Direct measurement of molecular motion in freestanding polystyrene thin films
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An optical photobleaching technique has been used to measure the reorientation of dilute probes in freestanding polystyrene films as thin as 14 nm. Temperature-ramping and isothermal anisotropy measurements reveal the existence of two subsets of probe molecules with differing dynamics. While the slow subset shows bulk-like dynamics, the more mobile subset reorients within a few hundred seconds even at T_g - 25 K (T_g is the glass transition temperature of bulk polystyrene). At T_g -5 K, the mobility of these two subsets differs by 4 orders of magnitude. These data are consistent with the presence of a high mobility layer at the film surface whose thickness is independent of polymer molecular weight and total film thickness. The thickness of the mobile surface layer increases with temperature and equals 7 nm at T_g.