Compliance Measurements of Confined Polystyrene Solutions by Atomic Force Microscopy

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The use of the atomic force microscope (AFM) as a local probe for elastohydrodynamic lubrication is discussed. Compliances are measured with a modified AFM that allows application of ac and dc force-displacement curves on end-grafted poly(styrene) chains in good (toluene) and poor (water) solvents. In toluene, the chains form a stretched brush whose elastic modulus is an order of magnitude larger than that of the collapsed layer in water. The dc force-displacement curves are compared to those previously obtained on similar systems with the surface forces apparatus.

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It is well known that polymers play an important role in the lubrication process as viscosity modifiers, dispersants, wear protective and anticorrosive coatings and easy-to-shear boundary layers. Hence functionalized and unfuctionalized polymers are used as additives to petroleum basestocks to improve friction and wear. In the past, the surface forces apparatus (SFA) and the atomic force microscope (AFM) have been successfully applied to study the rheological properties of polymer films [1–4] and diluted polymer liquids [5–7]. AFM measurements on ultrathin self-assembled polymeric films have shown that it is possible to simultaneously measure morphology, friction, and viscoelastic mechanical properties on the submicrometer scale [8]. The strength of the AFM is its local sensitivity to a diverse number of material properties. In liquids, however, only the SFA has been used to study material properties in confined geometries since it was believed impossible to confine liquids with the strongly limited contact area of AFM. In this paper we show experimentally that when the lateral mobility is decreased quantitative confinement measurements with a nanometer contact area are possible, as theoretically predicted [9].

We present an elastohydrodynamic lubrication study using a modified AFM approach on polymer brushes in contact with solvents. We have chosen a polymer whose lateral mobility is restricted by grafting one end to the solid substrate. This system is similar to one previously studied by SFA [6,7] and provides a direct comparison of the two techniques. The approach is based on the AFM modulation technique used by various groups to measure distance dependent interaction forces [10]. In this way, we show that material properties of liquids, such as viscosity and elastic compliance, can be measured in the same way as in dynamic SFA measurements [2].

A commercially available Topometrix AFM with silicon cantilevers was used. The bar-shaped cantilevers' spring constants c_L were 0.32 and 0.33 N/m, with resonance frequencies of 16 kHz corresponding to a cantilever mass m_L of 3.2×10^{-11} kg. The cantilevers were mounted on a piezoelement which could be modulated normal to the sample surface (*z direction*) [Fig. 1(a)]. All measurements were conducted at a temperature of 25.0 ± 0.1 °C. Two types of force approach curves were carried out, as shown in Fig. 1(a): (a) dc *approach curves* and (b) ac *approach curves*. During all approach curves, the feedback control of the system was switched off. The dc *approach,* also known in the literature as force-displacement curves, provides information about the static force that is acting on the cantilever during a steady velocity approach. The force gradient provides information about the compliance of the

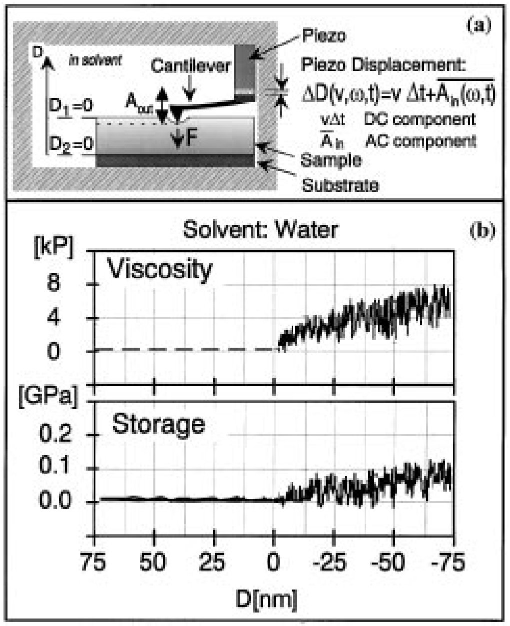

FIG. 1. (a) ac/dc-compliance method. (b) Simultaneous measurement of the dynamic storage modulus J and viscosity η' on PS in water.

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sample. The ac *approach* was performed by superimposing on the dc approach a small modulation amplitude of 5.5 nm at a modulation frequency of 3 kHz. This approach supplies storage and loss moduli. Scaling and the determination of zero value for distances we obtain from the combination of the ac and dc approaches.

A thin film of a monodisperse diblock copolymer of poly-4-vinylpyridine (P_4VP) (polymerization index $N_{\mathrm{P4VP}} = 20$) and poly(styrene) ($N_{\mathrm{PS}} = 200$) was spun cast form toluene solution onto a native oxide covered silicon (100) substrate and annealed in vacuum at 170 °C. Under these conditions the P_4VP block has been shown to adhere strongly to the silicon surface forming a PS brush [11]. Unattached polymer was rinsed off with pure toluene. A film thickness of $t_0 = 5 \pm 1$ nm was determined by ellipsometry, corresponding to a grafting density of 664 $\text{Å}^2/\text{chain}$.

The neutron experiments were performed in either water or toluene, as described in Ref. [12], on the H-9A reflectometer at Brookhaven National Laboratory.

Topographical AFM images in air and in water, both considered poor solvents for PS, revealed islandlike structures. These features, which are a function of the grafting density, have been shown [11] to occur when a stretched polymer brush is removed from a good solvent. The unfavorable interactions with the bad solvent causes the chains to collapse and associate on the surface forming islandlike structures [11]. Force-displacement curves in water were measured on top of the interconnected structures. We define D as the total displacement of the cantilever towards the sample (i.e., piezo movement in the z direction). $D = 0$ is determined from the ac measurements. In Figs. 2(a) and 2(b) we show the dc approach curves in water and toluene on bare silicon and on the PS layer covered silicon surface. The measured force F is given by $\Delta F = c_L \Delta z_L = c_S \Delta z_S = c_{\mathrm{eff}} \Delta D$, where Δz_S is the sample indentation, Δz_L is the cantilever deflection, c_L is the cantilever spring constant, c_s is the sample spring constant, and c_{eff} is the effective spring constant of the two-spring system. In contact ΔD is equal to the sum of Δz_S and Δz_L. We see in Fig. 2(a) that the force-displacement slope c_{eff} measured on the polymer film in water changes with displacement. For the first 4 nm after contact, the effective spring constant is on average about half of the cantilever spring constant $\overline{c}_{\mathrm{eff}} \cong 0.5 c_L$. At larger loadings, the effective spring constant continuously approaches the cantilever spring constant. This indicates that the film deforms and stiffens under high load. When the effective spring constant becomes comparable to the cantilever spring constant it is not possible from the dc approach alone to determine whether the cantilever is probing a highly compressed polymer or the bare substrate. The ac viscoelastic response, on the other hand, can be used to discriminate between the PS film and the substrate.

In order to investigate the viscoelastic behavior of the polymer film and ac approach was applied. The experimental setup is shown in Fig. 1(a). A sinusoidal z modulation is applied to the cantilever which results in a sinusoidal force on the liquid and/or sample beneath. Storage (in-phase) and loss (out-of-phase) moduli can then be measured. The results during an ac approach of the brush covered silicon substrate in water is shown in Fig. 1(b). The piezo displacement was set to zero when the ac response reached its maximum (cf., discussion below). Positive displacement values are used in the out-of-contact regime and negative values in the contact regime. From Fig. 1(b) we can immediately see that even at large negative displacement values D we observe a finite viscosity and a very small storage moduli. This suggests that in water the tip does not penetrate through the PS film to the Si substrate.

Figure 3 shows the neutron reflectivity spectra plotted as a function of the transverse momentum vector obtained from the grafted deuterated PS (dPS) layer in water and in air. The solid lines are fits obtained with the concentration profiles in the inset according to the algorithm described in Ref. [12]. In Fig. 3 we can see a statistically significant shift to higher frequency in water which can be related

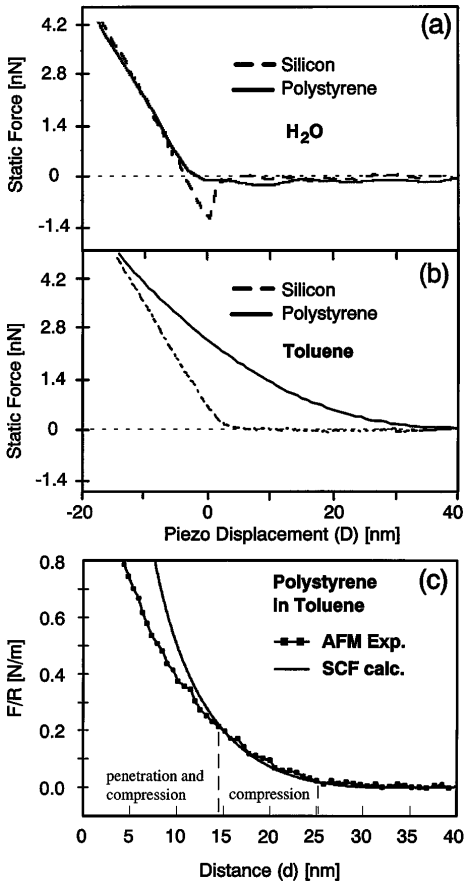

FIG. 2. (a,b) dc force-displacement curves in (a) water and (b) toluene. (c) Distance corrected plot of (b) (i.e., $\Delta d = \Delta D - \Delta F / c_L$, cf. text) normalized with a fitted contact radius $R = 2.2$ nm is compared with SCF calculations.

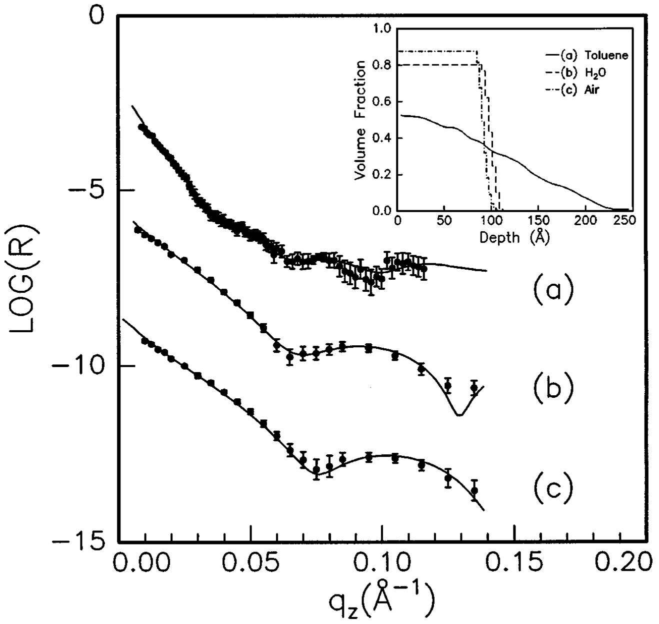

FIG. 3. Neutron reflectivity data of predeuterated PS on silicon in air, water, and toluene.

to a 7% increase in film thickness (inset of Fig. 3). Collapsing the PS brushes in air after exposure to good solvent produces a porous morphology where some water may penetrate [11].

We discuss the thin polymer film in water in terms of linear viscoelastic theory as a very concentrated solution or melt. For a linear viscoelastic material, the stress tensor $\sigma(t)$ can be related to a complex viscosity η^*. The real part η' and imaginary part η'' of the complex viscosity correspond to the viscous loss and the storage capability, respectively [2].

Since the Reynolds number is very small, we can follow the calculation developed by Montfort and Hadziioannou [2] for SFA experiments. Solving the equation of motion for a z modulation which consists of the inertial force $F_i = m_L(d^2z/dt^2)$, the restoring force of the cantilever spring $F_R = c_L z$, the surface force $F_s = F_0 + c_{\mathrm{eff}}(h - h_0)$, and the hydrodynamic forces $F_H(t) = 6\pi R^2\sigma(t)/h(t)$ [$\sigma(t)$ is the stress tensor] we obtain [2]

$$\eta' = [(h_0c_0)/(6\pi R^2)]A'\frac{\sin\phi}{\omega}\,,$$
$$\eta'' = \frac{h_0}{6\pi R^2\omega}\,[c_0/[A'\cos\phi - 1] + c_{\mathrm{eff}}]\,, \qquad (1)$$

where $A' = A_{\mathrm{in}}/(A_{\mathrm{in}} - A_{\mathrm{out}})$, $c_0 = (c_L - m_L\omega^2)$, η' is the dynamic viscosity, A_{in} is the modulation amplitude, A_{out} is the response amplitude, h_0 is the uncompressed film thickness, and ϕ is the phase shift. The experimental measured asymptotic behavior of the amplitude [$A_{\mathrm{out}}^{(0)} = \lim_{\omega\to 0} A_{\mathrm{out}}(\omega)$ and $A_{\mathrm{out}}^{(\infty)} = \lim_{\omega\to\infty} A_{\mathrm{out}}(\omega)$], and the frequency ω_m of the minimum phase shift ϕ_m, can then be related within the Maxwell model to the characteristic rheological parameters of the system, the zero shear rate viscosity, and storage modulus η_0 and J_0 which are determined with$(A_{\mathrm{in}} - A_{\mathrm{out}}^{(\infty)})/A_{\mathrm{in}} = |J_0/\alpha - c_{\mathrm{eff}}/c_L + 1|^{-1}$, $\alpha = c_L h_0/6\pi R^2$, and $\omega_m^2(\eta_0/J_0)^2 = A_{\mathrm{out}}^{(\infty)}/A_{\mathrm{out}}^{(0)}$ [2]. The contact area of the tip with the sample was estimated from measurements of the resolution of CaF$_2$ step edges to be 5 ± 2 nm^2. A modulation of 5.5 nm (rms) at a frequency of 3 kHz produced a response of 0.55 nm and a phase shift close to 90°. The dynamic viscosity can be calculated from Eq. (1) to $\eta' = 2100 \pm 600$ P and the dynamic storage modulus $J = \omega\eta''$ at $\omega = 3$ kHz from Eq. (1) to 0.15 ± 0.05 GPa. A minimum frequency ω_m of 500 ± 100 Hz, an amplitude ratio of the high frequency and zero frequency response of 10, and a zero-shear-rate storage modulus J_0 of 0.1 ± 0.03 GPa could be determined. Using the equation for the zero shear rate, we obtain $\eta_0 63 \pm 23$ kP for the collapsed PS film in water. This value is similar to that obtained for a bulk PS melt of comparable molecular weight at 135 °C. The interpolated zero-shear-rate storage modulus J_0 is larger than that of the PS melt ($J_0 \sim 10^{-3}$ GPa [13]) but is still an order of magnitude smaller than that of bulk (glassy) PS at room temperature. Hence both the viscosity and storage modulus are consistent with an altering of the film surface due to the penetration of water observed within the neutron reflection data.

It is interesting to note in Fig. 1(b) that the loss and storage signals for the brush film in water are rather "noisy." Both the viscosity value and the storage modulus observed indicate that the PS chain is not completely glassy and has finite mobility. In contrast to the SFA, the contact area of the AFM cantilever tip is roughly the size of the collapsed PS chains. Calculations show that under these conditions it is possible for part of the grafted chain to escape from under the compressing surface [14]. These "*escape transitions*" can lead to hysteresis in the mechanical response of the film, which may explain the observed discontinuities or "noise" of the modulus plots shown in Fig. 1(b).

While the PS chains in a poor solvent such as water collapse in order to minimize the interaction with the solvent, they stretch in a good solvent [7]. The amount the polymers stretch, i.e., the density profile, can be calculated using self-consistent mean field theory (SCF) [5].

To compare our results with SCF calculations for the energy required to compress the brush we plot F/R, where F is the measured force and R is the radius of the probe curvature, as a function of the probe-silicon distance d [Fig. 2(c)]. The actual compression of the brush can be obtained from the displacement D by $\Delta d = \Delta D - \Delta F/c_L$ and $\Delta h = h_0 - \Delta d$, respectively. The effective length of the brush h_0 is most accurately measured

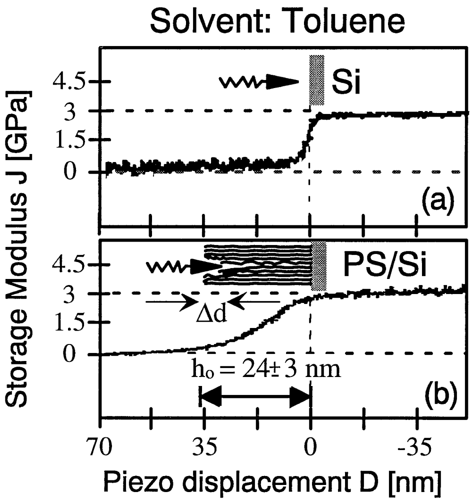

FIG. 4. The elastic modulus of (a) bar silicon in toluene and (b) PS in toluene. The polystyrene chains are 24 ± 3 nm (h_0) extended into the solvent.

from the distance between the plateaus in the ac storage modulus curve (Fig. 4). From the ac approach curves we can see that the cantilever penetrates after a displacement of 35 ± 3 nm through the PS brush and comes in contact with the bare silicon substrate. $D = 0$ is therefore defined by the position where the storage modulus of the PS brush saturates to the value of the bare Si surface. The height h_0 of the brush can then be estimated by substituting $D = 35 \pm 3$ nm, $\Delta F = 3.6$ nN, and $c_L = 0.33$ N/m to obtain $\Delta d = h_0 = 24 \pm 3$ nm. This value is in good agreement with that measured by neutron reflection (Fig. 3) and estimated from SCF [7].

In Fig. 2(c) we plot F/R as a function of d. The SCF calculation of Milner which has been shown to provide a good fit to the SFA measurements on other PS brushed in toluene [5] corresponds well to our experimental values in the first 10 nm of the brush [Fig. 2(c)]. As the brush is increasingly compressed, the calculated F/R increases faster than the experimental values. Additional viscosity measurements indicate that as the compression of the brush increases, the tip begins to penetrate within the brush. The lateral motion of the chains from under the AFM tip decreases the compression and hence the energy required to obtain a given displacement of the tip. This explanation is supported by the measurement of the phase shift of the compliance (a measure of dissipation) which starts to increase after a probe-silicon distance of 16 ± 3 nm is reached.

In Fig. 4 we show the storage modulus of the Si surface in toluene with and without the grafted PS brush. In contrast to the viscous response of the collapsed PS brush in water [Fig. 1(b)], the response of the brush in toluene is much more elastic. From Eq. (1) we can calculate an average dynamic elastic modulus $J = 1.5 \pm 0.5$ GPa. This value is approximately an order of magnitude larger than that in water and only a factor of 2 smaller than that of bulk PS at 25 °C. For the grafting density considered here, $s = 6.64$ nm^2/chain, only a few polymer molecules are directly involved in the estimated average contact area of 5–20 nm^2. On the other hand, the magnitude of F/R we observe at the brush surface, where the modulus is determined, is approximately the same order of magnitude as that measured with the SFA. It is therefore reasonable to assume that we are observing a collective response involving many chains in the brush rather than just the few in the contact area.

These results illustrate that it is possible to quantify the mechanical measurements performed with the AFM in analogy to results previously derived for the SFA. The area of confinement with the AFM is much smaller than that of the SFA. The chain dynamics can therefore be significantly faster, being determined mainly by interactions with only the substrate surface [15]. Consequently, the AFM can be a useful tool to measure material properties in equilibrium such as the viscosity and shear modulus of thin films.

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[1] R. M. Overney *et al.*, Nature **359**, 133 (1992).
[2] J. P. Montfort and G. Hadziioannou, J. Chem. Phys. **88**, 7187 (1988).
[3] H. Yoshizawa, Y.-L. Chen, and J. Israelachvili, J. Phys. Chem. **97**, 4128 (1993).
[4] H.-W. Hu and S. Granick, Science **258**, 1339 (1992).
[5] S. T. Milner, Eurphys. Lett. **7**, 695 (1988).
[6] M. Tirrell, S. Patel, and G. Hadziioannou, Proc. Natl. Acad. Sci. U.S.A. **84**, 4722 (1987).
[7] H. J. Taunton *et al.*, Macromolecules **23**, 571 (1990).
[8] R. M. Overney *et al.*, Langmuir **10**, 1281 (1994).
[9] U. Landman and W. D. Luedtke, MRS Bull, **18**, 36 (1993).
[10] M. Salmeron *et al.*, Langmuir **9**, 3600 (1993).
[11] W. Zhao *et al.*, Macromolecules **27**, 2933 (1994).
[12] T. P. Russel, Mater. Sci. Rep. **5**, 171 (1990).
[13] R. W. Herzberg, *Deformation and Fracture Mechanics of Engineering Materials* (J. Wiley, New York, 1976).
[14] G. Subramanian, D. R. M. Williams, and P. A. Pincus, Europhys. Lett. **29**, 285 (1995).
[15] X. Zheng *et al.*, Phys. Rev. Lett. **74**, 407 (1995).