

Dilution Wave and Negative-Order Crystallization Kinetics of Chain Molecules

G. Ungar,^{1,*} P. K. Mandal,^{1,†} P. G. Higgs,² D. S. M. de Silva,¹ E. Boda,¹ and C. M. Chen^{2,‡}

¹*Department of Engineering Materials, University of Sheffield, Sheffield S1 3JD, United Kingdom*

²*School of Biological Sciences, University of Manchester, Stopford Building, Oxford Road, Manchester M13 9PT, United Kingdom*

(Received 17 April 2000)

We show that the crystal growth rate of a very long-chain *n*-alkane C₁₉₈H₃₉₈ from solution can decrease with increasing supersaturation and follow strongly negative order kinetics. The experimental behavior can be well represented by a theoretical model which allows the molecule to attach and detach as either extended or folded in two. The obstruction of extended-chain growth by unstable folded depositions increases disproportionately with increasing concentration. As a consequence of this abnormal kinetics, a “dilution wave” can propagate and trigger a folded-to-extended-chain transformation on its way.

PACS numbers: 87.15.Nn, 64.70.Dv, 81.10.Aj, 81.10.Dn