Abstract Submitted for the MAR09 Meeting of The American Physical Society

Examination of Nonliquidlike Behaviors in Molten Polymer Films¹ Z.H. YANG, Boston University, Y.J. WANG, Hong Kong U. of Sci. and Tech., L. TODOROVA, O.K.C. TSUI, Boston U. — Several experiments have shown that polystyrene (PS) films with thicknesses of $h \approx 2R_G$ (where R_G is the radius of gyration of the polymer) exhibited nonliquidlike behaviors even in the molten state. By measuring the surface spectrum of PS films subjected to different thermal annealing, we show that similar nonliquidlike behaviors can be produced if the annealing time is below $\tau(q_{lc}^{eq}(h))$, the relaxation time of the capillary wave mode with wave vector equal to the lower-cutoff wave vector $q_{lc}^{eq}(h)$, which characterizes the equilibrium surface spectrum. At the same time, annealing above $\tau(q_{lc}^{eq}(h))$ recovers the liquid behaviors. Because $\tau(q_{lc}^{eq}(h))$ often amounts to days and even years, insufficient annealing constitutes a likely cause for the nonliquidlike behaviors. Nonetheless, the previously suggested strong pinning of the polymer chains to the substrate can also be a cause. To elucidate the origin of the observed nonliquidlike behaviors, we measure the surface dynamics of PS films with $h = 2R_G$ to $8R_G$ undergoing the glass-to-rubber transition and find that they are all the same. Our result favors insufficient annealing to be the cause of the observed nonliquidlike behaviors.

¹We thank support of NSF (DMR0706096) and ACS PRF (47882AC5). L. T. thanks support of the Boston University UROP program.

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Date submitted: 20 Nov 2008

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