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Confinement in thin polymer films near Tg leads to factors of 10 to 1000 reductions in dye translational diffusion JOHN TORKELSON, HUI DENG, MANISH MUNDRA, Northwestern University — A breakthrough time/fluorescence resonance energy transfer method is used to measure out-of-plane translational diffusion coefficients of small-molecule dyes in thin polymer films near the glass transition temperature, Tg. The bulk translational diffusion coefficient is a strong function of dye size, increasing by a factor of 100 in polystyrene when dye molecular volume decreases by 25%. Reduction in PS film thickness below 500 nm leads to a factor of 1000 decrease in Disperse Red 1 diffusion coefficient while reduction below 140 nm leads to slightly more than a factor of 10 decrease in decacyclene diffusion coefficient. At a thickness less than 100 nm, the diffusions coefficients for the two dyes are identical with error. Similar effects have been observed in poly(methyl methacrylate) and polysulfone films at Tg + 3 K. These effects are not directly correlated with the Tg-confinement effect in these polymers as the length scales for confinement effects are much smaller in the case of Tg and in some of the polymers both diffusivity and Tg decrease with confinement.

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