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Freezing of Polymer Thin Films and Surfaces: The Small Molecular Weight Puzzle STEPHAN HERMINGHAUS, RALF SEEMANN, MPI for Dynamics and Self-Organization, D-37073 Goettingen, KARIN JACOBS, Saarland University, D-66123 Saarbruecken, KATHARINA LANDFESTER, University of Ulm, D-89069 Ulm — Experimental observations (ellipsometry, scanning force microscopy (AFM), and nuclear magnetic resonance (NMR)) of the freezing behavior of thin supported films as well as the free surface of atactic polystyrene are reported, taken at a particularly small molecular weight of 2 kg/mol. Remarkably, we find the same effect of reduction of the glass transition temperature, Tg, as observed earlier with much longer molecules. Furthermore, surface melting is observed by NMR, with the molten layer thickness similar to what has been observed with larger molecular weight. We conclude that molecular geometry effects cannot account for these observations, and that a consistent explanation must be presentable in a continuum picture. Based on the capillary wave spectrum of the free surface and of the supported films, we present such a model, and find that it accounts very consistently with all observations made so far with polystyrene.

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