471c Structural Relaxation of Nanoconfined Glassy Polymer Systems Studied by Fluorescence Measurements

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Polymers confined to nanoscopic geometries have shown a substantial deviation in the glass transition temperature (Tg) relative to that of the bulk material. How these deviations in Tg alter the structural relaxation of polymeric glasses confined to nanoscopic geometries has emerged as a key question that needs to be addressed for both scientific and technological reasons. Here the effect of nanoconfinment, surfaces, and interfaces on structural relaxation of glassy polymers is investigated by a fluorescence method. Rotor dyes are used as probes (< 0.2wt%) dispersed in the polymer or as labels covalently attached (< 1 label/400 repeat units) to the polymer. Fluorescence intensity increases as local specific free volume / local mobility surrounding the dye decreases, exhibiting a nearly linear change with logarithmic aging time. For ultrathin PMMA films, which have attractive polymer-substrate interactions, a reduction in physical aging rate is observed compared to the bulk. For ultrathin PS films, which lack polymer-substrate interactions, the physical aging rate is nearly identical to that of the bulk. Using a multi-layer method we are able to determine a distribution of physical aging rates across supported PMMA films; relative to bulk there is a reduction in physical aging rate at the free-surface and an even greater reduction in physical aging rate at the substrate.