Surface Mobility of Polymeric Systems of Varying Chain Lengths ROHIT MALSHE, GREGORY TOEPPERWEIN, MARK EDIGER, LIAN YU, JUAN DE PABLO, University of Wisconsin — Thin films of polymeric material can exhibit drastically altered glass transition temperatures, mechanical responses, and overall dynamics as compared to the bulk. Differences in surface and bulk mobility are often cited as a primary explanation for such differences, but it has remained difficult to quantify local mobility as within the film. We have recently shown that decay constants from Mullins' surface diffusion model correspond directly to surface mobility for small-molecule glasses. In the current work, we examine long-chain polymers via two types of systems: polymeric pillars where the cross sections evolve from square to circular, and large particles which sink into polymeric thin films. For the pillars, we use Mullins' model to interpret changes in curvature. It is found that Mullins' decay constants correspond to relaxation times that can be identified with distinct segmental relaxation processes. Such decay constants exhibit a strong dependence on chain length and temperature. For the particle-thin film systems, we relate the rate of particle sinking to various measures of local mobility in the film. This setup is a direct analog to recent experimental work. The results presented here provide a connection between surface shape transformations, mobility, and diffusion.

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