Abstract Submitted
for the MAR17 Meeting of
The American Physical Society

Molecular Weight Dependence of the Intrinsic Size Effect on T_g in AAO Template-Supported Polymer Nanorods: A DSC Study TONG WEI, SHADID ASKAR, Department of Chemical and Biological Engineering, Northwestern University, ANTHONY TAN, Department of Materials Science and Engineering, Northwestern University, JOHN TORKELSON, Department of Chemical and Biological Engineering, Northwestern University — We have investigated how the intrinsic size effect modifies the glass transition temperature (T_g) and fragility of template-supported polystyrene (PS) nanorods in the absence of free surfaces and attractive polymer-substrate interactions. Template-supported nanorods of different molecular weight (MW) were prepared by melt infiltration; rod diameter (d) varied from 24 nm to 210 nm. The T_g- and fragility-confinement effects were characterized using differential scanning calorimetry. T_g-confinement effects are observed for PS nanorods MW $\geq$ 900 kg/mol; greater perturbations to T_g are observed with increasing MW (*e.g.*, in 24 nm rods, $T_{g,rod}$ – $T_{g,bulk}$ = -3.2 C for 900 kg/mol PS, whereas $T_{g,rod}$ – $T_{g,bulk}$ = -7.4 C for 3,840 kg/mol PS). Intrinsic size effects can account for the MW-dependent behavior in PS nanorods. Comparing the length scale of the confining dimension, d, to that of the polymer radius of gyration, R_g. Perturbations to T_g were observed when $d < 2R_g$. This result indicates that changes in polymer chain conformations due to confinement is important in perturbing T_g in template-supported PS nanorods. We also determined that the T_g-confinement is accompanied by a fragility-confinement effect. The fragility of 33-nm-diameter, 2,000 kg/mol PS nanorods is reduced 24% from the bulk value.

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Date submitted: 10 Nov 2016 Electronic form version 1.4