

Depth Profiling of Density Fluctuations within a Polymer Film by using Diffuse X-ray Scattering

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Introduction

The properties of polymer chains in thin films can differ from their properties in bulk polymers because of factors such as chain distortions at both the vapor and solid interfaces, free ends at the vapor interface, pinning at the solid interface, and polymer-substrate van der Waals interactions. It has been observed in several experiments that the value of the glass transition temperature T_g can change in thin polymer films when compared with the bulk polymers [1]. While x-ray reflectivity and diffuse scattering measurements have probed the structure and dynamics of the polymer surface [2, 3, 4], information about the interior of the film must be inferred from models that connect bulk behavior to the resulting surface deformations.

For the present measurements, we have used grazing incidence x-ray illumination to measure the bulk diffuse scattering from the structure inside the film. In order to separate bulk and surface effects, the measurements were performed at angles below the critical angle for total external reflection. Here, an evanescent wave penetrates with an exponentially decaying intensity over length scales from a minimum of 4.57 nm down to the film depth. At wave vectors that are small relative to the inverse of the inter-monomer spacing, the bulk diffuse scattering is expected to be independent of the wave vector and proportional to the isothermal compressibility. Consequently, we are able to probe the depth dependence of the compressibility of the polymer film.

Methods and Materials

Samples were prepared by dissolving polystyrene ($M_w = 123K$, $M_w/M_n = 1.06$) in toluene and by spin casting onto optically flat silicon substrates with dimensions of $18 \times 18 \times 0.25$ mm. The silicon surface was treated with a buffered oxide etch to ensure good polymer adhesion. After coating, the films were annealed in vacuum of approximately 10^{-2} torr for 12 hours at 150°C . Scattering measurements were performed by using a temperature-controlled sample chamber integrated with the spectrometer vacuum environment. The specularly reflected beam was intercepted by a beam stop fitted with a Si positive intrinsic negative (PIN) diode, which was used to normalize the beam intensity. There were no windows between the sample and beam stop, which yielded a measurement free of background scattering. Diffuse scattering was measured with a charge-coupled

device (CCD) that was fiber-coupled to an optical scintillator and corrected for flat field and fiber distortions.

Results

In this experiment, we were looking for trends in the bulk diffuse intensity as a function of depth and temperature around the glass transition. For polystyrene, the T_g is 100°C and the critical angle is 0.188° . The samples were measured at incident angles of 0.11° , 0.12° , 0.13° , and 0.14° , covering a range of penetration depths of 5.63, 5.93, 6.32, and 6.84 nm (as compared to the sample thickness of 147 nm). The sample temperature was increased in incremental steps of 5°C over a range from 50 to 150°C .

Figure 1 displays the scattering measured on the CCD. The bright wedge in the center of the image is the specular scattering from the surface of the film. At a fixed value of the scattering vector, the intensity of the surface scattering varies as the product of the illuminated area and the absolute square of the x-ray transmission factor. These two factors yield a net linear dependence of intensity with angle θ below the critical angle θ_c . The intensity of the bulk scattering is further scaled by the penetration depth $\Lambda = \lambda/4\pi(\theta_c^2 - \theta^2)^{1/2}$. Here, λ is the x-ray wavelength. Figure 2 shows the variation of the scattering within the box of Fig. 1a (shown by the black line) and Fig. 1b (red line). The angular dependence of these curves agrees with the predictions based on a decomposition into surface and bulk components.

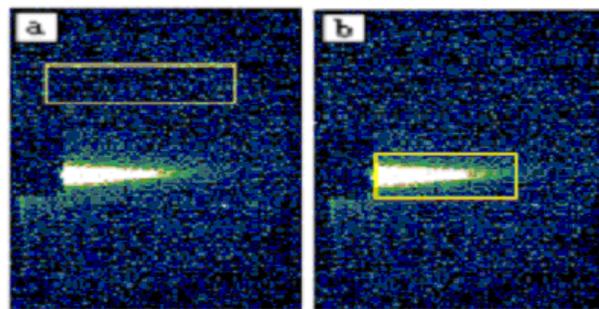


FIG. 1. Measured diffuse scattering from (a) bulk and (b) the surface of a polystyrene film supported on Si.

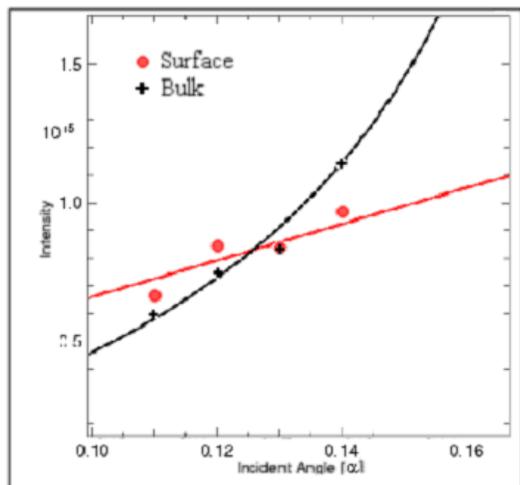


FIG. 2. Integrated intensity from the surface (red line) and bulk (black line) regions indicated in Fig. 1.

The data have been arbitrarily scaled in the y direction to fit on the same graph. The lines indicate the expected scaling for surface (black) and bulk (red) intensities with angle.

The variation of the integrated bulk diffuse intensity as a function of temperature and incident angle is displayed in Fig. 3. No trends in the intensity as a function of temperature or incident angle are apparent in the present data. However, we cannot rule out variations that are smaller than the random variations (~20%) between measurements. The large random variation in intensity with the angle most likely results from misalignment of the sample upon heating and from the difficulty of obtaining an exactly identical sample alignment after the temperature is changed.

Discussion

We have measured both surface and bulk scattering from polystyrene films supported on Si substrates as a function of angle and temperature. Analysis of the angular dependence of the intensity has permitted a decomposition of the scattering into its surface and bulk components. An initial search for trends in the bulk diffuse scattering with temperature above and below the glass transition was inconclusive. Since this initial measurement, the beamline has been re-fitted with a PIN diode detector mounted on a pseudo two-theta arm that has an angular resolution of order 1 millidegree. This should greatly reduce intensity fluctuations due to sample misalignment between temperature changes.

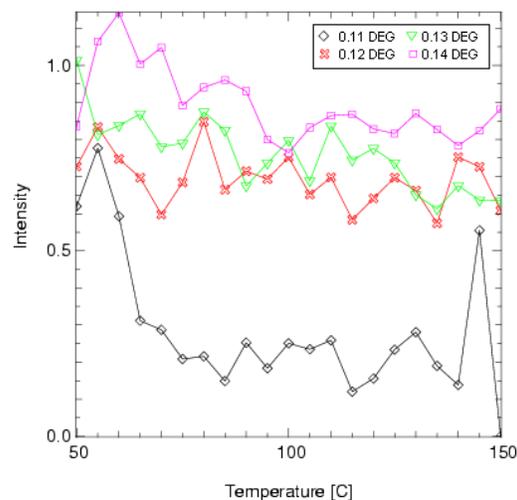


FIG. 3. Integrated bulk diffuse intensity versus temperature for measured incident angles of 0.11° , 0.12° , 0.13° , and 0.14° .

Acknowledgments

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References

- [1] J.L. Keddie, R.A.L. Jones, and R.A. Corey, *Europhys. Lett.* **27**, 59-64 (1994).
- [2] M. Tolan, *X-ray Scattering from Soft-Matter Thin Films* (Springer-Verlag, Berlin, Heidelberg, Germany 1999).
- [3] H. Kim, A. Ruhm, L.B. Lurio, J.K. Basu, J. Lal, S.K. Sinha, D. Lumma, and S.G.J. Mochrie, *Phys. Rev. Lett.* **90**(6), 8302 (14 February 2003).
- [4] L.B. Lurio, H. Kim, A. Ruhm, J.K. Basu, J. Lal, S.K. Sinha, and S.G.J. Mochrie, *Macromolecules* **36**, 5704 (2003).