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Confinement in Melts of Chains with Junction Points, but No Ends[1] MARK FOSTER, QIMING HE, YANG ZHOU, FAN ZHANG, Dept. of Polymer Science, The University of Akron, CHONGWEN HUANG, Dept. of Polymer Engineering, The University of Akron, SURESH NARAYANAN, X-ray Science Division, Argonne National Laboratory — Measurements of surface fluctuations of 4-arm star and "8-shaped" analogs of the same polystyrene (PS) chain show that elimination of chain ends is much more important in dictating the fragility in a thin film than is the introduction of a branch point in the molecule. Both the viscosities derived from surface fluctuations and rheological measurements for the 8-shaped PS manifest a lower value than the 4-arm star PS analog, with the discrepancy increasing as the temperature approaches the glass transition temperature, $T_{\mathrm{g,bulk}}$. Comparison among different chain topologies shows the effect of the number of chain ends and junction point on the viscosity. The viscosity behavior of the 8-shaped PS is quite different from that of the star analog, but similar to that of the simple cycle analog. The fragility of the 8-shaped molecule in the thin film is reduced relative to that in the bulk, manifesting a nanoconfinement effect.

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Mark Foster
Dept. of Polymer Science, The University of Akron

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