A Broad Perspective on the Dynamics of Highly Confined Polymer Films

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ABSTRACT

The manner in which the dynamics of a polymer are affected by thin film confinement is of technological significance, impacting thin film applications such as lubricants, adhesives, and chemically amplified photoresists. In this manuscript we use specular X-ray reflectivity (SXR), beam positron annihilation lifetime spectroscopy (PALS), and incoherent neutron scattering (INS) to study the influence of thin film confinement on the apparent glass transition temperature $T_g$ and the thermal expansion coefficients of thin polycarbonate (PC) films. Both the SXR and PALS indicate a significant suppression of $T_g$ when the film thickness becomes less than 200 Å. However, the INS measurements suggest an increase in the apparent $T_g$ below this same length scale. These disparate estimates of the thin film $T_g$ seem to indicate that each technique is sensitive to slightly different aspects of the glass formation process. However, all three agree that thin film confinement results in reduced thermal motion, regardless of the precise temperature that is ‘designated’ as the thin film $T_g$.

INTRODUCTION

In recent years, the number of studies focusing on the glass transition $T_g$ and dynamics of polymer thin films has increased dramatically. This body of literature is now so vast that it is nearly impossible to reference all of the germane contributions to the field. This attention is in part driven by industry’s need to better understand the thermophysical behavior of exceedingly thin polymer films (i.e., photolithography, coatings, adhesives, lubricant films, etc.). In bulk, $T_g$ is typically associated with the temperature beyond which there is a sudden decrease in the polymer viscosity, dramatic softening, enhanced mobility or diffusion, etc. Consequently, most applications are designed for use well below the $T_g$ of any of their polymeric components. However, in exceeding thin films, it is well known that confinement affects strong $T_g$ deviations, with the exact nature of the shift depending on the specific polymer/substrate pairing. The expectation is that all of the thin film properties will follow their bulk analogs. For example, a decrease in the apparent glass transition of a thin film is often interpreted as evidence for increased mobility, which would then lead to effects such as increased small molecule diffusion. In a photoresist film, such a scenario could lead to blurring of the lithographic image.

In this work we use three independent experimental techniques, specular X-ray reflectivity (SXR), positron annihilation lifetime spectroscopy (PALS), and incoherent neutron scattering (INS) to study an identically prepared set of polycarbonate (PC) films over a wide temperature range. In the bulk, each of these techniques is sensitive to a material parameter that goes through a discontinuous change at $T_g$. By comparing all three techniques on the same set of films, one obtains a broad perspective of how confinement affects the dynamics of thin polymer films.
EXPERIMENTAL

An identical series of films was prepared for each set of experiments by dissolving PC (GE Plastics [1] grade ML 4535-11N with a molecular mass average of 36.3 kg/mol and PDI = 1.4) into cyclohexanone at mass fractions ranging from 0.28 % to 5.00 %. These solutions were filtered (0.45 Teflon filter) and spun at 2000 rpm onto Si wafers with a freshly prepared native oxide (hydrophilic) surface. Prior to each measurement, the films were annealed for 6 h to 12 h at 200 °C under a vacuum of 10^{-5} Pa to ensure solvent removal.

SXR allows one to measure the film thickness with angstrom-level precision. By performing SXR measurements as a function of temperature, a thermal expansion curve is generated for the film. As with most amorphous materials, a discontinuity or kink in the expansion curve typically occurs at T_g. This has been widely used to characterize the glass transition of polymer thin films, and details of this measurement technique are reported elsewhere [2]. Note that all measurements, including the SXR, PALS and INS, are done under a vacuum of 10^{-5} Pa or better.

Similar to SXR, PALS is recognized technique for characterizing the glass transition in thin polymer films [3,4]. Specifically, PALS quantifies the nm-sized defects in the electron density (packing inefficiencies) through the ortho-positronium lifetime \( \tau_{o-Ps} \). To be registered by PALS, these defects must persist for one nanosecond or longer. Such inhomogeneities expand significantly with temperature, which is registered by an increase in \( \tau_{o-Ps} \). Like the macroscopic expansion of the film, a discontinuity is typically encountered at T_g in both thin films and bulk glasses. Again, the specific details of the experimental equipment are reported elsewhere [3,4].

Unlike SXR and PALS, INS is a new technique for characterizing the dynamics and the glass transition in thin polymer films. The measurements reported here are based on a Debye-Waller factor analysis of the Q dependence of the elastic incoherent neutron scattering intensities. Near absolute zero, most materials have zero mobility and the resultant neutron scattering is purely elastic. As temperature increases, thermally activated dynamical processes lead to a decrease in the intensity of the elastically scattered neutrons, and a corresponding increase in the number of inelastic scattering events. The incoherent scattering intensity \( I_{inc}(Q) \) is often approximated by the Debye-Waller factor where:

\[
I_{inc}(Q) \propto e^{-\frac{1}{3}Q^2<u^2>}
\]

where \( Q \) is the scattering vector and \( <u^2> \) is the amplitude or mean-square atomic displacement of the thermally activated motions. In this framework, the slope of \( ln(I_{inc}(Q)) \) vs. \( Q^2 \), which can be tracked as a function of temperature, yields \( <u^2> \).

The INS experiments are done at the NIST Center for Neutron Research on the High Flux Backscattering Spectrometer (HFBS) [5]. This spectrometer has an energy resolution of 0.8 \( \mu \)eV, which means that \( <u^2> \) reflects the motions 200 MHz or faster; slower motions appear as elastic scattering. The INS signal is dominated by H, which has a scattering cross section \( \approx 20 \) times larger than either C or O, and nearly 40 times larger than Si. In other words, the polymer should dominate the incoherent scattering for our PC films supported on Si wafers. To obtain
sufficient scattering signal from the thin films, (13 to 15) Si wafers (dia. = 75 mm) were broken into rectangular strips and placed in a sample cell (= 1 mg to 10 mg of PC in the cell). The spectrometer operates with a neutron wavelength of 6.27 Å over a Q range of 0.25 Å\(^{-1}\) to 2.0 Å\(^{-1}\). The fact that the first Bragg peak for Si occurs at Q ≈ 2.67 Å\(^{-1}\) further ensures that the dynamics of the Si substrates contribute negligibly to the scattering intensity. Further details of these thin film \(<\mu^2>\) measurements are reported elsewhere [6].

RESULTS AND DISCUSSION

Fig. 1 summarizes the SXR thin film thickness measurements as a function of temperature. The expansion curves are presented in terms the percent change in film thickness relative to a reference thickness, \(\delta h/h_0\) (arbitrarily the reference temperature is defined to be 180 °C). Each curve represents an average of 2 to 4 heating and/or cooling cycles and is offset vertically (by a constant addition indicated in the legend) for clarity. Error bars of ± 0.25 % indicate the typical standard uncertainty in the spread for the 2 to 4 isothermal thickness values averaged over all isothermal data sets.

![Graph showing percent change in film thickness as a function of temperature](image)

**Figure 1.** The percent change in film thickness, \(\delta h/h_0\), as measured by specular X-ray reflectivity, in reference to the overall thickness at 180 °C \((h_0)\). The curves are offset vertically for clarity by a value indicated in the legend. The extrapolated intersection of the fits, indicated by the solid lines, defines the apparent \(T_{g,x}\), as described in the text. The error bars indicate typical standard uncertainties in film thickness from multiple measurements.

In the 717 Å film, we observe a “kink” in the expansion curve nominally coincident with the calorimetric \(T_g\) of PC \((T_{g,c} = 150 °C)\). Linear fits to the regions above and below this kink, indicated by the solid lines, establish an intercept that is identified as the apparent glass transition \(T_{g,x}\) of the film as measured by SXR. A similar fitting procedure is used to extract the kink temperatures from the remaining films in Fig. 1, with the solid lines indicating the data points included in each fit. \(T_{g,x}\) appears to decrease with the decreasing film thickness, as summarized in Fig. 4.

Fig. 1 also reveals that the magnitude of the coefficient of thermal expansion (from the slopes of the linear fits) decreases as the film thickness is diminished. The expansion coefficients for both the glassy (\(\beta_{x,g}\)) and rubbery (\(\beta_{x,r}\)) regions (i.e., below and above \(T_{g,x}\) respectively) are summarized in Fig. 5. Interestingly, \(\beta_{x,g}\) takes on a negative value in the thinnest (60 Å) film. Unfortunately there is not adequate room to address this negative \(\beta_{x,g}\) in
this short manuscript. However, we have done extensive research on this phenomenon and can demonstrate that the effect not an experimental artifact. The results of these studies will be published shortly.

The complimentary $\tau_{Ps}$ versus temperature PALS data are presented in Fig. 2 for a similar range of PC films. For the range of $\tau_{Ps}$ values in Figure 2, the proportionality between cavity size (diameter, assuming a spherical cavity) and $\tau_{Ps}$ is approximately linear, corresponding to cavities approximately 5 Å to 6 Å in diameter. As with the SXR data, each curve is an average of multiple (2 to 5) heating and/or cooling curves. The error bars represent the standard uncertainty in the fitted lifetimes obtained from the PFPOSFIT algorithm [7], also averaged over the multiple (2 to 5) isothermal lifetime measurements. Figure 2 also compares the thin film data to the bulk PALS measurement [8] for a similar PC. The expansion curves are vertically offset by a constant (indicated in the legend) to facilitate comparison.

![Figure 2](image-url)

**Figure 2.** Thermal variations of the ortho-positronium lifetimes, $\tau_{Ps}$, as a function of film PC film thickness. Once again, the curves are offset vertically for clarity by a constant addition indicated in the legend. The intersection of the fits, indicated by the solid lines, defines the apparent $T_{g,p}$ as described in the text.

We caution that the absolute $\tau_{Ps}$ lifetimes should not be taken too literally; the thermal variations of $\tau_{Ps}$ are robust and the primary emphasis of this work. In each film there is a kink in the thermal variation of $\tau_{Ps}$, similar to the bulk data where the discontinuity is known to coincide with the calorimetric $T_{g,c}$. A least squares fitting routine is used to extract the apparent PALS glass transition temperatures, $T_{g,p}$, from the intersection of linear fits above and below the kink, analogous to the SXR analysis. A PALS coefficients of thermal expansion above ($\beta_{p,r}$) and below ($\beta_{p,g}$) $T_{g,c}$ is similarly defined by the slopes of these fits. The $T_{g,p}$'s and expansion data are summarized in Fig. 4 and 5, respectively. As with the SXR data, there is a decrease of $\beta$ with increasing confinement. In the 75 Å film, $\beta_{p,g}$ becomes slightly negative which is qualitatively similar to $\beta_{c,g}$ for the 60 Å film. Although the error bars on $\beta_{p,g}$ are large for this 76 Å film, the non-intuitive negative coefficient of thermal expansion appears to be supported by two independent techniques.

Fig. 3 shows the $\langle u^2 \rangle$ versus temperature plots from the incoherent elastic neutron scattering data [6]. Clearly $\langle u^2 \rangle$ decreases strongly as the degree of thin film confinement increases. This indicates a reduction of the overall particle mobility (i.e., more elastic scattering) with confinement. As described elsewhere [6], the Debye-Waller analysis was performed on the low Q data ($Q < 1.0 \text{ Å}^{-1}$) which means that $\langle u^2 \rangle$ emphasizes the longer length scale atomic
motions, with frequencies faster than 200 MHz. For example, motions like methyl group rotations or phenyl ring flips probably dominate \( \langle u^2 \rangle \).

**Figure 3.** The mean square atomic displacement \( \langle u^2 \rangle \), normalized to zero at \(-225^\circ C\), as a function of PC film thickness. The solid lines indicate linear fits used to extract the apparent \( T_{g,u} \). Standard uncertainties in \( \langle u^2 \rangle \) are on the order of the size of the data markers.

In addition to the decreasing \( \langle u^2 \rangle \) relative to the bulk, confinement shifts the softening point where \( \langle u^2 \rangle \) begins to rapidly increase to higher temperatures. In the bulk this crossover often coincides with the calorimetric \( T_{g,c} \) [9,10]. Once again, the corresponding kinks in the thin films are tentatively referred to as the apparent \( \langle u^2 \rangle \) glass transitions \( T_{g,u} \). Fig. 4 and 5 show that \( T_{g,u} \) increases with confinement. This trend is in stark contrast to \( T_{g,x} \) and \( T_{g,p} \) which shift to lower temperatures with decreasing film thickness. At this time we do not completely understand why the trends in the INS data diverge from the PALS and SXR. The SXR, PALS, and INS measurements apparently become sensitive to different aspects of the glass transition in thin films in a manner that is property specific. However, as with the SXR and PALS data, a \( \beta_{u,g} \) can be defined by a linear fit through the data below the kink. Fig. 5 shows that \( \beta_{u,g} \) decreases with level of confinement, in accord with the trends observed in \( \beta_{x,g} \) and \( \beta_{p,g} \). Thus while the discontinuity or apparent glass transition
temperature seems depend on the measurement technique, the trends in the thermal expansivity are qualitatively consistent, indicating reduced mobility. This is important because only focusing on the shift of a kink temperature, it is possible that one could come to the conclusion that a reduced apparent $T_g$ corresponds to enhanced mobility. Clearly caution must be exercised when identifying and interpreting kinks in the temperature dependence of a thermophysical parameter in relation to the glass transition.

![Graph](image)

**Figure 5.** Film thickness ($h$) variation of the various thermal expansion coefficients ($\beta$) as defined in the text. The error bars represent the standard uncertainty in the slopes from the linear fits in Figs. 1, 2, & 3.

REFERENCES

1. Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply the material or equipment identified is necessarily the best available for this purpose.


