

Kinetic Traps in Polymer Adsorption. 1. Polystyrene Displaced by Polyisoprene at 12 °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

Received December 7, 1993; Revised Manuscript Received May 20, 1994*

ABSTRACT: Sequential adsorption experiments were performed to determine the kinetics of polymer displacement. Protio-polystyrene (PS) and deuterio-*cis*-polyisoprene (PI) were allowed to adsorb sequentially at 12 °C, from dilute solution in carbon tetrachloride, onto a single surface of oxidized silicon. Whereas the net surface excess equilibrated rapidly, the individual populations of PS and PI equilibrated far more slowly. The adsorption of PI was enthalpically favored, but PS arrived first at the surface, so initially-adsorbed PS was displaced. This displacement was strongly nonexponential in time. When desorption kinetics were fitted to the stretched-exponential function as suggested by theoretical considerations, the power of time, β , increased from $\beta \cong 0.2$ for the PS chains of lowest molecular weight (M_{PS}) to a limiting value, $\beta \cong 1/2$, for the highest M_{PS} . The time constant for desorption, τ_{off} , depended only weakly on M_{PS} . The minimal molecular weight dependence of τ_{off} in this PS-PI system contrasts with our findings in the PS-PMMA [poly(methyl methacrylate)] system and is tentatively attributed to the fact that less PI adsorbed at any instant in time, the higher the M_{PS} . However, the pronounced nonexponential desorption confirms previous experience, as well as expectation based on a simple kinetic model. This gives corroborative evidence that $\beta \cong 1/2$ is the limiting value to be expected of simple diffusion-limited desorption.

Introduction

Scientific interest, stemming from the fundamental and technological importance of materials and processes involving polymer-surface interaction, has provoked much study of the static structure of adsorbed chains at equilibrium.¹⁻⁴ The kinetics of the approach to equilibrium have also received some theoretical⁵⁻⁹ and experimental (see below) attention. On general principles, one expects that adsorption should involve kinetically- and energetically-controlled processes: the diffusion of chains to the surface, the attachment of a fraction of the chains' possible adsorption sites, followed by rearrangements of the chain structure toward equilibrium. The mechanisms which govern the concurrent diffusion, attachment, and relaxation have proven difficult to resolve, and it is fair to say that a full understanding is not yet in hand.

Adsorption usually occurs too quickly to yield much quantitative information regarding the kinetics of segmental attachment or the mechanism by which polymers join and are incorporated into the growing layer. But while adsorption may occur on inconveniently short time scales, desorption tends to occur more slowly and over a more forgiving time scale.

Early work in this area showed that, although typically little or no polymer can be desorbed by dilution, exchange does occur against molecules of higher molecular weight or even of similar molecular weight.¹⁰⁻¹⁶ However, these displacement kinetics occur over exceedingly long time scales—for example, up to a day¹⁵ or longer¹⁶ for polystyrene. In this early work, quantitative kinetic quantities were difficult to obtain, however.

Quantitative analysis of the exchange of polymer between the adsorbed state and free solution was pioneered by Pefferkorn, Varoqui, and co-workers, and a simple bimolecular exchange of molecules between surface and solution was suggested.^{12,17,18} Later work showed a rich

variety of other possibilities.¹⁹⁻²³ Evidence of slow conformational relaxations in adsorbed layers, even under conditions where the mass adsorbed does not change, has also accumulated.^{19-22,24-26}

In another approach to these same problems, this laboratory has undertaken kinetic studies of the displacement of one polymer by a chemically different polymer. The initial notion was to introduce constraints on diffusive motion within adsorbed layers in a controlled way: a strongly adsorbing polymer, by looping around a weakly adsorbing polymer, would tend to pin the latter to the surface.²⁷ This was accomplished experimentally by adsorbing poly(methyl methacrylate) (PMMA) onto a previously-adsorbed layer of polystyrene (PS). The surface excess of PMMA quickly reached steady state with minimal desorption of PS, and the ensuing desorption kinetics of PS were analyzed as it depended on temperature,²⁷ molecular weight, and chain topology (linear or branched).^{28,29} A strong dependence on temperature was also noted in the poly(dimethylsiloxane)-polyisoprene system²⁹ and in the PS-polyisoprene system.⁹ The experiments were consistent with the chief predictions of a kinetic model (see below).⁹

This paper extends these studies to a more complex—but arguably more common—situation: in which adsorption of the overlayer polymer continues as the initially-adsorbed polymer undergoes desorption. The constraints on desorption are then no longer constant, and the applicability of the kinetic model is not obvious *a priori*. The chief conclusion of the study which follows is that, although simple molecular weight scaling of the desorption kinetics cannot be expected (because the constraints on desorption change according to the molecular weight), nonetheless the desorption is highly nonexponential with a specific nonexponential form that has a simple physical interpretation (see below).

* Abstract published in *Advance ACS Abstracts*, July 1, 1994.

Analysis of Data

The present experiments were undertaken to test a recently-proposed model of Douglas⁹ which examines two limiting kinetic regimes of the adsorption-desorption process. The model predicts that when rate-limited by diffusion from a surface, desorption will be nonexponential in time. This is in contrast to classical expectations and numerous findings for the adsorption of small molecules.^{7,8,24,25} On the other hand, when the enthalpy of attachment is rate-limiting, the classical exponential desorption behavior^{7,8,25} is of course predicted.

If diffusion is "fast" and chain conformations are equilibrated on the experimental time scale, the model invokes equilibrium arguments and expects an activated desorption process, exponential in elapsed time and exponential in the polymer molecular weight. This follows from the expectation that the free energy change with desorption, ΔF , should scale with the interaction per segment, α , and the molecular weight, M , so that the desorption time constant (τ_{off}) scales as

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

The rate of diminution of the surface excess, $\Gamma(t)$, is then exponential, since the rate of the desorption is taken to be proportional to the surface concentration. Note that $\tau_{\text{off}} \sim e^M$ is predicted from an activation energy argument; the argument does not suppose that all segments desorb at once and is consistent with the observation¹⁹ that detachment occurs piecemeal. Experimentally, this fast diffusion regime has been realized,¹⁹⁻²¹ though rarely, as most polymer systems exhibit slow relaxation and diffusion.

If molecular motions are so sluggish that diffusion competes with activated processes in its time scales, the above equilibrium arguments become inappropriate. Experimentally, this can be encountered at low temperatures^{9,28,29} or in situations where relaxations become constrained or glasslike.^{9,19,27,28} The simplest kinetic regime occurs if diffusion is rate-limiting. The steady-state flux from the surface $R(t)$ is given by

$$R(t) = (D/\pi t)^{1/2} \quad (2)$$

and the desorption in this regime is modeled as the product of the flux and the surface concentration:

$$d\Gamma/dt = -R(t) \Gamma(t) \quad (3)$$

When surface depletion is accounted for (Γ_0 is the surface excess before the exchange), integration of eq 3 leads to an intrinsically nonexponential desorption rate,⁹

$$\Gamma(t)/\Gamma_0 \sim \exp[-(t/\tau_{\text{off}})^\beta] \quad (4)$$

where $\beta = 1/2$. It also follows from this model that the desorption time constant, τ_{off} , scales as the inverse of the diffusion coefficient in the vicinity of the surface.

Central to the interpretation of experiment with respect to this model is the understanding that the $\beta = 1/2$ prediction stems from the experimental geometry of *homogeneous diffusion-limited desorption from a planar surface*. When the surface is "fractal" or the coverage is inhomogeneous, $\beta < 1/2$ is expected.⁹

The arguments presented above imply that stretched-exponential kinetics, with $\beta \approx 1/2$, should describe a general class of physical processes that are rate-limited by diffusion at a surface. This contrasts with the usual view that surface on-off processes are characteristically rate-limited by the

Table 1. Characteristics of the Polymer Samples

	M_w	supplier	M_w/M_n
PS	43 900	Toyo Soda	1.01
	96 400	Toyo Soda	1.01
	220 000	Polymer Lab, Amherst, MA	1.03
	355 000	Toyo Soda	1.02
	706 000	Toyo Soda	1.05
	1 260 000	Toyo Soda	1.05
PI	3 840 000	Toyo Soda	1.04
	154 500	Steve Smith	1.03

equilibrium energy of adsorption, and therefore the desorption-adsorption kinetics should be exponential. The origin of the nonexponential kinetics in this model does not support the common interpretation of a distribution of relaxation times or of predominantly collective motions; they are simply a logical consequence of the experimental geometry.

Experimental Section

The experiments were performed at the University of Illinois using an IBM IR-44 Fourier transform infrared spectrometer in the mode of attenuated total reflection. A cylindrical silicon crystal was fitted into a steel Circle Cell, purchased from Spectra-Tech, Inc., and secured by Teflon O-rings. The cell was mounted in a thermostated steel jacket. The temperature was controlled using a Lauda RCS water bath and was held constant at 12.0 °C to within 0.05 °C.

The polymer systems studied were protio-polystyrene (PS) of various molecular weights and deuterio-*cis*-polyisoprene (PI) in solution in carbon tetrachloride. The spectrograde carbon tetrachloride was purchased from Sigma-Aldrich and used as received. The characteristics of the polymers are listed in Table I. The net segment-surface interaction energies were evaluated by us following the protocol of Cohen-Stuart.^{24,25} These values are $\chi_s \approx 1$ for PS and $\chi_s \approx 2.9$ for h-PI. As we are using deuterated PI, the surface-segment interaction is assumed to be slightly larger than the corresponding h-PI, by $\approx 0.03kT$, due to the isotope effect.^{30,31} As the segment-surface interaction energies far outweigh the small tendency toward incompatibility of PS and PI (on the order of $0.01kT$), no surface demixing is expected.

The PI was synthesized at Procter and Gamble. Deuterio-isoprene monomer, purchased from Cambridge Isotopes Labs, was purified by distillation under vacuum following the reaction of dibutylmagnesium, purchased from Lithium Corp. of America, with trace impurities to form nonvolatile magnesium salts. The polymerization was performed in sealed, clean, dry reactors purchased from Chemco Pressure Reactors, the use of which is described elsewhere.³² To a clean reactor was added a fresh supply of cyclohexane, purchased (Pure Grade) from Phillips Petroleum, and the desired amount of purified 1,1-diphenylethylene, purchased from Kodak. The reactor was heated to 60 °C and titrated by dropwise addition of *sec*-butyllithium, purchased from LithCo. Once a persistent yellow color was achieved, the calculated amount of *sec*-butyllithium was charged to the reactor to give the desired molecular weight. A period of 15 min was allowed to elapse to permit complete addition of the butyllithium to the 1,1-diphenylethylene, at which time the desired amount of purified deuterioisoprene was added. After an additional 90 min, to allow for complete conversion of the isoprene, the reaction was terminated with degassed isopropyl alcohol. The contents of the reactor were pumped out under pressure and precipitated into a slightly acidic methanol/isopropyl alcohol mixture. The precipitated mixture was stabilized with Irganox 1010, vacuum dried, and stored.³²

The cell and crystal cleaning techniques and experimental preparation were described previously.²² The experiments always began by collecting an empty cell spectrum followed by solvent spectrum. Protio-PS solution, 1 mg/mL in CCl₄, then replaced the pure solvent in the cell, the adsorption was monitored for 1 h. The PS solution was then replaced by a solution of 150K molecular weight PI (1 mg/mL in CCl₄ unless otherwise noted). Spectra were collected at 1-min intervals for 15 min immediately following the exchange. Subsequent scans were collected at 15-

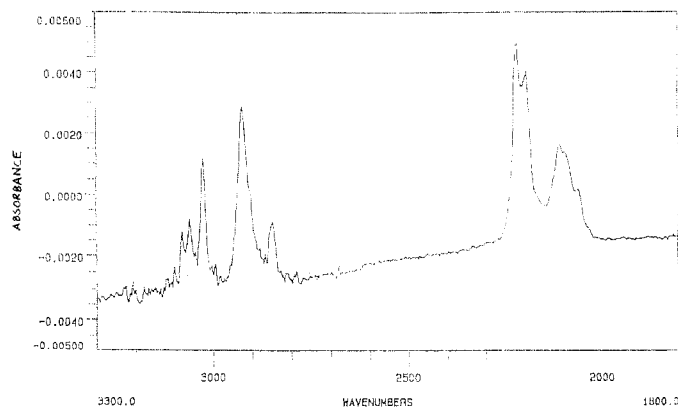


Figure 1. Representative infrared spectrum of polystyrene and deuterated polyisoprene coadsorbed onto silicon oxide from CCl_4 . Absorbance is plotted against wavenumber. Absorbance peaks at 3085, 3059, 3027, 2923, and 2850 cm^{-1} are integrated to determine the mass of PS on the surface. The peaks between 2000 and 2300 cm^{-1} are integrated to determine the PI mass adsorbed.

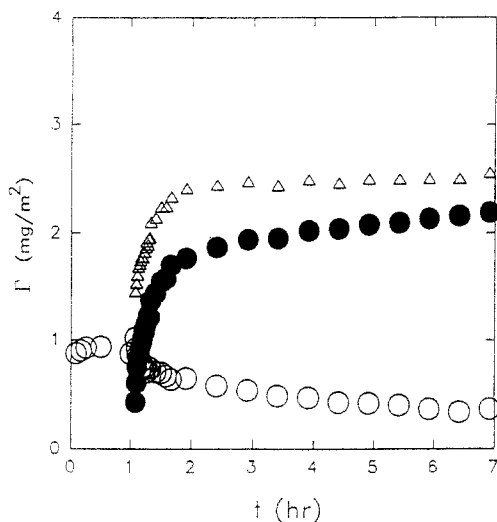


Figure 2. Surface excess of polymer, Γ , in mg/m^2 , plotted versus the elapsed time of the experiment. The open circles follow the adsorption of 355K PS from a 1 mg/mL solution in CCl_4 . When first adsorbed onto a bare silicon surface, the PS adsorption reaches a plateau quickly. After 1 h, the 150K PI (1 mg/mL solution in CCl_4) is exposed to the surface, and the PS is displaced by incoming PI chains. The filled circles indicate PI adsorption. The open triangles show the total surface excess of PS plus PI.

or 30-min intervals for several hours. The adsorption spectra, ratioed to solvent spectra, were base-line-corrected using the autobase-line function in the IBM PCIR software.³³ The peak areas were determined by curve-fitting mixtures of Lorentzian and Gaussian peaks using Spectracalc Software.³⁴ Calibrations for the solution correction and the relation between infrared absorptivity and mass adsorbed are described elsewhere.^{30,31}

Results

Figure 1 shows a representative ATR spectrum during the sequential adsorption of polystyrene and deuteriopolyisoprene. It is ratioed to a spectrum of pure CCl_4 . Absorbance is plotted against wavenumber, and the surface excess was determined¹⁹ from the integrated intensity of peaks centered at 3085, 3059, and 3027 cm^{-1} (polystyrene ring vibrations) and those at 2923 and 2850 cm^{-1} (CH_2 backbone stretches).³⁵ The peaks of PI between 2020 and 2280 cm^{-1} are integrated and calibrated to determine the mass of PI adsorbed on the crystal surface.

A typical experiment proceeded as shown in Figure 2. Protio-PS (in this example, 355K PS in 1 mg/mL solution

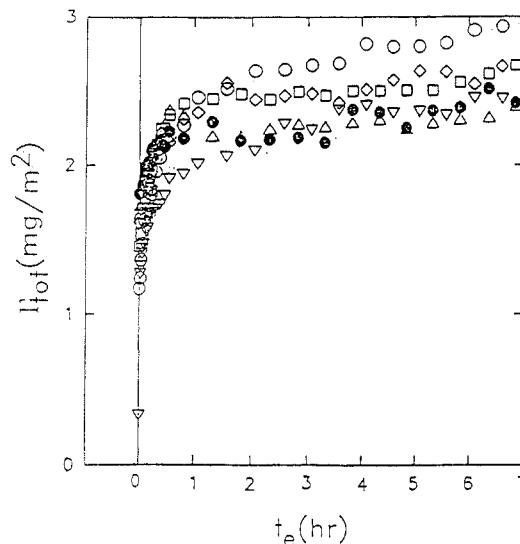


Figure 3. Summed mass of the polymers adsorbed, Γ_{tot} , plotted versus the time after the exchange of PS for PI solution, t_e . The Γ_{tot} reaches a plateau value of approximately 2.5 mg/m^2 regardless of the molecular weight of the PS initially adsorbed (open circles, 43K PS; triangles down, 96K PS; squares, 355K PS; triangles up, 706K PS; diamonds, 1.26M PS; filled circles, 3.84M PS).

in CCl_4) is adsorbed from dilute solution onto the oxidized silicon crystal surface. The surface excess reaches a plateau almost immediately. After 1 h, the PS solution was replaced by one of PI (150K PI in 1 mg/mL solution in CCl_4). The PS chains desorb as the PI chains, possessing the higher surface affinity, diffuse to the surface. Figure 2 also records the evolution of total mass adsorbed.

Self-Adjusting Surface Composition. Figure 2 also illustrates a striking feature of the exchange. Within the hour immediately following the exchange of solutions, the surface population adjusts to within 5% of its plateau value, which remains fairly constant throughout the experiment. However, the exchange of PI for PS continues for hours. Otherwise stated, the adjustment of the composition of the adsorbed layer takes longer than that of the total surface excess. It is interesting that the same total mass adsorbed is maintained during the compositional equilibration.

Figure 3 displays, for all experiments, the evolution of the total mass adsorbed following the exchange. Although the molecular weights of the initially adsorbed PS chains varied from 43.9K to 3.84M, the total mass adsorbed following an exchange with 150K PI solution reached roughly the same plateau value of approximately 2.5 mg/m^2 (scatter $\approx 0.5 \text{ mg}/\text{mL}$) at steady state.

The data summarized in Figure 4 show that, regardless of the molecular weight, the mass of the PS remaining on the surface following an exchange reached about 0.5 mg/m^2 . The longest chains, $M_{\text{PS}} = 3.84\text{M}$, behave differently from the other molecular weight systems. Desorption in the case of this extreme M_{PS} occurred most slowly, apparently for times longer than the duration of the experiment. It appears that the amount of mass remaining might, at longer times, eventually reach the same plateau value exhibited by the smaller chains. The general similarity for the different molecular weight systems is remarkable, especially when one considers the variances in molecular weight between the PS and PI species competing for the surface.

Kinetic Behavior. Even though the total mass on the surface at steady state is consistent between experiments regardless of M_{PS} , the data in Figure 4 shows that the underlying kinetics of PS desorption (and of the con-

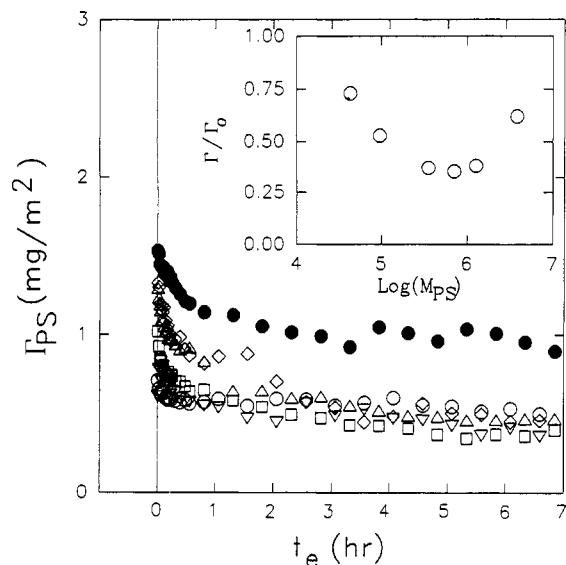


Figure 4. Surface excess of PS, Γ_{PS} , plotted versus the time following the exchange of PS for PI solution, t_e . At $t_e = 7$ h, the surface excess of PS fell to approximately the same level, 0.5 mg/m², regardless of the PS molecular weight, in spite of the fact that the mass adsorbed before the exchange, as well as the rate of subsequent desorption, depended on the PS molecular weight. It is speculated that, at still longer t_e , the sample of largest molecular weight (3.84M) would also reach this same level of surface excess (open circles, 43K PS; triangles down, 96K PS; squares, 355K PS; triangles up, 706K PS; diamonds, 1.26M PS; filled circles, 3.84M PS).

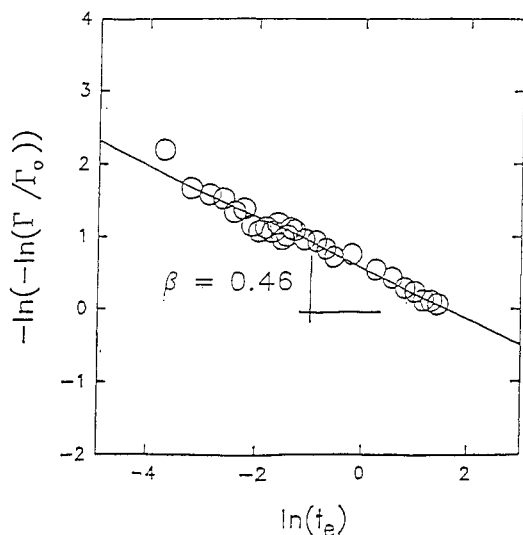


Figure 5. Example of the fit of desorption kinetics to the stretched-exponential function. The vertical axis is an algebraic manipulation of $\Gamma(t)/\Gamma_0$ to linearize the data. The horizontal axis is the logarithmic time after the exchange of solutions (in hours). The line through the data gives the slope, β , and the point where the ordinate is zero is τ_{off}/β . This is the same experiment shown in raw form in Figure 2.

comitant PI adsorption) varied considerably. For quantitative comparison to the Douglas model and the previous PS-PMMA experiment,⁹ the stretched-exponential fit to the data (defined in eq 4) is chosen. Figure 5 illustrates the linearization method as well as the quality of this fit: the natural log of the negative natural log of the surface excess of PS, normalized to its value before the exchange, is plotted versus the natural log of time. Although the vertical axis plots values that are difficult to interpret physically, the slope, β , and the point where the ordinate equals zero, $t \sim \tau_{off}$, are physically meaningful. The slope, β , represents the extent of deviation from exponential

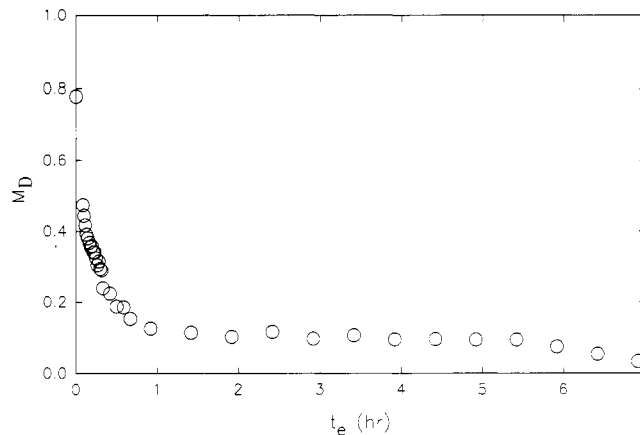


Figure 6. Example of the decay of the fractional deficit, M_D , defined in the text. This is the same experiment shown in raw form in Figure 2.

desorption behavior: the lower β is, the more nonexponential the desorption curve. The time constant, τ_{off} , indicates the time to remove $1/e$ of the original layer adsorbed. The data shown in this graph correspond to the desorption following the exchange of 355K PS by 150K PI shown in raw form in Figure 2.

While the desorption of the original PS layer represents one central theme of this study, the evolution of the PI overlayer merits attention as well. For simplicity, we assumed the total plateau value of mass adsorbed to represent a saturated surface layer. We monitor the approach to this saturation in terms of a fractional deficit, M_D , where $M_D(t)$ is the total mass adsorbed at steady state minus the summed mass of PS and PI adsorbed at any elapsed time, t , normalized to the plateau mass adsorbed. Thus, M_D indicates the fraction of "sites" available to the incoming chains during the approach toward layer saturation. (Note that a weakness of this interpretation is that one imagines the filling of available sites, whereas we quantify this as mass. This distinction should be noted when developing a physical picture of the surface population.)

Figure 6, in which M_D is plotted against elapsed time, shows the time-dependent loss of sites available to the incoming PI chains. The data were consistent with a stretched-exponential form; the resulting values of β are included in Figure 7.

In interpreting these observations, we note that the kinetic model by Douglas, discussed above for desorption, has also been extended to the case of adsorption.⁹ Similar predictions result: $\beta = 1/2$ is expected for adsorption to a homogeneous planar surface and deviation from $\beta = 1/2$ is expected where "heterogeneity" and surface site saturation are accounted for. That the adsorption of incoming PI chains through a layer of desorbing PS and already adsorbed PI shows $\beta < 1/2$ kinetics is therefore not surprising.

To better understand the interplay between adsorption and desorption in this system, the kinetic behavior is compared for experiments displacing adsorbed polystyrene of different molecular weights while keeping the M_{PI} constant. Figure 7 (circles) displays the change in the form of the desorption as the molecular weight of the original chain is varied. Lower molecular weight chains demonstrate increasingly nonexponential behavior, with β values as low as 0.2. As chains increase in size, β approaches 0.5 as a limiting value.

The form of the growth in surface excess for PI adsorption is summarized by the squares in Figure 7. It is apparent that, during the displacement of small PS chains,

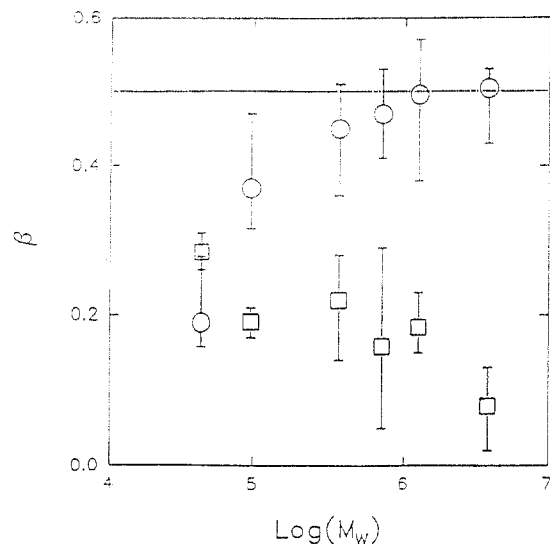


Figure 7. Index of time in the stretched-exponential fit, β , plotted versus the log of the molecular weight of the initially-adsorbed PS layer. Circles indicate desorption kinetics of PS, and squares indicate adsorption kinetics of PI. One observes the increase of β to a limiting value of $\beta \approx 0.5$, a large M_{PS} for desorption kinetics. The complementary β for PI adsorption kinetics decreases with M_{PS} . This reflects the fact that PI adsorption is increasingly slower than exponential.

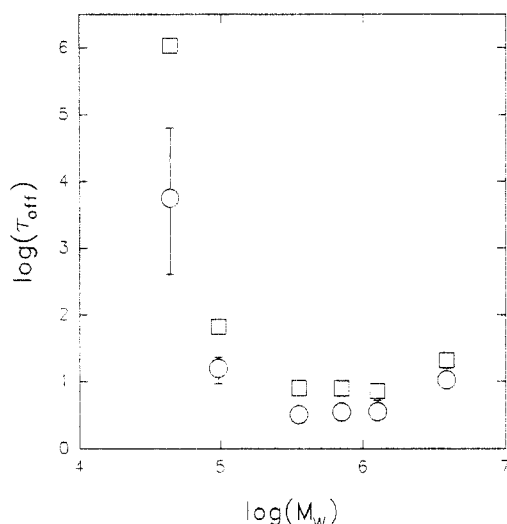


Figure 8. Logarithmic τ_{off} of PS plotted versus the logarithmic M_{PS} (circles). The logarithmic mean time constants of PS (calculated as described by eq 5), $\langle \tau_{off} \rangle$, are plotted versus the logarithmic M_{PS} (squares). The τ_{off} show little dependence on molecular weight, but are somewhat larger for the lowest M_{PS} . This can be rationalized by observing that the less PI adsorbed, the higher the PS molecular weight.

the PI which adsorbs to saturate the surface joins the adsorbed layer rather quickly. When larger PS chains must first be displaced, the PI adsorption (or the decrease in sites available, M_D) is presumably more hindered as PS chains of high molecular weight contribute to surface site saturation. Thus, significantly lower values of β are measured as compared to the adsorption over smaller PS chains. The dependence of PI adsorption on PS molecular weight implies that the PI chains cannot adsorb until space is made available through PS desorption.

Figure 8 (circles) summarizes the time constants of PS desorption, τ_{off} , calculated from the stretched-exponential fits. Low molecular weight chains ($M_w < 100\,000$), which showed very low values of β (0.2–0.3), are seen to have the longest desorption time constants. The desorption time constants of longer PS chains ($M_w > 200\,000$) are lower

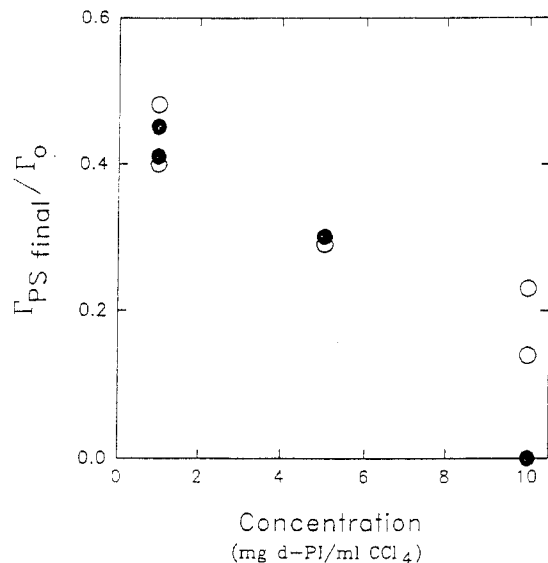


Figure 9. Fraction of the original PS layer at $t_e = 8$ h plotted against the concentration of the PI exchange solution. With increased solution concentration, more and more PS was desorbed, for both $M_{PS} = 96K$ (filled circles) and $M_{PS} = 3.84M$ (open circles). These data indicate that the PS adsorption was reversible.

and did not change significantly with further increases of molecular weight. Figure 8 (squares) also plots the mean desorption times, $\langle \tau_{off} \rangle$, calculated as is customary, by the relation describing the stretched-exponential function,

$$\langle \tau_{off} \rangle = \beta^{-1} \Gamma(\beta^{-1}) \tau_{off} \quad (5)$$

where Γ here is the gamma function.³⁶ These mean values follow the time constants exactly. The data in Figure 8 suggest (weak) a minimum value for the desorption time constant, indicating a tradeoff between the space available to the chains on the surface and in the surface layer and the mechanism involved in desorption. While longer chains presumably move more slowly, shorter chains might seem to take significant time to desorb as a result of the increased volume accessible to them for lateral diffusion (only center of mass motion from the surface is measured experimentally).

Reversibility. The issue of reversibility of adsorption is explored in Figure 9. In principle, one possibility that could explain the nearly identical mass adsorbed after long t_e , regardless of M_{PS} (as illustrated in Figure 2), is that portions of the chains were irreversibly bound to the surface. Figure 9, however, rules out that notion by showing that a higher concentration of PI exchange solution resulted in more PS desorption. In fact, when the concentration of PI in the exchange solution was sufficiently high, all the originally adsorbed PS polymer was removed. This shows that the PS adsorption is reversible and that no chemical interaction has taken place in the original layer. The graph shows that, for both low (96.4K PS) and high (3.84M PS) molecular weight chains, raising the exchange PI solution concentration had a similar effect. It is interesting to note that when high concentrations of PI solutions are used, the rate of exchange increased only slightly, and the reason for this is not yet clear.

Discussion

When describing the dynamics of polymers adsorbing at solid surfaces, or even the steady-state on-off dynamics that underlies an overall equilibrium, one must confront

several challenging issues. Namely, (1) the energetics, or the affinity of each chain segment for the surface, (2) the history, or the sequence of arrival and rearrangement of the chains, and (3) the kinetics, or the mechanism of chain transport to and from the surface.

The Mass Adsorbed. The chief conclusion of this study is that the *total* surface excess adjusts faster than that of the individual components. This contrasts with previous experiments in which PS was exchanged with PMMA,^{9,27,28} the PMMA overlayer adsorbed immediately and remained constant in mass, while the PS continued to desorb, resulting in an overshoot of the total mass adsorbed. In the present PS-PI system, a constant level of the total mass adsorbed is quickly attained, while the exchange of PI for PS proceeds fairly symmetrically in mass for hours. This interrelated on-off exchange, also suggested by a study of PS displaced by PS in CCl₄,²² is suspected to be common. The prediction⁹ that τ_{off} should scale inversely with the diffusion coefficient cannot be expected to hold in these systems where the composition of the overlayer changes with time.

It is also noteworthy that the total mass adsorbed was so constant (2.5 ± 0.5 mg/m²) regardless of M_{PS} and that a similar level of PS ($0.5 \pm .07$ mg/m²) remained persistently adsorbed after long exchange times. These observations are also consistent with previous studies (see below) and are suspected to be common.

In previous work where h-PS was displaced by deuterio-PS in CCl₄,²² it was proposed that persistent retention of some part of the first polymer species adsorbed indicates inhomogeneous adsorption. Work by Varoqui and Pfefferkorn^{12,17,18} similarly indicates two populations of adsorbed polymer chains, one easily removable and the other more tightly bound. Their picture of the adsorbed layer consists of a fraction of chains bound in a flat of conformation, occupying contiguous surface sites, around which the remainder of the chains bind loosely to a low density of remaining unoccupied sites. One might extend this picture to speculate that chains of lower M should adsorb relatively flat, relative to chains of higher M which would form a higher proportion of loops. This line of argument can explain why, in the experiments reported in this paper, the fraction of the PS layer remaining after a long elapsed time decreased with increasing M_{PS} .

We note also that this study and the previous work with PS/CCl₄²² also agree in showing increased displacement after long t_e , the higher the concentration of displacer polymer in the exchange solution. The quantitative relation between the exchange solution concentration and the driving force for displacement remains to be explained.

It is interesting to consider why the total mass adsorbed was so constant throughout the displacement process. A recent approach to such a problem postulates that adsorption-desorption occurs at a quasi-equilibrium steady state.²⁴ A free energy argument predicts that the steady-state surface composition is proportional to the bulk solution composition, modified by the entropy of mixing and the difference in segmental surface affinities of the two chains. This line of argument would leave major points unclear, however. First, much previous work indicates that progress toward equilibrium is slow (on the order of the hours to tens of hours) even for loosely adsorbing systems. Steady-state total mass adsorbed, however, was achieved in less than 4 h in the present experiments. Second, the exact form of the relationship, the free energy equation, is unclear, and therefore no quantitative checks presently exist. Finally, we have shown that the desorption-adsorption behavior is in part kinetically controlled,

that is, diffusion-limited, and therefore that arguments based solely on equilibrium notions are inappropriate. Most likely, some combination of the enthalpic surface affinity, entropic mixing, and kinetic trapping govern the steady-state surface excess and composition, of which a quantitative description remains as yet unclear.

Time Scale of Desorption Kinetics. When considering the kinetics of the desorption, one must acknowledge not only the effects of molecular weight and chain connectivity on the center of mass diffusion of the chains but also the possible hindrance imposed by the adsorption of the incoming displacer chains. Comparisons can be made to diffusion through melts,³⁷⁻⁴⁰ gels,^{41,42} or solutions exposed to entropic barriers,^{43,44} in those systems entanglements or physical obstacles hinder diffusion. Previous work confirmed the limiting features of $\beta \cong 1/2$ and τ_{off} scaling with the inverse diffusion coefficient.^{9,28} The present study has relaxed this idealized case when the displacement overlayer was constant during the desorption and addresses the more general case of gradual overlayer adsorption.

An attempt was made to quantify the time dependence of overlayer adsorption in terms of the decay of the fractional deficit, M_{D} , as shown in Figures 6 and 7. For much of the range of M_{PS} we found $\beta < 1/2$ for the desorption kinetics, a result which implies either heterogeneity (in the framework of the Douglas model⁹) or inapplicability of this kinetic model. In strong support of the basis applicability of this kinetic approach, we find the predicted limiting behavior, $\beta \cong 1/2$, for sufficiently large M_{PS} .

Conclusion

A kinetic theory which predicts intrinsically nonexponential desorption^{9,28} has been examined in a new experimental system. Under appropriate conditions, diffusion may become slower than the rate of detachment of chains from the surface and becomes the rate-limiting factor in polymer desorption. In this study, we report the results of sequential adsorption experiments in which PS is allowed to adsorb first ($\chi_s \cong 1$ for PS) and then is displaced by PI ($\chi_s \cong 2.9$ for h-PI). Working at a temperature of sluggish polymer mobility (12 °C), we corroborate the prediction of $\beta = 1/2$ for this diffusion-limited regime and show that when $\beta < 1/2$, nonhomogeneous hindrances to diffusion must be considered. However, as the desorption took place through an overlayer of PI which varied according to the molecular weight of the PS, no simple relation between τ_{off} and the molecular weight of PS was observed.

The total mass adsorbed reached steady state considerably more rapidly, during the displacement process, than the mass adsorbed of either PS or PI. In other words, the adsorbed mass of PI and PS changed in concert, such that the total mass adsorbed remained roughly constant regardless of the level of the adsorbed components. To understand the mechanism of this mutually dependent exchange will be a goal of future experiments.

Acknowledgment. At the University of Illinois, we appreciate financial support from the Exxon Corp., an NSF Fellowship (H.M.S.), and the taxpayers of the United State through Grant NSF-DMR-91-01509 (Polymers Program).

References and Notes

- (1) Cohen-Stuart, M. A.; Cosgrove, T.; Vincent, B. *Adv. Colloid Interface Sci.* **1986**, *24*, 143.
- (2) de Gennes, P.-G. *Adv. Colloid Interface Sci.* **1987**, *27*, 189.

- (3) Takahashi, A.; Kawaguchi, M. *Adv. Polym. Sci.* **1982**, *46*, 1.
- (4) Howard, G. J. In *Interfacial Phenomena in Apolar Media*; Eicke, H., Parfitt, G. D., Eds.; Marcel Dekker: New York, 1987; p 281.
- (5) Kislenco, V. N.; Berlin, A. D.; Moldovanov, M. A. *J. Colloid Interface Sci.* **1993**, *156*, 508.
- (6) Poland, D. *Macromolecules* **1991**, *24*, 3361.
- (7) de Gennes, P.-G. *C.R. Acad. Sci. (Fr.)* **1985**, *301*, 1399; **1986**, *302*, 765.
- (8) Dijt, J. C.; Cohen-Stuart, M. A.; Fleer, G. J. *Macromolecules* **1992**, *25*, 5416.
- (9) Douglas, J. F.; Johnson, H. E.; Granick, S. *Science* **1993**, *262*, 2010.
- (10) Granick, S. In *Physics of Polymer Surfaces and Interfaces*; Sanchez, I., Ed.; Manning Publications: Stoneham, MA, 1992.
- (11) Kawaguchi, M. *Adv. Colloid Interface Sci.* **1990**, *32*, 1.
- (12) Pefferkorn, E.; Carroy, A.; Varoqui, R. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1997.
- (13) Cosgrove, T.; Prestidge, C.; King, S.; Vincent, B. *Langmuir* **1992**, *8*, 2206.
- (14) Kawaguchi, M.; Anada, S.; Nishikawa, K.; Nobuhiro, K. *Macromolecules* **1992**, *25*, 1588.
- (15) Furusawa, K.; Yamamoto, K. *J. Colloid Interface Sci.* **1983**, *96*, 268.
- (16) Grant, W. H.; Smith, L. E.; Stromberg, R. R. *Faraday Discuss. Chem. Soc.* **1975**, *59*, 209.
- (17) Pefferkorn, E.; Haouam, A.; Varoqui, R. *Macromolecules* **1988**, *21*, 2111.
- (18) Pefferkorn, E.; Haouam, A.; Varoqui, R. *Macromolecules* **1989**, *22*, 2677.
- (19) Frantz, P.; Granick, S. *Phys. Rev. Lett.* **1991**, *66*, 899.
- (20) Johnson, H. E.; Granick, S. *Macromolecules* **1990**, *23*, 3367.
- (21) Frantz, P.; Granick, S. *Macromolecules*, in press.
- (22) Schneider, H.; Granick, S. *Macromolecules* **1992**, *25*, 5054.
- (23) Billowits, G. F.; Durning, C. J. *Macromolecules* **1993**, *26*, 6927.
- (24) Cohen-Stuart, M. A.; Fleer, G. J.; Scheujtens, J. M. H. M. *J. Colloid Interface Sci.* **1984**, *97*, 515.
- (25) Van der Beek, G. P.; Cohen-Stuart, M. A.; Fleer, G. J. *Macromolecules* **1991**, *24*, 3553.
- (26) Cohen-Stuart, M. A.; Tamai, H. *Macromolecules* **1988**, *21*, 1863.
- (27) Johnson, H. E.; Granick, S. *Science* **1992**, *255*, 966.
- (28) Johnson, H. E.; Douglas, J. F.; Granick, S. *Phys. Rev. Lett.* **1993**, *70*, 3267.
- (29) Johnson, H. E. Ph.D. Thesis, University of Illinois, Urbana, IL, 1993.
- (30) Leonhardt, D.; Johnson, H. E.; Granick, S. *Macromolecules* **1990**, *23*, 685.
- (31) Frantz, P.; Leonhardt, D.; Granick, S. *Macromolecules* **1991**, *24*, 1868.
- (32) Smith, S. D.; Noda, I.; Marcott, A.; Dowrey, E. In *Polymer Solutions, Blends, and Interfaces*; Noda, I.; Rubingh, D. N., Eds.; Elsevier: Amsterdam, The Netherlands, 1992, p 43.
- (33) PC/IR Software, Nicolet Analytical Instruments, 5225-1 Verona Rd., P.O. Box 4508, Madison, WI 53711.
- (34) Spectracalc Software, Galactic Industries Corp., 395 Main St., Salem, NH 03079.
- (35) Painter, H.; Coleman, H. *Appl. Spectrosc.* **1984**, *38*, 184.
- (36) Degiorgio, V.; Bellini, T.; Piazza, R.; Mantegazza, F.; Goldstein, R. *Phys. Rev. Lett.* **1990**, *64*, 1043.
- (37) Douglas, J. F.; Hubbard, J. B. *Macromolecules* **1991**, *24*, 3163.
- (38) Kremer, K.; Grest, G. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1707.
- (39) Herman, M. *Macromolecules* **1992**, *25*, 4925.
- (40) Herman, M.; Tong, P. *Macromolecules* **1992**, *25*, 6638.
- (41) Pajevic, S.; Bansil, R.; Konak, C. *Macromolecules* **1993**, *26*, 305.
- (42) Rotstein, N. A.; Lodge, T. P. *Macromolecules* **1992**, *25*, 1316.
- (43) Muthukumar, M.; Baumgartner, A. *Macromolecules* **1989**, *22*, 1937.
- (44) Lodge, T. P.; Wheeler, L. M. *Macromolecules* **1989**, *22*, 3399.