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Surface Dynamics of “Dry” Homopolymer Brushes¹

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The dynamics of the surface height fluctuations of polymer melts can be profoundly altered by tethering of the chains. Surface height fluctuations on layers of covalently tethered, nearly monodisperse polymer chains synthesized by atom transfer radical polymerization were studied using x-ray photon correlation spectroscopy. The data reveal that both polystyrene and poly(*n*-butyl acrylate) “brushes” have structure at the surface with length scales in the region of 620 nm to 3100 nm, but the surface features show no relaxation in a time window of 0.1 seconds to 1000 seconds, even at temperatures more than 130 °C above the glass transition temperature of corresponding untethered chains. This remarkable alteration of the dynamics is compared with the suppression of fluctuations on this length scale anticipated by thermodynamic theories. The alteration of surface dynamics by tethering has implications for wetting, friction, and adhesion.

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