Overshoots as polymers adsorb

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An overshoot in the time-dependent mass adsorbed from dilute solution was observed for poly(dimethylsiloxane) and *cis*-polyisoprene adsorbed onto single oxide surfaces. However, no overshoot was observed for poly(methyl methacrylate) and polystyrene, suggesting the possibility that the overshoot reflects transient surface-induced crystallization.

(Keywords: adsorption; surface properties; crystallization)

Introduction

Adsorption to an initially uncovered surface generally climbs montonically with time, with an asymptotic approach towards the equilibrium level[1,2]. In fact, a well developed body of research shows that the kinetics with which polymers adsorb is proportional to the fraction of empty surface sites[3,4] up to fairly high surface coverages (perhaps 50–80% of the equilibrium surface coverage). The rate of adsorption for these early stages is determined by the rate of diffusion through the surrounding bulk medium[5,6]. This Langmuir-type transient adsorption picture has been found to hold for adsorption of homopolymers[7,8] and block copolymers[9] from solution and also for adsorption from the melt[10].

Less well understood are the processes that occur during the final stages of adsorption. Equilibration kinetics at high surface coverage are considerably slower than would be expected if diffusion through the bulk were rate determining[2]. It has been proposed that the rate-determining step stems from penetration of the previously adsorbed layer[11,12] as well as configurational changes of the already adsorbed chains[13,14]. This laboratory's previous studies of the adsorption of the amorphous polymers, polystyrene (PS)[15] and poly(methyl methacrylate) (PMMA)[16], confirm the natural presumption that changes in the mass adsorbed during the final changes of equilibration would be monotonic.

In this communication we describe two other systems, poly(dimethylsiloxane) (PDMS) and *cis*-polyisoprene (PI), in which, during the final stages of adsorption, an overshoot of surface coverage was observed. Possible explanations of this qualitatively new behaviour are discussed.

Experimental

Infra-red spectroscopy in the mode of attenuated total reflection (a.t.r.) was employed to measure adsorption to the oxide surface of a silicon or a germanium infra-red prism. Methods described previously were used to collect the infra-red spectra and to calibrate the adsorbed mass per unit area (the surface excess)[15,16], as well as to prepare the surface of the a.t.r. prisms[17]. The samples were dissolved at dilute concentrations in carbon tetrachloride (Fisher) at concentrations of ~1 mg ml^{-1}. Experiments were performed at 25°C. In the course of adsorption, the surface excess was calibrated from the Si–O and Si–CH_3 vibration bands located near 1055 and 1260 cm^{-1} (PDMS), from the C=O band near 1750 cm^{-1} (PMMA), or from the C–H stretch bands near 2900 cm^{-1} (PI).

The PDMS ($M_w = 183\,000$; $M_w/M_n = 1.04$) was synthesized by anionic polymerization at the University of Cincinnati. The PI ($M_w = 205\,000$; $M_w/M_n = 1.04$) was purchased from Pressure Chemical Co. (Here M_w and M_n refer to the weight-average and number-average degrees of polymerization, respectively.)

Results and discussion

Generally the initial rate of adsorption occurred too rapidly to measure with the available time resolution, resulting in behaviour as shown in *Figure 1*. Here the mass adsorbed per unit area (Γ) is plotted against elapsed time for PMMA adsorption onto silicon oxide. The mass adsorbed jumped quickly to a value near plateau, with small monotonic increases afterwards. This was also characteristic of PS adsorption, as has been reported elsewhere[15] for PS samples of a wide range of molecular weight (up to 3.5×10^6 g mol^{-1}).

An example of the different adsorption kinetics of PDMS is shown in *Figure 2*. The mass adsorbed is again plotted against elapsed time. In contrast to *Figure 1*, a maximum in Γ was attained within the first 20 min of the experiment. This was followed by a slow desorption (~4 h) to a steady state. Note that at early times, the mass adsorbed was approximately 30% higher than at steady state.

This same qualitative effect was also found for PI, as shown in *Figure 3*. Here the maximum in mass adsorbed took longer to develop (~1 h), but was again approximately 30% higher than at steady state.

The inevitable polydispersity and heterogeneity of synthetic polymers raises legitimate questions about whether these observations could reflect the competitive

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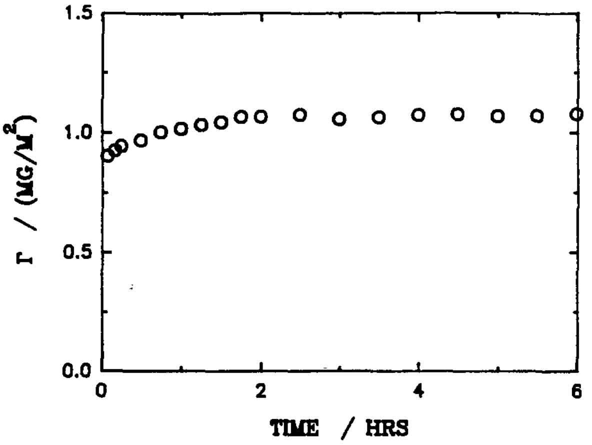

Figure 1 Surface excess (mass per unit area) of poly(methyl methacrylate) ($M_w = 107000$; $M_w/M_n = 1.10$) plotted against elapsed time during adsorption from carbon tetrachloride solution (~ 1 mg ml^{-1}) onto initially bare silicon oxide at 25°C

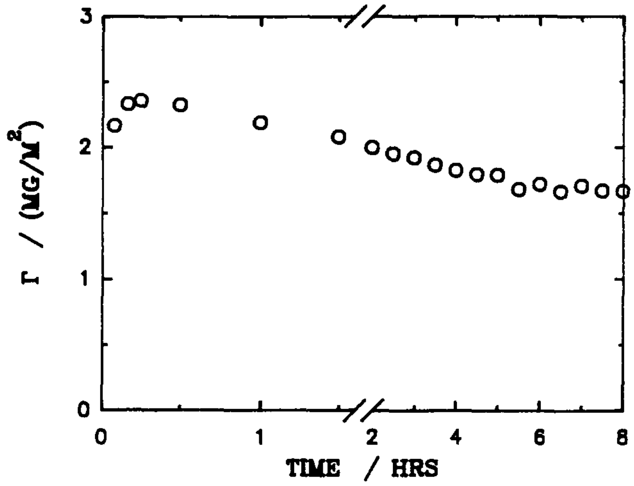

Figure 2 Surface excess (mass per unit area) of poly(dimethylsiloxane) ($M_w = 183000$; $M_w/M_n = 1.04$) plotted against elapsed time during adsorption from carbon tetrachloride solution ($\sim$0.2 mg ml^{-1}) onto initially bare germanium oxide at 25°C

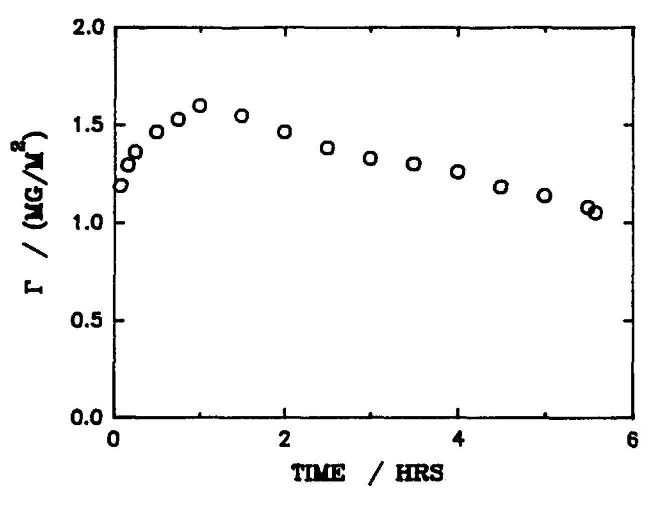

Figure 3 Surface excess (mass per unit area) of *cis*-polyisoprene ($M_w = 205000$; $M_w/M_n = 1.04$) plotted against elapsed time during adsorption from carbon tetrachloride solution ($\sim$1 mg ml^{-1}) onto initially bare silicon oxide at 25°C

adsorption of two (or more) different species[15,18]. If the species of higher adsorption had more rapid rate of access to the surface, and was later displaced as the experiments progressed, this would rationalize the observations. However, the infra-red spectra were examined throughout the experiments for rogue peaks that would indicate trace contaminants of different chemical composition than the polymers; these were not observed. In addition, because large chains diffuse more slowly, it is hard to argue that trace amounts of high molecular weight species would be responsible for the initially high adsorption. One would expect initially adsorbed species of low molecular weight to be displaced by species of higher molecular weight, not the converse. Although one cannot directly rule out the possibility of sample heterogeneity effects, this appears to be an unlikely explanation.

Originally we were also prepared for the possibility that spreading of chains towards their equilibrium adsorbed conformations might universally give rise to a transient overshoot of the mass adsorbed. A portion of the initially adsorbed chains might spread progressively onto the solid surfaces, becoming attached at an increasing number of adsorption sites[16], and thereby leaving fewer adsorption sites available for other adsorbed chains. But, as noted above, experiments did not show this phenomenon for the amorphous polymers, PS and PMMA. Presumably this implies that in the final stages of adsorption, the rate of spreading is faster than the rate of adsorption.

A more interesting possibility, noted by Oono[19], is that tendencies towards surface-induced crystallization might play a role. The equilibrium bulk crystallization temperature of PI ($T_m \approx 35°C$)[20] is higher than the temperature of these experiments (although surely depressed by the presence of solvent). For PDMS it is somewhat lower ($T_m \approx -40°C$)[20]. However, it is clear from several points of view that an external ordering field elevates T_m[21–24]. Thus, bulk samples of PI can be impelled to crystallize under strain[21]. Similarly, more recently it was discovered from computer simulations that when a simple liquid is placed immediately at a solid surface, a frozen layer, a single particle or a few particles thick, may form[22]. Indeed, computer simulations indicate that the tendency towards surface crystallization of simple fluids has no direct connection to T_m in the bulk, but rather is dominated by surface interactions[23,24]. This argument is also consistent with some unusual crystallization effects that have been observed for silica-filled siloxane elastomers, which may also be explained in terms of a preorientation of the chains at the surface by the filler[25].

For the above reasons, a plausible possibility is that surface-induced crystallization may have occurred in the course of the adsorption depicted in *Figures 2* and *3*. But if crystallization were incompatible with optimal molecular packing in the adsorbed state[26], the mass adsorbed would lessen as time progressed, in accordance with observations.

Detailed studies at different temperatures as well as more comprehensive studies of the time dependence of the infra-red dichroism are in progress and will be reported in due course.

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