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Effect of Molecular Architecture on Polymer Melt Surface Dynamics

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The dynamics of the thermally stimulated surface height fluctuations in a polymer melt dictate wetting, adhesion, and tribology at that surface. These surface fluctuations can be profoundly altered by tethering of the chains. One type of tethering is the tethering of one part of a molecule to another part of the same molecule. This tethering is found in both long chain branched polymers and in macrocycles. We have studied the surface fluctuations with X-ray Photon Correlation Spectroscopy for melts of well-defined, anionically polymerized polystyrenes of various architectures, including linear, 6 arm star, pom-pom, comb and cyclic architectures. For linear chains, the variation of surface relaxation time with in-plane scattering vector can be fit using a hydrodynamic continuum theory (HCT) of thermally stimulated capillary waves that knows nothing of the chain architecture. Assuming the theory is applicable, apparent viscosities of the films may then be inferred from the XPCS data. For unentangled linear chains, the viscosity inferred from XPCS data in this manner is the same as that measured by conventional bulk rheometry. The HCT does a reasonable job of describing the variation of relaxation time with scattering vector for long branched chains also, but only if a viscosity much larger than that of the bulk is assumed. The discrepancy between the viscosity inferred from surface relaxation times using the HCT and that derived from conventional rheometry grows larger as the bulk Tg is approached and is different for each long chain branched architecture. However, for densely branched combs and cyclic chains different behaviors are found. Acknowledgement: Thanks to NSF (CBET 0730692) and the Advanced Photon Source, supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science, under contract No. W-31-109-ENG-38.