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Order of Magnitude Decrease in Dye Diffusion in Nanoconfined Polymer Films: Fluorescence Nonradiative Energy Transfer Technique
HUI DENG, MANISH MUNDRA, JOHN TORKELSON, Northwestern University
— A fluorescence nonradiative energy transfer/multilayer film technique was used to determine the diffusion coefficient of the dyes decacyclene and Disperse Red 1 in supported polystyrene (PS) films as a function of film thickness. Previous studies on the glass transition temperature (Tg) of PS show a decrease in Tg as films are nanoconfined. This Tg-reduction is due to the enhanced role of the polymer/air interface which results in a region of increased polymer mobility as thickness is reduced. However, dye diffusion coefficients decrease upon film nanoconfinement, with the onset of diffusion coefficient reduction appearing at film thicknesses much thicker than the onset of Tg-confinement effects. These results can be explained by the fact that Tg reflects the longer time side of the polymer relaxation time distribution while dye diffusion reflects the shorter time side of the relaxation distribution. We hypothesize that confinement suppresses the shorter time side of the relaxation distribution which results in the observed decrease in diffusion coefficients.

Hui Deng
Northwestern University

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