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Polymer Film Surface Fluctuation Dynamics in the Limit of Very Dense Branching MARK FOSTER, BOXI LIU, Dept. of Polymer Science, The University of Akron, SURESH NARAYANAN, X-ray Science Division, Argonne National Laboratory, DAVID T. WU, Chemical Engr. and Chemistry Dept., Colorado School of Mines — The surface height fluctuations of melt films of densely branched comb polystyrenes of thicknesses greater than 55nm and at temperatures more than 23 C above the $T_{g,bulk}$ can be rationalized using the hydrodynamic continuum theory (HCT) known to describe melts of unentangled linear and cyclic chains. Film viscosities (η_{XPCS}) for three combs inferred from fits of the HCT to X-ray Photon Correlation Spectroscopy (XPCS) data are the same as bulk viscosities (η_{bulk}) measured with rheometry. For the comb most like a star polymer and the comb closest to showing bulk entanglement behavior, η_{XPCS} is greater than η_{bulk}. However, the values of $\eta_{XPCS} - \eta_{bulk}$ are much smaller than those seen for less densely branched polystyrenes. We conjecture that the smaller magnitude of $\eta_{XPCS} - \eta_{bulk}$ for the densely grafted combs is due to a lack of interpenetration of the side chains when branching is very dense. While data of relaxation time versus T for cyclic chains virtually collapse to a single curve when $T_{g,bulk}$ is accounted for, that is not the case for combs. $T_{g,bulk}$ and specific chain architecture both play important roles in determining the surface fluctuations. Acknowledgements: NSF CBET 0730692, CBET-0731319, DURIP W911NF-09-1-0122.

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