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Shear-Induced Desorption in Polymer Brushes

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Polymer chains tethered to a surface have been investigated extensively by numerous experimental, theoretical and simulation studies, and their equilibrium properties are now well-understood.[1−9] At sufficiently high grafting density in good solvent, such end-attached chains extend away from the surface due to excluded volume interactions, this elongation being counterbalanced by an entropic restoring force, to produce a layer of stretched chains known as a "polymer brush" . The response of polymer brushes subjected to shear flow has received considerable attention in recent years, but remains essentially controversial with several theoretical and computational efforts presenting a range of conflicting predictions. These include scaling theories and Monte Carlo, molecular dynamics, and Brownian dynamics simulations with predictions for the brush height under shear ranging from little or no change[10−13] to a significant increase[14−17] or even to a decrease[18,19] relative to its equilibrium value. While these investigations primarily deal with permanently grafted brushes, the question of brush desorption under shear appears to have been little explored, except for the theoretical work of Aubouy et al.[17] Force measurements between brushes in oscillatory shear[20] have indicated the emergence of additional repulsion above a certain shear velocity, suggesting possible swelling of the brush, while neutron reflection measurements in steady plane Poiseuille flow at very high shear rates detected no measurable change in brush height or volume fraction profile.[21,22]

Here we report the results of a neutron reflectivity study on the volume fraction profiles of end-adsorbed polystyrene brushes in good solvent (toluene) under conditions of strong shear flow in plane Poiseuille geometry. Our aim was to determine whether the volume fraction profiles are affected by strong shear, and to explore the relationship between chain detachment and applied shear rate. We have used highly asymmetric polystyrene−poly(ethylene oxide) (PS−PEO) block copolymers, where the shorter PEO block anchors the chain onto a quartz substrate from toluene solution. This system has been extensively studied by numerous techniques[8,9] and is well-characterized. The block copolymers were obtained from Polymer Laboratories Ltd. and their molecular characteristics are presented in Table 1.

The polymers were adsorbed onto the face of a quartz slab of dimensions 50 mm × 100 mm × 10 mm from a deuterated toluene (ACROS, 99.5% D) solution at a concentration of 0.1 mg/mL over a period of 10−15 h at 23 ± 1 °C. The quartz plate constitutes part of a flow cell made of Teflon and described in detail elsewhere,[23] that allows laminar flow of solvent through gaps in the range of 0.2−1.0 mm in plane Poiseuille geometry and at shear rates ranging from 10 s^{-1} to 60 × 10^3 s^{-1}. The shear rate at the solid−liquid interface is calculated from the measured flow rate assuming a parabolic velocity profile. As the adsorbed brush thickness is typically of order 0.01% of the gap, the quoted shear rates are effectively valid at the outer extremity of the brush. A neutron beam is allowed to enter the quartz plate from its side and is reflected from the quartz/*d*-toluene interface, where the polymer is adsorbed. The neutron reflection experiments were carried out at the EROS reflectometer of LLB−Saclay[24] with a neutron wavelength λ in the range 2−30 Å. Time-of-flight techniques were employed to measure the intensity of reflected neutrons as a function of scattering vector $|\vec{Q}| = Q = (4\pi/\lambda) \sin\theta$ at a fixed angle of reflection $\theta = 0.75° \pm 0.025$.

Table 1. Molecular Characteristics of PS−PEO Block Copolymers

PS−PEO block copolymer	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	PEO content (wt %)
80K	80 × 10^3	1.07	5.0
147K	147 × 10^3	1.09	1.3
184K	184 × 10^3	1.10	4.0
239K	239 × 10^3	1.10	2.3
322K	322 × 10^3	1.19	2.4
497K	497 × 10^3	1.18	1.2

The reflectivity profiles measured under static (i.e., zero shear) conditions were in very good agreement with those obtained previously from the same or similar polymers adsorbed on quartz from *d*-toluene.[9] A typical result is shown in Figure 1. As reported before,[9] the volume fraction profiles are found to have a parabolic shape.

The aim of the present study, however, is to concentrate on the behavior of the brush under strong shear flow. On increasing the shear rate, $\dot{\gamma}$, the reflectivity profiles obtained from a given brush are observed to remain unchanged within the experimental error over a period of many hours of continuous shear flow, provided a critical value $\dot{\gamma}_c$ is not exceeded. When the shear rate is raised above $\dot{\gamma}_c$, however, rapid desorption is observed. Typical results are shown in Figure 1 and 2. In Figure 1 the reflectivity profiles of PS−PEO (80K) are shown at two shear rates below $\dot{\gamma}_c$, in addition to the zero shear measurement. The inset shows the volume fraction, $\varphi(z)$, profiles. Figure 2 shows the reflectivity profiles of PS−PEO (80K) at zero shear and after 30 min at a shear rate 52820 s^{-1}. The inset shows the $\varphi(z)$ profile corresponding to each reflectivity curve. The adsorbance, Γ (which is given by the area under the $\varphi(z)$ profile), as a function of shear rate for PS−PEO (80K and 497K) is shown in Figure 3. Clearly, the adsorbance remains essentially unchanged until shear rates $\dot{\gamma}_c \approx 52000$ and 2700 s^{-1} are reached, respectively, but drops sharply above these values of shear rate. All polymers studied in this investigation exhibited a qualitatively similar behavior, but the value of $\dot{\gamma}_c$ was different for each polymer brush. On further examination we observed that $\dot{\gamma}_c$ depends on the mean interchain spacing, s. The latter is given by $s = (M/N_A\Gamma)^{1/2}$, where M is the molecular weight, Γ is obtained from each $\varphi(z)$ profile, and N_A is Avogadro's number.

Table 2 shows the values of *s* found for the different brushes of varying molecular weights of the PS−PEO block copolymers. As expected, *s* increases with increasing M in end-adsorbed (as opposed to chemically grafted) brushes, its value being determined by a balance between the osmotic repulsion that a chain

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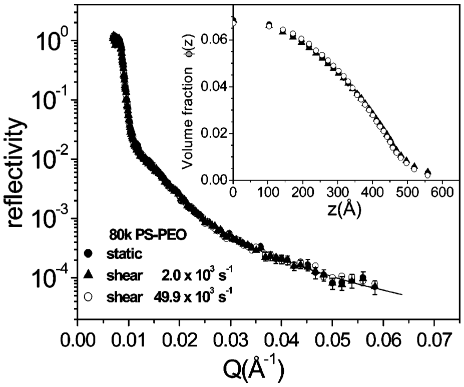

Figure 1. Reflectivity profile of PS−PEO 80K end-adsorbed on quartz from *d*-toluene at a concentration of 0.1 mg/mL over a period of 12 h at 23 ± 1 °C, after which the brush was subjected to shear flow. $\dot{\gamma} = 0\ s^{-1}$ (static) (●), $\dot{\gamma} = 2.0 \times 10^3\ s^{-1}$ (▲), and $\dot{\gamma} = 49.9 \times 10^3\ s^{-1}$ (○). Each reflectivity curve was measured after exposure of the polymer brush to shear flow for at least 1 h at the specified shear rate. The reflectivity profiles measured at these shear rates are identical, within the experimental error, while the corresponding least-squares fits based on a parabolic density profile are indistinguishable (continuous line). Inset: Best-fit parabolic volume fraction profiles for 0 s^{-1} (static) (●), 2.0 × $10^3\ s^{-1}$ (▲), and 49.9 × $10^3\ s^{-1}$ (○), respectively.

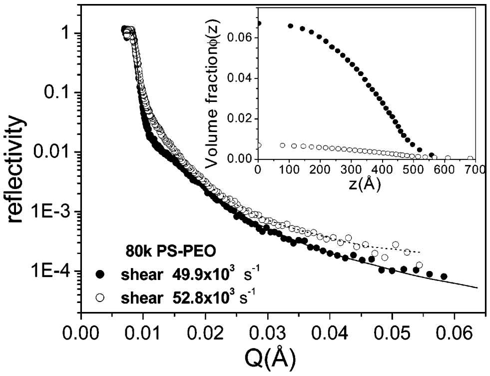

Figure 2. Reflectivity profile of PS−PEO 80K brush measured at 0 s^{-1} (static) (●), (as in Figure 1) and 52.8 × $10^3\ s^{-1}$ (○), after 1 h exposure to shear flow. Since the solvent (toluene) is deuterated while the polymer is hydrogenous the increase in reflectivity observed at 52.8 × $10^3\ s^{-1}$ indicates desorption. The continuous lines are least-squares fits based on parabolic volume fraction profiles for 0 (●), and 52.8 × $10^3\ s^{-1}$ (○) (see inset).

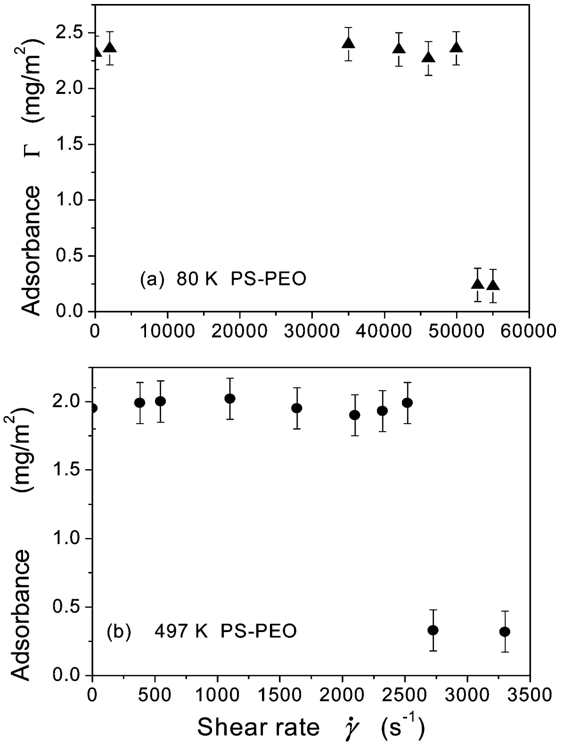

Figure 3. (a) Adsorbance values of PS−PEO 80K brush, and (b) PS−PEO 497K brush calculated from the area under the volume fraction profile determined at each shear rate. Each point on the adsorbance plateau is obtained from the corresponding reflectivity profiled measured after exposure of the brush to shear flow for 1 h at each particular shear rate. The adsorbance remains constant, within the experimental error, until a shear rate threshold is reached. Above this threshold, rapid desorption occurs with a sharp drop in Γ within 5 min of exposure to shear flow.

Table 2. Adsorbance Γ (at Zero Shear Rate), Interchain Spacing *s* of Unperturbed Brush, and Desorption Threshold (Critical Shear Rate) $\dot{\gamma}_c$ for All Polymers Studied

PS−PEO block copolymer	Γ (mg/m^2)	*s* (Å)	$\dot{\gamma}_c$ (s^{-1})
80K	2.32 ± 0.15	76 ± 3	52800 ± 5000
147K	2.70 ± 0.15	96 ± 3	26900 ± 2500
184K	1.90 ± 0.15	127 ± 5	11200 ± 1000
239K	1.63 ± 0.15	156 ± 6	5700 ± 400
322K	2.10 ± 0.15	160 ± 6	5500 ± 400
497K	1.95 ± 0.15	206 ± 7	2700 ± 200

experiences within the brush, and the sticking energy of its anchor block on the substrate.[8,9] As found in earlier studies[8,9] PS−PEO block copolymers such as those used here are known to possess sticking energies in the region of 6−8k_BT for substrates such as mica or quartz. Figure 4 shows the dependence of $\dot{\gamma}_c$ on s,[25] which clearly follows a power-law of the form $\dot{\gamma}_c \sim s^{-3}$.

We recall that in the Alexander−de Gennes scaling approach to semidilute polymer brushes in good solvent it is convenient to view the brush as a string of "blobs" of size ξ , with $\xi \approx s$. Consider the outermost blob of an end-adsorbed chain that is exposed to shear flow.

The characteristic Zimm relaxation time of such a blob is

$$\tau \cong \frac{\eta \xi^3}{k_B T} \tag{1}$$

where η is the solvent viscosity, k_B is the Boltzmann constant, and T is the absolute temperature. The behavior exhibited in Figure 4 suggests that the onset of desorption occurs at some critical value of the Weissenberg number W, i.e. $W_c = \dot{\gamma}_c \cdot \tau$. Thus

$$\dot{\gamma}_c = W_c \tau^{-1} \cong W_c \frac{k_B T}{\eta \xi^3} \tag{2}$$

which gives the power-law of Figure 4 since $\xi \approx s$. The above scaling expression for τ (eq 1) contains, as usual, an unknown prefactor. Furthermore, the value of W_c (of order 1) is also unknown. We may, however, obtain a value for the ratio of these constants from our data. Writing $\tau = C\eta\xi^3/k_BT$, where C is the unknown prefactor, it is obvious that C/W_c can be extracted from the intercept of the straight line of Figure 4. Taking the bulk value of the solvent (toluene) viscosity (ca. 0.6 mPa•s) we find $C/W_c = 270 \pm 40$.

We may compare this result to the predictions of existing theories concerning the values of the prefactor C and the critical Weissenberg number W_c. This prefactor has been reported to have the value of $(3\pi)(5.7) \approx 54$ by Doyle et al.[18] and $4\pi^3 \approx 124$ by Grest.[12] Concerning the effect of shear rate on brush

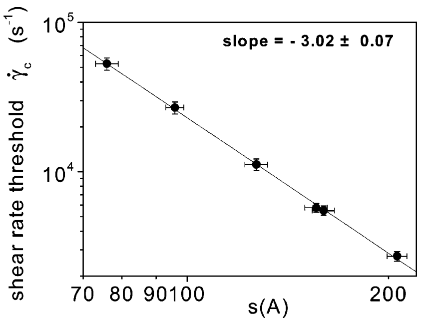

Figure 4. Dependence of desorption threshold (i.e., critical shear rate) $\dot{\gamma}_c$ on interchain spacing s (or mean blob size of unperturbed brush, ξ). The values of s and $\dot{\gamma}_c$ are presented in Table 2. The log−log plot yields a slope of -3.02 ± 0.07 confirming a power-law of the form $\dot{\gamma}_c \sim s^{-3}$ (or $\dot{\gamma}_c \sim \xi^{-3}$) (see eq 2).

structure, typically one would expect shear-related effects to occur when $W \geq 1$.[16] Early attempts to predict the behavior of brushes under strong shear flow were based on the Alexander−de Gennes model and assumed *uniform* stretching for all chains in the brush.[10,14] The "dual-chain" model of Aubouy et al.,[17] however, whereby *nonuniform* stretching is allowed and only a subset of chains is assumed to be exposed to the flow ("dragged" chains) while the remainder are protected deeper inside the brush layer ("quiescent" chains), suggests a much higher degree of brush susceptibility to solvent flow. In particular, this model predicts a discontinuity in the fraction, f, of extended chains at a critical shear rate. That is, the system is predicted to respond to shear by reducing f sharply, thereby exposing a small fraction of chains to a much higher tension (leaving the rest protected from flow) rather than exposing all chains to an equal but lower tension. This effect leads to a discontinuous (first order) swelling transition at a certain critical value of $W \ll 1$ for *grafted* chains. For *end-adsorbed* chains the model predicts a sharp increase in the rate of desorption at the swelling transition (i.e., as the threshold value of W is reached). This value of W is shown to depend on the mean number of blobs per chain, n_b, of the unperturbed brush. For n_b values corresponding to our experiment (ca. 6−8), the desorption rate is predicted to diverge when $W \geq 0.2$.[17]

This is consistent with our experimental results, particularly if we adopt the prefactor for eq 1 reported by Doyle et al.,[18] i.e. $(3\pi)(5.7)$. This gives $W_c = (3\pi)(5.7)/270 \approx 0.2$ in remarkably good agreement with the "dual-chain" model. (Alternatively, if the prefactor $4\pi^3$ is employed, we obtain $W_c \approx 0.45$). It is interesting, however, that the volume fraction profile shows no evidence of change just before the onset of desorption (see Figure 1) even though one would expect chains to extend before detachment. It is plausible, therefore, that any chain extension may be offset by tilting in the direction of the flow thus leaving the brush height unchanged, or that the fraction of any strongly extended chains at the critical shear rate may be too small to measurably alter the reflectivity profile, which gives an average brush height resulting from contributions from *all* chains, including quiescent ones. This view appears to be supported also by molecular dynamics simulations,[12] which show that only a small fraction of chains are strongly stretched under shear flow. Thus, as dragged chains are rapidly removed from the brush layer by the flow when $\dot{\gamma} > \dot{\gamma}_c$, they are replaced by formerly quiescent chains that become dragged and are in turn removed. This process then continues, giving rise to rapid desorption. Of course, once desorption sets in, the volume fraction profile is affected dramatically as a result of a sharp drop in adsorbance (see Figure 2).

In a recent study Ivkov et al.[22] investigated the effect of solvent flow on a polymer brush by neutron reflectometry. These authors found no change in the volume fraction profile of a chemically grafted, dense polystyrene brush (of $M_w = 83 \times 10^3$ g mol^{-1} with $s = 28$ Å) in toluene at the highest ever reported rates of shear ($\dot{\gamma} = 130 \times 10^3$ s^{-1}).[22] Our results suggest, however, that $\dot{\gamma}_c$ for such a brush would be expected to exceed 10^6 s^{-1},[26] and consequently its profile should remain unperturbed at $\dot{\gamma} = 130 \times 10^3$ s^{-1}, this value being roughly a factor of 8 lower than that required to test the possible occurrence of a swelling transition. Finally, the existence of a desorption threshold, as found in our experiments, may suggest that the additional forces observed above a certain shear velocity in the study by Klein et al.[20] could be associated with desorption.

In conclusion, we have used neutron reflectometry to study end-adsorbed polystyrene brushes exposed to shear flow in good solvent. The brush volume fraction profiles show no evidence of change with increasing $\dot{\gamma}$ below a shear rate threshold $\dot{\gamma}_c$, which is found to depend on the brush interchain spacing (or equivalently, the mean blob size) and is shown to increase with s^{-3} (or ξ^{-3}). A discontinuous transition in desorption rate is observed when $\dot{\gamma} = \dot{\gamma}_c$ (corresponding to a critical Weissenberg number $W_c < 0.5$) with a rapid and sharp reduction in adsorbance for $\dot{\gamma} > \dot{\gamma}_c$. The absence of any observable change in the volume fraction profile just before the onset of desorption suggests that the desorption process is probably mediated by only a small fraction of strongly extended chains dragged by the shear flow. Our results may have important implications in colloidal stability and lubrication since our findings demonstrate the existence of a limiting shear rate above which substrates are rapidly stripped of their protective layer of adsorbed polymer. Furthermore, the quantitative relationship we have established between brush structure and brush susceptibility to shear flow for end-adsorbed polymers may be of predictive value in determining or even tuning the response of a brush to a given shear flow regime.

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(25) The desorption threshold, $\dot{\gamma}_c$, is found to depend only on *s* but not on M. Brushes formed at lower adsorbance of the same polymer (same M but different s) yielded results (not shown) in complete agreement with the "master plot" of Figure 4.

(26) Extrapolation of the straight line shown in Figure 4 to $s = 28$ Å indicates a $\dot{\gamma}_c$ value of ca. 1.03×10^6 $s^{-1.}$

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