X-ray Photon Correlation Spectroscopy on Polymer Films with Molecular Weight Dependence

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Introduction

Thin polymer films are currently of great interest [1] for basic scientific reasons and because of their importance in a variety of technological applications (e.g., coatings, adhesives, biocompatible surfaces for medical implants, computer disk drives). In many aspects, the basics with regard to the conformation and dynamics of polymer chains in thin polymer films are still not well understood. An example is the dynamic behavior of polymeric thin films near the glass transition.

Recently we investigated the dynamics of supported polymer films by probing fluctuations in surface height as a function of lateral length scale by using x-ray photon correlation spectroscopy (XPCS) [2]. The measurements were performed on polystyrene (PS) films with a molecular weight (M_w) of 123×10^3 g/mol and thicknesses varying from 84 to 333 nm at temperatures above the PS glass transition temperature. Within a range of wave vectors spanning 10^{-3} to 10^{-2} nm^{-1}, good agreement was found between the measured surface dynamics and the theory of overdamped thermal capillary waves on thin films. Quantitatively, the data can be accounted for by using the viscosity of bulk PS.

In this study, we employed XPCS on several different molecular weights of PS in order to verify the molecular weight dependence found in our earlier studies with 123×10^3 g/mol.

Materials and Methods

Our films were prepared by dissolving PS in toluene and then spin-casting onto optically flat silicon substrates. PSs with a M_w ranging from 30×10^3 to 650×10^3 g/mol were used in this study. These samples were then annealed in a vacuum for 12 h at 150°C to ensure complete solvent removal. The thicknesses of the PS films were kept between 160 and 180 nm for all the molecular weights.

XPCS experiments were performed at sector 8-ID at the APS. They employed monochromatic radiation with an x-ray energy of 7.66 keV. The experimental geometry is illustrated schematically in Fig. 1. By arranging for the x-ray incidence angle (0.14°) to lie below the critical angle for total external reflection (0.16°), we were able to restrict the x-ray penetration into the film to a depth of 9 nm, far thinner than any of the films studied here. Thus, scattering from the film-substrate interface is negligible, and only fluctuations of the polymer/vacuum interface are probed. Moreover, with x-rays, it is possible to access in-plane wave vectors that are larger (out to 10^{-2} nm^{-1} in these experiments) than those that can be easily achieved with optical methods. The off-specular diffuse scattering of the rough polymer surface was recorded with a direct-illumination charge-coupled device (CCD) camera, located 3545 mm downstream of the sample.
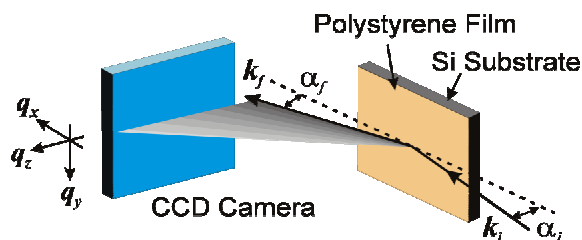

FIG. 1. The experimental setup for XPCS in reflectivity geometry.

Results

Figure 2 shows the best fit relaxation time constants (shown in symbols) as a function of in-plane wave vectors $q_\parallel$ for the ~170-nm-thick films of different molecular weights of PS at 160° and 170°C. The time constants
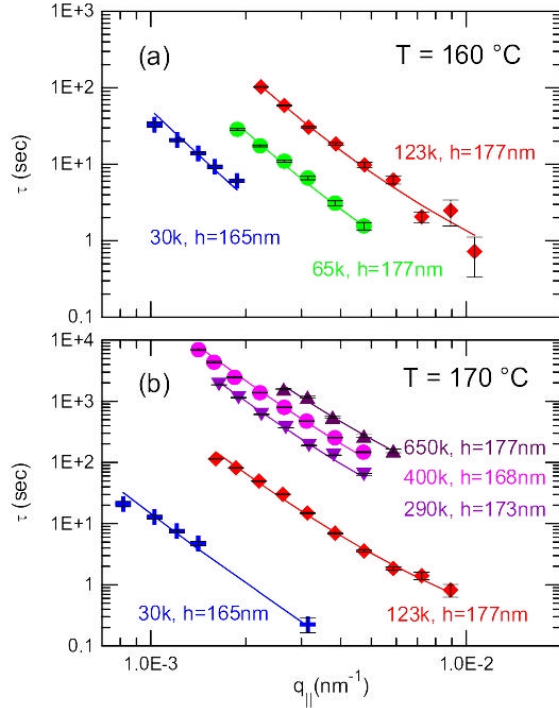
FIG. 2. *Measured time constant (τ) vs. in-plane wave vector (q$_\parallel$) for the ~170-nm-thick films of different molecular weights of PS at 160°C (a) and 170°C (b). The lines correspond to the calculation shown in Eq. (1).*

FIG. 3. *Viscosity of thin-film PS (squares) and bulk PS (circles) having different molecular weights as a function of temperature.*

were extracted from the intensity autocorrelation function. The time constants are faster in lower molecular weights and faster at higher temperature, as expected. Lines correspond to Eq. (1) [2] deduced from the theory [3] for the time dependence of surface height relaxations as well as for the wave vector, film thickness, and temperature in a viscous liquid. The relaxation time constant   is

$$ 2\ \text{H}/\ q_\parallel \text{F} , \qquad (1) $$

where   = viscosity,   = surface tension, F = $\sinh(q_\parallel h)\cosh(q_\parallel h) - q_\parallel h$, and H = $\cosh^2(q_\parallel h) + (q_\parallel h)^2$, with h being the thickness.

From the excellent agreement between the experimental data and theory, one can determine the ratio   / . By using the surface tension of PS [4] at each temperature, we obtained the viscosity of PSs with different molecular weights at each temperature shown in Fig. 3.

Discussion

Good agreement between the experimental results and conventional theory permits us to determine the film viscosity. A comparison between the values for viscosity obtained from these data and those for bulk PS reveals an
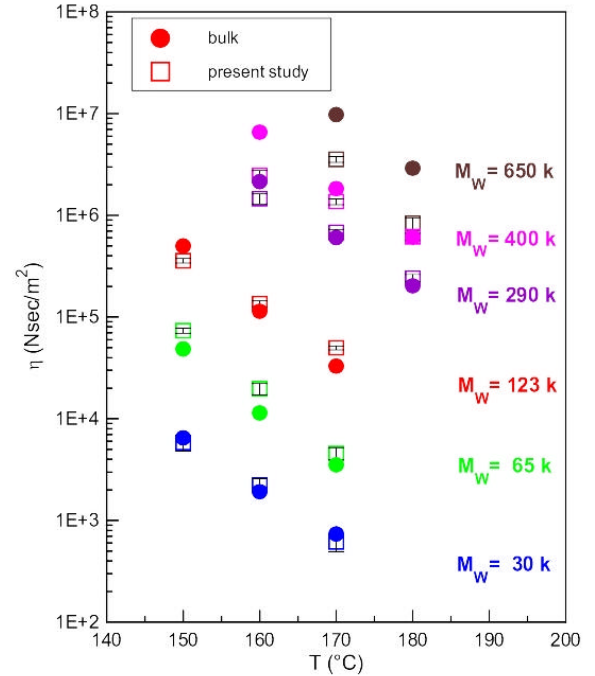
interesting result. Quantitatively, the data can be accounted for by using the viscosity of bulk PS with lower molecular weight. In higher-molecular-weight PS, the viscosity of thin film is lower than that of bulk PS. The behavior of higher-molecular-weight PS can be interpreted as an indication of the existence of a liquid surface layer having a lower viscosity than bulk PS, or it can be a result of the segregation possibly dominant in higher-molecular-weight PS.

Acknowledgments

References

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