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Tg and Structural Recovery of Single Ultrathin Films

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The behavior of materials confined at the nanoscale has been of considerable interest over the past two decades. Here, the focus is on recent results for single polystyrene ultrathin films studied with ultrafast scanning chip calorimetry. The T_g depression of a 20 nm-thick high-molecular-weight polystyrene film is found to be a function of cooling rate, decreasing with increasing cooling rate; whereas, at high enough cooling rates (e.g., 1000 K/s), T_g is the same as the bulk within the error of the measurements. Structural recovery is also performed with chip calorimetry as a function of aging time and temperature, and the evolution of the fictive temperature is followed. 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 temperatures as high as 15 K above nominal T_g and to aging times as short as 0.01 s. The aging behavior and relaxation time-temperature map for single ultrathin films are compared to those for bulk material. Comparison to behavior in other geometries will also be discussed.