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Spreading of Polymer Films at the Molecular Scale: Conformation, Orientation, and Fractionation. MICHAEL BARRETT, University of North Carolina at Chapel Hill, ALPER NESE, KRZYSZTOF MATYJASZEWSKI, Carnegie Mellon University, SERGEI SHEIKO, University of North Carolina at Chapel Hill — Previously, we have reported that comb-like polymer macromolecules undergo a plug-flow with an insignificant contribution of molecular diffusion (*Phys.* Rev. Lett. 93, 206103, 2004). It was also suggested that the composition of the flowing polymer melt was the same both inside the fluid reservoir (drop) and in the precursor film. This work called into question the macroscopic picture of polymer spreading. Through molecular imaging by AFM, we observe that macromolecules spread at different velocities depending on their size. We show that flow causes the molecules to align perpendicular to the flow direction We have also identified specific molecular conformations, such as hairpins, that become more abundant in spreading films. Lastly, we demonstrate that chain entanglements hinder permeation of long macromolecules from the drop to precursor film. These findings shed light on the molecular mechanism of spreading of polymer melts on natural, i.e. heterogeneous, substrates.

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