Surface Dynamics of Polymer Brushes in the Melt State: An XPCS Study

MARK D. FOSTER, BULENT AKGUN, GOKCE UGUR, WILLIAM J. BRITTAINE, Univ. of Akron, Akron, OH 44325-3909, SURESH NARAYANAN, X-ray Science Division, Argonne National Lab, Argonne, IL 60439, HEEJU LEE, SANGHOON SONG, HYUNJUNG KIM, Dept. of Physics, Sogang Univ., Seoul 121-742, Korea, ZHANG JIANG, SUNIL K. SINHA, Dept. of Physics, Univ. of California San Diego, La Jolla, CA 92093 — The suppression of long-wavelength modes of surface fluctuations on a molten polymer brush has been demonstrated using direct measurements of dynamics for the first time. The surface dynamics of densely grafted polystyrene brushes of reasonably monodisperse chains were investigated by X-ray photon correlation spectroscopy. Within the range of time and length scale investigated, 0.2 s to 1000 s, and 200 nm to 5 μm, there were no detectable dynamics on the brush surfaces, even 130°C above the polymer bulk glass transition temperature. A comparably thick film of untethered chains has a q-dependent surface relaxation time of the order of 30 s, indicating that the tethering of the chains alters the surface relaxation rate by at least 3 orders of magnitude. Such a suppression of long wavelength fluctuations on the surface of a molten brush was predicted by Frederickson and co-workers.