

Anomalous Surface Dynamics in Supported Polystyrene Films Near the Glass Transition

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The reduction of the glass transition temperature (T_g) in thin supported polymer films is of great interest. One proposed explanation is that close to the surface region there exists a thin layer with very low viscosity. In order to testify this possibility, we applied X-ray photon correlation spectroscopy (XPCS) to measure surface dynamics of polymer films. The samples were polystyrene (PS) films on hydrophobic silicon substrates with various molecular weights ($M_w = 11-900$ kg/mol). The film thickness ranges from 40 nm to 320 nm. These samples were annealed at 170°C in high vacuum for approximately 24 hours. The XPCS measurements performed at the beamline 8-ID-I in the Advanced Photon Source, Argonne.

In the wave vector range $10^{-3}-10^{-1}$ nm⁻¹, at just above T_g , we have found a relaxation mode of the surface fluctuations at least 100 times faster (for $M_w = 129k$) than the capillary wave theory predicts. Surprisingly, this mode does not show much molecular weight dependence. When the temperature increases far above T_g (>150C), the surface relaxation becomes normal, as predicted by capillary wave theory [1]. Using the theory developed [2] in the previous work, the results cannot be explained with a model having bilayer of a thin low viscous layer on top. The failure of fitting of the bilayer model clearly indicates that, within the current experimental resolution, the possibility of the existence of a thin less viscous layer near the surface can be excluded. Hence, in our current study, the anomalous surface dynamics at close to T_g , faster than predicted with a bulk viscosity, is not a result of the surface phenomena, and must arise from within the film.

[1] H. Kim, et al., Phys. Rev. Lett. **90**, 068302 (2003).

[2] Z. Jiang, et.al., Phys. Rev. E **.74**, 011603 (2006).