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Mechanisms Affecting Glassy Dynamics in Thin Polymer Films

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Numerous studies have documented changes in the glass transition temperature (Tg) with decreasing thickness for thin polymer films less than ˜100 nm in thickness. However, understanding of the fundamental mechanisms causing this phenomenon are still unknown. We have demonstrated that two separate mechanisms can act simultaneously to propagate enhanced mobility from the free surface deeper into the interior of the film resulting in two distinct reduced Tgs within single high molecular weight (MW) free-standing polystyrene films [1]. These two transitions, which can be separated by up to 60 K, show qualitatively different behaviors. The lower transition is MW dependent and appears to be unique to high MW chains, while the upper transition is MW independent and appears to be common across multiple glass forming systems such as polymers, small molecules, and colloids. We believe this more universal mechanism induces a gradient in dynamics near the free surface that propagates in via a mechanism related to cooperative motion [2].

Physical aging studies on polymer films are also underway to elucidate the stability and glassy dynamics of these thin films. For thick films (220-1800 nm) in which there are no Tg reductions, we find that the physical aging rate depends strongly on stress caused by thermal expansion mismatch between film and support. This stress, applied to the films as they are quenched into the glassy state, can nearly double the physical aging rate when changing the frame material from polycarbonate to silicon [3]. How stress and mechanical deformation impart mobility to polymer glasses has been studied primarily for materials where the glassy state was formed stress free. In contrast, we investigate the stability of polymer glasses after stress is applied during the formation of the glassy state (vitrification). Using a unique jig, constructed to apply a known stress to free-standing films during the thermal quench, we find that stress values above a threshold result in less stable polymer glasses with faster physical aging rates [4].

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