

Fluorescence Recovery after Photobleaching Measurements of Polymers in a Surface Forces Apparatus

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ABSTRACT: The surface forces apparatus has been combined with fluorescence recovery after photobleaching to measure translational diffusion of polymer confined between mica sheets. This article presents findings using polydimethylsiloxane with number-average molecular weight $M_n = 2200 \text{ g mol}^{-1}$, the chains end-labeled with soluble fluorescent dye. Melts with thickness 10 nm display a translational diffusion coefficient (D) with a bulk component and a slower component assigned to surface diffusion. Reduction of thickness to 1.8 nm causes mobility to split into two populations—an immobile fraction

(immobile on the time scale of 30–60 min) and a mobile fraction who's D slow only weakly with diminishing film thickness. However, when load causes the confining mica sheets to flatten, D of the mobile fraction drops by up to an additional order of magnitude, depending on the local pressure that squeezes on the polymer. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part B: Polym Phys* 48: 2582–2588, 2010

KEYWORDS: diffusion; fluorescence; imaging; interfaces; melt; optics

INTRODUCTION When the thickness of polymer melt films is decreased to the order of molecular dimensions, the mechanical relaxation times are prolonged by many orders of magnitude and the film becomes less fluid-like.^{1–5} On the practical side, this has evident possible implications for understanding interfacial properties including fracture properties of polymer composites, polymer surface glass transition, biocompatible coatings, adhesion, and lubrication. While prolonged relaxation times are also qualitatively observed when small-molecule fluids are confined,⁶ the viscoelastic properties of chain molecules are decidedly more complex. Apart from computer simulations of confined polymer melts, the surface forces apparatus (SFA)^{3–5} and atomic force microscopy^{1,2} have been prominent experimental tools in understanding such properties. However, from mechanical properties such as force, friction, and viscoelastic response, the underlying molecular motions can only be inferred. To this end, complementary direct measures of molecular mobility are desirable, in the same instrumental apparatus that is widely used to measure surface forces.

To measure directly diffusion in these confined geometries—the Brownian motion that would underlie linear viscoelastic response—requires the use of fluorescence-based methods.⁷ Earlier experiments from this laboratory and others concerned diffusion in confined small-molecule fluids but were limited by the need to study diffusion of unattached dye.^{8–10} Fluorescence measurements by others have been used to

study the structural relaxation of glassy polymers near surfaces and interfaces, with mainly spin coated films.^{11–16} This study, in which for the first time we study diffusion in polymer melts between mica sheets in a surface forces apparatus, takes instead the approach of attaching fluorescent dye to fluid polymer chains. It turns out that as chains are sufficiently slower to diffuse than unattached dye, that this requires the implementation of new fluorescence methods, beyond the fluorescence correlation spectroscopy (FCS) that we used previously.^{8,9} This is why we implement here fluorescence recovery after photobleaching (FRAP) within a specially designed surface forces apparatus so that the thickness of the polymer film can be measured directly. This is considered to be the first implementation of the FRAP method within the mica surface forces apparatus.

EXPERIMENTAL

The experiments were performed at the University of Illinois.

Fluorescent Labeling of Polymer

Amino-terminated PDMS (P1308-DMSNH2; Polymer Source) was purchased with number-average molecular weight $M_n = 2200 \text{ g mol}^{-1}$ and polydispersity specified by the manufacturer to be $M_w/M_n = 1.15$. This molecular weight corresponds to ~ 30 repeat units.

For fluorescence experiments, a great difficulty is that most of the usual fluorescent dyes are developed for use in

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aqueous media, and that others may adsorb or lack the needed photophysical properties. After screening a large number of candidate dyes, Bodipy-FL succinimidyl ester (D-2184; Molecular Probes) was selected as the fluorescent probe because of its good photostability, high quantum efficiency, solubility in nonpolar solvent, and low propensity to adsorb on mica surfaces from PDMS melt. We confirmed that the free dye did not adsorb to mica, as was also done in the course of FCS experiments.^{8,9} After dissolving free dye in the polymer sample, the detector focus was scanned in the *z* direction with the mica sheets far apart, confirming no excess fluorescence peak at either the mica surface.

The PDMS was end-labeled in chloroform (spectroscopic grade, Fisher) by condensation using a molar ratio of polymer to dye of 1:2 for 1 h. The mixture was first blown dry with nitrogen, and was then redissolved in *n*-heptane. Multiple extractions were performed by adding methanol nonsolvent of PDMS to remove excess free dye with < nM concentration of free dye in the methanol phase while the labeled PDMS remained in the *n*-heptane phase. Typically, the extraction was performed five times. The final yield of this reaction is higher than 60%. The concentration of dye in the polymer phase was found to be negligibly small.

In the FRAP experiments that we conducted, the molar ratio of labeled to unlabeled polymer chains was 1:10000. The unlabeled chains consisted of methyl-terminated PDMS (P3342-DMS; Polymer Source) with $M_n = 2400 \text{ g mol}^{-1}$ and $M_w/M_n = 1.18$.

FRAP within a Surface Forces Apparatus

Two key modifications were made in adapting the SFA for spectroscopy. The first was to work around the design paradox that while thickness is normally measured using multiple beam interferometry between silver coatings, the use of reflective silver is incompatible with spectroscopy, as laser excitation and fluorescent emission does not pass through it appropriately. Instead, the mica was coated with dielectric coatings designed to render them transmissive at the excitation and emission wavelengths of the dye but reflective at higher wavelengths at which interference fringes could be obtained for distance determination. Improving on the choice of dielectric coatings in the original such coatings made in our laboratory,^{8,9} the dielectric coatings used for this study consisted of 9–11 alternating layers of HfO_2 and SiO_2 , giving rise to a high reflectivity window in a desirable wavelength range, as we have reported elsewhere.⁷ The wavelength window, controllable by adjusting the coating thickness, is decided by the spectral response of the excitation and emission of the fluorescent dye. These coatings are stable at operating laser power ranges and have low background fluorescence, making them well suited for this application.

The needed thickness of each coating, to produce the desired optical transmission window, was controlled by monitoring transmission at 625 nm using an optical monitor within an E-beam evaporator. Evaporation of the dielectric coating was deemed complete when the transmission in the reflective window was lower than 12%. The coatings were produced

using electron-beam deposition in the Center for Microanalysis of Materials at the University of Illinois.

The second modification was to redesign the apparatus to be so compact in size and with mica sheets located so close to a microscope objective that it can sit on the stage of an optical microscope. The original method to do so in our laboratory did not allow fine-tuning of the distance; mica sheets were either far apart or squeezed close together, without the possibility of making measurements at intermediate thickness.^{8,9} Improving on this, the apparatus was redesigned with the goal of maximizing mechanical symmetry. To change the distance between mica surfaces, they were displaced relative to one another using a closed-loop piezoelectric actuator with <1 nm accuracy (Nano P-10, Mad City Lab, Madison, WI). Finally, the sample within the working distance of the high N.A. objective was needed for high-resolution fluorescence measurements. This was accomplished by redesigning the position of the sample relative to its location in the traditional surface forces apparatus, the distance between the polymer sample and the microscope objective being < 2 mm. Although not measured in the experiments reported here, shear responses and force-distance profiles of the confined fluids can be obtained with this redesigned apparatus in a way similar to a conventional SFA.

This apparatus was placed on a Zeiss Axiovert 200 inverted microscope, in the optical configuration shown in Figure 1. Fluorescent dye in the confined PDMS melt was excited using a 488 nm CW (continuous wave) laser. The laser beam was split into two, namely, the bleach beam and the probe beam, with almost all power directed into the bleach beam. Both beams were directed into an objective lens (LD Plan-Neofluar Zeiss, 63x, N.A. = 0.75) via a dichroic mirror and was tightly focused to a diffraction-limited spot. The laser power was modulated with the use of neutral density filters.

The bleach beam power at the sample was kept constant at 4.3 mW and the total energy experienced by the sample was varied by changing the exposure time. As for the probe beam, its power was kept to 5 μW or less to avoid heating and photo-degradation of the dye. This was verified by ensuring absence of photobleaching over extended periods of time and monitoring constant photon counts from the sample in control experiments. The bleach beam power reaching the sample could be controlled to be as high as 100 mW. The final bleach power was controlled by selecting, with the help of a shutter, the exposure time of the bleach beam.

The fluorescent probes within the confined region were first photobleached by brief exposure to the bleach beam, typically for 30 msec. By virtue of diffusion, polymers from the unexposed area with their intact fluorescent probes diffuse back into the bleached spot. The intensity recovery in the bleach spot due to this inflow of unbleached molecules is monitored by the probe beam, as is standard to do using the FRAP technique. The emitted fluorescence signal was collected through the same objective, collinearized, focused through a 30 μm pinhole onto an APD (avalanche photon detector) based photon counting module (SPCM-AQR-14, Perkin Elmer

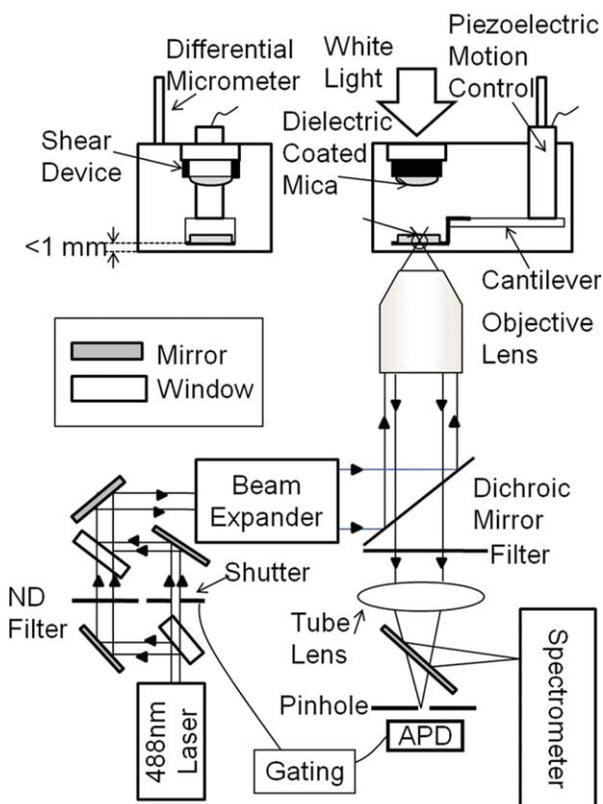


FIGURE 1 Schematic diagram showing how the optical setup to allow the performance of FRAP, fluorescence recovery after photobleaching, within a surface forces apparatus. The position control is achieved by the combination of differential micrometer and closed-loop piezoelectric device. This design can achieve motion control with the step size less than 0.5 nm, and can be stable for several hours. The bottom cylindrical lens is selected to be within 1 mm from a high N.A. long working distance microscope objective to collect the optical signal from the area of interest. In this diagram, ND denotes neutral-density filter and APD denotes avalanche photodiode.

Optoelectronics). The digitized output was collected by a NI-PCI-6281 data acquisition board (National Instruments Inc.) and correlated by a Labview based software.

Long time exposure, even to weak probe laser beams, eventually caused photobleaching. To prevent such photobleaching, exposure to the probe beam was controlled by a shutter such that it was exposed to the probe beam for 2 seconds in every 5-second cycle. Thus each fluorescence recovery curve was obtained with an accumulation of hundreds of such probing cycles.

The diameter of the bleached spot was $\sim 1 \mu\text{m}$, calibrated as described below. Although in principle one can expect polymer diffusivity to depend on location of the diffusing chains relative to the mica surfaces, in practice this could not be measured, as the film thickness of nm was less than the optical vertical resolution of μm . The small size of the bleached spot precluded direct confirmation of how the recovery times scaled with size of the bleach spot; to remedy this, we

explored systematically dependence on the power of the bleach beam, as described below. Thickness of the thin films was measured before and after each FRAP experiment to ensure that the thickness of the film remained unchanged throughout an experiment.

Measurements were made at room temperature, usually 20–22 °C.

Mica Preparation

Mica was glued onto crossed cylindrical lenses using heat-cured glue that we found to be exceptionally free of fluorescent background (Sylgard 184 Silicone Elastomer Kit, Dow Corning). Immediately before each experiment, it was tape-cleaved using the method of Frantz and Salmeron¹⁷ and a droplet of polymer was added. Experiments were performed in a sealed chamber in the presence of P_2O_5 to scavenge adventitious humidity. The chamber was also purged with argon gas overnight before the experiment to remove excess humidity.

Equilibration

The approaching rate used to reach a certain thickness in a SFA for small-molecule experiments affects the mechanical response.^{18–20} In the experiments reported here, the thickness was changed slowly, in steps of 5 nm or less, with care taken to ensure that the sample reach equilibrium after each perturbation. At least 10 min elapsed between steps. Once a desired thickness was achieved, the system was equilibrated for 2 h before FRAP experiments were initiated.

RESULTS

Fluorescence intensity did not over the workable experimental time scale return to its initial intensity before photobleaching, except for diffusion in the bulk polymer melt, as illustrated in Figure 2. This loss of fluorescence did not reflect photobleaching of background fluorescence (dielectric coatings or mica). For the present initial report of experimental findings we do not analyze this aspect, which is still under investigation, but focus instead on those chains that are mobile over our observation time window. Therefore I_0 in eq 1 below represents the recovered intensity during the experimental time window. The diffusion coefficients (D) that we inferred represent the most mobile polymers within the confined sample.

In parallel experiments, the bulk diffusion coefficients of free dyes (D_{bulk}) and tagged PDMS chains in unlabelled PDMS melt were measured using FCS. A single diffusion process for the tagged PDMS chains was inferred from inspection of the autocorrelation curves, the curves being described well by a 1-component fit. A translational diffusion coefficient consistent with literature values for this molecular weight was obtained.

DATA ANALYSIS AND CHOICE OF EXPERIMENTAL CONDITIONS

Using the experimental methodology described below, the recovery time after photobleaching was quantified. Figure 3

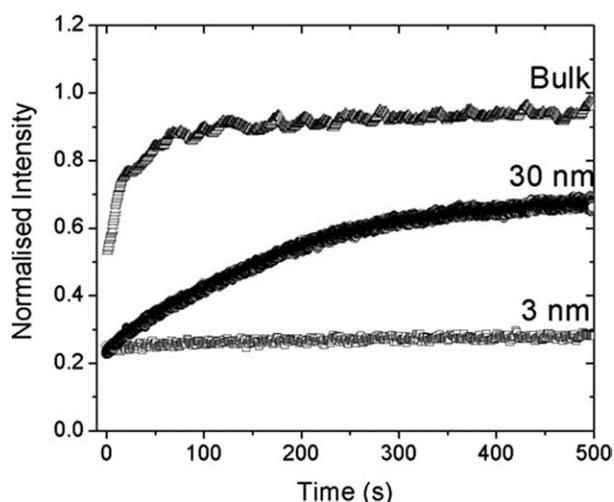


FIGURE 2 Typical fluorescence intensity recovery curves taken from FRAP experiments in this study. Fluorescence is plotted against time for bulk sample, a film 30 nm thick, and a film 3 nm thick. In the bulk, recovery over the experimental time scale is complete within experimental uncertainty, but not so for thin films.

shows the recovery time plotted against exposure time; one sees that the recovery time grew significantly with increasing exposure time, except for the shortest exposure times. This probably partially stems from larger size of the bleached spot, the larger the exposure time. There were no indications, at low bleach power, of photochemical crosslinking. Pragmatically, it caused us to limit the bleaching time to <30 msec. Laser power within the probe beam did not matter, however. This was demonstrated in experiments where

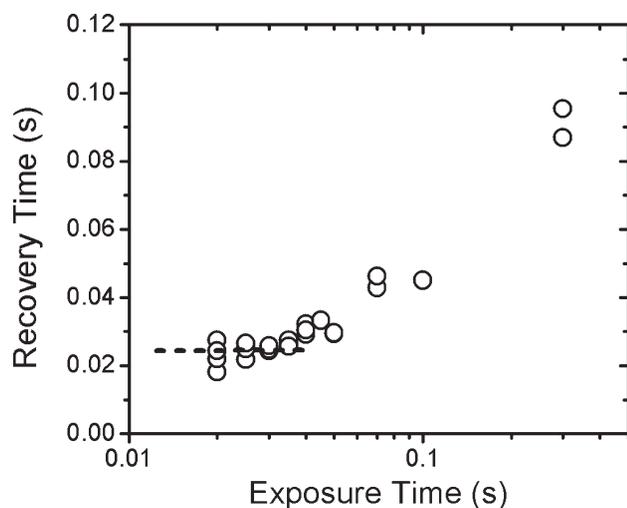


FIGURE 3 The recovery time after photobleaching bulk unconfined polymer is plotted against the time that the sample was exposed to the high power bleach beam. Longer exposure time gave longer recovery time indicating that the width of the bleached spot increased with exposure time. Subsequent experiments were performed in the regime indicated by the dotted line, <30 msec exposure time, in which data the recovery time did not depend on power of the bleach beam.

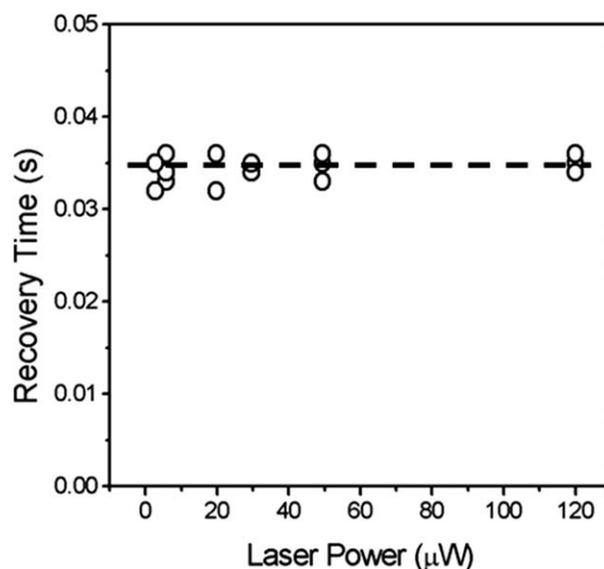


FIGURE 4 The recovery time after photobleaching bulk unconfined polymer is plotted against the power of the probe beam. The bleach time was 30 msec. There is no change in the characteristic time for the range of probe beam power used, as indicated by the dotted line through the data.

the probe beam power was varied over a wide range, as illustrated in Figure 4.

To analyze this data, the time dependence of fluorescence intensity was measured. This intensity within the bleached spot, I , varied with time, t , and the characteristic time of recovery for this diffusion process, τ , was obtained. Figure 5 shows a typical fluorescence recovery curve and compares it to predictions from eq 1. For one single Brownian diffusion process, fluorescence recovery curves should obey the equation shown below:²¹

$$I(t) = I_0 \times \left[1 - \frac{A}{\left(1 + \frac{t}{\tau}\right)} \right] \quad (1)$$

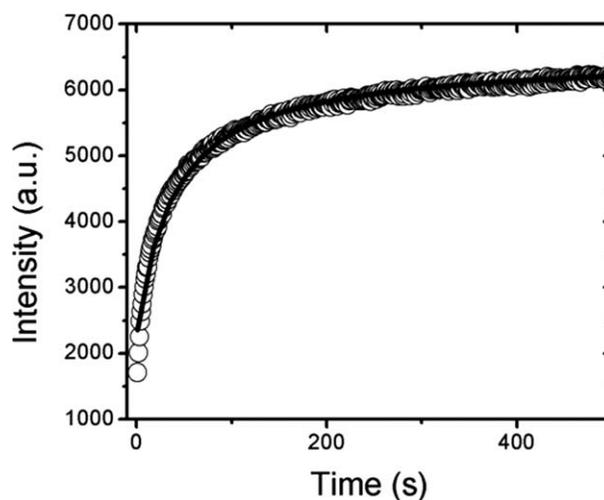


FIGURE 5 Typical fluorescence recovery curve of the mobile population, showing fit to eq 1.

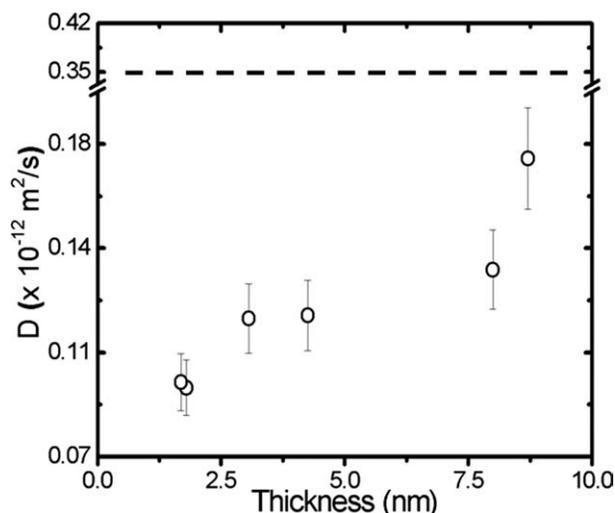


FIGURE 6 Diffusion coefficients of the mobile fraction are plotted against thickness of the confined melt with negligible load squeezing the films together. The dotted line shows the surface diffusion coefficient of the same unconfined sample, evaluated after adsorption onto a single mica sheet from the melt.

where I_0 and A are fitting constants which represent the final recovered intensity plateau and the extent of photobleaching in the bleached spot. The diffusion coefficient, D can be calculated using

$$D = \frac{\omega^2}{4\tau} \quad (2)$$

where ω , the diameter of the bleached spot needs to be known. To do so, ω was calibrated by measuring the characteristic recovery time of this polymer and using it with its known bulk diffusion constant of $7 \times 10^{-12} \text{ m}^2 \text{ sec}^{-1}$, verified by control experiments. The bleach spot diameter was thus estimated to be $1 \mu\text{m}$ when exposing the sample to identical experimental bleaching conditions as in the experiment. Within the experimental uncertainty, data in these experiments was consistent with eq 1.

How D Depends on Thickness

We measured using FRAP experiments the D_{surface} , the surface diffusion coefficient of polymers at the mica-melt interface when they are not confined by a second surface. Parenthetically, it is worth explaining how it is possible to measure diffusion at a single mica surface, given that PDMS dewets mica. These measurements were performed not strictly at a single surface but rather between two mica surfaces widely separated ($\sim 2 \text{ mm}$), the melt forming a meniscus between the two surfaces. To measure diffusion of PDMS on one sole mica surface, the optical focus was on the lower mica surface and FRAP measurements were made there. The result was that D_{surface} was $0.35 \times 10^{-12} \text{ m}^2 \text{ sec}^{-1}$, 20 times slower than the D for the bulk melt, which we measured using fluorescence correlation spectroscopy to be $7 \times 10^{-12} \text{ m}^2 \text{ sec}^{-1}$. Relative to these baselines, thickness-dependent measurements were compared.

The weak dependence on film thickness, summarized in Figure 6, is striking. Relative to surface diffusion, D measured at a thickness of 10 nm is half this value, and D measured at a thickness of 2 nm is just a factor of two smaller than this, although each of these cases is accompanied by an increasing in the absence of fluorescence recovery over the available time window of measurements, illustrated in Figure 2. It seems that decreasing the film thickness has minor influence on the mobility of the faster process, which has D on the same order of magnitude as for surface diffusion itself. Further improvement of the experimental setup will be needed to better quantify how the immobile fraction depends on film thickness.

This linear decrease of mobile fraction with decreasing film thickness (Fig. 7) is consistent with a model in which the mobility of this mobile fraction is described simply by two populations, one surface population and another not attached to the surface. But to pursue this line of reasoning would be premature since the role of the immobile fraction remains to be quantified with experiments in which the recovery process can be monitored over times long enough to observe more complete recovery.

How D Depends on Location within a Hertzian Contact

The measurements discussed to this point refer to polymer confined between crossed cylinders of mica sheets with radius of curvature $\sim 2 \text{ cm}$; the absence of visible flattening of those sheets confirmed that minimal normal load squeezed the sheets together. As we now describe, normal load caused additional slowing down of translational diffusion of the mobile chains.

For small-molecule fluids, propane diol and octamethylcyclotetrasiloxane (OMCTS), this laboratory reported previously that the diffusion coefficient of unattached probe fluorescence dye varied by nearly two orders of magnitude according to position within a Hertzian contact spot; this observation

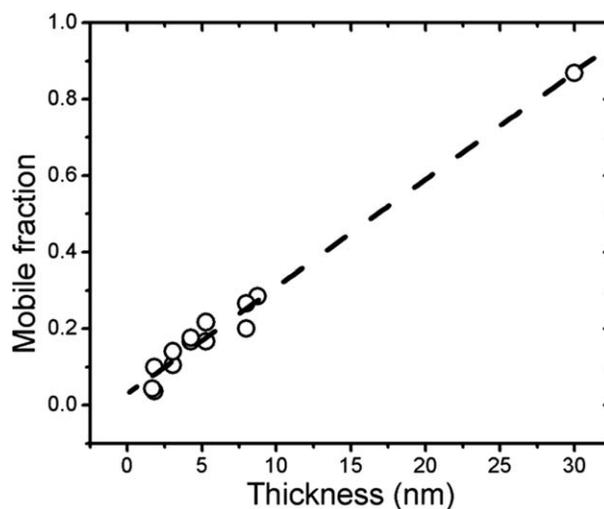


FIGURE 7 The mobile fraction evaluated from data illustrated in Figure 2, evaluated after 500 sec, is plotted against film thickness. The empirical linear relation, denoted by dashed line through the data, suggests a two-population model as described in the text.

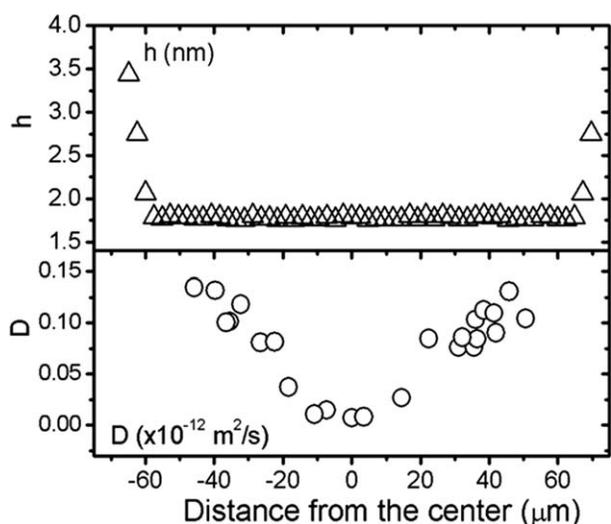


FIGURE 8 A film 1.8 nm thick, formed after equilibration for 3 days. Panel A: Thickness measured by multiple beam interferometry, plotted against distance from the center of the flattened contact region. Panel B: Diffusion coefficient (D) of the mobile fraction, plotted against distance from the center of the center. Note that D is slowest at the center, most rapid at the edges.

was tentatively interpreted as the influence of different local pressure squeezing the films together in the normal direction.^{8,9} Such differential pressures occur because when crossed cylinders in a surface forces apparatus are squeezed together, glue underneath the mica sheets deforms under external load, giving rise to a circular confinement region whose thickness is constant but with whose local normal pressure obeys Hertzian contact mechanics,²² sample closest to the center of the confined region experiencing the highest normal pressure.

By probing D at different positions within the confinement region, one can correlate changes of D with normal pressure, P for a constant thickness. For this set of experiments, the polymer melt was squeezed in a way similar to the procedures outlined for thickness dependence. The only difference was that, once no further reduction of actual thickness was observed with interference fringes, additional force was applied in steps until a contact area with diameter $\sim 120 \mu\text{m}$ was formed. As both the bleach and the probe beam diameters were much less than the diameter of the confined region, spatially resolved measurements were possible.

Figure 8 (top) illustrates that the thickness was constant across the contact spot, within the experimental resolution of 0.02 nm; this measurement was made using multiple beam interferometry in the traditional way.²³ Accompanying this, Figure 8 (bottom) illustrates that in this study of a film 2 nm thick, D was most rapid near the edge of the flattened contact and slowest at its center, implying a 10-fold drop of diffusion coefficient. Simple principles of contact mechanics allow one to deduce, knowing the modulus of the glue, the normal load that squeezed the films together to cause such flattening.²² The results of that calculation, shown in Figure 9, show that as the local normal

pressure increased from 50 kPa close to the edge of the confined area, to 300 kPa at its center, the data split into one region of minimal pressure dependence near the edge of the contact, and a second region of large pressure dependence near the center. The semilogarithmic plot in the inset of Figure 9 highlights this. If interpreted in the language of activation volume as this laboratory did previously for small-molecule fluids⁸ the apparent activation volume for mobile chains near the center of the contact would be large, 200 nm^3 -molecule. However, the tremendous loss of configurational entropy of chains in extreme confinements does not rule out the possibility of the onset of a pressure-induced glass transition at a pressure as low as 250 kPa. This might be consistent with the observation that liquids under confinement has sluggish relaxation.^{1-4,24-26} Some elastomers in particular have been known to have a long transition regime before the onset of pressure induced glass transition.^{27,28} However, such high activation volumes have never been reported before for polymers and are contrary to the idea that polymers move in units of segments.²⁹ Further experiments are needed to clarify the physical meaning of these numbers.

CONCLUSIONS

Over the years, nanorheology experiments with the surface forces apparatus and atomic force microscopy have shown that the shear viscosity of confined melts does not deviate from the bulk behavior until the thickness of the confined melt is about 5–6 times the radius of gyration, R_g , beyond which point the viscosity starts to increase dramatically.¹⁻⁴ For the present sample, this onset distance would be around 10 nm. The lack of complete fluorescence recovery in the data, over the available experimental window, suggests that slow-moving chains may dominate viscosity measurements.

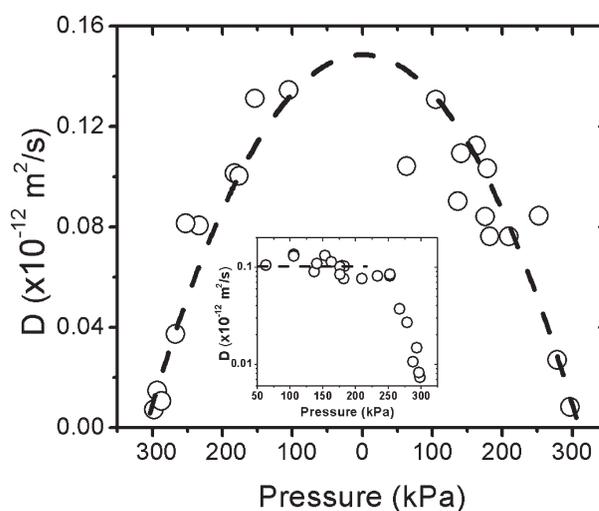


FIGURE 9 Diffusion coefficient plotted against Hertzian load pressure calculated from the data in Figure 8. The inset, a semilog plot of the same data, underscores that the data split into one region of minimal pressure dependence near the edge of the contact (dashed line), and a second region of larger pressure dependence near the center.

This may become quantifiable in the future when longer FRAP observation time windows become possible. The polymer oligomer studied in this investigation (selected for this initial study because of its low viscosity, hence relatively rapid equilibration) should be generalizable, in the future, to longer chains than this.

These direct measurements of confined polymer diffusion suggest mobility to be heterogeneous, even for a polymer oligomer—slowest for chains adsorbed on the surface and more rapid for those chains without physical attachment to it. The strong apparent dependence on local pressure, suggesting a heightened response to this standard thermodynamic variable, may be conjectured to reflect the known increased density fluctuations near the surface as a result of ordering in direction of compression and loss of configurational entropy as a result of adsorption, resulting in possibly glasslike behavior. Now that the feasibility of experiments of this kind is established and the experimental platform has been developed, the path is becoming clear in which later experiments should continue, especially to quantify the distinction between fast-moving and slow-moving chains, the FRAP observation of which is the main contribution of this study.

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