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Effect of Confinement in Ultrathin Films on Translational Diffusion in Polymers near the Glass Transition MANISH K. MUNDRA, JOHN M. TORKELSON, Northwestern University, Evanston, Illinois 60208 — A novel, extremely simple fluorescence-based multilayer method, based on breakthrough time assuming Fickian diffusion, has been developed to measure the impact of nanoscale confinement near free surfaces or polymer-substrate interfaces on translational diffusion in amorphous polymers near the glass transition temperature, Tg. With decreasing polystyrene film thickness, two dye molecules, Disperse Red 1 and decacyclene, exhibit reductions in their diffusion coefficients associated with translational diffusion away from the silica substrate interface and toward the free surface of the film. The effect of confinement on translational diffusion is much greater for the smaller dye, Disperse Red 1, with as much as an order of magnitude reduction in its translational diffusion coefficient being observed in the most confined film relative to its value in bulk polymer.

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