Kinetics of Polymer Adsorption and Desorption

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We study adsorption-desorption kinetics of polymer chains at a solid surface. Protio polystyrene, adsorbed from cyclohexane to a single surface of oxidized silicon, was displaced by deuterio polystyrene. A single time constant, τ_{off}, described displacement for a significant time (1–2 h). An aging effect, in which τ_{off} continued to increase even after mass adsorbed had equilibrated, implied surprisingly slow rearrangements of adsorbed chains in the direction of conformational equilibrium. After equilibration, τ_{off} increased exponentially with length of adsorbed chains.

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Polymer chains are exceptionally prone to adsorb—a phenomenon with consequences in areas which range from biology to tribology—because even small preferential adsorption per segment adds up to enormous preferential adsorption per chain. The bulk of experimental and theoretical research has addressed the spatial distribution of segments at equilibrium, as summarized in Refs. 1 and 2. However, interesting time dependence is associated with achievement of equilibrium as chains adsorb onto an initially bare surface. Even at overall adsorption equilibrium there is a steady-state traffic of macromolecules between the adsorbed state and the unadsorbed state.[3,4]

The dynamics of these processes is a largely unsolved problem. In this Letter, we report what we believe to be the first measurements of adsorption-desorption kinetics in which the polymer chain length was varied. We distinguish three time scales: for diffusion to and adsorption onto an initially bare surface (rapid), for ensuing surface rearrangements (slow and history dependent), and for displacement. The displacement time constant τ_{off} grew exponentially, in the system we studied, with the chain length. The significance of these observations is to paint a picture of surface dynamics qualitatively different from what had been expected theoretically,[1,5–7] and also to set new criteria for equilibration of adsorbed layers.

The surface coverage of polystyrene, adsorbed to oxidized silicon from cyclohexane, was monitored *in situ* using Fourier-transform infrared spectroscopy in the mode of attenuated total reflection. The experimental protocol was the same as described elsewhere,[8] with the exception that the silicon surfaces were cleaned in oxygen rather than in argon plasma. Cyclohexane (Baker) was freshly distilled and dried (molecular sieves). The temperature was 30.0 °C. This is the Θ temperature T_Θ of deuterio polystyrene (PS-d) in cyclohexane and is close to (4.5 °C less than) T_Θ of protio polystyrene (PS-h) in cyclohexane.[9] PS-d and PS-h are miscible at the concentrations used.[9] Characteristics of the protio and deuterio polystyrenes (Toyo Soda and Polymer Laboratories) are given in Table I.

These are flexible linear chains. The net segment-surface interaction enthalpy is $\chi_s \approx 1.8kT$ on the related surface, silica[10] (k is the Boltzmann constant and T is the absolute temperature). The adsorption isotope effect, which slightly favors adsorption of the deuterio isotope, is $0.04kT$ per segment.[11] In order to avoid repulsive osmotic interactions between adsorbed chains and incoming chains as the source of a possible kinetic bottleneck, this system has the advantage of being a near-Θ solvent for both polymers.

Control experiments showed that desorption, when the solution was replaced by the same pure solvent, was too small to measure on a time scale of hours. This is typical;[3,4] the activation energy to peel all segments off the surface at once is so high that the process is kinetically blocked. Substantial displacement occurs only with concomitant adsorption of other molecules, originally free in solution.[3,4]

Figure 1 illustrates the sequence of each experiment. First, the PS-h solution ($N_w = 5750$ in this example) was exposed to the surface. The adsorbed mass reached steady state rapidly (< 30 min). Later the solution of PS-h was replaced by a solution of PS-d ($N_w = 5500$ in

TABLE I. Characterization of the polymer samples. N is the degree of polymerization. Γ_0 is the adsorption of PS-h prior to its displacement by PS-d. The ratio N_w/N_n of the weight-averaged to the number-averaged degree of polymerization, known as the polydispersity index, 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 of protio PS is 104 g/mole.

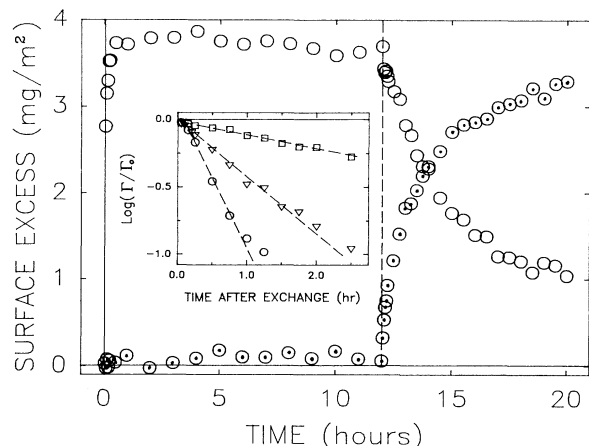| Sample	N	N_w/N_n	Γ_0 (mg/m^2)
Protio	1 150	1.04	2.5
	3 550	1.02	3.5
	5 750	1.06	3.8
	10 800	1.05	5.8
Deuterio	5 500	1.05	· · ·

FIG. 1. An illustrative experiment. Adsorbed mass is plotted against time. The first PS-h solution (1 mg ml^{-1}, N_w =5 750) was exposed to the silicon-oxide surface. After a waiting time this solution was replaced by a PS-d solution (1 mg ml^{-1}, N_w =5 500) and the ensuing exchange kinetics was monitored. Inset: The effect on displacement kinetics of changing the waiting time before replacing protio by deuterio polymer solution. The time-dependent adsorbed amount of PS-h (Γ), normalized by the surface excess just before replacing the solution (Γ_0), is plotted logarithmically against linear time after replacement. Circles, 30-min aging; triangles, 2-h aging; squares, 12-h aging.

FIG. 2. Displacement time constants plotted against aging times of the initially adsorbed PS-h layer (N_w =5 750). Circles: 0.1 mg/ml. Squares: 1.0 mg/ml. Time constants of the exponential fits to the data (dashed lines) are 23 and 7.6 h, respectively.

this example) of the same solution concentration. The ensuing time-dependent displacement of PS-h was accompanied by adsorption of PS-d. Because adsorption of the deuterio isotope is preferred,[11] at first PS-d adsorbed more rapidly than PS-h desorbed. The resulting overshoot in the mass adsorbed 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. Control experiments, in which the degree of polymerization and the solution concentration of the deuterio polymer were varied, showed 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 system.[12]

First we discuss the displacement kinetics and its striking dependence on aging time. In the inset of Fig. 1, one sees that a single time constant described displacement for a significant time (1–2 h). In order to simplify the issue, only the exponential decay is discussed below (deviations from exponential decay after this time are believed to reflect reorganization of the initially adsorbed layer during the course of displacement). We remark that simple exponential behavior was not expected when this study was begun; it 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.
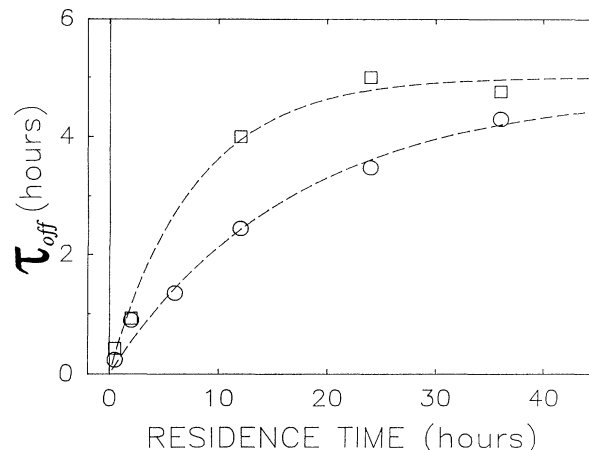
The aging time before replacement of the solution was also varied, as summarized in Fig. 2. The displacement time constants which describe these data, τ_{off}, increased with the surface residence time before replacing the solution. They extrapolated to zero when the residence time was short and they approached a plateau of 5 h in two solution concentrations (1.0 and 0.1 mg ml^{-1}).

It is likely that this slowing down of τ_{off}, with increasing aging time, reflected rearrangements of 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 kinetic scheme of adsorption: diffusion of the incoming chain from the bulk solution to the surface (rapid on the time scale of these experiments), adsorption, 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,[7,8] thereby reducing the flux of chains between the surface and solution. As may be seen in Fig. 1, this restructuring of the conformations of adsorbed chains occurred even after the mass adsorbed had reached steady state.

It is not clear that one should seek universality in the surface rearrangement time τ_{aging}, the time required to equilibrate τ_{off}. It is true that τ_{aging} did increase with the degree of polymerization of the adsorbed chains; other variables held constant. However, it was also sensitive to experimental conditions. Systematic experiments in this regard were performed with the chains of a matched number of segments, $N \approx 5\,500$. Figure 2 shows that steady-state displacement kinetics was achieved after approximately 7.6 h (solution concentrations of 1.0 mg/ml) but was achieved more slowly (after approximately 23 h)
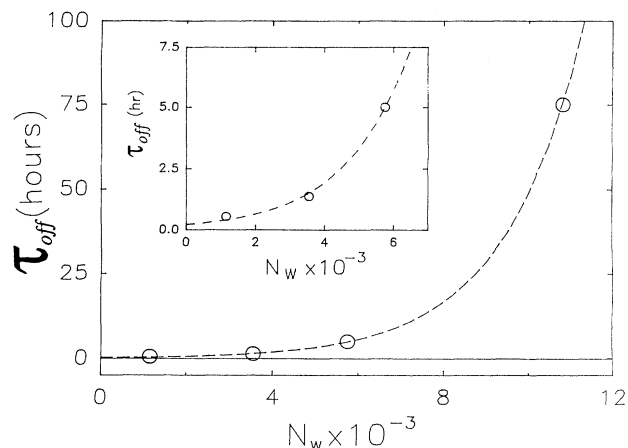
900

FIG. 3. Equilibrated time constant for displacement plotted against degree of polymerization of adsorbed PS-h.
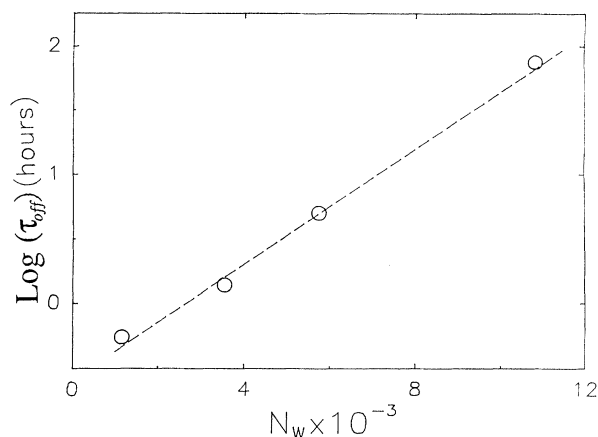

FIG. 4. Log-linear plot of Fig. 3, showing that the equilibrated displacement time constant increased exponentially with the chain length of adsorbed polymer.

when the chains adsorbed from solution concentrations of 0.1 mg/ml. This history dependence has a bearing on interpreting inconsistencies between various other kinetic studies, in which the surface residence time of the polymer was apparently not controlled.

We should note that an effect of surface residence time was previously suggested by studies of protein macromolecules,[13] although it does not appear to have been recognized previously in the context of homopolymer adsorption. 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.

What of the *equilibrated* displacement time, which may be expected to be more universal? The systematic increase of equilibrated τ_{off} with increasing length of the adsorbed chains, when challenged by the PS-d species with $N = 5500$, is shown in Fig. 3. (The steady-state mass adsorbed also increased with chain length, as listed in Table I. The surface bound fraction of segments can be estimated.[14]) In Fig. 3, one sees that τ_{off} increased from 0.5 ($N = 1150$) to approximately 80 h ($N = 10800$), and that the rate of increase was more rapid than linear. It is intriguing that these data are described by a simple exponential relationship: $\tau_{\text{off}} \simeq e^{aN}$. This is shown in Fig. 4, where the logarithmic time constant is plotted against the number of segments N; the line drawn through the data has slope $a = 5 \times 10^{-4}$. The conflicting reports over the years regarding the reversibility or irreversibility of polymer adsorption become easier to appreciate in view of this extreme sensitivity of τ_{off} to N. When N was large, the rate of displacement was strongly quenched.

In fact it is not obvious that the barrier height for displacement should be proportional to the number of segments. While this would be trivial *if* all of the adsorbed segments were released at once, that possibility is ruled out by the fact that desorption of adsorbed chains into pure solvent did not occur on the experimental time scale. Rather, the much faster 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. Explanation of the exponential growth of τ_{off} with N must involve concerted motion at the many points where the polymer chain is adsorbed.

A weaker dependence on N ($\tau_{\text{off}} \simeq N^{-1/4}$) was previously predicted.[1,5-7] The key physical assumption was that penetration of incoming chains into the previously adsorbed layer was rate controlling. In fact, detachment from the previously adsorbed layer was rate controlling, as noted above.

In suggesting the underlying mechanism, there is an analogy to be made with the longest relaxation time τ_1 of a chain which dangles from a polymer network. In a network, the reason that τ_1 grows exponentially with N is believed to be that the dangling chain, in order to relax, must first adventitiously diffuse to the point of its attachment to the network.[15] Polymer chains pinned to a surface by intertwining with other adsorbed chains could escape by an analogous mechanism. Alternatively, displacement could result simply from the stochastic time-dependent detachment of many linked segments. Which of these approaches (or others) captures the essential physics of adsorption-desorption exchange is not yet clear because an exponential relationship can be justified in many ways. The matter may be decided experimentally by using adsorbed chains of shorter length.

The results presented here have fundamental implications in setting new criteria for equilibration of conformations within adsorbed polymer layers. They expose a

new picture of what controls the dynamics of adsorbed polymer chains.

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