

Kinetic Traps in Polymer Adsorption. 2. Polystyrene Displaced by Polyisoprene at 50 °C

Hildegard M. Schneider and Steve Granick*

Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801

Steve Smith

Miami Valley Laboratories, Procter and Gamble Corporation, Cincinnati, Ohio 45239

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ABSTRACT: We analyze adsorption-desorption kinetics at significantly higher temperatures than in the accompanying study (Schneider, H. M.; Granick, S.; Smith, S. preceding paper in this issue) so as to contrast enthalpic, detachment-limited desorption with the diffusion-limited regime. The experiments involve measurements of protipolystyrene (PS) and deuterio-*cis*-polyisoprene (PI) adsorbed sequentially onto oxidized silicon from a dilute solution in carbon tetrachloride at 48.5 °C. The time dependence of the displacement of PS by PI is analyzed as it depends on the PS molecular weight (M_{PS}). In contrast to behavior at low temperature, if M_{PS} is sufficiently low ($<10^5$), the PS desorption is a simple exponential in elapsed time, as expected for desorption that is rate-limited by segmental surface detachment. Larger M_{PS} chains, however, even at this elevated temperature, display kinetics that is strongly nonexponential in time. When fit to a stretched exponential as suggested by a simple kinetic model, the power of time is $\beta \approx 0.6$, near the $\beta = 0.5$ limit expected for diffusion-limited desorption. In contrast to behavior at low temperature, a prominent overshoot of PI surface excess occurred for adsorption onto PS of low molecular weight. This overshoot, which is also seen for PI adsorption onto a bare surface, is tentatively attributed to initially rapid unequilibrated adsorption, followed by conformational rearrangement of adsorbed PI.

Introduction

The adsorption and desorption of polymers at surfaces has been intensively studied, but there is as yet no all-encompassing model of the process.¹⁻¹⁹ Much of the information comes from work in which only the total amount adsorbed could be quantified by the experimental methods which were employed. More recently, attention has been focused on the adsorption of one polymer species, followed by its displacement by another polymer species.¹⁰ The interplay of adsorption and desorption in these experiments always occurs under the conditions of high surface coverage. In this respect it differs fundamentally from adsorption onto an originally-bare surface. It has become clear that the surface composition can change drastically with time even under conditions where the total amount adsorbed is constant.¹

The preceding paper investigated the desorption of protipolystyrene (PS) from oxidized silicon by exchange with deuteriopolyisoprene (PI) at 12 °C. The nonexponential kinetics predicted by a simple kinetic model for diffusion-limited desorption through a homogeneous overlayer were observed, so long as the molecular weight of PS (M_{PS}) was sufficiently high. The desorption kinetics of low M_{PS} chains, also highly nonexponential, showed indications of heterogeneity in the overlayer. The mutual dependence of the adsorption and desorption processes was also clearly demonstrated. However, at this low temperature, displacement did not go to completion over the experimental time scale. This observation, which did not depend upon the molecular weight of the species being desorbed, suggested a metastable state in which a fraction of the original layer remained trapped. The nature of the trapped layer was not entirely clarified but was expected to result in large part from hindered mobility at the low experimental temperature.

This same PS/PI system is investigated in this paper at higher temperature, 48.5 °C. The idea is that the increased

mobility at higher temperatures should encourage progress toward equilibrium, switching the rate-limiting step to segmental surface detachment rather than the diffusion-limited kinetics which we inferred at lower temperature. Higher temperature also improves the solvent quality, thereby lessening somewhat the intensity of the segment-surface interaction parameter (χ_s). The behavior of the system at low and high temperatures is compared to better understand the mechanisms of equilibration and generality of the interdependent exchange processes.

Experimental Section

The experimental method has been described in the accompanying paper¹ in detail. These experiments are identical except that the temperature is held constant at 48.5 °C. The polymers were at a concentration of 1 mg/mL in CCl_4 .

Results

The sequence of a typical experiment is shown in Figure 1. Surface excess is plotted versus elapsed time. Initially, PS is adsorbed from dilute solution onto the oxidized silicon crystal. After 1 h, the solution is exchanged with one of PI. Two experiments are plotted in Figure 1 to illustrate the dependence on PS molecular weight.

Several features should be noted in Figure 1. First, PS desorption proceeded to completion for chains of low M_{PS} and at a more rapid rate than for the chains of higher M_{PS} . Both these features contrast with the behavior in this same system at lower temperature; in particular, such differences according to molecular weight were not seen.¹ The final notable item in Figure 1 concerns the overshoot of PI adsorption. This unusual phenomenon, not seen at lower temperature,¹ and its change with the molecular weight of PS are illustrated more fully in Figure 2.

Overshoot Mass Adsorbed. Figure 2 shows that the PI adsorption onto PS of low molecular weight always shows an overshoot. Surface excesses of PI (top) and PS

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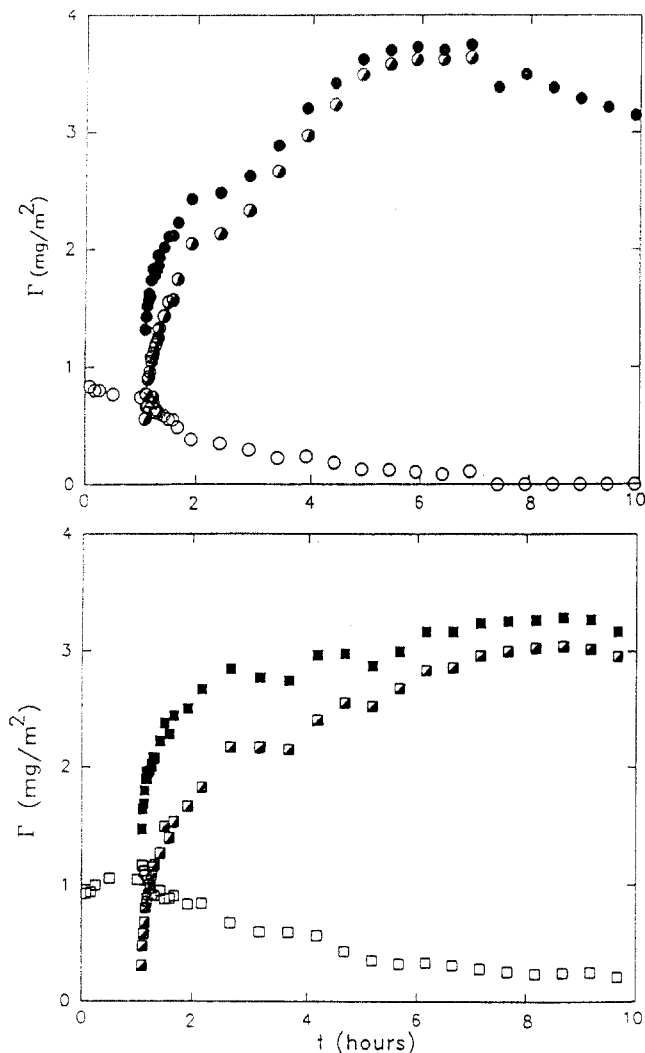


Figure 1. Surface excess of PS and PI plotted versus elapsed time. (Top panel) The exchange of 355K PS by 150K PI (open circles, PS; half-filled circles, PI; filled circles, PS + PI). (Bottom panel) The exchange of 3.84 M PS by 150K PI (open squares, PS; half-filled squares, PI; filled squares, PS + PI). The line indicates the time at which the PS solution was exchanged for the PI solution.

(bottom) are plotted against time elapsed after the exchange of PS for PI solution, t_e . The overshoot decreases with an increase in the molecular weight of the PS initially adsorbed, such that for the PS of highest molecular weight no overshoot in PI adsorption is observed. The rate of the PI adsorption also changes with PS molecular weight. When short PS chains are displaced, PI mass builds up relatively quickly. When longer PS chains are displaced, the PI takes longer to reach its overshoot maximum. However, at the time at which our experiments terminate, about 9 h after the exchange, the PI mass adsorbed has not reached steady state, leaving unclear the question of what would be the equilibrium surface population. Obviously, it is necessary to look more quantitatively at the rates of adsorption, displacement, and overlayer rearrangement to try to resolve the parameters and mechanisms which determine the time-dependent surface composition.

Kinetic Analysis. The kinetic data are described by values derived from empirical fits. As in previous work,^{1,15,16,20} and for continued comparison with the expectations of a simple kinetic model,¹⁶ we first consider the stretched-exponential function to quantify the desorption of PS. In such a fit a power of time, $\beta < 1$, indicates

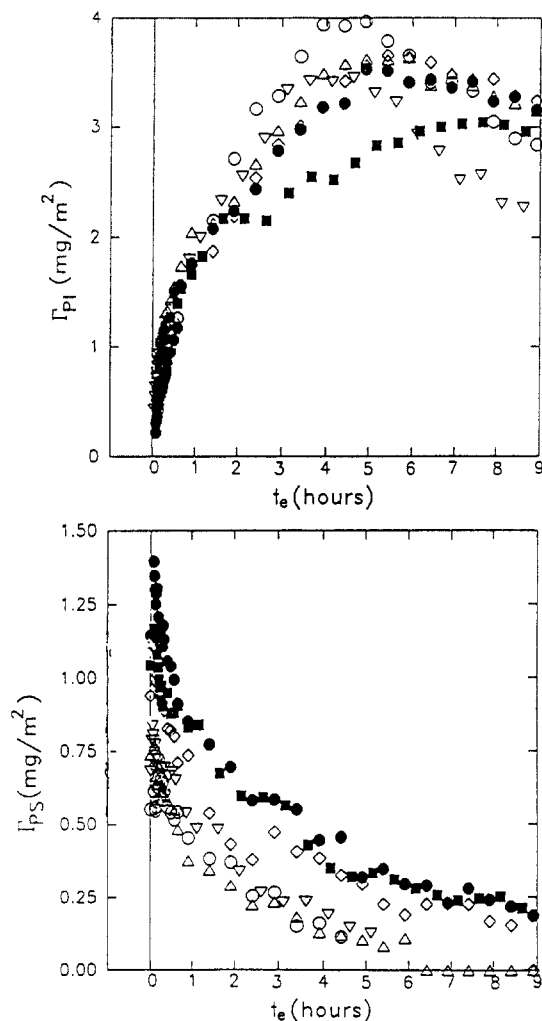


Figure 2. (Top panel) Surface excess of PI, Γ_{PI} , plotted against time after exchange of PS for PI solution, t_e . With increasing M_{PS} , the PI adsorption and its overshoot becomes less (open circles, 43.9K PS; triangles down, 96.4K PS; triangles up, 355K PS; diamonds, 706K PS; closed circles, 1.26M PS; closed squares, 3.84M PS). (Bottom panel) Surface excess of PS, Γ_{PS} , plotted versus t_e . Symbols are the same as above.

that desorption is slower than a single exponential. The data in Figure 3, as an example, show the excellent quality of such a fit.

Because of the complexity of this experimental situation, in which the PS encounters a changing PI environment in the course of desorption in contrast to the assumptions of the model which predicts stretched-exponential kinetics, we also attempted exponential fits. The inset of Figure 3, a semilogarithmic plot, shows that two exponential time constants are also consistent with the data in the main part of Figure 3. Semilogarithmic plots of desorption for other M_{PS} are shown in Figure 4. In particular, the kinetics are consistent with being single exponential for PS of sufficiently low molecular weight ($M = 96\,400$ in this example) but is consistently nonexponential for PS of high molecular weight ($M = 1\,260\,000$ and $3\,840\,000$ in this example), indicating at least two time constants with a crossover region. Clearly, nonexponential kinetics are seen for $M > 300\,000$.

Adopting a two-constant fit, τ_{fast} at early times and τ_{slow} at later times, gives the dependence on M_{PS} shown in Figure 5. The parameter τ_{fast} is independent of M_{PS} ; τ_{slow} increases slightly with M_{PS} . However, in view of the inability of the fit to describe the crossover region, the questionable superiority of this two-constant fit to the two-constant

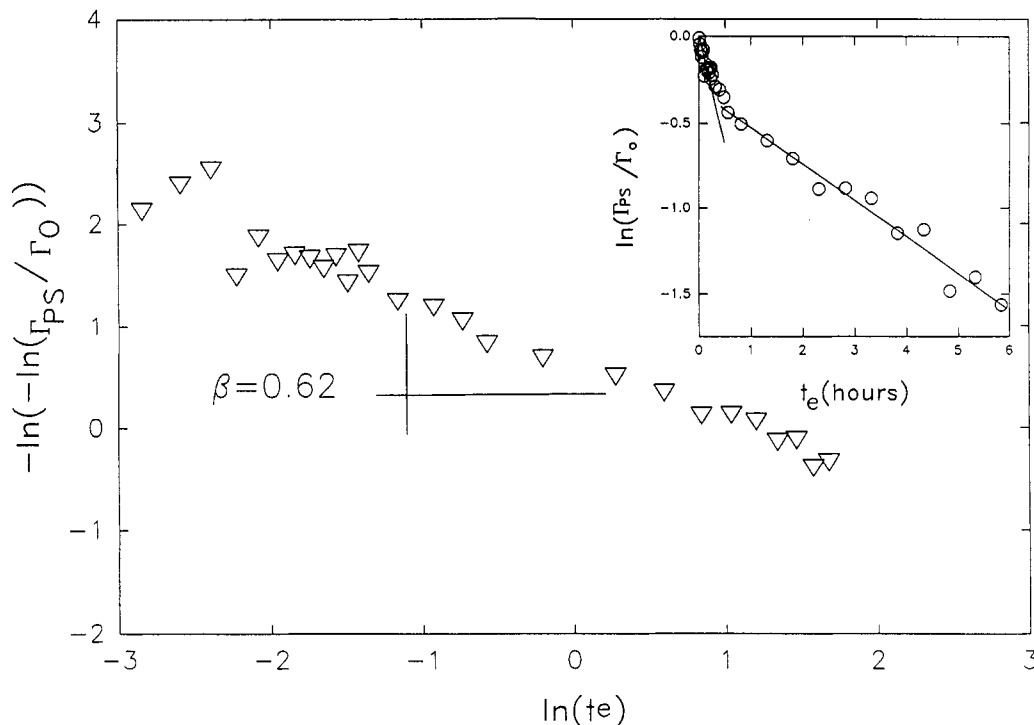


Figure 3. Comparison of stretched-exponential and exponential fits of PS desorption kinetics. The main graph shows a linearized form of the stretched-exponential function. Here Γ_0 is the PS mass adsorbed just prior to the exchange of PS for PI solution, and t_e is time elapsed after the exchange of solutions. The inset shows a semilog plot of the same data. These are the same data shown in raw form in Figure 1 (top panel).

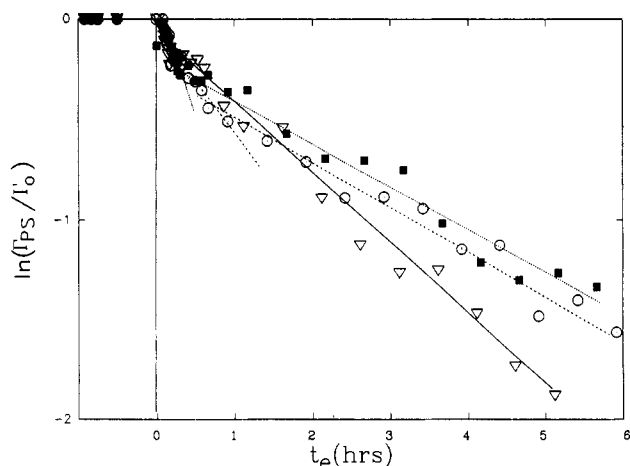


Figure 4. Semilogarithmic plots of PS desorption. At low M_{PS} (triangles, 96K PS) the desorption is exponential, but not at higher M_{PS} (dotted circles, 1.26M PS; filled squares, 3.84M PS).

stretched-exponential fit, and for better comparison with results of the previous paper and theoretical expectations, we employ in the following discussion the stretched-exponential relationship.

Figure 6 analyzes the total adsorption kinetics—PI adsorption modified by PS desorption—using the notion of a fractional deficit, M_D , introduced in the previous paper.¹ The variable M_D is plotted against elapsed time. Here, we consider the total mass adsorbed at the peak of the surface excess overshoot to represent a saturated surface layer. This peak in mass, minus the adsorbed mass at any time t , normalized by the peak adsorption, gives one a rough idea of the degree to which the surface layer is unsaturated; this is referred to as the fractional deficit, M_D . The decay of M_D with time quantifies the slow approach toward surface saturation. The kinetics which follow the overshoot are discussed below. From Figure 6 we see that these adsorption kinetics are even more strongly nonexponential than the desorption kinetics of PS.

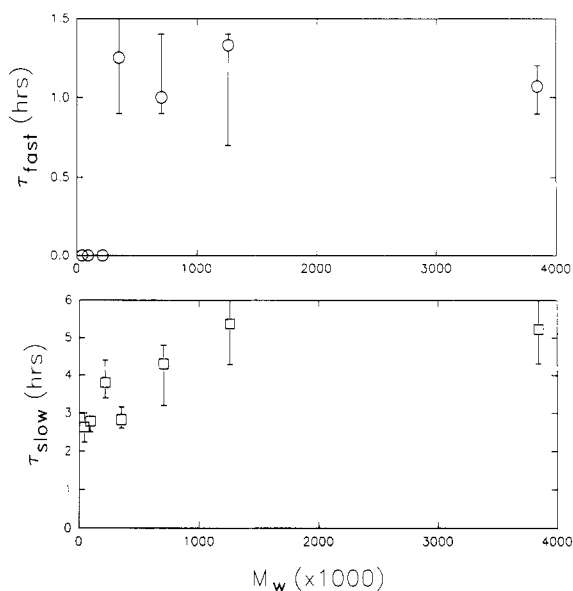


Figure 5. Time constants τ_{fast} and τ_{slow} , calculated from exponential analysis of desorption data (as in Figure 4), plotted versus molecular weight of the desorbing PS. Low molecular weight chains ($M < 300\,000$) can be described by a single exponential, and this time constant is arbitrarily assigned to τ_{slow} .

Comparison of the power of time in the stretched-exponential analysis, β , is a convenient way to analyze how the form of these kinetics varies with M_{PS} . Figure 7 compares the values of β that are derived for both the desorption of PS and for the adsorption. These events are most rapid when low molecular weight PS chains are displaced, and desorption follows a single exponential, $\beta = 1$. However, β decreases with increasing M_{PS} until it stabilizes, at $M_{PS} > 300\,000$ at $\beta \approx 0.65$. The decrease of M_D is highly nonexponential in every case, beginning at $\beta \approx 0.5$ and stabilizing at $\beta \approx 0.3$. When one compares to the corresponding results at lower temperature (preceding paper), one notes that, despite the quantitative differences

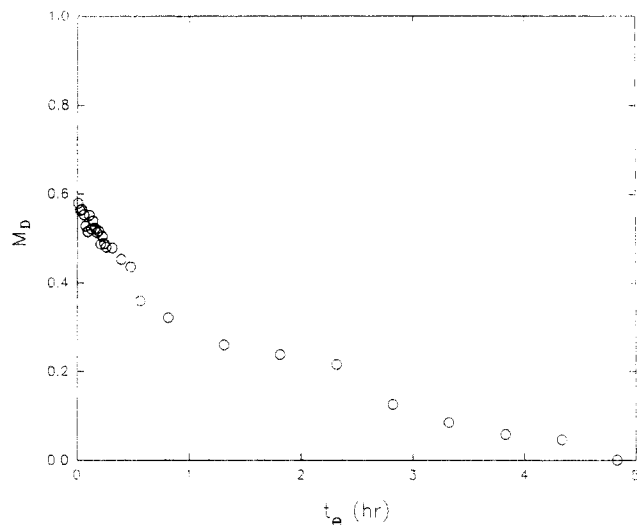


Figure 6. Analysis of the approach to surface saturation (the filling of the fractional deficit, M_D), as described in the text. Here t_e is the time elapsed after the exchange of PS for PI solution.

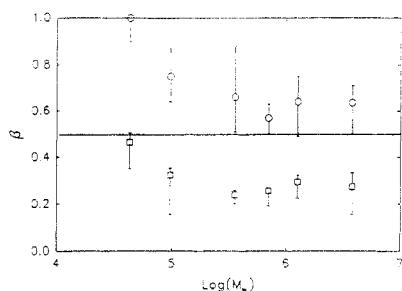


Figure 7. Power of time in the stretched-exponential fit, β , plotted versus the logarithmic molecular weight (M_w) of PS.

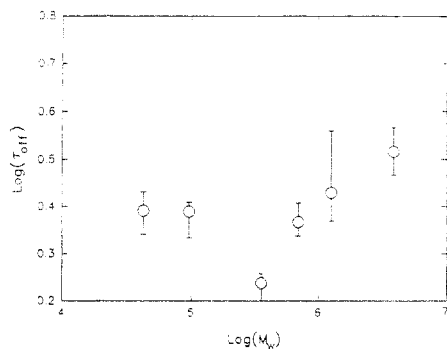


Figure 8. Logarithmic desorption time constant of PS, τ_{off} , plotted against the logarithmic PS molecular weight.

in values of β (extent of nonexponentiality), the trend for the values of β for the adsorption and desorption to change in concert is a point in common.

The time constants for PS desorption, τ_{off} , were also compared for different M_{PS} . This can be interpreted physically as the time at which $1/e$ of the original amount adsorbed is removed. Figure 8 shows τ_{off} plotted against M_{PS} on log-log scales. One observes that τ_{off} is at first independent of molecular weight ($M = 43\,900$ and $96\,000$), decreases at an intermediate molecular weight, and increases slowly for chains of the highest molecular weight. In such a comparison, however, it is more meaningful to also take into account the associated changes in β . As is customary in the study of glassy kinetics,²¹ the mean desorption times, $\langle \tau_{off} \rangle$, were calculated by the relation which describes the stretched-exponential function,

$$\langle \tau_{off} \rangle = \beta^{-1} \Gamma(\beta^{-1}) \tau_{off} \quad (1)$$

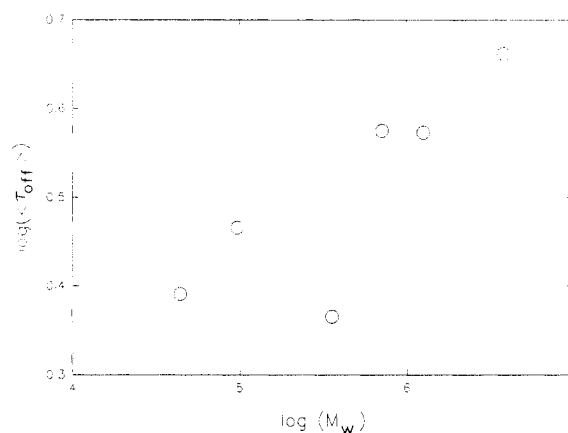


Figure 9. Mean desorption time constant of PS, $\langle \tau_{off} \rangle$, calculated as described in the text, plotted versus the logarithmic molecular weight of PS.

where Γ here is the gamma function.²¹ The resulting $\langle \tau_{off} \rangle$ are plotted against M_{PS} , on log-log scales, in Figure 9. This measure of the rate of desorption increases more consistently with increasing M_{PS} .

Discussion

While there is no accepted model of the adsorption-desorption process, two limiting regimes have been proposed.^{15,16,20} Energetics of segmental detachment is expected to govern dynamics when diffusion is rapid. Transport from the surface can become hindered, however, to the point that this diffusion process becomes rate-limiting. In the preceding paper, we reported the results of sequential adsorption experiments in which the strongly nonexponential kinetics, $\beta = 0.5$, predicted for diffusion-limited desorption through a homogeneous overlayer, were recovered for high molecular weight desorbing PS. In addition, changes in the PI adsorption occurred in concert with the PS desorption and were shown to depend on M_{PS} .

The current work confirms that adsorption-desorption processes are interdependent even at higher temperature. At this higher temperature, diffusion is no longer rate-limiting in the desorption of low M_{PS} chains; single-exponential kinetics are observed. For high M_{PS} chains, however, the parameter β again tended toward $\beta = 0.5$. It is speculated that further increases in molecular weight might slow diffusion to the point that diffusion-controlled desorption kinetics, $\beta = 0.5$, would be cleanly recovered.

It is also interesting to consider the progress toward equilibrium at the two temperatures. In these experiments one would expect, at equilibrium, to totally displace the originally-adsorbed PS layer. At the present high temperature, we proceed closer to this state than at low temperature, where motions were slowed to the point that some PS chains remained adsorbed regardless of molecular weight over the experimental time scale, leaving a metastable kinetically trapped fraction.¹ At this high temperature, the short chains are mobile enough to escape completely, and only the longest M_{PS} chains leave a fraction trapped.

We now discuss the spectacular overshoot of PI adsorption, which was most strong for adsorption onto the more easily-desorbed low molecular weight chains. An overshoot has been seen previously in several other systems, in particular for PI adsorption onto an initially-bare surface.²² In this previous study we speculated that, as the PI adsorbs onto a bare surface, many chains attach at first loosely to the surface but that, as time passes, reorganization occurs such that some chains must desorb to optimize packing

of the remaining chains. It is therefore consistent, in the current study, to see a less prominent overshoot in cases where the PI adsorption was slowed down by the presence of long PS chains which we slow to desorb. The lingering presence of the highest M_{PS} chains apparently slowed attachment to the point that no overshoot occurred.

This speculation is also consistent with findings at low temperatures, as reported in the preceding paper,¹ where diffusion and adsorption were slowed even more and, correspondingly, no overshoot occurred for any of the M_{PS} that were studied. It is also consistent with the pioneering experiment of Pefferkorn and Elaissari,²³ in which the rate of polyelectrolyte supply to a solid surface was varied. They found that at slow adsorption rates the change in mass adsorbed was monotonic in time. But at high rates of adsorption an overshoot in the total mass indicated initial packing of chains in isotropic conformations, followed by desorption due to competition for surface sites during structural relaxations. Computer simulations²⁴ were consistent with this interpretation.

Finally, we consider the contrast between constant total adsorbed mass¹ and the present case of higher temperature, where nothing of the sort is found. The constant total adsorbed mass found in ref 1 is discussed at length in that paper. At higher temperatures the adsorbed mass does not reach steady state over the experimental time scale. Rather, mobility is enhanced and the layer continues to evolve with time. In light of the higher mobility at higher temperature, we do not expect a recurrence of the metastable surface excess found in ref 1, and none is observed.

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