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Dramatic alteration of Tg of polystyrene confined in cylindrical nanopores GI XUE, CHAO TENG, JIE XU, LINLING LI, Nanjing University — Vitrification of polystyrene melt infiltrated in AAO template was greatly altered by geometrical confinement. DSC detected two distinguish Tgs for PS slowly cooled from the melt in nanopores. One was at a lower temperature than the bulk Tg and the other was at a higher temperature. The deviation between the two Tgs could reach as big as 60 °C and increased with decreasing pore size. Surprisingly, Tg for the PS nanorodes recovered back to the bulk value when the template was removed, indicating the importance of the interfacial interaction. The major factor which induced such a strong confinement is the cooling rate. The coefficient of thermal expansion (CTE) of AAO template is about one order lower than that for PS. The mismatch of CTEs causes a strain induced stress during cooling: the PS chains tend to shrink and to de-wet from the walls; meanwhile the interfacial interaction tends to hold the chains back. The chains are subjected to a high residual stress by a fast cooling and would peel off from the wall. When the cooling rate is sufficiently slow, and the stress was relaxed during cooling. Then the chains were still stick on the wall, resulting in a strong interfacial constraints for chains.

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