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Abstract
X-ray photon correlation spectroscopy, an emerging technique for studying the slow dynamics of condensed matter, has been employed to probe surface fluctuations on thin supported polymer films as a function of in-plane wavevector, film thickness, temperature, and molecular weight of the polymer. The measurements were performed on thin polystyrene (PS) films of thicknesses ranging from 84 to 333 nm above the glass transition temperature. The lateral length scales probed are at least ten times smaller than those accessible in conventional dynamic light scattering. We find excellent agreement between the measured surface dynamics and the theory of overdamped thermal capillary waves on thin viscoelastic films. The values of the viscosity obtained from these data show good agreement with those of bulk PS.

1. Introduction

For conventional x-ray sources, the coherence length of radiation at the sample is typically less than a micron in the directions transverse to the beam and a few tens of nanometres in the longitudinal direction. In this case the sample scatters from a large number of incoherently scattering volumes, which results in the conventional scattering averages which appear in

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the correlation functions determining the scattering. However, if the x-ray beam is highly monochromatic and highly collimated, as is the situation at present-day third generation synchrotron sources, then the coherence lengths can be of the order of tens of microns and the whole sample can scatter coherently. In general, due to interference effects, this results in the phenomenon of speckle in the scattered beam. As the atoms fluctuate in time, these speckles move in and out of the detector or a detector pixel, thus yielding a time-dependent scattered intensity. The time autocorrelation function of such speckled scattering patterns yields the characteristic relaxation times of the sample [1]. This is completely analogous to the techniques of dynamic light scattering; however, the length scales studied can be much smaller and optically opaque systems can be studied [2]. For example, x-ray photon correlation spectroscopy (XPCS) measurements have been carried out of the equilibrium dynamics of a binary alloy near its critical point [3], of Brownian motion of gold colloids diffusing in glycerol [4], and of the equilibrium dynamics of block-copolymer micelles in a homopolymer matrix [5] and of non-equilibrium dynamics of phase separation in a binary glass [6] in small-angle scattering geometry. More recently, the capillary wave dynamics on liquid glycerol surfaces has been performed in reflection geometry [7].

In this paper, we have applied this new method of XPCS for probing the surface dynamics of thin polymer films as a function of lateral length scale. The short wavelength of the radiation and the slow timescales that are characteristic of XPCS extend the phase space accessible to scattering studies with visible light or neutrons. In surface x-ray photon correlation spectroscopy (SXPCS), highly coherent x-rays impinge on the polymer surface at grazing incidence. Studying the dynamics of thin polymer films near and above the glass transition temperature is interesting for the following reasons.

(1) In many technological applications of thin polymer films, it is important to understand relaxation at the surface and buried interfaces.
(2) The transition from a molten state to a glass is one of the least-well understood phenomena in physics.

An especially important effect that occurs in polymer films is an unusual depression of the glass transition temperature compared with the bulk material [8–14]. Among the proposed explanations for this effect is the notion that a thin low-viscosity surface layer remains at temperatures below the glass transition temperature, even when the rest of the film has already entered the glass state. According to this view, the surface effect is usually minimal compared to the behaviour of the bulk, but it starts to dominate the polymer behaviour as the film thickness decreases. The slow surface modes in viscoelastic liquid films have been predicted to be strongly overdamped capillary waves where the relaxation times are determined by the viscosity, the surface tension, the film thickness, and the wavelength of the capillary waves [15, 16]. However, 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.

2. Experiment

Polymer films were prepared by dissolving polystyrene (PS) of $M_W = 123\,000$ g mol^{-1} ($M_W/M_n = 1.08$) in toluene which was then spun cast onto optically flat silicon substrates that were cleaned by Pirhana etch. 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 ranged from 80 to 333 nm. The XPCS experiments were performed at beam line
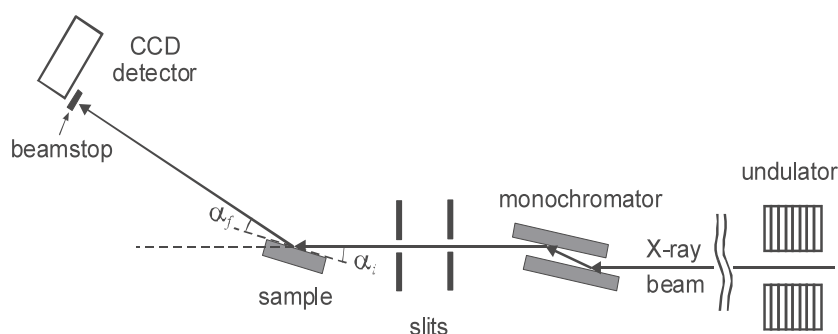
Figure 1. The experimental setup for surface x-ray photon correlation spectroscopy.

8-ID at the Advanced Photon Source (APS). A germanium (111) channel-cut double-bounce monochromator located 64.4 m from the source and an adjustable slit system 40 cm upstream of the sample were used to prepare a coherent monochromatic x-ray beam with a wavelength of 0.16 nm and a cross section of 20×20 $\mu\mathrm{m}^2$. In this configuration, the pixel size of the charge-coupled device (CCD) of 22.5×22.5 $\mu\mathrm{m}^2$ corresponds to the theoretical speckle size. By using a CCD as detector, the signal-to-noise ratio of the correlation function is improved since the signal from many CCD pixels can be correlated and then averaged over pixels with equivalent wavevector transfers. The experimental geometry is illustrated schematically in figure 1. 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 wavevectors up to 10^{-2} nm^{-1}, where van der Waals interactions are negligible [17], could be accessed. The off-specular diffuse scattering [18–20] from the polymer surface was recorded with a direct-illumination CCD camera, located 3.55 m downstream of the sample. 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. 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.

3. Results and discussion

The results obtained by conventional off-specular diffuse scattering from our polymer surfaces show good agreement with the static scattering calculated within the distorted wave Born approximation on the basis of the capillary wave model. It confirms that the surface morphology is governed by capillary waves. In addition, these measurements confirm that the surface tension of the polymer films is thickness independent and agrees with the bulk surface tension [21] to within the experimental accuracy (±25%). We have published the detailed results on the surface tension and surface roughness of supported polystyrene films in the same range of thicknesses and at the same temperatures elsewhere [22].

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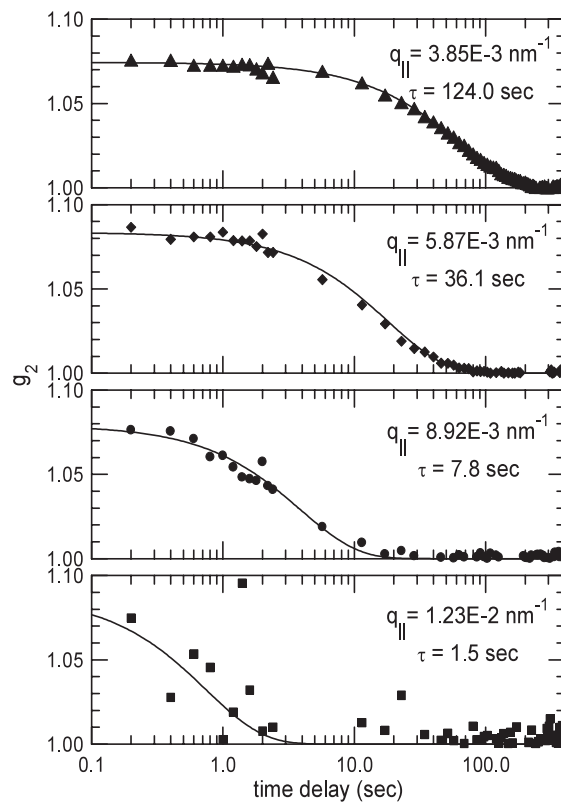
Figure 2. Autocorrelation functions obtained at four different in-plane wavevectors measured on a sample of thickness 84 nm at 160 °C (shown as symbols), compared with single-exponential fits (shown as curves). The time constant τ at each $q_\parallel$ is also displayed.

The normalized intensity–intensity time 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 wavevector transfer $\mathbf{q}$ at time t'. In equation (1), the angular brackets refer to averages over time t', and t denotes the delay time [23]. In figure 2, experimental correlation functions acquired from the 84 nm thick film at 160 °C are shown as symbols for four different in-plane wavevectors $q_\parallel$. The curves show single-exponential fits, i.e., $g_2 = 1 + \beta \exp(-2t/\tau)$, where β is the speckle contrast and $\tau = \tau(q_\parallel)$ is the relaxation time for equilibrium surface height fluctuations. At higher $q_\parallel$, the relaxation time is faster. The temperature dependence of the relaxation times on a film with fixed film thickness shows that the time constants at higher temperature are faster at a given $q_\parallel$. In each case, however, the $q_\parallel$ dependence is similar, with larger length-scale asperities relaxing more slowly than smaller ones. The time constants on films of different thickness at a fixed temperature decrease monotonically with increasing thickness. The fact that the surface dynamics depends 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. From the theory [16] of the dynamics of capillary waves on viscous liquid films, we have earlier deduced [24] the expression for the relaxation time τ for capillary waves as a function of the
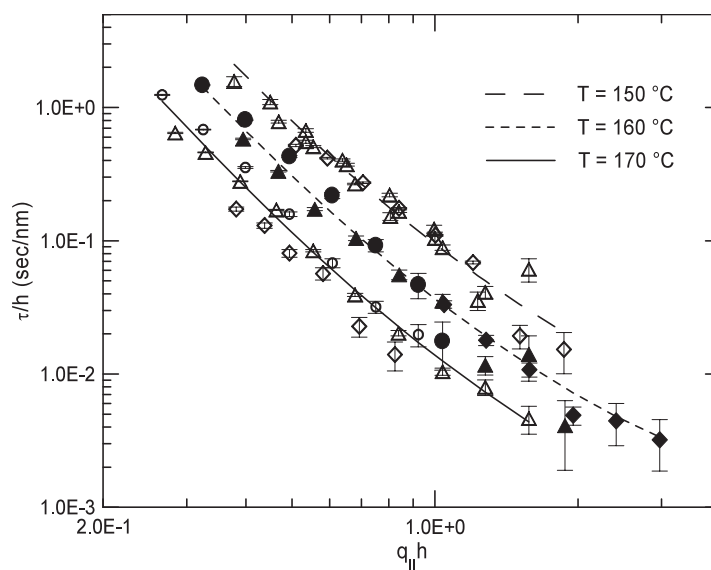
Figure 3. τ/h versus $q_\parallel h$ for film thicknesses 84 nm (circles), 170, 177 nm (triangles), and 312.5, 318, 333 nm (diamonds). Measurements were performed at 150, 160, and 170 °C. The curves represent least-squares fits based on equation (2).

Table 1. Viscosity of thin polystyrene (PS) film (present study) and bulk PS at various temperatures. ($\times 10^5$ N s m^{-2}).

Temperature (°C)	Present study	Bulk
150	3.58 ± 0.90	5.04
160	1.35 ± 0.34	1.14
170	0.50 ± 0.13	0.33

viscosity, η, the surface tension, γ, the thickness, h, and the in-plane wavevector, $q_\parallel$, in the overdamped regime. From that expression, τ/h should be solely a function of $q_\parallel h$ and directly proportional to the ratio η/γ as shown in equation (2).

$$\frac{\tau}{h} \approx \frac{2\eta}{\gamma} \frac{\left[\cosh^2(q_\parallel h) + (q_\parallel h)^2\right]}{(q_\parallel h)\left[\sinh(q_\parallel h)\cosh(q_\parallel h) - q_\parallel h\right]}. \tag{2}$$

To test the predicted scaling behaviour, we have plotted the experimental quantity τ/h versus $q_\parallel h$ for different film thicknesses at 150, 160, and 170 °C in figure 3. At each temperature, data from different samples collapse to form a universal single curve, confirming the anticipated scaling with film thickness.

Experiment and theory (equation (2)) show excellent agreement, with only a single fit parameter, the ratio η/γ. Knowing the surface tension (γ) at each temperature [22], we may obtain the film viscosity (η), because the fits to τ/h versus $q_\parallel h$ determine η/γ. The viscosity obtained from these fits and is tabulated in table 1 together with the corresponding bulk viscosity interpolated from [25] for a molecular weight of 123 000. Evidently, bulk and film viscosities agree within the accuracy of our measurements. However, it looks as if the temperature dependence of the film viscosity might be slightly less steep than that of the bulk viscosity.
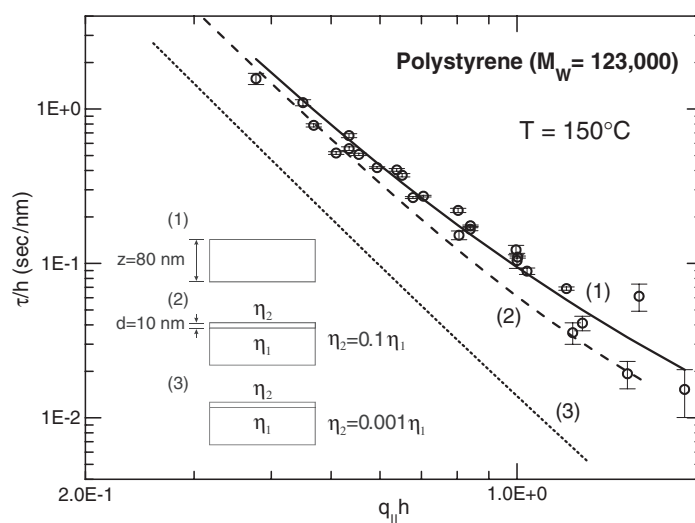
Figure 4. Comparison between the data at 150 °C (circles) and various model curves. The solid curve (1) corresponds to equation (2) based on the tabulated bulk viscosity of polystyrene [25]. The inset shows the schematic diagram for each calculated curve: for a homogeneous film as well as for two inhomogeneous films according to the two-layer model described in the text. The total film thickness is 80 nm. Line (1) (solid curve) was calculated for a homogeneous film, line (2) (dashed curve) was calculated for a surface layer of thickness 10 nm having 10 times less than the viscosity derived from our XPCS data for a homogeneous film model, and line (3) (dotted curve) was calculated for a surface layer of thickness 10 nm having 1000 times less than the viscosity derived for a homogeneous film model.

In addition, it is possible to derive limits on the extent to which viscosity inhomogeneities may be present in the film. For example, we have examined the specific model of Kawana and Jones [11], which hypothesizes a lower viscosity surface layer of thickness 10 nm with a viscosity of only one-tenth of the bulk viscosity. The relaxation times are calculated based on a Navier–Stokes equation with nonslip boundary conditions and continuity of the stress field across the interface. It was assumed that the two layers resulting from this model have different viscosities but the same density and no interfacial tension. The comparison between our experimental data and calculations with (1) a surface layer with 10 times lower viscosity and (2) one with 1000 times lower viscosity is shown in figure 4. The latter model, however, does not fit the observed data as can be seen from the figure (curve (3)). We are thus able to rule out a 10 nm thick surface layer with a dramatically reduced viscosity, e.g. by a factor 1000 compared to the bulk viscosity. We cannot rule out, however, a slightly less viscous surface layer of thickness 10 nm, or a low-viscosity layer even thinner than 10 nm.

4. Summary

Among the many new possibilities of research with x-ray beams from third generation synchrotrons, one of the most exciting opportunities is to investigate the dynamics of condensed matter on molecular length scales using x-ray photon correlation spectroscopy (XPCS). In this work, we demonstrated this technique in particular to determine the dynamics of surface height fluctuations which goes beyond characterizing the equilibrium configuration of a surface via reflectivity and diffuse scattering measurements. With this surface x-ray photon correlation spectroscopy (SXPCS) technique we measured the relaxation times of overdamped capillary

waves for thin polystyrene films of molecular weight $123\,000$ g mol^{-1} at various temperatures above the glass transition temperature T_g, and we verified scaling relations for τ/h versus $q_{\parallel}h$ as predicted by the theory of such capillary waves. We used these results and an analysis of the static off-specular scattering [22] to obtain viscosities and surface tensions for these films at various temperatures. The results are in good agreement with bulk values interpolated to the molecular weight of our polymer material. The extension of our investigations to a wider range of molecular weights and thinner films is in progress in order to test what is the dominating length scale controlling the surface dynamics.

Acknowledgments

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