanol. The poly(styrene sulfonic acid) was neutralized rapidly—to prevent the formation of sulfone cross-links—by immersing the grafted surface in a 0.5 M $NaHCO_3$ solution. After rinsing with pure water, a poly(styrene sulfonate sodium salt) brush was obtained.

Some "free" poly(styrene sulfonate sodium salt) was also synthesized in bulk following the same receipe: 0.104 g (10^{-3} mol) of polystyrene was dissolved in 0.3 mL of distilled dichloroethane, an excess of acetyl sulfate solution (3 mL, 3 × 10^{-3} mol) was added, the mixture was stirred for 5 h at 60 °C, and the reaction was terminated by the addition of 5 mL of methanol. The polymer was extracted with water, the aqueous phase was dialyzed during 48 h, and the polymer was freeze-dried. The solid polymer was redissolved in pure water. An aliquot was titrated with 0.01 N sodium hydroxide solution. The sulfonation yield was found to be about 65% for the protonated chains and about 40% for the deuterated ones. (These values were also obtained by elemental analyses and IR spectra—see the Supporting Information). The rest of the polymer was neutralized with a 0.5 M $NaHCO_3$ solution. Finally, the aqueous solution of poly(styrene sulfonate sodium salt) was dialyzed before being freeze-dried. Films of these free chains (either with sodium or with alkylammonium counterion) were spin-coated on silicon prism, and IR-ATR absorption spectra were recorded. They exhibited the same absorption bands as those of the corresponding brushes; in particular, no shift due to some grafting-induced anisotropy was observed. These measurements allowed us to calibrate the IR-ATR experiments as explained above.

Ellipsometry and IR-ATR Measurements. The thickness h_{dry} of the dry PS brush was measured by ellipsometry using a SD2300 PLASMOS apparatus. h_{dry} corresponds to an average of about 100 measurements all over the surface of the silicon block, each of them being an average over a surface of area of 30 × 10 μm^2. The deviation

from the average did never exceed 5%. The refractive index of the PS layer was assumed to be 1.6.

The grafting density σ_{PS} is related to h_{dry} via the following equation:

$$\sigma_{PS} = \frac{a^2}{D_{PS}^2} \quad \text{with}$$

$$D_{PS}(\text{Å}) = \left(\frac{h_{dry}(\text{Å}) \times 0.1 \times d(\text{g cm}^{-3}) \times 6.022}{M_w(\text{g mole}^{-1})} \right)^{-1/2}$$

a being the size of the styrene monomer ($a = 5.1$ Å), d (in g cm^{-3}) the PS density and M_w(g mole^{-1}) the PS molecular weight. $d = 1.06$ g cm^{-3} (respectively $d = 1.14$ g cm^{-3}) for protonated (respectively deuterated) polystyrene.

Infrared spectra were recorded on a Magna IR 50 (Nicolet) spectrometer with a resolution of 2 cm^{-1}. For these measurements, the silicon block had a trapezoidal shape ($80 \times 10 \times 1.5$ mm^3 with an angle of 22°30′) which allowed the IR beam to penetrate and reflect 26 times on the great base where the polymer was grafted. The number of reflections did not vary from more than 1 for two different prisms. This means that if the same experiment (same conditions of sample preparation) was repeated on two different silicon prisms, the results did not vary from more than 4%.

As explained above, two bands were used for the determination of the strongly bound fraction δ and the sulfonated fraction α: 2924 and 3026 cm^{-1} (for protonated brushes). δ and α were obtained within a certain degree of uncertainty whose origin is 2-fold: the reproducibility of the data collection itself which was of the order of 4% and the determination of the baseline. In the latter case, the overlap with other bands could contribute to increase the error bar on δ and α up to 15%.

Neutron Reflectivity. NR can be used to gain information about the structure of planar surfaces, both liquid and solid, at a length scale between a few Å and a few thousandths Å. The experimental procedures and setup were described in detail elsewhere.[16] In essence, neutron reflectivity is not different from light reflectivity. It is sensitive to the scattering length density profile (which corresponds approximately to the refractive index) in the direction normal to the interface $Nb(z)$. In the context of polymer interfaces, this technique is especially powerful because it can distinguish between H and D atoms, allowing the layer structure to be revealed if selective deuteration is used.

Supporting Information Available: The preparation and the characterization of the free PSS−Na samples are described in more detail (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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