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Structural Relaxation of Stacked Ultrathin Polystyrene Films

YUNG P. KOH, SINDEE L. SIMON, Texas Tech University — The kinetic behavior of stacked polystyrene ultrathin films is investigated by differential scanning calorimetry (DSC) and compared to the behavior of bulk polystyrene. The fictive temperature (T_f) was measured as a function of cooling rate and as a function of aging time for aging temperatures below the nominal glass transition temperature (T_g). The stacked thin films show enthalpy overshoots in DSC heating scans which are reduced in height but occur over a broader temperature range relative to the bulk response for a given change in fictive temperature. The cooling rate dependence of the limiting fictive temperature, T_f' is also found to be higher for the stacked thin film samples; the result is that the magnitude of the T_g depression between the thin film sample and the bulk is inversely proportional to the cooling rate consistent with other results in the literature. We also find that the rate of physical aging of the stacked thin films is comparable to the bulk when aging is performed at the same distance from T_g ; however, when conducted at the same aging temperature, the thin film samples show accelerated physical aging due to their depressed T_g values. This result is in contrast to recent work in the literature on PMMA ultrathin films and on o-TP confined in nanopores.

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