Abstract Submitted
for the MAR07 Meeting of
The American Physical Society

Why Does the Effect of the Free Surface on the Tg-Confinement Effect Depend So Strongly on Polymer Species? JOHN M. TORKELSON, MANISH K. MUNDRA, Northwestern University, Evanston, Illinois 60208 — The effect of confinement on the glass transition temperature in thin polymer films has been heavily examined in the case of polystyrene and poly(methyl methacrylate). However, related effects have seen very limited study in other polymer systems. Here we demonstrate that simple adjustments to the polymer repeat unit structure leading to a greater requirement for cooperativity of the segmental mobility associated with Tg result in larger effects of the Tg-confinement effect. This is seen both with regard to the magnitude of the reduction in Tg at a given film thickness and with regard to the film thickness at which reductions in Tg from the bulk value are observed. Sets of data in which an increase in the size of a rigid side group (polystyrene vs. poly(4-methyl styrene) vs. poly(t-butyl styrene)) or an increase in the polymer backbone rigidity (polystyrene vs. polycarbonate vs. polysulfone) lead to an increase in the Tg-confinement effect will be described.

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Date submitted: 20 Nov 2006 Electronic form version 1.4