New Paradigms for Polymer Crystallization

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The ordering process of topologically connected chains into a crystalline state is distinctly different from that of low molar mass substances. One of the key differences arises fundamentally from entropic barriers due to substantial reduction in configurational entropy of the system during the ordering process. We have derived a new theoretical model with the following essential features: (1) For a single lamella, the free energy landscape exhibits many metastable states (separated by free energy barriers), and a globally stable state. Among the metastable states, even the first viable state with its free energy just below that of the melt is long-lived, due to the barrier for thickening. The thickness of this long-lived metastable state increases with temperature. However, if enough time is granted for this metastable state to evolve, then the equilibrium thickness would be reached for each temperature. The equilibrium thickness decreases with temperature, until the approach of the equilibrium melting temperature. The equilibrium melting temperature does not correspond to that of extended chain dimensions. (2) The lateral growth faces a free energy barrier, due to temporal crowding of entangled chains at the growth front. A general formula is derived for the growth kinetics of the growth front, providing a crossover description for crystallization of low and very high molar mass polymer chains. The predictions are compared with available experimental data.