

Abstract Submitted
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Thin films of linear polymer exhibiting no Tg-confinement effect: Correlation with low bulk fragility JOHN TORKELSON, LAWRENCE CHEN, Northwestern University — Recently, two studies have demonstrated a strong connection between the magnitude of the Tg-confinement effect in thin, supported films of linear polymer that lack significant attractive interactions with the substrate and the value of bulk polymer fragility (See *Macromolecules* 2013, 46, 6091 and *Macromolecules* 2016, 49, 5092.) Here, we discuss experimental work which extends these results to polymers with very low bulk fragility values, about 70. With decreasing bulk fragility, we observe a reduction in the Tg-confinement effect until, at sufficiently low values of bulk fragility, Tg is unchanged from its bulk value at thicknesses of about 20 nm. That is, the Tg-confinement effect is eliminated down to thicknesses of 20 nm by virtue of the fact that the fragility, which reflects chain segment packing frustration, cannot be reduced by confinement as the bulk value is already very low. With these new results, a total of twelve linear polymers are shown to exhibit a one-to-one correlation of the strength of the Tg-confinement effect and the bulk fragility value. We also note that an exception to this correlation has been observed with films of linear PMMA that lack attractive interactions with its substrate. Possible reasons for the exceptional behavior of PMMA will be discussed.

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