Surface and Bulk Dynamics of Diblock Copolymer Films

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Introduction

In thin polymer films, the dynamical properties of a polymeric material are altered compared to its bulk properties. In several studies reduced glass transition temperatures were found in thin films.[1] Opposite trends have been reported for free-standing and supported thin films, indicating that interactions with the substrate can alter the dynamics. While free-standing films tend to have faster dynamics, the behavior of supported films has been controversially discussed in the past.[1] An obvious explanation for slowed dynamics would be that the polymer chains are bound to the static substrate through attractive forces, whereas on the other hand there is some evidence for the presence of a more mobile layer at the surface of polymer systems, which could render a thin film more liquid-like as a whole.

Most of the current knowledge about the dynamics of thin polymer films stems from light-scattering experiments, but it is mostly free-standing films and, indirectly, surfaces of semi-infinite polymeric materials that have been investigated so far. One reason for that is that multiple scattering and heterodyning render dynamic light scattering on thin films very complicated. At beamline 8-ID, we have begun to investigate the dynamics of thin polymer films using photon correlation spectroscopy in the x-ray regime (XPCS). An advantage of this technique is that high momentum transfers and short length scales can be examined, down to the characteristic length scales of polymer chains. Another feature of particular interest when studying thin films is the total external reflection of x-rays from condensed matter, which in principle enables depth-resolved investigations of the dynamical properties of thin films and should allow one to distinguish between surface and bulk dynamics.

Due to the scattering length density difference between vacuum and condensed matter, surfaces with static or capillary wave roughness always give rise to an x-ray scattering signal. In situations where it is well-known how the surface dynamics is determined by the dynamics of the whole film, the latter is indirectly accessible even to experimental techniques that are only sensitive to the surface. In more complicated cases, e.g., polymer brushes or microstructured materials, it would be desirable to be able to probe the dynamics of the bulk of the film directly and, if possible, obtain depth-resolved information. First experiments of this kind have now been started at 8-ID. As density fluctuations within a homogeneous material would normally provide too weak a scattering contrast, we investigate multicomponent systems, like block copolymers, to obtain sufficient scattering contrast from the bulk.

Methods and Materials

At beamline 8-ID, a Ge(111) channel-cut and an adjustable slit system 40 cm upstream of the sample are used to prepare a coherent monochromatic x-ray beam with a wavelength of 1.62 Å and a cross section of 20 × 20 microns. A series of speckle diffraction images are recorded with a CCD detector 3 m downstream of the sample and analyzed off-line.[2] In this configuration, the CCD pixel size of 22.5 microns corresponds to the theoretical speckle size. Systems with characteristic times between 0.1 s and 200 s can be investigated.

We examined diblock copolymer films of polystyrene and polydimethylsiloxane. PS(176.4k)-*b*-PDMS(9.3k) powder was purchased from Polymer Source, Montreal, and dissolved in toluene. Films of thicknesses between 390 Å and 4450 Å were prepared by spin coating onto silicon wafers and annealing in vacuum at 160°C. In order to be sensitive to the film dynamics only and to minimize heterodyning with substrate signals, the incident beam impinged on the surface at a grazing angle slightly below (for surface dynamics) or above (for bulk dynamics) the critical angle of total reflection of the polymer. The penetration depth of the x-rays could thus be restricted to less than 200 Å.

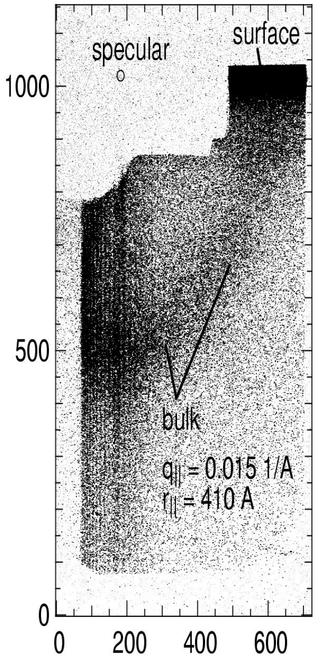

FIG. 1. Diffuse scattering images obtained in reflection geometry from PS-b-PDMS films in comparison with images from PS films.

Results

Figure 1 shows the diffuse scattering from a PS-*b*-PDMS copolymer film. The horizontal streak is the signal originating from the surface roughness; its shape results from the asymmetric resolution geometry. Lines of constant $q_{||}$ basically correspond to equi-intensity lines; note, however, that q_z varies along these lines.

In the copolymer data, there is an additional ring of scattering centered around the specular beam. Here, equi-intensity lines correspond to lines of constant $q = |(\mathbf{q}_{\|}, q_z)|$, as opposed to $q_{\|}$. The geometrical shape of this scattering signal on the image is very different from the surface signal; the ring of scattering can be interpreted as (more or less) isotropic bulk scattering from the copolymer film, modified by the transmission function $T(\alpha_f)$. It is found to be most intense for angles of incidence between the critical angle of the copolymer (0.14) and the one of the silicon substrate (0.22). As expected for a bulk signal, the ring is enhanced when the x-rays are transmitted through the vacuum-copolymer interface but reflected from the copolymer-substrate interface. It originates from the spatially varying x-ray scattering length density within the copolymer film.

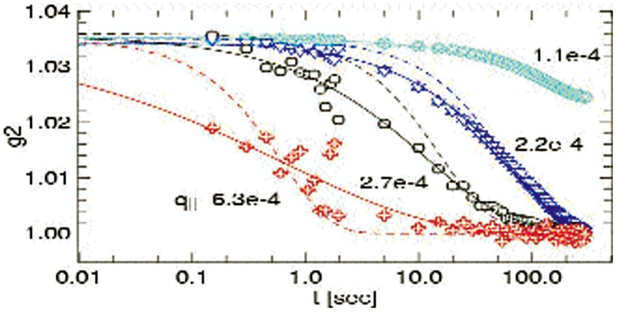

FIG. 2. Correlation functions (surface signal) from a 4000 A film at 180 °C at various q||-positions. The dashed lines are exponential fits. The solid lines are stretched exponentials and fit the data much better.

We studied the dynamics of the surface signal as a function of temperature and film thickness by recording a series of CCD images. The delay time between two images was 0.15 s. After an integrated exposure time of 200 s, the beam was moved to a fresh region on the sample surface. Radiation damage of the films was found to be irrelevant within the measurement time of 200 s. The correlation functions of the surface signal at different $q_{\|}$-positions are shown in Fig. 2. Interestingly, some correlation functions could not be fitted with single exponential curves but show a stretched exponential dependence. Measurable dynamics sets in above 120°C. The fitted characteristic times, so far based on single exponential fits, are plotted in Fig. 3. As expected we find that the dynamics are faster at higher momentum transfer/shorter length scales, at higher temperature, and in thicker films (see Discussion). For the given molecular weight of our samples, the dynamics of the thinnest films tend to become too slow to be measured at low temperature, especially at low $q_{\|}$.

Discussion

Neglecting the difference between the relatively short PDMS section and the long PS section in the block-copolymer chains, our results are basically consistent with the ones from our experiments on polystyrene homopolymer films (see report by H. Kim et al.). However, most correlation functions have a stretched exponential form, and, based on the current state of the data analysis, the exact $q_{\|}$-dependence of the characteristic times seems to deviate from Jäckle's theory of thin films of simple viscoelastic liquids.[3] Overall the surface dynamics due to capillary waves is slower according to the higher molecular weight of the copolymer samples. For comparison, further experiments will be carried out on copolymer films of lower molecular weight in the future.

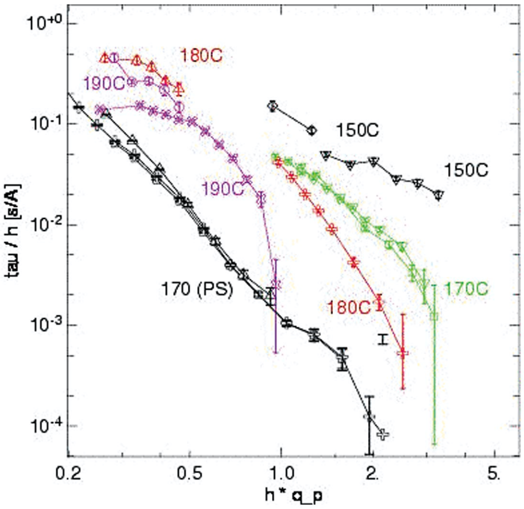

FIG. 3. Characteristic times τ plotted versus $q_{\|}$ for various temperatures and film thicknesses. Both axes are rescaled by the film thickness h to test the scaling law predicted by Jäckle.[3]

The origin of the ring of scattering was identified as bulk scattering from the inhomogeneous x-ray scattering length density within the copolymer material. It is located at a distance q=0.015 Å from the specular beam, which corresponds very well to the position at which we found a peak in the bulk static structure factor, as determined from regular small-angle measurements on annealed bulk material in glass capillaries. This q-value corresponds to about twice the radius of gyration of the copolymer, which points to the presence of spherical micelles in the films.

The analysis of the dynamics of this scattering signal is in progress. It seems to show considerably slower dynamics than the surface signal, which would corroborate speculations about a more mobile layer at the surface of polymer films.[1] We believe that heterodyning between the bulk and the surface signal can be neglected in q-regions where the two signals do not overlap. Further analyses of the statics and dynamics of the ring-shaped scattering feature are in progress, and we envisage that more materials and a larger variety of systems will be investigated with this technique in the near future.

Acknowledgments

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