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Distinct Thermophysical and Interfacial Properties Associated with Low Molecular Weight Cyclic Polystyrene in Bulk and Confined States: Tg and Fragility¹ LANHE ZHANG, Northwestern University, RAVIN-DER ELUPULA, SCOTT GRAYSON, Tulane University, JOHN TORKELSON, Northwestern University — Cyclic or ring polymers represent an exciting class of topologically distinctive polymers. The influence of "end-to-end" tethering and the unusual conformational properties associated with cyclic topologies have led to polymer dynamics significantly different from the linear counterpart. Bulk cyclic polystyrene (c-PS) exhibits very weak T_{g} - and fragility-molecular weight (MW) dependences compared to linear PS. In stark contrast to the substantial $T_{\rm g}$ -confinement effects in linear PS, a nearly completely suppressed confinement effect is discovered in low MW c-PS. The cyclic topology strongly restricts polymer-substrate interactions. Therefore, the near elimination of the T_{g} -confinement effect in c-PS originates mainly from a very weak perturbation to $T_{\rm g}$ near the free surface. Upon nanoscale confinement, linear PS films have been shown to have significantly reduced fragility compared to bulk. Despite having similar bulk fragility as high MW linear PS, low MW c-PS films show major suppression in fragility reduction with decreasing thickness. Due to a lack of chain ends, properties associated with the ring structure are not prone to be perturbed by either MW reduction or confinement. This result indicates a strong correlation between the susceptibility of fragility perturbation and the susceptibility of $T_{\rm g}$ perturbation, caused by chain topology and/or by confinement.

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