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New Measurements of the Effects of Confinement on the Glass Transition Temperature of Freely Standing Polymer Films JOHN TORKELSON, SOYOUNG KIM, CONNIE ROTH, Northwestern University — Pioneering work by the Dutcher group (PRL 77, 2002 (1996)) a dozen years ago led to the first measurement of the Tg-confinement effect in freely standing polymer films. Their studies were especially intriguing because of the observations of very large Tg reductions relative to bulk Tg and a strong molecular weight dependence of the Tg-confinement effect. Such a molecular weight dependence is absent in the Tg-confinement effect of supported polymer films. Because of experimental difficulties associated with freely standing films, especially when the films are less than 100 nm thick, only a few related experiments have been reported by other research groups. Here we describe new results involving the measurement of Tg via the temperature dependence of fluorescence intensity of dyes labeled at trace levels to the polymer chains. Present measurements on freely standing films of poly(methyl methacrylate) (PMMA) have demonstrated reductions in Tg relative to bulk values of 20 to 25 K in films of 25-40 nm thickness. Tg reductions of at least 5 K are observed when PMMA films are 80 nm thick. Studies are also underway with polystyrene films and with polymers of different molecular weight.

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