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Reduced Calorimetric Tg in Confined Thin Polymer Films with Controlled Interface GI XUE, JIAO CHEN, DONGSHAN ZHOU, Department of Polymer Science and Engineering, Nanjing University — When most prior studies on thin polymer film have shown that glass transition temperature (Tg) decreases under nano-confinement, differential alternating current (AC) chip calorimetric method shows little dependence of Tg on thickness for supported film. To reveal this contradiction, we have manipulated a free-interface by spin-coating polystyrene with an immiscible surfactant [tetraoctylammonium bromide (TOAB)], which had a melting point lower than Tg of polystyrene. When the sample was heated during AC chip measurement, TOAB molecules assembled on the interface and became a mobile layer. As a result, Tg was reduced for ultra thin polymer film. Moreover, stacked free-standing polymer films also show Tg dependence on thickness. The releasing of interface stresses caused by spin-coating is the major reason for reduction of calorimetric Tg. These data unambiguously show that thickness dependence of Tg is an intrinsic property of thin polymer film confined by geometry and dimensions.

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