Observing a true liquid behavior on polymer thin film surfaces

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Introduction

On liquid surfaces, thermal excitations induce capillary waves with a long wave length cutoff due to gravitation [1]. The power spectrum associated with capillary waves can be expressed as $S(k) = (k_B T/\gamma)(k^2 + k_c^2)^{-1}$, where the cutoff $k_c = \sqrt{\rho g/\gamma}$ (1 to 10 cm^{-1}), and ρ and γ are the liquid density and its surface tension, respectively, and g is the gravitation. Theoretically, on liquid thin film surfaces, the cutoff is simply modified by substituting g with $g_{eff} = g + F/(\rho d)$, where F is the effective interaction force per unit area (e.g., van der Waals forces) and d the thickness of the film. For $d < 1$ µm, $g_{eff} >> g$, resulting in a much larger cutoff k_c than that for bulk liquid surfaces. Such interaction prevents the long-range correlations that a free liquid surface possesses while essentially not affecting the short wavelength fluctuations. The shift of k_c to larger values can be visualized by x-ray diffuse scattering measurements, a well-suited technique for obtaining quantitative information about such thermal excitations. Whereas bulk liquids have been investigated extensively [2], there are only a handful of quantitative investigations on liquid thin films [3, 4], mainly due to difficulties in preparing samples with well-controlled film thickness and interfacial environment. Recently, we have attempted to study the surface behaviors of ultrathin polymer films for elucidating the capillary wave properties on liquid thin film surfaces and for investigating the substrate effects on these properties [5, 6]. However, the true liquidlike behavior has never been observed even if the polymer film thicknesses were much larger than the radius of gyration (R_G) and the polymer glass transition temperature (T_g). In such a case, strong confinement was thought to be responsible for the absence of the liquid surface properties. In this report, the surfaces of molten poly(tert-butyl acrylate) (PTBA) thin films on a silicon substrate have been investigated by specular and diffuse x-ray scattering. We have demonstrated the surface of the polymer thin films exhibits modified capillary wave fluctuation, possibly due to the attracting van der Waals interaction between the substrates and the thin films. The observed capillary wave scattering is strongly dependent on the thin film thickness. When the film thickness is close to or only a few times larger than R_G, the low frequency cutoff of the wave-vector transfer along the surface (q_x) shifts to higher frequencies as the film thickness decreases. Furthermore, a signature of free liquid capillary scattering, namely, the changing of the exponent in the diffuse scattering power-law as a function of momentum transfer normal to the surface, q_z, was clearly observed for thicker films.

Methods and Materials

To investigate the polymer film surfaces, PTBA with a molecular weight of 350 K and R_G = 138 Å was used. The films, with thickness ranging from 130 to about 2000 Å, were spun cast onto polished silicon wafers. The x-ray reflectivity and diffuse scattering measurements were performed at the SRI-CAT 1-BM-C beamline of the Advanced Photon Source (APS). During the experiment, the films were kept under a helium environment and on a heating stage with temperature adjusted to 70–90° C, well above T_g at 45° C. With an x-ray flux close to 10^{11} photon/s at the sample surface, radiation damage would occur within one hour of exposure monitored by fast x-ray reflectivity scans. Therefore, data collection time for each sample was limited to 40 minutes or less to ensure minimum radiation damage to the polymer thin film [7].

At the polymer surface, the scattering function $S(\mathbf{q})$, which is proportional to the observed intensity $I(\mathbf{q})$ at point, $\mathbf{q}$, in reciprocal space, can be expressed as Equation (1) [2]:

$$S(q_{x,}, q_z) = \frac{(\Delta\rho)^2 e^{-q_z^2\sigma^2}}{q_z^2} \int_0^\infty e^{q_z^2 C(X) - \delta_{q_x}^2 X^2} \cos(q_x X) dX, \qquad (1)$$

where $C(X)$ is the displacement-displacement correlation, $C(R)$, is defined as $\langle z(\mathbf{r}) z(\mathbf{r}+\mathbf{R})\rangle_{\mathbf{r}}$, averaged in the direction of normal to the diffraction plane (y-direction), with $z(\mathbf{r})$ being the displacement of the surface contour relative to an arbitrary origin at the lateral position $\mathbf{r}$, σ is the rms roughness and $\Delta\rho$ is the electron density contrast at the polymer/air interface. Wide-open slits in the y-direction leads to a $q_x^{\eta-1}$ power-law decay of the diffuse scattering [2], where $\eta = (1/2)Bq_x^2$, and $B = k_B T/\pi\gamma$ (k_B: Boltman constant, T: temperature).

Results

The transverse diffuse scattering curves for the thickest film with $d = 2018$ Å measured at various q_z are shown in Figure 1. The capillary wave properties that a free liquid surface possesses have been readily observed in the data. The diffuse scattering intensity follows $I(q_x) \propto q_x^{\eta-1}$. The relationship between η and q_z^2 is illustrated in the inset in the figure. The slope in the linear fit yield $B = 5.5\ \AA^2$ corresponding to $\gamma = 28\ mN/m$, which is close to the value for a free molten PTBA surface at this elevated temperature (90°C).

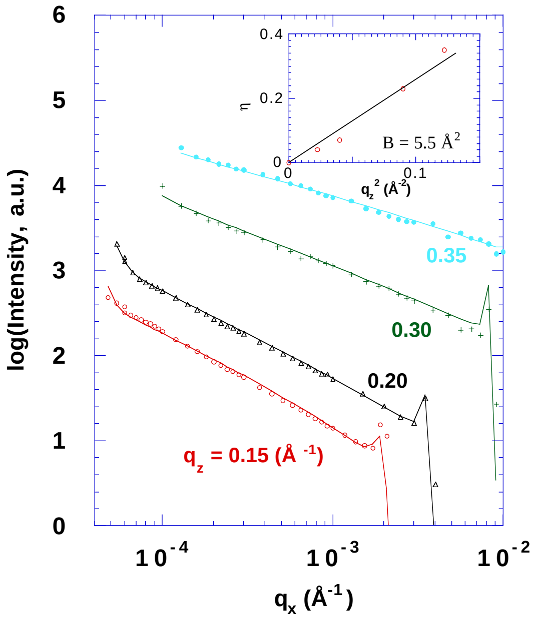

Figure 1: Transverse diffuse scattering from the sample with $d = 2018$ Å. The fits to the data using capillary wave scattering theory (Equation 1) are shown as lines.

The much thinner films show very different behavior. Figure 2 shows the diffuse scattering curves for the sample with $d = 131$ Å at $q_z =$ 0.20 and 0.25 Å^{-1}. It can be seen that two regions of scattering exist. They are separated by the low-q cutoff, k_c, observed as the "bend" in the curves. Below the cutoff (long wavelength region), the scattering is suppressed and is relative flat. Above the cutoff, the scattering curve resumes the power-law relationship with q_x indicating that the film thickness does not affect the capillary waves in the low wavelength region.

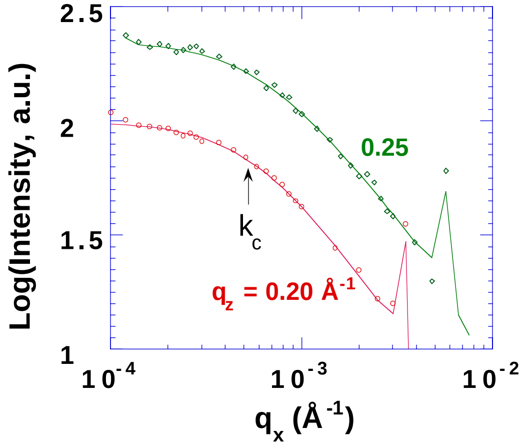

Figure 2: Transverse diffuse scattering from the sample with $d = 113$ Å. The fits to the data using modified capillary wave scattering theory (incorporating thin film effect) are shown as lines.

The experimental data and their fits show that the cutoff moves to larger q_x as film thickness decreases, as demonstrated in Figure 3. In the inset, the relationship between $\log(k_c)$ and $\log(d)$ is plotted and the slope of the linear fit is –1.4. This slope does not agree with the value of –2 predicted by the van der Waals interaction model [5, 6]. The disagreement may imply that the thin films, especially, the films with thicknesses only a few times larger than RG, are not completely in a homogeneous molten state. The film close to the substrate may still be an amorphous solid [8]. Therefore, the liquid film thickness is less than the polymer film thickness. A detailed analysis is still in process.

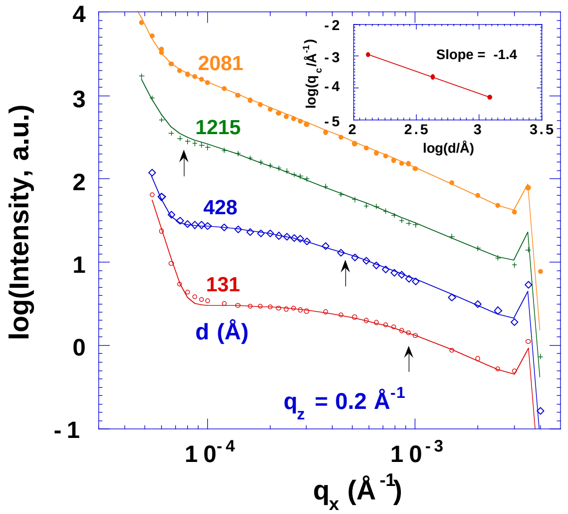

Figure 3: Transverse diffuse scattering scan for the samples with various polymer thicknesses at $q_z = 0.2$ Å^{-1}. The fits to the data using modified capillary wave scattering theory (incorporating thin film effect) are shown as lines. The arrows indicate the cutoff locations. The inset depicts $\log(k_c)$ vs. $\log(d)$(circles: k_c obtained from the diffuse scattering data, line: linear fit yielding a slope –1.4).

Discussion

The x-ray diffuse scattering data in this work have demonstrated that: 1) for PTBA thin films with thickness above 1,000 Å, the surface is liquidlike with modifications possibly due to the van der Waals interaction between the film and the substrate; and 2) for PTBA films with thickness close to or only a few (< 5) times larger than R_G, a less pronounced change of the exponent in the power-law in the transverse diffuse scattering data suggests that the films could be confined like in the case of PS films on silicon [6], where substrate-induced confinement is present even for films with thickness many times greater than R_G.

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