Mesomorphic State in Early Stage Crystallization of Polyethylene
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— The kinetic pathway by which a molten polymer transforms into a multi-length scale, semi-crystalline structure upon cooling is an unsolved problem in polymer physics, yet it is critical to the processing, properties and ultimate performance of these materials. Here we utilize Raman spectroscopy to probe the early stage crystallization kinetics of a high-density polyethylene during low undercooling. The importance of Raman as a tool stems from its ability to measure the mass fraction of conformations that are in consecutive trans sequences (locally straight) but are not in an orthorhombic configuration, which we term non-orthorhombic continuous-trans (NOCT). We find that the Raman peaks indicative of NOCT precede the appearance of the peak which indicates orthorhombic crystallinity. We analyze the spectra within the context of a three-state conformational model to extract the mass fractions of the NOCT and the orthorhombic conformational states as crystallization proceeds. Concomitant birefringence and turbidity measurements indicate that this NOCT state can be understood as a separate mesomorphic phase which emerges from the melt state and precedes crystallization.