Dramatic role of fragility in determining the magnitude of $T_g$ perturbations to ultrathin film layers and near-ininitely dilute blend components

CHRISTOPHER EVANS, JOHN TORKELSON, Northwestern University, NORTHWESTERN UNIVERSITY TEAM — Using fluorescence, we measure the glass transition temperatures ($T_g$) of ultrathin (11-14 nm) polystyrene (PS, bulk $T_{gb} = 103 \, ^\circ C$) layers which can be tuned over $\sim 80 \, ^\circ C$ when sandwiched between two bulk neighboring layers of poly(4-vinyl pyridine) (P4VP), polycarbonate, poly(vinyl chloride) (PVC) or poly(tert-butyl acrylate). Between P4VP, an ultrathin PS layer has its dynamics slaved and reports the $T_g$ of bulk P4VP. In contrast, an ultrathin PS layer is weakly perturbed ($T_g = 97 \, ^\circ C$) when placed between PVC. These perturbations to the PS $T_g$ become evident even for layers 10s of nanometers in thickness. Additionally, binary blends were prepared with 0.1 wt% PS components surrounded by the same neighboring polymers as in the trilayers. The $T_g$ reported by an ultrathin PS layer and a 0.1 wt% PS blend component are the same for a given polymer pair indicating that the $T_g$ perturbations in these two systems arise from a common physical origin. The strength of perturbations to PS correlate with the fragility of the neighboring domain in both blends and multilayers indicating that it is a key variable in determining the strength of $T_g$-confinement effects. Fragility also tracks with the magnitude of $T_g$-confinement effects observed in single layer polymer films supported on silicon wafers.