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Molecular Weight Dependent and Independent Glass Transition Temperature Reductions Coexisting in High MW Free-Standing Polystyrene Films JUSTIN PYE, CONNIE ROTH, Dept of Physics, Emory University — Using transmission ellipsometry, we have measured the thermal expansion of ultrathin, high molecular weight (MW), free-standing polystyrene films over an extended temperature range. For two different MWs, we observed two distinct reduced glass transition temperatures (Tgs), separated by up to 60 K, within single films with thicknesses h less than 70 nm. The lower transition follows the previously seen MW dependent, linear Tg(h) behavior, while we also observe the presence of a much stronger upper transition that is MW independent and exhibits the same Tg(h) dependence as supported and low MW free-standing films. This represents the first experimental evidence indicating that two separate mechanisms can act simultaneously on thin free-standing polymer films to propagate enhanced mobility from the free surface into the material. The change in thermal expansion through the transitions indicate that ∼90% of the film (matrix) solidifies at the upper transition with only ∼10% of the material remaining mobile, freezing in at the lower transition. Surprisingly, when we compare our results to the existing literature, and especially the low MW free-standing film data, we conclude that the upper transition encompasses the free surface region and associated gradient in dynamics. This leaves open the question about where the small (∼10%) fraction of material that has ultrafast, MW dependent dynamics resides within the film.

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