Molecular Modeling of Polymer Crystallization and the Effect of Nucleating Agents

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Technical Summary

The microstructure in a semicrystalline polymer material ultimately determines its material properties. Despite the abundance of research into the semicrystalline microstructure and its evolution during crystallization, a clear description of its development remains elusive. The advent of advanced computing and algorithms, however, have promoted molecular modeling of polymer crystallization, providing a new perspective on the development of the microstructure. This thesis revisits and challenges many aspects of microstructural development in macromolecular materials by applying new modeling techniques and recent technologies.

Through atomistic simulations of n-alkane crystallization, this thesis presents new molecular evidence of surface nucleation processes that contribute to the propagation of the crystal growth front in a macromolecular system. Crystallization in polymeric systems has long been theorized to proceed by "secondary nucleation." In this work, molecular dynamics (MD) simulations were engineered to probe this surface nucleation process by systematically inducing crystal growth for a system of macromolecules. In a novel application of mean first passage time analysis, the critical surface nucleus sizes, waiting times, and surface nucleation rates were extracted from atomically-detailed molecular trajectories using a layer-by-layer approach.

Insight from MD simulations was used to build a new kinetic model to describe the structure and rate of advancement of the growth front during crystallization. In the model, solidification occurs through the mechanisms of surface nucleation and lateral spreading of the solid phase within layers in the vicinity of the growth front. Transformation within each layer is described by an equation similar to the two-dimensional variant of the Johnson−Mehl−Avrami equation. The kinetic model is computationally efficient and predictive of important macroscopic observables.

Finally, this thesis presents the first computational screening of nucleating agents for macromolecular crystallization. Screens were conducted for two families of crystal materials: tetrahedrally coordinated materials isomorphic to diamond and silicon, and 2D, hexagonally coordinated materials isomorphic to graphene. The induction time for heterogeneous nucleation was shown to depend strongly on crystallographic registry between the nucleating agent and the critical nucleus, but the severity of this registry requirement weakened with increasing strength of attraction to the surface of the nucleating agent. In an unprecedented find, the substrate rigidity also significantly influenced heterogeneous nucleation.

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