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Polymer Lateral Diffusion at the Solid−Liquid Interface

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Diffusion is always fundamental, yet problematical to measure at surfaces. Indeed, focus is intense upon the dynamics of flexible polymers in the bulk[1] but not yet regarding polymers at the solid−liquid interface.[2,3] The reason is the historical paucity of suitable experimental methods by which to obtain direct, quantitative data. This limitation has been removed with the advent of experiments based on detecting fluorescence from single molecules. Prior studies from this laboratory presented data[4,5] and possible theoretical models[5] for polymer chains diffusing, at the solid−liquid interface, at concentrations so dilute that there was minimal chain−chain interaction of the molecules. This left unanswered the important question of polymer−polymer interactions when the surface coverage was raised above the dilute limit. Indeed, a long history of studying polymer diffusion in bulk (three-dimensional) solutions shows that the influence of interactions between the diffusing objects is enormous.[1]

In this study, we present what we believe to be the first experiment to study polymer surface diffusion over the full concentration range, from minimal chain−chain interaction (dilute) to predominant chain−chain interaction (concentrated). A provocative nonmonotonic dependence is shown − the surface mobility at first increases with increasing surface concentration, and then decreases abruptly. This behavior is quite unlike the concentration dependence known for polymers in bulk solution[1] and was not anticipated in this area of study, but can be rationalized by the speculative interpretation presented below.

The sample was poly(ethylene glycol) (PEG). Starting from the parent sample, amine-terminated at one end and methoxy-terminated at the other end (Shearwater Polymers, Inc.), the fluorescent label, Alexa 488 (Molecular Probes, Inc.), a derivatized rhodamine green molecule with exceptionally bright fluorescence and stability against photodegradation, was attached at the amine terminus. The number-average degree of polymerization of the PEG was 244 (number-average molecular weight before labeling of $M_n = 10\,800$ g mol^{-1}), and the ratio of weight-average to number-average molecular weight was 1.02. The surfaces were fused silica cover slides (ESCO Products) treated with condensed octadecyltriethoxysilane (OTE) to render them hydrophobic using methods described previously,[5] and the polymers were allowed to adsorb to it from in 1 mM aqueous phosphate buffer at pH = 8.4. This hydrophobic surface was selected because PEG of this modest chain length does not adsorb to hydrophilic (unmodified) silica surfaces but does adsorb to these hydrophobic surfaces, with sticking energy $\approx 0.5\ k_BT$ per repeat unit.[5] The surface concentration of adsorbed polymer was quantified by parallel experiments using Fourier transform infrared spectroscopy in the mode of attenuated total reflection (FTIR-ATR).[5]

To reach levels of surface coverage higher than dilute, first the labeled chains were allowed to adsorb to a dilute concentration from nanomolar solution such that the fluorescence signal came from ≤ 1 molecule on the average, then the solution was rinsed copiously to remove residual nonadsorbed polymer, and finally unlabeled polymer from the same batch was added from solutions of higher concentration. Control experiments showed no desorption of the fluorescent-labeled polymer into the bulk (<5% over the experimental time scale of 8−10 h). This is to be expected from the prohibitively large activation energy for all segments of the adsorbed chain to leave the surface simultaneously. Therefore, the diffusion that we measured was strictly lateral, in the plane of the solid−liquid interface.

A mode locked Ti-sapphire laser with a pulse width < 100 fs provided the source for two-photon fluorescence excitation. The raw data consisted of temporal fluctuations of the photon counts within the small volume (effectively a planar area since diffusion was in the plane of the surface) created by the focused laser beam as labeled polymers diffused through it; the intensity of fluorescence fluctuated,[6,7] and from the rate of fluctuations the translational diffusion is implied.[5,7]

In the graph presented below, each datum is the average of 10−20 experiments performed at different locations on the surface. Fits of these data to the simplest reasonable model, a single species diffusing laterally, determined the mutual diffusion coefficient in the plane of the surface (D), which at dilute coverage, as was the case here, equals the translational diffusion coefficient. Usually the measurements began 1 h after adsorption, but control experiments showed no difference when up to 12 h were allowed for equilibration, signifying that the chain conformations equilibrated even at the shortest equilibration times. Figure 1 shows D plotted against adsorbed concentration.

In Figure 1, the most dilute surface coverage is 2.8×10^{-4} mg m^{-2}, which amounts to 240×240 nm^2 per molecule. To estimate the overlap surface concentration c_{2D}*, we suppose by Occam's razor the same persistence length as for PEG in bulk solution and good solvent thermodynamic conditions on the surface just as in bulk aqueous solution. In a good solvent, the radius of gyration of a 2-D (two-dimensional) chain scales at the $^3/_4$ power of degree of polymerization.[8−10] It follows that $c_{2D}^* \approx 0.05$ mg m^{-2}, which is far on the low end of the concentration scale in Figure 1. Finally, note that pressure−area isotherms of PEG monolayers at the air−water interface show that dense 2-D surface coverage amounts[11] to ~0.4 mg m^{-2}. It is tantalizing that the precipitous slowing-down in Figure 2, at $c \approx 0.4$ mg m^{-2}, is close to the expected close-packed density of 2-D chains,[11] but no quantitative explanation is offered at this time. Higher concentrations surely reflect loop-train-tail conformations with an increasing proportion of loops.

It is reasonable to ask if the findings at high surface coverage were influenced by the known susceptibility of PEG to aggregation and crystallization.[12−14] If so, a single diffusion process would not be observed, as aggregation and crystallization are known to produce objects of polydisperse size, and the data were inconsistent with this. Figure 2 contrasts representative autocorrelation functions in the extreme cases of dilute and concentrated surface coverage.

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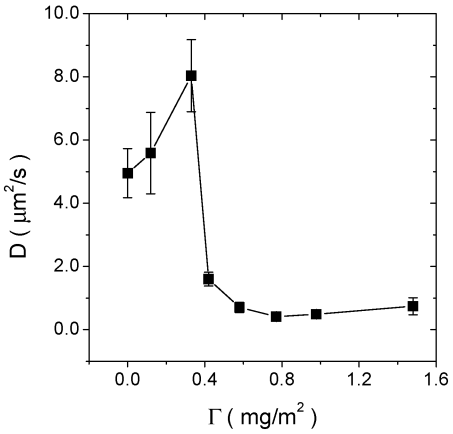

Figure 1. Lateral diffusion coefficient of PEG (M_n = 10 800 g mol^{-1}) at the solid−liquid interface in aqueous environment at pH = 8.4 is plotted against adsorbed concentration. The error bars are the standard deviation measured in 10−20 repeated experiments at different spots on the test surface.

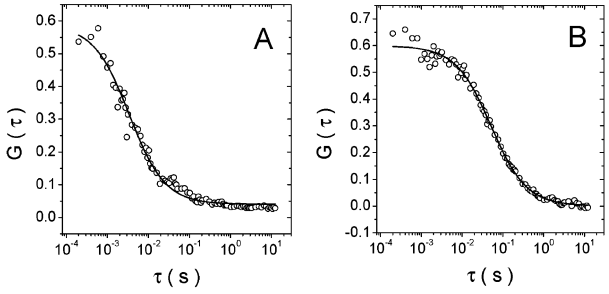

Figure 2. Fluorescence intensity−intensity autocorrelation function, normalized to unity at short times, for PEG (M_n = 10 800 g mol^{-1}) at the solid−liquid interface in aqueous environment at pH = 8.4. Panel A shows illustrative data taken at dilute surface coverage, 2.8×10^{-4} mg/m^2; panel B shows illustrative data taken at concentrated coverage, 0.77 mg/m^2. The improved fit to the model of a single process of translational diffusion demonstrates that the restrictions on diffusion were more homogeneous when the surface coverage was high.

In the former case, we interpret occasional small deviations from the model of a single diffusion process to reflect the influence of unavoidable inhomogeneities in the surface chemistry and topographical makeup. This was observed sometimes (e.g., Figure 2a) and in many other experiments not observed (Figure 2b), probably because of surface chemical heterogeneity in experiments such as that illustrated in Figure 2a. The main point is that this was not an issue when the surface coverage was larger. Neighboring chains apparently presented a more homogeneous environment than did the underlying solid surface itself.

To test more directly the alternative hypothesis that the changes in lateral mobility in Figure 1 could reflect a new surface conformation of the polymer, perhaps helices,[12−14] we performed additional in-situ ellipsometry experiments of layer thickness, using a sensitive phase-modulated ellipsometer constructed in this laboratory after a known design.[15] In this design, measurements are made near the Brewster angle to enhance the sensitivity. The raw data were ellipticity, $\rho \equiv Im(r_p/r_s)$, where r_p and r_s are the complex reflection amplitudes for p and s polarizations, respectively. The result was that ellipticity was directly proportional to surface coverage measured independently by FTIR-ATR. This in turn signifies that the differential refractive index of PEG at the surface was independent of surface coverage, which argues strongly against the alternative hypothesis. Having with these control experiments done our utmost to rule out trivial explanation, we proceed to a speculative interpretation.

Conformations of adsorbed chains lie at the heart of this matter. In this field of study, chains at the most dilute surface coverage are believed to adopt "pancake" conformations, flat against the surface, because general considerations show that the enthalpy gained outweighs the entropy lost.[16] At higher surface coverage, it is not so; chains adopt fuzzy "loop-train-tail" conformations instead, because sufficient chains are present to coat the surface with adsorbed segments without sacrificing so much conformational entropy.[2] When one considers that the transition between these limiting regimes should on physical grounds be continuous, it is reasonable to suppose that the speeding up of D, in the regime where the surface coverage was larger than c_{2D}* but less than a monolayer, may reflect the smaller number of adsorption sites as chain conformations shifted from pancake toward loop-train-tail conformations. The enhancement of mobility reflects fewer chain segments hopping on the surface. The abrupt slowing down at higher surface coverage is phenomenologically reminiscent of "jamming"[17] that has been much discussed in recent literature in connection with three-dimensional systems.

In summary, these measurements quantify, for what we believe to be the first time, how polymer self-diffusion at the solid−liquid interface compares when the surface coverage is concentrated or dilute. The results are significant because, unlike the case in bulk solution, the dependence on surface coverage was not monotonic. Indeed, a reasonable guess might have anticipated precisely the opposite finding − simply that chains would diffuse faster and faster with increasing surface coverage as their conformations switched from "pancake" to "loop-train-tail". This expectation was confirmed up to a point, and then was found to fail. Crowding by neighboring chains appeared to dominate instead.

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