Kinetic Traps in Polymer Adsorption: Exchange of Polystyrene between the Adsorbed State and a Good Solvent

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ABSTRACT: The conformations of polystyrene (PS) adsorbed onto silicon oxide from carbon tetrachloride (CCl₄) were investigated through measurements of exchange rates between the adsorbed state and free solution. Infrared spectroscopy in attenuated total reflection (FTIR-ATR) was used to measure PS adsorbed onto oxidized silicon from dilute carbon tetrachloride solution at 25.0 °C. Protiopolystyrene (PS-h; M_w = 575 000 or 96 400) was allowed to adsorb for a variable time from a solution of concentration 1 mg mL⁻¹; then this solution was replaced by a solution of deuteriopolystyrene (PS-d; M_w = 550 000 or 85 000) at the same concentration. An initial rapid exchange was completed over periods of minutes. No subsequent exchange was detectable over periods up to 10 h, indicating that a major fraction of the adsorbed polymer was kinetically trapped. With increasing surface residence time before exchange, the rapid exchange rate slowed moderately and the trapped fraction (T_f) increased. For exchange of chains of matched chain length, after a residence time of 16 h, $T_f \approx 0.6$ ($M_w \approx 550\,000$) and $T_f \approx 1.0$ ($M_w \approx 90\,000$). However, T_f extrapolated to zero for residence times less than 1 h. In addition, PS-h could be entirely displaced by CH₂Cl₂, indicating for this reason also that the adsorption was reversible in spite of being kinetically metastable. The higher trapped fractions after increased equilibration are tentatively interpreted to reflect logjammed states induced by steric hindrance between intertwined adsorbed chains.

Introduction

Motives for this study are the following. First, the problem of polymers at surfaces deserves understanding, owing to its interesting complexities and technological ramifications. Second, although the static structure of adsorbed chains has usually been considered,[1–4] the dynamics of these systems are also of intrinsic interest.[5–7] Above all, the dynamics of the adsorption process and subsequent surface mobility must be inherently related to the time scales of adsorption equilibrium.

Previous studies from this laboratory considered near-Θ solvent situations. First, an absorption isotope effect[8–10] and carboxylic acid chain end effect[8–10] were quantified concerning polystyrene (PS) adsorption onto silicon oxide from cyclohexane. Next, the dependence of the segmental sticking energies on the silicon surface preparation was explored.[11] The adsorption–desorption dynamics were probed in a weakly adsorbing system, polystyrene in cyclohexane,[12] and in a strongly adsorbing system, poly(methyl methacrylate) (PMMA) in carbon tetrachloride.[13] In the polystyrene–cyclohexane system, it was noted that adsorption–desorption rates continued to slow down for a considerable time after the adsorbed amount had equilibrated. This aging effect indirectly indicated slow rearrangements of the adsorbed chains in the direction of equilibrium.[12] These studies were recently extended to mixed PS–PMMA systems.[14]

In this paper, the adsorption and desorption of polystyrene in carbon tetrachloride onto an oxidized silicon surface are described. The relationship between residence time and desorption was investigated. Molecular weight was varied to investigate surface reorganization, solvent quality, and surface mobility effects.

Experimental Section

The experiments were performed using an IBM IR-44 Fourier transform infrared spectrometer (FTIR) equipped with a mercury–cadmium telluride detector. The internal reflection element (IRE) was a silicon rod with conical ends. The angle of incidence, calculated by the method of Sperline and co-workers,[15] was 35°. The rod was fitted into a Circle Cell purchased from Spectra-Tech, Inc., and was mounted inside a thermostated steel jacket.

Table I
Characteristics of the Polymer Samples

sample	M_w	M_w/M_n	source
protio	575 000	1.06	Polymer Lab., Amherst, MA
	96 400	1.01	Tosoh Corp., Japan
deuterio	550 000	1.05	Polymer Lab., Amherst, MA
	87 000	1.05	Polymer Lab., Amherst, MA
	85 000	1.02	Polymer Lab., Amherst, MA

The polymer systems studied were deuterio- and protiopolystyrenes (PS) of various molecular weights in solution in carbon tetrachloride. The characteristics of these polymers are summarized in Table I. The spectroscopic-grade carbon tetrachloride was purchased from Fisher. Initially it was used as received. In later experiments it was used after purification by passage through silica gel, but no changes in the solvent spectra or in the subsequent adsorption of PS were detected, confirming the quality of the as-received solvent. The work was performed at 25.0 °C, resulting in moderately good solvent quality conditions.[16,17]

At the end of an experiment, the IRE crystal was cleaned in ethyl acetate with an ultrasound for approximately 10 min and stored in a Teflon boat immersed in this same solvent. Before use, the crystal was removed from the ethyl acetate, rinsed in dilute (3%) hydrofluoric acid for 45 s, rinsed with deionized filtered water, and blown dry with nitrogen gas. It was then subjected to oxygen plasma for 5 min. The stainless steel elements of the Circle Cell were also cleaned in the ultrasound following each experiment and then stored in nitric acid for a minimum of 10 h.

In preparation for a new experiment, the cell was rinsed with deionized filtered water and soaked in acetone for 15 min. A jet of nitrogen gas was used to completely dry the cell. Teflon tubing and screws used in solution delivery were cleaned in the ultrasound. Methylene chloride was forced through the tubes to dislodge any remaining polymer. The tubes and screws were also dried with nitrogen gas.

The experiments normally began approximately 15–30 min after the assembly was secured in the FTIR. A control experiment described below showed that this waiting time was not critical. The waiting time allowed the chamber to be well purged by the continually flowing nitrogen. An empty cell spectrum was collected. The cell was then filled with CCl₄, and after approximately 45 min, another spectrum was taken. The protio polymer solution then replaced the pure solvent, and multiple spectra
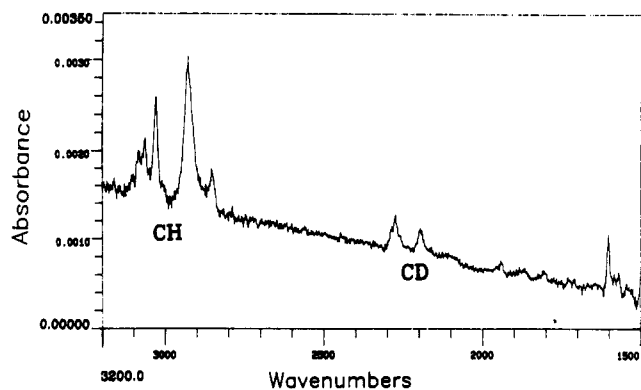
Figure 1. Infrared spectrum, measured in attenuated total reflection, of PS-*d* and PS-*h* jointly adsorbed onto silicon oxide from a CCl$_4$ solution of concentration 1.0 mg/mL. Absorbance is plotted against wavenumbers. Note regions of polystyrene C–H vibrations (3000–2830 cm^{-1}) and of C–D vibrations (2306–2066 cm^{-1}) whose integrated intensities were used to calculate surface excess plotted in succeeding figures. This spectrum has been ratioed to one of the pure solvent.

Figure 2. Displacement experiments performed to determine the segmental adsorption energy of PS onto silicon oxide from CCl$_4$. The surface excess of PS (M_w = 575 000), normalized by the surface excess from pure CCl$_4$, is plotted against the volume fraction of the displacer (CH$_2$Cl$_2$). From the intercept on the abscissa, χ_s = 1.3 was estimated.

were collected. After a given residence time, the solution of protio polymer was replaced by the solution of deuterio polymer. The exchange of these species at the surface was recorded by spectra collected immediately upon exchange. The isotope effect was probed by following the pure solvent spectra with about a 50/50 mixture of protio- and deuteriopolystyrene solution.

For early tests, the procedure of data collection limited the scan intervals to 5 min. Unfortunately, at least 75% of the CH mass to be lost was already gone at this point, rendering it impossible to fit any meaningful function to the kinetic data. A modified procedure was implemented, such that immediately after exchange of solutions, sets of 130 scans were taken at 1-min intervals. This modification gave a clearer view of the rates of desorption.
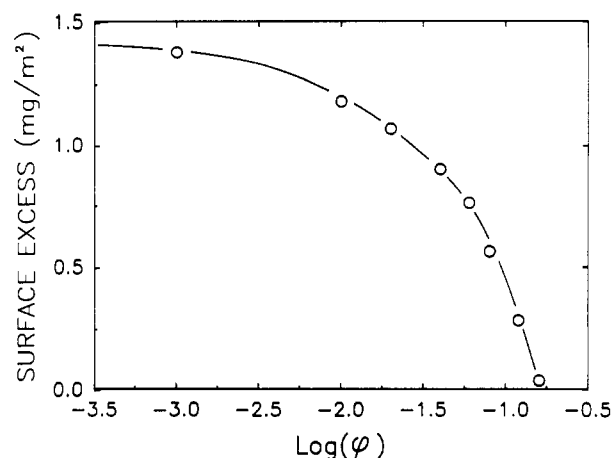
The ratioed spectra were base-line-corrected using the auto-base-line function in the IBM PC/IR software.[18] The peak areas were determined after curve-fitting Lorentzian functions using Spectracalc software.[19] The curve fitting involved normalizing the peak areas by the resolution at which the data were taken. In these experiments, the resolution was either 2 or 4 cm^{-1}.

Calibrations of the mass adsorbed per area (the surface excess) were performed as has been described elsewhere.[10]

Results

Figure 1 shows a representative ATR spectrum of protio- and deuteriopolystyrene, ratioed to a spectrum of pure CCl$_4$. Absorbance is plotted against wavenumbers. To quantify the surface excess, the areas integrated of protiopolystyrene were the peaks between 3011 and 2830 cm^{-1} and those of deuteriopolystyrene between 2306 and 2066 cm^{-1}. As has been discussed by Painter,[20] the peak centered at 3085 cm^{-1} is the meta, ortho asymmetric stretch; the peak at 3059 cm^{-1} is the para vibration; the peak at 3027 cm^{-1} is the symmetric stretch of the polystyrene ring; and the peaks at 2923 and 2850 cm^{-1} represent the asymmetric and symmetric CH$_2$ stretches, respectively. For the deuterio species these vibrations are shifted to lower wavenumbers and are centered at 2273 cm^{-1} for the ring vibration and at 2194 and 2101 cm^{-1} for the asymmetric and symmetric CD$_2$ stretches, respectively. The lower vibrational energy of the deuterio polymer at the aromatic ring is thought to cause a preferential adsorption of the deuterio species, resulting in an adsorption isotope effect.[8–10]

Segmental Sticking Energy. The χ_s parameter is defined as the difference in adsorption energy (units of *kT*) between a polymer segment and a solvent molecule.[21] The segmental adsorption energy may be decreased by adding a monomeric displacer to the polymer–solvent

solution.[22] At a certain displacer volume fraction, termed the critical volume fraction ϕ_c, the polymer is completely displaced. An elegant technique, developed by Cohen-Stuart et al.,[22] provides a relationship between this point and the segmental adsorption energy. The paper by van der Beek et al.[23] gives a practical description and application of this theory.

Rough estimates of this parameter were made, assuming athermal conditions for simplicity and for minimization of parameters, as in the original theory. Errors incurred by this approximation were calculated in ref 24 to be commonly less than 5% of the χ_s value.

Figure 2 shows a typical displacer experiment. The polymer solution was admitted into the ATR cell, and ample time is allowed for equilibration. To obtain a value of the surface excess at infinite dilution, the polymer solution was replaced by pure solvent. This data point was treated as displacer volume fraction ϕ = 1 × 10^{-3} for purposes of logarithmic plots, since control experiments using that volume fraction showed findings indistinguishable from ϕ = 0. The displacer volume fraction was then incremented with methylene chloride (Fisher) until the C–H peaks were no longer visible.

From the extrapolated intersection with the ϕ axis, χ_s ≈ 1 was calculated[11] in the manner described in more detail elsewhere.[11] This is a relatively weak segmental adsorption energy.

Adsorption Isotope Effect. We have discussed previously an approach to analyze the competitive effects of isotopic labeling, concentration in solution, and molecular weight.[8–10] Figure 3 illustrates a competitive adsorption of a 65/35 mixture by weight of protio- and deuteriopolystyrene of matched chain length. Equilibration was rapid, the surface excess stabilizing within 15 min. The surface excess of the deuterio sample was close to that measured noncompetitively, while the surface excess of the protio sample was barely detectable, an order of magnitude less.

This trend toward selective adsorption of the deuterio samples was also found in cyclohexane solution,[8–10] but the magnitude in CCl$_4$ is less. In cyclohexane the effect is ≈80 J mol^{-1} segment^{-1}.[10] In other words, the difference in χ_s, for protio- and deuteriopolystyrene in protiocyclohexane, is ≈0.03.

In the present system, 575 000 PS-*h* replaced by 550 000 PS-*d*, calculated as described previously,[10] the adsorption isotope effect is found to be ≈5 J mol^{-1} segment^{-1}. This
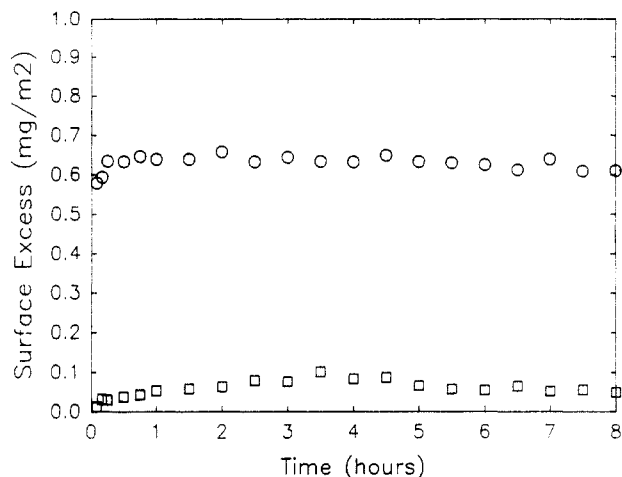
Figure 3. Illustration of the preferential adsorption of the deuterio species. The surface excess (mass per unit area) of protio- and deuteriopolystyrenes is plotted against the elapsed time when adsorbed competitively from a 65/35 mixture by weight in carbon tetrachloride solution at 25.0 °C. Squares: PS-h, M_w = 575 000. Circles: PS-d, M_w = 550 000.
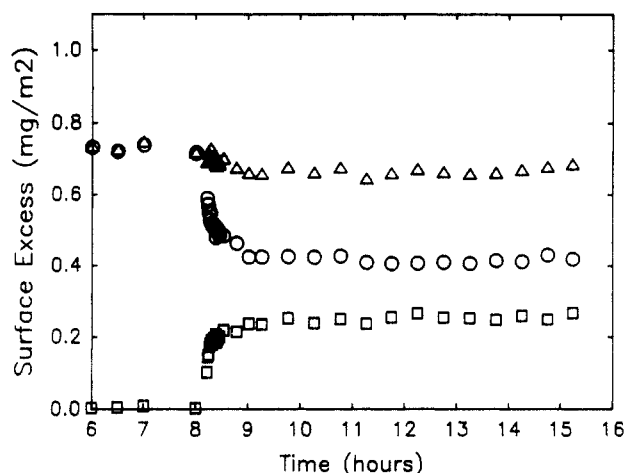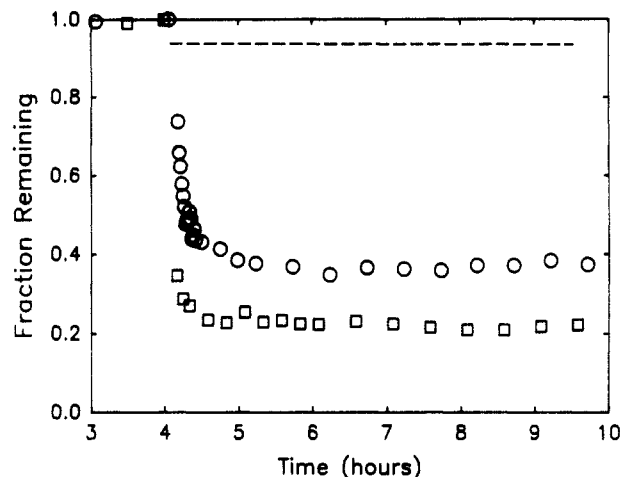

Figure 4. Surface excess of protio- and deuteriopolystyrene plotted against elapsed time. After 8 h, PS-h of solution concentration 1 mg/mL was replaced by PS-d of solution concentration 1 mg/mL. Triangles: total mass of PS. Circles: PS-h. Squares: PS-d.

was confirmed at 25 °C and also at 40 °C. In other words, the difference in χ_s, for protio- and deuteriopolystyrene in CCl$_4$, is $\approx 2 \times 10^{-3}$. The reasons that these seemingly small enthalpic differences cause large changes in the overall adsorption, when added up over many adsorption sites, have been discussed previously in quantitative terms.[10] A dependence of the adsorption isotope effect on the chemical composition of the fluid and solid support is consistent with other studies.[39]

Reversibility of Adsorption in Exchange Experiments. Having estimated the segmental adsorption energy and the magnitude of the isotope effect in this system, the kinetics of sequential adsorption were probed. Control experiments showed that desorption, when the solution was replaced by the same pure solvent, was too small to measure on a time scale of hours. This is typical;[25] the activation energy to peel all segments off the surface at once is so high that the process is kinetically blocked.

Figure 4 illustrates the sequence of exchange experiments. Surface excess is plotted against elapsed time. The time-dependent adsorption of PS-h was followed for some time (8 h in this example), and then this solution was replaced by PS-d at the same solution concentration. The adsorption of PS-h onto the initially-bare surface

Figure 5. Surface excess of protiopolystyrene plotted against elapsed time. After 4 h, PS-h of solution concentration 1 mg/mL was replaced. Dotted line: replaced by pure CCl$_4$. Circles: replaced by PS-d (M_w = 85 000) of solution concentration 1 mg/mL. Squares: replaced by PS-d (M_w = 550 000) of solution concentration 1 mg/mL.

consistently reached a steady state within 15 min. The level of adsorption was constant within experimental error, ±0.05 mg/m², until the solution of deuterio polymer replaced the original solution. In Figure 4, one sees that, although the individual species adsorbed changed significantly, the *total* surface excess remained constant after the exchange of two polymers of matched chain lengths.

An initial rapid exchange between the adsorbed state and the free solution was completed within minutes. No subsequent exchange was detectable over periods up to 10 h, indicating a significant trapped fraction. In the initial stages of adsorption and desorption, the symmetry of the kinetics is noteworthy.

Experiments to investigate the reversibility or irreversibility of these trapped states are summarized in Figure 5. The time-dependent surface excess of PS-h (M_w = 575 000), normalized by the surface excess before replacing the solutions, is plotted against elapsed time. Circles denote displacement by PS-d (M_w = 85 000); the pattern of initial rapid displacement, followed by a trapped fraction, is the general pattern we always observed. The squares in Figure 5 depict displacement by PS-d of higher molecular weight (M_w = 550 000). It is evident that the initial displacement was more rapid and that the trapped fraction was lower. As discussed above, other control experiments showed that adsorbed PS-h was entirely displaced from the surface when CH$_2$Cl$_2$ was added to the solution.

These observations show conclusively that adsorption was reversible. The high levels of the trapped fraction do not signify, for example, adventitious chemical attachment of some segments to the surface. Rather, they describe a situation where, although desorption was blocked with respect to the given driving force, further desorption was always possible when the driving force was increased.

Changes in Desorption Kinetics following Aging of the Adsorbed Layer. The surface residence time of PS-h before exchange of solutions was varied. Increased residence times might allow for rearrangements of adsorbed species, which might in turn retard the desorption kinetics, as was found previously under near-θ conditions of solvent quality.[12]

Time constants for the initial (rapid) desorption of PS-h are plotted in Figure 6 as a function of aging time before exchange. The time constants were estimated as the time for the surface excess to reach 1/e of the steady-state level
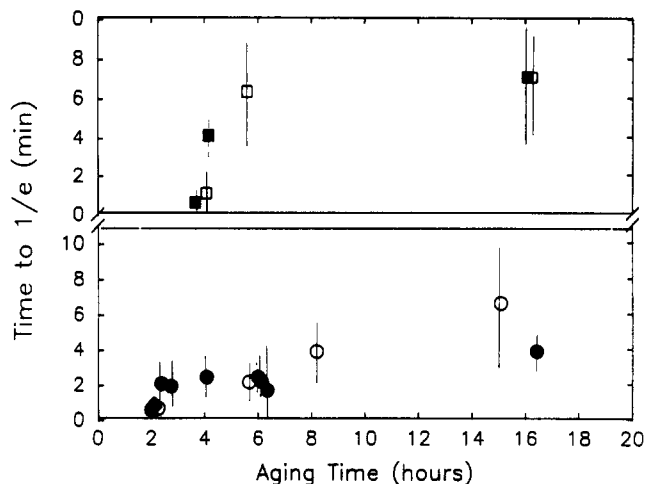
Figure 6. Time constants for the initial (rapid) desorption after exchange of solutions. The time to desorb $1/e$ of the surface excess of PS-h is plotted versus the residence time. Bottom graph (circles): displacement by PS-d (M_w = 550 000). Top graph (squares): displacement by PS-d (M_w = 87 000). The open circles and squares denote that M_w of PS-h = 96 400. The filled circles and squares denote that M_w of PS-h = 575 000. The diamond indicates a 96.4K PS-h/550K PS-d exchange following a 6-h solvent age time.
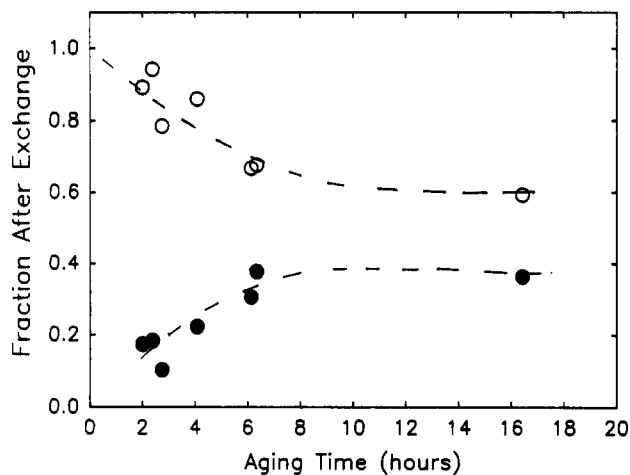

Figure 7. Trapped fractions of PS-h (M_w = 575 000) and PS-d (M_w = 550 000), plotted against aging times of the initially-adsorbed PS-h layer. The trapped fraction is the steady-state surface excess after exchange, normalized to the surface excess of PS-h before exchange. Filled circles: PS-h. Open circles: PS-d. Note the symmetry of the two curves.

reached at long times. The relatively large error bars reflect the rapidity of the exchange. Time constants were ≈1–2 min after an aging time of 2 h and were ≈6 min after an aging time of 16 h. Thus a moderate slowing of this process was evident.

For the exchange of PS-h and PS-d of matched molecular weight (M_w = 575 000 and 550 000, respectively), the fractions of PS-h and PS-d at steady state are plotted in Figure 7 as a function of the aging time. It is evident that the proportion of trapped species increased with increasing aging time, while the proportion of invading PS-d at steady state decreased. Even after 16 h of aging time, plateau levels of these quantities were not attained. In the discussion below, the trapped fraction obtained in these experiments is denoted T_f.

The possibility of system specificity was investigated by varying the molecular weights of both the protio and deuterio polymer. As may be noted in Figure 5, it was observed that the first (rapid) desorption process was somewhat more rapid, the larger the molecular weight of the invading polymer.
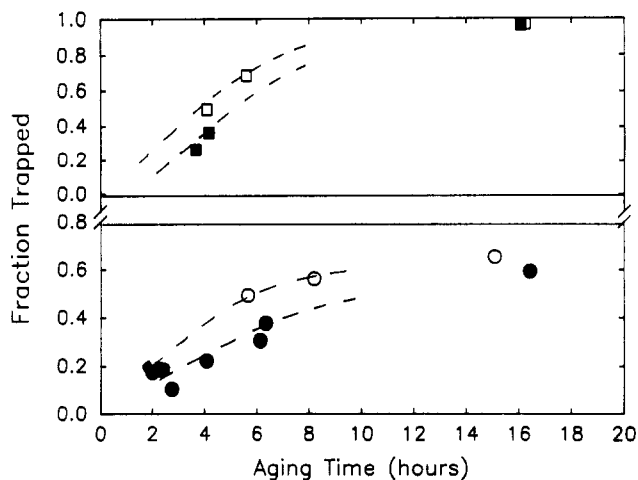
Figure 8. Trapped fractions of PS-h plotted against aging times of the initially-adsorbed PS-h layer. Lower molecular weight polymers are thought to rearrange more quickly and thus to be more difficult to remove during early exchanges then their longer chain counterparts. Symbols: same as in Figure 6.

In Figure 8, one sees that the PS-h sample of lower molecular weight was generally associated with higher T_f (at constant aging time). The exact relationship between T_f and molecular weight remains unclear because of scatter in the data, but the qualitative effect is clear. In Figure 8, T_f is plotted against aging time for the displacement of two PS-h species (M_w = 96 400 and 575 000).

In a control experiment, the cell was allowed to stand in pure CCl_4 for 6 h before the adsorption experiment was initiated. This experiment matched, in adsorbed mass and in kinetics, the results obtained with those measured on the same system after a normal 45-min solvent bath before initiating the experiment. This test of whether the aging effects described above might have reflected changes in chemistry of the silicon oxide surface, rather than structural changes in the adsorbed polymer layers, thus gave a null result.

Discussion

The adsorption of polymers at solid surfaces and especially the dyamics of these chains remain fundamental problems, as yet only peripherally understood. The multitude of system-specific and general environmental factors that affect the process account for much of the confusion. By studying the microscopic dynamics of specific systems under well-controlled conditions, general principles will eventually be understood.

Time Scales of Adsorption and Desorption. As was already indicated by our previous investigations of near-Θ solvent systems,[12] several distinct time scales are involved: τ_{on}, τ_{off}, and τ_{aging}. Adsorption onto the initially bare surface (τ_{on}) is rapid. As has been demonstrated several times in the past,[26,27] adsorption kinetics obey the simplest Langmuir kinetics up to a surface coverage of at least 50%. Conformational reorganization in the adsorbed state (τ_{aging}) is accomplished much more slowly.[12] This is inferred from the observation that the desorption time constant (τ_{off}) decreases over periods of hours to days for PS chains of molecular weight ≈5 × 10^5.[12]

The present study has confirmed this aging effect in a moderately good solvent system. In addition, one sees here that τ_{aging} increased with the molecular weight of the adsorbed chains, in the sense that the increase in T_f with aging time, was more rapid for the PS-h of lower molecular weight. This supports the notion of surface rearrangements, which would be accomplished more quickly

for smaller chains. It is also broadly consistent with findings concerning PS adsorbed from cyclohexane under near-Θ solvent conditions.[12]

Differences from Θ Solvent Conditions. In this study, desorption proceeded in two steps. The initial desorption step was always accomplished within the span of less than 10 min, but there remained a significant trapped fraction (T_f). The trapped fraction showed no subsequent decay with elapsed time. We emphasize that the population of kinetically trapped chains appears to have been reversibly adsorbed in the sense that T_f decreased, the higher the driving force toward desorption.

The two-step desorption in these experiments contrasts with our results in cyclohexane under near-Θ solvent conditions, where a single time constant described desorption for a significant time.[12] However, also noted in those experiments was that the rate of desorption slowed down after 1–2 h. This is then consistent with the results of the present study, although quantitatively different.

In interpreting these differences, it should be borne in mind that the segmental adsorption energy is estimated to be χ_s = 1.3 in CCl$_4$ but χ_s = 2.1 in cyclohexane.[24] However, no explanation in terms of these differences in χ_s is offered at the present time.

Comparison with Other Studies. The above picture of the dynamics of the adsorption process is broadly consistent with previous studies of PS–CCl$_4$ systems. The earliest work on this system explored the preferential adsorption of chains of high molecular weight onto silica particles from polydisperse mixtures.[28,29] Although measurements of exchange dynamics were not made, the surface excesses measured in one study[28] agree nearly quantitatively with those in the present study.

An innovative series of papers by Varoqui, Pefferkorn, and co-workers investigated the steady-state exchange of tritium-labeled polystyrene between silica particles and CCl$_4$ solution.[25,30–32] The solution concentrations were extremely low, 0.01 mg mL^{-1} or less. At solution concentrations less than 0.007 mg mL^{-1}, the polymer flux to[25,30] and from[31,32] the solution to the surface was found to have a well-defined single, long relaxation time, which obeyed first-order kinetics. A theory for adsorption onto a two-dimensional lattice was successful in describing the data.[25,30] On the basis of the published rate constants,[31] we infer that exchange would be complete after about 20 h. These exchange experiments were performed after 3 days of aging.[31]

At concentrations in the range 0.007–0.01 mg mL^{-1}, the surface excess was larger than could be accommodated in a monolayer and the exchange dynamics could not be described by a single relaxation time.[31] For any given total surface coverage, the desorption time constant increased continuously with the extent of exchange. The interesting proposal was made that some chains (the earliest to adsorb) were tightly adsorbed into a quasi two-dimensional state and that other chains (which adsorbed later) adsorbed more loosely. This is reminiscent of qualitative ideas suggested, with respect to experiments in a Θ system, by Furusawa and co-workers.[33] In the present study, we did not observe the gradual exchange reported in those studies. Instead, we observed an initial rapid desorption of a fraction of the adsorbed amount, after which time the composition of the surface layers remained constant.

Unfortunately, direct comparison with the present findings is not warranted. Our solution concentrations were at least 100 times higher. We note also that the surface excess measured in those studies was higher (a

factor of 3–6) than those reported here or earlier.[28] This discrepancy could be accounted for by the differences between the systems, including surface preparations, surface area available for adsorption, or the higher polydispersity of the radioactive-labeled polymers.

Finally, we note that while a strong dependence of the surface excess on the temperature[30–32] has been reported, that effect was limited to exceedingly low polymer concentrations. An extrapolation to our solution concentrations would predict no effect detectable by our methods.

The phenomenology of tightly and loosely adsorbed polymers also comes from a recent study of adsorption during shear or elongational flow in a Θ solvent system[34] and from studies of protein surface diffusion.[35,36] Possible explanations are considered in the following section.

Energy Landscapes in Polymer Adsorption. As just noted, the speed with which the polymer is displaced in these experiments is consistent with the previous notions[31,32] of two types of binding, tight and loose. With increasing residence time on the surface, it is natural to presume that the system tended to rearrange in the direction of equilibration. The central result of this study is that the tightly bound fraction increased so considerably with increasing aging time.

Customary explanations seem unsatisfactory in the present system. (1) In work with proteins and other molecules of variable affinities for the surface, the presence of ordered aggregates[35] or multilayers[36] has been suggested. But as the molecules used in this study were relatively monodisperse, uncharged, and atactic, the cause of the binding difference should, in principle, be more general than this. (2) Surface inhomogeneities have also been advanced as a possible cause.[34,36] But explanations based on surface inhomogeneities should not apply to the present system since we found simpler exchange kinetics in experiments conducted under near-Θ conditions, using silicon surfaces prepared in the same manner as those in the present study. (3) The proposition that the first polymers to arrive from solution adsorb in flatter conformations, and therefore more tightly,[30,31,33] seems unlikely in view of the trends with increasing aging time. One would expect an increasingly homogeneous layer as time elapsed, if this explanation held, whereas experimentally, the trapped fraction, T_f, increased with increasing residence time. (4) It has been suggested that the segmental density at a surface may become so high that the local segmental concentration would correspond to that of a bulk glass.[37] This picture, however, is difficult to imagine for polymers in good solvent; the extended bulk conformations and favorable polymer solvent interactions make such a glasslike density seem unphysical.

A different mechanism to reach a logjammed state, described elsewhere,[14,38] involves steric hindrance such that chains cannot readily glide past one another. Recalling that the trapped fraction extrapolated to zero for residence times less than 1 h, we tentatively suggest that the higher trapped fractions after increased equilibration reflect the degree to which chains on the surface have become intertwined during the aging process prior to exchange. This suggestion is consistent with the observation that the polymers of lower molecular weight displayed a higher trapped fraction than the long chains when the aging time was short. Indeed, one expects that shorter chains would intertwine more rapidly than longer chains.

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