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The kinetic substrate length in nucleation-controlled crystallization in polyethylene fractions

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The concept of a substrate length L is essential in the understanding of the regime I→II growth rate transitions in melt-crystallized lamellar polymers. The present work deals with the actual magnitude of L in polyethylene fractions as determined strictly from the kinetics of crystallization. With the help of an improved value of the activation energy of transport in the melt, and a more precise method of analysis than was employed heretofore, it is found from published growth rate measurements on polyethylene fractions that L is within about a factor of two of 0.77 μm at the regime I→II transition. The value of L is independent of the equilibrium melting temperature $T_m^0(\infty)$ assumed in the analysis. It is shown that L is much larger than a just stable surface nucleus. A brief summary is given of what is known about L from a kinetic point of view, and possible correlations with morphological features are mentioned. It is conjectured that L may relate to the mean distance between surface defects that have the capacity to terminate strip completion. In the course of the study, better values of the pre-exponential factors N_0 and C_0 that govern the absolute growth rates in regimes I and II, respectively, are obtained. A revised numerical value is given for the pre-exponential factor in the Lauritzen 'Z' test. This is based partly on the new value of C_0, and partly on a reformulation of the problem.

(Keywords: polymer crystallization; regime I; regime II; substrate length; Lauritzen 'Z' test; polyethylene; poly(L-lactic acid))

INTRODUCTION

The substrate length L plays an important role in theories of nucleation-controlled growth in chain systems, and is essential to the interpretation of a number of effects that are observed experimentally. Notable among the latter are the regime I→II transitions found in nucleation-controlled lamellar crystallization in polyethylene fractions[1,2]; these transitions cannot be understood within any extant conceptual framework without reference to a substrate length L. Though the reality of L is hardly to be doubted because of the existence of the regime I→II rate transitions, its physical origin has been a puzzle, as was recently pointed out by Frank[3]. In order to approach the question of the physical origin of L, it is deemed useful to have at our disposal a determination of its actual value as derived from crystallization kinetics that is reliable within specified limits. The principal objective of this paper is to obtain such an estimate from published growth rate data on polyethylene fractions that crystallized from the melt in the chain-folded lamellar mode. The input value of the activation energy for transport in the present determination is more accurate than that used previously, and certain approximations in the analysis have been removed. The determination of L requires that estimates of the values of the pre-exponential factors that govern the absolute growth rates in regimes I and II be obtained. These factors are of interest in themselves, and expose some interesting problems related to nucleation theory as it pertains to crystallization in chain systems.

Some other topics will be addressed. It will be shown that the length of a just stable surface nucleus is much less than L. While it is not certain that any connection between L as determined by kinetics and some morphological feature exists, comment will be given on a possible relationship. A summary of what is known about L from a kinetic point of view is given. Note is made of a possible new concept for explaining the physical origin of L.

It is useful to comment briefly at the outset on the subject of regime transitions. Three regimes of crystallization are known to occur in nucleation-controlled polymer crystallization. Within a specified regime, a definite relationship exists between the surface nucleation rate i and the observable lineal growth rate G. The quantity i is strongly dependent on the undercooling ΔT and for polymers varies as $\exp[-K_g/T(\Delta T)]$ near the melting point. In regime I, which occurs nearest the melting point, $G_I = b_0 iL$, where b_0 is the layer thickness. Here one nucleation act causes completion[2] of the substrate of length L. In the next lower regime, denoted II, multiple nucleation occurs on the substrate of length L, and the growth rate becomes[4,5] $G_{II} = b_0(2ig)^{1/2}$. The variation with temperature of the substrate completion rate g is much less than that of i, so $G_{II} \propto i^{1/2}$. Thus, in regime II the growth rate is independent of L. Experimentally, the regime I→II transition appears clearly in polyethylene fractions as an abrupt change in slope of the growth rate at a reproducible undercooling in a G *versus* T plot[1]. In a plot of $\ln G + Q_R^*/RT$ *versus* $1/T(\Delta T)$, the change of slope at the transition is very close to the theoretical value of two and is insensitive to the activation energy for reptation Q_R^* employed in the analysis. Accurate growth rate data are available for polyethylene

fractions $M_z = 26\,500$ to $203\,600$ crystallizing in the lamellar chain-folded mode in both regimes I and II, and the undercooling ΔT_t at the transition is fairly accurately known for the various fractions[2]. As implied earlier, a consideration of the absolute value of the preexponential factors of the expressions describing the growth rate in regimes I and II leads to a 'kinetic' estimate of L at the transition. Below regime II, another regime is known in polyethylene[6] where $G_{III} \propto i$ again, but is not of primary interest here.

The importance of the concept of L is stressed again by the fact that nucleation-controlled growth in polymer crystals is observed to be lineal, i.e., the growth rate is independent of the size of the perimeter of the crystal or the overall dimension of the growth front. In the case of regime I growth, this points directly to the fact that the growth face on the crystal edge is somehow divided up in a natural way into regions of approximately constant length L. Then the mean growth rate associated with each region will be given by $G_I = b_0 i L$ with the result that the observable growth rate will be lineal in time, rather than an increasing power of time as would be the case if the active substrate length were for instance the continuously enlarging perimeter of a platelike crystal or a set of line elements of increasing length and number on the surface of an expanding sphere.

ESTIMATE OF SUBSTRATE LENGTH L IN POLYETHYLENE FRACTIONS

First we will give a brief outline of the framework of surface nucleation controlled growth as it applied to lamellar polymers in such a manner as to bring out the relationship between L, the absolute growth rate, and the regime I$\rightarrow$II transition.

The surface nucleation rate in stems s^{-1} cm^{-1} is given by

$$i \equiv S_T/L = S_T/n_s a_0 \qquad (1)$$

where S_T, the total flux across the barrier system shown in *Figure 1*, is given by[2,6,7]

$$S_T = \frac{1}{l_u} \int_{2\sigma_e/(\Delta f)}^{\infty} [N_0 A_0 (A-B)/(A-B+B_1)]\mathrm{d}l \qquad (2)$$

where l is the thickness of the lamella. The quantity n_s is the number of stems of width a_0 that comprise the substrate L, so that $L = n_s a_0$ as shown in equation (1). The symbol N_0 represents the number of reacting species and we assume that it is proportional to n_s as

$$N_0 = C_0 n_s \qquad (3)$$

where C_0 is a numerical constant that controls the absolute growth rate. This constant can be determined experimentally, and plays a significant role in defining the magnitude of L in one of the two methods that will be given.

In the above expressions the elementary process rate constants are[2,6,8]

$$A_0 = \beta_g \exp[-2b_0\sigma l/kT] \qquad (4)$$

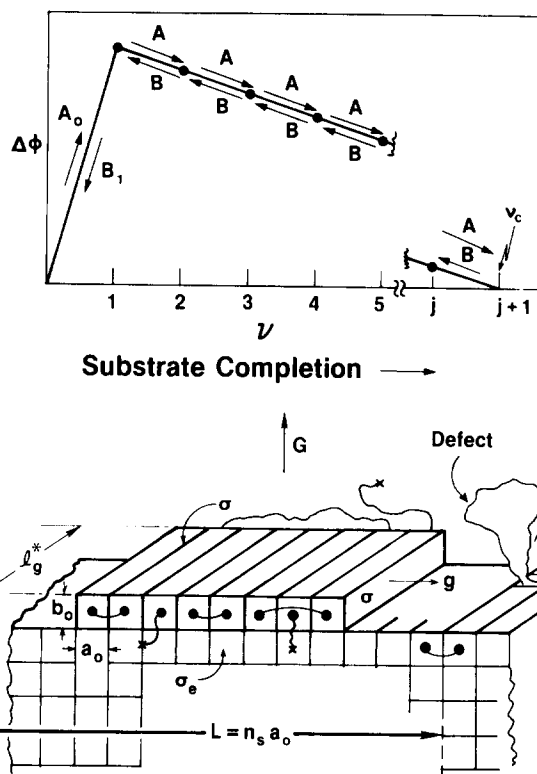$$B_1 = \beta_g \exp[-a_0 b_0 l(\Delta f)/kT] \qquad (5)$$

Figure 1 Surface nucleation processes in a chain-folded lamellar polymer. The lower diagram illustrates schematically one type of surface defect that could block substrate completion ('omega' defect). The basic molecular morphology depicted here (in highly schematic fashion) is deliberately invested with some non-adjacent re-entry events to show that it is of the 'variable cluster' type

for the forward and backward reactions, respectively, for the first ($v = 1$) stem, and

$$A = \beta_g \exp[-q/kT] \qquad (6)$$

$$B = \beta_g \exp[-a_0 b_0 l(\Delta f)/kT] \qquad (7)$$

for the forward and backward reactions in each step of the substrate completion process ($v \geqslant 2$). The rate constants given refer to the case[7] $\psi = 0$, which is entirely adequate for the development to follow. The quantity l_u is the length of the chain unit, and σ_e is the fold surface free energy $q/2a_0 b_0$ where q is the work of chain folding, and $a_0 b_0$ the cross-sectional area of the chain. The driving force for crystallization Δf is given to a sufficient approximation by

$$\Delta f = (\Delta h_f)(\Delta T)/T_m \qquad (8)$$

where Δh_f is the heat of fusion (commonly given in erg cm^{-3}), and ΔT the undercooling $T_m - T$. The lower limit of integration in equation (2) corresponds to the thinnest possible lamella[2,6,7].

The force of crystallization acts to reel the molecules onto the substrate[2], and this is opposed by the friction coefficient associated with reptation in the melt as represented by the retardation factor β_g. This applies of course only to a molecule that has not simultaneously nucleated in two or more places, either on the same lamella or another—such doubly nucleated molecules cannot be reeled onto the crystal, except for small clusters deriving from 'slack', and lead to the amorphous component[6]. Based on previous work[2], we give two alternative expressions for β_g. The first is a modified Eyring expression

$$\beta_g = (\kappa/n)(kT/h)\exp(-Q_R^*/RT) \qquad (9)$$

where κ is a numerical constant to be determined by experiment and n the number of units in the polymer chain. (In treating the data, we use $n = n_z$ where n_z is the 'z' average chain length[2].) The alternative, derived from a consideration of the friction coefficient associated with reptation in the melt, is[2]

$$\beta_g = \{(kT/n\xi_0 a_0 b_0)\exp[Q_R^*/RT_0]\}\exp(-Q_R^*/RT) \quad (10)$$

where Q_R^* is the activation energy for reptation, ξ_0 the friction coefficient per chain unit for reptation, and T_0 a reference temperature that for polyethylene we shall set at the regime I→regime II transition temperature, which is 129.0°C or 402.2 K in the high molecular weight limit[2]. The activation energy for reptation is of course the same as that of centre-of-mass diffusion, and this is known to be close to 23 kJ mol^{-1} (or 5500 cal mol^{-1}) for long n-hydrocarbons[9]. The friction coefficient $\xi_0 = 3.56 \times 10^{-10}$ erg s cm^{-2} (3.5×10^{-13} J s m^{-2}) is known from centre-of-mass diffusion data by a method given by DiMarzio *et al.*[10], and outlined in a recent paper[2].

It will prove to be advantageous in what follows to use equation (9) with the κ implied by equation (10). With κ independently determined, the way is open to estimate L from growth rate data. It is seen that equations (9) and (10) are equivalent when

$$\kappa = (h/\xi_0 a_0 b_0)\exp(Q_R^*/RT_0) = 9.60 \qquad (11)$$

where in calculating κ we have set $a_0 b_0 = 18.9 \times 10^{-16}$ cm^2. This method of determining κ, which greatly facilitates the estimation of L by a straightforward procedure to be illustrated shortly, was not used previously mostly because a Q_R^* value that was somewhat too high was employed that gave an unacceptably high κ. The value of κ given by equation (11) is well within the range of expectation[2].

In what follows we shall give experimental values relevant to polyethylene for quantities of interest. Most of these are from ref. 2 as revised according to an analysis with $Q_R^* = 5500$ cal mole^{-1} (23 kJ mol^{-1}) rather than $Q_R^* \simeq 7000$ cal mole^{-1} (29.3 kJ mol^{-1}). In expressions where the undercooling is involved, the numerical values given all refer to the case where the undercooling is measured from $T_m^\circ(\infty) = 418.7$ K = 145.5°C. (In dealing with fractions of moderate molecular weight, the melting point T_m° was corrected downward from $T_m^\circ(\infty)$ by appropriate procedures[2].) The question of what occurs when a different $T_m^\circ(\infty)$ is assumed will be dealt with subsequently.

The growth rate in regime I is defined as $G_I \equiv b_0 i L$ and with the above developments leads to[2,4,6,7]

$$G_I = (C_I/n)\exp(-Q_R^*)RT)\exp[-K_{g(I)}/T(\Delta T)] \quad (12a)$$

where

$$C_I = \kappa b_0(kT/h)p_i C_0 n_s = 9.24 \times 10^{12} \text{ cm s}^{-1} \text{ (experimental)}$$
$$(12b)$$

$$p_i = \frac{1}{l_u}\left[\frac{kT}{2b_0\sigma} - \frac{kT}{2b_0\sigma + a_0 b_0(\Delta f)}\right] = 0.760 \text{ at } 402.2 \text{ K}$$
$$(12c)$$

and

$$K_{g(I)} = 4b_0\sigma\sigma_e T_m/(\Delta h_f)k$$
$$= 1.910 \times 10^5 \text{ deg}^2 \text{ (experimental)}$$

C_I and $K_{g(i)}$ are values obtained directly from the experiments for the case where $Q^* = 5500$ cal mole^{-1} is used in the analysis. In the above, σ is the lateral surface free energy, which has a value close to 12.0 erg cm^{-2} for polyethylene. This value of σ is based on the fact that $\sigma\sigma_e \simeq 1063$ erg^2 cm^{-4} as estimated from experimental data giving $K_{g(I)} = 1.910 \times 10^5$ deg^2, which with $\sigma_e \simeq 90$ erg cm^{-2} (0.090 J m^{-2}) gives the value of σ just cited. In earlier work[2] only the first term in the brackets in equation (12c) was used in calculating p_i, and this led to some error in one of the methods employed to estimate L.

Observe that the only quantity in the above expressions that is related to L, namely n_s in $n_s \equiv L/a_0$, is in the preexponential factor C_I. The value of C_I is known experimentally, but C_0 in equation (12b) must be determined or eliminated with the help of an additional expression to find $n_s = L/a_0$. The necessary relation is found in C_{II}, the preexponential for the growth rate G_{II} in regime II. This is developed below.

The quantity G_{II} is defined as $b_0(2ig)^{1/2}$ where g is the substrate completion rate. The latter is given by[2,6]

$$g \equiv a_0(A - B) = a_0\beta_g f\exp(-q/kT) \qquad (13a)$$

where

$$f = 1 - \exp[-a_0 b_0\delta(\Delta f)/kT]$$
$$= 1 - \exp[-a_0(\Delta f)/\sigma] = 0.341 \text{ at } 402.2 \text{ K}$$
$$(13b)$$

In the above expressions δ is the extra length $kT/b_0\sigma$ that adds to the classical value $l^* = 2\sigma_e/(\Delta f)$ in defining the initial lamellar thickness l_g^*. This is required so that the substrate completion process $v \geqslant 2$ represented in *Figure 1* can take place with the formation of a stable surface patch; it is readily seen from equation (13) that the case $\delta = 0$, which corresponds to the 'classical' approach, allows no substrate completion whatsoever. It is the feature of $\delta > 0$ that, among others, sets the treatment outlined above apart from classical nucleation theory. Theories with $\delta = 0$ are fundamentally incorrect when applied to lamellar systems because they do not permit substrate completion[2,6,11].

It follows from the above that

$$G_{II} = (C_{II}/n)\exp(-Q_R^*/RT)\exp[-K_{g(II)}/T(\Delta T)] \quad (14a)$$

where

$$C_{II} = \kappa b_0(kT/h)(2p_i f)^{1/2}C_0^{1/2}\exp(-q/2kT)$$
$$= 5.20 \times 10^6 \text{ cm s}^{-1} \text{ (experimental)} \qquad (14b)$$

and

$$K_{g(II)} = 2b_0\sigma\sigma_e T_m/(\Delta h_f)k = 0.955 \times 10^5 \text{ deg}^2 \text{ (experimental)}$$
$$(14c)$$

The numerical values given above for $K_{g(I)}$, $K_{g(II)}$, C_I and C_{II} were obtained for the polyethylene fractions from plots

of the type shown schematically in *Figure 2* for the case $T_m^\circ(\infty) = 145.5°C$. The condition $K_{g(I)} = 2K_{g(II)}$ was imposed, which the experimental data[2] show is an excellent approximation for $T_m^\circ(\infty)$ values in the vicinity of 144 to 145°C. Also, Q_R^* was set at 5500 cal mole^{-1}.

From the pre-exponential factors in equations (12b) and (14b) one thus finds

$$n_s = 2\kappa b_0 (kT/h)(C_I/C_{II}^2) f \exp(-q/kT) \qquad (15)$$

$$= 1690$$

Values of κ, C_I and C_{II} have already been given. The work of chain folding q is taken as ~ 4900 cal mole^{-1} (20.5 kJ mol^{-1}), which through $\sigma_e = q/2a_0b_0$ corresponds to $\sigma_e = 90$ erg cm^{-2}. The temperature T is set at 402.2 K, which is the observed regime I→II transition temperature in the high molecular weight limit. The numerical value of f in equation (13) was calculated with $\sigma = 12.0$ erg cm^{-1} (0.012 J m^{-2}), $\Delta h_f = 2.8 \times 10^9$ erg cm^{-3} (2.8×10^8 J m^{-3}) and $\Delta T = T_m^\circ(\infty) - T_t = 418.7 - 402.2 = 16.5°C$. (The value $\Delta T_t = 16.5°C$ holds for all the fractions within $\pm 0.4°C$ even though T_m° falls with decreasing
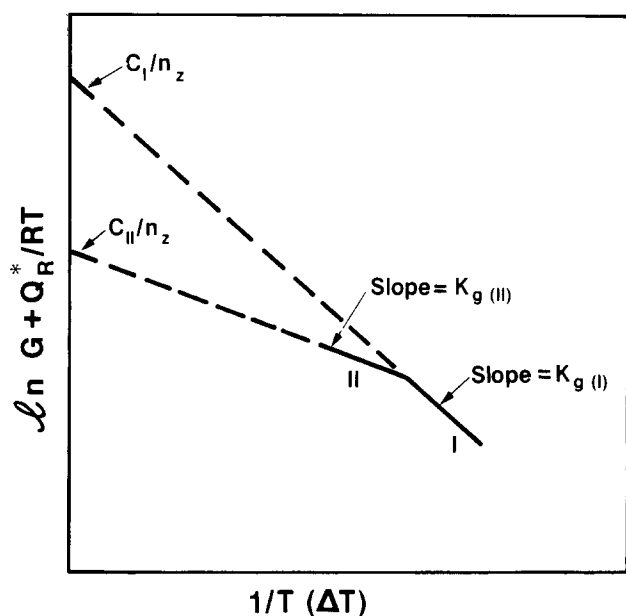

Figure 2 Plot illustrating method of determining slopes $K_{g(I)}$ and $K_{g(II)}$ and preexponential factors C_I and C_{II} for polyethylene fractions (schematic). Solid lines represent region where data are available. Regime II→III transition not shown

molecular weight[2].) Thus we find the value of n_s cited in equation (15) for polyethylene fractions $M_t = 26\,500$ to $M_t = 203\,600$ at the transition temperature.

With $a_0 = 4.55 \times 10^{-8}$ cm, the value of n_s given corresponds to $L = n_s a_0 = 0.77\ \mu m$. This is in reasonable accord with earlier estimates of[2] $\sim 0.6\ \mu m$ and[8] $\sim 0.5\ \mu m$ that were however considerably less certain because κ was not as closely bounded as it is in the present case. The new value $L \sim 0.77\ \mu m$ supersedes these estimates, as well as one of[2] $0.11\ \mu m$, and a preliminary estimate of[1] ~ 5 to $10\ \mu m$ (see later).

In what follows concerning the Lauritzen 'Z' method[4] of estimating L, we shall need a value of C_0. From the foregoing it is easily derived that

$$C_0 = C_{II}^2 \exp(q/kT)/(2p_i f)[\kappa b_0(kT/h)]^2 = 2.15 \times 10^3 (16)$$

In previous work we employed a constant equivalent to C_0 that was designated[2] '$\bar{z}C_nP_0$' that took on a value of $\sim 1.5 \times 10^4$. The present treatment is considerably more precise with regard to the value of this constant.

The effect of changes of the assumed equilibrium melting point $T_m^\circ(\infty)$ of polyethylene in the high molecular weight limit is shown in *Table 1*. With the C_I, C_{II} and K_g values shown for each assumed $T_m^\circ(\infty)$, the experimental growth rates in each regime are accurately reproduced. The principal change from earlier work is in C_I and C_{II}, which are both lower because the data fit was carried out with $Q_R^* = 5500$ cal mole^{-1} rather than $Q_R^* = 7000$ cal mole^{-1}. The growth rates G_I and G_{II} are equal at ΔT_t, and have the correct slopes on either side of T_t. The absolute growth rate at ΔT_t in all cases is $3.0 \times 10^{-5}\ n_z^{-1}$, which is the experimentally observed value in cm s^{-1} at the transition for all of the fractions. For the range of $T_m^\circ(\infty)$ commonly quoted[12] for polyethylene, which is $145.5 \pm 1°C$, C_0 varies from 5.55×10^2 to 9.82×10^3. Observe that L is very nearly invariant with changes in the assumed $T_m^\circ(\infty)$. A value of $T_m^\circ(\infty)$ in the vicinity of 142°C or slightly less has sometimes been suggested for polyethylene[13]; this leads to $C_0 \sim 50$ and $\sigma\sigma_e \simeq 700$ erg^2 cm^{-4} (7×10^{-4} J^2 m^{-4}), but does not change L or any essential physical interpretation in the present paper.

Another method of estimating n_s and thus L is afforded by a consideration of the 'Z' test given by Lauritzen[4]. If the dimensionless quantity

$$Z = iL^2/4g = in_s^2 a_0^2/4g \qquad (17)$$

is unity or larger, multiple nucleation occurs on the

Table 1 Estimates of C_0, n_s and L for polyethylene fractions[a]

| Assumed $T_m^\circ(\infty)$ (°C) | Input data | | | | | Results | | | | |
	ΔT_t (°C)	$K_{g(I)}$ (deg$^2 \times 10^{-5}$)	$K_{g(II)}$ (deg$^2 \times 10^{-5}$)	$\sigma\sigma_e$ (erg^2 cm^{-4})	σ (erg cm^{-4})	C_I (cm s^{-1})	C_{II} (cm s^{-1})	C_0	n_s	L (μm)
146.5	17.5	2.132	1.066	1186	13.2	4.18×10^{13}	1.11×10^7	9.82×10^3	1678	0.76
145.5	16.5	1.910	0.955	1063	11.8	9.24×10^{12}	5.20×10^6	2.15×10^3	1690	0.77
145.0	16.0	1.800	0.900	1010	11.2	4.11×10^{12}	3.47×10^6	9.60×10^2	1689	0.77
144.5	15.5	1.700	0.855	952	10.8	2.38×10^{12}	2.64×10^6	5.55×10^2	1689	0.77
144.0	15.0	1.602	0.801	897	10.0	9.96×10^{11}	1.71×10^6	2.33×10^2	1685	0.77

[a] All K_g and C_I and C_{II} values based on analysis of data with $Q_R^* = 5500$ cal mole^{-1}. L is calculated $n_s a_0$ with $a_0 = 4.55 \times 10^{-8}$ cm, then converted to μm. The experimental ΔT_t values are accurate to $\sim \pm 0.4°C$ and for a given $T_m^\circ(\infty)$ apply to all five fractions, which ranged from $M_t = 2.65 \times 10^4$ to $M_z = 2.03 \times 10^5$ in molecular weight ($n_z = 1900$ to 14 450). The preferred equilibrium melting temperature is $145.5 \pm 1°C$. The value of σ is calculated from $\sigma\sigma_e$ using $\sigma_e = 90$ erg cm^{-2}

substrate, and the system is in regime II, and $G_{II} \propto i^{1/2}$. If Z is 0.1 or less, the system crystallizes in regime I where one nucleus completes the substrate, and $G_{I} \propto i$. Because i has such a strong variation with undercooling, Z changes from 0.1 to 1 over a short temperature range, thus explaining the relative abruptness of the regime I→II transition. The critical value of Z, denoted Z_c, where the transition occurs, is 0.5. From the above we find

$$n_s = 2Z_c^{1/2}(g/i)^{1/2}/a_0 \qquad (18)$$

With $\quad i = (C_0 p_i \beta_g/a_0)\exp[-K_{g(II)}/T(\Delta T)] \quad$ and $g = a_0 \beta_g f e^{-q/kT}$ this gives

$$n_s = 2Z_c^{1/2}(f/p_i)^{1/2}C_0^{-1/2}\exp(-q/2kT\exp[K_{g(II)}/T(\Delta T_i)]$$

$$= 2394\,Z_c^{1/2} \simeq 1693 \qquad (19)$$

This corresponds to $L = 0.77\ \mu m$. Identical values of n_s are found for all the different assumed values of $T_m^\circ(\infty)$. A plot of Z as a function of ΔT for various values of L is shown in *Figure 3*. This illustrates the abruptness of the regime I→II transition, and shows how the transition temperature T_t increases as L increases.

Thus, by two different though not totally independent routes we arrive at the conclusion that the substrate length in polyethylene is close to $0.77\ \mu m$. It is this apparently spontaneous break-up or confinement of the growth front that requires a physical explanation.

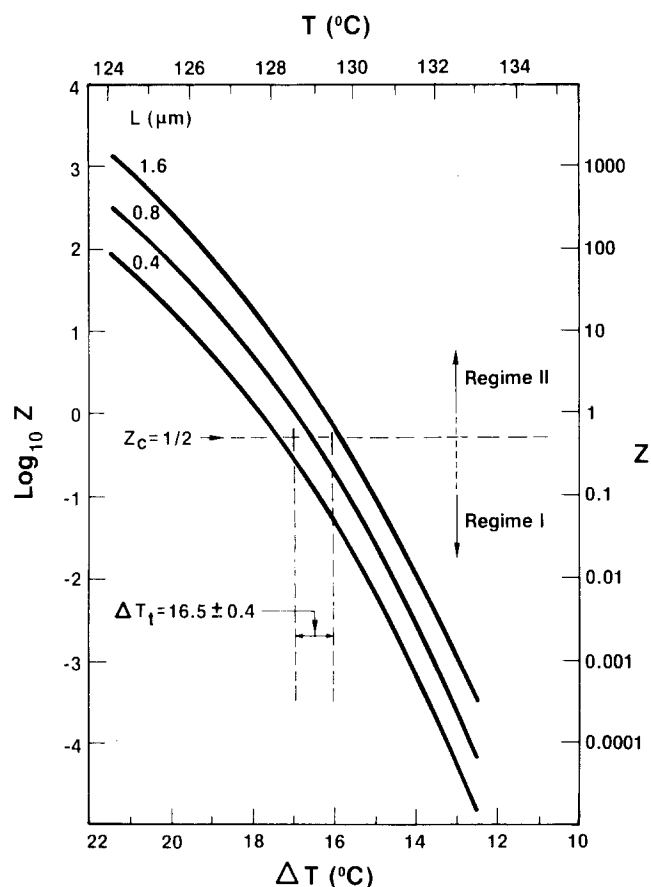Though it is parenthetical to the main discussion, it is

T (°C)

Figure 3 Lauritzen 'Z' plot for polyethylene. $T_m^\circ(\infty)$ set at 145.5°C = 418.7K in calculating ΔT_t. The temperature scale at the top of the graph applies only to a high molecular weight fraction whose melting point is near $T_m(\infty)$; the ΔT scale at the bottom refers to $T_m^\circ - T$ and is valid for all fractions. See text for details

worth pointing out that the value of L and C_0 arrived at here for polyethylene permits a closer calibration of the numerical constants that should be used in employing the Lauritzen 'Z' test to determine which regime is present in polymer crystallization. From the current work we find for polyethylene

$$Z \simeq 1.2 \times 10^3 (L/a_0)^2 e^{q/kT} e^{-X \cdot T(\Delta T)} \qquad (20)$$

where X is the trial value of K_g. The factor 1.2×10^3 is $p_i C_0/4f$. In our first work[1] on the subject, the value of C_0 was not known and the pre-exponential factor was given as ~ 40 rather than 1.2×10^3. Though this did not lead to an erroneous identification of the regimes involved, it did lead to an estimate of L for polyethylene of ~ 5 to $10\ \mu m$, which was too large by a factor of about ten. The estimate of L given in the present paper is substantially more accurate. Equation (20) is recommended on a trial basis for the Lauritzen 'Z' test for regime determination and estimates of L in other polymers. (See later for application to poly(L-lactic acid).)

The value of n_s or L calculated by the procedures given above depends on the work of chain folding q. In the first (equation (15)), it depends on $\exp(-q/kT)$ and in the second, (equation (19)), it depends on $\exp(-q/2kT)$. If an error of 10% in q is assumed, the error in L in the first case would be a factor of 1.85, and 1.36 in the second. We feel confident that $L = 0.77\ \mu m$ is correct to within a factor of about two or less.

It is evident that ΔT_t is not strongly dependent on molecular weight. There is a small variability in ΔT_t from one molecular weight to another, and in duplicate runs on the same sample, that comes to ± 0.4°C in the average value[2] $\Delta T_t = 16.5$°C. The error in ΔT_t in the various fractions is random, and does not reflect any clear trend in L with molecular weight. The experimental error in ΔT_t could obscure a molecular weight dependence of L as strong as $n^{\pm 1/2}$, but not as large as $n^{\pm 1}$, as may be judged by a consideration of *Figure 3*. The value of L deduced earlier and in *Table 1* is best regarded as an average for all specimens where n_z varied from 1900 to 14450, the logarithmic mean being $\bar{n}_z = 5250$. If there is a molecular weight dependence of L, it will have to be determined experimentally by some method other than that outlined here. To this we must add that the same is true of any dependence on T or ΔT that L may have; the methods for determining L given here provide an estimate of this quantity only at ΔT_t.

LOWER BOUND OF L

It is useful to define a lower bound for L that is predicated by surface nucleation theory. The value of L in a temperature range where crystallization occurs cannot be less than the length of a stable surface nucleus. We shall calculate this length in terms of v, the number of stems on the substrate. A critical number of stems, denoted v_c, is required before the surface patch enters the stable (i.e., negative) region (*Figure 1*).

The free energy of formation of a surface patch of a chain-folded lamellar crystal is

$$\Delta\phi_v = 2b_0\sigma l - a_0 b_0 l(\Delta f) + (v-1)a_0 b_0[2\sigma_e - l(\Delta f)] \quad (21)$$

This expression is consistent with the rate constants given in equations (4)–(7). Setting $\Delta\phi_v$ equal to zero gives

$$v_c = 2(a_0\sigma_e - \sigma l)/a_0[2\sigma_e - l(\Delta f)]] \qquad (22)$$

In lamellar crystallization, the long polymer molecule chooses its own stem length which according to nucleation theory is[7,11,14]

$$\langle l \rangle = l_g^* = 2\sigma_e/(\Delta f) + \delta \qquad (23)$$

where to a first approximation that is sufficient for the purpose at hand

$$\delta \simeq kT/b_0\sigma \qquad (24)$$

Inserting equation (23) into equation (22) yields

$$v_c = \frac{4\sigma\sigma_e}{(\Delta f)^2} \cdot \frac{1}{a_0\delta} - \frac{2}{(\Delta f)}\left[\frac{\sigma_e}{\delta} - \frac{\sigma}{a_0}\right] \qquad (25)$$

Using values of σ, σ_e and Δh_f quoted elsewhere in this article, v_c can be calculated at various undercoolings. In the range where crystal growth rates have been measured for polyethylene fractions ($T_x \simeq 123°C$ to $130.3°C$), v_c is much less than the estimates given earlier for n_s. In this temperature range v_c varies from ~ 30 to 75, while the best estimate of n_s, which is known experimentally only at $\Delta T_t = 16.5$ or $\sim 128.5°C$, is ca. 1690. (More exact expressions for δ are known[7,14], and lead to somewhat smaller values of v_c.) This finding reassures us on an important point; namely, there is in the present application no internal contradiction in surface nucleation theory in that the substrate $L = n_s a_0$ is easily large enough in the temperature range mentioned to sustain numerous stable surface patches as is required in regime II. An additional point is that one readily sees in equation (25) again that theories with $\delta = 0$ are inadmissable.

SUMMARY OF INFORMATION CONCERNING KINETIC VALUE OF L AND REGIME I→II TRANSITIONS IN POLYETHYLENE

Below we summarize what is known concerning the 'kinetic' substrate length L and regime I→II transitions in polyethylene. This forms a useful prelude to the discussion to follow. Unless otherwise noted, all comments refer to crystallization of polyethylene from the melt. Brief mention is made of a I→II transition that was found in poly(L-lactic acid).

(1) Within the context of currently known concepts, the existence of regime I→II transitions requires that L exist as a real physical phenomenon. This point is emphasized again by the fact that lineal growth is observed in regime I. The latter could not occur unless some physical agency divided up the growth front into units of mean length L.

(2) The magnitude of L in polyethylene appears to be within a factor of about two of 0.77 μm at the regime I→II transition. This corresponds to roughly 1700 or so stems.

(3) In the temperature range where crystallization rates can be measured in polyethylene, L is much larger than a just stable surface nucleus.

(4) The regime I→II transition occurs in the range $\Delta T \simeq 16.5 \pm 0.4°C$ for fractions $n_z = 1900$ to $n_z = 14540$ for $T_m^\circ(\infty) = 145.5°C$. From this it is inferred that L does not depend on molecular weight any more strongly than $n^{\pm 1/2}$.

(5) In fractions, the regime transition is quite distinct, but it is diffuse in specimens with a broad distribution[1].

(6) So far as if known, regime I→II transitions occur only in lamellar chain-folded polymers, and then only

rarely. Specifically, they have been found in polyethylene[1], and a poly(L-lactic acid) fraction[15] crystallized from the melt. The rarity of I→II transitions is probably partly connected with the fact that they naturally occur most clearly only in fractions, and then only at high temperatures where crystal growth rates are normally exceedingly slow and therefore inconvenient to measure. In high molecular weight fractions, the distinct I→II transition appears to be replaced by regime II[15] or 'mixed' I and II[2] behaviour.

(7) The temperature dependence of L, if any, is not known from kinetic experiments—L is known from such experiments only at the regime I→II transition. It is worth noting, however, that a regime I→II transition of the sharpness observed experimentally in melt-crystallized fractions is consistent not only with a constant L, but also with one that varies as say $L \propto \Delta T$ or $1/\Delta T$. This is readily deduced from *Figure 3*. The sharpness of the transition is mainly a result of the enormous change of the nucleation rate i with undercooling, and is not dependent on L being absolutely constant with undercooling.

(8) There is no compelling evidence that a regime I→II transition occurs in the crystallization of chain-folded polyethylene single crystals from dilute solution, though circumstantial evidence has been presented suggesting a rather gradual I→II transition[16]. The presence of a diffuse I→II transition is supported to an extent by the slightly convex upward shape of the $\ln G$ versus $1/T(\Delta T)$ plots and the reasonable values of $\sigma\sigma_e$ obtained by assuming 'mixed' regime I and II in the analysis of the growth data on the fractions[16].

DISCUSSION

The chief conclusions concerning the magnitude and known behaviour of L as derived from growth kinetics have already been given, and need not be repeated. It remains to discuss what relationship L has, if any, with morphological features observed in melt-crystallized polyethylene, and what physical phenomenon might cause the growth front to break up into sections of mean length L. We shall also comment briefly on the absolute value of C_0, application of the approach presented here to poly(L-lactic acid), and the validity of the nucleation model of lamellar growth as it is supported by the presence of regimes I, II and III.

Bassett, Hodge and Olley have recently summarized their work on the morphology of melt-crystallized polyethylene fractions[17]. In quenched specimens, they find by electron microscopy a lamellar width of ~ 0.7 to 1 μm. We would note here that quenched specimens have a tendency to crystallize in the lower part of regime II or just in fregime III[6], which is in the region of 115 to 120°C. It is in such quenched specimens that one might expect the observed lamellar width to most closely approach the characteristic length associated with the growth front. We observe that the lamellar width quoted above that was observed directly by electron microscopy is quite close to the value of $L \simeq 0.77$ μm that we have found here by strictly kinetic methods. Our kinetic determination of L refers to a growth temperature that is in the range of $\sim 126°C$ to 129°C, depending on the molecular weight of the fraction. While the similarity of the observed lamellar width in quenched specimens and the kinetic value of L for melt-crystallized polyethylene may be adventitious, it is nevertheless worthy of note. We mention further in this

connection that evidence of the presence of 110 facets on the order 1 μm in length has been found by Keller and Sawada[18] in degradation fragments derived from melt-crystallized polyethylene (both quenched and isothermally grown at 129°C). As the authors suggest, these quite possibly represent growth tips, and we note the similarity of the dimensions found in their experiments to the kinetic estimate of $L \sim 0.77$ μm given in the present work. In any event, it strikes us as reasonable that the 'persistence length' L determined from kinetic data, which is clearly a property associated with the growth front, should have some morphological manifestation. Here we have suggested that the most likely connection is with the initial width of the lamellar growth tip.

Bassett *et al.* have shown that the matured lamellar width in polyethylene fractions appears to slowly increase with increasing crystallization temperature[17,19]. Their work also suggests, though again there is considerable scatter, that the matured lamellar width is smaller the higher the molecular weight. As implied earlier, the matured lamellar width probably does not closely reflect the characteristic length associated with the growth tip (except perhaps in quenched specimens) and we therefore do not suggest that L should necessarily exhibit the variations with temperature and molecular weight cited above for the overall lamellar width. If there is a correlation between L and a morphological feature, it is likely, as implied above, that L will be associated with the nature of the initial width of the growth tip. This highlights the fact that direct measurements of the dimensions of the actual growth tip, though difficult for a melt-crystallized system, would be worth considerable effort. Meanwhile, it is obvious that it would be advantageous to develop an understanding of the physical origin of L of sufficient validity to permit the construction of a theory of its behaviour.

Some years ago, Keith and Padden showed conclusively that short chain species are excluded during the lamellar crystallization process and congregate at the growth front and at the lamellar surfaces and edges[20,21]. Even though the presence of such short chain material was deliberately minimized by prior precipitation from dilute solution[1] in the polyethylene fractions used here to estimate L, it is quite certain that some shorter chain 'impurities' were present in the final melt-crystallized samples, and that segregation therefore occurred. Keith and Padden originally suggested on the basis of thin film studies that under certain conditions the diffusion coefficient of the rejected species D, in combination with the lamellar growth rate G, defined a linear dimension D/G that was of the order of magnitude of the lamellar width. Following this, one might be tempted to construct a theory for L beginning with this concept. However, the current view of Keith and Padden is that in a spherulitic bulk system that D/G refers to a dimension of the system other than the lamellar width[22]. In summary, segregation certainly occurs in the crystallization of fractions, but it is now thought that D/G does not predict the width of the lamellae or the growth tip. Accordingly, we do not at this juncture attempt to extend the D/G concept to explain the origin of L, but shall instead seek an alternative type of approach.

One rather general proposition immediately presents itself as a possible origin for L. It could be assumed that L represents the mean distance between defects on the

substrate that are capable of interrupting substrate completion. While a number of types of 'blocking' defects can be envisioned, the following will serve as an illustration. The defect might be a quasi-random coil amorphous structure, which in its most extended form resembles the Greek letter Ω. This is shown schematically in *Figure 1*. In its normal state, the amorphous defect would resemble a hemisphere or disc on the substrate. Such an amorphous defect that was pinned on the substrate for at least a time could be of either equilibrium or kinetic origin, and if large enough, would for its lifetime be able to block substrate completion. In fact, the defect need only cover a portion of a stem on the surface of length δ as given by equation (24) to strongly inhibit substrate completion. It is now widely understood that some 'mistakes', such as non-adjacent re-entries, are formed in the kinetic process of putting down the substrate, especially in melt crystallization where the resulting loop contributes significantly to the amorphous phase[6,23-26]. The 'omega' defect mentioned above could form as another type of 'mistake' by double nucleation of a chain on the same niche. Alternatively (or in addition) such a defect could form as part of an equilibrium surface roughness effect, for instance by drawing in a pendant cilium. The free energy of formation of an 'omega' defect from a pendant cilium, loose non-adjacent loop, or interlamellar link is not large since little or no new amorphous chain need be generated, and very little new 'σ' surface need be exposed. In this model, the I→II effect would not appear if the lifetime of the defect was too short or if chain stiffness impeded its formation. This implies that the appearance of a I→II transition may be somewhat unusual. This and related topics will be discussed in a subsequent paper.

The quantities $N_0 = C_0 n_s$ and C_0, which control the absolute growth rates in regimes I and II, respectively, are of interest. The actual value and possible physical origin of n_s has in effect already been discussed above in the comments on L, since this quantity is given by $a_0 n_s$. This focuses attention on C_0, which is seen in *Table 1* to have a value ranging from $\sim 2.3 \times 10^2$ to 9.8×10^3 depending on the assumed value of $T_m^\circ(\infty)$. One simple explanation of the general magnitude of C_0 is to assume that N_0 represents the number of $-CH_2-$ units on the active surface in regime I multiplied by a coordination number C_n. This leads to the proposition that $N_0 = C_0 n_s \simeq C_n \bar{z} n_s$, i.e.,

$$C_0 \simeq C_n \bar{z} \qquad (27)$$

where $\bar{z}$ is l_g^*/l_u, the number of $-CH_2-$ units in a single stem of length l_g^*. At the regime I→II transition, $\bar{z} \simeq 157$, which with C_n assumed to be 6 leads to the estimate $C_0 \sim 10^3$. This is satisfactory in that it falls approximately in the mid-range of the C_0 values in *Table 1*, for $T_m^\circ(\infty) = 145.5 \pm 1$°C and eliminates the need to introduce a configurational path degeneracy[2] P_0, but still suffers from the somewhat arbitrary value of C_n. Nevertheless, equation (27) appears to give the correct order of magnitude for C_0. A refinement of this estimate would be most useful.

A comparison of L for polyethylene with that for another polymer is only possible for poly(L-lactic acid). With equation (20), the values of the 'kinetic' L quoted by Vasanthakumari and Pennings[15] are revised downward to ~ 0.25 μm, which is satisfactory. All other quantities

given by them, such as K_g, σ and σ_e, together with the basic interpretation, remain unchanged.

We close by observing that the presence of regime transitions in polyethylene fractions crystallized from the melt provides strong support of a general character for the surface nucleation model proposed elsewhere for all regimes[2,6,7] and outlined in some detail for regimes I and II in the first part of this work. The occurrence of the regime I→II transitions in the polyethylene fractions on a consistent basis, and the fact that the growth in regime I is lineal, points straightaway to the existence of a substrate length L, which has been shown here to be *ca.* 0.77 μm. Also the fact that the experimentally observed change in the nucleation exponent K_g at the I→II transition is very close to a factor of two is consistent with the theory, which states that $G_I \propto i$ and $G_{II} \propto i^{1/2}$. It is important to note that these results clearly imply that there is in these two regimes a substrate completion process that takes place at a rate g after the initial nucleation act that consists of stems filling in the niches. (There is no requirement that the chain folding in substrate completion be fully regular, though it is certain that very considerable adjacent and very near adjacent re-entry must occur to prevent a density paradox at the lamellar surface[3,6,23-26].) The same surface nucleation model that leads to the I→II transition when substrate-stopping entities are active demands the occurrence of a regime II→III transition at a crystallization temperature below the I→II transition. The II→III transition occurs when the surface nucleation rate becomes so high that the spacing ('niche separation') between the various multiple nuclei characteristic of regime II attains its minimal value[6]. Then the filling in of the rough and niche-laden substrate is actually largely effected by the surface nucleation acts themselves so that $G_{III} \propto i$, with the result that substrate completion at a rate g in the sense applicable in regimes I and II is no longer pertinent to the overall kinetics; in the lower portion of regime II and in regime III the regularity of the chain folding will be near a minimum, and will conform to the 'variable cluster' model of molecular morphology[6]. The clear-cut occurrence of the II→III transition in polyethylene[6,27], poly(oxymethylene)[6,28], i-polypropylene[29], poly-D-(-)3-hydroxybutyrate[30] and poly(*p*-phenylene sulphide)[31] thus lends credence to the general nature of the surface nucleation and growth process that has been proposed, including the proposition that substrate completion in regime II (and regime I if it is present) takes place after the initial nucleation act largely by the addition of stems to niches. (We mention this latter point because it has in one instance been doubted that niches are probable sites for addition of stems[13]). If alternative overall models

of lamellar growth in melt-crystallized polyethylene are proposed, they must be consistent with (or predict) the I→II and II→III rate transitions, since these are unmistakeably exhibited by the experimental data.

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