Influence of Shear on Polymer Adsorption Kinetics

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Kinetics of poly(methylmethacrylate) adsorption onto a single surface from dilute carbon tetrachloride solution is reported. From stagnant solution the well-known steady-state plateau level of mass adsorbed is approached at long times. However, the mass adsorbed resumes its rise when moderate shear flow is initiated. For adsorption onto an initially bare surface, at a shear rate of 3 sec^{-1}, there is no sign of plateau on the logarithmic time scale.

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Little is known about either the characteristic rates or the mechanisms of surface motions and relaxations of adsorbed polymer layers. The bulk of experimental and theoretical work concerning polymers at surfaces has addressed what happens at equilibrium, as summarized in several reviews.[1-4] However, interesting time dependence is associated with the achievement of equilibrium as polymer adsorbs onto an initially bare surface. Even at overall adsorption equilibrium, a steady-state flux of macromolecules between the adsorbed and nonadsorbed states is expected.[5,6] Recently[6] we applied Fourier-transform infrared spectroscopy in the mode of attenuated total reflection to study the adsorption, from dilute carbon tetrachloride (CCl_4) solution, of polymethylmethacrylate (PMMA) onto single germanium surfaces. We concluded, from the exchange of hydrogenated and deuterated species, that PMMA of molecular weight ca. 60000 g/mole displayed a residence time on the surface of at least several hours. In the present Letter we examine the effects of polymer molecular weight and shear flow on the kinetics and achievement of equilibrium. This was more problematical than anticipated.

The experimental aspects are described in detail elsewhere.[6] In brief, adsorption onto the surface of a cylindrical infrared prism is monitored with use of the attenuated-total-reflection infrared Circle Cell optics sold by Spectra-Tech, Inc. The adsorbing surface is the inner of two concentric cylinders of diameters approximately $\frac{1}{4}$ and $\frac{5}{16}$ in. The penetration depth of the evanescent wave is far larger than the characteristic thickness of the adsorbed polymer layer (ca. the radius of gyration). Therefore, the peak intensities do not contain information concerning segment distribution as a function of depth but represent, by Beer's Law, the surface excess of adsorbed polymer *in toto*. In the present experiments, the solution concentration of polymer, 0.1 mg/ml, was sufficiently low to be a negligible contribution (ca. 1%) to the total signal. Anionically polymerized atactic PMMA standards were purchased from Polymer Laboratories and used as received. Their characteristics are listed in Table I.

The attenuated-total-reflection prism used was Amtir, an alloy of germanium, arsenic, and selenium. Energy transfer in attenuated-total-reflection mode is more efficient for this material than for the germanium prism we used[6] previously, thus enhancing the experimental sensitivity. The prism was prepared before each experiment according to the following protocol: reflux for several hours in ethyl acetate, ultrasound in ethyl acetate for 10 min, treatment for 2 min in oxygen-purged argon-ion plasma, and immediate commencement of the experiment with use of distilled solvents that had been dried over type-4A molecular sieves. Experiments were performed at 24- 26 °C in CCl_4, a poor[7] solvent; no temperature dependence was detected in repeated runs. At each stage of the experiments, the spectra were examined for infrared absorption bands indicating the presence of contaminating surface species; if these were encountered the experiment was aborted. Spectra reported here are based on the collection of 800 interferograms taken on an IBM Model IR-44 Fourier-transform infrared spectrometer with a spectral resolution of 8 cm^{-1}, and represent a time average of 3 min. A rough calibration indicates a surface coverage of 1.5 mg/m^2 per unit of integrated intensity of the PMMA carbonyl peak.

Initially, we pumped the polymer solutions past the surface as a matter of routine. The shear rate, calculat-

TABLE I. Characteristics of the polymethylmethacrylates studied. M_p is the polymer molecular weight. The ratio, M_w/M_n, of the weight-averaged molecular weight to the number-averaged molecular weight, known as the polydispersity index, is a measure of the dispersion of polymer molecular weight in a sample. A ratio of 1 implies that all polymer chain lengths in the sample are equal.

Code	M_p (g/mole)	M_w/M_n
A	7700	1.15
B	49000	1.07
C	107000	< 1.10
D	400000	1.14
E	750000	1.12

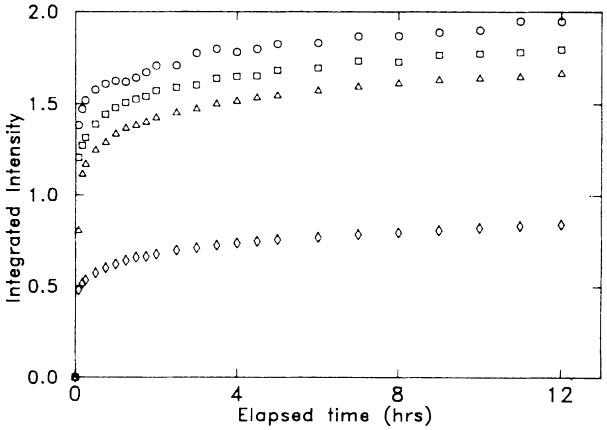

FIG. 1. Integrated intensity of carbonyl peak of PMMA plotted against time. $M_p = 7700$, lozenges; $M_p = 107\,000$, triangles; $M_p = 400\,000$, squares; $M_p = 750\,000$, circles. Shear rate is 3 sec^{-1}.

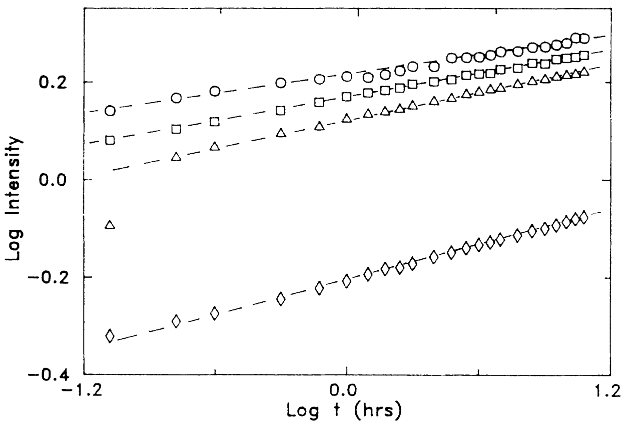

FIG. 2. Log-log representation of the data plotted in Fig. 1. Symbols same as in Fig. 1.

ed with the assumption of a linear velocity gradient, was 3 sec^{-1}. We reasoned that the rate of adsorption should involve, in principle, three steps: diffusion (or flow) to the surface, configurational rearrangements in the surface layer to accommodate arriving macromolecules, and rearrangements in the surface layer which result in exchange between the surface-bound state and the free solution. It was expected that a modest amount of flow would not seriously affect adsorption and might prevent diffusion to the surface from being rate limiting.

The results of a large number of experiments are summarized in Fig. 1. The integrated intensity of the carbonyl (1733 cm^{-1}) peak of PMMA is plotted against elapsed time for experiments involving PMMA of four molecular weights from 7700 to 750000 g/mole. Our data show an increase in mass adsorbed with increasing chain length for all times. Exceptions to this trend were seen in occasional runs. We believe this difficulty in obtaining absolute quantitative reproducibility to be due to problems in reproducible surface preparation. The isotherms in Fig. 1, each representing the average of two separate experiments, are all of high affinity; i.e., the bulk of mass adsorbed occurs before the first datum point is taken at 5 min elapsed time. Beyond this point, the mass adsorbed rises less than 50% over 12 h. Between 8 and 12 h elapsed time, the change in mass adsorbed is always less than 6%. It would be natural to conclude, if the data were more scattered, that the isotherms were settling into a plateau.

A different interpretation is suggested by Fig. 2. In this figure, the data of Fig. 1 are plotted on a log-log scale. The data for the four different molar mass polymers all appear to fall on straight lines over two decades of time, suggesting empirically that the mass adsorbed follows a power law in the elapsed time over the time scales investigated. The slopes of 0.066, 0.081, 0.093, and 0.117 correspond to polymer molecular weights of 750000, 400000, 107000, and 7700, respectively, implying faster kinetics for the smaller chain lengths. On the logarithmic time scale there is no suggestion that a steady-state amount of mass adsorbed is even approached.

The failure to reach plateau in mass adsorbed was initially worrisome. It contrasts with a large body of data in the literature.[1-4] In those cases, however, it happens that most of the rate measurements were made from stagnant solution, if onto single surfaces,[8,9] or from gently agitated solution, if onto colloidal particles.[10,11] Indeed, few studies exist which used single surfaces. For adsorption onto colloidal particles, rates have been reported to be faster when magnetic stirring was used rather than tumbling,[11] indicating the sensitivity of adsorption kinetics to experimental detail. Apparently, only one study[12] has systematically probed adsorption of high polymers onto a single surface as a function of shear rate—but the rates involved were much higher than in the present case (100–7800 sec^{-1}). Furthermore, it is unclear whether all previous experiments had the necessary signal resolution to detect the small deviations from the apparent adsorption plateau, at long times, that we observe.

Figure 3 illustrates what happened when PMMA of molecular weight 49000 g/mole was adsorbed from stagnant, dilute CCl_4 solution, i.e., in the absence of macroscopic flow past the surface. It is striking that under this condition, a plateau in the mass adsorbed *is* observed. In addition, the path to plateau is slower than under conditions of shear flow at 3 sec^{-1}. The log-log slope for the early-time stagnant-adsorption data in Fig. 3 is only 0.025, about $\frac{1}{4}$ that obtained in the case of flowing solutions. The control experiment consisted of the determination of what occurred, after the plateau was reached under stagnant conditions, if flow was then initiated. Figure 3 shows that in this case the rate of mass adsorp-

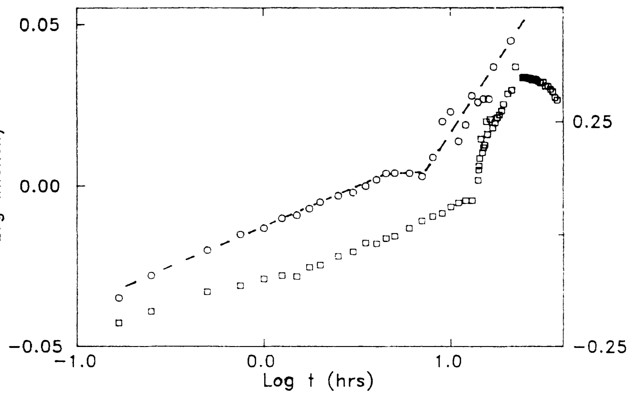

FIG. 3. Logarithmic intensity of carbonyl peak of polymer B (circles) and of C-H peaks of polyisoprene ($M_w = 135000$; $M_w/M_n = 1.04$) (squares) plotted against logarithmic time. Initial adsorption is from stagnant solution. At 8.5 h (polymer B) and 12 h (polyisoprene), flow was begun with shear rate 3 $\sec^{-1}$. At 24 h, polyisoprene flow was stopped. Left ordinate: PMMA. Right ordinate: polyisoprene.

tion *resumed* its rise with an increased log-log slope and no sign of plateau even after twelve additional hours.

The molecular-weight dependence of these high-affinity isotherms is in agreement with both theory and previous experiment.[1-4] The faster kinetics for smaller chain lengths, as indicated by the slopes of the log(adsorption) versus log(time) plots, is intuitively reasonable but does not appear to have been reported previously. It may reflect the increased mobility of the smaller chains in both rearranging to accommodate later-arriving chains and exchanging with other chains in solution.

The curious and unexpected feature is the effect of low shear flow past the surface. While a steady-state plateau was reached under stagnant solution conditions, under steady-shear-flow conditions no hint of plateau was seen for polymers differing in molecular weight by a factor of 100. Contrary results, of flow-*inhibited* adsorption, were found in a study of polystyrene in cyclohexane near the θ temperature.[12] In these experiments, however, the shear rates were much larger, ranging from 100 to 7800 $\sec^{-1}$. The present experiments suggest that different rates of shear flow have profoundly different consequences on polymer adsorption.

Our central experimental finding is the lack of equilibration under flow. The changes that we observe are small but well beyond the bounds of experimental uncertainty. The origin of the empirical power laws, in particular whether they reflect true scaling behavior or are only apparent, is unclear at present. Being in poor solvent conditions, one might suspect phase separation to mediate the effects of flow. Since we do not appear ever to reach equilibrium, this issue is difficult to address conceptually. Included in Fig. 3 are preliminary findings which indicate a similar flow effect for a different polymer in a better solvent, poly(isoprene) in carbon tetrachloride.

Although "multilayer" formation has no place in modern theories of polymer adsorption,[1-4] a number of workers over the years have interpreted their data in terms of this rather vague notion.[13] More recently, Barham *et al.*[14] reported perturbations of the viscosity in thin capillaries so large as to suggest the production, under flow, of layers up to several microns thick. This was noticed[14] for PMMA, polystyrene, and several other polymers of high molecular weight, in good solvents as well as poor ones. Also for the polystyrene-mica system,[15] failure to attain an adsorption plateau under conditions of gentle stirring has been noted. The proposal has been advanced[14] that solution polymer becomes entangled with the adsorbed layer, so that macromolecules could become trapped at the wall even though they are not physically attached to it. The data presented here for species of much lower molecular weight than in the above studies are qualitatively consistent with this picture. However, the increased mass adsorbed under flow (cf. Fig. 3) was modest. Moreover, it is not reasonable that a species with molecular weight as low as polymer A could become entangled.

What is difficult to assess as a cause of the continuing buildup of polymer is the possible role of stress-induced diffusion.[16] In this picture the adsorbed amount could reach a new plateau in the presence of flow, a prediction for which we have no experimental evidence, but which we cannot rule out since experimental events proceeded on a logarithmic time scale. The higher shear rate near the surface produced by increased polymer concentration could act to reorient the polymer chains with respect to the surface. This reorientation, involving fewer adsorption sites per chain, could liberate additional space at the surface to which additional polymer molecules could diffuse.[17] It is true that given our low molecular weights and low macroscopic shear rate, stress-induced diffusion in unbounded liquids would be weak compared to Brownian motion. In the present context of high concentration gradients occurring in the adsorbed layer, the relative strength of the effect is unclear.

As de Gennes has emphasized,[4] virtually all the available theories of adsorbed polymer structure[1-4] are based on the assumption of a state of thermodynamic equilibrium. The rich kinetics we observe suggests that this assumption is restrictive. Elucidation of more difficult nonequilibrium questions of motion and relaxation in surface layers seems required for a full explanation.

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