

occur under dilute growth conditions. Quasielastic light scattering measurements then reveal exponential growth in time, as opposed to the critical growth observed close to the gel point. This exponential growth and the observed dimension of $D \cong 2$ indicate nonequilibrium cluster formation via reaction-limited aggregation. Thus different preparative pathways can be used to modify the structure of silica gels.

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Exchange Kinetics between the Adsorbed State and Free Solution: Poly(methyl methacrylate) in Carbon Tetrachloride

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ABSTRACT: Adsorption and desorption rates at high surface coverage are reported for poly(methyl methacrylate) (PMMA) adsorbed from dilute carbon tetrachloride solution ($1 \text{ mg}\cdot\text{mL}^{-1}$) onto a single silicon oxide substrate at 30.0°C . The method of measurement was infrared spectroscopy in attenuated total reflection. The polymer fractions studied were deuterio (d-PMMA) and protio (h-PMMA) with matched degrees of polymerization $N_w \approx 570$ and 640 , respectively. No adsorption isotope effect was expected, nor noted experimentally. The rapid adsorption of d-PMMA onto the initially bare surface was followed for 1 h, at which time the ambient solution was changed either to a solution of h-PMMA or to pure CCl_4 . Desorption of d-PMMA after this time was linear in the elapsed time over 6 h, with rate on the order of $1\% \text{ h}^{-1}$, and this rate was the same into a solution of h-PMMA as into pure CCl_4 at 30 and 40°C . The infrared bound fraction, i.e., the fraction of segments in direct contact with the surface, was also measured. During adsorption onto initially bare surfaces, the average bound fraction took the constant level $p \approx 0.25$ throughout the experiments. However, for h-PMMA penetrating the preadsorbed d-PMMA layer after this polymer was allowed to adsorb for 1 h, the average bound fraction was $p \approx 0.1$ at elapsed times of minutes but rose to $p \approx 0.2$ after 6 h. This indicates that incoming chains underwent spreading at the surface. Control experiments with stearic acid in CCl_4 showed that adsorption-desorption kinetics in this system were more rapid than the experimental time scale. This suggests that despite slow rearrangements of the overall chains, rearrangements may have been rapid at the level of individual segments. The surface excess adsorbed amount in this PMMA system was dominated by sluggish relaxation and, by inference, by metastable nonequilibrium states.

Introduction

What physical picture should one imagine of polymers at a surface? It has long been known that the mass adsorbed usually amounts to more than a monolayer of repeat units; therefore presumably the segments of chains between adsorption sites loop into solution. Much theoretical attention has been given to describing the spatial distribution of segments at equilibrium. Tails at the ends of the macromolecules dangle dozens or hundreds

of angstroms into solution; loops of various sizes also dangle into solution; and the entire structure is anchored to the surface by only a fraction of the potential adsorption sites. The resulting concentration profile decays roughly exponentially with distance from the surface, and its characteristic thickness is predicted to be of the same order as the correlation length. For polymers adsorbed from dilute solution, this distance is of the same order as the radius of gyration of an isolated chain in solution. On the experimental side, information of a definitive quan-

titative nature is difficult to obtain because of the extremely low mass of an adsorbed layer, typically only 1–10 mg·m⁻². There are a number of recent reviews of what occurs, or is predicted to occur, at static equilibrium.^{1–3}

Another experimental approach to exploring adsorbed polymer layers is to consider the underlying microscopic dynamics. Little is known yet quantitatively about the rates and the mechanisms of the mobility of polymers in thin interfacial regions. Most of the rate measurements one finds are qualitative, made to determine the contact time necessary to reach steady-state levels of adsorption. However, there are at least two motives for seeking to understand dynamics. One is to understand surface motions and relaxations, in particular the dynamics that must underlie an overall adsorption equilibrium. This is important in both pure and applied science where the use of adsorbed polymers is ubiquitous. A second motive is to firmly assess the conditions for reversibility or irreversibility in the adsorption process. The conditions are not yet known under which it is appropriate to make the common assumption of equilibrium configurations at smooth featureless surfaces. By exploring the rate of relaxation from one adsorption state to another, one may seek to gain understanding about the energy barriers that separate various equilibrated or metastable states.

If displacer molecules (initially in free solution) have the same chemistry and number of segments as do native molecules which previously were adsorbed to steady state, then the kinetics of exchange may reflect the rates that underlie overall adsorption equilibrium. Fascinating measurements in this vein have been made by Varoqui and co-workers.^{4–7} In their original experiments,⁴ tritium-labeled polyacrylamide ($M_w = 1.2 \times 10^6$, $M_w/M_n = 1.3$) was adsorbed to steady state from water onto glass beads of unusually well-defined surface chemistry and particle morphology. The solution was then changed to a solution of the same, but unlabeled polymer, and radiation counts in the supernatant were monitored with elapsed time. The first 15 min saw a rapid drop of 5–10% in the surface population of radioactive polymer; for the next 8 h the rate of exchange slowed; and during the final 9 h the rate of exchange obeyed second-order kinetics. Second-order kinetics at long times were also consistent with the observed linear dependence of rate on the solution concentration of displacer, so that a simple bimolecular exchange of molecules between surface and solution was suggested. Such an exchange was modeled by de Gennes^{8,9} in analogy to quantum-mechanical tunneling.

More recently, these studies using tritium tracers were continued in a nonaqueous system, the adsorption of polystyrene ($M_w = 3.6 \times 10^5$, $M_w/M_n = 1.6$) onto silica beads from carbon tetrachloride.^{5–7} Studies with rather dilute solutions showed that up to a well-defined solution concentration on the order of 10 µg/mL, the rates of mass flux into solution from the adsorbed state were consistent with a single relaxation time on the order of 25 h. At higher concentrations the exchange kinetics were an order of magnitude faster but no longer fit a single relaxation time. Results were interpreted to reflect a change of the adsorbed layer structure with increasing solution concentration: from adsorption in a flat conformation to adsorption as a "hairy carpet". All in all, these studies confirmed the earlier conclusion⁴ of long-lived adsorbed states. Recent experiments involving aqueous poly(ethylene glycol) chains on colloidal silica particles are also consistent with this general conclusion.¹⁰

We have been working with single solid surfaces rather than colloidal particles. In earlier work, we established

Table I
Characteristics of the Poly(methyl methacrylates) Studied^a

code	M_w	M_w/M_n	N_w^b
d-PMMA ^c	57 000	1.08	570
h-PMMA ^d	64 000	<1.09	640

^a Manufacturer's data based on gel permeation chromatography. Since protio standards were used for calibration, the molecular weight data of the deuterio sample refer to the protio equivalent. ^b Number-average degree of polymerization. ^c Deuterio species. ^d Protio species.

the feasibility of using Fourier transform infrared spectroscopy (FTIR) in the mode of attenuated total reflection (ATR) for studying adsorption of PMMA onto the single surface of an infrared prism. We showed that protio/deuterio labeling could be used to follow the self-exchange of PMMA between the adsorbed state and free solution.¹¹ The system, PMMA in CCl₄, was chosen for experimental convenience. The intense carbonyl peak of PMMA can be measured with good precision, and CCl₄ is nearly transparent in the infrared spectrum. In addition, since we wished the osmotic interactions between adsorbed chains and incoming chains to be weak, CCl₄ has the advantage of being a poor solvent for PMMA, with the θ temperature for protio-PMMA reported to be ca. 27 °C.²⁰

In our first study,¹¹ the polymer solutions were pumped gently through the measurement cell in order to limit diffusion as the rate-controlling process in adsorption. Later we examined the effects of shear flow on the kinetics and achievement of equilibration as PMMA adsorbed onto an initially bare surface.¹² A rich kinetics turned out to be associated with the presence of low levels of shear flow (3 s⁻¹ macroscopic shear rate). Shear flow is a complication avoided in the present work.

In this study, we examine rates of adsorption and desorption in the absence of externally driven flow. The infrared technique used gives information not just about the rates of change of the mass adsorbed in toto but also about the rates of change of the fraction of adsorbed segments. By using a combination of h-PMMA and d-PMMA with matched degrees of polymerization, ca. 600, we quantify the adsorption-desorption exchange kinetics, at high surface coverage, between the adsorbed state and free solution.

Experimental Section

Infrared spectra were collected on an IBM IR-44 Fourier transform infrared spectrometer (FTIR) equipped with a mercury cadmium telluride detector. The attenuated total reflection optics (Circle Cell) were purchased from Spectra-Tech, Inc. The infrared beam sustained roughly seven internal reflections as it traveled the length of a cylindrical prism with an angle of incidence of 45°. The prism was mounted inside a thermostated steel jacket.

Anionically polymerized poly(methyl methacrylate) (PMMA), deuterio and protio standards of similar degree of polymerization, were purchased from Polymer Laboratories and were used as received. Their characteristics are listed in Table I. Tacticities were stated by the manufacturer to be ca. 53% syndio, 40% hetero, and 7% isotactic.

Silicon ATR prisms were employed. As purchased, the surfaces had been polished with 1/4-µm diamond paste. Energy transfer in the attenuated total reflection mode is more efficient for silicon than for the germanium prism we used previously,¹¹ thus enhancing the experimental sensitivity. Reproducibility of the experiments was better than with the Amtir alloy prism which we also used previously.¹² Before each experiment the thermostat cell for the infrared prism was disassembled and cleaned (soaked in nitric acid, rinsed in water and acetone, and dried under dry nitrogen).

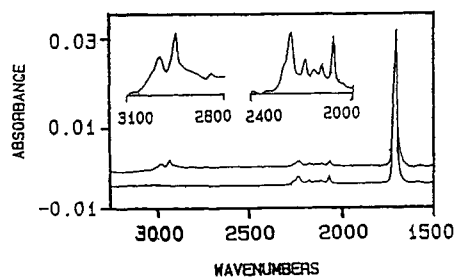


Figure 1. ATR infrared spectra of d-PMMA and h-PMMA adsorbed onto silicon from a solution of concentration 1 mg/mL. Note regions of carbonyl vibration (1729 cm^{-1}), of carbon-hydrogen vibration (2953 and 3018 cm^{-1}), and of carbon-deuteron vibration (2079 cm^{-1}) plotted in succeeding figures.

The prism was prepared before each experiment with the following protocol: reflux for several hours in ethyl acetate, ultrasound in ethyl acetate for 10 min, treat in oxygen-purged argon ion plasma for 1 min. After these ministrations, the experiment was begun immediately using freshly distilled solvents that had been dried over type-4A molecular sieves. First a spectrum was collected of the dry cell, and then a spectrum was collected of the cell filled with carbon tetrachloride. Polymer solution was not added until 30–60 min after the cell had been filled with CCl_4 ; this improved the base-line stability. Under ambient conditions such as those we used, it is well-known that silicon is covered by a native oxide layer.¹³

We briefly review the method of attenuated total reflection. When a beam of light strikes the interface between a medium of high refractive index n_1 and a medium of lower refractive index n_2 , light is totally reflected at the boundary if the angle of incidence θ is larger than the critical angle, $\theta_c = \sin^{-1}(n_2/n_1)$. At the point of reflection, an evanescent wave of exponentially decreasing intensity penetrates the second medium for distances on the order of a wavelength. The depth of penetration d_p , defined as the distance normal to the surface at which intensity falls to $1/e$ of the value at the surface, is given by¹⁴

$$d_p = \frac{\lambda}{2\pi n_1 [\sin^2 \theta - n_{12}^2]^{1/2}}$$

where λ is the light wavelength in a vacuum and $n_{12} = n_2/n_1$. An ATR correction was applied arbitrarily to account for the differences in d_p at various wavelengths. In our experiments the first medium was the Si prism and the second medium was the polymer solution. Some of the incident radiation was adsorbed at the vibrational bands of the adsorbed PMMA layers, giving rise to the absorbance reported below.

The refractive index of Si is 3.42 and that of CCl_4 is 1.41. In these experiments with dilute CCl_4 solution, the penetration depth was $d_p = 0.48\ \mu\text{m}$ at the carbonyl stretch of 1729 cm^{-1} . At every wavelength, the penetration depth was far larger than the characteristic thickness of the adsorbed polymer layer (ca. the radius of gyration). Therefore the measured polymer peak intensities did not contain information about segment distribution as a function of depth but represented the surface excess of adsorbed polymer in toto.

The spectra were examined at each stage of the experiments for infrared adsorption bands indicating the presence of contaminating surface species, and the experiment was aborted if contamination was encountered. Measurements reported here employed the Happ-Genzel apodization. They are based on the collection of 800 interferograms with a spectral resolution of 8 cm^{-1} and represent a time average of 3 min.

The solution concentration of PMMA in the experiments reported below was 1 mg/mL. However, in repeated runs using solutions of concentration between 0.1 and 1 mg/mL, no concentration dependence was detected.

Results

Representative Spectra. Figure 1 shows ATR spectra recorded for d-PMMA and h-PMMA in carbon tetrachloride, ratioed to the spectrum of the sample cell containing pure CCl_4 . Absorbance is plotted against wave-

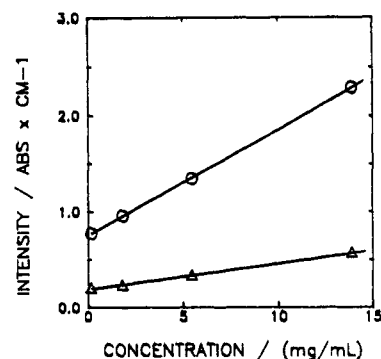


Figure 2. Integrated peak intensities for h-PMMA plotted against solution concentration as described in the text: (O), 1729-cm^{-1} carbonyl peak; (Δ) C-H stretches.

numbers. The carbonyl peak of PMMA, centered at 1729 cm^{-1} , dominates. In addition, d-PMMA shows a series of carbon-deuteron vibrations in the region $2000\text{--}2300\text{ cm}^{-1}$, and h-PMMA shows a series of carbon-hydrogen vibrations in the region $2800\text{--}3100\text{ cm}^{-1}$.

The infrared absorption peaks were integrated for purposes of tracking the surface excess. By Beer's law, both peak height and integrated peak intensity would be proportional to polymer concentration. However, the latter measure is more reliable in the context of the present experiment, where oscillator line shapes might be broadened by local changes in environment during the course of adsorption.

Quantification of the Surface Signal. The usefulness of ATR for quantitative work generally depends on using films much thinner than the penetration depth of the radiation and on having low energy loss as a result of the adsorbed layer. The conditions for Beer's law to hold to a good approximation have been discussed by Harrick¹⁴ and others.^{15–17} When they are not satisfied, the ATR signal is not necessarily linear in concentration because the reflectivity of the interface is not linear in solution concentration. The absorption bands in ATR may be shifted or distorted in frequency or line shape because the reflectivity, which depends on the refractive index of the sample, changes abruptly at frequencies near the sample's absorption peak. However, adsorption losses were low for the present adsorbed PMMA layers, as is illustrated in Figure 1.

Owing to the large penetration depth of the evanescent wave, the measurements included contributions from oscillators in the isotropic polymer solutions in addition to those within the adsorbed polymer layers. Accounting for this solution contribution was straightforward. First PMMA was adsorbed until the mass adsorbed had reached a plateau; then PMMA solutions of a range of concentrations were added in rapid succession. Since the mass adsorbed is insensitive to solution concentration over this range of dilute solution concentrations,^{1–3} the intercept at $c = 0$ represented signal from the adsorbed layer. The additional signal at finite concentrations was the contribution from PMMA in solution.

In Figure 2 the integrated intensities of both the carbonyl peak and C-H vibrations measured by ATR are plotted for h-PMMA as a function of solution concentration. The relationship is remarkably linear up to the highest concentration investigated, 14 mg/mL. With this slope, it was straightforward to calculate the solution contribution that corresponded to a given solution concentration. For the PMMA data reported below, this calibrated solution contribution was subtracted from the raw values of integrated peak intensity.

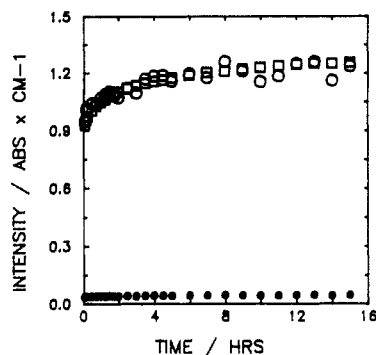


Figure 3. Integrated peak intensities for d-PMMA plotted against elapsed time during adsorption onto initially bare surface: (\square) 1729-cm^{-1} carbonyl peak; (\bullet) 2079-cm^{-1} C-D peak; (\circ) C-D peak normalized to the carbonyl peak.

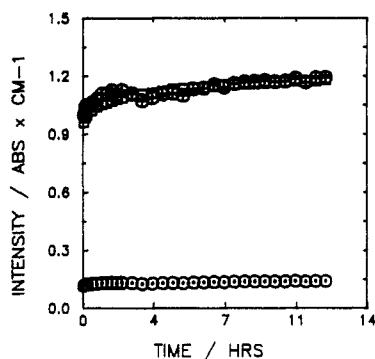


Figure 4. Integrated peak intensities for h-PMMA plotted against elapsed time during adsorption onto initially bare surface: (\square) 1729-cm^{-1} carbonyl peak; (\circ) C-H peaks, (\bullet) C-H peaks normalized to the carbonyl peak.

This calibration of the solution signal also allows one to calibrate the absolute level of PMMA adsorbed. The integral of the exponentially decaying evanescent wave, integrated from the surface to deep into the solution, is easily shown to be proportional to $c \cdot d_p$ (the bulk solution concentration is c , the penetration depth is d_p). Because the PMMA layer thickness is small compared to d_p ,¹⁻³ the evanescent wave decays to a negligible extent as it samples the adsorbed layer. It follows that a peak intensity (1729-cm^{-1} carbonyl peak) of 0.23 absorbance unit $\cdot\text{cm}^{-1}$ corresponded to a surface excess of 1 mg/m². Figures 2 and 3 show that the carbonyl peak intensity at plateau adsorption was $1.1\text{--}1.2$ absorbance units $\cdot\text{cm}^{-1}$ for both d-PMMA and h-PMMA after 10 h of adsorption. Therefore the mass adsorbed was $4\text{--}5$ mg $\cdot\text{m}^{-2}$.

To compare the relative surface excess of h-PMMA and d-PMMA mixtures during competitive adsorption, the intensities of the C-H and C-D peaks were normalized to the intensity of the carbonyl peak. Figures 3 and 4 show this normalization for the time-dependent adsorption of d-PMMA and h-PMMA, respectively, onto initially bare silicon surfaces. Integrated intensities of the carbonyl peak and of the C-H or C-D peaks are plotted against the elapsed time. Also plotted are the normalized peaks: the C-H or C-D peaks after multiplication by a constant factor. The agreement between the two sets of measurements is excellent, demonstrating that the relative peak intensities contained equivalent kinetic information.

No Isotope Effect on Adsorption. Presumably, PMMA adsorbs at the carbonyl group, so no protio-deuterio adsorption isotope effect was expected. Nor was an adsorption isotope effect observed during co-adsorption from a 50:50 mixture of d-PMMA and h-PMMA. In

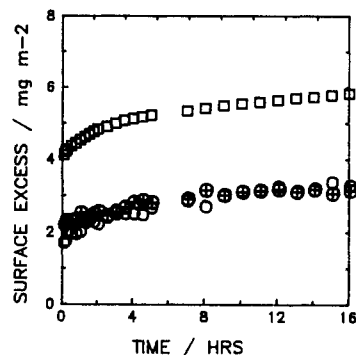


Figure 5. Surface excess plotted against elapsed time during competitive adsorption of a 50:50 mixture (by weight) of d-PMMA and h-PMMA onto initially bare surface: (\square) 1729-cm^{-1} carbonyl peak; (\bullet) normalized C-H peaks; (\circ) normalized 2079-cm^{-1} C-D peak.

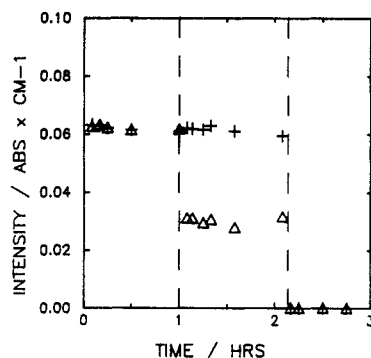


Figure 6. Infrared peak intensities of stearic acid normalized to carbonyl peak plotted against elapsed time for a sequence in which the liquid solution was first d-stearic acid in CCl_4 , then a 50:50 mixture of d-stearic acid and h-stearic acid in CCl_4 , and finally pure CCl_4 as described in the text: (+) carbonyl peak, representing the total mass; (Δ) d-stearic acid.

Figure 5 the course of the adsorption is plotted against time elapsed for a period of 16 h. One sees that the total surface excess was comparable to that for the pure isotopic isomers adsorbed separately (cf. Figures 3 and 4), suggesting that the physical process of adsorption was not affected by mixing the isotopes. Furthermore, the levels of the normalized protio and deuterio peaks were the same within the experimental uncertainty, each one-half of the total, which demonstrates that neither isotope adsorbed preferentially.

Experiments with h- and d-Stearic Acid. In principle, the above observation might have been limited by kinetic barriers to equilibration in view of the very slow equilibration, which we will describe below. Indeed, the protio isotope of stearic acid was previously found to adsorb preferentially from hexadecane onto aluminum oxide.¹⁸ Therefore it seemed worthwhile to further check the possibility of an adsorption isotope effect using stearic acid. Stearic acid of course contains a carbonyl group as does PMMA, and an eventual isotope effect might be expected to be exaggerated owing to the long alkane tail.

Figure 6 shows the results of experiments using stearic acid (Cambridge Isotopes) in carbon tetrachloride (1 mg/mL). First d-stearic acid was allowed to adsorb for 1 h. Next the ambient solution was replaced by a 50:50 mixture (by weight) of d-stearic acid and h-stearic acid. Finally the solution was replaced by pure CCl_4 . As will be reported in detail elsewhere, no preferential surface segregation of either isotope was observed. In addition, the equilibration time in response to each change in solution conditions was rapid—more rapid than the experimental time scale.

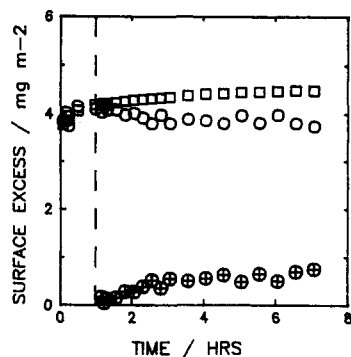


Figure 7. Surface excess plotted against elapsed time. After 1 h, d-PMMA of solution concentration 1 mg/mL was replaced by h-PMMA of solution concentration 1 mg/mL. (\square) Total mass of PMMA; (\circ) d-PMMA; (\oplus) h-PMMA.

Desorption into Ethyl Acetate. In principle, one could conceive that the slow desorption of PMMA, which we describe below, might have resulted from irreversible attachment of the PMMA to the surface at a small number of reactive sites. A control experiment was therefore performed in which, after d-PMMA had adsorbed for 1 h, the polymer solution was changed to undiluted ethyl acetate. The C-D peaks of PMMA disappeared, indicating that the ethyl acetate displaced PMMA from the surface, in other words, that the PMMA chains were reversibly adsorbed.

Replacement of d-PMMA in Solution by h-PMMA in Solution. Figure 7 shows the time-dependent adsorption from d-PMMA solution for 1 h, followed by replacement of this solution by h-PMMA solution. The carbonyl peak tracks the total mass of PMMA adsorbed. Also plotted are individual levels of h-PMMA and d-PMMA adsorbed. Two methods of calculating the surface excess of h-PMMA gave consistent results. One method was to calculate directly from the normalized intensities of the carbon-hydrogen vibrations, but these calculated quantities proved to be noisy owing to noise in the spectra in the region of the C-H vibrations. Therefore the h-PMMA data shown in Figure 7 were calculated as the difference between the total mass adsorbed (carbonyl peak) and the surface excess of d-PMMA. The surface excess of d-PMMA was calculated from the normalized carbon-deuteron 2079-cm^{-1} peak, using the calibrated relationship between intensity and mass described above.

In Figure 7 the total amount adsorbed continues to rise, upon replacing the solution, in the same way as is shown in Figures 3 and 4 for continued adsorption of the same polymer species. However, these changes in the surface excess are accompanied by the time-dependent loss of the native population of deuterio species, with concomitant time-dependent invasion by the protio species. The rate of mass adsorption is plotted on a magnified scale in Figure 11.

Replacement of d-PMMA in Solution by Pure Solvent. In other experiments, the solutions of d-PMMA were replaced after 1 h by pure carbon tetrachloride. Figure 8 shows the normalized 2079-cm^{-1} peak of the deuterio species plotted against hours elapsed after this exchange. Included for comparison are data replotted from Figure 7. Within the experimental uncertainty, the rate of desorption into pure CCl_4 at 30°C was the same as into the PMMA solution.

Figure 8 includes the result of a similar experiment carried out at 40°C to check the generality of this conclusion. Within the experimental scatter, the rate of de-

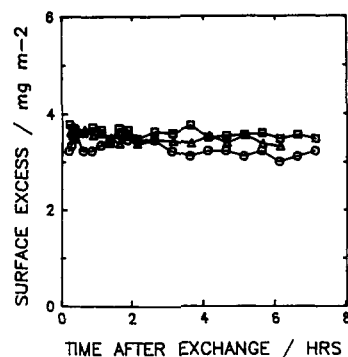


Figure 8. Desorption kinetics of d-PMMA. Surface excess is plotted against elapsed time after exchange of ambient solution: (\blacktriangle) exchange with solution of polymer h-PMMA at 30°C ; (\square) exchange with pure CCl_4 at 30°C ; (\circ) exchange with pure CCl_4 at 40°C .

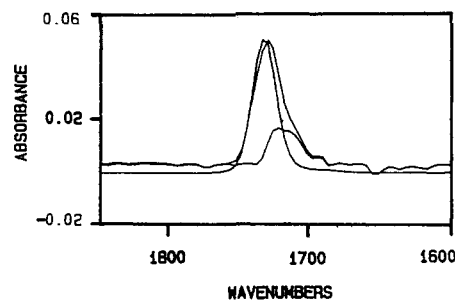


Figure 9. Absorbance of d-PMMA plotted versus wavenumber in the region of carbonyl absorption to illustrate the subtraction used to calculate the bound fraction. Three spectra are shown: ATR spectrum as measured (spectrum with hump at low wavenumber), liquid transmission spectrum (symmetric spectrum), and the residue after subtracting the other two spectra as described in the text.

sorption was not affected by the difference in temperature.

Fraction of Adsorbed Segments. It has long been known that when PMMA adsorbs by hydrogen bonding, the carbonyl peak is displaced to lower frequency (lower wavenumber).¹⁹ From the relative intensities of "bound" and "free" carbonyl peaks, it is traditional to calculate the "bound fraction", i.e., the fraction of segments in direct contact with the surface.^{1-3,34}

Figure 9 illustrates the raw data: a transmittance spectrum of the carbonyl peak of PMMA in CCl_4 solution compared to an ATR spectrum. It is evident that the ATR spectrum is not symmetric about 1729 cm^{-1} but shows a distinct hump on the low-wavenumber side, as expected. In order to separate this asymmetric peak into two populations, the transmittance spectrum shown in Figure 9 was subtracted digitally from the ATR spectrum, yielding the remainder illustrated in Figure 9.

This subpeak, centered at ca. 1715 cm^{-1} , was rather broad. This is consistent with the reasonable expectation that adsorbed segments found themselves in a distribution of environments. In future work, spectra taken with resolution higher than 8 cm^{-1} might permit analysis of line shape. For present purposes, the fraction of adsorbed segments was calculated by dividing the integrated intensity of the subpeak by the intensity of the entire carbonyl peak, after correcting this latter intensity for the solution contribution.

For adsorption of d-PMMA onto the initially bare silicon surface, Figure 10 shows the time evolution of the bound fraction and Figure 3 shows the evolution of the mass adsorbed. Within the experimental uncertainty, the bound fraction was constant at the level $p \approx 0.26$ from 5

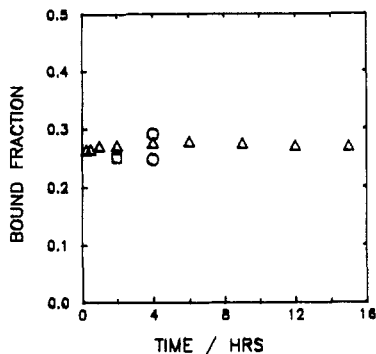


Figure 10. Bound fractions of PMMA plotted against elapsed time during adsorption onto initially bare surface: (Δ) kinetics showing the evolution of bound fraction for d-PMMA in a single experiment; (\circ) d-PMMA in two other independent experiments; (\square) h-PMMA in an independent experiment.

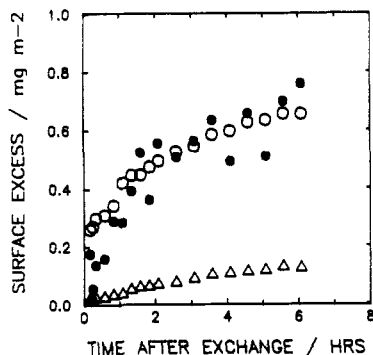


Figure 11. Total h-PMMA carbonyl peak and its bound subpeak, plotted against elapsed time after exchange of d-PMMA solution for h-PMMA solution at $t = 1$ h: (\circ) surface excess of h-PMMA calculated by digital subtraction of ATR spectra; (\bullet) surface excess of h-PMMA replotted from Figure 7; (Δ) subpeak representing the bound fraction, calculated by digital subtraction.

min to 15 h, even though the mass adsorbed during this time increased by a factor of 1.3. This finding of constant bound fraction was initially surprising to us. One might have expected that the chains which arrived late on the surface would be bound at fewer adsorption sites. However, a large number of repeated experiments confirmed the empirical observation.

Although the calculated bound fraction was quite constant in a given experiment, this number ranged from $p = 0.23$ to $p = 0.28$ in repeated experiments. The mass adsorbed in these repeated experiments varied less. The extent to which this difficulty in obtaining absolute quantitative reproducibility might reflect scatter in processing the data or true differences between the experiments in the arrangement of PMMA segments at the surface is not known at present. Examples of three calculations obtained in independent experiments at the elapsed time $t = 4$ h are included in Figure 10. Also included for comparison is the bound fraction of h-PMMA (calculated at $t = 2$ h for the same experiment as is depicted in Figure 4). For h-PMMA, the bound fraction was found to be 0.24, in good agreement with the measurements for d-PMMA.

Changes with time in the fraction of adsorbed segments were, however, significant for the invasion of h-PMMA into a preadsorbed layer of d-PMMA. Data showing the time evolution of invasion of the invading chains are shown in Figures 11 and 12. Figure 5 shows the evolution of the mass adsorbed in this same experiment. To make these calculations, two digital subtractions were needed. From each spectrum taken after the

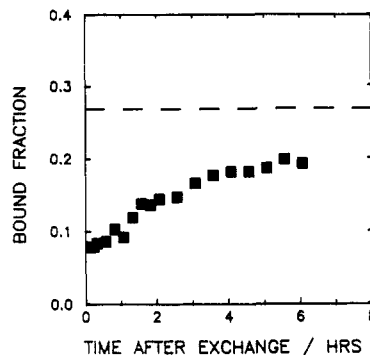


Figure 12. Bound fraction of h-PMMA plotted against elapsed time after exchange of d-PMMA solution for h-PMMA solution at $t = 1$ h as described in the text. The dashed line shows the bound fraction measured during adsorption onto the initially bare surface. The surface excesses of h-PMMA and d-PMMA in this same experiment are plotted in Figures 7 and 11.

solution was changed to one of h-PMMA, the spectrum taken immediately before the exchange was subtracted in such a way that carbon-deuteron peaks of adsorbed d-PMMA accounted for the solution contribution. This removed the contributions of adsorbed d-PMMA and also of d-PMMA in solution for the carbonyl peak. After correcting for small differences in the concentrations of d-PMMA and h-PMMA in solution, this difference spectrum for the carbonyl peak was interpreted to represent the carbonyl peak of adsorbed h-PMMA. Then from this spectrum of the carbonyl peak, the transmission spectrum of h-PMMA was subtracted in the same manner illustrated in Figure 7 to obtain the subpeak of the carbonyl peak attributed to bound h-PMMA.

Repeated experiments gave consistent results, despite the extensive data processing involved. Figure 11 shows the data used to calculate the time-dependent bound fractions shown in Figure 12. Plotted as a function of time after exchange are the surface excess amounts of h-PMMA and of the subpeak corresponding to the bound fraction. The surface excess of h-PMMA has been calculated two different ways: by digital subtraction of the ATR spectra in the manner just described and as the difference between the total carbonyl peak intensity and the intensity of the normalized C-D peak as described above in the discussion of Figure 7. While it is true that small numbers were involved, it is evident that the two calculations are in excellent agreement. In addition, one notices that even after 6 h of elapsed time, the mass adsorbed of invading chains was only ca. $0.6 \text{ mg}\cdot\text{m}^{-2}$, i.e., $<10\%$ of the total surface excess.

The time evolution of the bound fraction of the incoming chains, calculated from the data in Figure 11, is plotted in Figure 12. The bound fraction was $p \approx 0.1$ on the time scale of minutes but rose to $p \approx 0.2$ after 6 h. Further work of this nature is in progress; the data plotted in Figure 12 for late times are clearly an average over a distribution of chain configurations, so that presumably chains that arrived just before a given measurement have $p < p_{\text{meas}}$, while chains that arrived much earlier have $p > p_{\text{meas}}$. However, these data suggest already that with increasing time spent on the surface, the incoming chains became attached at more and more potential adsorption sites.

Discussion and Conclusions

The purpose of this study was to explore the mobility of adsorbed chains. Quantitative measurements were made

of the rates with which amorphous, flexible polymer chains adsorbed from solution to a solid surface exchanged with labeled polymers originally in free solution.

A picture emerges of sluggish turnover between the adsorbed state and free solution. After rapid deposition of polymer onto the initially bare surface, subsequent adsorption and desorption rates were remarkably slow. When d-PMMA solution was exchanged for h-PMMA solution, one expects that at equilibrium the invading h-PMMA chains would have replaced the initially adsorbed chains completely. Instead, as illustrated in Figures 7 and 8, the extent of replacement was a fraction less than 0.1 even after 6 h. In this respect, the chains were irreversibly bound over the experimental time scale of hours.

As a means to address the rate of equilibration at the segmental level, parallel experiments were carried out with stearic acid. The surface excess of stearic acid in CCl_4 responded promptly, faster than the instrumental resolution, to replacement of the isotopic species in solution. In this respect we recall that a polymer may be irreversibly adsorbed in two respects, as Barford and Ball have noted.^{21,22} If attachment to the surface is irreversible at the level of each repeat unit, then of course the chain is adsorbed irreversibly also. However, the chain taken as a whole may be adsorbed firmly even though the individual repeat units are in thermal equilibrium between the adsorbed and unadsorbed states. The experiments with stearic acid suggest that chain adsorption in these experiments was irreversible in the latter sense.

If one supposes that individual PMMA repeat units were in thermal equilibrium but that the overall adsorbed population of chain macromolecules was not, what is the correct picture to visualize of the structure of these polymer layers? Additional information was provided by the infrared bound fraction, p . The average bound fraction took a constant value throughout the experiments, $p \approx 0.25$, in the course of adsorption onto the initially bare surfaces. One might have expected this value to evolve with time under conditions when the total amount of polymer was increasing. To find that the mean bound fraction was constant, within experimental uncertainty, is consistent with the picture that the chain structure was generally slow to rearrange.

However, exchange experiments showed that as chains arrived at a surface where the surface coverage of polymer was high to begin with, their bound fraction was at first less ($p \approx 0.1$) and afterward grew with time. This suggests that with increasing time, adsorbing chains did undergo a spreading process on the surface. The time scale of this process was at least hours—considerably slower than the adsorption-desorption kinetics of stearic acid (a species with a single carbonyl group). The kinetics of evolution of the bound fraction is under further investigation.

The finding of average bound fraction $p \approx 0.25$ is consistent with the independent estimate that the surface excess was $4\text{--}5 \text{ mg}\cdot\text{m}^{-2}$. It implies that the surface coverage of segments in direct contact with the surface was $\approx 1 \text{ mg}\cdot\text{m}^{-2}$, which is monolayer coverage by PMMA determined from surface pressure measurements at the water-air interface.²³ The volume fraction directly at the surface thus appears to have been close to unity. Surface motions and relaxations of a collective nature may then be expected to be correspondingly slow, in qualitative agreement with the present findings.²⁴

When literature data are surveyed,^{1-3,34} one notices that the finding $p \approx 0.25$ is on the low side. Essentially only with polystyrene were similar values of the infrared bound

fraction estimated (see the tabulated review in ref 1). For example, $p \approx 0.2$ in the study by Kawaguchi and co-workers of polystyrene adsorbed from cyclohexane onto colloidal silica at the θ temperature.²⁶ In many other systems, including one previous study of PMMA adsorbed from CCl_4 onto colloidal silica,²⁷ $p \approx 0.5\text{--}0.6$ or higher for chains with degrees of polymerization similar to those studied here. This range of estimates of p in the literature is difficult to assess. In part it certainly reflects the density of surface hydroxyl groups in different systems. The density of surface hydroxyl groups is large on colloidal silica and was unfortunately not known in our experiments. In addition, as Cohen-Stuart and co-workers have emphasized,²⁸ an infrared measure of the bound fraction based on the frequency shifts of carbonyl groups (or, in the case of the adsorbed polystyrene, of hydroxyl groups on silica²⁶) is expected to respond only to hydrogen bonding; it is blind to segment-surface interactions which occur by weak physisorption rather than a hydrogen bond. In view of these considerations, the extent to which it is useful to compare the absolute values of the bound fraction derived from infrared spectroscopy in different systems is not clear to us. Rather we wish to emphasize the relative values, as discussed above.

What of the mass flux to and from the surface at high surface coverage? In principle, one may consider at least three stages of an adsorption process: diffusion of incoming chains from bulk solution to the surface, changes in the conformations of the incoming chains as they penetrate the preexisting layer, and concomitant rearrangements, in the already adsorbed layer, to accommodate the incoming chains. In the experiments described here, the rates of adsorption and desorption did not depend on the solution concentration over the range of concentrations investigated. This suggests that the second and third stages were rate limiting. In addition, the rate of desorption into a solution of finite polymer concentration was not distinguishably different from that into pure solvent. These considerations suggest that desorption of chains from the surface was rate limiting for this PMMA system.

It has long been known that the desorption of adsorbed chains, when solution is replaced by pure solvent, is typically small,^{4-7,29} exceedingly slow,³⁰ and largely insensitive to temperature,^{31,32} in general agreement with the present findings. The accepted interpretation is that the activation energy to peel all segments off the surface at once is prohibitively high. More recent experiments also showed that the outward flux in polyacrylamide and polystyrene systems was more rapid in the event of exchange into a polymer solution than into pure solvent.⁴⁻⁷ This behavior was notably absent in the present system. In the previous studies the reasonable interpretation was given that exchange could proceed piecemeal, a small number of segments at a time, with lesser activation energy because of the lesser cooperativity required. We speculate that the different response of the present system may stem from a difference in segmental interaction with the surface (higher in this system). Unfortunately, a quantitative measure of the segmental interaction energy in this system is not yet in hand.

In summary, this polymer system retained a long memory of its adsorption history. The mass flux between surface and solution was small on the time scale of hours. The time evolution of the infrared bound fraction of incoming chains was slow, preliminary results showing that the time scale over which the bound fraction increased was at least hours. At the same time, parallel experiments

with stearic acid suggested that the layers may have been in thermal equilibrium at the segmental level. Barford and Ball have developed a nonequilibrium theory of the spatial distribution of segments in a layer of this nature.^{21,22} However, we are not aware of models for the dynamics in a nonequilibrium system, though the reptation of an adsorbed chain has been considered.³³

This finding of sluggish rearrangement is in general agreement with the picture that emerges from other recent kinetic experiments on other polymer systems⁴⁻⁷ and raises questions about the generality of the usual statistical-mechanical assumption that adsorbed polymer layers are in a state of thermodynamic equilibrium.¹⁻³ To draw conclusions about the possible universality of this situation would be premature. For the present, we conclude that the kinetic barriers with respect to the equilibration of populations, on the surface and in solution, were large in this system. By inference, the surface excess adsorbed amount was dominated by metastable nonequilibrium states.

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References and Notes

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