Neutron Reflectivity Study of Poly(4-vinylpyridine)–Deuterated Polystyrene (P_4VP–dPS) Diblock Brushes

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The concentration profiles of end-grafted polymer brushes in solution have been an area of extensive study both theoretically[1-6] and experimentally.[7-9] More recently the focus has shifted to the effects of laminar shear[10] and mixed solvents[11] on the brush profile. Both of these issues impact in many design applications. Shear plays an important role in the effectiveness of lubrication by a polymer layer of moving components, while in a mixed solvent it has been shown that a brush can trap a layer of a liquid that would not normally wet the solid surface.[11] In order to effectively profile the grafted polymers under these conditions, it is important for the chains to be irreversibly bound to the substrate. This allows the grafting density of the brush to be kept constant while the chemical and mechanical properties of the liquid matrix are varied. In this paper we show that this may be conveniently accomplished using poly(4-vinylpyridine)–deuterated polystyrene (P_4VP–dPS) block copolymers. P_4VP strongly hydrogen bonds to the silica surface, and hence large grafting densities can be obtained with small P_4VP end blocks. Strongly grafted polymers using chemically reactive end groups have also been reported by several groups.[12-14] In contrast to these systems, the block copolymers produced comparable or larger maximum grafting densities without the need for any special procedures to remove the excess free end molecules which compete for surface sites, or special storage precautions for the unreacted polymers. In addition, the maximum grafting density was not sensitive to the preparation of the silica surface. Similar results were obtained on surfaces used as received from the manufacturer, those with oxides grown in chromic acid or the Shirake technique, and those from which the oxide layer was stripped in hydrofluoric acid.

The block copolymers used in the experiments reported here consisted of 18 P_4VP units and 130 dPS units and were synthesized as described in ref 15. Films between 100 and 130 Å thick, where the precise thickness was measured by ellipsometry, were spun from a toluene solution onto silicon wafers 3 in. in diameter and 0.5 cm thick. The samples were annealed in a vacuum of 10^{-4} Torr at 150 °C to allow P_4VP to react with the surface. Atomic force microscopy (AFM) examination of the samples after annealing (Figure 1) shows micelles approximately 0.2 μm in diameter and 130 Å high segregating on the sample surface when the film thickness is greater than 90 Å. The size and density of the micelles are seen to increase with the initial thickness of the film. When the film thickness is greater than 130 Å, large surface domains ≥ 1.5 μm in diameter occur on the sample surface. These domains have a uniform height which is equal to the layer spacing in the ordered bulk structure of diblock films, and therefore we expect that the internal structure is the same. Rinsing the samples in toluene, a good solvent for PS, reduced the thickness of all samples from an as-spun thickness of approximately 100 Å down to 70–80 Å corresponding to a grafting density of 4.5×10^{-3} chains/Å^2. Agitation of the samples in the solvent was done to simulate shear experiment conditions, and no further reduction in film thickness was observed. AFM microscopy showed that the micelles, not being directly bound to the silicon surface, were removed by this process. Therefore, the maximum grafting density is limited by the competition between grafting and micelle formation. It should be noted that the same maximum grafting density was also obtained simply by adsorbing P_4VP from solution. The main advantages of spinning and heating were that the grafting density could be more closely controlled by varying the film thickness below the maximum value and annealing drives away any excess toluene solvent.

Concentration profiles of the dPS segments in solution were investigated by neutron reflectivity.[16] The experiments were performed on the H-9A reflectometer at the Brookhaven National Laboratory High Flux Beam Reactor. The neutron wavelength was fixed by pyrolytic carbon monochromators to be 4.16 ± 0.02 Å, and slit settings were adjusted to fix the resolution at a constant value of $\Delta q_z/q_z = 0.02$, where q_z is the momentum transfer prependicular to the sample surface. The reflectometer has a horizontal geometry. Silicon substrates were placed face down to seal a Teflon trough filled with the desired solvent (not containing any polymer) lying flat on the sample table. Each time the solvent was changed the silicon wafer with the brush was carefully washed and heated to remove the previous liquid. The experimental temperature was held at 25 °C by an external heat lamp. CCl_4, rather than toluene, also a good solvent for PS, was chosen since the absence of hydrogen minimizes the incoherent component of the neutron scattering.

The results are shown in Figure 2. Figure 2c is the reflectivity spectra obtained initially without solvent. Figure 2a is the spectrum obtained with carbon tetrachloride (CCl_4) solvent, and Figure 2b is the spectrum obtained in cyclohexane. The data acquisition time for these spectra was approximately 24 h. The data were normalized to the direct beam through the silicon wafer. Following the cyclohexane point, the brush was stored in CCl_4 for 20 days, dried, and remeasured in air to check the amount of polymer desorbed. The data are shown in Figure 2d. Figure 3 shows the profiles which were used to produce the solid line fits to the data. The CCl_4 data were fit with a modified parabolic profile of height $h = 215$ Å. This value is approximately 7 times the radius of gyration of the brush in the melt and confirms that the grafting interaction is strong enough to sustain significant stretching of the brush. The value of h is in good agreement with the calculations of Milner, $h = 220$ Å, for a brush of this grafting density in a good solvent. Changing the solvent to cyclohexane, a solvent of intermediate quality for PS at 25 °C, is seen to decrease the brush to a parabola of $h \simeq 150$ Å. This is also consistent with the simulations of Grest and Murat[17] where the increasingly unfavorable interactions between the solvent and the brush are insufficient to overcome the loss in entropy due to stretching. It should be noted that the profile for the brush in CCl_4 is not a simple parabola but has a diffuse "foot" section. This feature has been explained by Milner[2,6] as arising from

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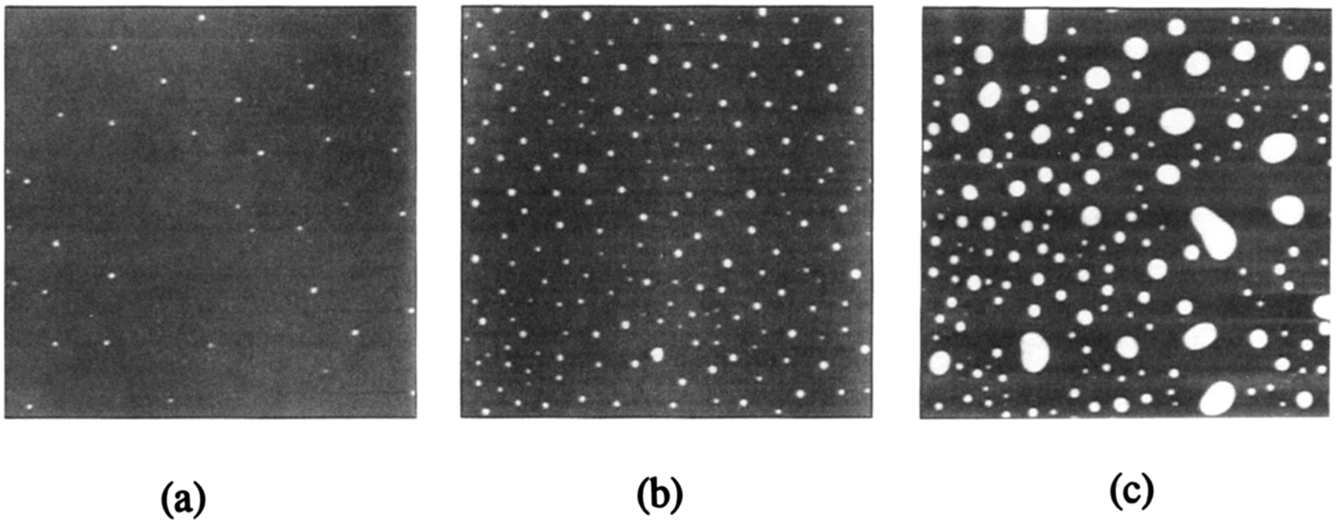

Figure 1. AFM topographs of thin P$_4$VP–dPS films on silicon. Thicknesses are 92 (a), 106 (b), and 130 Å (c). The image area is 15 × 15 μm.

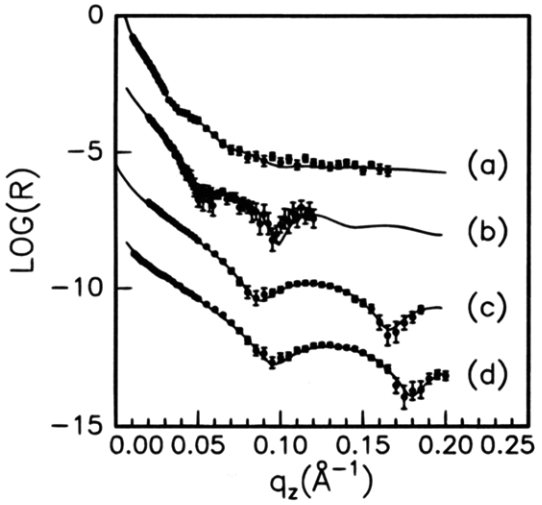

Figure 2. Neutron reflectivity spectra for a P$_4$VP–PS grafted layer (a) in contact with CCl$_4$, (b) in contact with cyclohexane, (c) before emerging into solvent, and (d) with solvent removed, after 20 days in storage in CCl$_4$.

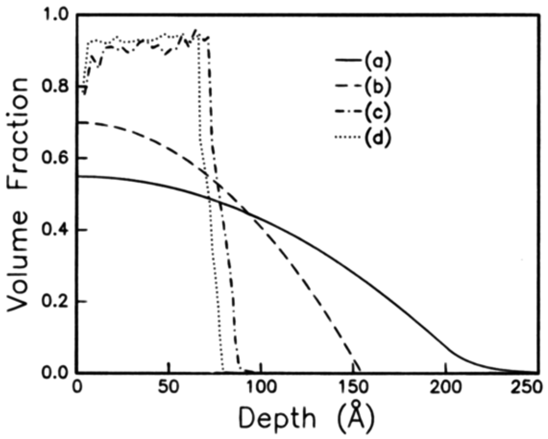

Figure 3. Volume fraction profiles used for neutron reflectivity calculations in Figure 2.

chain end fluctuation in the otherwise stretched brush. As can be seen from the data, these fluctuations become less pronounced as the brush height is decreased as cyclohexane.

The air spectra were fit to a simple uniform layer. The solid line corresponds to the initial thickness of 100 Å prior to solvent immersion. From the profile in CCl$_4$, one obtains a total amount of adsorbed polymer of $Z^* = 78$ Å, or approximately 22% of the chains were desorbed after 20 h in CCl$_4$. Immersion in cyclohexane for another 20 h changes Z^* by only a small amount to 75 Å. The dotted uniform profile corresponds to the data obtained after 20 days in CCl$_4$. From the figure it can be seen that Z^* has only decreased to 71 Å even after prolonged exposure to a good solvent where the chains were significantly stretched.

In conclusion, we have found that the P$_4$VP–dPS diblock copolymers strongly adsorb to silicon surfaces and provide a convenient and stable system for studying brushes in static solution and under shear.

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