

MOLECULAR SIMULATION OF NUCLEATION FROM FLOWING POLYMER MELTS

by

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TECHNICAL SUMMARY

During processing, flow drastically accelerates the kinetics of polymer crystallization, altering the morphology and properties of the resulting material. The earliest stage of flow-induced crystallization, known as flow-enhanced nucleation (FEN), is challenging to study experimentally due to the small spatiotemporal scale over which it occurs. Non-equilibrium molecular dynamics (NEMD) simulation, which operates at short time and length scales, has proven to be a useful tool for investigating this stage. Using NEMD, FEN was studied in *n*-eicosane (C20), *n*-pentacontane (C150) and their blends. Analysis of these simulations provided insight into the underlying mechanism and constitutive relationships that govern FEN.

A method was developed to extract kinetic rates and critical parameters from direct simulations of nucleation events. It is based on the first-passage time statistics of a stochastic process obeying the classical nucleation theory (CNT) and utilized a novel approximation for the first-passage time distribution. Using this method, FEN in C20 was determined to occur through both a reduction in the barrier to nucleation and enhanced diffusion. Mechanistically, the barrier reduction is consistent with CNT with an extra driving force due to flow-induced stretching and orientation.

In FEN simulations of C150, intense fluctuations gave rise to domains with high local alignment on the Kuhn length-scale. Upon quenching, the nucleation of small crystallites occurred preferentially within these domains. This behavior is at odds with CNT and indicates a more complex mechanism at play. The C150 simulations were further utilized to draw correlations between the nucleation rate and the response of the melt to the applied flow field. Based on the fidelity of the observed correlations, empirical models reported in the literature were evaluated for their consistency with the NEMD data, and new models are proposed for data that do not comport with existing ones.

In bimodal blends of C20 and C150, nucleation kinetics were found to depend on the degree to which both the long and short chains are deformed. This result conflicts with experimental evidence that the nucleation rate in a polydisperse melt is determined only by the high molecular weight component.

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