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Homogeneous crystal nucleation from the melts of flexible n-alkanes by molecular simulation PENG YI, GREGORY C. RUTLEDGE, Massachusetts Institute of Technology — Homogeneous crystal nucleation from a dense melt is particularly interesting for chain molecules due to their anisotropy and conformational flexibility. We report our molecular simulation study of the homogeneous crystal nucleation from n-alkane melts. For short n-alkane (C20) (J.Chem.Phys. 135, 024903), the nucleation trajectory was sampled using brute force molecular dynamics (MD) simulations at about 20% supercooling and the nucleation free energy was sampled using the Monte Carlo (MC) umbrella sampling method for temperatures ranging from 10% to 20% supercooling. In the MD simulation, we identified the induction period unambiguously and calculated the nucleation rate through a mean-first-passagetime analysis. A typical critical nucleus consists of a bundle of stretched segments organized into a cylindrical shape. The remaining CH2 groups form a disordered interfacial layer. By fitting the free energy curve sampled by MC to the cylindrical nucleus model, the crystal-melt interfacial free energies are calculated. We have found good agreement between the melting temperature and the interfacial free energies obtained in our simulation and those from experiment. For a long n-alkane above the entanglement length (C150), MD simulation of nucleation was performed at super-cooling as small as 15%. Chain folding was observed during the nucleation stage, and thickening of crystallites was observed during the subsequent crystal growth. The resulting crystal-amorphous interface is characterized in terms of loops, bridges and tails.

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