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Fragility Nanoconfinement Effect in Thin Polymer Films: Novel Characterization by Ellipsometry TIAN LAN, Department of Materials Science and Engineering, Northwestern University, JOHN TORKELSON, Department of Materials Science and Engineering, Department of Chemical and Biological Engineering, Northwestern University — A novel ellipsometry-based method was introduced to determine kinetic fragility in polymer films and to investigate the effect of nanoscale confinement on polymer fragility. Three systems were studied: polystyrene (PS), polycarbonate (PC), and PS doped with small molecule diluents of 1,10-bis-(1-pyrene)decane (BPD). In bulk-like films, fragility index measured by ellipsometry agreed very well with that by differential scanning calorimetry. With confinement, a dramatic decrease in fragility was observed in highly fragile PS and PC. The fragility decreased by 58% from 166 to 69 in PS and by 65% from 214 to 75 in PC as film thickness decreased from bulk to 27-28 nm; a substantially muted response was observed in the strongest of the three: PS + 2 wt% BPD, where the fragility decreased only 21% from 134 to 106 from a bulk film to a 27-nm-thick film. The larger fragility-confinement effect in more fragile polymers strongly correlates with a previous discovery of the T_g-confinement effect: the strength of the T_g-confinement effect increases with increasing fragility of bulk polymers. It indicates that bulk fragility is associated with the susceptibility of polymers to effects of nanoscale confinement.

Tian Lan
Dept of Materials Science and Engineering, Northwestern University

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