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The Distributions of T_g Values and Physical Aging across Thin and Ultrathin Polymer Films and within Polymer Nanocomposites

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Polymeric glass formers can exhibit amazing changes in glass transition temperature, T_g, relative to bulk when subject to nanoconfinement. At present there is no detailed understanding of this effect nor, until recently, was there a method to determine how far from the surface or interface these effects propagate into the glass former. We have developed a simple, fluorescence / multilayer method that has yielded the first determination of the distribution of T_g values across supported polymer films, revealing that the enhancement of dynamics at a surface affects T_g several tens of nanometers into a polystyrene (PS) film. The extent to which T_g dynamics smoothly transition from enhanced to bulk states depends strongly on nanoconfinement. When films are sufficiently thin that a reduction in thickness leads to an overall T_g reduction, the surface-layer T_g actually increases with a reduction in overall thickness whereas the substrate-layer T_g decreases. These results indicate that the gradient in T_g dynamics is not abrupt and that the size of a cooperatively rearranging region is much smaller than the distance over which interfacial effects propagate. There is no MW dependence of the T_g-nanoconfinement effect in PS; thus, the effect cannot be attributed to radius of gyration, segregation of chains ends to the free surface, or entanglement reduction. However, the effect is strongly dependent on added diluent, repeat unit structure and attractive polymer-substrate interactions: added diluent reduces or even suppresses the effect; poly(4-tert-butylstyrene) exhibits a T_g reduction at a thickness of 300-400 nm, far beyond the thickness at which T_g reductions are observed in PS; and poly(2-vinyl pyridine) (P2VP), which can undergo hydrogen-bonding with hydroxyl units on the surface of glass, exhibits enhancements in T_g at thicknesses below 300 nm. We have also developed an approach for characterizing physical aging in thin and ultrathin films, revealing that the distribution of physical aging is distinct from that of T_g.