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Structure of Polymer Brushes under Shear Flow in a Good Solvent

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The equilibrium structure of polymer brushes (strongly stretched chains terminally attached to a surface) and the interaction of brush-bearing surfaces have been studied extensively and are now well-understood.[1−12] Much less is known, however, on the behavior of brushes under shear.[13−16] Force measurements between brushes in good solvent under lateral *oscillatory* shear indicate additional repulsion above a certain shear velocity,[17] suggesting possible extension of the chains. Theoretical calculations of the brush layer thickness (L_0) under shear, on the other hand, have produced mixed predictions ranging from no significant change[13,18] to substantial increase[14,19−22] or even to a decrease[23,24] of L_0 relative to its equilibrium value. We have used neutron reflectivity to probe *directly* the density profile of polystyrene brushes in toluene (a good solvent) under *steady* shear flow. We find that the reflectivity profiles remain insensitive to strong shear, but above certain shear rates substantial chain desorption is abruptly observed. There is no indication of a monotonic increase in L_0 or any evidence of shear thinning as a function of shear rate. Our results demonstrate the remarkable robustness of polymer brushes under high shear and have direct technological implications on dispersion stability and rheology.

Experimental Section. The structure of a polymer brush under steady laminar shear flow in a good solvent was investigated using the technique of neutron reflectivity.[25] This technique allows determination of the brush layer thickness (or brush height) and is an effective nanometer-scale probe of the polymer segment density profile normal to the grafting surface.[7] To accomplish this, we have constructed a cell designed to have plane Poiseuille flow, with both walls stationary and the fluid pumped between them.[26] The upper plane is defined by the polished surface of a quartz slab which serves as the adsorbing surface. The lower plane is formed by a shallow trough, precision milled into the top of a Teflon block so as to create a flow chamber beneath the quartz. The depth of the trough can be varied in the range 0.3−2.0 mm depending on the shear rate required. The macromolecule used was a polystyrene (PS)−poly(ethylene oxide) (PEO) diblock copolymer of 184×10^3 molecular weight and polydispersity index 1.10, the details of which have been reported before.[9] This polymer is known to adsorb terminally onto quartz or mica from toluene (a good solvent) and to form a well-defined polymer brush.[7,9]

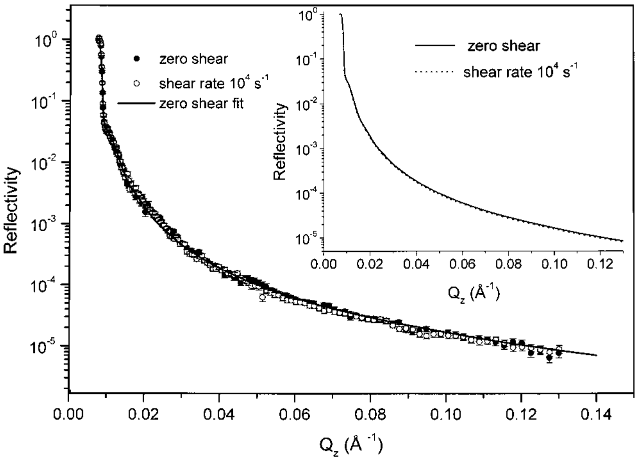

Figure 1. Neutron reflectivity data of PS−PEO diblock copolymer brush at zero shear (●) and at $\dot{\gamma} = 10^4$ s^{-1} (○). The continuous line is the best fit to the zero shear data based on a parabolic volume fraction profile (see Figure 2). Inset: fits to the zero shear (—) and $\dot{\gamma} = 10^4$ s^{-1} (- - -) data based on parabolic volume fraction profiles (see Figure 2). The experimental points are not shown for reasons of clarity. The PS−PEO diblock copolymer ($M_w = 184 \times 10^3$) was adsorbed onto quartz from *d*-toluene as described in the text.

The cell was assembled by clamping the quartz crystal against the Teflon block with the aid of a machined sealing lip. Flow was effected by means of a speed-adjustable pump, operating in a closed loop between a reservoir and the cell. Shear rates in the range $1 \times 10^1 - 2 \times 10^4$ s^{-1} could be attained under conditions of laminar flow, the highest recorded Reynolds number being ca. 770 at the upper limit of the shear rate range. Extreme care was taken to clean the quartz and the Teflon components prior to assembly as described before.[7] The cell was filled with a 0.1 mg/mL polymer solution in *d*-toluene. Adsorption onto the quartz and subsequent equilibration were allowed to occur over a period of 6 days. The measurements were made on the SPEAR reflectometer at LANSCE, Los Alamos, and on the CRISP reflectometer at ISIS, UK, using time-of-flight methods, which allow measurement of the neutron reflectivity as a function of Q_z, the perpendicular component of the scattering vector. The results obtained from both reflectometers were reproducible within the experimental error. Typical counting times were in the region 30−180 min, while the statistical error at the lowest measured values of the reflectivity was better than 10%.

Results and Discussion. Figure 1 shows the neutron reflectivity profile of the brush under conditions of zero shear and a shear rate, $\dot{\gamma}$, of 10^4 s^{-1}. The two profiles are essentially identical within the experimental error. Other shear rates ranging from a few hundred s^{-1} to several thousand s^{-1} were also employed and always produced reflectivity profiles (not shown) indistinguishable from those at zero shear rate. The data are

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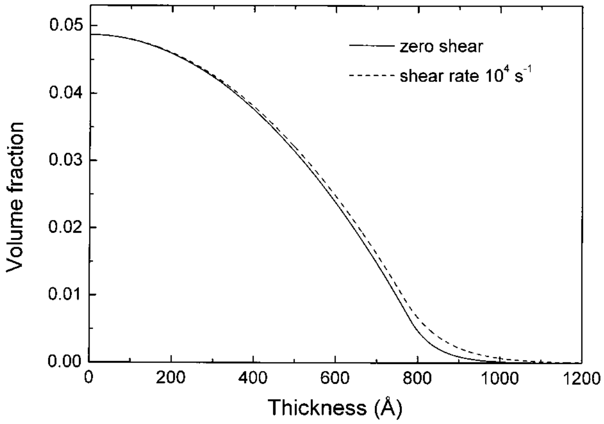

Figure 2. Parabolic brush volume fraction profiles extracted from the fits shown in Figure 1. The brush profile at $\dot{\gamma} = 0$ (—) is nearly identical to that at $\dot{\gamma} = 10^4$ s^{-1} (- - -). Small differences between the profiles are within the experimental error.

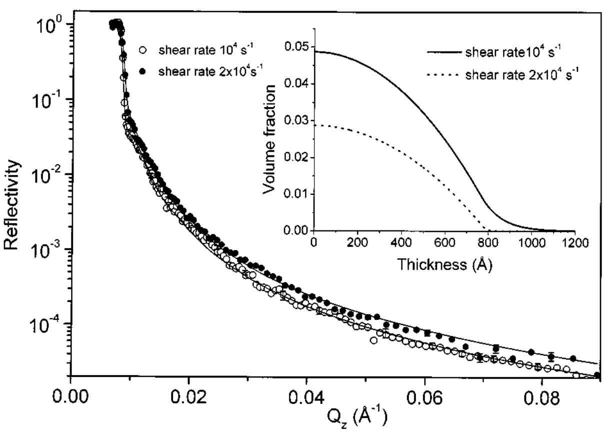

Figure 3. Neutron reflectivity data of the PS−PEO brush at $\dot{\gamma} = 10^4$ s^{-1} (○) and $\dot{\gamma} = 2 \times 10^4$ s^{-1} (●). The continuous lines are the best fits based on a parabolic brush profile in each case (see inset). Inset: parabolic volume fraction profiles at $\dot{\gamma} = 10^4$ s^{-1} (—) and $\dot{\gamma} = 2 \times 10^4$ s^{-1} (- - -) showing significant desorption at the higher shear rate (see text).

well-described by a parabolic density profile as described previously,[7] and there is little discernible difference between the fits (shown in the inset for reasons of clarity). This is further underlined by the parabolic profiles (see Figure 2) extracted from the fits where the small differences between the static profile and that obtained under shear (the latter showing an apparent slight extension of the brush height) are within the experimental error. These results clearly demonstrate that what would normally be regarded as rather high rates of shear (i.e., 10^4 s^{-1}) fail to produce any significant change in the brush structure, the height and profile of the brush remaining essentially intact under shear.

The insensitivity of the reflectivity profiles and hence the brush structure to shear extends to higher shear rates until at ca. 2×10^4 s^{-1} substantial *desorption* of the chains is observed. This can be seen in Figure 3, which shows the reflectivity profile and brush density profile (inset) at shear rates of 10^4 and 2×10^4 s^{-1}, respectively.

As the area under the volume fraction profile of the brush is proportional to the adsorbance, it is evident that at $\dot{\gamma} = 2 \times 10^4$ s^{-1} a significant amount of polymer has been forced to desorb[27] under the action of the drag forces to which the chains have been subjected at these very high rates of shear. (We recall that the brush under investigation is not chemically grafted to the quartz surface, but rather is an "equilibrium" brush where the grafting density and brush height result from a balance between the osmotic stretching of the dangling chains and the adsorption energy of the anchoring blocks.) Such desorption is clearly absent at lower shear rates where the reflectivity profiles remained unchanged under prolonged continuous shearing action lasting for many hours (in excess of 8 h in some experiments). Furthermore, there is no evidence to suggest that desorption increases gradually as the shear rate is increased. It appears instead that at some "critical" shear rate roughly estimated between 1.5×10^4 and 2×10^4 s^{-1} desorption emerges abruptly, while at lower shear rates no measurable desorption is observed within the time scale of our experiments.

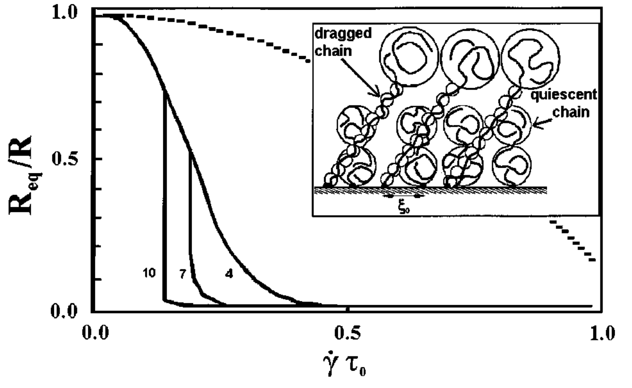

Figure 4. Dependence of desorption rate, R, on the dimensionless shear rate $\dot{\gamma}\tau_0$ for the dual chain model[21] (continuous curves). R_{eq} is the equilibrium desorption rate (i.e., at $\dot{\gamma} = 0$). Different curves correspond to brushes with different numbers of "blobs", n_b, at equilibrium ($n_b = 4$ (highest curve), 7 (middle curve), and 10 (lowest curve)). The broken line is for the corresponding single-chain model, where all chains are assumed to behave alike. Note that for the brushes used in our study $n_b \approx 8$, while at the highest shear rates employed in our experiments $\dot{\gamma}\tau_0 \lesssim 0.1$. Inset: schematic diagram of the dual-chain brush.[21] The system exposes a subset of the chains to the shear flow (dragged chains) while the rest remain protected from flow (quiescent chains). The shear flow which penetrates into the layer only up to a distance ξ_0 exerts a drag force $F = 6\pi\eta\dot{\gamma}\xi_0^2$ on each chain. Here, ξ_0 is the characteristic size of the blob in the outer extremity of the brush, and η is the solvent viscosity. (Adapted from ref 21.)

These results appear to lend support to the "dual-chain" model of Aubouy, Harden, and Cates[21] whereby the behavior of grafted polymer layers in strong solvent shear flows is described under the assumption that only a subset of chains are exposed to the flow (dragged chains), leaving the remainder protected (quiescent chains) deeper in the adsorbed layer, where the flow is screened. This model predicts a discontinuous (first order) swelling transition at a certain critical shear rate for *grafted* chains. This effect is associated with the dynamics of the part of the dragged chain exposed to the flow. In the case of *end-adsorbed* block copolymer brushes the model predicts a strong increase in desorption at the swelling transition (i.e., as the critical shear rate is reached), leading to the type of catastrophic removal of chains from the interface as observed in our experiments.

The predictions of the dual-chain model are summarized in Figure 4, which shows the divergence of the desorption rate at various critical rates of shear, depending on the average number of "blobs"[28] of the static brush. It is noteworthy that allowing nonuniform stretching produces qualitatively and quantitatively different predictions from the corresponding model in which all chains are assumed to behave alike. In particular, while the latter predicts a gradual increase in desorption with increasing $\dot{\gamma}$, the dual-chain model predicts a dramatic jump in desorption rate at much smaller values of $\dot{\gamma}$, i.e., $\dot{\gamma}\tau_0 \ll 1$, where τ_0 is the Zimm relaxation time of a blob of the unperturbed brush[29] (see Figure 4). In our experiment, strong desorption is observed at shear rates corresponding to $\dot{\gamma}\tau_0 \lesssim 0.1$, whereas in the context of models based on the Alexander−de Gennes-type ansatz that all chains stretch alike, much higher dimensionless shear rates $\dot{\gamma}\tau_0 > 1$ would be required to produce any significant change in desorption (see Figure 4).[30]

It remains to consider the force measurements of Klein et al.[17] between brushes in good solvent under oscillatory shear, where additional repulsion was observed above a critical shear velocity which these authors attributed to extension of the chains. The end-attached polystyrene employed in that study was very similar in molecular weight and sticking energy to the one used in our experiments, yet we find no such extension in our measurements at comparable shear rates. This discrepancy is probably peculiar to the oscillatory shear mode employed by Klein et al. in contrast to the steady shear flow regime of our experiment. It is also possible, however, that the effect observed in the force experiments might be associated with chain desorption above a certain shear velocity, as found in the present study.

In conclusion, we have measured the reflectivity profiles of polymer brushes in a good solvent under steady shear flow at the highest ever reported rates of shear in plane Poiseuille geometry. These experiments are the first attempt to *directly* probe the structure of a brush subjected to high shear. Our results do not support predictions of a monotonic increase in brush height[14,19,20,22] as a function of the shear rate. Furthermore, our experimental findings clearly disagree with the shear thinning effect predicted for steady flow regimes by Brownian dynamics methods.[23,24] The insensitivity of the reflectivity profiles to strong shear observed in our experiments coupled with the abrupt emergence of desorption at very high rates of shear, but still within $\dot{\gamma}\tau_0 \lesssim 0.1$, are consistent with the notion of a discontinuous transition occurring above a critical shear rate.[21] An interesting result that emerges from our study is the robust nature of the polymer brush structure under vigorous shear flow. The brush profile shows no evidence of changing gradually with increasing shear rate. Thus, below the critical shear rate for desorption, end-adsorbed brushes may be expected to remain virtually unperturbed in many practical applications involving strong shear flow regimes. These observations may have important implications in the stabilization and rheology of colloidal dispersions, as well as the tribological properties of surfaces and interfaces.

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(27) The desorption measurements and profile (Figure 3) do not correspond to equilibrium values but represent a kind of "snapshot" during desorption. The kinetics of this process is still under investigation.
(28) For fixed grafting density, the number of "blobs" of an Alexander−de Gennes brush increases linearly with the molecular weight. In the case of an "equilibrium brush" (see text) the grafting density and the brush height result from a balance between the osmotic stretching of the dangling chains and the sticking energy of the anchoring blocks. For such a brush of a *given* molecular weight, the number of blobs is a direct measure of the adsorption energy.
(29) τ_0, the characteristic relaxation time of a blob in the unpertrubed brush, is given by $\tau_0 \cong \eta\xi_0^3/k_BT$, where ξ_0 is the blob size and η the solvent viscosity.
(30) Polydispersity may, to some extent, enhance the desorption process. This is because longer chains protruding out of the main brush structure are more susceptible to the effects of solvent flow and should be the first ones to be pulled off the interface. Their departure would leave the brush more exposed to the flow and more vulnerable to further chain detachment.

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