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Microscopic kinetic model for polymer crystal growth¹ WENBING

HU, Department of Polymer Science and Engineering, Stat Key Lab of Coordination Chemistry, School of Chemistry and Chemical Enginnering, Nanjing University Linear crystal growth rates characterize the net result of competition between growth and melting at the liquid-solid interfaces. The rate equation for polymer crystal growth can be derived with a barrier term for crystal growth and with a driving force term of excess lamellar thickness, provided that growth and melting share the same rate-determining steps at the growth front. Such an ansatz can be verified by the kinetic symmetry between growth and melting around the melting point of lamellar crystals, as made in our recent dynamic Monte Carlo simulations. The profile of the growth/melting front appears as wedge-shaped, with the free energy barrier for intramolecular secondary crystal nucleation at its top, and with the driving force gained via instant thickening at its bottom. Such a scenario explains unique phenomena on polymer crystal growth, such as chain folding, regime transitions, molecular segregation of polydisperse polymers, self-poisoning with integer-number chain-folding of short chains, and colligative growth rates of binary mixtures of two chain lengths.

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