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Effects of molecular weight and tacticity on the Tg of poly(methyl methacrylate) films supported by silica¹ KUN GENG, FEI CHEN, OPHELIA TSUI, Boston University Physics Department — The glass transition temperature (T_g) of poly(methyl methacrylate) (PMMA) films supported by silica is studied as a function of film thickness at different molecular weights $(M_{\rm w})$ for different polymer tacticities. The $T_{\rm g}$ confinement effect is found to depend on the $M_{\rm w}$ and tacticity. For the films with a low $M_{\rm w}$ of 2.5 kg/mol, $T_{\rm g}$ is depressed for the atactic films, consistent with previous results. In contrast, the films with a higher syndiotactic content exhibit $T_{\rm g}$ enlargement as thickness decreases. We tentatively suggest this to be caused the influence of chain stiffness on the $T_{\rm g}$ that dominates at low $M_{\rm w}$ and varies with tacticity. For sufficiently high $M_{\rm w}$, the effect of chain stiffness is expected to be small. At $M_{\rm w} = 50$ kg/mol, the $T_{\rm g}$ confinement effect of the atatic and more syndiotactic films reverses from that observed of the low- $M_{\rm w}$ counterpart films. We suggest the chain stiffness effect to be negligible at this $M_{\rm w}$, and attribute the opposite $T_{\rm g}$ confinement effect to be caused by a competition between the surface $T_{\rm g}$ and the substrate $T_{\rm g}$ in these films. The $T_{\rm g}$ found of bilayers made of the atatic and more syndiotatic PMMAs with this $M_{\rm w}$ supports our attribute.

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Kun Geng Boston University Physics Department

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