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Role of Entropic Barriers in Controlling Polymer Diffusion in Polystyrene Nanocomposites PHILIP GRIFFIN, WEI-SHAO TUNG, University of Pennsylvania, JEFFREY METH, Dupont, NIGEL CLARKE, University of Sheffield, RUSSELL COMPOSTO, KAREN WINEY, University of Pennsylvania — Polymer diffusion in polymer nanocomposites (PNCs) is significantly modified relative to the neat state. While it is suspected that nanoparticle-induced confinement plays a key role in the diffusion process, a detailed understanding of this process remains nonetheless elusive. We present recent studies of the temperature dependent polymer center-of-mass tracer diffusion coefficient in an athermal PNC comprising polystyrene and phenyl-capped, spherical silica NPs using elastic recoil detection. We find that the polymer tracer diffusion coefficient in the PNC relative to the bulk decreases with increasing nanoparticle concentration and is unexpectedly more strongly reduced at higher temperatures. This unusual temperature dependence of polymer diffusion in PNCs cannot be explained by the reptation model or a modified version incorporating an effective tube diameter, but instead it is the direct result of entropic free energy barriers imposed on polymer chains under confinement.

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