

Events at the Growth Face as Revealed by Concentration Dependence of Crystallization Rate of Long Alkanes

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INTRODUCTION

It is by now well known that monodisperse *n*-alkanes, long enough to exhibit chain folding, show a minimum in crystal growth rate with increasing supercooling ΔT . The minimum occurs near the transition from extended-chain (E) and once-folded chain growth (F),¹ or from once-folded to twice-folded growth.^{2,3} The anomaly is attributed to the self-poisoning or pinning effect whereby, as transition temperature is approached from above, the unstable once-folded overgrowth diverges and virtually stops the growth of extended-chain crystals.⁴ Preliminary solution-crystallization experiments have shown a similar kinetic anomaly as a function of increasing concentration.⁵ Here we present a more detailed study of concentration dependence of crystal growth rate, resolved into step initiation and step propagation rates. The study confirms the strongly negative reaction order in the range of strong poisoning, and an order of 2 to 3 for folded-chain secondary nucleation in the range of weak poisoning, giving support to the idea of a 2-dimensional secondary nucleus.