

Peering into the Interfaces of Nanoscale Polymeric Materials

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It is well known that the physical and mechanical properties of ultrathin polymer films differ substantially from the bulks, the so-called “nanoconfinement” effects. There is now growing evidence that the air/polymer interface and the polymer/substrate interface play crucial roles in these nanoconfinement effects concurrently. Hence, it is anticipated that the local quantities and structures of ultrathin polymer films are heterogeneous in the direction normal to the film surface, depending on the interplay between these interfaces. It was this unanswered question that motivated the present study. Here I present our X-ray photon correlation spectroscopy (XPCS) results on the interfacial dynamics of polymer chains determined by the Brownian motion of gold nanoparticles embedded in the melt as markers. The results are intriguing to show the presence of a topmost reduced viscosity layer as well as the formation of a very thin immobile (adsorbed) polymer layer on the substrate surface at temperatures far above the bulk glass transition temperature. In addition, we found that the effect of the adsorbed layer propagates into the film interior, resulting in the long-range perturbation on the local viscosity. Since irreversible chain adsorption from the melts during thermal annealing is general regardless of the magnitude of attractive segment/solid interactions, the formation (and the effect) of the adsorbed layer is unavoidable. I will also discuss the effects of the adsorbed layers on film stability and pattern formation of various ultrathin polymer films.