Landscape of Polymer Morphology under Isothermal & Non-isothermal Crystallization

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Spatio-temporal emergence of polymer morphology has been investigated theoretically based on time dependent Ginzburg-Landau equation (known as TDGL - Model A), by coupling non-conserved crystal order parameter and temperature field. In the description of the total free energy, a double-well local free energy density signifying metastability of crystal ordering is combined with a non-local free energy term representing interface gradient. The coupled heat conduction equation has a latent heat source along the moving crystal growth front, which is proportional to the temporal variation of crystal order parameter. Two-dimensional calculations are carried out using material parameters and experimental conditions to elucidate morphology development during polymer crystallization. Important control parameters are the supercooling and anisotropy. For the crystallization with vanishing anisotropy, due to self-generated thermal field, which is caused by the liberating latent heat at the growth front, the crystal-melt interface became unstable. In the simulation under the condition of deep supercooling, lamellar branching occurs within the growing polymer spherulites, which is consistent with the experimental findings of poly(ethylene oxide) crystallization from supercooled melt. Furthermore, we confirm the occurrence of various single crystal forms including faceted hexagonal patterns, nonfaceted snowflakes and dense branching morphology. The landscape of these morphological textures has been established as functions of anisotropy of surface energy and driving force, supercooling. We found crystalline anisotropy is necessary for steady growth of the tips of side branches which appeared in snowflake patterns. With decreasing crystallization temperatures, the simulations showed the morphology of the single crystals changes from a nucleation-controlled faceted hexagonal plate to the nonfaceted snowflake-like pattern as evidenced by experiments. Finally, we applied an external thermal gradient in the temperature field, and the emergence of structural gradient with epitaxial lamellar growth at the chilled wall and spherulites in the bulk was revealed.

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