X-ray Photon Correlation Spectroscopy Study on Dynamics of the Free Surface in Entangled Polystyrene Melt Films

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Abstract. 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. Recent studies show that the properties of the free surface region are crucial in determining the anomalous glass transition temperature ($T_g$) reduction of polymer thin films. In this study, by embedding “dilute” gold nanoparticles in polystyrene (PS) thin films as “markers”, we could successfully probe the diffusive Brownian motion which tracks the local viscosity both at the free surface and within the rest of the single PS thin film far above bulk $T_g$. The technique used was X-ray photon correlation spectroscopy with resonance-enhanced X-rays that allows us to independently measure the motion in the regions of interest at the nanometer scale. We found the presence of the surface reduced viscosity layer in entangled PS thin films at $T>>T_g$.

1. Introduction

It is well known that a nanoconfinement effect can play an important role in determining the mechanical and rheological properties of polymer thin films. With the advent of increasing miniaturization, lubricant films of this thickness have become commercially relevant and hence it is important to investigate the effect on a more fundamental level. So far, intensive experimental and theoretical studies have focused on the relationship between the glass transition temperature ($T_g$) and the chain dynamics in polymer thin films (see, for examples, Refs. [[1, 2]]. However, $T_g$ values are often said to average over the entire film so that the information is an ensemble average including both a polymer/substrate interface and polymer/air interface. By using x-ray photon correlation spectroscopy with gold nanoparticles as “markers”, we measured the Brownian motion of the gold particles at the free surface and the center of the polymer film independently. All of the gold relaxation functions were well described by a single exponential function and the enhanced surface dynamics was observed at all temperatures far above the $T_g$. These indicate that the origin of the enhanced surface mobility is not heterogeneous dynamics due to the glass transition. Further, we found that the gold dynamics tracked the viscosity of the polymer matrix and the viscosity of the free surface showed $\eta \propto M_w^{3.4}$, which is known as the power law variation for entangled polymers.

2. Experimental

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Four different molecular weights of polystyrene (PS, Mw=123, 200, 290, and 400 kg/mol) having narrow polydispersions (Mw/Mn=1.02-1.05) were investigated. Thiol-functionalized (octadecanethiol (C18H37SH)) gold nanoparticles were prepared by using the one phase synthesis method developed[3]. The average radius of the core gold particles and the thickness of the C18H37SH (shell) layer were approximated to be 15 Å and 13 Å, respectively. Solutions of PS were first prepared in toluene. The Au nanoparticles were then added to the PS solutions, which were further sonicated for 30 min. The weight percentages of the gold nanoparticles were fixed to 4%. PS/gold thin films were prepared by spin-casting onto HF etched Si substrates and annealed for 1 day in vacuum of 10^-3 Torr at T=170 °C >T_g, in order to remove residual solvents and spin-induced stress. TEM experiments gave us the evidence that the individual Au particles were dispersed in the PS polymer matrix even after the XPCS experiments.

In order to study the surface dynamics alone, we used a “markers” X-ray photon correlation spectroscopy (XPCS) technique that serves a “fingerprint” of the motion of the gold nanoparticles in polymer matrices. Furthermore, by intensifying the probing electrical field in the regions of interest for XPCS experiments, we could successfully differentiate the nanoparticles motions at the surface from the rest of the film by using the following two modes: (i) The “surface-mode” with the incident angle (\(\alpha_i=0.15^\circ\)) below the critical angle of the total external reflection of PS (0.16° with the x-ray energy of 7.5 keV used for the experiments). This allows us to study the surface area (about 90 Å depth) since the electric field intensity (EFI) decays exponentially into the film. (ii) The “resonance-mode” with the incident angle just above the critical angle where the first-resonance enhancement of the EFI in the polymer film takes place. Resonance-enhanced x-rays (REX), which are generated by the interference of x-ray plane waves reflected and refracted at the two interfaces of the film in air, are significantly intensified at the position close to the center of the film [4]. We found that the resonance enhanced x-ray intensity at the first resonance mode (i.e., at the incident angle (\(\theta\) of 0.168° for a 1280 Å film) is 53.5 times higher than that of the incident beam and the intensity near both interfaces can be eliminated[5]. It should be noted that the incident angle for the first resonance mode depends on the film thickness and second-order (\(\theta=0.184^\circ\)) and third-order (\(\theta=0.200^\circ\)) REXs can be also produced within the film. Consequently, a series of XPCS experiments at the two different modes allow direct investigation of the gold motion at the topmost surface area in a single thin film.

![Fig.1 Measured g2 at T =176 °C for the PS (M_w=123 kg/mol)/Au film at (a) the surface mode and (b) resonance mode. The solid lines are the best single exponential fits described in the text.](image-url)
The XPCS experiments were performed at the beam line 8-ID at the Advanced Photon Source (APS), Argonne National Laboratory. The details of the experiments have been described elsewhere[6]. XPCS measures the normalized intensity-intensity time autocorrelation function, $g_2(q, t)$

$$g_2(q, t) = \frac{<I(q, t'I(q, t+t')>}{<I(q, t')>2}$$

where $I(q, t')$ refers to the scattering intensity at the in-plane wave vector transfer $q$, and at time $t'$. The brackets $<$ > refer to averages over time $t'$ and $t$ is the delay time. $g_2(q, t)$ is related to the normalized intermediate structure factor $[f(q, t)]$ via $g_2(q, t) = 1 + A[f(q, t)]^2$, where $A$ is the speckle contrast. $g_2$ at each $q$ could be fitted by using a single exponential function, $f(q, t) = \exp(-t/\tau)$, where $\tau$ is the characteristic relaxation time of the function.

3. Results and Discussion

Fig. 1 shows representative $g_2$ functions at five different $q$ values at the surface mode (Fig. 1(a)) and the resonance mode (Fig. 1(b)) at 176°C. The thickness of the PS($M_w$=123 kg/mol)/Au film was 1280 Å. The solid lines are best-fits of the exponentially decaying autocorrelation function to the experimental data. Fig. 2 shows the $q$ dependences of the $\tau$ values obtained at both modes at 176°C. From the figure we can see that all the $q$ dependences followed the power-law behavior of $\tau \propto q^{-2}$, indicating the diffusive motion of the gold nanoparticles in the polymer matrix. From the best-fits to the data (the solid lines) with the relationship of $\tau = 1/Dq^2$, where $D$ is the diffusion constant of the gold particles, the $D$ values were estimated to be 345Å²/s for the surface mode and 235Å²/s for the resonance mode, respectively. It indicates that the Brownian diffusive motion of the gold particles is approximately 50% faster at the surface than near the center of the film. It should be emphasized that the enhanced gold dynamics at the surface (~50%) could be observed for the PS/Au films (~130 nm thickness) regardless of temperatures (156 ≤ T ≤ 186 °C) and molecular weights of the polymers used in this study.

In order to investigate the origin of the enhanced gold dynamics, we calculated the theoretical $D$ values using the Stokes-Einstein (S-E) law for diffusion of isolated particles in a viscous medium, i.e., $D = k_BT/6\pi\eta R$, where $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $R$ is the effective radius of the thiol-functionalized Au particles (28 Å), and $\eta$ is the viscosity of the entire film. The averaged film viscosity for the PS/Au thin film was estimated to be $3.5 \times 10^4$ (Ns/m²) at T=176 °C by using bilayer dewetting measurements[7]. Substituting the measured $\eta$ value for the PS($M_w$=123 kg/mol)/Au nanocomposite thin film into the S-E law gave us the calculated $D$ values of 331Å²/s, showing that the experimental $D$ values obtained from the XPCS experiments are very close to the calculated $D$ values. Therefore, we can conclude that the thiol-functionalized gold nanoparticles have
a very weak interaction with the polymer such that the Brownian motion of the nanoparticles tracks the viscosity of the matrix. Consequently, the XPCS results clearly demonstrate that the enhanced Au dynamics is due to the presence of the reduced viscosity layer at the topmost surface of the single polymer film at $T >> T_g$.

We further investigated the local viscosity of the surface and center regions calculated by the S-E law. Interestingly, we found the well-known relationship of $\eta \propto M_w^{3.4}$, which is known as the power law variation for entangled polymers[8], in both the surface and resonance modes[5]. This finding indicates that the polymer chains are indeed entangled even at the surface region within the thickness of 90 Å and the chain dynamics is still governed by the pure reptation mechanism.

The next question to be clarified is whether this surface reduced viscosity layer is present regardless of the film thickness. Our preliminary XPCS experiments with different thicknesses of the PS/Au films gave us the evidence that the surface layer is perturbed when a distance from the substrate is close to 600 Å and the further reduction of the distance down to about 300 Å obliterates the surface layer to a great extent. We believe this is attributed to the presence of a “dead” layer which is strongly bound to the substrate and hence remains on the substrate even after thorough rinsing with a good solvent [9]. Further studies will provide a new insight into the mechanism of the nanoconfinement effect on the rheological property of polymer thin films.

4. Conclusion

In summary, by using the marker XPCS technique in conjunction with resonance-enhanced x-rays, we found the existence of the surface enhanced layer in the liquid polymer thin films with ~1300 Å thickness. The viscosity of the free surface layer was about 30 % lower than the rest of the film. Moreover, we found that the emergence of the surface enhanced layer was strongly related to the entanglement of the polymer chains, resulting in the well-known relationship of $\eta \propto M_w^{3.4}$ at the free surface of polymers. We believe that the methodology described here would open up a new avenue to explore in-situ and surface perturbation (such as oscillatory in the case of atomic force microscopy)-free dynamics at specific surfaces and interfaces of polymer films or membranes to be used for interdisciplinary materials research.

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