

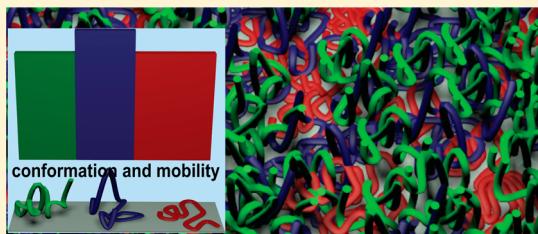
Revisiting Polymer Surface Diffusion in the Extreme Case of Strong Adsorption

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Supporting Information

ABSTRACT: Revisiting polymer surface adsorption with a level of quantification not possible at the time of earlier seminal contributions to this field, we employ fluorescence microscopy to quantify the in-plane diffusion of end-labeled polystyrene adsorbed onto quartz and mica from cyclohexane solution, mostly at 25 °C. Care is taken to prohibit a surface-hopping mechanism, and the experimental techniques are adapted to measurements that persist for up to a few days. The main conclusion is that we fail to observe a single Fickian diffusion coefficient: instead, diffusion displays a broad multicomponent spectrum, indicating that the heterogeneity of surface diffusion fails to average out even over these long times and over distances (~600 nm, the diameter of a diffraction-limited spot) greatly exceeding the size of the polymer molecules. This holds generally when we vary the molecular weight, the surface roughness, and the temperature. It quantifies the long-believed scenario that strongly adsorbed polymer layers (monomer–surface interaction of more than $1k_B T$) intrinsically present diverse surface conformations that present heterogeneous environments to one another as they diffuse. Bearing in mind that in spite of adsorption from dilute solution the interfacial polymer concentration is high, ramifications of these findings are relevant to the interfacial mobility of polymer glasses, melts, and nanocomposites.



INTRODUCTION

Challenging an extensive literature on polymer adsorption, which viewed polymer adsorption as irreversible when the monomer–surface interaction exceeds the thermal energy $k_B T$,^{1–4} recent studies show provocative cases in which adsorbed polymers diffuse from spot to spot on surfaces by hopping first off the surface and then back onto it.^{5,6} However, this refers to cases of weaker adsorption where chains are so tenuously adsorbed that they are prone to desorb. In a favorable polymer–surface system in which the sticking energy could be varied, single-molecule observation revealed that increasing the sticking energy removed the hopping mechanism.⁵ With this in mind, the recent quantification of the hopping-derived surface lateral mobility^{5,6} makes it interesting to revisit the other extreme of strong adsorption. Our survey of the literature shows, to the best of our knowledge, no prior quantification of in-plane surface diffusion in the limit of strong adsorption.^{7–9}

There are several difficulties in contemplating such an experiment. First, single-molecule methods used to study cases of weak adsorption cannot, for technical reasons (see below), be used when diffusion is much slower. We solve this difficulty by adapting an older experimental technique, fluorescence recovery after photobleaching (FRAP). Second, because it can be problematical to demonstrate satisfactorily the absence of a condition, there is the difficulty of how to demonstrate the absence of off-surface hops. But because hops tend to drive polymer to desorb, the quantity adsorbed diminishes

continuously with time when hopping occurs,^{5,6} so this can be checked by monitoring the amount adsorbed. In this study, we confirm that the amount adsorbed remains essentially constant. This condition is obtained by the process of sample preparation. The surface layers were prepared by polymer adsorption followed by extensive solvent rinses; we waited hours for the loosely bound chains to desorb after each rinse. No reduction in the surface fluorescence intensity was observed after at least 20 such rinses.

The question then becomes to decide what sorts of findings would be expected on the basis of the existing physical understanding of this system. At one extreme, one would expect a kind of dynamic heterogeneity, as is routine now to expect for polymer glasses;^{10,11} in this view, no single average diffusion coefficient would be meaningful, but instead one should expect a spectrum. At the other extreme, one would expect heterogeneity to average out, provided that experiments could be performed over time scales that were sufficiently long. Seeking to address this difficulty, the experiments presented below extended for at least 12 h and in some cases for up to 80 h.

In designing the experiments reported below, the system was selected to consist of polymer films that, to preclude bulk diffusion, were molecularly thin: polystyrene dissolved in

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cyclohexane, a θ solvent, was allowed to adsorb onto quartz to saturated surface coverage at a temperature (25.0 °C) below the θ temperature (34.5 °C). This method of depositing polystyrene is known to have a thickness of roughly the radius of gyration while avoiding bulk phase separation at this temperature.^{12–15} Such ultrathin polymer films can even be peeled off the substrate when immersed in water.¹⁶ Satisfying the desideratum of strong segmental adsorption characteristic of the systems that we seek to model and precluding interfacial migration by adsorption–desorption,⁴ the relative segment–surface interaction, in favor of replacing surface-bound cyclohexane by surface-bound polymer segments, is known from the literature to be $\epsilon \approx 2k_B T$.¹⁷ Here, the desorption of an entire chain molecule with many constituent adsorbed segments becomes energetically unfavorable because it requires the collective detachment of all adsorbed monomers all at once.^{2,3} Such irreversibility of adsorption, even when an adsorbed layer is exposed to pure solvent, was also confirmed by many earlier experiments on adsorbed polymers under solvent rinsing, in which desorption took place only under very high shear flow.^{18–23} An interesting irony is that despite the intuition of many polymer scientists that surface diffusion of strongly adsorbed layers is slow and heterogeneous, the evidence is indirect.^{3,4,17,21–28} Beyond the hopping experiments noted above, there exist few direct measurements of polymer interfacial mobility, with these being only at low to moderate surface coverage.^{7,8,29} An artistic representation of diverse conformations that can be anticipated for strongly adsorbed polymer layers is shown in Figure 1.

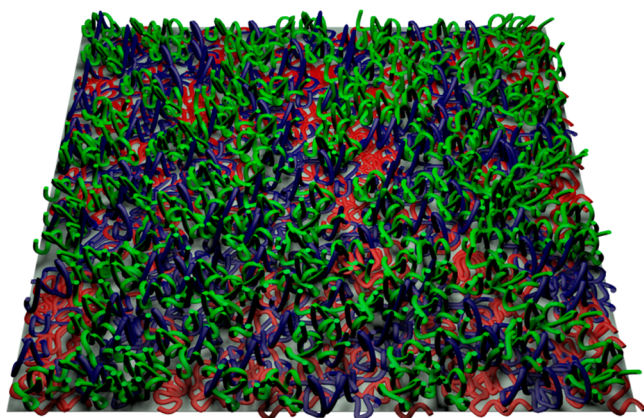


Figure 1. Hypothetical scheme of strongly adsorbed polymer layers with a broad conformational distribution and resulting dynamical heterogeneity. In this article, the surface is the solid–liquid interface. Different colors represent different levels of bound fraction per chain. With increasing bound fraction, one has green–blue–red.

EXPERIMENTAL SECTION

Preparation of Adsorbed Polystyrene Layers. Polystyrene was end-labeled with a fluorescent probe, one per chain, by reacting amine-terminated polystyrene (Polymer Source Inc.) with a neutral-charged lipophilic dye, BODIPY succinimidyl ester (493/503, Life Technologies), by which the influence from preferential dye adsorption was minimized.⁷ Unattached dye molecules were removed by repeated precipitation (>5 times) of THF-dissolved polymer solutions into methanol. The final products were vacuum dried for a week at room temperature and then stored in a –20 °C freezer. Three polymer samples were examined (33, 120, and 300 kDa with polydispersity indexes of <1.04, 1.04, and 1.18 respectively). Below, the data refer to

PS 300 kDa unless mentioned otherwise. The diffusion coefficient in dilute bulk solution was $\sim 15 \mu\text{m}^2/\text{s}$, as determined by us using two-photon fluorescence correlation spectroscopy, FCS, as described below and in Supporting Information.³⁰

The adsorbed polymer films were prepared by allowing dilute solutions (0.01 mg/mL) of labeled polystyrene in cyclohexane to adsorb onto quartz (fused, SPI Supplies) cleaned thoroughly by piranha solution ($v(98\% \text{H}_2\text{SO}_4)/v(30\% \text{H}_2\text{O}_2) = 3:1$) followed by treatment in an oxygen plasma cleaner (Harrick Scientific).⁵ The root-mean-square roughness is 0.55 nm, examined previously in this laboratory by AFM.⁷ The temperature was 25.0 °C unless specified otherwise, controlled by a commercial thermal stage with ± 0.1 °C resolution (Instec Inc.). After 24 h of equilibrium time, the sample was rinsed extensively with pure solvent, cyclohexane. The rinsing was repeated for >20 times (multiple rinses each time) within another 12 h to the point that no further chains desorbed. The surface excess, proportional to the fluorescence intensity, was monitored *in situ* through a diffraction-limited laser spot as described below in the section regarding the FRAP protocol.

The uniformity of the adsorbed layer, free of phase-separated domains, was confirmed by mapping out the fluorescence intensity at various spots. A control experiment showed that while still-lower temperatures produced phase separation (Figure S1), the films were homogeneous at 25 °C, as further validated by fluorescence imaging as summarized in Figure 2a. Ellipsometry resolved the film thickness in

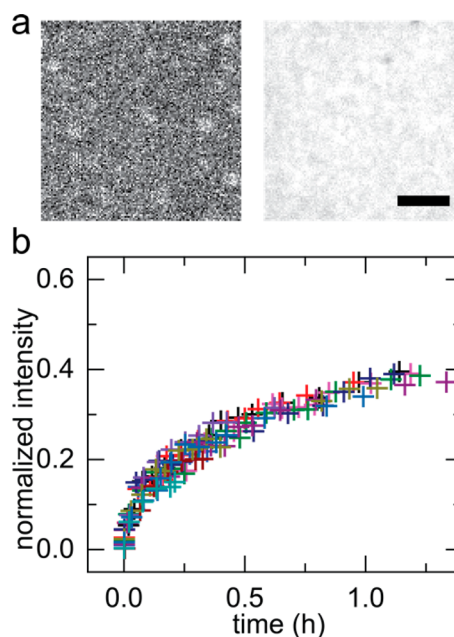


Figure 2. (a) Images of fluorescent end-labeled polystyrene at (left) dilute surface coverage and (right) high surface coverage at 25 °C, demonstrating that the adsorbed films are uniform in both cases. Each bright spot represents a chain, and the two images are on the same intensity scale. The scale bar is 2 μm . (b) Example of more than 10 individual measurement for each condition. The final FRAP curve is the average of them.

the dried state, 3.6 nm for 300 kDa PS (1.5 nm, 2.2 nm for 33 kDa and 120 kDa PS, respectively). Considering that the thickness with cyclohexane present should be ~ 10 nm for this system,^{13,14} the volume fraction of the adsorbed film should be $\sim 40\%$. This is consistent with a surface excess of $\sim 4 \text{ mg}/\text{m}^2$, known from prior experiments in this laboratory.¹²

FRAP Protocol and Analysis. The single-molecule experiments that this laboratory employed previously⁵ to measure surface diffusion do not apply for strongly adsorbed chains because their diffusion is prohibitively slow, so much so that fluorescent dyes lack the photostability required to measure this slow diffusion. For an example

of how slow, this study concerns polymer diffusion slower than 10^{-16} m^2/s , i.e., slower than 10^{-4} $\mu\text{m}^2/\text{s}$ in units that are more system-friendly. Therefore, our measurements of interfacial mobility employed fluorescence recovery after photobleaching (FRAP).³¹

Fluorescence recovery after photobleaching (FRAP) was measured after bleaching a diffraction-limited spot using a home-built one-photon confocal microscope.³¹ This experimental approach presented the advantage of having a well-defined bleaching area defined by the Gaussian illumination beam and also high time resolution of data acquisition. The laser beam (488 nm, continuous wave) was split into two by a dichroic mirror. The bleach beam and the probe beam were directed into a 63 \times air objective (NA = 0.75, Zeiss) via a dichroic mirror and were tightly focused onto a diffraction-limited spot ($\omega \approx 0.3$ μm is the half width of the Gaussian beam). The bleaching beam at the sample was kept at ~ 4 mW power. As for the probe beam, its power was kept at ~ 0.03 μW power, which is particularly weak in minimizing the heating and photodegradation of the dye. The surface excess during sample preparation (adsorption and rinsing) was also measured by this probe beam.

FRAP measurements began with photobleaching the fluorescent probes within the surface by brief exposure to the bleach beam for 30–100 ms. Polymers from unexposed areas of the sample, carrying intact fluorescent probes, diffused back into the bleached spot. The fluorescence intensity recovery in the bleach spot, whose source was this inflow of unbleached molecules, was monitored by the probe beam. The emitted fluorescence signal was collected through the same objective, collimated, and focused through a 30 μm pinhole onto an APD (avalanche photodetector). The acquisition time for each data point was 1 s. An automatic shutter was used to allow the probe beam to excite the sample for only 5 such data points, and each fluorescence recovery curve was obtained by repeating this operation 5–10 times. We further corrected for residual unavoidable photobleaching from the probe beam as described in the Supporting Information (Figure S2). Ultimately, more than 10 curves were acquired for each experimental condition and averaged for analysis (Figure 2b)

RESULTS AND DISCUSSION

To measure in-plane surface diffusion, one should avoid desorption/readsorption events. Before initiating measurements, we waited at least 24 h after adsorption, a time sufficient to reach the estimated conformational equilibration in this system.¹⁷ Then the surface excess decreased gradually in the course of the solvent rinse but after a sufficient number of rinses reached an absolute plateau that corresponds to no further desorption. Although it is true that earlier experiments on a similar polymer–surface system under continuous solvent rinsing showed that desorption could be produced by very strong shear flow,^{18,20,32} in the present study our intermittent rinsing was carried out gently with minimal flow. Moreover, we realized that, after rinsing, segments tend to reoccupy the surface sites vacated by the loosely bound chains that had desorbed. Therefore, before initiating photobleaching experiments after rinsing, we waited an additional 40 h to allow time for this step of conformational equilibrium. The experimental design is summarized in Figure 3a. Upon exposing the previously bare surface to polymer solution, the amount adsorbed reached a plateau rapidly, within 1 h. The solvent rinse step caused the fluorescence intensity to drop by $\sim 20\%$ as loosely bound chains left the surface. A qualitative inspection of the raw data revealed less mobility the longer that chains sat in the adsorbed state, even after the amount adsorbed had reached a plateau (Figure 3a). This tendency held even without the step of careful rinsing: the recovery within 1 h amounted to 60% (1–3 h into the experiment) and 40% (12–24 h into the experiment) but remained at 40% when we waited even longer (up to 80 h), suggesting that conformational equilibration had

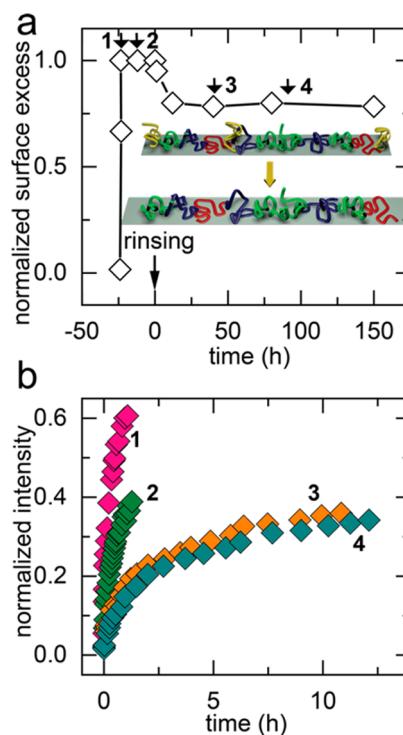


Figure 3. (a) Data showing the fluorescence intensity, normalized to the plateau adsorption, plotted against time before and after rinsing at time = 0. Four different stages are marked: 1–3 h (1), 12–24 h (2) before rinsing, and 12–40 h (3) and >40 h (4) after rinsing. The inset illustrates the desorption of loosely bound chains upon solvent rinsing. (b) Data showing FRAP curves plotted against time at four different stages identified in (a). Each curve is the average of more than 10 individual measurements.

been achieved by that time, as illustrated in Figure S3. However, after we rinsed to remove loosely adsorbed chains, recovery became even slower by a factor of 10. In experiments initiated after rinsing, only 40% of the fluorescence intensity was recovered during the first 10 h after bleaching (Figure 3b), and only 50% was recovered even 72 h after bleaching.

Our quantitative analysis pertains to experiments in this regime. Below, we argue that a single diffusion coefficient cannot fit this data, even if one considers solely the mobile fraction that contributes to fluorescence recovery.

To test whether the sluggish mobility came from the surface crowding effect due to the high local density, we compared it to diffusion in bulk polymer solution at various concentrations. Given the known thickness of films in the dry and wet states, we estimated the local volume fraction to be $\phi \approx 0.4$ for adsorbed PS 300 kDa. The bulk diffusion of polystyrene of this molecular weight in cyclohexane at this concentration at this same temperature is shown in Figure 4. Specifically, measurements were performed for PS 300 kDa at different volume fractions of up to $\phi = 0.4$ using two-photon FCS (Supporting Information). A technical point is that diffusion at surfaces did not contribute to these measurements because the focal point was kept at least 50 μm above the surface. For example, the diffusion coefficient is $D \approx 0.01$ $\mu\text{m}^2/\text{s}$ for $\phi = 0.4$; the time to traverse the diffraction-limited area of a FRAP experiment would be ~ 5 s, which is orders of magnitude more rapid than the ~ 10 h recovery times that we measured for surface diffusion. Evidently, bulk diffusion cannot explain these findings.

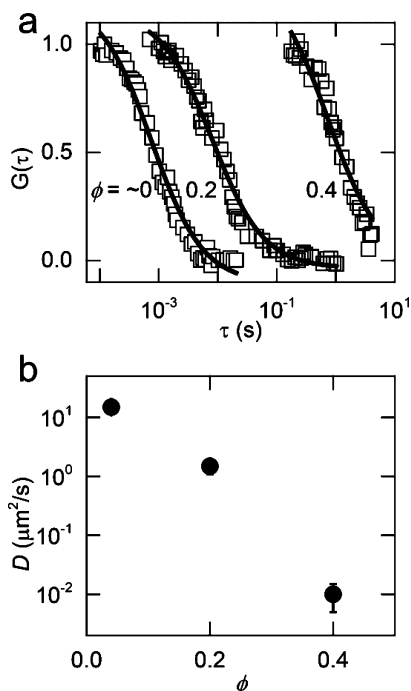


Figure 4. Bulk diffusion coefficient plotted against volume fraction ϕ for PS 300 kDa in cyclohexane solution at 25 °C. (a) Illustrative raw data: fluorescence correlation spectroscopy, with the autocorrelation function plotted against logarithmic time, in dilute solution with $\phi \approx 0$, and concentrated solutions with $\phi = 0.2$ and $\phi = 0.4$. Lines are fits of the data to a Fickian diffusion process. (b) Fitted diffusion coefficient D is plotted against volume fraction on a semilogarithmic scale.

For surface diffusion, the raw data split into one portion that is so slow as to appear immobile even on a time scale of hours in the FRAP experiments and another portion that displayed mobility on the scale of hours. To quantify the diffusivity of the mobile fraction, we use the Axelrod equation.³³ Fluorescence intensity recovery curves under a Gaussian beam with large bleaching depth of $K \gg 4$ can be described by the following equation

$$F(t) = F^0 \sum_i \nu_i K^{-\nu_i} \Gamma(\nu_i) R_i + F_0 \left(1 - \sum_i R_i \right) \quad (1)$$

where F^0 and F_0 are the fluorescence intensities before and just after bleaching with $F_0 = F^0 K^{-1} (1 - e^{-K})$, $\nu_i = (1 + 2t/\tau_i)^{-1}$, and $\tau_i = \omega^2/4D_i$ ($\omega \approx 0.3 \mu\text{m}$ is the half width of the Gaussian beam and D_i is the diffusion coefficient for each component) and R_i is the ratio of the mobile component. There exists a broad spread of diffusion species, so i could be 1 to a large number. For simplicity and to minimize the number of fitting parameters, we consider only two species, namely, $i = 1$ and 2 denoting a fast and a slow diffusion mode. By this approach (model 1 in Figure 5a), the raw data is fitted well as a bimodal distribution, and analysis quantifies its fast and slow diffusive modes (Figure 5b, see also Supporting Information). The characteristic diffusion times ($\tau_i = \omega^2/4D_i$) are 0.16 ± 0.08 h and 2.1 ± 0.8 h with relative fractions of 0.15 ± 0.06 and 0.26 ± 0.04 , respectively.

This sorts the response spectrum into three fractions: fast, slow, and immobile on the experimental time scale. Even the fastest of these is ~ 2 orders of magnitude slower than bulk

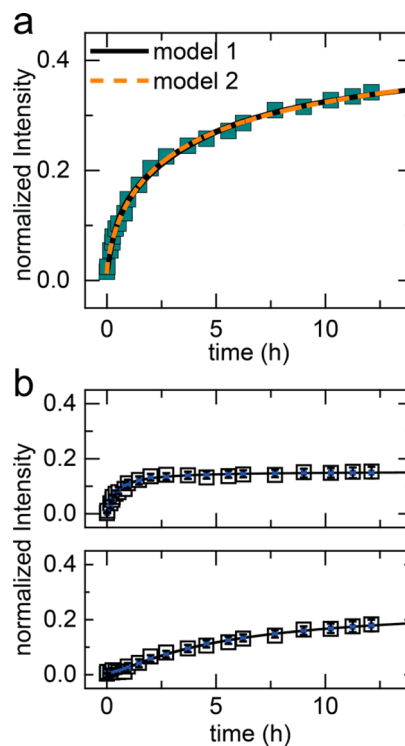


Figure 5. Fluorescence recovery curves plotted against time for adsorbed PS 300 kDa. (a) Fitted by model 1 (two components) and model 2 (anomalous diffusion). (b) Decomposition into a fast (top) and a slow (bottom) diffusive mode using the nonlinear error estimation described in the Supporting Information. Their diffusion times are 0.16 ± 0.08 h and 2.1 ± 0.8 h, respectively.

diffusion at this volume fraction. Alternatively, another fitting model (model 2) considers anomalous diffusion

$$F(t) = F^0 \nu K^{-\nu} \Gamma(\nu) R + F_0 (1 - R) \quad (2)$$

where $\nu = (1 + 2(t/\tau)^\alpha)^{-1}$ and α is a power of time. Thus, a fit subdiffusion yields empirically $\alpha = 0.5$, a subdiffusion (Figure 5a). Then the diffusion time is 0.7 ± 0.2 h with a mobile fraction of 0.51 ± 0.03 . The data are described equally well by models 1 and 2, and both analyses agree in suggesting that the relaxation time distribution is broad.^{34,35}

Similar dynamic heterogeneity was observed for the samples whose molecular weight was lower. With fluorescence intensity plotted against time, their representative FRAP recovery curves are shown in Figure 6. The recovery time and the fraction of the seemingly immobile chains decrease with decreasing molecular weight. Nonetheless, the seemingly immobile, the fast, and the slow diffusive modes coexist for all of these samples, indicating that a broad distribution of chain conformations holds regardless of the molecular weight.

The fitting results are summarized in Figure 7a,b. Note that the seemingly immobile fraction is a relative quantity that depends strongly on the acquisition time. Regarding the mobile fraction, in classical polymer science the center-of-mass diffusion coefficient (D) scales with the degree of polymerization N as N^{-1} and N^{-2} for Rouse and reptation mechanisms, respectively, for 2D random coils in the θ -solvent situation that we study, whereas the data in Figure 7 tend toward the former. To rationalize this, one argument can be that friction is proportional to fN , where f is nearly independent of N , but the comparison against only three molecular weights is at best

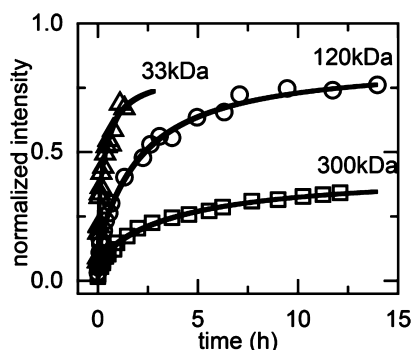


Figure 6. Molecular weight dependence of multicomponent surface diffusion. FRAP recovery curves plotted against time for three molecular weights indicated. The solid lines are fit to model 1.

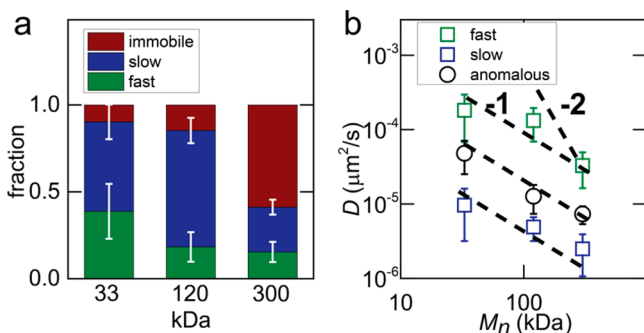


Figure 7. (a) Fitted mobility fraction of immobile, slow, and fast populations and (b) fitted diffusion coefficients based on model 1 (bimodal, fast and slow) and model 2 (anomalous diffusion). The dashed lines indicate $D \approx N^{-1}$ and $D \approx N^{-2}$, where N is the degree of polymerization. Note that because of a shorter acquisition time for that case, the immobile fraction for 33 kDa PS might be overestimated.

suggestive, though we could not resist embarking on this analysis because more adequate models and longer observation times are unavailable. From the argument, the pattern of broad surface diffusivity is confirmed, which applies to all of the polymer samples that we studied.

The spread of diffusivity further holds when the surface roughness and temperature are varied. To compare the possible influence of surface roughness, we contrasted the above-mentioned diffusion (on quartz) to diffusion on muscovite mica (freshly cleaved) that had been cleaved to be atomically smooth. To compare the possible effect of temperature, we contrasted the above-mentioned data taken at 25 °C to other data taken at 35 °C. Examples of the raw data are summarized in Figure 8 in plots of fluorescence intensity against recovery time, and their analysis using eq 1 confirms multicomponent diffusivity but the quantitative differences are also interesting. First, one notices that diffusivity was somewhat more rapid on mica than on quartz, even though it is known that the roughness of quartz is also low, ~ 0.55 nm.⁷ From Lifshitz theory, one can expect that the monomer–surface interaction on the mica surface is stronger as a result of its higher permittivity ($\epsilon_{r,\text{mica}} = 7.0 > \epsilon_{r,\text{quartz}} = 3.8$).³⁶ Therefore, it is likely to stem primarily from the difference in surface roughness, but a firm disentanglement, which matters more, was beyond the scope of this study. Second, one notices that diffusivity at the higher temperature was slightly slower. Though this may seem surprising because better solvent quality may be expected to amount to a weaker monomer–surface attraction, notice also

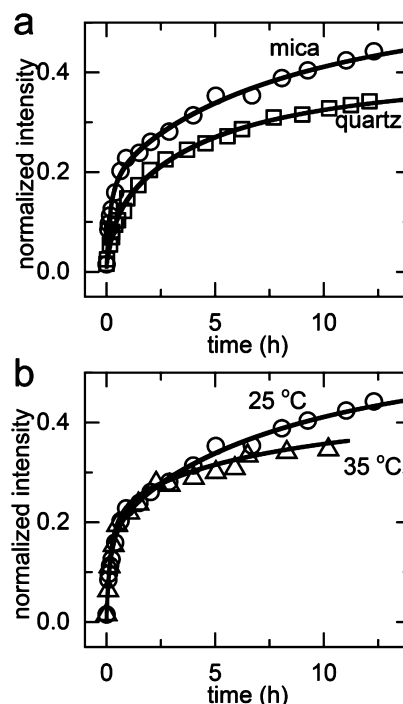


Figure 8. Influence of surface roughness and experimental temperature. (a) FRAP recovery curves plotted against time for PS 300 kDa at 25 °C, comparing quartz and mica surfaces. (b) FRAP recovery curves plotted against time for PS 300 kDa adsorbed onto mica, comparing experiments at 25 and 35 °C. The solid lines are fitted to model 1 with fast, slow, and immobile fractions. The fitting parameters for the quartz surface are given in the above text. For diffusion on mica, the fitting parameters are $R_1 = 0.21 \pm 0.04$, $R_2 = 0.41 \pm 0.07$, $\tau_1 = 0.10 \pm 0.04$ h, and $\tau_2 = 2.93 \pm 0.94$ h for 25 °C and $R_1 = 0.27 \pm 0.05$, $R_2 = 0.24 \pm 0.10$, $\tau_1 = 0.10 \pm 0.03$ h, and $\tau_2 = 3.89 \pm 1.12$ h for 35 °C.

that the amount adsorbed at 35 °C was only 40% of that at 25 °C (under 0.03 μW illumination, the fluorescence intensities are ~ 1200 and ~ 3000 counts/s, respectively). This suggests that flatter polymer conformations with accompanying higher bound fractions at the higher temperature produced slower diffusion.

CONCLUSIONS

Direct measurements of polymer lateral surface diffusion have been presented in strongly adsorbed molecularly thin films where chains intertwine not only with one another but also with the surface. Multicomponent diffusivity is observed and interpreted to originate in a broad spectrum of polymer conformations such that fast diffusion times increase roughly in proportion to the molecular weight whereas a large population of chains are so slow to diffuse that they appear to be immobile over extended times on the order of hours. This pattern held when we varied the polymer molecular weight, surface roughness, and temperature. Recognizing that the physical origins are pertinent to ideas about mutual pinning,³⁷ local constraints,³⁸ and hypothesized glass transition induced by adsorption,³⁹ we also note the relevance of these physical issues to broader interests in the dynamics of polymer glasses,^{40–42} melts^{43–45} near surfaces, nanocomposites,^{1,46} and polymer–filler systems.^{1,43–46} The interfacial dynamics reported here should influence the adhesion, friction, and dynamical–

mechanical response, extrapolating the physical ideas that are quantified in this model system.

■ ASSOCIATED CONTENT

● Supporting Information

Imaging of adsorbed polymers. Two-photon FCS measurements. FRAP data analysis. Imaging of phase-separated regions. Calibration allowing the correction of FRAP curves for photobleaching. FRAP curves plotted against time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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