Kinetic Traps in the Crystallization of Sustainable Polyethylene-Like Materials

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Bio-sourced polyethylene-like polymers have been synthesized as possible substitutes for commodity polymers derived from fossil fuel feedstocks. Their crystalline and mechanical properties are of interest in the path to developing a more sustainable, circular plastics economy. We are interested in understanding their solidification behavior from the melt and the semicrystalline morphology acquired under different crystallization modes. Recent studies of polymorphism, melting behavior and crystallization kinetics of polyethylenes with moieties placed at an exact equal distance along the backbone will be presented with especial focus on the crystalline properties of precision polyethylenes with acetals and esters, under rapid and isothermal crystallization from the melt. All display unusual discrete crystallization rate minima with increasing crystallization temperature. Such inversions in the temperature coefficient of the crystallization kinetics correlate with transitions between crystalline structures differing in packing symmetry (polymorphs), or in a step-increase in crystal thickness (see schematics below). At the rate minima, the level of crystallinity is very low. Hence, the rate minima are "kinetic traps" of relevance in processing these materials from the melt. The origin of the rate minima will be discussed.

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