Surface Dynamics of Polymer Films

Hyunjung Kim,[1,2,3] A. Rühm,[4,5] L. B. Lurio,[4,6] J. K. Basu,[1,7] J. Lal,[8] D. Lumma,[4] S. G. J. Mochrie,[9] and S. K. Sinha[1,2]
[1]*Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439*
[2]*Department of Physics, University of California San Diego, La Jolla, CA 92093 and LANSCE, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*
[3]*Department of Physics, Sogang University, Seoul 121-742, Korea*
[4]*Center for Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*
[5]*Max-Planck-Institut für Metallforschung, Stuttgart, Germany*
[6]*Department of Physics, Northern Illinois University, DeKalb, Illinois 60115*
[7]*Materials Research Laboratory, University of Illinois, Urbana-Champaign, Illinois 61801*
[8]*Intense Pulsed Neutron Source, Argonne National Laboratory, Argonne, Illinois 60439*
[9]*Departments of Physics and Applied Physics, Yale University, New Haven, Connecticut 06520*
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The dynamics of supported polymer films were studied by probing the surface height fluctuations as a function of lateral length scale using x-ray photon correlation spectroscopy. Measurements were performed on polystyrene (PS) films of thicknesses varying from 84 to 333 nm at temperatures above the PS glass transition temperature. Within a range of wave vectors spanning 10^{-3} to 10^{-2} nm^{-1}, good agreement is found between the measured surface dynamics and the theory of overdamped thermal capillary waves on thin films. Quantitatively, the data can be accounted for using the viscosity of bulk PS.

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The surface dynamics of viscoelastic liquid films have been evaluated by several authors [1,2] and it can be shown that the slow modes are strongly overdamped capillary waves where the relaxation times are determined by the viscosity, the surface tension, the film thickness, and the wavelength (or equivalently the wave vector) of the capillary wave. To our knowledge there have been no experimental tests of how well these theories apply to polymer films. In particular, it is unclear to what extent these theories are still valid in situations where the film thickness approaches the typical length scale of the polymer chains, i.e., the radius of gyration (R_g), and how satisfactorily fluctuations over certain lateral length scales are described by these theories. In this Letter, we present the first experimental verification of the theoretical predictions for the thickness, wave vector, and temperature dependence of the capillary wave relaxation times for supported polymeric films above the glass transition temperature (T_g). We used the emerging technique of x-ray photon correlation spectroscopy (XPCS) as a means to study the dynamics of small-scale surface height fluctuations [3].

The experiments described here enable us in principle to set some limits on the extent to which the viscosity of the film develops inhomogeneities [4–9] as a function of depth in a certain temperature range above the bulk T_g. This is of particular interest in the context of the following issues related to the dynamical properties of thin supported polymer films: various contradictory findings regarding the mobility of the polymer chains at the free surface relative to the bulk [10,11]; indications of an immobile viscoelastic layer adjacent to the substrate arising from an analysis of near-specular diffuse scattering in quenched polymer films [12]; and predictions on the basis of a generalized reptation model [13] that long-range motion of polymer chains is hindered in thin films, resulting in an increase in viscosity.

Our films were prepared by dissolving polystyrene (PS) of $M_W = 123\,000$ g/mol and $M_W/M_n = 1.08$ in toluene and then spin casting onto optically flat silicon substrates. These samples were then annealed in vacuum for 12 h at 150 °C to ensure complete solvent removal. The thicknesses of the PS films investigated by XPCS were 84, 170, 177, 312.5, and 333 nm as measured by x-ray reflectivity and ellipsometry. The XPCS experiments were performed at beam line 8-ID at the Advanced Photon Source (APS) and employed monochromatic radiation with an x-ray energy of 7.66 keV. The experimental geometry is illustrated schematically in Fig. 1(a). By arranging for the x-ray incidence angle (0.14°) to lie below the critical angle for total external reflection (0.16°), we were able to restrict the x-ray penetration into the film to a depth of ∼9 nm, far less than any of the film thicknesses studied here. Thus, scattering from the film-substrate interface is negligible, and only fluctuations of the polymer/vacuum interface are probed. In-plane wave vectors up to 10^{-2} nm^{-1}, where van der Waals interactions are negligible [14], could be accessed.

The off-specular diffuse scattering from the polymer surface was recorded with a direct-illumination charge-coupled device (CCD) camera, located 3545 mm downstream of the sample. A CCD image of the time-averaged diffuse scattering from the 84 nm-thick film at 160 °C is shown in Fig. 1(b). In comparison, Fig. 1(c) represents the

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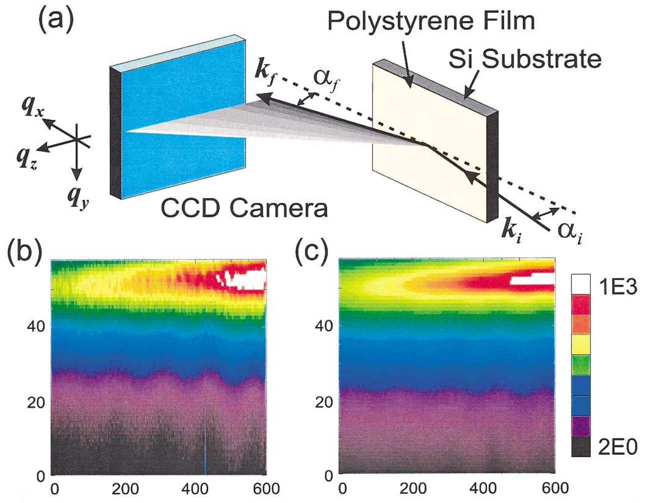

FIG. 1 (color). (a) Scheme of the experimental setup for XPCS in reflectivity geometry. (b) CCD image of time-averaged diffuse scattering. (c) Fit to capillary wave model for a sample of thickness 84 nm at 160°C. Axes are labeled with pixel numbers.

static scattering calculated within the distorted wave Born approximation on the basis of the capillary wave model [15]. There is good agreement between the data and the model, which confirms that the surface morphology is governed by capillary waves. Furthermore, the surface tension deduced from the static scattering is consistent with that of bulk PS (31.4 mN/m at 150 °C [16]) and is independent of film thickness.

The beam dimensions were $20 \times 20\ \mu\text{m}^2$, comparable to the x-ray coherence lengths of 7 and 90 μm in the horizontal and vertical directions, respectively [17]. As a result, the polymer surface is partially coherently illuminated, giving rise to a speckled scattering pattern which varies in time as the surface modes undergo random thermal fluctuations. The normalized intensity-intensity time autocorrelation function, g_2, then yields the sample's surface dynamics. The typical flux was $\sim 8 \times 10^8$ photons/sec. To avoid x-ray sample damage, the x-ray exposure of any position on the sample was limited to about 10 min, after which time the sample was shifted to illuminate a fresh area.

The intensity autocorrelation function is

$$g_2(\mathbf{q}, t) = \frac{\langle I(\mathbf{q}, t')I(\mathbf{q}, t' + t)\rangle}{\langle I(\mathbf{q}, t')\rangle^2}, \tag{1}$$

where $I(\mathbf{q}, t')$ is the scattering intensity at wave vector transfer $\mathbf{q}$ at time t'. In Eq. (1), the angular brackets refer to averages over time t' and t denotes the delay time. Our methods for determining g_2 are described in detail in Ref. [17]. Representative experimental correlation functions acquired from the 84 nm-thick film at 160 °C are shown as symbols in Fig. 2 for four different in-plane wave vectors $q_{\|}$. The lines represent single-exponential fits, i.e., $g_2 = 1 + \beta \exp(-2t/\tau)$, where β is the speckle contrast and $\tau = \tau(q_{\|})$ is the relaxation time for equilibrium surface height fluctuations. The parameters varied in each fit were β and τ. Evidently, the model provides a good description of our data.

The $q_{\|}$ dependence of the best-fit relaxation times is displayed in Fig. 3(a) at three different temperatures for the 177 nm-thick film. The time constants decrease with increasing temperature. At each temperature, however, the $q_{\|}$ dependence appears to be similar, with larger length-scale asperities relaxing more slowly than smaller ones. Shown in Fig. 3(b) are the relaxation times at 160 °C for three films of different thickness. The time constants decrease monotonically with increasing thickness. The fact that the surface dynamics depend on film thickness demonstrates that, although our measurements are sensitive only to surface motions, those motions in turn depend on molecular movements throughout the film.

Explicit predictions for the time dependence of surface height relaxations, as well as for the wave vector, film thickness, and temperature dependence of the relaxation time, can be deduced from the theory given in Ref. [2]. Specifically, using parameter values appropriate for a highly viscous polymer liquid, capillary modes on the surface of PS should be strongly overdamped, which is consistent with the observed single-exponential decay of

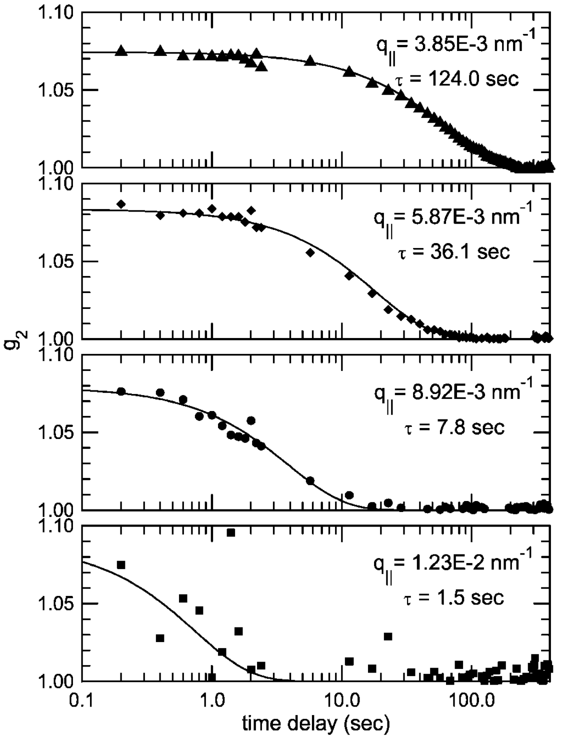

FIG. 2. Autocorrelations obtained at four different in-plane wave vectors measured on a sample thickness of 84 nm at 160 °C (symbols), compared with single-exponential fits (lines). The time constant τ at each $q_{\|}$ is also displayed.

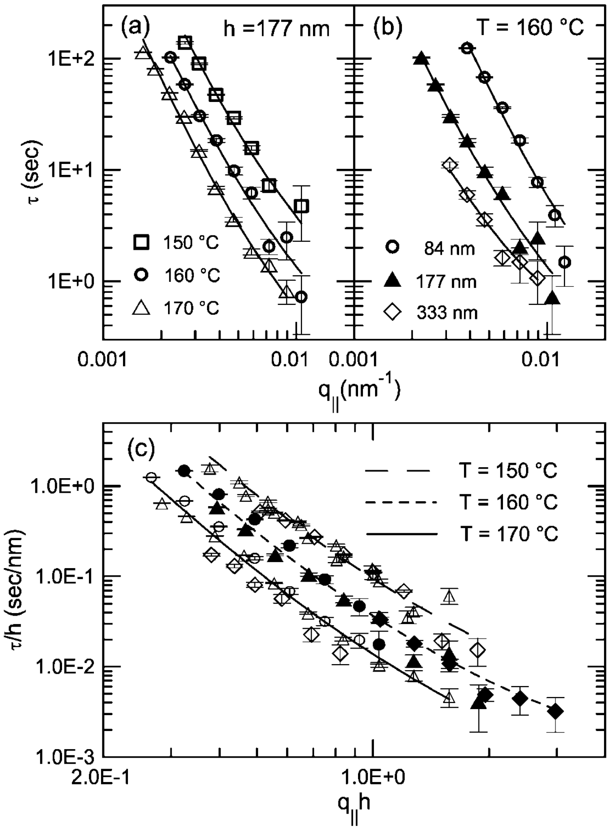

FIG. 3. (a) Measured time constant τ vs in-plane wave vector $q_{||}$ for the 177 nm-thick film at 150 °C (squares), 160 °C (circles), and 170 °C (triangles). (b) τ vs $q_{||}$ at 160 °C for films of thickness 84 nm (circles), 177 nm (triangles), and 333 nm (diamonds). (c) τ/h vs $q_{||}h$ for film thicknesses 84 nm (circles), 170, 177 nm (triangles), and 312.5, 318, 333 nm (diamonds). Lines represent least-squares fits based on Eq. (2).

intensity autocorrelations. In addition, we find that the corresponding relaxation time, $\tau(q_{||})$, is

$$\tau \simeq 2\eta H/\gamma q_{||}F, \tag{2}$$

where η is the viscosity (assumed uniform throughout the film), γ is the surface tension, and F and H are defined as follows: $F = \sinh(q_{||}h)\cosh(q_{||}h) - q_{||}h$ and $H = \cosh^2(q_{||}h) + q_{||}^2h^2$, with h the film thickness.

Equation (2) indicates that τ/h should be solely a function of $q_{||}h$ and directly proportional to the ratio η/γ. To test the predicted scaling behavior, we plotted the quantity $\tau(q_{||})/h$ versus $q_{||}h$ for different film thicknesses at 150, 160, and 170 °C in Fig. 3(c). At each temperature, data from different samples collapse to form a single curve, confirming the anticipated scaling with film thickness. Excellent agreement between experiment and theory [Eq. (2)] is achieved with a single fit parameter, the ratio η/γ. This is strong evidence that the dynamical capillary wave theory is satisfactory, and that its premise of a wave vector and thickness independent viscosity is appropriate for the films studied here.

Knowing the surface tension (γ) at each temperature, we may obtain the film viscosity (η), because the fits to $\tau(q_{||})/h$ versus $q_{||}h$ [Fig. 3(c)] determine η/γ. The viscosity obtained from these fits is plotted versus temperature in Fig. 4(a), together with the corresponding bulk viscosity interpolated from Ref. [18] for a molecular weight of 123 000. Evidently, bulk and film viscosities agree within the accuracy of our measurements. However, the temperature dependence of the film viscosity might be weaker than that of the bulk viscosity.

Now, if we reconsider these results in the context of possible inhomogeneities in our films, the question arises as to whether the good agreement with bulk properties really tells us that there is no surface layer of substantially lower viscosity, as suggested by various authors [4–8,11]. To answer this question and to determine the sensitivity of our measurements, we also calculated the relaxation times for an *inhomogeneous* film composed of two layers of differing viscosities. Details of these calculations will be published elsewhere. They are based on the Navier-Stokes equation with nonslip boundary conditions and continuity of the stress field across the interface. For simplicity, we took the densities of the two layers to be equal and for there to be no interfacial tension between them. The viscosity of the surface layer enters through the Navier-Stokes equation as a local quantity that is characterized by the average chain mobility in that layer. Even if some polymer chains in a high-mobility surface layer were restricted in their motion over large lateral distances due to interaction with the more viscous layer underneath, the surface layer would, for the purposes of calculating the capillary wave dynamics, act as a lower viscosity layer. This is because the amplitude of motions executed by particles in a film undergoing capillary wave fluctuations can be calculated to be of the order of 1 nm or less in both the vertical and lateral direction, so no flow of polymer chains over large lateral distances is involved.

To permit comparison with our data, we hypothesized, following Kawana and Jones [6], the existence of a high-mobility surface layer of thickness 10 nm. This layer rests on the remainder of the film, which we assumed to have the viscosity obtained from the fits shown in Fig. 3(c) [see Fig. 4(a)]. The viscosity of the surface layer is assumed to be 10 times lower. Our calculations then predict that for a (hypothetical) inhomogeneous film of total thickness 80 nm held at 150 °C the capillary wave relaxation times are approximately 70% of the relaxation times of the homogeneous film [see dashed line in Fig. 4(b)]. We judge this to represent the limit of accuracy of our measurements, but we can conclude that at this temperature an inhomogeneity in viscosity with a 10 times lower viscosity near the surface can only affect a surface layer thinner than 10 nm.

In summary, using XPCS we have measured the relaxation times of overdamped capillary waves for thin liquid polystyrene films of molecular weight 123 000 at

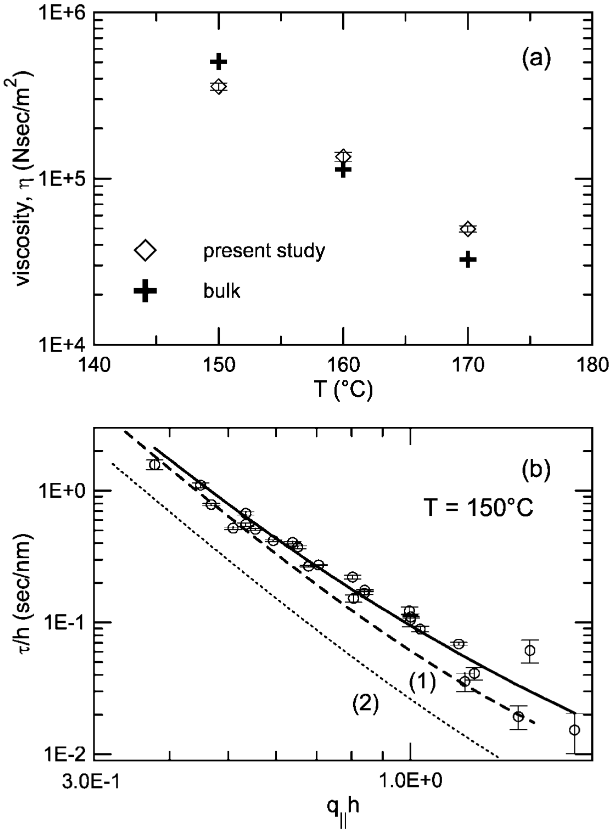

FIG. 4. (a) Viscosity of thin-film PS (diamonds) and bulk PS (crosses) as a function of temperature. (b) Comparison between the data (circles) and various model curves. The solid line corresponds to Eq. (2) and is also shown in Fig. 3(c). The other two lines represent fits for inhomogeneous films according to the two-layer model described in the text. The total film thickness is 80 nm (dashed line, 1) and 20 nm (dotted line, 2), respectively. In both cases the viscosity of the high-mobility surface layer of thickness 10 nm is 10 times less than the measured viscosity given in (a) at $T = 150\,^\circ\mathrm{C}$.

various temperatures above T_g, and we verified for the first time scaling relations for τ as a function of wave vector and film thickness as predicted by the theory of such capillary waves. We used these results and an analysis of the static off-specular scattering to obtain (postulated uniform) viscosities and surface tensions for these films at various temperatures which are in good agreement with bulk values interpolated to the above molecular weight. On the basis of these data, together with a supplementary calculation of the capillary wave relaxation times for inhomogeneous thin films, we can rule out the existence of a more than 10 nm thick surface layer with a viscosity less than one tenth of the bulk viscosity.

Our measurements provide an important constraint on theories seeking to elucidate the temperature and depth dependence of the viscosity near a polymer surface. It is important, however, to extend these measurements to a wider range of M_W and thinner films in order to test what is the dominating length scale controlling the surface dynamics: the polymer radius of gyration or the much smaller depth over which the packing density of chain segments [9] changes near the free surface. If the latter, then there should not be much difference between the bulk viscosity of PS and the viscosity obtained here for the investigated film thicknesses. Larger differences might only be manifested in films thinner than ~20 nm. For such thin films it would have a marked influence on the viscosity if the outer high-mobility surface layer was indeed 10 nm thick [see dotted line in Fig. 4(b)]. Such experiments would also provide a crucial test of the theory of Semenov [13] which predicts an increase of the film viscosity as the film thickness decreases.

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