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Reduced Viscosity of the Free Surface in Entangled Polymer Melt Films

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By embedding ''dilute'' gold nanoparticles in single polystyrene thin films as ''markers'', we probe the local viscosity of the free surface at temperatures far above the glass transition temperature (T_g). The technique used was x-ray photon correlation spectroscopy with resonance-enhanced x-ray scattering. The results clearly showed the surface viscosity is about 30% lower than the rest of the film. We found that this reduction is strongly associated with chain entanglements at the free surface rather than the reduction in T_g.

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The dynamics of polymer chains near the surface of a melt and within thin films remains a subject of inquiry along with the nature of the glass transition in these systems (See, e.g., Refs. [1,2]). According to the Monte Carlo [3] and molecular dynamics [4] simulations, chain end groups tend to localize at polymer-air or polymer-substrate interfaces even without strong interaction forces of the chain end groups. By using a simple scaling analysis, Mayes [5] showed that such end enrichment at the air/polymer interface is extended within a distance nearly equal to the radius of polymer gyration (R_g). There are multiple experimental techniques for studying the surface glass transition temperature (T_g) in polymer thin films, and the above concept has been intensively discussed to explain the anomalous T_g reduction for substrate-supported polymer thin films ([1,2]). However, *in situ* dynamics at the free surface of single polymer thin films remains unclear due to the lack of experimental techniques that allow direct comparisons of these as a function of a distance from the surface. To overcome the difficulty and explore the details of the free surface, we utilized a ''marker'' x-ray photon correlation spectroscopy (XPCS) technique using gold nanoparticles (by taking advantage of the inherent strong x-ray contrasts) embedded in a polystyrene (PS) matrix. In addition, the use of resonance-enhanced x-ray scattering [6] for XPCS enabled us to intensify, by more than 1 order of magnitude, the probing electrical field in the regions of interest within single PS thin films. In this Letter, we show the first experimental evidence of the reduced viscosity in the near-surface region at $T \gg T_g$ due to reduced entanglements.

Six different molecular weights (M_w) of PS ($M_w = 30$, 65, 123, 200, 290, and 400 kDa) having narrow polydispersities ($M_w/M_n = 1.02$–1.05) were investigated. Thiol-functionalized (octadecanethiol ($C_{18}H_{37}SH$)) Au nanoparticles were prepared by using the one phase synthesis method [7]. The average radius of the core Au particles was 15 ± 2 Å based on small-angle x-ray scattering experiments and the thickness of the $C_{18}H_{37}SH$ (shell) layer was approximated to be 13 Å [8]. Solutions of PS were first prepared in toluene. The Au nanoparticles (the volume fraction was 0.2%) were then added to the PS solutions, which were further sonicated for 30 min. PS/Au thin films were prepared by spin-casting onto HF etched Si substrates and annealed for 1 d in vacuum of 10^{-3} Torr at $T = 170\,^\circ\mathrm{C} \gg T_g$ of PS, in order to remove residual solvents and to relax strains induced in the spinning process. We confirmed that the Au nanoparticles were homogenously dispersed in the PS matrix before and after the XPCS experiments using transmission electron microscopy (data are not shown) [9].

The XPCS experiments were performed at the beam line 8-ID at the Advanced Photon Source (APS), Argonne National Laboratory. The details of XPCS have been described elsewhere [10]. XPCS measures the normalized intensity-intensity time autocorrelation function, $g_2(q_\parallel, t) = \langle I(q_\parallel, t')I(q_\parallel, t'+t)\rangle / \langle I(q_\parallel, t')\rangle^2$, where $I(q_\parallel, t')$ refers to the scattering intensity at the in-plane wave vector transfer ($q_\parallel$) and at time t'. The brackets $\langle\rangle$ refer to averages over time t' and t is the delay time. $g_2(q_\parallel, t)$ is related to the normalized intermediate structure factor [$f(q_\parallel, t)$] via $g_2(q_\parallel, t) = 1 + A[f(q_\parallel, t)]^2$, where A is the speckle contrast. The two different modes were used for the present XPCS study: (i) With the incident angle (θ) of 0.15° set below the critical angle of the total external reflection of PS ($=0.16°$ at the x-ray energy of 7.5 keV), the scattering intensity is dominated by a surface region of thickness of about 90 Å [10]. We assign this experimental configuration as the "surface mode" hereafter. (ii) With the incident angle set just above the critical angle ($\approx 0.17°$), known as "the first resonance mode" [6], where resonance enhancement of the electric field intensity (EFI) in a polymer film takes place (Fig. 1), resonance-enhanced x rays (REX) are significantly intensified at the position close to the center of the film, while the scattering signal from an air/polymer interface (as well as a polymer/Si interface) can be eliminated (the inset of Fig. 1). We assign this experimental configuration as the "resonance mode" hereafter. Hence, XPCS in conjunction with the two different modes enables us to extract the Au motion at the free surface alone.

Representative g_2 functions for the Au nanoparticles at the surface mode are shown in Fig. 2(a). The thickness of the PS($M_w = 123$ kDa)/Au film was 1280 Å. In order to avoid the effect of T_g ($= 100\,°\mathrm{C}$ for PS), the measurements were made at temperatures of 156, 166, 176, and 186 °C in vacuum. The g_2 function at each $q_{\parallel}$ could be fitted by a single exponential function, $f(q_{\parallel}, t) = \exp[-(t/\tau)]$, where τ is a characteristic relaxation time of the Au nanoparticles. The solid lines in Fig. 2(a) are the best-fits to the experimental data. As shown in Fig. 2(b), we can see the power-law behavior of $\tau \propto 1/q_{\parallel}^2$ for both modes, indicating the diffusive motions of the Au nanoparticles at the surface and the center of the film. From the best-fits to the data (indicated by the solid lines) with the relationship of $\tau = 1/2Dq_{\parallel}^2$, where D is the diffusion constant of the Au particles [11], the D values for the surface mode (D_{sur}) and the resonance mode (D_{res}) were determined as a function of temperature. These D values are summarized in Table I where we can see that the Brownian motion of the Au particles is approximately 50% faster at the surface than at the center of the film regardless of temperature [13].

To discuss the origin of the enhanced Au dynamics at the surface, we calculated the theoretical values (D_{SE}) based on the Stokes-Einstein (S-E) law [14], i.e., $D_{\mathrm{SE}} = k_B T/6\pi R_E \eta$, where k_B is the Boltzmann constant, T is the absolute temperature, R_E is the effective radius of the thiol-functionalized Au particles ($= 28$ Å), and η is the film viscosity [15]. The average film viscosity of the PS/Au thin film, which is often different from the pure PS film [12], was measured independently by using bilayer dewetting experiments [12]. As summarized in Table I, the experimental D values for the PS/Au film were of the same order of magnitude as the predicted values, although the D_{SE} values correspond to the average of the local D values associated with different viscosity across the film. Hence, it is reasonable to conclude that the interaction between the PS and nanoparticles is weak enough so that the Brownian motion tracks the viscosity of the polymer matrix [16]. Consequently, the XPCS results give us the important conclusion that the enhanced Au dynamics is due to the presence of the reduced viscosity layer at the topmost

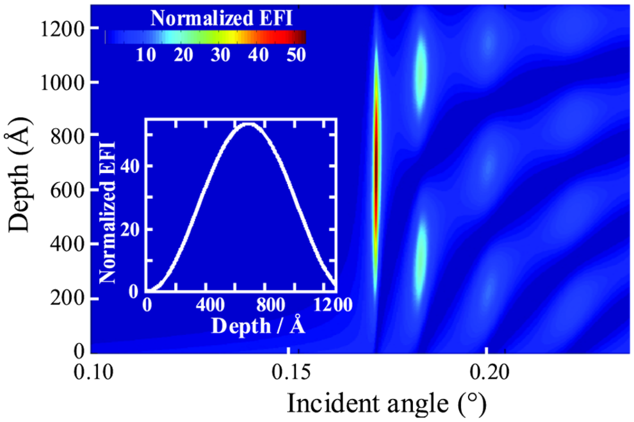

FIG. 1 (color online). Calculated EFI for a PS/Au film with the thickness of 1280 Å as functions of the depth from the air/polymer interface and the incident angle of x rays. The EFI distribution was generated by the interference of 7.5 keV x-ray plane waves reflected and refracted at the two interfaces in the film in air. As shown in the inset, the normalized resonance-enhanced x-ray EFI profile at the first resonance mode ($\theta = 0.168°$) is 53.5 times higher than that of the incident beam and the tail near the polymer/air interface can be eliminated. Second-order ($\theta = 0.184°$) and third-order ($\theta = 0.200°$) REXs can be also produced within the film.

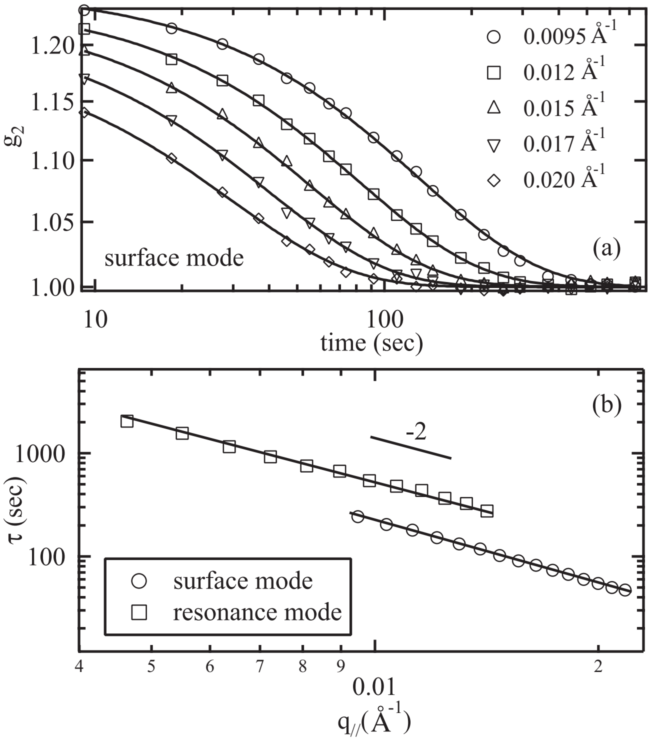

FIG. 2. (a) Measured g_2 at $T = 156\,°\mathrm{C}$ for the PS($M_w = 123$ kDa)/Au film at the surface mode. The solid lines are the best single exponential fits described in the text. (b) Log-log plot of τ vs $q_{\parallel}$ at $T = 156\,°\mathrm{C}$ for the surface mode and resonance mode. The solid lines correspond to the best fits of the relationship ($\tau = 1/2Dq_{\parallel}^2$) to the data.

TABLE I. Measured and calculated diffusion coefficients of the Au nanoparticles embedded in the PS ($M_w = 123$ kDa) matrix at four different temperatures.

T(°C)	D_{sur}(Å^2/s)	D_{res}(Å^2/s)	D_{SE}(Å^2/s)	η(N s/m^2)[a]
156	45	30	50	2.2×10^5
166	170	110	182	6.3×10^4
176	345	235	331	3.5×10^4
186	780	530	844	1.4×10^4

[a] Determined by bilayer dewetting experiments [12].

surface of the single polymer film at $T \gg T_g$. Similar conclusion was recently drawn by Bodiguel and Freigny [17] who used dewetting experiments for PS thin films on a liquid surface. However, as they pointed out, the dewetting experiments used provide a simple average of the local viscosity across the entire film so that the depth dependence of the local viscosity is strongly model-dependent. On the other hand, Fakhraai and Forrest showed the presence of enhanced surface mobility in PS thin films cooled below T_g [18]. However, the phenomenon is in a nonequilibrium glassy state. Hence, our finding is the first direct evidence of a reduced viscosity layer at the surface of the rubbery PS film in thermal equilibrium [19].

The next question to be addressed is whether the reduction in the surface viscosity is associated with a surface T_g change. To estimate the corresponding T_g change, we utilized the temperature scaling of the viscosity (η). Figure 3 shows η for the PS($M_w = 123$ kDa)/Au film as a function of temperature. The solid lines correspond to the best-fits to the data with the Williams-Landel-Ferry (WLF) equation [20], $\log(\eta(T)/\eta(T_0)) = -c_1(T - T_0)/(T - T_\infty)$, where T_0 is a reference temperature chosen, c_1 is a numerical constant, and T_∞ is a fixed temperature at which, regardless of the arbitrary choice of T_0, $\log(\eta(T)/\eta(T_0))$ becomes infinite. The best fits to the data gave us $c_1 = 4.0 \pm 0.5$ and $T_\infty = 42 \pm 2$ °C for the surface mode, and $c_1 = 4.0 \pm 0.5$ and $T_\infty = 47 \pm 2$ °C for the resonance mode, respectively. Hence our conclusion is that the T_g values (50 °C above T_∞ for PS [21]) for the surface and the center of the film are almost bulklike (~100 °C) [22]. This is inconsistent with the T_g measurements of a fluorescently labeled surface film by which Ellison and Torkelson [23] showed a large decrease in T_g (32 °C below bulk T_g) at the topmost PS surface (140 Å thickness) when the film was thicker than 600 Å. This discrepancy indicates that the reduction in the surface viscosity is not related to the decrease in T_g but inherent to the nature of the free surface in a rubbery PS film.

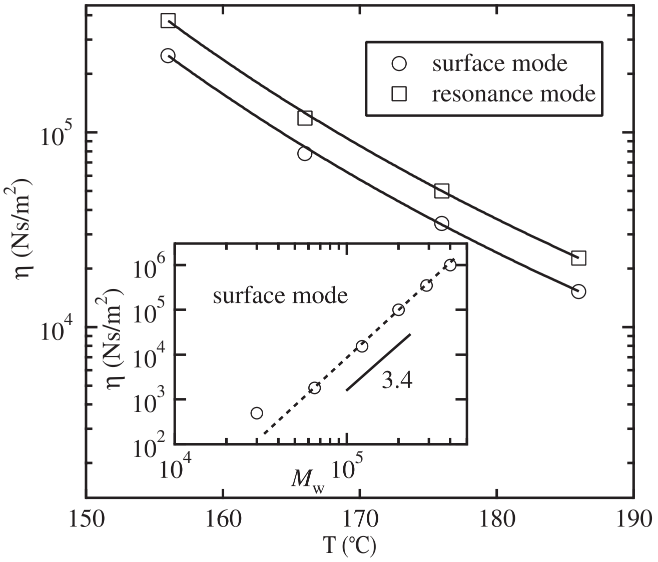

FIG. 3. Temperature dependences of the viscosity of the PS($M_w = 123$ kDa)/Au film (open symbols). The solid lines correspond to the best-fits of the WLF equation to the data with $c_1 = 4.0 \pm 0.5$ and $T_\infty = 42 \pm 2$ °C for the surface mode and $c_1 = 4.0 \pm 0.5$ and $T_\infty = 47 \pm 2$ °C for the resonance mode, respectively. In the inset, a log-log plot of the viscosity of the PS/Au film against M_w of PS at $T = 186$ °C is shown.

In order to further explore the surface reduced viscosity, we performed the XPCS experiments for the PS/Au films with the nearly same thickness (~1300 Å) but composed of different molecular weights (30 kDa $\leq M_w \leq$ 400 kDa). Note that the critical molecular weight (M_c) of PS, at which entanglement effects become apparent, is $M_c \sim$ 36 kDa [24]. All the XPCS results showed the single exponential decay functions of the Au motions for both the surface mode and resonance mode at the given temperatures (156 °C $\leq T \leq$ 186 °C). As summarized in Fig. 4, the enhancement of the Au diffusion at the free surface relative to the film center, $D_{\mathrm{sur}}/D_{\mathrm{res}}$, became less pronounced as M_w approached M_c, while the $D_{\mathrm{sur}}/D_{\mathrm{res}}$ values remained nearly constant (~1.5) at $M_w \geq$ 123 kDa. Especially, the enhancement almost vanished at

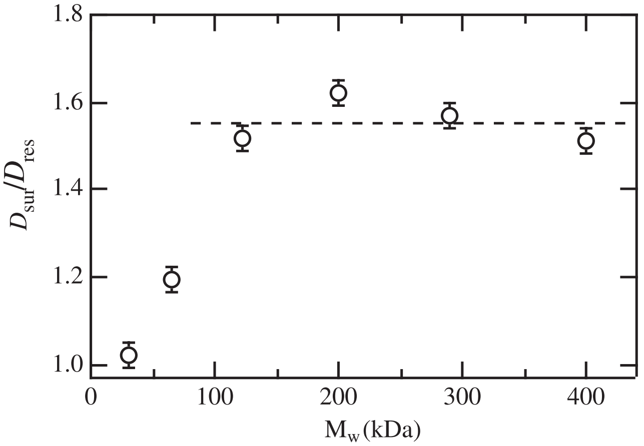

FIG. 4. Ratio of $D_{\mathrm{sur}}/D_{\mathrm{res}}$ for the PS/Au films (about 1300 Å in thick) as a function of M_w of PS measured at $T = 156$ °C.

$M_w = 30$ kDa, suggesting that the viscosity reduction at the surface is related to the chain entanglements. The inset of Fig. 3 shows a log-log plot of η vs M_w for the surface mode at $T = 186\,^{\circ}\mathrm{C}$ where we can see the well-known relationship of $\eta \propto M_w^{3.4}$ [25] except for the lowest M_w (30 kDa), indicating that the Au motion is probing primarily entangled dynamics in the surface region, although the diameter of the Au nanoparticles (56 Å) is somewhat smaller than the tube diameter for entangled PS (about 90 Å [26]). We therefore conclude that the reduced viscosity in the surface region is due to reduced entanglements that arise from the fact that the depth of the near-surface region being probed (ca. 90 Å depth) is comparable to the tube diameter.

In summary, by using a marker XPCS technique using Au nanoparticles in conjunction with resonance-enhanced x-ray scattering, we could probe the local viscosity of free surface of single PS melt films at $T \gg T_g$. The viscosity at the free surface is about 30% lower than the rest of the film and the reduction in viscosity can be extrapolated back to only a 5 °C decrease in T_g compared to the bulk. Moreover, we found that the reduced viscosity can be attributed to reduced entanglements at the surface.

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[9] Based on the in-plane structure factors of the small-angle x-ray scattering pattern from the film, the interparticle spacing of the nanoparticles was estimated to be 2200 Å. This is in good agreement with the average interparticle distance (l) of ~2000 Å predicted from the equation of $l \cong d[(\pi/6\phi)^{1/3} - 1]$, where d and ϕ are the average diameter and volume fraction of homogeneously dispersed filler particles, respectively.

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[16] In addition, the applicability of the S-E law to the PS/Au film is consistent with a previous report [V. Ganesan *et al.*, J. Chem. Phys. **124**, 221102 (2006)] which demonstrated that the S-E law is valid only for polymer nanocomposite systems that meet the condition of $R_g > R_E \gg a$, where a is the correlation length for a polymer generally considered as the size of a monomer unit.

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