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The distribution of Tgs in bulk and nanoconfined polymer films measured by a novel fluorescence method CHRISTOPHER J. ELLISON, JOHN M. TORKELSON — We have recently developed (Nature Mater., 2, p695, 2003) fluorescence approaches that have allowed the direct measurement of Tg in specific layers 10-15 nm in thickness near interfaces and in between. This novel approach has made possible the unique characterization of the distribution of Tgs in bulk and ultrathin polymer films where it has been observed that the distribution in Tgs is highly dependent on the type of interfacial interaction (as at the free surface or substrate) and the degree of nanoconfinement. These measurements have revealed that interfacial effects almost entirely explain Tg deviations observed in ultrathin polymer films and that these interfacial effects have the ability to impact the properties (Tg and associated cooperative segmental dynamics) of material that is even tens of nanometers away from an interface. For example, these measurements have indicated that the 14 nm nearest the free surface of a relatively thick polystyrene (PS) film has a Tg that is reduced by more than 30 K and that this Tg reduction at the free surface influences material even 30 nm away from that interface.

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