The Dynamics of Confined Polycarbonate Chains Probed with Incoherent Neutron Scattering

C. L. Soles, J. F. Douglas, R. M. Dimeo* and W. L. Wu

Polymers Division, NIST, Gaithersburg, MD, 20899-8541

*NIST Center for Neutron Research

ABSTRACT

The mean-square atomic displacement <u^2> of thin (1015 Å to 75 Å) polycarbonate films supported on Si wafers is measured using incoherent elastic neutron scattering. The value of <u^2> is determined by fitting the scattering intensity data to the Debye-Waller factor and we find that <u^2> is diminished with decreasing film thickness. When the film thickness is comparable to the unperturbed dimensions of the macromolecule two characteristic temperatures start to emerge in the <u^2> data, one above and the other below the bulk Tg . Furthermore, preliminary results with a different polymer suggests that <u^2> does not depend on the probing direction, i.e. the in-plane and the out-of-plane <u^2> were found to be identical within the experiment uncertainty.

INTRODUCTION

Material properties of thin films can deviate substantially from their bulk values. Many recent experimental results indicate a critical film thickness, on the order of the macromolecular size, for properties deviations. This length scale is much greater than what is required for similar deviations in small molecule compounds. For polymeric materials these changes have potential ramifications in a range of thin film applications such as photolithography, protective coatings, lubricants, adhesives, etc. Of particular interest are surface induced changes in the polymer mobility as reflected in the glass transition temperature, Tg, and the viscoelastic properties that depend on Tg. Deviations in a polymer's dynamical properties can introduce deleterious behavior relevant to a variety of thin film applications, e.g., an increase in Tg and the viscosity of a lubricating film or a decrease in Tg and enhanced transport through a barrier film. It is therefore important to develop fundamental methods to study these finite-size or confinement effects.

In this work, we present the first incoherent elastic neutron scattering measurements directly probing the chain dynamics of supported polymer films. From the one phonon approximation, the incoherent elastic neutron scattering intensity is proportional to the Debye-Waller factor where $I_{inc}(Q) \propto \exp(-1/3Q^2<u^2>)$. In this representation, Q is the scattering vector and <u^2> the mean-square displacement of the scattering entities.

EXPERIMENT

Thin polycarbonate (PC) (GE Lexan ML-4235 [1]; Mw= 36.3 kg/mol) films were spin cast from cyclohexanone solutions onto silicon wafers (75 mm diameter, <100> surface, thickness ~ 0.3 mm) with freshly prepared oxide surfaces. Four sets of films with typical thickness values of 75 Å , 128 Å , 298 Å , and 1015 Å, as determined by specular X-ray reflectivity, were studied. Approximately 13 to 15 wafers of each film thickness were broken into approx 20 x 50 mm^2 strips and placed in a cylindrical, thin-walled aluminum cell. This resulted in roughly 0.6 mg to 7.1 mg of PC in the sample cell in comparison to 52 g to 58 g of Si. The cell was mounted on the High Flux Backscattering Spectrometer (HFBS) on the NG2 beam line at the NIST Center for Neutron Research [2] and cooled to 50 °K under vacuum. The spectrometer operated in the Fixed Window Mode (stationary Doppler drive) with the elastic intensities recorded over a Q range of 0.25 Å^{-1} to 2.0 Å^{-1}. The sample temperature (T) was ramped at 0.5 °K/min (1014 Å films) to 0.1 ° K/min (75 Å films) up to 525 °K. The HFBS energy resolution of 0.85 µeV (FWHM) implies that dynamics on a time scale of 200 MHz or slower are considered static.

Neutron scattering in polymers is typically dominated by H which has a total scattering cross-section approximately 20 times greater than either C or O, and nearly 40 times larger than the Si substrate. Given that there is nearly 100 times more Si than PC in the sample cell, it might seem unreasonable to extract dynamical information from the polymer. However, with a neutron wavelength of 6.271 Å, the accessible Q range of the HFBS spectrometer is just below the first Bragg peak of Si (Q ~ 2.67 Å^{-1}). This ensures that the dynamics of Si are nearly transparent to the spectrometer.

RESULTS AND DISCUSSION

For a harmonic solid, the intensity of the elastically scattered neutrons decreases linearly with T. In contrast, the motions of a polymer can be strongly anharmonic and non-vibrational, producing a non-linear thermal decrease in the scattered intensity. Such a non-linear decrease has been observed at a fixed Q for all the PC films. In Fig. 1 where <u^2>, normalized to zero at 40 °K, is plotted as a function of T for both the bulk and thin film samples. Clearly, <u^2> is diminished as the film thickness decreases, suggesting that confinement reduces the amplitude of the atomic movements.

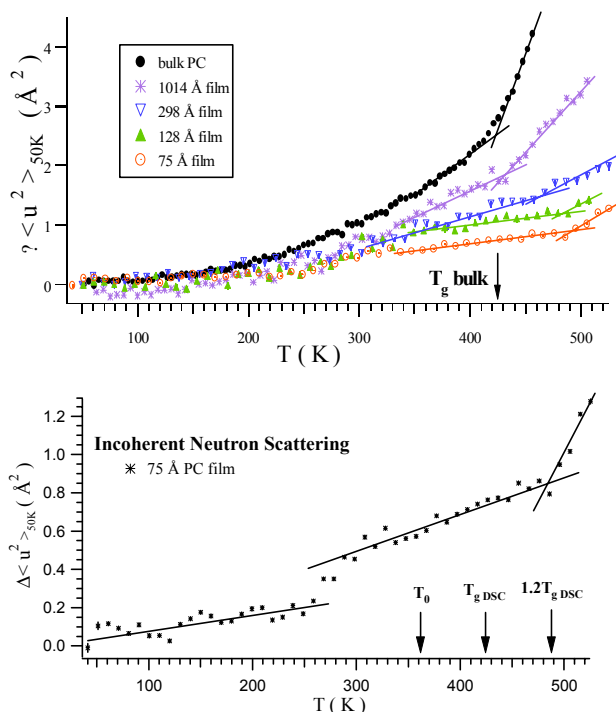**Figure 1.** (a) <u^2> as function of temperature for both the bulk and confined PC films. (b) The result for the 75 Å sample is expanded to emphasize the step-like feature between 250° K and 350° K. The standard uncertainty from the counting statistics are less than the size of the data points.

Specular X-ray reflectivity measurements of film thickness as a function of T provide an established method to estimate the apparent Tg of thin films. Fig. 2 compares the thermal expansion in terms of D, a percent change in thickness, for the 720 Å and 75 Å PC films on identical substrates. The break in the expansion is close to the bulk Tg (DSC) for the thicker film, but is apparently shifted to lower T in the thinnest film. At first this seems to contradict the apparent increase in Tg observed in <u^2>. However, a close up of the result of the 75 Å film (Fig. 1b) reveals a step-like feature in <u^2> between 250 ° K and 350 °K that is absent from the thicker films and bulk material. This step-like feature appears close to the apparently reduced Tg appeared in the reflectivity data of Fig. 2.
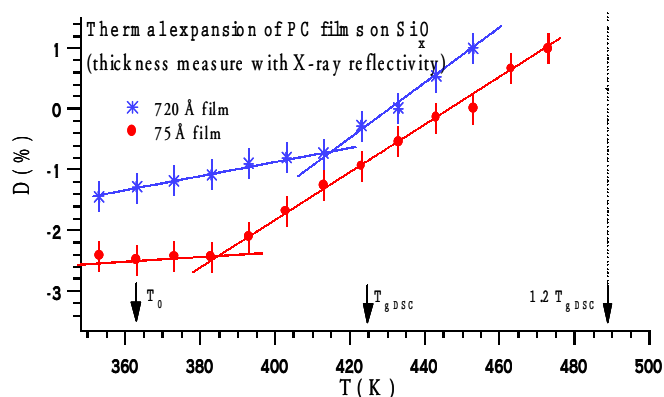
Figure 2. Thermal expansion of a thick (720 Å) and thin (75 Å) PC film determined by specular X-ray reflectivity. The error bars denote the typical standard deviations from multiple measurements.

At this time it not clear how the features in Fig. 1 relate to the glass transition. The high T break in the thermal dependence of $<u^2>$ occurs at $\sim 1.2 T_g$ (bulk) for the 75 Å films. Unfortunately, the X-ray reflectivity data does not extend to this T because of instrumental limitations.

There is precedent for observing multiple characteristic T's in bulk glass-forming liquids. A variety of evidence [5-7] indicates that changes in the dynamics of supercooled liquids occur above T_g at T $\sim 1.2 T_g$. These changes include deviations in the Stokes-Einstein and Debye-Einstein relations, a bifurcation of the a and b relaxation processes, and the breaking of ergodicity as predicted by mode coupling theory. It seems interesting that the break in $<u^2>$ for highly confined PC films also occurs near 1.2 T_g(bulk). Similarly, a sub-T_g(bulk) characteristic temperature is predicted by fitting viscosity or relaxation data to the Vogel-Fulcher equation (e.g., $\eta \sim \eta_\infty$ exp $[mT_0/(T-T_0)]$). Experimental evidence [6] and theoretical arguments by Adam-Gibbs [8] suggest that the configurational entropy stops varying well below ($\sim 50° K$) T_g(bulk), at a T very near T_0. The lower temperature cross-overs in both $<u^2>$ and reflectivity data for D occur close to a range of estimates (340 °K < T_0< 375 ° K) for the Vogel-Fulcher T_0 for PC.

The ramifications of these observations need to be established by extending the measurements to a broader range of confined glasses. These results raise several interesting questions, however. For example, it is not clear why the two characteristic temperatures become pronounced in the thin film geometry. Beside the observation that thin film confinement causes a decrease in $<u^2>$, the question of directional dependence of $<u^2>$ is also an interesting one. In other words, is the value of $<u^2>$ measured along the plane of confinement different from that perpendicular to the plane or along the thickness direction. The answer to this question is expected to shed some light about the origin of the observed decrease in $<u^2>$.

As demonstrated in Fig. 2 that $<u^2>$ was measured from the Q dependence of the elastic neutron intensity. By placing a stack of supported films with its surface either parallel to or perpendicular to the direction of the smallest Q vector, defined by the position of the nearest detector off the beam stop, one can get a semi quantitative answer to this question. The first sample we tried is 420 Å poly methyl methacrylate (PMMA) film of 1.7M molecular weight. In a similar study to be published later we found that this thickness is sufficient to observe a confinement effect in $<u^2>$. Thick films are preferred for this type of neutron measurement since the signal is rather weak and is linearly proportion to film thickness. The result (Fig. 3) suggests that the magnitude of $<u^2>$ does not depend on orientation, i.e. the out-of plane amplitude and the in-plane one are identical.
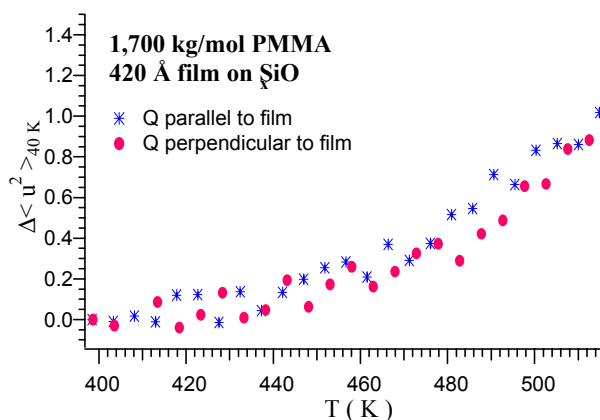

Figure 3. $<u^2>$ results of a stack of supported PMMA films; one set of data was collected with sample surface nearly parallel to the scattering vector and the other set perpendicular to the scattering vector.

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 that the material or equipment identified is necessarily the best available for this purpose.
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