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The Glass Transition Temperature of Polymer Nanoparticles under Soft and Hard Confinement CHUAN ZHANG, YUNLONG GUO, RODNEY PRIESTLEY, Department of Chemical and Biological Engineering, Princeton University — When confined to the nanoscale, the glass transition temperature (T_g) of polymers can deviate substantially from the bulk, i.e., the T_g-confinement effect. Due to ease of processing, most studies have focused on the size-dependent T_g of thin films, while few have extended investigations to other geometries. As polymers confined in higher geometrical dimensions become the enabling material in technologies ranging from drug delivery to plastic electronics, a greater understanding of size effects on T_g is warranted. Here, we investigate the effect of soft and hard three-dimensional confinement on the T_g of polymer nanoparticles. Via modulated differential scanning calorimetry, we show that T_g decreases with size for bare polymer nanoparticles, i.e., the case of soft confinement while T_g is invariant with size for silica-capped polymer nanoparticles, i.e., the case of hard confinement. These results suggest that the free surface is a key factor in T_g reductions of three-dimensionally confined polymer.

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