A Simple Kinetic Model of Polymer Adsorption and Desorption

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A model of the desorption and adsorption of a polymer layer at a planar surface indicates a transition from exponential kinetics at high temperatures to nonexponential kinetics (stretched exponential with index one-half) at lower temperatures where these processes are diffusion-limited. Measurements of polystyrene desorption through polyisoprene overlayers show this predicted transition. Corroborative results are obtained for polystyrene desorption through polymethylmethacrylate overlayers. This identification of two distinct kinetic regimes suggests a unifying perspective from which to analyze polymer and biopolymer mobility at surfaces.

The kinetics of polymer adsorption and desorption is fundamental in many polymer and biomedical applications. Although equilibrium surface structure and composition have been much discussed (*1*), it is also important to understand the rate of passage from one equilibrium state to a new one. Classically, these processes are expected to be exponential in the elapsed time (*2–9*), as is found experimentally for small molecules at the solid-gas interface (*10*), but recent experiments and simulations have cast doubt on the generality of this behavior (*11–14*). Nonexponential rate processes at solid-liquid and liquid-liquid interfaces are also observed experimentally in many other contexts, among them sensory physiology, such as photoreception (*15*); charge transport at electrodes (*16*); and membrane polarization (*17*). There is no accepted interpretation of the striking nonexponential regularities that are observed.

Here, a simple theoretical model is presented that potentially provides a unified perspective. We show, and support with experiments, that desorption is nonexponential in time when it is rate-limited by diffusion away from the surface rather than by energetics of surface detachment. This regime stands in contrast to the situation when desorption is rate-limited by the energetics of surface detachment, in which case desorption is exponential and extensions of classical Langmuir kinetics are appropriate.

The model considers two limiting kinetic regimes. First, at high temperatures we expect a rate process to be determined by equilibrium parameters, leading to an activated rate process in which a system decays exponentially from an initial state. This situation is analogous to isotopic radioactive decay. For the particular case of polymer desorption, the free-energy change upon desorption (ΔF) should be extensive in the polymer molecular weight (M) (*18–20*), so that the desorption time constant, τ_{off}, should increase in proportion to chain length

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

Here, the parameter α is expected to scale with the polymer-surface interaction (*20*), k_B is the Boltzmann constant, and T is absolute temperature. The rate of desorption is taken to be proportional to the surface concentration, $\Gamma(t)$, which leads to exponential decay of $\Gamma(t)$. These considerations as to time and molecular weight dependence agree with prior polymer desorption experiments (*21*).

The second kinetic regime arises at lower temperatures, where the molecular mobility becomes sluggish for reasons that have been widely discussed (*11, 14, 22*). We then suppose that the equilibrium ΔF no longer controls the kinetics and that desorption is governed by diffusive flux from the surface. The steady-state flux $R(t)$ per unit concentration from a planar surface equals (*23*)

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

where D is the center-of-mass diffusion coefficient of the molecule. In a more general treatment, $R(t)$ also reflects irregularity of the surface and the type of diffusion process, Fickian or not (*20*). The short-time variation of $R(t)$, when Eq. 2 requires modification, has also been considered (*23*). In any case, we model desorption rate as proportional to the product of $R(t)$ and the surface concentration $\Gamma(t)$. This superficially resembles the process that led to Eq. 1, but unlike that case, the desorption rate is time-dependent because of the intermittency of surface detachment

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

Interpretation of this type of pseudo first-order kinetic process for diffusion-limited reactions has been discussed (*24*). In the absence of surface depletion, the desorption rate is simply $R(t)$. With depletion of the surface concentration, integration of Eq. 3 with $R(t)$ given by Eq. 2 gives

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

where the exponent β equals ½ in this model. Here, Γ_0 is the steady-state mass per area adsorbed at $t = 0$.

The adsorption of the incoming layer can be described by a similar kinetic model, leading to the symmetric prediction

$$\Gamma(t)/\Gamma_\infty \sim 1 - \exp[-(t/\tau_{\text{on}})^{\beta}] \quad (5)$$

Expansion of Eq. 5 for small t leads to a $t^{1/2}$ increase of the surface concentration for simple diffusion-limited adsorption onto a plane surface, where $\beta = 1/2$. At later times, this standard result (*2*) for the steady-state diffusion-limited increase of the surface concentration is altered by the adsorption of polymer chains, which limits further adsorption. Equation 5 accounts for this saturation phenomenon, and $\Gamma(t)$ approaches a limiting steady-state level, Γ_∞, for very long times.

Although the idea that kinetics may change from an energy-controlled process at high temperatures to a diffusion-controlled process at lower temperatures may seem obvious (the analogous transition from liquid to glass is well known), no previous models are known that stress the implications of such a transition for surface desorption-adsorption. From this point of view, the adoption of the diffusion-limited rate in Eq. 2 follows reasonably (*25*), leading to stretched exponential relaxation where the exponent β has a specific geometrical interpretation. Another feature of the model, as opposed to a variety of other arguments that also lead to stretched exponential kinetics, is the predicted variation

$$\tau_{\text{off}} \sim D^{-1} \quad (6)$$

which compares favorably with the data below.

To investigate these predictions experimentally, we studied the displacement of a weakly adsorbed polymer [deuterio polystyrene (d-PS)] by a more strongly adsorbing polymer [cis-polyisoprene (PI)] at an oxidized silicon surface. From previous studies, we know that the displacement of PS is rate-limited by PS surface desorption (*11, 21*), so this experiment allows us to focus on the desorption process (see Fig. 1 for solution conditions and Table 1 for the linear polymers that were studied). We found that PI displaced PS from the limited surface area, as would be predicted from net segment-surface interaction energies (Table 1). Adsorption was measured by infrared spectroscopy in attenuated total reflection as described elsewhere (*11, 21*).

First, the PS solution was exposed to a bare surface of silicon oxide. The mass per

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Table 1. Characteristics of the flexible linear polymers. The ratio M_w/M_n of the weight-averaged to the number-averaged molecular weight is a measure of the dispersion of chain lengths in a sample. A ratio of 1 implies that all chain lengths are equal.

Sample	M_w	M_w/M_n	χ_s* (kT)
d-PS	550,000	1.05	0.8
h-PS	19,600	1.01	0.8
	43,900	1.01	
	96,400	1.01	
	220,000	1.03	
	355,000	1.02	
	465,000	1.04	
	575,000	1.06	
	706,000	1.05	
PI	205,000	1.04	2.9
PMMA	146,000	1.04	4.1

*Net segmental enthalpy change upon replacement of a surface-bound polymer segment by solvent; evaluated by the method of Cohen Stuart and co-workers (*9*).

area adsorbed (Γ) reached steady state rapidly and was independent of the experimental temperature (Fig. 1). After 1 hour, the PS solution surrounding the adsorbed layer was replaced by PI solution. The PI adsorbed rapidly as described elsewhere (*11*), and PS commenced to desorb. The average desorption time, $<\tau_{off}> \equiv \int [\Gamma(t)/\Gamma_o]dt$, was calculated.

The parameters β and $<\tau_{off}>$ were obtained by fit to the stretched exponential function at various temperatures between 0° and 50°C (Fig. 2). Note that the rate of desorption followed single-exponential kinetics above 40°C but strongly nonexponential kinetics ($\beta \approx 1/2$) below 20°C. The rapid rise of τ_{off} over a narrow range of decreasing temperature, which suggests a "glassy" response, has been much discussed but is not understood quantitatively (*11, 14, 22*). The observation $\beta \approx 1/2$ in this diffusion-controlled regime agrees with the expectation based on Eq. 4.

We remark that in the system studied, *D* refers to PS diffusion through the PI overlayer that provides a kinetic barrier to its detachment. More generally, *D* refers to bulk diffusion outside a surface-bound layer. This implies (see Eq. 6) that the functional dependence of τ_{off} at a fixed temperature is the same as that of D^{-1}. This prediction is particularly interesting in the polymer desorption context because so much is known about *D* in polymer solutions. For example, experiments indicate that *D* of polymers in solution varies as M^{-2} to M^{-3} (entangled linear chains) and as e^{-M} (star-branched entangled chains); the appropriate molecular interpretation continues to be discussed (*26*). Therefore, Eq. 6 contains specific predictions concerning the dependence of τ_{off} on the chain length and architecture of the desorbing species. In a system where the overlayer density was held constant and the desorbing species was varied, control experiments confirmed this prediction about molecular weight dependence and linear star distinction in the control of τ_{off} (*12*).

What happens in the case of surface heterogeneity? It is interesting that Eq. 4 can be interpreted to state that the desorption rate is related to the survival probability of a random walk initiating from the surface; that is, to the fraction of random walk paths that do not touch the surface after time *t*. From this point of view, one appreciates that if the surface is rough or "fractal" or if its coverage is inhomogeneous, the escape probability is altered so that $\beta \neq 1/2$ (*20*).

To investigate this idea experimentally, we studied the displacement of a homologous series of weakly adsorbed polymers [protio polystyrene (h-PS)] by a different, more strongly adsorbing polymer [deuterio poly(methyl methacrylate) (PMMA), M = 146,000]. The molecular weight of h-PS was varied over a wide range (Table 1). The desorption kinetics (Fig. 3) empirically fit the stretched exponential function (Eq. 4) satisfactorily (Fig. 3, inset). The parameters β were obtained by fit to the stretched exponential function at the fixed temperature of 25°C (Fig. 4) (*27*). One expects small PS chains to be most sensitive to irregularity in the deposition of more strongly adsorbing PMMA. The observed monotonic rise from $\beta \approx 1/4$ (short PS) to a limiting value $\beta \approx 1/2$ (large PS) confirms the theoretical expectation in a second experimental system.

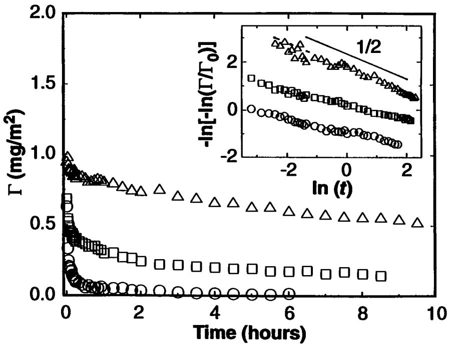

Fig. 3. Illustrative experiments in a second system at the fixed temperature of 25°C. Mass adsorbed per area (Γ) is plotted against time. First, a PS solution (1 mg ml^{-1} in CCl_4) was exposed to the oxidized silicon surface. After 1 hour, the PS solution was replaced by a PMMA solution (PMMA not shown in graph; M_w = 146,000; 1 mg ml^{-1}). The molecular weight of PS was 43,900 (circles), 220,000 (squares), or 706,000 (triangles). **(Inset)** The satisfactory fit of these data to a linearized form of Eq. 4.

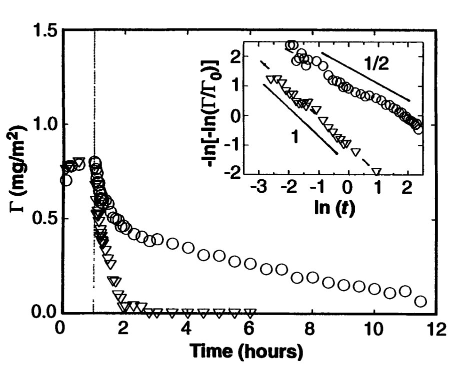

Fig. 1. Illustrative experiments. Mass adsorbed per area (Γ) is plotted against time. First, a PS solution (M_w = 550,000; 1 mg ml^{-1} in CCl_4) was exposed to the oxidized silicon surface. After 1 hour, the PS solution was replaced by a PI solution (PI not shown in graph; M_w = 205,000; 1 mg ml^{-1}). The temperature was 0° (circles) or 45°C (triangles). **(Inset)** The satisfactory fit of these data to a linearized form of Eq. 4.

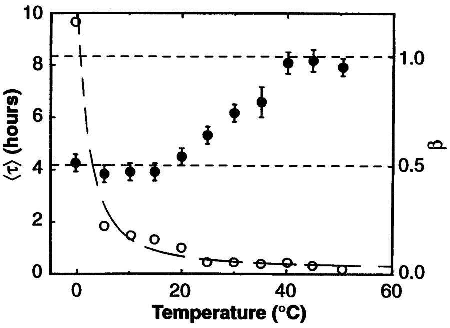

Fig. 2. Influence of temperature on desorption kinetics. A PS solution (M_w = 550,000; 1 mg ml^{-1} in CCl_4) was exposed to the oxidized silicon surface. After 1 hour, the PS solution was replaced by a PI solution (M_w = 205,000; 1 mg ml^{-1}), and the ensuing desorption kinetics of PS was analyzed. Open circles: $<\tau_{off}>$, the average desorption time. Filled circles: β. Note that β = 1 describes exponential desorption.

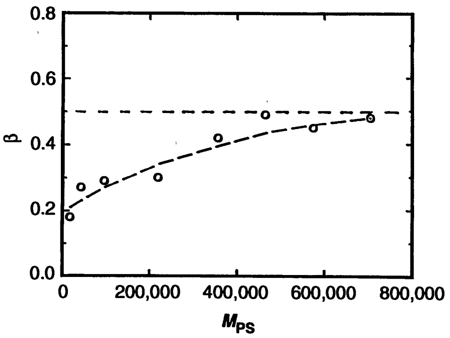

Fig. 4. Influence of molecular weight of the desorbing species on the desorption kinetics at the fixed temperature of 25°C. First, a PS solution (indicated molecular weight; 1 mg ml^{-1} in CCl_4) was exposed to the oxidized silicon surface. After 1 hour, the PS solution was replaced by a PMMA solution (*M* = 146,000; 1 mg ml^{-1}), and the ensuing desorption kinetics of PS was analyzed. The limiting value β ≈ ½ is predicted by Eq. 4.

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 equilibrium energy of adsorption and therefore the desorption-adsorption kinetics should be exponential. The origin of the nonexponential kinetics in our 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. Kinetic processes that fall into this category are expected to be widespread, in fields from tribology to biology.

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Molecular Light Emission Induced by Inelastic Electron Tunneling

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Light emission from molecular layers has been induced by inelastically tunneling electrons in a tunneling junction. The fast quenching of molecular emission on metal surfaces was suppressed by use of the "transparent conductor" indium-tin-oxide for the junction electrodes. The emission measurements have been made in squeezable tunneling junctions as small as 10^{-9} square centimeters, coated with 9-10 dichloro-anthracene layers. At a bias of 2.5 to 3.5 volts, yields of 5000 photons per microcoulomb were observed. Evidence for the molecular origin of the emission is given. This method shows good prospects for use in the imaging of chromophores on surfaces with atomic resolution.

The appearance of the scanning tunneling microscope (STM) inspired the birth of a wide class of scanning probe microscopes (SPMs). In addition to their excellent spatial resolution, SPMs are useful for probing the nature of species on the surface. Impurities or perturbed states on a surface are routinely measured with an STM by scanning with a variable bias (*1*). Spectroscopy of local densities of states can be probed with current voltage curves of the tunneling current (*2*). Images of adsorbed molecules and molecular layers have been viewed on surfaces (*3*). Vibrational spectroscopy of a single molecule adsorbed on a surface has been recorded (*4*) with current voltage spectroscopy. However, spectroscopic mapping of specific molecules on surfaces has not been reported so far.

Optical spectroscopy is a possible probe of adsorbed molecules. However, the spatial resolution of conventional optical spectroscopy is limited by the wavelength of the excitation source. Substantial effort has been directed toward overcoming the intrinsic resolution limits of the light microscope. The most promising solution is probably the near field microscope (*5*), which scans an object close to its surface with a small aperture while monitoring light transmission or fluorescence. In spite of recent progress (*6*), this microscopy is yet in its infancy and is limited to ~100 Å in spatial resolution.

To overcome such limitations, one could excite molecules on surfaces by inelastic tunneling processes in the STM and record their light emission. Such a method would combine the high spatial resolution of the STM for excitation with the specificity of the fluorescence spectroscopy in order to scan and identify with atomic resolution chromophores on surfaces.

Light emission from STM junctions has been previously observed. Gimzewski, Berndt, and co-workers have explored inverse photoemission (*7*), electron hole recombination in semiconductors (*8*), and plasmon emission from solid-state surfaces (*9*). Recently, the same group observed enhanced photon emission from small metallic particles on surfaces (*10*). However, no reports of light emission from molecules adsorbed on surfaces in STM junctions are known.

Two processes are fundamental to molecular light emission in STM junctions: molecular excitation by inelastic tunneling, and the quantum efficiency of light emission. Theoretical estimates of the cross section for the excitation process (*11*) (about 10^{-17} cm^2 for electronic excitations) predict millions of excitations per second for typical tunneling currents (nanoamperes) in the STM. However, the quantum efficiency for light emission of molecules adsorbed on conductive surfaces is very low (*12*) (of the order of 10^{-6}), precluding a measurable emission rate from the excited molecules.

The very low emission efficiency from molecules adjacent to metallic and semiconductor surfaces is caused by the fast deexcitation processes (*13*) governed by energy transfer to nonradiative surface excitations (Auger processes). We replaced

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