Dynamics of Polymer Films Near the Glass Transition

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Introduction

The properties of thin polymer films have been of considerable interest lately, as they differ in some respects from those of bulk polymers.[1,2] In particular, the nature of the glass transition in polymer films is not yet completely understood and has been the subject of controversy.[3] To shed more light on the glass transition in polymer films, we have investigated the dynamics of surface capillary waves in polystyrene films using x-ray photon correlation spectroscopy (XPCS).[4] The measurements were performed at temperatures higher than the glass transition temperature and were analyzed in terms of the theory of overdamped thermal capillary waves on thin viscoelastic films.

Materials and Methods

The experiments were performed at the IMM-CAT's beamline 8-ID at the Advanced Photon Source (APS) and employed undulator x-ray radiation with a photon energy of 7.66 keV. We employed XPCS in the reflectivity geometry shown in Fig. 1 (a). The sample is illuminated coherently, resulting in a random speckle pattern that varies in time as the sample experiences thermal fluctuations. The x-ray beam impinges on the film at grazing incidence and correlation functions are obtained from intensity-intensity time-autocorrelation of the fluctuations of the speckles corresponding to the off-specular scattering by the capillary waves. The beam size was 20 × 20 μm², and the distance between the sample and the detector was 3.5 m. The detailed experimental setup is presented elsewhere.[5] Polystyrene (M_W = 123 000 g/mol, M_W/M_n =1.08) was dissolved in toluene and spun cast onto a hydrophilic silicon substrate. The thicknesses of the samples were 841, 1767, and 3332 Å. The samples were annealed in high vacuum for ~12 h at 150ºC (T_g ~ 100ºC). Figure 1 (b) shows the CCD image of time-averaged diffuse scattering from a 841-Å film at 160°C along with a fit to the expected structure factor for capillary waves.[6] The fit shows good agreement with the experimental data, indicating that capillary waves suffice to explain the scattering.

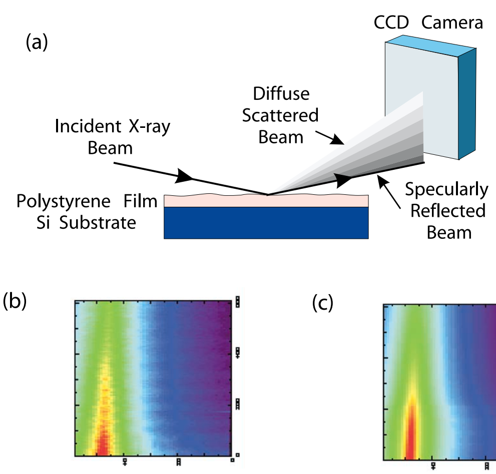

FIG. 1. (a) The schematic reflectivity geometry in XPCS. (b) The CCD image of time-averaged diffuse scattering and (c) the fit to capillary wave model with a sample having thickness of 841 Å at 160°C.

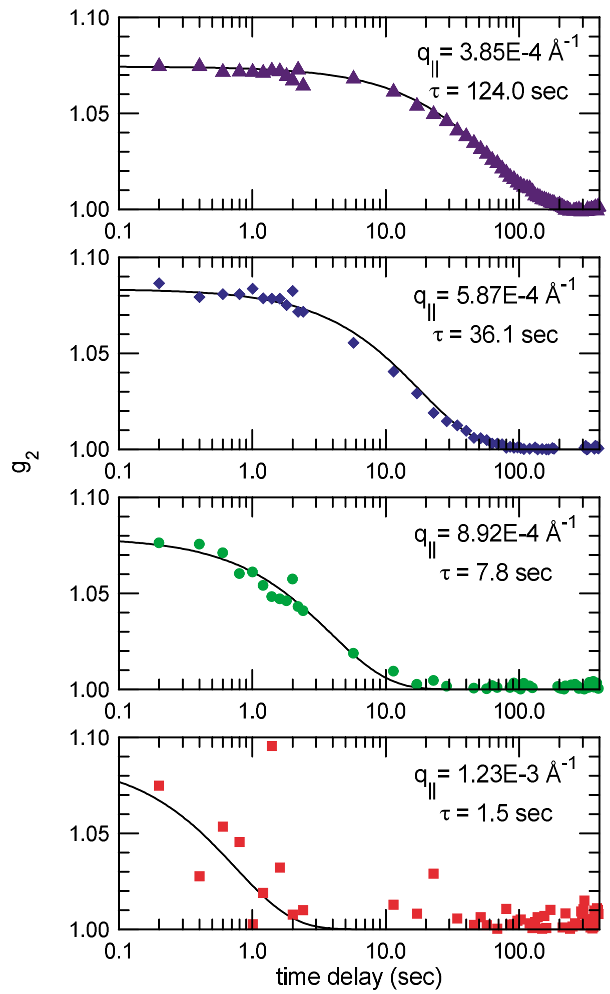

FIG. 2. The correlation functions obtained at four different in-plane q-values measured in a sample thickness of 841 Å at 160°C (shown in symbols) are compared with single exponential fits (shown in lines). The time constant τ at each q is also shown in the figure.

Results and Discussion

Correlation functions in an 841-Å sample at 160°C are compared with single exponential fits, expected for overdamped capillary waves, in Fig. 2. The in-plane wavevector dependence of τ at several temperatures is then displayed in Fig. 3. The symbols show the experimental data and the lines are the fits based on the

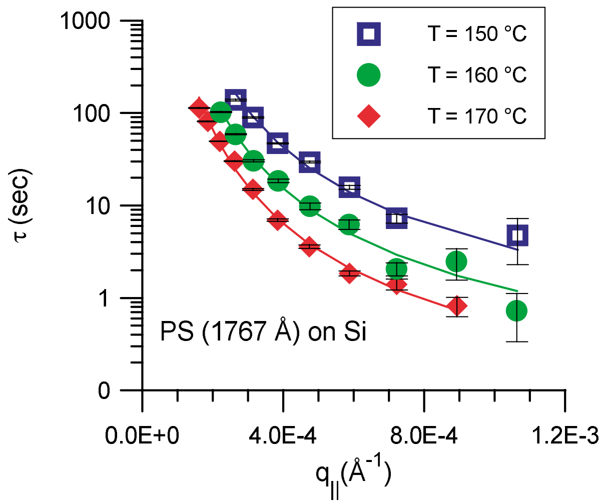

FIG. 3. The time constant as a function of wavevector at several temperatures measured in a sample thickness of 1767 Å (shown in symbols) are compared with the fits to the theory (shown in lines).

theory of Jäckle.[7] The time constant at a given in-plane wave-vector decreases with increasing temperature and film thickness. From the capillary model, one obtains the ratio of the viscosity to the surface tension.[8] If one assumes the bulk surface tension, the resulting viscosities are also consistent with the bulk values. Thus, this experiment finds no evidence of different behavior in the glass transition in the bulk or near the surface.

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