T_g and Structural Recovery of Nanoconfined Polystyrene

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The behavior of glass-forming materials confined at the nanoscale has been of considerable interest over the past two decades with conflicting results sparking debate. Here, I will discuss recent work from my laboratory focusing on the glass transition and associated structural relaxation kinetics of nanoconfined polystyrene using a Mettler Toledo Flash differential scanning calorimeter (DSC). The advantages of the Flash DSC include sufficient sensitivity to measure enthalpy recovery for a single 20 nm thick film, as well as extension of the measurements to aging times as short as 0.01 s and to aging temperatures as high as 15 K above nominal T_g since high fictive-temperature glass can be created by the fast cooling rates (1000 K/s). Confinement geometries studied include ultrathin films, supported rods, and stacked rods. The T_g depression of thin films is found to be a function of cooling rate, decreasing with increasing cooling rate; whereas, at the highest cooling rates, T_g is the same as the bulk within the error of the measurements. Results for rods also depend on cooling rate, but with supported rods showing elevated T_g's relative to the bulk. Structural recovery is performed as a function of aging time and temperature, and the evolution of the fictive temperature is followed. The aging behavior and relaxation time-temperature map for single ultrathin films will be compared to those for bulk material, as well as to those for nanoconfined rods and stacked samples. The results will also be discussed in the context of current controversies in the field.