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New insight into surface melting in ultrathin polymer films: a combined surface x-ray scattering study TADANORI KOGA, Chemical and Molecular Engineering Program, Dept of Mat. Sci. and Eng., Stony Brook University, Y. WANG, M. RAFAILOVICH, J. SOKOLOV, Dept of Mat. Sci. and Eng., Stony Brook University, A. TIKHONOV, D. SCHULTZ, M. LEE, ChemMatCARS, The University of Chicago, X. LI, J. WANG, Advanced Photon Source, Argonne National Lab. — The crystallization of ultrathin polymer films on solid substrates has been studied for decades due to its importance in determining interfacial properties of coatings. Numerous groups have demonstrated that the rate of crystallization, crystal orientation, and density of nucleation points can be very different from bulk. We previously observed that, by using the shear modulation force microscopy (SMFM) measurements, the surface melting temperature (T_s) of polyethylene (PE) thin films decreased by 40 $^\circ$C relative to the bulk melting temperature (T_m) when the thickness was close to the lamellar domain spacing ($\sim$15 nm). This large depression can't be explained by the classical Thomson-Gibbs equation. In order to delve deeper into the mechanism of the surface melting, we integrated a variety of in-situ surface-sensitive scattering techniques, i.e., grazing-incidence x-ray diffraction (GID), grazing-incidence small-angle x-ray scattering (GISAXS), and diffuse scattering. We will present the detailed x-ray results and shed new light on the mechanism.

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