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Effect of Chain Stiffness on the Glass Transition Temperature of Polymer Thin Film¹ KUN GENG, FEI CHEN, Boston University Department of Physics, OPHELIA TSUI, Boston University Department of Physics and Division of Materials Science and Engineering — The glass transition temperature (T_g) of poly(α -methyl styrene) (PAMS) films supported by silica is studied as a function of film thicknesses from ~17 to ~168 nm at three molecular weights of 1.3, 20 and 420 kg/mol. For the 20 and 420 kg/mol films, the glass transition temperature decreases with decreasing film thickness, consistent with previous results. But for the 1.3 kg/mol films, it becomes independent of the film thickness. We tentatively suggest the T_g depression to be caused by free volume excess at the polymer-air interface and that its influence diminishes at low enough molecular weights because of a chain stiffness effect. Besides PAMS, we contemplate that silica-supported poly(methyl methacrylate) (PMMA) can be another potential candidate for such an effect since published data shows that chain stiffness also affects the T_g of this polymer. Preliminary results supporting this conjecture will be discussed.

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