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Polymer Melt Diffusion inside Nanoscale Cylindrical Pores.

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Polymers in composites and inside porous media are frequently confined to spaces that are comparable to or even smaller than their mean end-to-end distances in the unconfined bulk state. Understanding the impact of nanoscale confinement on both polymer structure and dynamics is critical during processing and in applications. Anodized aluminum oxide (AAO) membranes with uniform cylindrical pores (diameters 18, 35, 55 or 80 nm) were filled with polystyrene (200 kDa) and then a thin layer of deuterated polystyrene was deposited on top. After annealing the concentration profile of the deuterated polymer was measured using elastic recoil detection and the center-of-mass polymer diffusion coefficient was determined. Melt diffusion is faster in AAO membranes with smaller pore diameters. This experimental finding is corroborated by coarse grain simulations with neutral interactions with the pore walls, although the increase is more pronounced in the simulations. Our simulations previously found that chain conformations slightly elongated parallel to the cylinder axis and compressed perpendicular to the cylinder and the number of entanglements per chain decreases as the cylinder diameter decreases. It is primarily the reduction in polymer entanglements that allows polymers to diffuse faster when the pore diameter is smaller in an athermal or weakly interacting system. Segmental dynamics have been measured using quasielastic neutron scattering. Polymer diffusion is cylindrical pores is now being studied at a fixed pore diameter as a function of molecular weight.