Probing polyethylene crystallization via simultaneous Raman scattering, rheology and microscopy KALMAN MIGLER, ANTHONY KOTULA, ANGELA HIGHT WALKER, NIST — The structure and rheology of polyolefins during crystallization is of critical importance to the polymer processing industry. Here we present simultaneous Raman scattering, rheological and optical microscopy measurements of crystallizing high density polyethylenes during quiescent and slow flow conditions. Raman scattering measurements during quiescent crystallization allow us to quantify three different mass fractions of chain conformers: an amorphous fraction, an orthorhombic crystalline fraction, and a fraction of chains that contain many consecutive trans bonds but are not part of the orthorhombic crystal. These non-crystalline consecutive trans (NCCT) conformers are generated as a precursor to crystallinity. Slow steady shear rates (1 s⁻¹) applied during isothermal crystallization experiments dramatically increase the crystallization rate as well as the amount of NCCT conformers produced. Optical measurements of sheared samples during crystallization reveal the formation of fiber structures that compositionally contain more NCCT conformers than the surrounding melt. The increase in the complex shear modulus commonly measured for crystallizing polyethylenes correlates with the growth of chain conformers and the appearance of spherulites within the melt.