

Exchange Kinetics of Adsorbed Polymer and the Achievement of Conformational Equilibrium

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ABSTRACT: We study adsorption-desorption kinetics of polymer chains at a solid surface. Protipolystyrene, adsorbed from dilute cyclohexane to a single solid surface of oxidized silicon, was displaced by deuterio-polystyrene. A single time constant, τ_{off} , described displacement for a significant time (1-3 h), followed by a period of slower desorption kinetics. An aging effect, in which τ_{off} continued to increase even after the mass adsorbed had equilibrated, implied surprisingly slow rearrangements of adsorbed chains in the direction of conformational equilibrium. After long aging times, ranging from hours to days, τ_{off} reached a plateau value. This equilibrated desorption time increased exponentially with the length of adsorbed chains.

Introduction

Much attention, both experimental and theoretical, has been devoted to describe the equilibrium state of adsorbed polymer layers.¹⁻³ Mass of polymer adsorbed, average layer thickness, and overall concentration profiles have been of concern. Despite the impressive progress that has been made, a nagging uncertainty exists with respect to putting these results from idealized equilibrated systems into context with more realistic situations. In fact, little is known about the conditions under which the assumption of equilibrium is appropriate.⁴ This uncertainty impedes progress of a number of fields which depend on the nature of interfacial properties of polymers.

Here we expand upon a previous communication.⁵ We distinguish three time scales in the development of an adsorbed layer: For diffusion to an initially bare surface, for attachment to the surface, and for equilibration of the adsorbed chains.^{1,4} Furthermore, even at overall adsorption equilibrium there is a steady-state traffic of macromolecules between the adsorbed state and the unadsorbed state.^{6,7} The interplay between these processes creates a complex system rich in dynamic possibilities. As a result, the reliable prediction of quantities such as the adsorbed mass and concentration profiles demands detailed knowledge of the dynamics. Thus, one motive for this study is to understand the surface motions and relaxations, in particular the dynamics which must underlie an overall adsorption equilibrium. A second motive is to assess the conditions for reversibility and irreversibility in the adsorption process.

Pioneering theory,⁸ experiments,⁹ and simulations¹⁰ by Pefferkorn, Varoqui, and co-workers endeavored to understand the kinetics of establishment of adsorption equilibrium. The critical assumption was that an adsorbed chain begins in a solution-like conformation but becomes progressively flatter until obstructed by excluded surface effects, such as interaction with other adsorbed chains, or until thermodynamic equilibrium has been attained. To test this hypothesis, a series of experiments was conceived in which the rate of polyelectrolyte supply to the surface was varied.^{9,10} They found that at slow adsorption rates equilibrium in total mass was achieved with only a small amount of polymer on the surface. It was surmised that this reflected coverage of the surface by very few flattened chains which prevented further adsorption. At high rates of adsorption an overshoot in total mass indicated initial

close packing of chains in isotropic conformations, followed by desorption due to competition for surface sites during structural relaxations.

Computer simulations were then undertaken to determine the total mass adsorbed under conditions similar to the experiment. In these simulations, flat disks were successively distributed on the surface according to the prescriptions of random sequential adsorption and were allowed to grow radially according to first-order kinetics. The experimental measurements of total mass adsorbed were accurately reproduced by the simulation.

Careful studies of conformational relaxations have also been carried out in Wageningen.^{11,12} Cohen Stuart and Tamai¹¹ used streaming potentials to infer the hydrodynamic thickness, δ_h , of poly(vinylpyrrolidone) as it adsorbed to the inside of a glass capillary. An overshoot of δ_h with time during adsorption was interpreted as an initial increase of δ_h during accumulation of polymer at the surface, followed by a reduction of δ_h as the chains relaxed to a flattened conformation. Further work by Dijt¹² studied the time scales of desorption of a low molecular weight polymer as it was displaced during competition with a population of simultaneously adsorbed chains of much greater molecular weight. It was speculated that as the large chains relaxed and attached more segments to the surface, they displaced segments of the shorter chains which were promptly released into the solvent. These studies show rather convincingly that time scales for reformation may be quite sluggish in certain cases, but it was difficult to obtain precise kinetic quantities.

Evidence of slow conformational relaxations in adsorbed layers has been accumulating in our laboratory,^{5,13} and a rich picture of chain dynamics has emerged from studies of kinetics of polymer exchange.^{14,15} In a recent study of polystyrene adsorbed from carbon tetrachloride, the relationship between surface residence time and the extent of polymer exchanged, when challenged by a displacer, implied slow (~ 10 h) conformational relaxations.

In this report, as in a preliminary earlier work,⁵ we examine rates of desorption of polystyrene from a single surface of oxidized silicon to infer changes in the structure of the layer. We find that a single time constant, τ_{off} , described displacement for a significant time (1-3 h), followed by a period of slower desorption kinetics. An aging effect, in which τ_{off} continued to increase even after the mass adsorbed had equilibrated, implied surprisingly slow rearrangements of adsorbed chains in the direction of conformational equilibrium. After long aging times,

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Table 1. Characterization of the Polystyrenes^a

sample	M_w	M_w/M_n	source	Γ_0 (mg/m ²)
protio	115 000	1.04	Polymer Laboratories	2.5
	355 000	1.02	Toyo Soda	3.5
	575 000	1.06	Pressure Chemical Co.	3.8
	1 080 000	1.05	Polymer Laboratories	5.8
deuterio	10 500	1.02	Polymer Laboratories	
	87 500	1.05	Polymer Laboratories	
	550 000	1.05	Polymer Laboratories	

^a Data are those of the suppliers.

ranging from hours to days, τ_{off} reached a plateau value, τ_{eq} . This equilibrated desorption time increased exponentially with the length of adsorbed chains.

Experimental Section

Infrared spectra were collected using a Nicolet IR/30 Fourier transform infrared spectrometer (FTIR) equipped with a mercury-cadmium-telluride detector. Experiments were performed in the mode of attenuated total reflection (ATR).^{16,17} The internal reflection element (IRE) at the heart of the CIRCLE optical assembly, obtained from Spectra-Tech, was a silicon rod with conical ends. In this geometry, the infrared beam entered the crystal with a 35 °C angle of incidence and sustained roughly 13 internal reflections.¹⁸ The prism was mounted inside a thermostated steel jacket.

Anionically polymerized atactic polystyrene (PS), protio (PS-*h*) and deuterio (PS-*d*) standards of various degrees of polymerization, were obtained from several sources and were used as received. Their characteristics are listed in Table 1. Polymer samples were dissolved in freshly distilled cyclohexane (Baker) at dilute concentrations of either 1.0 or 0.1 mg/mL. The experiments were thermostated at 30 °C, which is the θ temperature, T_θ , for PS-*d* in cyclohexane.¹⁹ For PS-*h* in cyclohexane, $T_\theta = 34.5$ °C, so that PS-*d* at the temperature of the experiment found itself in a slightly better solvent than did PS-*h*. PS-*d* and PS-*h* are both miscible at the concentrations used.

These are flexible linear chains. The net segment-surface interaction enthalpy under the conditions of this experiment is $\chi_s = 2.1kT^{20}$ (k is the Boltzmann constant and T is the temperature). The adsorption isotope effect, which slightly favors the adsorption of the deuterio isotope, is $0.04kT$ per segment.²¹ To avoid repulsive osmotic interactions between adsorbed chains and incoming chains as a source of a possible kinetic bottleneck, this system has the advantage of being a near θ solvent for both polymers. In these experiments with dilute cyclohexane solution, the penetration depth of the infrared evanescent wave was $d = 0.27$ μm at the largest carbon-hydrogen stretch of 3050 cm^{-1} . At every wavelength, the evanescent wave sampled the interfacial region to a depth far larger than the thickness of the adsorbed layer (ca. the radius of gyration). Therefore the measured polymer peak intensities did not contain information about segment distribution as a function of depth but represented the surface excess of adsorbed polymer *in toto*.

The spectra were observed at each stage of the experiments for infrared adsorption bands indicating the presence of contaminating surface species, and the experiment was aborted if contamination was encountered. Measurements reported here are based on the collection of 800 interferograms with a spectral resolution of 8 cm^{-1} and a time average of 3 min. Calibrations of the mass adsorbed per area (surface excess) and corrections for the contribution from polymer in solution are described elsewhere.^{16,17,22}

At the end of an experiment, the silicon IRE was degreased in ethyl acetate with ultrasonic agitation for ~10 min and stored in a bath of the same solvent. Before use, the crystal was successively rinsed with deionized filtered water, rinsed in dilute (5%) hydrofluoric acid for 45 s, rinsed again with water, and blown dry with nitrogen gas. It was then exposed to oxygen plasma (100 W, rf) for 5 min. Finally, it was allowed 10 min to cool and equilibrate in the reduced-pressure oxygen before installation in the stainless steel cell. This treatment has been shown²⁰ to reproducibly cultivate an oxidized surface (primarily

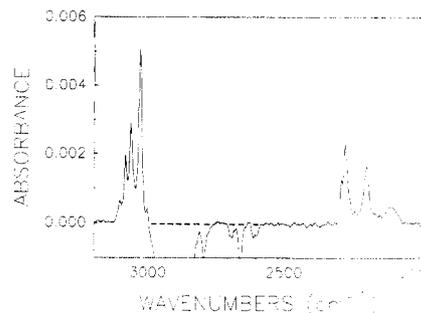


Figure 1. Infrared spectrum of PS-*h* and PS-*d* adsorbed jointly onto silicon from a cyclohexane solution of 0.1 mg/mL. Absorbance is plotted against wavenumbers. From the integrated intensities of the polystyrene C-H ring vibrations (3000–3150 cm^{-1}) and of the C-D vibrations (2000–2300 cm^{-1}), the surface excess plotted in succeeding figures is calculated.

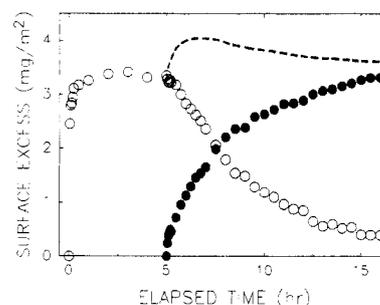


Figure 2. Illustration of the sequence of each exchange experiment. Surface excess (mass-area⁻¹) is plotted versus time. First PS-*h* solution (open circles, 1 mg·mL⁻¹, $M_w = 575$ 000) was exposed to the silicon surface. After a waiting time, in this case 6 h, this solution was replaced by PS-*d* solution (filled circles, 1 mg·mL⁻¹, $M_w = 550$ 000) and the ensuing adsorption-desorption kinetics were monitored. The dashed line represents the total mass adsorbed, PS-*h* + PS-*d*, to show the mass overshoot.

SiO₂), while minimizing the amount of organic contamination and surface silanol groups.

The Teflon and stainless steel components of the CIRCLE cell were cleaned in the ultrasonic ethyl acetate and then stored in nitric acid for a minimum of 10 h. In preparation for a new experiment, the cell was rinsed with deionized water and soaked in acetone for 15 min. A jet of N₂ gas was used to dry the cell. The Teflon input tubes and fittings were rinsed with methylene chloride and dried with N₂ gas. The experiments normally began ~15–30 min after the assembly was secured in the spectrometer. Control experiments¹³ showed that this waiting time had no effect on the quantity of mass adsorbed or the time scale of exchange. The cell was then filled with freshly distilled cyclohexane and, after ~30 min, a background was collected. Polymer solution was not added until 30–60 min after the cell had been filled with cyclohexane; this improved baseline stability, perhaps reflecting desorption of adsorbed gasses.

Results

The Exchange Experiment. Figure 1 shows a representative spectrum of PS-*h* and PS-*d* adsorbed jointly and ratioed to a background spectrum of pure cyclohexane. Absorbance is plotted against wavenumbers. PS-*h* shows a series of carbon-hydrogen vibrations in the region 3000–3150 cm^{-1} , and PS-*d* shows a series of carbon-deuteron vibrations in the region 2000–2300 cm^{-1} . These C-H and C-D peaks are due to stretching vibrations on the polystyrene ring and the deuterated methylene groups, respectively. The negative peaks may be attributed to the depletion of cyclohexane from the surface.

Figure 2 illustrates the sequence of each experiment. First, a dilute PS-*h* solution ($M_w = 575$ 000 in this example) was exposed to the bare silicon oxide surface. By monitoring the C-H stretches, the growth of the surface

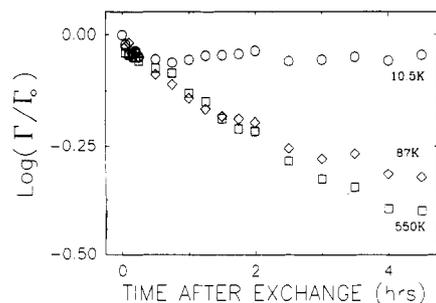


Figure 3. Logarithm of the adsorbed mass of PS-*h* ($M_w = 575\,000$), normalized by the surface excess just before replacing the solution, potted during displacement by PS-*d* of various molecular weights. Squares, $M_w = 550\,000$; diamonds, $M_w = 87\,000$; circles, $M_w = 10\,500$. In each experiment solution concentrations of 1.0 mg/mL and surface residence times of 12 h were used.

excess with time was observed to quickly (<1 h) reach a steady-state value. Beyond this adsorption time, the layer was allowed a residence time (5 h in this example) for equilibration of the layer. The state of the layer was then probed by challenging its occupation of the surface by introducing a solution of PS-*d* ($M_w = 550\,000$ in this example) of the same solution concentration. Control experiments showed that the rate of solution flow into the cell had no influence on the outcome of the experiments reported below. The ensuing time-dependent displacement of PS-*h* was accompanied by adsorption of PS-*d*.

Upon careful inspection one sees that the apparent symmetry in the adsorption/desorption kinetics is broken in the early time of the exchange. Because adsorption of the deuterio isotope is preferred,²² adsorption of the PS-*d* commenced immediately after introduction of the solution, with little desorption of PS-*h*. The resulting overshoot in the total mass adsorbed (see the dashed line of Figure 2) supports the picture of a transient state in which invading and detaching chains wormed their way in and out of the surface layer by the sequential attachment and detachment of adsorbed segments, as discussed below. This overshoot was absent when displacement proceeded with chains of equal segment-surface interaction strength (backbone-deuterated polystyrene).²³

It is reasonable to ask how the invading chains influence the kinetics of exchange. Could the kinetics of exchange depend on an entropic adjustment of the total free energy change upon desorption due to the mismatch of chain size between the escaping and invading chains? To pursue this question, a series of experiments was performed in which displacement of a PS-*h* layer ($M_w = 575\,000$, aged 12 h) was induced by deuterated polystyrenes of a variety of molecular weights. These experiments, plotted in Figure 3, show that the desorption rate is independent of molecular weight of the polymeric displacer. However, the steady-state quantity displaced decreased with decreasing molecular weight of the invading chains. This is due to the entropic preference for larger chains to remain at the interface.^{22,24,25} Thus, it is evident that displacement of PS-*h*, i.e., detachment from the surface, was rate controlling. That this process is rate controlling was also found in a different polymer system²⁶ and molecular architecture.¹⁵

When logarithm of normalized mass is plotted against linear time (Figure 4), one finds that the displacement of PS-*h* may be described by a single time constant for a significant time (~ 2 h), followed by a period of slower desorption which may also be fit by a single time constant. The second process was observed to continue until complete removal of the initial layer, but this could be

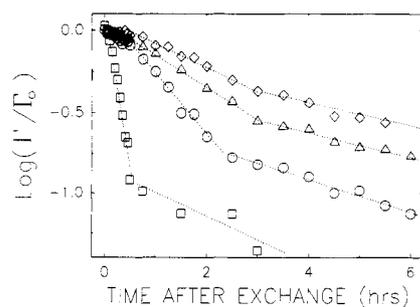


Figure 4. Kinetics of exchange and the effect on displacement kinetics of changing the waiting time before replacing protio by deuterio polymer solution. The time-dependent normalized surface excess of PS-*h* is plotted logarithmically against linear time after replacement. Squares, 30-min aging; circles, 6-h aging; triangles, 12-h aging; diamonds, 24-h aging.

determined only when experimental conditions allowed data collection after long times on the scale of the specific desorption kinetics (up to 3 days). We remark that simple exponential behavior was not observed when this study was begun but depended on meticulous preparation of the surface, as referred to above. By contrast, exchange was nonexponential, actually consistent with following a power law in time, when the surface was chemically heterogeneous.²⁹

Delay before Desorption. The time delay between initial adsorption of PS-*d* and release of PS-*h* from the surface was evident in all experiments as an extrapolation of the linear fit to a nonzero time at the onset of desorption. This transient state was observed to persist for 10–30 min. The data roughly show that this time delay grew with molecular weight of the initial layer and with increasing concentration of the PS-*d* solution, supporting a picture of a dense overlayer formed by the aggressive invading chains. Thus, the PS-*h* required an additional time to diffuse through topological constraints imposed by the PS-*d* barrier. However, due to poor reproducibility, a quantitative analysis is avoided at this time.

Variation of Residence Time. A series of experiments was performed in which the residence time before replacement of the initial PS-*h* solution was varied, as summarized in Figure 4. Again, for residence times ranging from 30 min to 36 h, the displacement kinetics may be separated into two distinct regimes, each with a single time constant. It is interesting to note that the point of crossover between the two kinetic regimes became less distinct at longer residence times.

Yet the most striking feature of this collection of experiments is the systematic dependence of the displacement kinetics on the residence time. As the adsorbed layer occupied the surface, the time constants for desorption increased, indicating that it became increasingly more difficult for the adsorbed chains to be removed. For the purpose of analyzing this trend, we will consider only the desorption during the initial kinetic regime (<3 h) and assign to each of these a value τ_{off} , the time for the surface excess to reach $1/e$ of the steady-state level reached at long times. These time constants, represented by the squares of Figure 5b, are plotted as a function of surface residence time. They extrapolated to $\tau_{\text{off}} = 0$ when the residence time was short and they approached a plateau, τ_{eq} , of 5 h at long times.

It also became clear that this aging process was sensitive to experimental conditions. Figure 5B shows that steady-state displacement kinetics was achieved after ~ 7.6 h (squares, solution concentration of 1.0 mg/mL) but was achieved more slowly (after ~ 23 h) when the chains adsorbed from a solution of 0.1 mg/mL (circles). Variations

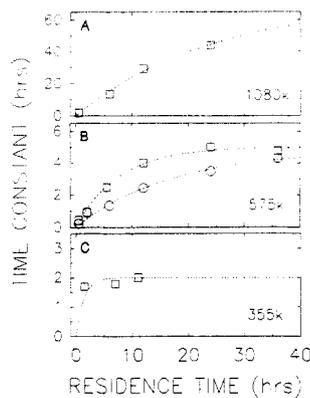


Figure 5. Displacement time constants, τ_{off} , plotted against aging times of the initially adsorbed PS-*h* of various molecular weights. A, $M_w = 1\,080\,000$; B, $M_w = 575\,000$; C, $M_w = 355\,000$. Squares and circles represent adsorption from solution concentrations of 1.0 and 0.1 mg/mL, respectively.

in temperature also exerted a marked influence on the aging time.²³ This history dependence has a bearing on interpreting inconsistencies between various other kinetic studies in the literature, in which the surface residence time was apparently not controlled.

One may argue that the increasing barrier to displacement may be caused by chemisorption or some highly specific interaction between the polymer and chemical heterogeneities on the surface. It is conceivable that the number of such strong attachments could increase with time as the surface chemistry evolved during an experiment. This is equivalent to proposing that the average segment-surface interaction enthalpy, χ_s , could somehow increase with time. To allay these fears, estimates of the χ_s parameter were made for a freshly adsorbed layer of PS-*h* and one that had been aged for 24 h, as shown in Figure 6.

To determine χ_s , the segmental adsorption energy of an adsorbed layer was decreased by adding a monomeric displacer (methylene chloride) to the polymer solvent solution²⁷ at an incrementally increasing displacer volume fraction ϕ_d . At a certain value of ϕ_d , termed the critical volume fraction ϕ_c , the polymer was completely displaced. An elegant technique, devised by Cohen Stuart et al.,^{27,28} provides a relationship between this critical point and the segmental adsorption energy. It is evident to the eye that the ϕ_c for these layers are roughly equal to each other; the quantitative description, which follows, shows that $\phi_c = 0.2$ and $\chi_s = 2.1$. Therefore, we may conclude that the average strength of the segment-surface interaction remained constant.

The actual differences between the two displacement experiments of Figure 6 deserve discussion. Analysis²⁷ shows that the slight dissimilarity between the ϕ_c values ($\phi_c = 0.18$ and 0.22) amounts to a difference in χ_s of less than $0.1kT$. This may be due to uncontrollable fluctuations in surface chemistry from one experiment to the next and will have little effect on the free energy change upon displacement.²⁰ The second issue concerns the difference between the surface excesses at low displacer volume fractions. When aged only 30 min (circles, Figure 6), 18% of the adsorbed mass was lost upon exchange of the polymer solution with pure solvent. The retention of all polymer composing the aged layer (squares, Figure 6) indicated a process by which loosely adsorbed chains became more secure with time by attaching more segments, as discussed below. Incidentally, the shape of the displacement curve is believed to contain information about the restrictions on polymer mobility due to lateral interactions between polymer molecules.³⁰

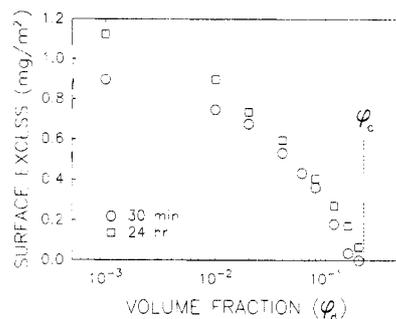


Figure 6. Displacement experiments to determine the segment-surface interaction enthalpy, χ_s , after different aging times. Circles, aged 30 min; squares, aged 24 h. The intersection with the x-axis gives the critical displacer volume fraction, ϕ_c .

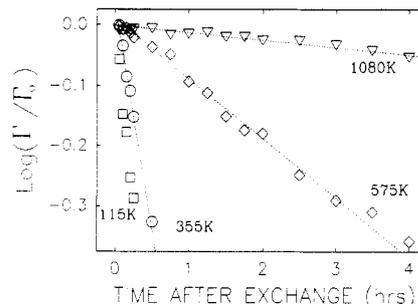


Figure 7. Adsorbed mass of four different PS-*h* of varying molecular weights during displacement by PS-*d* ($M_w = 550\,000$). Triangles, $M_w = 1\,080\,000$; diamonds, $M_w = 575\,000$; circles, $M_w = 355\,000$; squares, $M_w = 115\,000$. In each experiment solution concentrations of 1.0 mg/mL and aging times of 12 h were used.

Variation of Molecular Weight. The influence of molecular weight on the reconfiguration process is displayed by the squares of Figure 5A-C. In each of these experiments, PS-*h* was adsorbed from a cyclohexane solution of 1.0 mg/mL concentration. After the specified residence time, the PS-*h* solution in the cell was exchanged with PS-*d* ($M_w = 550\,000$) solution of the same concentration. As before, desorption time constants, τ_{off} , were obtained from the initial displacement kinetic regime. The increase of τ_{off} may be empirically described by a saturating exponential (dashed lines, Figure 5). We make no attempt to justify exponential behavior at this time; this is merely a suitable empirical fit to be used for the purpose of quantitative comparison.

From the exponential fits of the 1.0 mg/mL data of Figure 5, we obtained values of the equilibrated desorption time, τ_{eq} , for a variety of molecular weights. The result is a dramatic increase of both τ_{eq} (from 2 h to 70 h) and the characteristic time to reach τ_{eq} (from <1 to 30 h). To emphasize the scale of this augmentation of τ_{eq} with molecular weight, Figure 7 shows a set of four experiments using a wide range of molecular weights making up the initial layer. In each case the PS-*h* solution was exchanged with PS-*d* ($M_w = 550\,000$) after 12 h, and we display only the data from the initial kinetic regime.

The systematic increase of τ_{eq} with length of adsorbed chains, when challenged by the PS-*d* species, is shown in Figure 8. One sees that τ_{eq} rose from 0.5 h ($M_w = 115\,000$) to ~ 70 h ($M_w = 1\,080\,000$) at a rate far more rapid than linear. When the logarithmic time constant is plotted against molecular weight, as in the inset of Figure 8, it appears that the data may be described by a simple exponential relationship: $\tau_{eq} \sim e^{\alpha M}$. The line drawn through the data has a slope $\alpha = 5 \times 10^{-6}$. The conflicting reports over the years regarding the reversibility and irreversibility of polymer adsorption become easier to appreciate in view of this extreme sensitivity of τ_{off} to M .

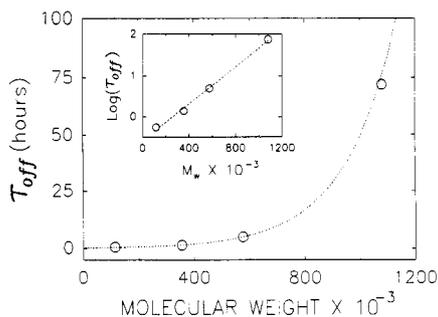


Figure 8. Equilibrated time constant for displacement plotted against molecular weight. Inset: log-linear plot of same data showing that the equilibrated displacement time constant increased exponentially with the chain length of adsorbed polymer.

When M was large, the rate of displacement was strongly quenched.

Discussion

Kinetics of Exchange. Although the simple kinetics described above, exponential in time elapsed and time constant exponential in M , remind us of the behavior of small molecules, the exchange *mechanism* must be fundamentally different. A strict analogy with small molecules would suggest that all of the adsorbed segments are released at once; however, that possibility is ruled out by the fact that desorption of adsorbed chains into pure solvent did not occur on the experimental time scale.¹³ Rather, the displacement into a polymer solution must have proceeded piecemeal, a small number of segments at a time, with lesser activation energy associated with this sequential process.

In Figure 3 one sees that a single time constant described displacement for a significant time (1–3 h) and for a large fraction of chains composing the layer (50–90%). Deviations from the initial exponential decay after this time may arise from a number of causes. One possible origin is that the remaining chains making up the initial layer may continue to evolve toward tightly bound conformations during the slow exchange process. This mechanism would cause a gradual slowing of desorption but would not account for the abrupt transition seen in the displacement of a layer with little aging (for example, squares of Figure 4). A more attractive scenario is that there could exist two distinct populations on the surface: a loosely bound layer making up the first kinetic regime, and a tightly bound layer making up the second. It has been suggested^{6–9} that in the limit of slow accumulation of polymer from dilute solution to a bare surface, the first chains to arrive will assume a flat conformation to maximize the number of segment–surface contacts. Experiments are underway in our laboratory to test this hypothesis.

The existence of distinct fast and slow desorption processes, both roughly obeying first-order kinetics, has recently been reported in the removal of adsorbed polysaccharides ($M_w = 40\,000$) from germanium by monomeric displacers.³¹ It was convincingly shown, by limiting the rate of transport of polysaccharides to the surface (as in the experiments of Pefferkorn^{6,7}), that the slow desorption was due to a tightly bound population which formed in early times when the surface comprised an abundance of potential adsorption sites.

The existence of tightly and loosely bound layers has also been reported in a recent study of adsorption during shear or elongational flow in a Θ solvent system³² and in studies of protein surface diffusion^{33,34} as discussed in ref

13. Further convincing evidence of dissimilar conformational populations has emerged in our laboratory from studies of polystyrene adsorbing from a good solvent (carbon tetrachloride).¹³

Equilibration of the Adsorbed Layer. To simplify the analysis, only the initial exponential decay is discussed below. It is likely that the slowing down of τ_{off} with increasing residence time reflected rearrangements of the adsorbed chains in the direction of conformational equilibrium. When chains first adsorb to a surface, one would not expect their conformations to be equilibrated. One may consider the following scheme of adsorption: diffusion of the incoming chains from the bulk solution to the interface (rapid on the time scale of the experiment), attachment to the surface, and conformational equilibration. The chains may be expected during this last stage to become bound more tightly to the surface, attached at more and more potential adsorption sites,^{4,13,35} thereby reducing the flux of chains between the surface and solution. As may be seen in Figure 2, this restructuring of conformations occurred even after the mass adsorbed had reached a steady state.

Although the time constants increased dramatically with aging time in the first kinetic regime, only a slight increase was observed for the second. When viewed as the desorption from two conformational populations, this suggests that the loosely bound group relaxed more than the tightly bound group. Perhaps the tightly bound chains were already very close to their lowest energy configuration. This scenario, in which a loosely bound population evolves toward the conformation of a more relaxed, tightly bound population, was previously suggested by measurements of hydrodynamic thickness. Cohen Stuart and Tamai¹¹ monitored the relaxation of δ_h for a variety of surface coverages of poly(vinylpyrrolidone) on glass and found that relaxation was more extensive when the surface excess was large.

In this model system of monodisperse polystyrene, the reconfiguration process apparently has little influence on the total mass adsorbed or on the time scale to reach this steady state. In general, we may expect that the time-dependent consumption of surface sites by some chains, in competition with others, may release some from the surface, creating an overshoot in mass. Such a process has been observed in our laboratory^{36,37} and in Wagenin- gen.¹² Thus, prediction of the time-dependent composition of an adsorbed layer requires detailed knowledge of the mechanisms and dynamics of equilibration. Regrettably, there exist no theories which link the kinetics of total mass equilibration with the dynamics of conformational equilibration. It is therefore difficult to predict, in any given system, which process of our kinetic scheme is rate limiting. As a rule of thumb, it is expected that as the segment–surface interaction is increased, the mobility becomes more sluggish, thus augmenting the time scales of chain relaxation. This expectation has been borne out in recent experiments on tightly bound binding systems in which relaxations from nonequilibrium conformations were essentially quenched.^{17,23}

Growth of τ_{off} with Molecular Weight. While there are many ways to justify an exponential growth of the equilibrated desorption time, τ_{eq} , with molecular weight,⁵ we presently discuss only the simplest. We continue the analogy with small molecules and expect the adsorption–desorption rate to be governed by equilibrium parameters. General considerations show that the free energy change upon desorption, ΔF , should grow linearly with the number and strength of polymer–surface interactions. Thus, as

discussed elsewhere,¹⁵ ΔF should be extensive in the molecular weight, M . The desorption time constant, τ_{off} , is then

$$\tau_{\text{off}} \sim \exp(\Delta F/k_b T) \sim \exp(\alpha M/M_0) \quad (1)$$

Here, M_0 renders the argument dimensionless and the parameter α is expected to scale with the polymer-surface interaction.

The argument presented above is valid as long as chain mobility is not restricted. If molecular mobility becomes sluggish or "glassy",^{15,38,39} then the desorption kinetics may no longer be controlled by the free energy. This case, in which topological constraints dominate the desorption process, has been studied in a different system.^{14,15,39} It has been shown that at low temperatures, in a regime of diffusive control, the desorption time scales as $M^{2.3}$, which evokes the behavior of the self-diffusion coefficient, D .^{15,39}

A weaker dependence on M ($\tau_{\text{off}} \sim M^{-1/4}$) was previously predicted.^{3,35,40} The key physical assumption was that penetration of incoming chains into the previously adsorbed layer was rate controlling. In fact, detachment from the layer was rate controlling.

Universality. We should note that an effect of surface residence time was previously suggested by studies of protein macromolecules.⁴¹ Studies with proteins might be complicated by other, more complex, effects of denaturation and strong binding to the surface at specific functional groups. The present study emphasizes the generality of the aging phenomenon in a simpler macromolecular system.

The ability to relate the time scales of equilibration to other studies of polymer/solvent/surface systems remains a formidable task due to the dependence of these quantities on the experimental conditions and history of the layer. For example, we have seen that the surface rearrangement time, the time to reach τ_{eq} , increased with decreasing solution concentration and with increasing degree of polymerization. However, it is encouraging that the equilibrated time constant, τ_{eq} , appears, based on the evidence available to date, to be insensitive to external conditions such as the concentration. We conclude that although a universal conformational distribution exists for a given polymer/solvent/surface system in its lowest energy configuration, the time scales to reach this state vary greatly with experimental conditions. It is relevant to compare this relaxed conformation with existing theoretical predictions which ignore the dynamics contained in the apparent history dependence.

Conclusion

This work has been presented with three goals in mind: to demonstrate the utility of the polymer exchange experiment as a probe of the structure and dynamics of adsorbed polymer, to investigate the mechanisms of chain mobility and exchange, and to construct a quantitative foundation for a time-dependent description of the distribution of conformations. We have examined a simple situation which, by enjoying freedom from the kinetic complexities of topological constraints,^{14,15,38} has provided a view of the kinetic processes from the perspective of equilibrium parameters. In this circumstance we expect, and give experimental evidence of, desorption that follows a single exponential in elapsed time and whose time constant grows exponentially with molecular weight.

Finally, these results have fundamental implications in setting new criteria for equilibration of conformations within an adsorbed layer.

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References and Notes

- (1) Cohen Stuart, M. A.; Cosgrove, T.; Vincent, B. *Adv. Colloid Interface Sci.* **1986**, *24*, 143.
- (2) Kawaguchi, M.; Takahashi, A. *Adv. Colloid Interface Sci.* **1992**, *37*, 219.
- (3) de Gennes, P.-G. *Adv. Colloid Interface Sci.* **1987**, *27*, 189.
- (4) Granick, S. In *Physics of Polymer Surfaces and Interfaces*; Sanchez, I., Ed.; Manning Publications: New York, 1993.
- (5) Frantz, P.; Granick, S. *Phys. Rev. Lett.* **1991**, *66*, 899.
- (6) Pefferkorn, E.; Carroy, A.; Varoqui, R. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1997.
- (7) Pefferkorn, E.; Haouam, A.; Varoqui, R. *Macromolecules* **1989**, *22*, 2677.
- (8) Varoqui, R.; Pefferkorn, E. *J. Colloid Interface Sci.* **1986**, *109*, 520.
- (9) Pefferkorn, E.; Elaissari, A. *J. Colloid Interface Sci.* **1990**, *138*, 187.
- (10) Pefferkorn, E.; Elaissari, A. *J. Colloid Interface Sci.* **1991**, *143*, 85.
- (11) Cohen Stuart, M. A.; Tamai, H. *Macromolecules* **1988**, *21*, 1863.
- (12) Dijt, J. C. Thesis, "Kinetics of Polymer Adsorption Desorption and Exchange", Landbouwwuniversiteit te Wageningen, 1993.
- (13) Schneider, H. M.; Granick, S. *Macromolecules* **1992**, *25*, 5054.
- (14) Johnson, H. E.; Douglas, J.; Granick, S. *Phys. Rev. Lett.* **1993**, *24*, 3267.
- (15) Douglas, J.; Johnson, H. E.; Granick, S. *Science*, in press.
- (16) Kuzmenka, D. J.; Granick, S. *Colloids Surf.* **1988**, *31*, 105.
- (17) Johnson, H. E.; Granick, S. *Macromolecules* **1990**, *23*, 3367.
- (18) These quantities were determined by the methods of Sperline et al.; Sperline, R. P.; Muralidharan, S.; Freiser, H. *Langmuir* **1987**, *3*, 198.
- (19) Strazielle, C.; Benoit, H. *Macromolecules* **1975**, *8*, 203.
- (20) Frantz, P.; Granick, S. *Langmuir* **1992**, *8*, 1176.
- (21) Leonhardt, D. C.; Johnson, H. E.; Granick, S. *Macromolecules* **1990**, *23*, 687.
- (22) Frantz, P.; Leonhardt, D. C.; Granick, S. *Macromolecules* **1991**, *24*, 1868.
- (23) Frantz, P.; Granick, S., in preparation.
- (24) Roe, R.-J. In *Adhesion and Adsorption of Polymers*; Lee, L.-H., Ed.; Plenum Press: New York, 1980.
- (25) Scheutjens, J. M. H. M.; Fleer, G. J. In *The Effect of Polymers on Dispersion Properties*; Tadros, Th. F., Ed.; Academic Press: New York, 1982.
- (26) Johnson, H. E.; Granick, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 523.
- (27) Cohen Stuart, M. A.; Fleer, G. J.; Scheutjens, J. M. H. M. *J. Colloid Interface Sci.* **1984**, *97*, 515.
- (28) van der Beek, G. P. *Macromolecules* **1991**, *24*, 6600.
- (29) Leonhardt, D. M.S. Thesis, "Study of Adsorption of Protio and Deutero Polystyrene", University of Illinois at Urbana-Champaign, 1990.
- (30) van der Beek, G. P. *Langmuir* **1989**, *5*, 1180.
- (31) Ishida, K. P.; Griffiths, P. R. *J. Colloid Interface Sci.* **1993**, *160*, 190.
- (32) Chin, S.; Hoagland, D. *Macromolecules* **1991**, *24*, 1876.
- (33) Tilton, R.; Robertson, C. R.; Gast, A. *J. Colloid Interface Sci.* **1990**, *137*, 192.
- (34) Burghardt, T. P.; Axelrod, D. *Biophys. J.* **1981**, *33*, 455.
- (35) de Gennes, P.-G. In *New Trends in Physics and Physical Chemistry of Polymers*; Lee, L.-H., Ed.; Plenum Press: New York, 1990.
- (36) Johnson, H. E.; Clarson, S. J.; Granick, S. *Polymer* **1993**, *34*, 1960.
- (37) Schneider, H.; Granick, S., submitted.
- (38) Chakraborty, A.; Adriani, P. M. *Macromolecules* **1992**, *24*, 2470.
- (39) Johnson, H. E.; Granick, S. *Science* **1992**, *255*, 966.
- (40) de Gennes, P.-G. *C. R. Acad. Sci.* **1986**, *302*, 765.
- (41) Norde, W. *Adv. Colloid Interface Sci.* **1986**, *25*, 267.