

The Bimodal Energy Landscape When Polymers Adsorb

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We describe the histogram of chain conformations that results when flexible polymers adsorb more quickly than the surface structure equilibrates. By infrared analysis of conformational substates in a model system (poly(methyl methacrylate) adsorbed primarily by hydrogen bonding onto oxidized silicon), this histogram was measured and found to be bimodal. One large population of chains spread into flattened conformations. A second large population of chains, finding less free surface available at the time of adsorption, became attached more tenuously. The history dependence of adsorption could be understood as the irreversible adsorption of objects with flexible shape. This interpretation differs decisively from the traditional considerations of minimizing the free energy.

When the conformations of adsorbed polymer chains are equilibrated, powerful methods of equilibrium statistical mechanics apply. Sophisticated theories describe this situation.^{1,2} Experimenters, on the other hand, have long been frustrated by the recurring problem of “trapped” adsorption, in which polymer chains deposit decidedly more quickly than the surface structure equilibrates.^{3–13} Conceptual understanding of this problem has been elusive because of the difficulty to make general statements about a problem where sample history necessarily plays a role.

Here we show that history dependence can be interpreted by an alternate approach, the irreversible adsorption of objects with flexible shape.^{14–16} More specifically, we show that polymer surface structure can originate in piecemeal deposition with differential spreading dictated by the still-uncovered surface area. This differs decisively from the prevailing view^{1,2} that chain conformations are selected such that free energy is minimized.

The model system was poly(methyl methacrylate) adsorbed from dilute solution onto oxidized silicon. Chains that adsorbed at low surface coverage spread to maximize their surface–segment contacts and remained in this flattened conformation as the surface coverage increased. Chains that adsorbed at surface coverage above roughly half were bound tenuously. The resulting spectrum of

adsorption substrates within the complete adsorbed layer was broad and bimodal.

Experimental Section

Poly(methyl methacrylate) (PMMA) was allowed to adsorb from dilute solution to a single surface of oxidized silicon. Table 1 lists the characteristics of the PMMA chains. The surface preparation, calibration of attenuated total reflection infrared signals,⁸ and modifications for using polarized radiation¹⁷ were described elsewhere. PMMA adsorbs mainly by hydrogen bonding.⁸ The net segment–surface interaction energy is $4k_{\text{B}}T^{12}$ (k_{B} is the Boltzmann constant and T is the temperature). The temperature was 303 K.

Results

The distinction between equilibrium at the segmental level and its potential breakdown at the molecular level has been emphasized on theoretical grounds.⁵ The hypothesis arose that the activation energy to release these polymer chains from multiple hydrogen-bonded contacts with the surface might be prohibitive. If so, chains deposited at low surface coverage might spread to occupy a disproportionately large number of potential adsorption sites and these flattened conformations might persist even after the surface coverage was saturated.

In initial experiments (circles, Figure 1A), polymer D was allowed to deposit uninterruptedly onto the initially bare surface. In parallel experiments (triangles and circles, Figure 1A), adsorption was halted at incomplete coverage and construction of the monolayer was completed with isotopically labeled molecules of matched molecular weight (polymer C). No desorption of polymer D occurred following adsorption of polymer C.

Sub-monolayers of polymer D displayed considerable orientation as measured by IR dichroism. Dichroic ratio is defined here as the ratio of absorptivity perpendicular to the surface and in one direction parallel to it.^{17,18} Dichroic ratio of unity indicates isotropy. Figure 1A shows, for the experiments shown in Figure 2A, the time-dependent dichroic ratio of the asymmetric methyl stretch (D_{CH_3}). The data show directional preference for stretch in the plane of the surface, $D_{\text{CH}_3} < 1$. This was most pronounced when surface coverage was least (Figure 1B, triangles). The mean segmental orientation of the earliest-adsorbed chains remained fixed in a state far more

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(18) The ATR intensities for plane-polarized radiation depend upon the absorption index in the two directions parallel to the surface (A_x and A_y) and perpendicular to the surface (A_z). Because the solution was stagnant, $A_x = A_y$.

Table 1. Characteristics of Atactic PMMA Polymers^a

sample	M_w	M_w/M_n
polymer A ^b	7 700	1.15
polymer B ^b	64 000	<1.09
polymer C ^c	90 000	
polymer D ^b	107 000	<1.10
polymer E ^b	1 300 000	1.06

^a These are flexible linear chains. The ratio of the weight-averaged to the number-averaged (M_w/M_n) 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. The molar mass of the repeat unit is 93 g mol^{-1} (protio PMMA) and 102 g mol^{-1} (deuterio PMMA). ^b Protio sample (Polymer Laboratories, Amherst, MA). ^c Deuterio sample (Polymer Standards Service, Mainz, Germany).

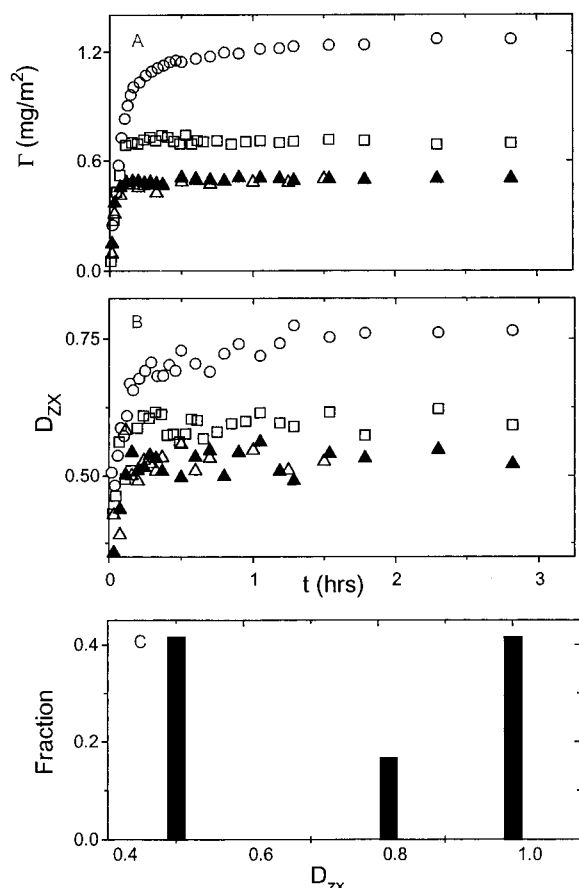


Figure 1. Adsorption of polymer D (0.01 mg mL^{-1} in CCl_4) plotted against elapsed time. (A) Mass adsorbed per area (Γ) during uninterrupted adsorption (circles). Alternatively, solution was replaced by polymer C solution at the same solution concentration (open symbols) or at 100-fold larger concentration (filled symbols) after 4 min (triangles) or after 8 min (squares). The Γ of polymer D was unaffected. (B) The dichroic ratio (D_{CH_3}) of the asymmetric CH_3 vibration for the experiments indicated in part A. Dichroic ratio of unity would indicate isotropy. Symbols are the same as for part A. (C) The histogram of dichroic ratio (D_{CH_3}) implied by part B.

distorted than the average over the entire layer (circles) and showed no time dependence.

Therefore when adsorption proceeded to completion, highly oriented chains were buried under a cover of more nearly isotropic chains.¹⁹ The distribution of dichroism in Figure 1B, shown in Figure 1C, shows that different fractions of the original layer were bound in energetically different situations. Pefferkorn and Varoqui proposed a similar "hairy carpet" model years ago,^{6,7} in which chains

(19) Analysis of other infrared active vibrations also indicated large kinetically stable deviations from isotropy. Dichroism of the asymmetric methyl stretch is not directly linked to backbone orientation.

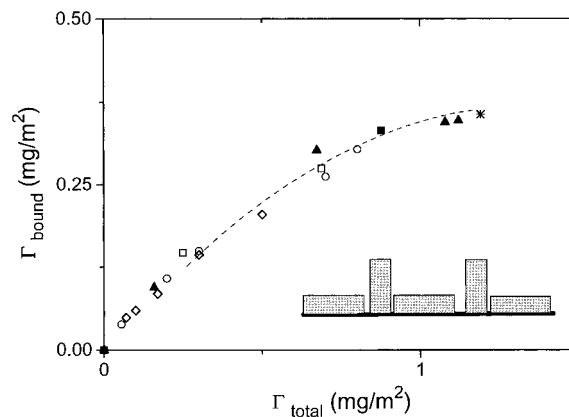


Figure 2. Bound mass (Γ_{bound} , hydrogen bonded to the surface) plotted against total mass adsorbed (Γ). Uninterrupted adsorption, from data in Figure 1 (dashed line). The following polymers were adsorbed to "starved" partial coverage from 0.01 mg mL^{-1} in CCl_4 : polymer A (open squares), polymer B (filled squares), polymer D (open circles), polymer E (diamonds). Also adsorbed to partial coverage were polymer B from CCl_4 at 0.08 mg mL^{-1} (star) and polymer D at 0.01 mg mL^{-1} from toluene at 303K. Inset shows a schematic sketch of the implied distribution, in which chains first to arrive at a surface adsorbed in a relatively flat conformation, while later-arriving chains adsorbed more loosely.

first to arrive at a surface adsorbed in a relatively flat conformation, while later-arriving chains adsorbed more loosely. The desirability of quantitative study was evident.

Summarized in Figure 2 are a large number of experiments examining the relation between mass adsorbed and extent of molecular distortion. Here as an indicator of molecular distortion, we show mass hydrogen bonded to the surface,⁷ Γ_{bound} , since this distortion parameter presented less experimental scatter than the dichroism discussed above. The Γ_{bound} was calculated from the intensity of the infrared carbonyl peak shifted to slightly lower wavenumber by hydrogen bonding.⁸ The experiments summarized in Figure 2 show that the total mass adsorbed (Γ) and Γ_{bound} were in one-to-one correspondence, regardless of molecular weight, solution concentration, choice of solvent, temperature, or dosage during adsorption. This indicated that impingement to the surface was slower than the rate of spreading.

Some of these data refer to uninterrupted adsorption as illustrated in Figure 1A. Other data (see figure caption) refer to experiments in which adsorption was halted at incomplete coverage by exposing the surface to pure solvent. Also shown is a control in which the solvent was changed from CCl_4 (near- θ solvent) to toluene (good solvent quality). Other control experiments found no difference when the temperature was raised to 323 K. Note that PMMA could be desorbed by adding polar displacer molecules, verifying the absence of chemisorption.⁸

The lack of time dependence is a definitive conclusion in spite of unavoidable scatter in the data. In addition the dichroism experiments (Figure 1) show that this certainly did not indicate equilibrated conformations but instead indicated "trapped" adsorption as noted above, except possibly at the highest surface coverages.²⁰

These heterogeneous surface structures were quantified by the histogram of bound fraction, p , plotted in Figure

(20) The distribution calculations are made on the hypothesis of total conformational stability. Figure 1 shows that this is correct at the earlier stage of adsorption, when polymers have the opportunity to arrange many surface-segment contacts, so the structure is frozen. It is true that chains deposited at very high surface coverage have fewer surface contacts, and such loosely bound polymers might experience exchange between bound and loop portions, but this does not affect the conclusion as to bimodality.

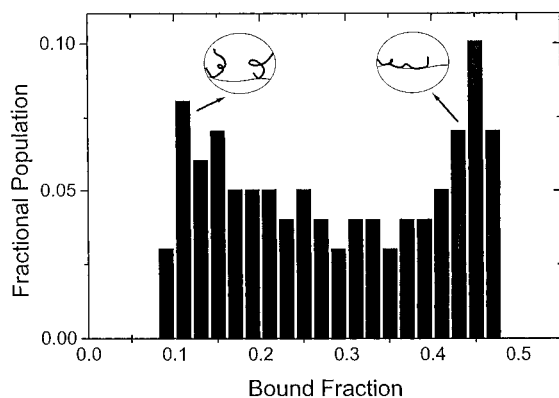


Figure 3. Histogram of bound fractions determined, for fractions separated by $\Delta p' = 0.02$, from the data in Figure 2. Evaluated at surface excess 1.2 mg m^{-2} to avoid propagation of errors as incremental differences became small. Inset shows schematic illustrations of chains with large and small bound fractions.

3. Here $p = \Gamma_{\text{bound}}/\Gamma$, bound mass adsorbed relative to total mass adsorbed. In brief, for sequential increments of total mass adsorbed, the change of Γ_{bound} was determined. This gave the histogram of the relative mass adsorbed, attributable to subpopulations of chains with equally-spaced bound fractions between 0 and 1. The most striking feature of the histogram in Figure 3 is the asymmetry. The broad distribution splits into two populations: those chains that met a bare surface and sank into highly-flattened configurations, and those that, meeting a nearly-saturated surface, became attached more tenuously.²⁰ Note that most other experimental techniques used to characterize polymer surface structure determine an averaged structure and are blind to this actual distribution of adsorption substrates or “energy landscape”.²¹

Discussion and Conclusions

This evokes problems similar to those of other scientific fields: the “parking problem” and random sequential

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adsorption. Here objects are deposited onto a plane one by one with random locations except that the same spot cannot be occupied by the same object.^{14–16} This is normally considered for rigid objects. The portion of the histogram in Figure 3 to the right of center suggestively involved only ≈ 0.2 of the possible $\approx 0.35 \text{ mg m}^{-2}$ bound mass. This level is close to the expected “jamming limit” (57% of surface sites^{14,15}) observed for colloids and certain proteins.¹⁶ Figure 3 shows that flexible polymers can continue to adsorb by adjusting their shape to adsorb at fewer and fewer surface sites.

Shape flexibility of polymer chains affords a mechanism for surface coverage to reach unity, unlike the often analyzed case of rigid objects.^{14–16} This picture of piecemeal surface deposition contrasts strongly with the expected intertwining of polymers at conformational equilibrium.^{1,2} An interesting implication is that the chains which adsorbed later, finding fewer and fewer surface sites available and becoming attached with fewer and fewer segments, should have had their center-of-mass located farther from the adsorption surface than those which arrived first. These chains might most influence the often studied^{1,2} hydrodynamic thickness.

The significance is both scientific and practical. On the practical side, a broad and bimodal conformational distribution has evident bearing on situations where the usefulness of polymers hangs on the tenacity of their surface attachment, especially adhesion. The scientific significance is that this interpretation of surface structure differs decisively from the customary view that the chain conformations are selected such that the free energy is minimized. However if surface impingement were comparable to or more rapid than the rate of spreading, as for concentrated solutions and melts, a different distribution should be expected.

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