Topological Influences on Polymer Adsorption and Desorption Dynamics

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The desorption of polymer chains through an overlayer of strongly adsorbed chains was studied to determine the influence of topological constraints on the polymer desorption process. The desorption time of linear chains fits a power law, M^a, where M is molecular weight and $a=2.3\pm0.2$. A comparison of linear and star-branched chains shows that desorption of star-branched chains was greatly suppressed. These findings are reminiscent of entanglement effects in bulk systems. They suggest a unifying perspective from which to analyze polymer mobility at surfaces.

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The adsorption of high polymers is fundamentally different from that of small molecules. We are concerned here with understanding the factors that control polymer mobility at surfaces [1,2]. Recently, anomalously slow mobility has been found for spreading of molten polymer onto adsorbing solids [3], adsorption and desorption rates from solution [4–6], and the viscoelastic dynamics of confined polymers [7,8]. The hypothesis has been advanced that topological interactions, traditionally referred to as "entanglements," may be responsible [3]. Entanglements may be more prominent in thin films than in the bulk [8,9].

There are two problems in testing this hypothesis. The first is the practical question of how to assess the influence of surface heterogeneity, which also could be expected to slow down the chain mobility. The second problem is how to introduce constraints on the diffusive motion in a controlled way. Recently, an experimental strategy was suggested to address these issues: a strongly adsorbing polymer, by looping around a weakly adsorbing polymer, would tend to pin the latter to a surface [10]. The impediments to desorption thus provided might be expected to be stronger than those of the possibly heterogeneous energetic attractions to the surface [10]. But only a single polymer was studied, leaving open the question of how the ensuing rates of desorption scale with polymer chain length and architecture.

In this Letter, we present the first comparison of linear and branched chains and the molecular weight scaling of the rate of desorption. The main result is that these effects are qualitatively the same as for the diffusion coefficient of entangled chains in a bulk medium. The significance of this observation is to suggest a unifying perspective from which to analyze the kinetics of polymer adsorption and desorption.

The surface coverage of a tactic polystyrene (PS) and polymethylmethacrylate (PMMA), adsorbed to oxidized silicon from carbon tetrachloride (CCl_4), was monitored *in situ* by Fourier-transform infrared spectroscopy in the mode of attenuated total reflection. Characteristics of these polymers are given in Table I. The protocols and calibrations are described elsewhere [6]. The net segment-surface interaction energies, evaluated by us using the method of Cohen Stuart and co-workers [11], are $\approx 1kT$ (PS) and $\approx 4kT$ (PMMA) at 25 °C (k is the Boltzmann constant and T is the absolute temperature). Control experiments verified that in the event of competitive adsorption from a 50:50 mixture in solution, PMMA adsorbed to the exclusion of PS. This result was expected because a small preferential adsorption per segment adds up to an enormous preferential adsorption per chain. Thus, a weakly adsorbing species is excluded from the limited surface area at equilibrium. The temperature of the experiments was fixed at 25.0 °C.

An illustrative experiment is shown in Fig. 1. First, a dilute PS solution (weight-averaged molecular weight $M_w=220000$, 1 mg mL^{-1}) was exposed to a bare surface of silicon oxide and the adsorbed mass per area (Γ) reached steady state rapidly. The resulting loop-train-tail configuration, in which polymer chains are attached to the surface by only a fraction of the potential adsorption sites, has been studied extensively [1]. After 1 h, the PS solution surrounding the adsorbed layer was replaced by

TABLE I. Characterization of the polymers studied. These are flexible linear chains. The ratio M_w/M_n of the weight-averaged to the number-averaged molecular weight is a measure of the dispersion of chain lengths in a sample. A ratio of 1 implies that all chain lengths are equal. The molar mass of the repeat unit is 104 g mole^{-1} (PS) and 93 g mole^{-1} (PMMA).

Sample		M_w	M_w/M_n
Ps	linear	43900	1.01
		96400	1.01
		220000	1.03
		355000	1.02
		465000	1.04
		706000	1.05
	3-arm star	165000 (55000 per arm)	
PMMA	linear	820000	1.04

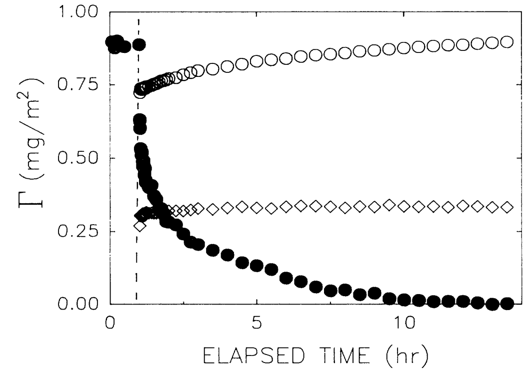

FIG. 1. An illustrative experiment. Mass adsorbed per area, Γ, is plotted against elapsed time. First a PS solution (M_w =220000, 1.0 mgmL^{-1} in CCl$_4$) was exposed to the oxidized silicon surface. After 1 h this was replaced by PMMA solution (M_w=820000, 0.1 mgmL^{-1} in CCl$_4$) for a period of 1 h, and the time-dependent surface coverages of PS and PMMA were measured. Control experiments showed that adsorption-desorption kinetics did not change with longer residence time before replacing the solutions. Filled circles: Γ(PS). Open circles: Γ(PMMA). Diamonds: mass adsorbed per unit area of PMMA segments hydrogen bonded to the surface.

a dilute (M_w=820000, 0.1 mgmL^{-1}) PMMA solution. After replacing the solutions, Γ of PMMA quickly reached steady state with minimal desorption of PS. In addition, the mass per area of PMMA segments hydrogen bonded to the surface (Γ_{bound}) was inferred from vibrational shifts of the carbonyl peak [10]. This value quickly reached a high level, ≈30% of full monolayer coverage, with only a modest subsequent increase. This indicates that desorption of PS took place by tortuous diffusion through a blanket of more strongly adsorbing PMMA.

The rate of decay of the surface PS concentration, Γ, was described empirically by the stretched exponential function

$$\Gamma(t)/\Gamma_0=\exp[-(t/\tau_{\text{off}})^{\beta}]\,. \tag{1}$$

Here Γ_0 is the steady-state mass per area adsorbed of PS before challenge by PMMA. For all of the cases studied here, $\beta=0.35\pm0.04$, indicating that the desorption was much slower than exponential. A dependence of β on the molecular weight of PMMA in the adsorbed overlayer warrants further exploration [12]. Elsewhere we argue that β reflects the regularity of the surface and the kind of diffusion process, Fickian or not [13]. For present purposes we do not insist on explaining the physical significance of β but rather emphasize simply that β, which quantifies the extent of deviation from exponential decay, was a constant in the empirical fit. It is then meaningful to analyze changes of the desorption time, τ_{off}, as the length of the linear chains is varied. Physically, τ_{off} can be interpreted as the time at which the surface excess had decayed to $1/e$ of its initial level.

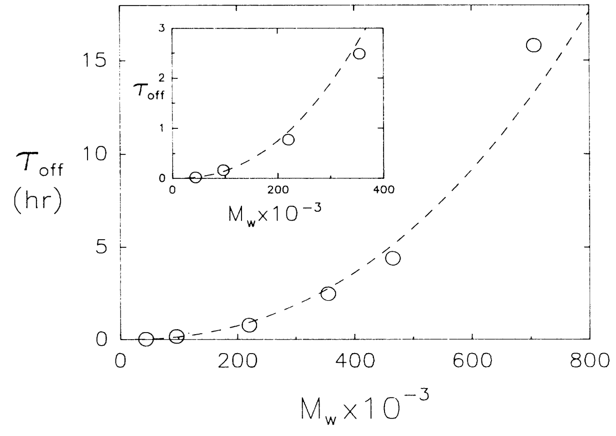

FIG. 2. Displacement time constants of PS plotted linearly against PS molecular weight.

The systematic increase of τ_{off} with increasing length of the adsorbed linear PS is shown in Fig. 2. One sees that τ_{off} increased more rapidly than in direct proportion to M, the molecular weight. It increased from 1 min (M=43900) to 10 min (M=96500) and to 16 h (M =706000). The range of $1\frac{1}{2}$ logarithmic decades in M, and nearly 3 logarithmic decades in τ_{off}, is sufficient to exclude an exponential dependence of τ_{off} with M.

In Fig. 3, τ_{off} is plotted against M on doubly logarithmic axes. The data are consistent with a power law,

$$\tau_{\text{off}}\sim M^{a}, \quad a=2.3\pm0.2\,. \tag{2}$$

This evokes the behavior of the self-diffusion coefficient (D) in the entangled bulk melt and in concentrated bulk solutions of linear chains [14,15], where D follows a power law in M with similar magnitude. The classical reptation prediction is $a=2$. In bulk systems the precise value of the power a appears to depend strongly on concentration and perhaps also on the experimental system, but experimental values fall in the range $a=2$ to 3 [14,15]. There are various models of entanglement interactions that accord qualitatively with this result

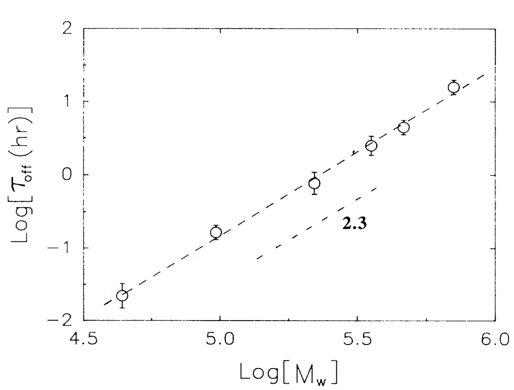

FIG. 3. Log-log plot of the data in Fig. 2. Empirical slope is 2.3±0.2.

[9,14,16]. In the present context, the point we wish to emphasize is the phenomenological similarity between known experimental results for diffusion in bulk systems, and the observations presented above.

Seeking corroborative evidence that this similarity might reflect a common origin, control experiments were then performed on a polymer system that, in the bulk, is believed *not* to relax by the same mechanism as linear chains. A well-known class of such chains are the branched molecules; the best-characterized branched molecules are the regular stars. Three-arm stars, generously donated by M. Antonietti of the University of Marburg, were prepared by joining anionically polymerized PS by reaction with methyltrichlorogermanium [17]. This synthesis procedure was important because the core of the star is not expected to adsorb selectively in these stars.

Figure 4 compares the desorption kinetics of a linear polymer and a three-arm star of matched molecular weight. The time-dependent surface excess $\Gamma(t)$ is plotted against the elapsed time on doubly logarithmic scales. One observes that the desorption of the linear chain was more rapid than a power law, but slower than a single exponential, as described by Eq. (1) [18]. By contrast, desorption of the star-branched molecule was hardly apparent on the logarithmic time scale. Quite similar suppression of the viscoelastic relaxation of stars is also found in the bulk [19], where the effect originates in retarded diffusion [14].

What of possible artifacts? One might question analysis in terms of stretched exponential relation—but as already noted, since the β parameter was constant, the scaling with M that we observe is not specific to the fitting function that was used. One might question whether desorption through a layer of molecular thickness can properly be considered to indicate translational diffusion of a molecule's center of mass; but, since the micron-scale penetration depth of the infrared evanescent wave was vast compared to the thickness of the adsorbed layers, it is clear that we measured center-of-mass motion rather than the detachment of individual segments from the surface. Finally, one might argue that the tendency of PS and PMMA to be incompatible in bulk mixtures might lead to phase segregation at the surface; but this is expected to be a second-order effect because the segmental tendency towards incompatibility ($\approx 0.04kT$ [20]) was much smaller than the intensity of the polymer-surface interaction, $\approx 1kT$, as specified above. The former effect may, it is true, have enhanced the driving force towards desorption.

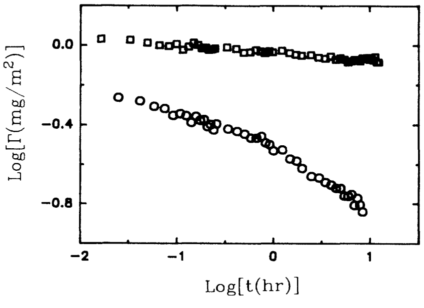

FIG. 4. Comparison of linear and star-branched molecules of matched molecular weight. The time-dependent adsorbed mass per area of PS during desorption, $\Gamma(t)$, is plotted logarithmically against logarithmic elapsed time. Circles: linear chain, $M = 220000$. Squares: 3-arm star, $M = 55000$ per arm.

With small molecules, the physical situation is qualitatively different from the case here. The desorption rates of small molecules are characteristically controlled by the free energy of adsorption [21]. In the present context, the free energy change upon desorption should be extensive in the polymer molecular weight [22-24] and therefore the desorption time constant τ_{off} should be *exponential* in the molecular weight if the desorption were governed by the free energy of adsorption. That this can happen is confirmed by prior experiments with *weakly* adsorbed polymers—protio PS displaced by deuterio PS [25].

The present study has addressed a new kinetic regime: that which arises when the flux from the surface is no longer rate limited by the energetics of surface detachment, but instead is controlled by the sluggish center-of-mass diffusion of the desorbing polymer away from the surface. In the system studied, this is diffusion of PS through the PMMA overlayer. More generally, it is diffusion to the outside of any surface-bound layer. This process can be described by a mathematical model which relates the desorption rate to the escape probability of the random walk initiating from the surface. This model indicates that τ_{off} scales as D^{-1} [13] and this prediction accords with the data in Figs. 2-4.

We suggest tentatively that topological interactions of the sort suggested by this study may be common in the adsorption of chain molecules. Solid surfaces are typically heterogeneous, both in chemical composition and in topography—not the uniform plane often assumed. Heterogeneity is expected to provide "hot spots" of strong attachment to the surface. Weakly adsorbed chains may thus be expected to thread through other chains that are more strongly adsorbed, leading to the effects of the kind studied here. This provides a new perspective from which to interpret the anomalously slow surface mobility that has been observed repeatedly over the years with synthetic polymers [1-8], as well as with proteins [26].

In summary, these are the first experiments to show the molecular weight dependence of polymer desorption times under conditions of strong topological constraints. The finding of an analogy with entanglements in bulk systems is significant because presently there is no accepted model of adsorption-desorption mechanisms [1,2]. Much theoretical modeling has taken the approach of extending classical Langmuir kinetics [1,27–30], but we have shown here that this approach is not always a good one —desorption may be rate limited by diffusion away from the surface rather than determined by energetics of surface detachment. By rational extension, there are implications for understanding events that occur in the course of lubrication, wetting, adhesion, and adsorption of proteins.

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