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Viscosity of Polymer Nanometer Films[1]

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Ample studies have shown that the T_g of polymer films can change visibly when the film thickness (h) is decreased below 100 nm. It implies that the viscosity (η) of the films can differ notably from the bulk. In this talk, I shall discuss the viscosity measurement performed on two systems - polystyrene and poly(methal methacrylate) on silicon oxide (PS/SiO$_x$ and PMMA/SiO$_x$) where the T_g decreases and increases with decreasing h, respectively. At low molecular weight (M_w), η of both systems can be described by a layer model. For PS/SiO$_x$, a two-layer model assuming the films to comprise a mobile layer on top of a bulklike layer is sufficient. For PMMA/SiO$_x$, a three-layer model including an additional slow substrate layer is needed. For PS/SiO$_x$, the layer model is also able to describe the data at high M_w. However, the M_w-dependence displays a qualitative change when the polymer size exceeds the estimated thickness of the surface mobile layer. Beyond that, the surface chains are partially embedded in the bulklike layer so cannot facilitate enhanced transport as in the low-M_w films. We hypothesize that the surface mobile layer operates in the low-M_w films, but a confinement effect in the high-M_w films in lowering η.

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