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The Tg-Nanoconfinement Effect and the Relaxation of Residual Stresses in Spin-Coated Films of Polystyrene and Styrene-Containing Copolymers: Characterization by Intrinsic Fluorescence. MANISH K. MUNDRA, CHRISTOPHER J. ELLISON, ROSS BEHLING, JOHN M. TORKELSON, Northwestern University, Evanston, IL 60208 — The glass transition temperatures (Tgs) of films of polystyrene (PS) and styrene (S)-methyl methacrylate (MMA) copolymers have been determined using intrinsic fluorescence from styrene units. The Tgs are measured by a break in the temperature dependence of fluorescence intensity measured upon cooling from the equilibrium liquid state. As the film thickness decreases below 50 nm, there is a substantial deviation in Tg from bulk Tg, with PS and high S-content copolymers exhibiting a reduction in Tg and high MMA-content copolymers exhibiting an increase in Tg. This is explained by a competition of free surface effects and the effects of attractive polymer-substrate interactions. As the intrinsic fluorescence is a combination of monomer and excimer fluorescence, it reflects the local conformational population. This is used to determine the conditions at which residual stresses induced by spin coating are relaxed away, leading to a steady-state conformational population and fluorescence signal independent of annealing time. Films must be heated to temperatures well above Tg (Tg + 30 K) for several minutes to achieve constant fluorescence independent of further annealing. Annealing for short times close to Tg is insufficient to achieve an equilibrium conformational population.

John M. Torkelson
Northwestern University

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