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Crystallization in Precision Polyolefins RUFINA ALAMO, ANINDYA GHOSAL, FAMU-FSU College of Engineering, Tallahassee Fl, EMINE BOZ, KENNETH WAGENER, University of Florida, Chemistry Department, Gainesville, Fl, RIQIANG FU, NHMFL, Tallahassee, Fl, ALAMO, GHOSAL, FU COLLABORATION, WAGENER, BOZ COL-LABORATION — Understanding the crystallization behavior of highly branched polyolefins can be accomplished with model polymers with well defined microstructures. Models for branched polyethylenes with precisely placed O, F, Cl or Br on each and every 19 carbons have been synthesized via acyclic diene metathesis (AD-MET) polymerization followed by hydrogenation. Compared to broad WAXS and DSC melting peaks of systems with a random distribution of the substituent, similar properties of precisely substituted polyolefins are very sharp, typical of the behavior of homopolymers. A uniform partitioning of the substituent between crystalline and non-crystalline regions, observed by NMR, relatively thick lamellar crystallites (240 A) and WAXS angular shifts, parallel the homopolymer-like crystallization behavior. In this series, orthorhombic isomorphic structures are maintained in O and F substituted polymers or up to a van der Waals radius of about 1.6 A, while accommodation of bulkier atoms in the lattice promotes the formation of a new triclinic form. A linear correlation between melting points and vdw radius in the halogen series is indicative to the degree to which each substitution perturbs the symmetry of the neighboring carbons in the lattice.

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