

Molecular Aspects of Flow-Induced Crystallization of Polymers

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Molecular aspects of polymer melt rheology play an extremely strong role in governing the processing-structure-property relations of semicrystalline polymers. Recent advances in experimental apparatus and methods have revealed that the dramatic changes in crystallization kinetics and morphology induced during shear follow a kinetic pathway. The rate of formation of oriented precursors is not limited by the usual activation barrier to nucleation, but instead occurs many orders of magnitude faster at a rate that tracks the dynamics of the polymer chains in the melt. Model polymers and their binary blends have shown that the relevant melt dynamics that control formation of the oriented, thread-like nuclei are those of the longest chains in the melt, and that the mechanism of the effect of the long chains is cooperative, greatly enhanced by long chain-long chain overlap. Thus, insights gained into the role of chain dynamics in the molecular mechanism of shear-enhanced crystallization may soon combine with parallel advances over the past decade regarding the dynamics of polydisperse melts to provide the underpinnings for truly predictive models of flow-enhanced crystallization of polymers.