Neutron Reflectivity Study of the Density Profile of a Model End-Grafted Polymer Brush: Influence of Solvent Quality

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Neutron reflectivity measurements are made on a chemically end-grafted polymer brush swollen over a range of temperatures above and below the theta point. Good agreement between the brush profiles and recent self-consistent field calculations and numerical simulations is obtained for temperatures in the vicinity of the theta point and in a good solvent. The expansion of the main body of the brush resembles a swelling gel, while the brush tail expands similarly to a polymer in solution.

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The equilibrium properties of tethered polymer chains ("brushes") have attracted continued attention in recent years. Tethered polymeric systems are important for the modification of interfacial properties, colloid stabilization, and numerous other applications and have been the subject of many theoretical, experimental, and simulation studies [1–15]. Most theories have focused on predicting the equilibrium density profile of end-anchored chains having a moderately high grafting density which are immersed in a good solvent. Recently, theoretical predictions for the density profile of polymer brushes in a solvent having varying excluded volume (i.e., solvent "quality") were estimated from analytical self-consistent field (SCF) theory by Zhulina [4], and complementary Monte Carlo (MC) simulations and molecular dynamics (MD) calculations were performed by Lai and Binder [5] and Grest and Murat [6], respectively. The present work provides experimental measures of the density profiles of a polymer brush from neutron reflectivity measurements and compares these results with recent theory.

Experimental verification of theoretical predictions for the brush density profile has been difficult because idealized grafting conditions are usually assumed. Most previously reported measurements on brushes involve end groups which are physically adsorbed [10–12] and thus too weak to tether strongly stretched chains, resulting in a lower overall grafting density which depends on solvent quality. Higher densities of adsorbed chains can be attained by increasing the polymer solution concentration [13], but this strategy leads to the formation of a wetting nongrafted layer on top of the end-adsorbed polymer layer.

A more controllable tethered polymer layer can be formed with chemically grafted brushes. Auroy *et al.* [14] studied such systems in porous media using small-angle neutron scattering (SANS) to determine the scaling of brush height with molecular weight and grafting density in good and poor solvents. They also studied the variation of the brush height with solvent quality in a mixture of solvents and by changing the temperature of the pure solvent. While they showed the profile to be roughly parabolic in a good solvent and more steplike in a very poor solvent, a comprehensive study of the variation of shape of the brush profile with solvent quality was not performed since this is difficult using SANS. Moreover, the SANS measurements were performed inside pores which are not the ideal flat surfaces considered by theory [2–9].

In the present Letter, we report neutron reflectivity (NR) measurements on chemically end-grafted polymer PS-$SiCl_3$ of $M_w = 105\,000$ ($M_w/M_n < 1.05$). The polymer was end-grafted onto a 10 cm diam × 5 mm thick polished silicon slab that was precleaned in a heated bath of 70% H_2SO_4/30% H_2O_2 (w/w). The grafting procedure is similar to that used in preparing a much lower molecular weight PS-$SiCl_3$ (8 K) brush reported earlier [15]. Typically, the $SiCl_3$ end group has been used in chemically grafting short chain alkyl molecules to silicon oxide surfaces via silanol chemistry. Our extension of this chemistry to polymeric system is useful since the anchoring group is pointlike, the grafting surface is planar, and the grafting density is controllable through variation of reaction time and solution concentration. Measurements on such a well characterized brush should be very useful in testing the rapidly developing theory of polymer brushes.

Dry film thicknesses [15] were characterized by x-ray reflectivity (XR), before and after the NR measurements. The dry film had a thickness of about 100 Å which translates into a coverage, $\Gamma \sim 10.5$ mg/m^2 or in terms of a dimensionless grafting density, $\sigma = (a/D)^2 = 0.027$, where $a = 6.7$ Å is the statistical segment size and D is the average distance between grafting sites [14]. NR measurements were performed at the NG7 reflectometer at NIST. The incident neutron beam entered through one edge of the silicon single crystal and reflected from the silicon-polymer-solvent interface with the reflected beam again traversing the crystal before exiting to the detector. A fixed wavelength of $\lambda = 4.1$ Å neutrons was used. Specular neutron reflectivity was obtained as a function of wave-vector transfer $q_z = 4\pi \sin\Theta/\lambda$, where Θ is the angle of incidence and reflection of the neutron beam with the silicon-solvent interface. Details of the NR technique,

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the solvent containing teflon cell, and the temperature control assembly can be found elsewhere [16]. NR data from a clean silicon slab in contact with pure solvents, deuterated toluene, or cyclohexane could be fitted with a scattering length density of silicon and solvents to be the same as known literature values. In addition an oxide layer of 20 Å was required to fit the data, whose thickness was kept constant at 20 Å in all of the fits to the grafted brush as well.

Figure 1 shows neutron reflectivity from the brush in a good solvent (d-toluene) at room temperature and in a temperature range between 53.4 °C and 14.6 °C, around θ (34 °C [17]) in a poorer solvent, d-cyclohexane. The temperature was repeatedly cycled to ensure reproducibility of data. The brush height (h) can be estimated from the raw data $h \sim \pi/q^*$, where q^* is the first minimum in the reflectivity oscillations corrected for refraction effects. Discretized real space profiles were generated by a finely meshed multilayer fitting algorithm [16] with fit parameters optimized to best fit the data. A simple error function profile did not satisfactorily fit the full set of data under varying solvent quality. Alternatively, the brush density profile is taken to have the form

$$\phi(z) = \begin{cases} \phi_s[1-(z/h)^2]^\alpha, & z<h, \\ 0, & z>h, \end{cases} \qquad (1)$$

which is motivated by analytic SCF calculations [3,4]. Here ϕ_s is the polymer volume fraction at the silicon oxide surface, h is the cutoff thickness of the profile, and α is the "profile exponent" which is taken to be a measure of the density profile shape. In the limit of infinitely long chains, the SCF calculations give $\alpha = 1$ for a good solvent and $\frac{1}{2}$ for a θ solvent. It was necessary to introduce a "tail" to the brush profile given by Eq. (1) to fit the data. In simulation of polymer brushes [5,6] this tail has its origin in the fluctuations of the brush at the outer interface due to finite chain length. We modeled this by convoluting Eq. (1) with a normalized Gaussian of full width at half maximum Δ (tail width) in a region spanning nearly $\pm 2\Delta$ about the cutoff length. In some cases this procedure introduced a very small discontinuity in the profile at the point where the convolution was stopped, however, its effect on the reflectivity is negligible. The maximum discrepancy between integrated polymer volume fraction obtained by NR and dry film XR was ±5%. Thus the data analysis is internally self-consistent. Polymer segment density profiles $\phi(z)$ obtained from fitting the NR data are shown in Fig. 2.

First, we consider the overall brush swelling with varying solvent quality. In a good solvent (d-toluene) the first minimum in the reflectivity in Fig. 1 occurs at a very low q^*, indicating a highly stretched brush. The brush height h is ~820 Å (Fig. 2), extending over nine times the radius of gyration in the melt, $R_g \sim 87$ Å. Such strong stretching is only possible when the brush is strongly tethered by chemically end grafting [14,15] (for comparison we note that maximum extension ratios are typically on the order of $\sim 5R_g$ in highly asymmetric diblock copolymers of PS-P2VP [10]). At the highest temperature (53.4 °C) measured in d-cyclohexane the brush height is ~450 Å, only one-half of its stretched length in d-toluene. Further reduction in solvent quality by lowering the temperature causes additional contraction of the brush in qualitative

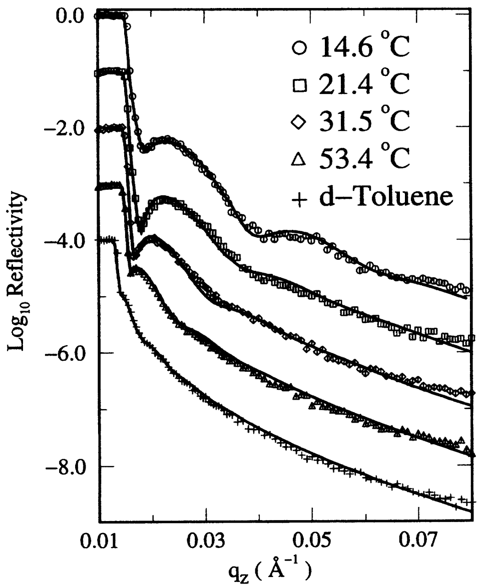

FIG. 1. Reflectivity data as a function of neutron momentum q_z ($= 4\pi \sin\Theta/\lambda$) from the end-grafted brush in d-cyclohexane at different temperatures (data at 9.5 °C and 41.5 °C have not been shown due to space limitations) and in d-toluene. Consecutive reflectivities have been offset from each other by a decade for clarity. Solid lines are reflectivities calculated from corresponding brush profiles shown in Fig. 2.

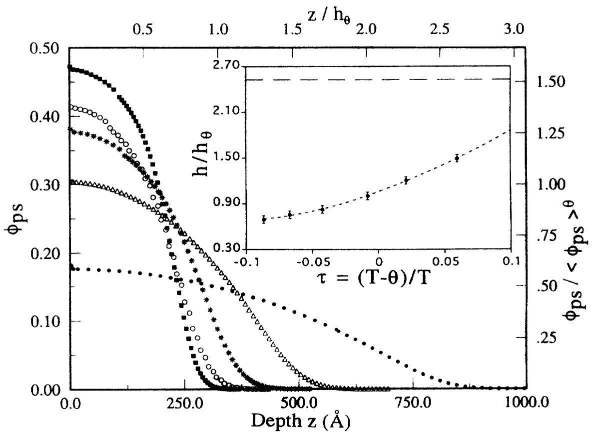

FIG. 2. Polymer volume fraction $\phi(z)$ as a function of distance from grafting surface in d-cyclohexane at 14.6 °C (■), 21.4 °C (○), 31.5 °C (*), 53.4 °C (△), and in d-toluene at 21 °C (●). (Actual density of points is ~10 time higher in calculations.) $\langle \phi_{ps} \rangle^\theta$ is the normalized layer density under theta conditions as discussed by Zhulina *et al.* [4]. The density profile shape accords with SCF predictions in theta and good solvents as indicated by Zhulina (Fig. 3 of Ref. [4]). Inset shows brush height normalized by its θ value as a function of dimensionless solvent quality, τ.

agreement with SCF calculations and MC and MD simulations on short chain systems. At approximately the bulk theta temperature of d-cyclohexane, the brush thickness is approximately $h_\theta \sim 325$ Å, while at the lowest measured temperature of 9.5 °C, $h \sim 225$ Å. In contrast, the fully contracted length for the dry film is 100 Å.

The inset of Fig. 2 shows h/h_θ, i.e., brush height normalized by its theta value, plotted as a function of the reduced temperature variable, $\tau = (T - \theta)/T$. At the θ temperature [18], $\tau = 0$, the brush chains are stretched from their ideal Gaussian configuration (dilute solution dimensions at theta point by a factor of about 3, reflecting the effect of interchain interactions, consistent with recent analytic and numerical (MC and MD) calculations [5,6]. The rise of h/h_θ with τ saturates for large τ [18] and fixed chain length, corresponding to the athermal limit. We have drawn a dashed line passing through the d-toluene point to represent the upper limit of the stretched brush height. Similarly, the extreme poor solvent case of a dry brush in air ($\tau \ll 0$) can be assumed to represent the lower limit of contraction of the end-grafted brush. Between these limits, a dashed line is drawn through all the data points to illustrate the smooth nature of swelling of the brush with increasing solvent quality about the θ point. This pattern of swelling is qualitatively similar to the temperature dependence of swelling of slightly cross-linked gels [19].

We next focus on the detailed shape of the brush density profile with varying solvent quality. Figure 3 illustrates the variation of the profile exponent α as a function of reduced temperature τ. In d-toluene we find that $\alpha = 1.0$ (i.e., a parabola) gave the best fit to the reflectivity data. Such a parabolic profile is consistent with self-consistent field theory [3,4] and numerical (MC [5] and MD [6]) calculations for densely grafted in *good* solvents. With reduction of solvent quality the layer contraction is accompanied by a decrease in the value of α, indicating a flattening of the profiles. The qualitative effect was also observed in recent numerical simulations [6]. Even at the highest temperature of 53.4 °C in d-cyclohexane, however, deviations from a parabolic profile can be seen so that the profiles are now "root parabolic" [i.e., $\alpha < 1$ in Eq. (1)]. Note that as the theta point it approached $\tau \sim 0$, we observe $\alpha \sim 0.5$, in accord with the SCF predictions of Zhulina *et al.* [4]. To our knowledge this is the first experimental verification of this prediction of SCF theory. Recent MD [6] and MC [5] calculations, on the other hand, have concluded that the theta solvent density profile is flatter than the SCF prediction of Zhulina *et al.* [4], but these treatments do not account separately for the tail as in the present fitting of the density profile.

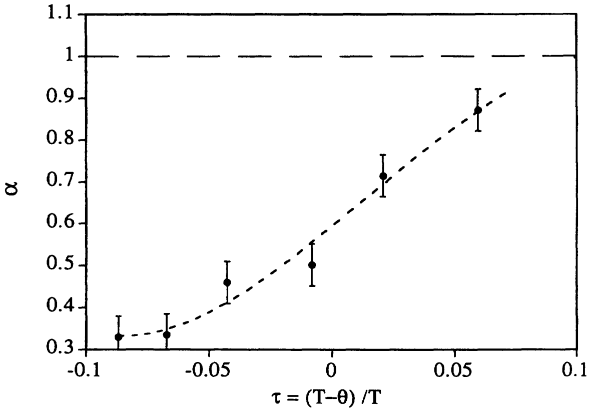

FIG. 3. Variation of profile exponent α with solvent quality τ. The dashed line is a guide to the eye passing through data points obtained from measurements in d-cyclohexane at different temperatures. The horizontal dashed line corresponds to a parabolic profile obtained in d-toluene.

The flattening of the density profile (reduction of α) with a lowering of temperature continues below the θ temperature, presumably approaching the uniform density profile seen for the dry film. At the lowest measured temperature of 9.5 °C we find $\alpha \sim 0.33$. Note, however, that the profile is still quite different from an ideal step profile ($\alpha = 0$). We have only obtained the step density profile [15] under extremely poor or nonsolvent conditions such as in D_2O by NR or in air as measured by x-ray and neutron reflectivity. While the shape exponent α matches the SCF prediction under good and theta conditions (where the theory is more reliable as in polymer solution theory of swelling), the prediction of a sharp drop of $\phi(z)$ to zero at the periphery of the brush below the θ point is not observed. Such sharp features would be difficult to observe experimentally, due to the smearing in $\phi(z)$ arising from finite chain fluctuation effects [5,6] and polydispersity. The polydispersity of the brush chains is small, however, ($M_w/M_n < 1.05$) and this effect should be largely independent of temperature. It is notable that the width of the brush tail is very sizable even under theta conditions ($\Delta_\theta \approx 130$ Å).

Figure 4 depicts the variation of the normalized tail width (Δ/Δ_θ) with solvent quality. Once again a dashed line representing the good solvent limit is indicated. Under these conditions the diffuse tail represents a substantial portion of the entire brush width and is a limiting factor in the accurate determination of the exponent α. Clearly, the fluctuations associated with finite chain length have an appreciable influence on real brush density profiles. We expect that the chains in this interfacial regime should be less stretched through interchain excluded volume interferences, and these "chain tips" can be expected to swell much like a chain in a semidilute or dilute solution. In accord with this intuitive view, observe that the shape of the dashed line through the data points is *sigmoidal.* This pattern is unlike the swelling of the brush itself and is indeed similar to the swelling of homopolymers in dilute solutions [20]. The extended brush tail should be important for problems involving interacting brushes where significant brush interpenetration may be expected on account of the diffuseness of the outer brush layer.

Another observation relating to the shape of the profiles in Fig. 2 is the lack of a detectable (greater than 15 Å)

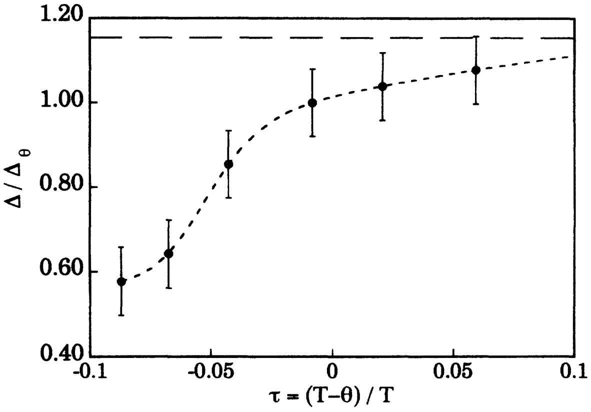

FIG. 4. Solvent quality dependence of brush interfacial width Δ in reduced θ parameters. Here, $\Delta_\theta = 130$ Å corresponds to the brush interfacial width at approximately the θ value. The horizontal dashed line corresponds to the upper limit in a good solvent, *d*-toluene.

depletion zone [11] of polymer near the silicon surface. Such a zone near the silicon oxide surface would be observable as a change in the asymptotic value of the reflectivity, owing to the large scattering length density jump at the surface created by the deuterated solvent relative to either the silicon oxide or the polymer. However, in all of our fits a simple error function interface of width 10 Å between the silicon oxide surface layer and the brush $\phi(0)$ gave satisfactory fits. The degree of surface depletion decreases with surface chain attraction in single chain theories of polymer adsorption [21] and numerical studies of segment density profiles performed [6]. Grest and Murat [6] show that the depletion zone is diminished by an attractive polymer surface interaction and suggest that it should be possible to observe depletion for nonadsorbing surfaces. We expect that a similar effect is responsible for the lack of an observed depletion zone in our brush. We note that the screening of polymer surface interactions is expected at high surface coverage, so that the depletion effect should also diminish with increased coverage σ. This effect could be explored by coating the adsorbing surface before attaching chains or by adding a strongly adsorbing specimen which is taken up at the surface.

In conclusion, we have observed the stretching and contraction of a model brush consisting of a chemically end-grafted PS, as a function solvent quality to make more stringent tests of modern brush theories. The density profile shape exponent α describing the shape of the brush profile in good and theta solvents accords with self-consistent field calculations which predict α equal to 1 and $\frac{1}{2}$, respectively. We observe that the main body of the brush swells differently from the diffuse tail, and analogies are drawn with the swelling of lightly cross-linked gels and polymers in solution, respectively. No discontinuity of brush density profile is observed below the theta point, nor is a surface depletion layer of polymer observed under good solvent conditions.

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