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Glass transition temperature and its distribution in nanoconfined free-standing polymer films SOYOUNG KIM, CONNIE ROTH, JOHN TORKELSON, Northwestern University — The confinement effect on the glass transition temperature (Tg) of free-standing polystyrene (PS) films is determined using the temperature dependence of a pyrene-label fluorescence intensity ratio. A strong confinement effect on Tg is evident at thicknesses $<$ 80-90 nm; a 41-nm-thick PS film (Mn = 701 kg/mol) exhibits a 47 K reduction in Tg relative to bulk PS. A strong molecular weight dependence of the Tg-confinement effect is observed, in reasonable agreement with the study by Dutcher group (PRE 2001). Employing multilayer films, measurements of Tg at specific locations within PS free-standing films are possible, e.g., a 14-nm-thick pyrene-labeled PS layer atop a 500-nm-thick PS free-standing film exhibits a 32 K reduction in Tg relative to bulk PS, the same level of free-surface effect on Tg as supported PS films. This study is the first to experimentally address the distribution of Tgs across free-standing films and provide a route to test the fundamental basis for the large Tg-confinement effect in free-standing films and in particular the theory proposed by de Gennes (EPJE 2000).

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