Reports

New Mechanism of Nonequilibrium Polymer Adsorption

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Nonequilibrium states of surface composition can be extremely long-lived when polymer chains adsorb competitively. In a model system (polymethylmethacrylate adsorbed from CCl_4 onto oxidized silicon previously saturated with polystyrene), it is shown that a weakly adsorbing polymer was sterically pinned to a surface by a more strongly adsorbing polymer. The dynamical evolution of the surface composition was strongly nonexponential in time and non-Arrhenius in temperature; the phenomenology is analogous to bulk glasses. This interpretation offers a new mechanism to explain why weakly adsorbing chains may bind to surfaces, as well as a direction in which to look for a method to release them.

The reliable prediction of which species in a macromolecular mixture will segregate to a surface is not yet possible (*1–5*). This impedes progress on a vast number of technological and biomedical problems (for example, lubricants, paints, foods, water purification, capillary zone electrophoresis, and biomedical materials). Although researchers in these fields have been well aware of possible nonequilibrium effects for a long time, the emphasis has been to understand equilibrium, and the classical models of polymer adsorption address the composition and structure of an adsorbed macromolecular layer based only upon relative free energies of interactions (*1–5*). Recent measurements, showing spectacularly sluggish rates of exchange between the adsorbed state and free solution (*6–9*), have emphasized the prominence of time-dependent effects.

In this report we address explicitly nonequilibrium surface states by using simple chain molecules in a model system. The experiments show that a weakly adsorbing polymer [polystyrene (PS)], is sterically pinned to an adsorbing surface by a more strongly adsorbing polymer [polymethylmethacrylate (PMMA)].

The surface coverage of PS and PMMA, adsorbed to oxidized silicon from carbon tetrachloride (CCl_4), was monitored in situ with Fourier-transform infrared spectroscopy in the mode of attenuated total reflection. Characteristics of these flexible linear polymer chains are given in Table 1. The experimental protocol and calibrations are described elsewhere (*8, 9*). The net segment-surface interaction energies, evaluated by us using the method of Cohen-Stuart *et al.* (*10*), are ~1.3 kT (PS) and ~4 kT (PMMA) at 25°C (k is the Boltzmann constant and T is the absolute temperature). Control experiments verified that in the event of competitive adsorption from a 50:50 mixture in solution, PMMA adsorbed to the exclusion of PS. This result was expected because a small preferential adsorption per segment adds up to an enormous preferential adsorption per chain, so that the weakly adsorbing species is excluded from the limited surface area at equilibrium (*1–5*).

The sequence of events when the weakly adsorbing (PS) chains adsorbed first in an experiment conducted at 40.0°C is shown in Fig. 1A. First, a dilute PS solution (weight-averaged molecular weight M_w = 706,000) was exposed to the bare oxide surface. The adsorbed mass per area (Γ) reached steady state rapidly (<10 min). The resulting loop-train-tail configuration, in which polymer chains are attached to the surface by only a fraction of the potential adsorption sites, has been studied extensively (*1–5*). After 1 hour, the PS solution surrounding the adsorbed layer was replaced by a dilute (0.009 mg ml^{-1}) PMMA solution (M_w = 146,000). Control experiments showed that the ensuing PS desorption kinetics did not change with longer residence time before replacement of the solutions. After replacing the solutions, Γ of PMMA reached steady state within 15 min with minimal desorption of PS, which corresponds to a large overshoot of the total mass adsorbed and supports the picture of a transient state in which detaching chains wormed their way slowly out of the surface layer. In addition, the mass per area of PMMA segments hydrogen bonded to the surface (Γ_{bound}) was inferred from vibrational shifts of the carbonyl peak (*8, 11*). Within 15 min this value also reached a high level, at ~40% of a full monolayer coverage (0.4 mg m^{-2}) with only a modest subsequent increase. Thus the desorption of PS took place by tortuous diffusion through a densely stapled blanket of more strongly adsorbing PMMA.

Experiments at higher PMMA solution concentration (1.0 mg ml^{-1}) also followed this pattern. The results of sequential adsorption experiments conducted at 40.0° and 25.0°C are shown in Fig. 1B. The Γ of PS and PMMA are plotted against elapsed time. Again Γ_{bound} of PMMA equilibrated within the same short time as in Fig. 1A and at the same level (~0.4 mg m^{-2}, corresponding to a lower bound fraction of segments in an average chain). Temperature did not affect the levels of PMMA adsorbed onto PS, nor did it affect the levels of PS adsorbed onto the initially bare surfaces. However, the PS must now desorb through

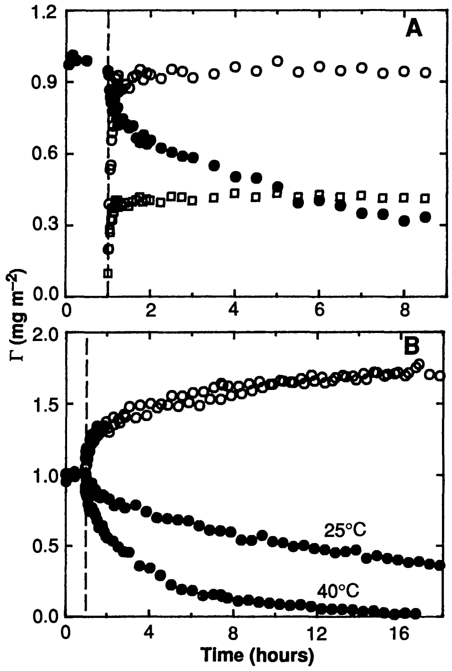

Fig. 1. Mass adsorbed per unit area (Γ) is plotted against elapsed time. First a PS solution (M_w = 706,000, 1.0 mg ml^{-1} in CCl_4) was exposed to the oxidized silicon surface. After 1 hour this was replaced by PMMA solution (M_w = 146,000 in CCl_4) of (**A**) lower concentration (0.009 mg ml^{-1}) or (**B**) higher concentration (1.0 mg ml^{-1}) and the ensuing kinetics of PS desorption and PMMA adsorption were measured. The temperature in (A) was 40.0°C and in (B) was 25° or 40°C. Control experiments showed that adsorption-desorption kinetics did not change with longer residence time before replacing the solutions: (●), Γ(PS); (○), Γ(PMMA); and (□), mass adsorbed per unit area of PMMA segments hydrogen bonded to the surface.

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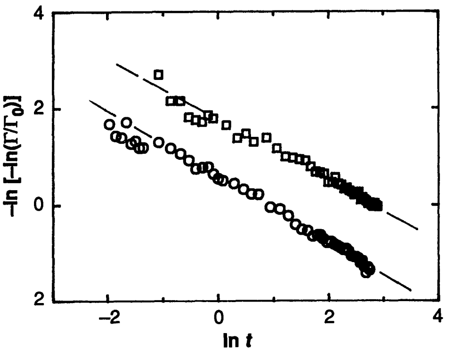

Fig. 2. Illustration of the quality of fits to stretched exponential desorption kinetics. The desorption data from Fig. 1B are plotted according to a linearized form of Eq. 1. The slope of these graphs equals $-\beta$. At the point where the ordinate equals zero, $t = \tau_{\mathrm{off}}$. (○) Experiment at 40.0°C. (□) Experiment at 25.0°C.

as much as 50 to 60% more PMMA mass adsorbed than in Fig. 1A. Desorption was dramatically slower at 25.0° than at 40.0°C.

The desorption rate of PS was slower than the single exponential that is predicted by the existing models (*1, 12*) of polymer surface dynamics, but, except at the lowest temperatures, it was faster than a power law in time. Empirically, the data were well fitted by the so-called stretched exponential function:

$$\Gamma(t)/\Gamma_0 = \exp\,[-t/\tau_{\mathrm{off}}]^{\beta} \qquad (1)$$

with $\beta \approx 1/2$. Here Γ_0 is the steady-state surface excess of PS before challenge by PMMA. The satisfactory quality of the fit is illustrated in Fig. 2, where the data are plotted according to Eq. 1 in linearized form. The effective time constant (τ_{off}) can be interpreted physically as the time to decay to $1/e$ of Γ_0. Relaxation that is so nonexponential stands in contrast to what happens when PS is displaced by a weakly adsorbing polymer, deuterio PS (*9*), in which case $\beta \approx 1$ for much of the desorption (see below). The physical significance of the finding that $\beta \approx 1/2$ is considered below.

Various control experiments were performed. Cis-polyisoprene (PI) was used in place of PMMA as the strongly adsorbing species, and polydimethylsiloxane (PDMS) was used in place of PS as the weakly adsorbing species. In both cases the desorption of the weakly bound species also followed stretched exponential kinetics ($\beta \approx 1/2$), suggesting the generality of the above behavior for systems where strongly adsorbing polymers adsorb onto weakly adsorbing polymers.

The parameters τ_{off} and β obtained by fit to Eq. 1 for temperatures between 25° and 50°C are shown in Fig. 3 for additional experiments of the type shown in Fig. 1B. Although a modest increase of β with T is apparent, the desorption was always strongly nonexponential.

Table 1. Characterization of the polymers studied. These are flexible linear chains. 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 of the chain lengths are equal. The molar mass of the repeat unit is 104 g mol^{-1} (PS) and 93 g mol^{-1} (d-PMMA).

Sample	M_w	M_w/M_n
h-PS*	706,000	1.05
d-PMMA†	146,000	1.04

*Protio sample (Toyo Soda, Tokyo, Japan). †Deuterio sample (Polymer Laboratories, Amherst, Massachusetts).

The desorption times τ_{off} tended to diverge near 25°C. Clearly τ_{off} did not increase in classical Arrhenius fashion; the apparent activation energy increased with decreasing temperature and was physically unrealistic, ~35 kT. However, the well-known Vogel-Fulcher equation for glasses (*13*) provides a reasonable description:

$$\tau_{\mathrm{off}} = \tau_{\mathrm{off}}\exp[E_0/(T - T_0)] \qquad (2)$$

with the realistic parameters $E_0 = 11.2$ and transition temperature $T_0 = 23.8$°C. At temperatures below T_0, desorption was effectively quenched. Computer simulations by Chakraborty and co-workers of the diffusion of single chains on a surface also show dynamical behavior suggesting glass-like motion (*13, 14*).

The possibility that the divergence of relaxation times stemmed simply from some intrinsic property of either PS or PMMA seemed unlikely on the basis of the experiments in which a lower solution concentration of PMMA (0.009 instead of 1.0 mg ml^{-1}) was used. If the polymer chains themselves were responsible, one would not expect different behavior depending on the amount adsorbed. Yet in the case of the lower Γ of PMMA associated with lower solution concentration of PMMA, as in Fig. 1A, the rates of PS desorption were found to depend minimally on temperature. They did, however, remain systematically nonexponential ($\tau_{\mathrm{off}} = 4 \pm 2$ hours independent of temperature over the range of temperatures indicated in Fig. 3, with $\beta = 0.5$ to 0.6). It seems reasonable that there may be a divergence of τ_{off} at lower temperatures than we could measure. Further experiments over a wider temperature range are needed to test the expectation that the temperature at the divergence of τ_{off} of the kind shown in Fig. 3 would depend on the density of pinning, the strength of segment-surface interactions, and the polymer architecture (*13*). For the present, we conclude only that the transition with temperature shown in Fig. 3 was surface induced, not an inherent property of the polymer systems we studied.

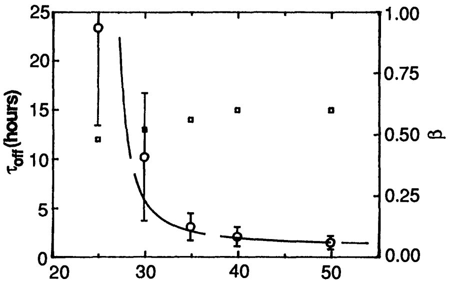

Fig. 3. Influence of temperature on desorption kinetics (1.0 mg ml^{-1} PMMA in CCl$_4$). Larger error bars at the lower temperatures reflect the uncertainty of extrapolating data to times longer than the experimental time scale: (○), τ_{off}; and (□) β. Dashed line is a fit to Eq. 2 as described in text.

Relaxation that follows Eqs. 1 and 2 is also encountered in many other complex random systems, especially bulk glasses (*15*). The difficult question of the molecular origin is debated, but the general physical significance is surely that diffusion is controlled by a distribution of nonequilibrium trapped states.

The physical interpretation that we suggest is the following. The segments of the strongly adsorbed PMMA chains trapped segments of the weakly adsorbed PS chains in virtual cages, bounded on one side by the impenetrable substrate and on the other side by the strongly adsorbed PMMA. The diffusion of PS chains over long distances, from the adsorbed state into free solution, involved tortuous motion through a distribution of steric constraints.

At the same time, the strongly adsorbed PMMA molecules that constituted the cage of a particular adsorbed PS segment were themselves caged by their own adsorption. As a result, the desorption of PS was also influenced by highly cooperative slow motions of the PMMA. One expects that the rearrangements of PMMA slowed down as the bound fraction increased. This result is consistent with the observation that the weakly bound chains desorbed, at 40°C, more slowly through the PMMA layer with the lower Γ but with the higher fraction of bound segments per PMMA chain.

The statistics of random adsorption imply a distribution of such caged states among the various PS chains, and this also must contribute to the nonexponential character of the relaxation. Whether the empirical result, $\beta = 1/2$, has fundamental significance is not known. This result is, however, the predicted time dependence of diffusive flux through a distribution of tortuous pores constructed by continuous random walks (*16*), to which this experimental system may be analogous. As the heterogeneity of constraints is lessened, we expect that β would increase in the direction of unity, which is qualitatively consistent with the dependence on temperature observed in these experiments. This would lead ultimately to exponential relaxation, $\beta = 1$ (*9*).

Long-lived nonequilibrium states thus can result from steric pinning of molecules to the adsorbing surface; they need not reflect strong adsorption to that surface. The ensuing dynamical evolution of the surface composition displays a phenomenology analogous to the forms of complex dynamics that are well known for conventional glasses. The dynamic constraints on desorption can actually give rise to a divergence of the effective relaxation time; the temperature at which this occurs is expected to depend on the strength of segment-surface adsorption and on the density of pinning. Further work in which the polymer molecular weights are varied shows that displacement is more rapid when the chain length of the weakly adsorbing species is less (*17*) but remains nonexponential. The physical model suggested here may also have a bearing on interpreting dynamic aspects of flexible proteins at surfaces.

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The Conformation of Fluid Membranes: Monte Carlo Simulations

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The conformation and scaling properties of self-avoiding fluid membranes with an extrinsic bending rigidity κ were studied with the use of Monte Carlo methods. For $\kappa = 0$, the results are consistent with branched polymer behavior at large length scales. There is a smooth crossover from a crumpled to an extended state with increasing κ, with a peak in the specific heat when the persistence length reaches the system size. The scale-dependent effective bending rigidity is a decreasing function of system size for all bare rigidities. These results indicate that fluid membranes are always crumpled at sufficiently long length scales.

MEMBRANES COMPOSED OF AMPHIPHILIC molecules, such as the monolayers of surfactant molecules at oil-water interfaces in microemulsions, the lipid bilayers that form biological membranes, as well as the layers of surfactant molecules in recently studied lyotropic liquid crystals, are highly flexible (nearly tensionless) surfaces. Membranes play a central role in determining the architecture of biological systems and provide the basic structural element for complex fluids such as microemulsions; an understanding of the statistical mechanics of these self-avoiding surfaces is therefore of considerable importance (*1, 2*).

In most cases of interest, these membranes are fluid, which means that the molecules can diffuse rapidly within the membrane surface and possess no reference lattice. In the absence of a lateral tension (*3, 4*), the shape of the membrane is governed by its bending rigidity κ. A membrane of linear size L exhibits transverse fluctuations (*5*) of extension $L_\perp \sim (kT/\kappa)^{1/2}L$ (where k is Boltzmann's constant and T is temperature) on length scales small compared to the persistence length (*6*) $\xi_p \equiv a \exp(c\kappa/kT)$, where a is a short-distance cutoff and $c = 4\pi/3$ (*7, 8*). However, as L approaches ξ_p, shape fluctuations have been predicted (*7, 8*) to reduce the bending rigidity and lead to a renormalized rigidity $\kappa_R = \kappa - (kT/c)\ln(L/a)$ in the limit of small kT/κ. On length scales $L \approx \xi_p$, the membrane should have an effective bending rigidity of the order of kT. At larger length scales ($L >> \xi_p$), membranes fluctuating at constant area are expected to have an extremely small bending rigidity and behave as crumpled (*9*) objects characterized by the absence of long-range orientational order of normals erected perpendicular to the local surface elements. For a fixed topology, the scaling behavior of self-avoiding fluid membranes at these length scales is expected to be the same as that of a branched polymer (*2, 10, 11*).

Several aspects of this scenario have, however, not yet been verified. Indeed, there is little evidence that self-avoiding fluid membranes with a finite bare bending rigidity really do crumple. It has been speculated (*2*) that self-avoidance may stabilize the effective bending rigidity at some finite value $\kappa \sim kT$ and therefore prevent crumpling. Furthermore, there is some controversy concerning the universality classes of the various models used to describe self-avoiding random surfaces (with $\kappa = 0$). The most widely studied models for these surfaces are constructed by taking the elementary 2-cells (plaquettes) on a hypercubic lattice and gluing them together in such a way that each edge is shared by exactly two plaquettes (*10*). For fixed topology, the long–length-scale behavior of this class of surface has been shown to be that of a branched polymer: the radius of gyration R_g of a surface of area S scales as $R_g^2 \sim S^\nu$ (*12*), with $\nu = 1$ in spatial dimension $d = 3$ (*10*). Recently, however, randomly triangulated surfaces of the type we consider here have been investigated for $\kappa = 0$ with the use of Monte Carlo techniques (*13*). A value $\nu \approx 0.8$ was reported, implying that such surfaces belong to a different universality class. Given the generality of the entropic mechanism behind branched polymer behavior, this discrepancy is troubling (*10, 11*).

In this report we present evidence that fluid membranes are crumpled at sufficiently large length scales for any value of the bare bending rigidity and that the crumpled state does indeed exhibit branched polymer behavior. Our conclusions are based on exten-

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