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Growth kinetics and morphology of polymer crystals[1]

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Originating from the nature of chain folding, polymer single crystals are quite unique in the growth kinetics and morphology. The developments of the understanding in the past 50 years are discussed and the unsolved important issues will be suggested. Polymer single crystals are thin lamellae with the thickness in the order of 10nm determined by the period of chain folding, which keeps a constant value for the isothermal crystallization. The growth of polymer single crystals is modeled by the kinetics of creation and annihilation of growth steps on a rectangular substrate with the pre-determined thickness. The growth face is therefore regarded as a one-dimensional substrate and the kinks and anti-kinks on the substrate correspond to the growth steps propagating in the opposite directions. The kinetic equations of those kinks proposed by Seto and Frank well describe the transition of growth regime as a crossover from single nucleation to multi-nucleation on the basis of the standard model of chain-folded polymer crystallization with surface nucleation proposed by Lauritzen and Hoffman. However, the analysis of the growth kinetics and morphology of single crystals having curved growth front suggests an unusual behavior of the step propagation velocity. The anomaly can be accounted for by a self-poisoning of the growth step interrupted by polymer chains with folding shorter than required. An entropic barrier of pinning proposed by Sadler and Gilmer is a possible candidate of the self-poisoning and is in accordance with recent computer simulation results suggesting the kinetics on a rugged free energy landscape having a resemblance to protein folding. Therefore, the quantitative evaluation of the kinetic barriers of surface nucleation and pinning has been an important issue. In addition, examination of the kinetics of melting will have valuable information because melting of a crystal must be free from nucleation but can still be limited by the entropic barrier.

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