On the growth rate maximum in extended-chain growth of crystals of linear paraffins

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Isothermal crystallization of a pure n-paraffin at temperatures near its melting point results in extended chain crystals whose growth rate–crystallization temperature curve exhibits a maximum and whose melting point appears to be lower than that expected. This behaviour can be explained in terms of polymer crystal nucleation theory with a model in which registration of chain ends is not perfect resulting in a transient layer of cilia on the crystal and to an end surface free energy σ' for that ciliated surface. The presence of the maximum, however, requires a *decreasing* nucleation rate with decreasing temperature—contrary to customary expectations. This can be shown to be a consequence of the crystallization of (essentially) fixed length stems: the combination of the relevant nucleation and backward reaction terms thus giving rise to the maximum. The temperature at which the maximum occurs is a function of the degree of imperfection at the end surface.

(Keywords: nucleation theory; n-paraffin crystallization; extended chains; end surface free energy)

Over the past three decades, the Lauritzen–Hoffman (LH) theory[1] of polymer crystal growth has been quite successful in explaining the main features of polymer crystallization. In addition, extensions of the theory permit its application to more subtle details of polymer crystallization, such as the effect of molecular weight[2]. Nevertheless, experimentalists occasionally produce observations which appear to be in violation with the LH theory and, hence, call its validity into question. One such example was the formation (from dilute solution) of polyethylene single crystals exhibiting curved edges. This case was treated recently[3,4] within the scope of the LH theory with a model, experimentally based, in which repulsion of the folds in the curved fold sectors resulted in lattice strain.

A more recent example arises from studies of the crystallization of certain long pure n-paraffins by Ungar and Keller[5], particularly n-$C_{246}H_{494}$ (C246). During isothermal crystallization from the melt near the melting temperature such materials form only extended-chain crystals. With decreasing crystallization temperature, the growth rate of C246 crystals first increased, then went through a maximum decreasing with further lowering of the temperature, eventually exhibiting a minimum at the temperature corresponding to the boundary between extended-chain and once-folded crystallization. A maximum in the crystal growth rate curve for polymers is not unexpected—it arises from the opposing temperature dependencies of the nucleation and transport processes. However, the maximum observed for C246 by Ungar and Keller occurs in the temperature range where only the nucleation process should have a significant effect—the transport term should be relatively temperature independent. Hence, the maximum must arise from the nucleation process alone which is an apparent violation of LH theory.

To explain such behaviour, Hoffman[6] has extended LH nucleation theory to apply to the crystallization of pure n-paraffins and to apply to crystallization in the extended-chain form. His approach is an extension of the earlier work[3,4] concerning the effect of lattice strain on the crystallization process and provides answers for the observed phenomena: (1) the apparent lowering of the melting point; (2) the maximum in growth rate at a temperature slightly below the melting temperature T_m; and (3) the existence of a minimum in the growth rate–temperature curve followed by a rapid increase in growth rate accompanying the onset of once-folding; all within the purview of nucleation theory.

The explanation that a maximum in the growth rate can occur under conditions where nucleation control is operative is counter to the collective experience with crystallizable polymers and has troubled other workers in the field. It is the purpose of this communication to elaborate the Hoffman treatment in order to clarify the reasons leading to (and the physics underlying) the observed behaviour in an attempt to satisfy some of these concerns.

The model employed by Hoffman[6] invokes a process in which complete registry of the chain ends is not attained during nucleation. The result is a transient layer of cilia on the surface (called 'kinetic ciliation' by Hoffman) which gives rise to an end surface free energy σ' characteristic of this disorder. Application of the procedures of LH theory[1] to this model leads to a growth rate expression for the crystallization of a molecule of extended length l_0 which may be written as

$$G \propto [\mathrm{TR}] \times [\mathrm{ST}] \times [\mathrm{BA}] \times [\mathrm{NU}] \qquad (1)$$

where the bracketed terms represent the individual contributions of the transport, strain, backward reaction and nucleation processes, respectively:

$$[\mathrm{TR}] = \exp(-Q^*/RT) \qquad (2a)$$

$$[\mathrm{ST}] = \exp(-2a_0 b_0 \sigma'/kT) \qquad (2b)$$

$$[\mathrm{BA}] = 1 - \exp[-(a_0 b_0/kT)(l_0\,\Delta G - 2\sigma')] \qquad (2c)$$

$$[\mathrm{NU}] = \exp(-b_0 \sigma l_0/kT) \qquad (2d)$$

All of the parameters appearing in equations (2a)–(2d), except for σ', are standard in LH theory: k and R are the Boltzmann and gas constants, respectively, T is the

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isothermal crystallization temperature, Q^* is the activation energy relevant to the transport process, a_0 and b_0 are the molecular width and molecular thickness of the crystallizing molecule, σ is the lateral surface free energy, and $\Delta G = (T_m - T)/T_m$ is the free energy of fusion at T with T_m being the equilibrium melting point of the material.

The temperature dependence of each of the terms in equation (1) is critical to an understanding of the observations. In the temperature range of interest, neither the strain [ST] nor the transport [TR] varies significantly with temperature and, hence, need not be considered further. The backward reaction term [BA] is relatively temperature independent except near the melting point where it decreases rapidly towards zero with increasing temperature. No combination of these three terms can give rise to a significant decrease in growth rate with decreasing temperature in the vicinity of the melting point. Thus, the observed behaviour must lie in the nature of the nucleation term [NU], i.e. the temperature dependence of the nucleation process must be opposite to that normally encountered in polymer crystallization.

A generalized nucleation term, applicable to both polymers and paraffins, may be written

$$[\mathrm{NU}]_{\mathrm{gen}} = \exp(-b_0\sigma l/kT) \qquad (3)$$

in which l is the length of the stem in the activated state for the nucleation process. For polymers crystallizing according to a chain-folding mechanism, l is a function of the crystallization temperature[1], $l \cong 2\sigma_e/\Delta G$, and the nucleation term becomes

$$[\mathrm{NU}]_{\mathrm{poly}} = \exp(-K_g/T\,\Delta T) \qquad (4a)$$

which, because of the inverse ΔT functionality, gives rise to the rapid increase in growth rate with decreasing temperature that is commonly encountered in crystallization of polymers (σ_e and K_g are the fold surface free energies and the nucleation constant, respectively). For n-paraffin crystallization near T_m in the extended-chain conformation, on the other hand, the stem length is *fixed* at (or near) the molecular length $l \cong l_0$. As a consequence of this restriction, the nucleation term (equation (2d)) exhibits an Arrhenius behaviour, i.e.

$$[\mathrm{NU}]_{\mathrm{par}} = \exp(-\mathrm{constant}/RT) \qquad (4b)$$

which *decreases* with decreasing crystallization temperature. Herein lies the reason for the apparent anomalous behaviour. For the n-paraffins, the nucleation and the backward reaction terms have opposing temperature dependencies with a resulting maximum in the growth rate in the vicinity of the melting point.

The situation is illustrated in *Figure 1* by calculations for the extended-chain crystallization of three n-paraffins discussed in the literature: $C_{192}H_{386}$ (C192), C246 and $C_{294}H_{590}$ (C294). These curves exhibit the general behaviour reported for C246 by Ungar and Keller[5]. For the calculations, regime II was assumed (choice of regime I instead would not affect the results) and values of the parameters appearing in equations (2a)–(2d) were taken as those appropriate to polyethylene[2]. The value of σ' was chosen to make the location of the maximum in the calculated curve for C246 agree with that observed. This value was then used to calculate the curves for the other two paraffins. For each paraffin, curves a and b illustrate, respectively, the overall growth rate dependence (equation (1)) and the behaviour of the nucleation term alone (equation (2d)) as a function of the isothermal crystallization temperature. The boundary between extended-chain and once-folded crystallization is demarked by the vertical line on the left of each set of curves. The analogous calculations with no strain component ($\sigma' = 0$) are indicated by the dotted lines.

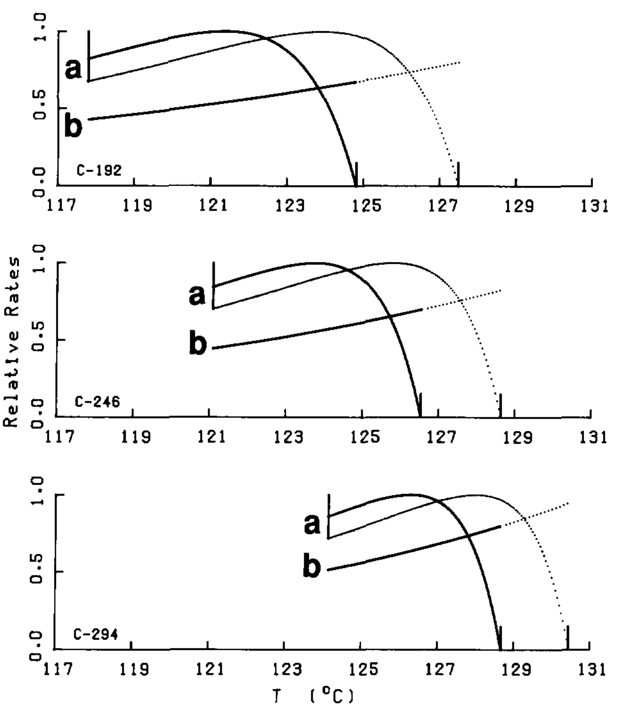

Figure 1 Effect (calculated) of molecular length and of σ' on relative rates as a function of temperature for the hydrocarbons: n-$C_{192}H_{386}$, n-$C_{246}H_{494}$, n-$C_{294}H_{590}$. (——) $\sigma' = 23\ \mathrm{erg\,cm^{-2}}$; (···) $\sigma' = 0\ \mathrm{erg\,cm^{-2}}$. Lines labelled (a): relative growth rates, G/G_0 scaled to a maximum value of unity. Lines labelled (b): 'nucleation' term (equation (2d)) scaled to a value of unity at $T = 131°\mathrm{C}$. Vertical lines on the left of the curves labelled (a) signify the temperatures for the onset of the once-folding region of crystal growth. Vertical bars on the abscissa of each figure denote values of the melting point appropriate for each paraffin length and σ' value

The calculated curve for C246 represents the observed behaviour in a satisfactory manner. Note that the presence of the surface ciliation term σ' also serves to depress the apparent melting point of an n-paraffin (solid line) below that for the perfect n-paraffin crystal (dotted line). A corollary of this is the expectation that the observed melting point (by d.s.c., say) of an n-paraffin might be expected to vary with crystallization temperature. Such behaviour has been reported for C192 by Stack *et al.*[7].

It is clear that in the crystallization of pure paraffins the restriction to a *fixed* stem length is the underlying cause of the maximum in the growth rate curve, independent of the existence or magnitude of an end surface term σ'. The *position* of the maximum is determined by the magnitude of σ'. The apparent violation of nucleation theory, therefore, can be satisfactorily explained.

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