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*
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We show that the crystal growth rate of a very long-chain n-alkane $C_{198}H_{398}$ 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.

Linear molecules shorter than ca. 15 nm crystallize as layers of extended chains (Fig. 1), while longer molecules such as most crystalline polymers fold [1]. Chain-folding in synthetic polymers has its origin in crystallization kinetics [2–4]. Among many peculiarities of chain-folded polymer crystallization is the weak dependence of crystal growth rate G on solution supersaturation $(c - c_0)/c_0$; i.e., $G \propto [(c - c_0)/c_0]^m$, where $0.2 \leq m \leq 1$ [5,6] (c_0 and c are concentrations of saturated and supersaturated solutions; m is the reaction order). The prevailing explanation is that the growing crystal experiences a local concentration higher than the bulk average due to adsorbed chains [7,8]. However, the present findings suggest that this may not be the full explanation.

Important kinetic and morphological features of synthetic polymers are masked by their polydispersity [6]. For this reason we are studying specially synthesized completely uniform n-alkanes as long as $C_{390}H_{782}$ [9]. These can be crystallized in conformations ranging from fully extended to folded in five, with chain ends at the lamellar surface (Fig. 1) [10]. The resulting quantization of lamellar thickness L can cause revealing singularities [11].

Here we measure the rates of growth of crystals of n-$C_{198}H_{398}$ from 1-phenyldecane solutions as a function of initial supersaturation and crystallization temperature (T_c). Crystal dimensions are measured directly from interference contrast micrographs captured during isothermal growth. Under certain conditions, such as $T_c = 98.6\,°C$ and 4.2 wt % initial concentration, the growth exhibits autoacceleration. This gives reasons to suspect an increase in the growth rate G with dilution, since supersaturation decreases during crystallization. The extrapolated initial longitudinal and transverse crystal growth rates G_b (along [010]) and G_a (along [100]), respectively, are plotted as functions of initial concentration c in Fig. 2 for $T_c = 98.0\,°C$. While at low c the growth rates increase with increasing c, a maximum is reached around $c = 1\%$. With a further increase in concentration the growth rates indeed decrease steeply to reach a minimum for c around 3%. Beyond this concentration $G_a(c)$ and $G_b(c)$ start rising once more.

The observed reaction order m for crystallization of the alkane becomes strongly negative, with $m \leq -5$, near the minimum in $G_a(c)$. There are a number of examples of chemical reactions of negative order with respect to one of the reactants [12]. However, these are complex reactions involving intermediates and, usually, a catalyst. The simplicity of the present system of a single compound crystallizing from a pure inert solvent is exceptional.

We have also determined G vs T_c for selected concentrations—see Fig. 3 for $c = 1.1$ and $c = 4.2$ wt %. The $G(T_c)$ data are in broad agreement with previously found T_c dependencies of crystallization rates from melt and solution [11,13,14]: These show a pronounced minimum near the melting/dissolution temperature of once-folded chain crystals [15].

A theory for the temperature dependence of crystal growth rates in monodisperse alkane crystals was already given [16,17]. A simple analytical model was presented that was solvable in one dimension, together with simulations in two dimensions [17]. Here we extend this idea to include both temperature and concentration dependence.
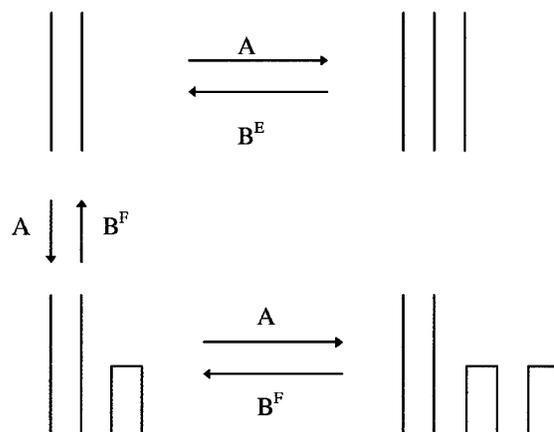
The formulation has been deliberately kept simple. Extended chains may bind to the growth surface at rate A if and only if there is already an extended chain on the surface. Folded chains may bind to the surface at rate A
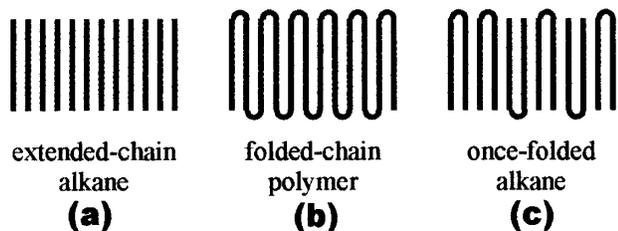
FIG. 1.   Schematic representation of sections through crystals of an (a) extended-chain n-alkane, (b) folded-chain polymer, (c) once-folded alkane ("hairpin" conformation).

whatever the current state of the surface. Extended chains escape from the surface at rate B^E, while folded chains escape at rate B^F. Following a very similar argument to that in [17] we find that growth rates of extended- and folded-chain crystals are

$$G^E = (1 - A/B^F)(A - B^E), \quad \text{if } B^E < A < B^F, \quad (1a)$$

$$G^F = A - B^F, \quad\quad\quad\quad\quad \text{if } B^F < A. \quad (1b)$$

The free energy changes on removal of one extended or one folded chain from the surface are

$$\Delta F^E = \varepsilon z - \sigma_{\text{ends}} - szT + kT \ln c, \quad (2a)$$

$$\Delta F^F = \varepsilon z - \sigma_{\text{ends}} - \sigma_{\text{fold}} - szT + kT \ln c, \quad (2b)$$

where z is the number of monomers per chain, ε and s are the energy and entropy change per monomer between the bulk of the crystal and the solution, and σ_{ends} and σ_{fold} are the excess free energies associated with the chain ends and the chain fold, respectively [2] (chains in solution are treated as an ideal gas). Hence we may write
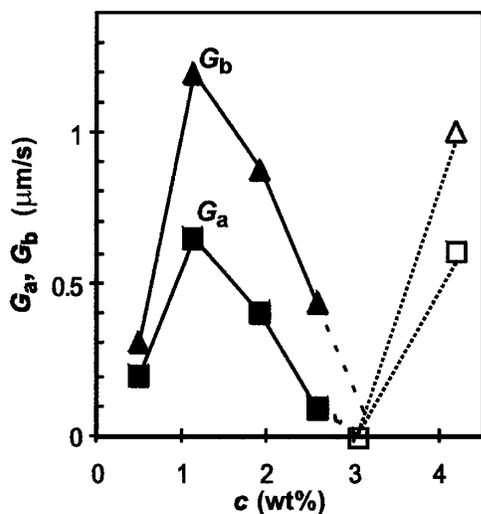
$$\frac{A}{B^E} = \exp(\Delta F^E/kT) = c\exp[-\alpha(1 - \theta^E/T)], \quad (3a)$$

$$\frac{A}{B^F} = \exp(\Delta F^F/kT) = c\exp[-\alpha(1 - \theta^F/T)], \quad (3b)$$

where $\alpha = sz/k$, $\theta^E = (\varepsilon/s) - (\sigma_{\text{ends}}/sz)$, and $\theta^F = (\varepsilon/s) - (\sigma_{\text{ends}} + \sigma_{\text{fold}})/sz$. By setting these two ratios equal to 1, we may calculate the temperatures of dissolution of the two crystal types as a function of chain concentration:

$$T_d^E = \theta^E/(1 - \ln c/\alpha), \quad (4a)$$

$$T_d^F = \theta^F/(1 - \ln c/\alpha). \quad (4b)$$

These two relationships give the phase diagram shown in Fig. 4(a). The symbols are measurements with $C_{198}H_{398}$, and the lines are fits of the theoretical curves. The predicted growth rate calculated along a horizontal section at $T = 98\,°C$ is shown in Fig. 4(b), which may be compared with the data in Fig. 2. The growth rates along two vertical sections at $c = 1.1\%$ and $c = 4.2\%$ are shown in Fig. 4(c) for comparison with Fig. 3.

This simple 1D theory is intended to give a qualitative explanation of the phenomena observed, and it cannot be used to give quantitative predictions of crystal growth rates. However, in [17] we did simulations of a 2D version of the model in which temperature was varied at fixed concentration. Very similar shapes of the growth curve were
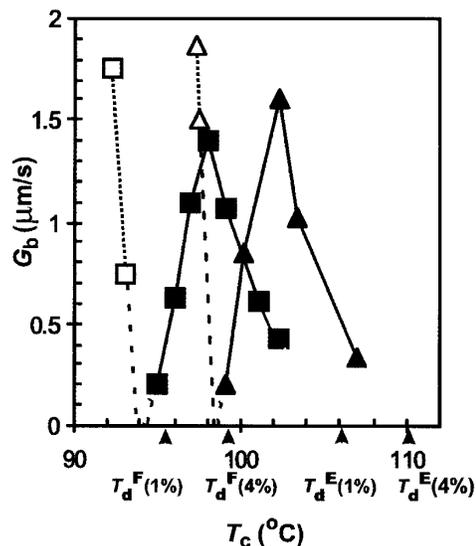

FIG. 2.   Initial crystal growth rate G_a and G_b of $C_{198}H_{398}$ vs solution concentration at 98.0 °C. ■, ▲: extended chain; □, △: once-folded chain crystals. Note the negative dG/dc gradient for $1\% < c < 3\%$.

FIG. 3.   Initial crystal growth rate G_b vs T_c from 1.1 wt % (■, □) and 4.2 wt % solutions (▲, △) of $C_{198}H_{398}$ in 1-phenyldecane. ■, ▲: extended chain; □, △: once-folded chain. The slope of the size vs time curves at zero size limit for crystals appearing first was taken to represent the growth rate at the known initial concentration. Dissolution temperatures of extended (T_d^E) and once-folded chain crystals (T_d^F) are marked.
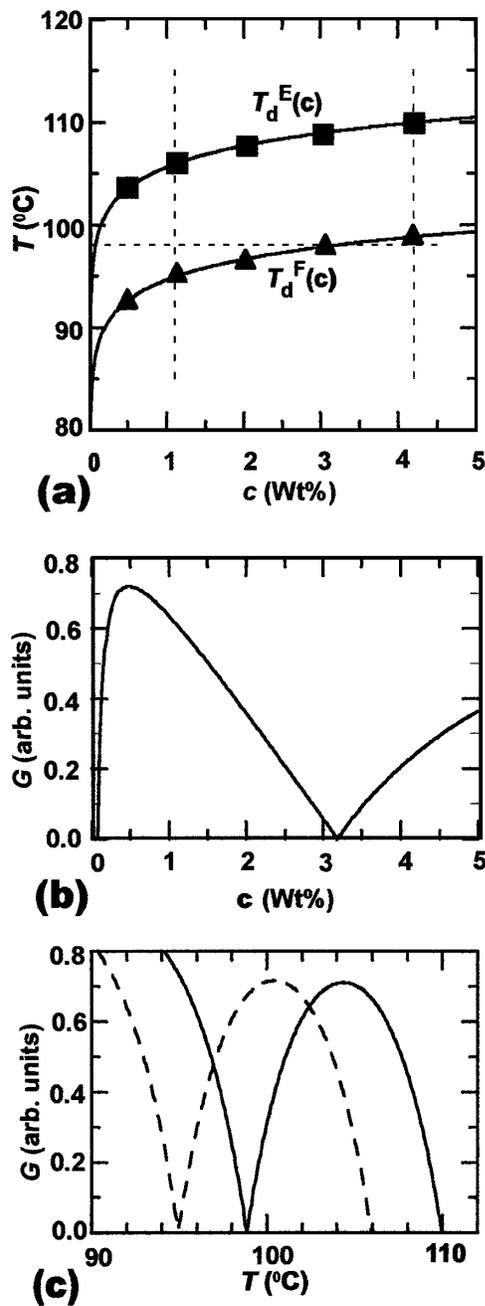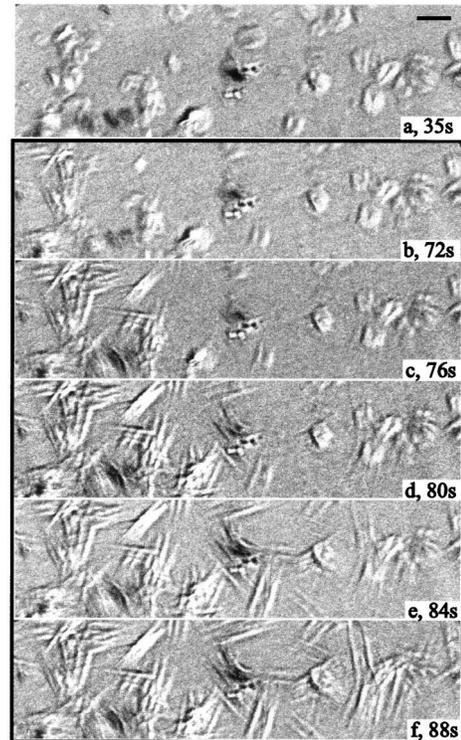
FIG. 5. Series of interference contrast optical micrographs of an initially 4.2 wt% solution of $C_{198}H_{398}$ at successive times (indicated) upon reaching $T_c = 97.4$ °C. The progress of the "dilution wave" is shown in (b)–(f), triggering the processes of crystallization of rodlike extended-chain crystals and simultaneous dissolution of folded-chain crystals. The rods form along the two {100} faces of the "truncated lozenge" shaped [21] folded-chain crystals, with a third parallel crystal often appearing in the middle. Bar = 20 μm.

FIG. 4. (a) Binary phase diagram n-$C_{198}H_{398}$–phenyldecane. Equilibrium liquidus curve $T_d^E(c)$ for extended-chain crystals and nonequilibrium curve $T_d^F(c)$ for once-folded chain crystals were calculated using Eq. (4), matched to the experimental dissolution temperatures (■, ▲). The fitting parameters used are $\alpha = 123$, $\theta^E = 392.8$ K, and $\theta^F = 381.4$ K. Experimental $T_d^E(c)$ and $T_d^F(c)$ values were determined *in situ* at a near zero heating rate [18]. (b) Crystal growth rate G calculated as a function of concentration at $T_c = 98.0$ °C—cf. Fig. 2. (c) G calculated as a function of T_c for $c = 1.1\%$ (dashed curve) and $c = 4.2\%$ (full curve)—cf. Fig. 3.

found to those in the 1D model. We therefore are confident that the 1D model captures the essense of the system behavior in a very straightforward way.

The observed negative dG/dc in Fig. 2 can thus be explained as follows. An increase in concentration increases the coverage by the "wrong" but nearly stable chain-folded depositions which "pin down" [3] the underlying molecules at the growth surface and hinder their full extension; chain extension cannot continue before the overlayer is detached. As expected, $G(c)$ behaves normally at low concentrations, with dG/dc positive (Fig. 2); with ΔF^F strongly positive the short lifetime of folded depositions leaves ample time for uninhibited extension of surface chains. With increasing c the obstructive chain-folded coverage increases out of proportion.

Analysis of crystal habits according to [19] shows that the process most suppressed by increased supersaturation is the initiation of new molecular layers on {100} faces [20]. Furthermore, morphological similarities with polyethylene suggest that a similar inhibitory mechanism also operates in crystallization of polydisperse polymers [21].

The autoaccelerated crystallization of the long alkane gives rise to a further phenomenon, described by the following example. Crystallization from an initially 4.2% solution at $T_c = 97.4$ °C results in pseudohexagonal plateletlike folded-chain crystals [Fig. 5(a)]. These cease

to grow after about 30 s as a metastable equilibrium is reached between folded-chain crystals and a pseudosaturated solution described by $T_d^F(c)$ in Fig. 4(a). As both nucleation and growth of extended-chain crystals are highly suppressed under these conditions, no visible change occurs for the next half a minute. After that, rather suddenly, the platelet crystals are replaced by highly elongated extended-chain crystals. The transformation takes several seconds and is solution mediated. It spreads from left to right in Fig. 5(b) at a rate of 13 μm/s [Figs. 5(b)–5(f)]. We assume that somewhere to the left of the area in Fig. 5 an extended-chain crystal successfully forms, thus depleting the surrounding solution. This in turn triggers the growth of other extended-chain crystals in the vicinity, as the inhibitory effect of high concentration eases. A "dilution wave" is thus generated. Ahead of it the system is in metastable equilibrium between folded-chain crystals and the $T_d^F(c)$ solution, while behind it the true equilibrium between extended-chain crystals and the $T_d^E(c)$ solution is established. The wave is self-sustaining, with the crystals in its way acting as "repeaters," maintaining the signal's amplitude and sharpness. The principle of inverse concentration dependence of crystallization rate may potentially be exploitable, e.g., in concentration switches controlling chemical or biochemical systems.

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*To whom correspondence should be addressed. Electronic address: g.ungar@sheffield.ac.uk

†On leave from Department of Physics, University of North Bengal, Siliguri-734430, India.

‡Present address: Department of Physics, National Taiwan Normal University, Taipei, Taiwan.

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