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**Making the Tg-Confinement Effect
Disappear in Thin Polystyrene Films: Good Physics vs. Inappropriate Analysis**

JOHN TORKELSON, LAWRENCE CHEN, Northwestern University — The Tg-confinement effect in polymers was first characterized in supported polystyrene (PS) films by Keddie et al. in 1994. Since then, many researchers have shown that (pseudo-)thermodynamic Tg measurements of supported PS films taken on cooling consistently yield the same qualitative results, with a decrease from bulk Tg beginning at 40-60 nm thickness and becoming very strong below 20 nm thickness. Some quantitative differences have been noted between studies, which may be ascribed to measurement method or the analysis employed. In 2004, we showed that the Tg-confinement effect in PS may be suppressed by adding several wt% of small-molecule diluents such as dioctyl phthalate. Recently, Kremer and co-workers (Macromolecules 2010, 43, 9937) reported that there was no Tg-confinement in supported PS films based on an analysis of the second derivative of ellipsometry data and use of a ninth order polynomial fit. Here, we demonstrate a new method for suppressing the Tg-confinement effect. In particular, PS made by emulsion polymerization yields no Tg-confinement effect as measured by ellipsometry or fluorescence, while PS made by anionic or conventional free radical polymerization yield strong Tg-confinement effects. The difference is hypothesized to result from surfactant in the emulsion polymerized PS. We also show that the absence of the Tg-confinement effect reported by Kremer is due to inappropriate analysis of ellipsometry data and that correct analysis yields Tg-confinement effects.

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