POLYMER BRUSH RESPONSE TO SOLVENT FLOW

The presence of polymer chains grafted or adsorbed onto a surface can dramatically alter the forces that affect interactions between surfaces. The equilibrium properties of such polymer brush systems have been studied for the past two decades, yielding general agreement between theory and experiment. Conversely, the non-equilibrium properties of polymer brushes are still under intense theoretical and experimental investigation. Of particular interest is the response of a brush to the frictional forces imposed by solvent flow. The behavior of polymer brushes subjected to flow has important technological implications for the rheology of colloidal dispersions stabilized by polymer layers, for the lubrication properties of polymer coated interfaces, for biocompatibility of medical implant devices, and for permeation flow through polymer-containing porous media [1].

The height of a polymer brush is determined by the equilibrium conformation of the tethered chains, which depends on both the grafting density and quality of solvent. The basic physics governing the static behavior of a polymer brush result from a competition between two opposing tendencies: 1) elastic contraction, as the chains attempts to maximize their entropy by adopting random walk configurations, and 2) monomer-monomer interactions, such as polymer-polymer repulsions, and polymer-solvent wetting [2, 3].

Polymer chain stretching in densely grafted brushes has been studied by many different techniques including surface forces apparatus [4], neutron reflectivity [5], and small angle neutron scattering (SANS) [6]. In general, there is good agreement with results from experiment, simulations and analytical calculations [3].

Oscillatory shear measurements performed with a surface forces apparatus suggest that the normal forces between a pair of brush surfaces are altered when sheared. However, these measurements do not give the actual brush profile either with or without shear. Effective hydrodynamic thickness measurements of polymer brushes under shear indicate a thickening of the brush; whereas neutron reflectivity experiments on adsorbed PS-PEO block copolymer brushes on a silica surface show no effect of shear on the brush density profile in good solvent, and a slight increase in poor solvent. These earlier reflectivity measurements were limited to shear rates of $\approx$ 10,000 s^{-1} [7] since the adsorbed PS-PEO block copolymer brushes have a tendency to come off the surface at higher shear rates.

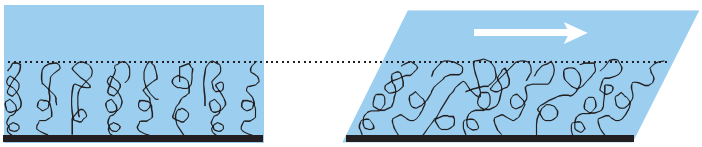

FIGURE 1. Schematic illustrating the effect of shear on grafted brushes predicted by Miao *et al.* [8] Such an effect would be consistent with the present data.

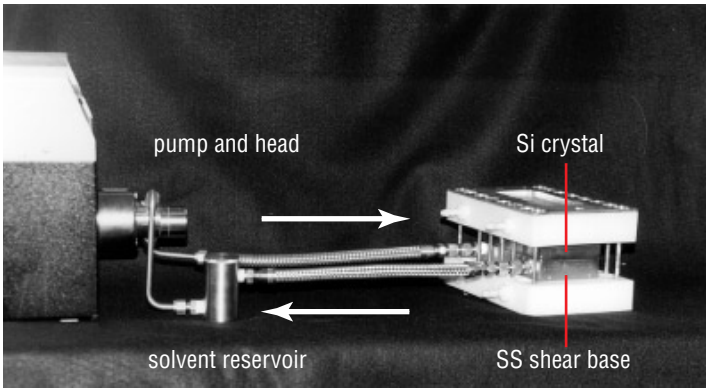

FIGURE 2. Shear cell. Arrows denote solvent flow direction. The polystyrene brush is grafted onto the Si crystal.

Predictions from theoretical calculations of brush profiles under shear span the gamut of possibilities, ranging from brush thickening to brush compression, including no effect of shear flow on the density profile [3]. Miao *et al.* [8] predict that the response of a brush to the solvent shear flow is displayed as chain tilting toward and chain stretching along the direction of flow. However, the overall conformational properties such as brush thickness remain essentially unaffected (Fig. 1).

We have performed neutron reflectivity measurements on a chemically grafted polymer in both good and poor solvents at shear rates over an order of magnitude greater than previously reported. Our neutron reflectivity experiments measure the segment density profile of the polymer brushes under shear in an experimental cell similar to the one used by Baker *et al.* [9], (Fig. 2). We use deuterated polystyrene (d-PS), 83 kg/mol, with a trichlorosilane end group to bind the d-PS brush chemically onto a single crystal Si surface [5]. We used a good solvent, toluene, and a poor

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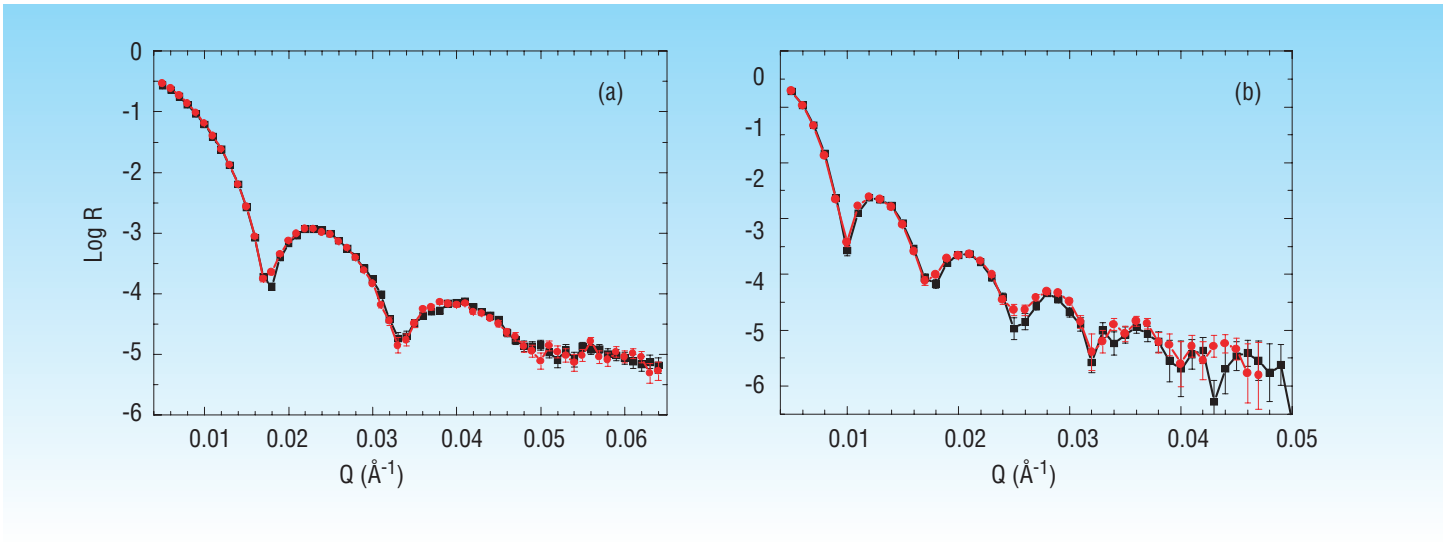

FIGURE 3. Representative shear data for deuterated polystyrene brush under shear in cyclohexane (a), and toluene (b). In both cases, black circles represent shear of 0 s^{-1}, whereas red squares represent data taken at 30,000 s^{-1}.

solvent, cyclohexane, as the solvent media. The dry brush height was measured by X-ray reflectivity to be 17.5 nm. Without shear the brush extends to 31 nm in cyclohexane and 75 nm in toluene. We measured the brush profile at several shear rates, up to 130,000 s^{-1}, yet we see no effect of shear on the brush density profiles in either solvent (Fig. 3). No desorption of the polymer brush was ever observed. In fact, the neutron reflectivity profiles at 0 s^{-1} and 130,000 s^{-1} look identical, indicating less than a 2 % to 3 % change in the brush density profile.

We have also been able to establish that the slight shear induced swelling reported by Baker *et al*. [7] for a poor solvent (cyclohexane), was probably due to frictional heating of the solvent. In high shear fields, heat generated from friction between the solvent and interior surfaces of the apparatus does not readily dissipate, causing a ≈ 2 °C to 3 °C rise in the temperature of the shear cell. We were able to demonstrate that the brush height in cyclohexane is unaffected by shear when the cell temperature is carefully controlled. An elevated cyclohexane temperature swells the brush as the solvent quality improves. Naturally, these effects were not observed in toluene.

Thus, our neutron reflectivity data represent the first comprehensive measurements of shear effects on the density profile of a grafted polymer brush into regimes that are predicted by some to display an effect. We cannot at this time determine if the brush responds as predicted by Miao *et al*. [8], or if there is insufficient solvent penetration into the brush to exert enough force on the chains to induce conformational changes. Future measurements will distinguish between these cases.

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