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Methacrylate-Based Polymer Films Exhibit Different Tg-Confinement Effects at High and Low Molecular Weight TIAN LAN, JOHN TORKELSON, Northwestern University — The effects of confinement on the properties of polymer films are important in applications related to photoresists. To optimize resolution, methacrylate-based polymers in photoresists are often low molecular weight (MW). Here, we have used ellipsometry and fluorescence to determine how the glass transition temperature, Tg, is affected by confinement in silica-supported films of low and high MW poly(1-ethylcyclopentyl methacrylate) (PECPMA) and poly(methyl methacrylate) (PMMA). With decreasing nanoscale thickness, Tg is nearly invariant at high PECPMA MW but decreases dramatically at low MW, with Tg- Tg(bulk) = -15 K in a 17-nm-thick film. Fluorescence studies of a single 20-nm-thick dye-labeled layer in multilayer PECPMA films reveal a much greater perturbation to Tg in the free-surface layer for low MW polymer. The effect of MW in PMMA films is even more striking; Tg increases with decreasing thickness for high MW but decreases for low MW. The strong influence of MW on the confinement effect in PECPMA and PMMA is in strong contrast to the previously reported invariance of the effect with MW in supported polystyrene films, reconfirmed in our study.

John Torkelson
Northwestern University

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