polymer papers

Theory of the substrate length in polymer crystallization: Surface roughening as an inhibitor for substrate completion

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A model is proposed for the physical origin of the substrate length L that appears in the customary treatment of the regime I→II growth rate transitions which occur in certain polymers during crystallization from the melt. (A previous analysis of growth rate measurements showed that $L \approx 0.77$ μm at the I→II transition in polyethylene). L is treated as a 'persistence length' between defects that have the capacity to inhibit substrate completion. The defects are pictured as resembling the Greek letter Ω (omega) in their most extended state; in their normal state they are represented as hemispherical or disc-like amorphous patches that are pinned onto the substrate. The omega defect can form on the substrate by drawing in a portion of one of the cilia, loose loops, or interlamellar links that are characteristic of the 'variable cluster' representation of the molecular morphology of lamellar semicrystalline polymers. The formulation relates L to the equilibrium free energy of formation of the omega defect, which is viewed as being principally entropic. Thus we derive $L \propto$(stem width)$\times \exp(-\Delta S/R)$. From the known value of L for polyethylene, it is determined that the experimental entropy of formation of the defect is $\Delta S_{\mathrm{expt.}} = -12.6 \pm 1.5$ cal mole^{-1} deg^{-1}. This is justified on basic grounds by first applying nucleation theory to estimate the number of chain units n_Ω in the defect of critical size. Then from partition functions for once- and twice-pinned polymer chains on a surface, which gives $\Delta S = -fR \ln n_\Omega$ with $f \sim 2.0$ to 2.5 depending on defect shape, one arrives at a theoretical estimate of ΔS for the omega defect in polyethylene that is in good agreement with the experimental value. This indicates that the omega defect model for L is reasonable on energetic grounds. It is shown further that the model is consistent in a number of respects with what is known about the I→II transition and L. Criteria for the occurrence of I→II transitions are presented, and the range of validity of the theory is discussed. It is noted that the I→II transition may be diffuse or absent in many cases, either because the equilibrium distribution is not attained or because the lifetime of the defects is too short in comparison with the residence time. Thus in many polymers, regime I may be missing so that regime II (with its locally rough growth front) will persist up to quite high temperatures, i.e., up to the practical limit of slow growth.

(Keywords: polymer crystallization; substrate length; regime I; regime II; regime III; omega defect; surface roughening; chain-folding; 'variable cluster' model; polyethylene; poly(L-lactic acid))

INTRODUCTION

Experimental growth rate studies have revealed the unmistakable presence of regime I→II growth rate transitions in polyethylene fractions crystallized from the melt in the lamellar chain-folded mode[1-4]. At this transition, the slope of the growth rate *versus* temperature curve falls off with descending temperature, leading to a definite break in the slope of the curve at a temperature T_t. The undercooling at which this occurs in polyethylene fractions is $\Delta T_t = 16.5 \pm 0.4$°C[2,4]. The regime I→II effect described here cannot be understood within the context of currently known concepts without the introduction of a substrate length, L, that has a fixed mean value in the vicinity of the transition. In the high temperature region, regime I, the growth rate is given by[5-7] $G_{\mathrm{I}} = b_0 iL$, where b_0 is the layer thickness, i the surface nucleation rate, and L the kinetic substrate length. Thus, in regime I, each primary surface nucleation act causes a layer of thickness b_0 and length L to add to the growth front, so that lineal growth results because of the fixed L. The value of L in regime I cannot for instance correspond to the increasing perimeter of a crystal since this would lead at a fixed temperature in this regime to a growth rate that increased with time; such non-linear growth is not observed experimentally. Below T_t, i.e., in regime II, multiple nucleation occurs on the substrate, and the growth rate is independent of L, naturally lineal in time, and proportional[5,6] to $i^{1/2}$ as in $G_{\mathrm{II}} = b_0(2ig)^{1/2}$. Here g is the substrate completion rate. The main purpose of this paper is to suggest a possible physical origin for the substrate length, L. The importance of the question of the origin of L was recently pointed out by Frank[8].

The substrate length, L, has a profound effect on the shape of the growth rate curves as a function of crystallization temperature and undercooling. The general expression for the growth rate in regime I, which is valid at $T \geqslant T_t$, is[2,3]

$$G_{\mathrm{I}} \equiv b_0 iL = (C_{\mathrm{I}}/n)\exp(-Q^*/RT)\exp[-K_{g(\mathrm{I})}/T(\Delta T)] \quad (1)$$

where the pre-exponential factor, C_{I}, contains L, and for the lower temperature regime II the result, valid at $T \leqslant T_t$, is[2,3]

$$G_{\mathrm{II}} \equiv b_0(2ig)^{1/2} = (C_{\mathrm{II}}/n)\exp(-Q^*/RT)\exp[-K_{g(\mathrm{II})}/T(\Delta T)] \quad (2)$$

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in which C_{II} does not contain L, and where $K_{g(\mathrm{I})}=2K_{g(\mathrm{II})}$. Thus, because $K_{g(\mathrm{I})}$ is twice $K_{g(\mathrm{II})}$, there is a relatively abrupt change in slope of a factor of two in plots of $\ln G+Q^*/RT$ *versus* $1/T(\Delta T)$ at the I→II transition. Also, the I→II transition temperature T_t is higher the larger the value of L. The nature of the change in growth rate at the regime I→II transition, which is readily observed experimentally, is shown schematically in *Figure 1*. (At still lower crystallization temperatures, regime III is entered[3], but this is not of primary interest here). In the above expressions R is the gas constant, n the number of monomer units in the dangling chain being drawn onto the substrate, Q^* the activation energy of transport (reptation) of the dangling chain, T the isothermal crystallization temperature, ΔT the undercooling, and i the surface nucleation rate, which is proportional to $\exp[-K_{g(\mathrm{I})}/T(\Delta T)]$. Explicit formulae for C_{I}, C_{II}, $K_{g(\mathrm{I})}$, and $K_{g(\mathrm{II})}$ have been given elsewhere[2-4,7,9]. In some applications, especially at low temperatures, $\exp(-Q^*/RT)$ is replaced by[7] $\exp[-U^*/R(T-T_\infty)]$. The pre-exponential constants C_{I} and C_{II} can be determined experimentally from growth rate measurements, and from these it is possible to extract a 'kinetic' value of L. In the case of polyethylene fractions crystallized from the melt, this comes to $\approx 0.77\ \mu$m within a factor of roughly two[4]. It is the physical origin and magnitude of this quantity that requires explanation.

We shall treat L as being associated with the mean distance between surface defects (in an equilibrium or quasi-equilibrium concentration) that have the capacity to interrupt substrate completion. The criterion for how large the defect must be to inhibit substrate completion is derived directly from previously established results of surface nucleation theory[7,9]. The formation of the defect, which is postulated to be amorphous in character, is treated as a type of equilibrium or quasi-equilibrium surface 'roughening' effect. For reasons to emerge shortly, we call the amorphous entity that interrupts substrate completion an 'omega' defect. This class of defect is possible only in chain systems, and will be especially prominent in lamellar chain-folded systems, which, because of their special features, provide ample opportunity for the formation of objects of the type postulated. The entropy of formation of the 'omega' defect in polyethylene will be estimated from the experimental value $L\approx 0.77\ \mu$m with the help of the treatment to be presented. This observed entropy of formation will then be shown to be reasonable in terms of the statistical mechanics of once- and twice-pinned random coils in the presence of a surface that restricts the phase space in which the portion of the chain of interest can develop its configurational entropy[10,11]. Some potentially useful predictions concerning the behaviour of L are given, and it will be shown that the theory seems consistent with what is now known about L and the regime I→II transition. It will be noted under what circumstances the I→II transition may be diffuse or absent. This involves a discussion of the relation of the time τ_d required to achieve the equilibrium 'free' defect distribution, and the lifetime τ_d^* of the 'impinged' defect that acts as a stopping agent for substrate completion to τ_s, the mean time for substrate nucleation and completion.

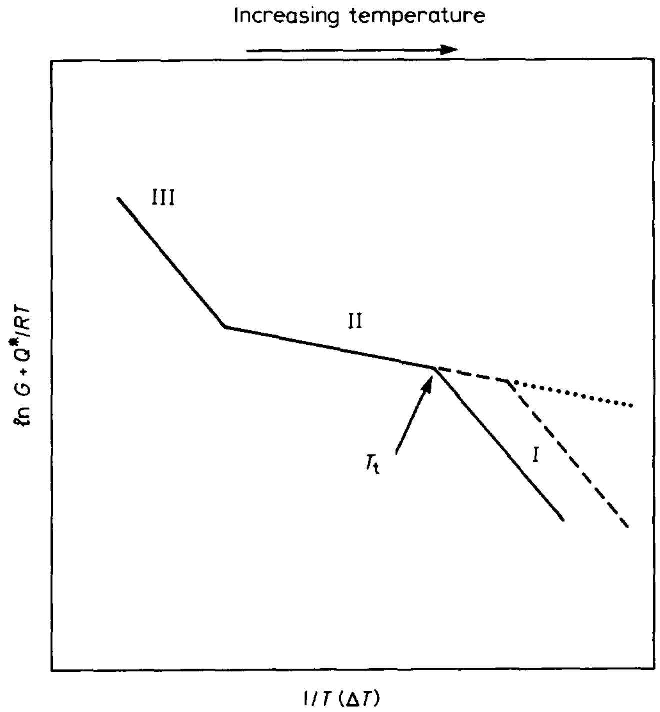

Figure 1 Regime transitions on a plot of $\log_e G+Q^*/RT$ against $1/T(\Delta T)$. (-----) shows increase of regime I→II transition temperature T_t caused by increase of L. Under certain specifiable circumstances, the I→II transition will often be diffuse or absent in which case the regime I effect is replaced by a continuation of regime II (·····) or 'mixed' I and II up to high growth temperatures (see text)

MODEL AND APPLICATION TO POLYETHYLENE

Background and model: The omega defect

We assume at the outset that in crystallization from the melt the substrate completion process can be inhibited by the occasional appearance on the surface near the lamellar edge of an amorphous structure called an 'omega' defect, which is of natural and spontaneous origin. The general nature of this defect is depicted in *Figure 2*. Below we shall formulate the probability of formation of such a defect, and show its relationship to the substrate length L.

One aspect of the 'omega' defect model depends on the irregularities in the chain-folding process in melt crystallization. Specifically, it is expected that cilia, loose loops, or interlamellar links resulting from the non-adjacent re-entry events that are characteristic of the 'variable cluster' model of chain folding[3,12,13] will provide a major source for the formation of an amorphous defect on the substrate. In its most extended state, this defect resembles the Greek letter Ω, hence the name[4]. In its normal state it is, of course, to be thought of as approximating random-coil or quasi-random-coil character. For example, an Ω defect can be formed on the substrate simply by pulling in part of a cilium (*Figure 2*, case (i)). It can regress by reversing the process. In such a situation there is no net change in the amount of amorphous material present, and no significant amount of new σ-type surface is exposed. A similar remark applies to the formation of the defect from an interlamellar link (case (ii)) or a loose loop (cases (iii) and (iv)), though in some of these instances some strain energy may be involved. In the event that the defect is formed by pulling a sharp adjacent re-entry fold into the substrate, as in case (v), *Figure 2*, considerable σ-type surface is exposed and a double row vacancy appears on the substrate; while the work of doing this is not

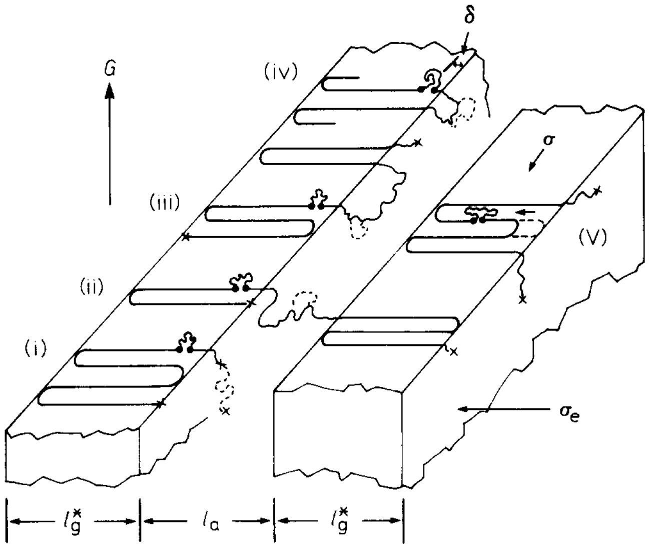

Figure 2 Structures allowing formation of omega defects in chain-folded systems. The overall scheme is based on the 'variable cluster' model[3,12,13] of molecular morphology in semicrystalline lamellar polymers. The symbol l_g^* is the initial lamellar thickness, and l_a the thickness of the amorphous phase. The amorphous and 'doubly pinned' defect forms most readily near the lamellar edge by drawing in a cilium (i), interlamellar link (ii), or loose loop (iii and iv). The width of each stem on the substrate is a_0

necessarily prohibitive, it will be shown subsequently to be substantially larger than for the others.

In the treatment that follows, we shall introduce a factor, f_a, that represents the fraction of surface stems that readily permit omega defect formation. While our results will not be highly sensitive to the estimate of f_a, it is still necessary to establish its bounds. The quantity, f_a, is essentially $1-p_{tf}$, where p_{tf} is the degree of 'tight' folding, i.e., it is equivalent to the degree of non-adjacent re-entry p_{nar}.

A 'tight' fold is simply a fold that involves proximate re-entry back into the lamella of origin *with no amorphous character in the intervening traverse*[3]. Specifically, 'tight' folds are composed of (a) strictly adjacent re-entries and (b) second- and third-nearest neighbour re-entries, all of which have no amorphous character between the point of exit and subsequent return. The 'gambler's ruin'[14] and related calculations[15] show unambiguously that

$$p_{tf} \geqslant 1-\frac{\rho_a}{\rho_c}\cdot\frac{l_b}{l_u}\cdot\frac{1}{3\cos\theta} \tag{3}$$

where ρ_a = amorphous phase density, ρ_c = crystal phase density, l_u = monomer length (1.27 Å for polyethylene), l_b = bond length (1.54 Å for polyethylene) and θ = the angle of tilt of the chains in the lamella as measured from the vertical. Equation (3) assures that no density paradox will occur at the lamellar surface, and holds for both the cubic lattice[14] and the rotational isomeric state model[15] of polyethylene and related molecules; it is valid even when an interfacial layer[16] is present. The 'gambler's ruin' results have been supported by recent calculations, and extended to include the effect of shorter chains[17].

The quantity $(\rho_a l_b/\rho_c l_u)$ in equation (3) is close to unity for polyethylene, and θ varies from 0°–34° at various places in a given lamella[18]. Accordingly the minimum value of p_{tf} ranges from ≈ 0.6 ($\theta = 34°$)–≈ 0.66 ($\theta = 0°$) for melt-crystallized polyethylene, i.e., the lamellar surface consists of well over one-half and up to two-thirds 'tight' folds depending on the local angle of tilt. We expect the minimal values of p_{tf} to hold in the present situation, which deals with melt-crystallization. Hence we estimate $f_a = p_{nar} = 1 - p_{tf}$ to be ≈ 0.33–≈ 0.4. In the calculations to follow we shall set $f_a \simeq 1/3$ for melt-crystallized polyethylene with the understanding that it may vary from ≈ 0.3–0.4 in melt-crystallized polyethylene depending on circumstances.

It is important to note that the issue here related to f_a involves the degree of 'tight' folding through the relation $f_a = 1 - p_{tf}$, and not the degree of strict adjacency. The degree of 'tight' folding is bounded with considerable precision by equation (3). This expression makes it clear that for vertical stems ($\theta = 0°$) at least two out of three of the events at the fold surface must involve a very early return to the lamella of origin with no intervening 'amorphous' loop[19]. If equation (3) is seriously violated by the assumption of too much random re-entry for a given θ, the appearance of an inadmissable density anomaly at the fold surface is a certainty on general topological grounds. (In the case of residual violations, it has been suggested by Keith and Padden that lamellar twist can result (see later)). With considerable justification, equation (3) may be regarded as a physical law (see *Footnote 1* below).

It is of interest to remark that in the case of solution-grown single crystals one must expect a higher degree of strict adjacency and tight folding than in the corresponding case of melt-crystallized polymer. Thus, for single crystals it follows that $1 - p_{tf} = f_a$ will be smaller than for melt-crystallized polymer. However, there are other important peculiarities that may affect the appearance of the regime I→II transition in the dilute solution case, and these will be brought out subsequently.

Probability of formation of omega defect of critical size and its relation to L

The equilibrium probability of formation of an omega defect of critical size may be written as

$$P_\Omega = f_a \exp(-\Delta G/RT) \tag{4}$$

where f_a is the fraction of 'active' stems on the substrate that allow ready formation of the defect, and ΔG the equilibrium free energy of formation of an omega defect of

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Footnote 1. There seems to be a convergence toward agreement on the point that for vertical stems ($\theta = 0°$) close to two out of three emergent stems must very soon return to the lamella of origin with an intervening sharp fold with no amorphous character, i.e., as a 'tight' fold, as we originally contended after arriving at equation (3)[14,15]. Counting first-, second- and third-nearest neighbour returns, Mansfield subsequently arrived at basically this same conclusion by Metropolis Monte-Carlo techniques, and also predicted theoretically for the first time the presence of a semi-ordered interfacial layer[16]. A minimum degree of 'tight' folding of two-thirds was also found by Leermakers *et al.*[17], and again directly confirming equation (3) for the case $\theta = 0°$. Still later, other investigators (see ref. 19) found for a cubic lattice with $\theta = 0°$ that $\approx 70\%$ of the chains soon returned to the lamella of origin. (These authors also found the interfacial layer.) The dependence of the degree of tight folding P_{tf} on the angle of tilt θ as given by equation (3) does not appear to be contested. Thus we deem it reasonable to regard equation (3) as an exact, or nearly exact, physical law that reflects the impact of topological constraints on the amount of non-adjacency $p_{nar} = 1 - p_{tf}$ that can be tolerated in a chain-folded lamellar system consisting of non-helical molecules. What remains at issue is the degree of strict adjacency. Here the theoretical prediction of the fraction of 'tight' folds that are strictly adjacent depends in one limit on details of the chain energetics, and in the other on the kinetics. Currently the various analyses of the experiments lead to discordant views concerning the degree of strict adjacency.

critical size. As described above, we shall use $f_a = 1/3$ in the calculations to follow. The quantity P_Ω is the probability that a stem of width a_0 will have a defect of the general type shown in *Figure 2*, cases (i) to (iv), that is large enough to interrupt substrate completion. (The criterion for establishing the critical size will be given in the next section.) It is assumed that the defect will occur most readily near a cilium, loose loop, or interlamellar link as depicted in *Figure 2*, so that P_Ω refers to a local equilibrium near the lamellar edge, and therefore does not depend on l_g^*.

It is explicitly pointed out that in writing equation (4) we assume the presence of an equilibrium distribution of omega defects of critical size near the lamellar edge, or at least a close approximation to such a distribution. There are two basic ways in which such a condition may come to exist that are consistent with the treatment. One assumption that will permit a close approach to the equilibrium distribution is to let the mean lifetime τ_d of a 'free' omega defect of critical size, i.e., one that is not in contact with the approaching new layer with which it will subsequently interact, be comparable to or somewhat less than the mean time τ_s associated with nucleation and completion of the substrate ($\tau_d \lesssim \tau_s$). (For reasons that will be brought out subsequently, one cannot use $\tau_d \ll \tau_s$.) The postulate $\tau_d \lesssim \tau_s$ in turn implies the presence of a sort of 'surface reptation' or 'inchworm' type of motion that allows the omega defect to work its way on and off the substrate when no over-layer is present. An alternative to the above is to assume that the 'kinetic' distribution of defects originally put down in the substrate completion process is similar to the equilibrium set; there is some justification for believing that this can occur under certain circumstances, as will be discussed in 'Theoretical estimates of the entropy of formation of the omega defect'. In this instance, equation (4) is approximately valid even if $\tau_d > \tau_s$. In summary, the theory to be given here for L is valid only under the assumption that either (a) the mean lifetime τ_d of the 'free' omega defect of critical size is comparable to or somewhat less than the mean time τ_s associated with nucleation and completion of the substrate ($\tau_d \lesssim \tau_s$) or (b) the 'kinetic' distribution is similar at the outset to the equilibrium one. The probable effects that will ensue if something approaching the equilibrium distribution is not attained will be noted in due course. To the above proviso that the equilibrium defect distribution shall be present must be added one of great importance that deals with the lifetime τ_d^* of the 'impinged' defects that act as stopping agents for substrate completion. This is given below.

Under the condition that the mean lifetime τ_d^* of an 'impinged' or 'stabilized' omega defect of critical size (i.e., one that is in contact with the new layer and engaged in stopping it) is considerably longer than the mean time τ_s required for substrate nucleation and completion so that $\tau_d^* \gg \tau_s$, the mean distance L between these 'stopping' defects is $L = a_0/P_\Omega$ to a good approximation. If the condition $\tau_d^* \gg \tau_s$ is not met, the substrate will overun the defects and L will become very large. (The derivation of $L = a_0/P_\Omega$ will be outlined subsequently in 'Defect lifetimes and the range of applicability of the treatment'.) Thus, under the joint restrictions that something close to the equilibrium defect distribution be present and $\tau_d^* \gg \tau_s$, we have

$$L = a_0/P_\Omega = (a_0/f_a)\exp(\Delta G/RT) \qquad (5)$$

where a_0 is the width of a single stem. Thus, the larger the free energy of formation, the more improbable the defect of critical size will be, leading in turn to a larger substrate length.

The dual provisos embodied in equation (5) (a) that the local equilibrium concentration of omega defects of critical size shall be established near the lamellar edge, which in one situation requires $\tau_d \lesssim \tau_s$ and (b) that the average value of L is given by a_0/P_Ω, which requires that $\tau_d^* \gg \tau_s$, raises the question of why and under what circumstances that the defect of critical size that has been impinged by the new layer might have a lifetime τ_d^* that is much longer than that of the 'free' or unimpinged defect. While this point will be dealt with further in 'Defect lifetimes and the range of applicability of the treatment', it suffices here to note that when the new substrate layer is in contact with a defect of critical size on the underlying layer some of the segments in the new layer will cover over the 'reptating' stem associated with the defect, thus increasing its lifetime. Alternatively, segments from the new layer could be viewed as blocking the 'inchworm' motion that allows regression of the defect, which could also greatly increase its lifetime. In any case, we see the interaction of the new substrate layer with an omega defect of critical size as creating the possibility of a long-lived 'stabilized' or 'impinged' defect of critical size such that $\tau_d^* \gg \tau_s$ even when $\tau_d \lesssim \tau_s$ for the 'free' or unimpinged defect. (In the situation where the initial 'kinetic' distribution is essentially equivalent to the equilibrium distribution, it is possible to have $\tau_d \sim \tau_d^* \gg \tau_s$ at the outset, in which case one need not invoke the stabilization-by-impingement mechanism.) As will be discussed in more detail later, the aforementioned provisos are important in determining the range of validity of the theory and the conditions under which regime I→II transitions will occur. It is of course clear that the twin conditions (a) that a fair approximation to the equilibrium defect distribution be present and (b) that the lifetime of the defect of critical size be considerably longer than the mean time required for substrate nucleation and completion ($\tau_d^* \gg \tau_s$) will not always be met. Nevertheless we shall proceed with the treatment with polyethylene in mind, since here it will emerge that the theory is successful for the case of melt-crystallized fractions $M_z \approx 2.5 \times 10^4 - \approx 2 \times 10^5$.

We now consider the case of melt-crystallized polyethylene fractions (see *Footnote 2* below). With the knowledge that $L = 0.77\ \mu\text{m} = 7.7 \times 10^{-5}$ cm at 402.2 K and $a_0 = 4.55 \times 10^{-8}$ cm for these fractions[4], and setting $f_a = 1/3$ and $T = 402.2$ K, the latter being the temperature at the regime I→II transition, one finds

$$\Delta G_{\text{expt}} = \Delta H - T\Delta S = 5063\ \text{cal mol}^{-1} \qquad (6)$$

If it is assumed that the free energy of formation is mainly entropic we have

$$L = (a_0/f_a)\exp(-\Delta S/R) \qquad (7)$$

where ΔS is the configurational entropy of formation of

Footnote 2. The data referred to here are spherulite and axialite growth rate measurements on five fractions $M_z = 26\,500–203\,600$ that all exhibited clear-cut I→II transitions at $\Delta T_t = 16.5°\text{C} \pm 0.4°\text{C}$ ($T_m(\infty) = 145.5°\text{C}$). The original data are given in ref. 1, and the best estimate of $L \simeq 0.77\ \mu\text{m}$ obtained therefrom is given in ref. 4. Fractions of higher molecular weight did not have a clear-cut I→II transition, but exhibited instead definite 'mixed' regime I and II behaviour[1].

the defect. In this case, which we consider sufficiently realistic for highly flexible chains, it is found at 402.2 K that

$$-\Delta S_{\mathrm{expt}} = 5063/402.2 = 12.6\ \mathrm{cal\,mol^{-1}\,deg^{-1}} \qquad (8)$$

to which we assign an error of $\pm 1.5\ \mathrm{cal\,mol^{-1}\,deg^{-1}}$ to account for the uncertainty in L.

The entropy of the system is lower after the omega defect has formed, so $\exp(-\Delta S/R)$ is a positive number greater than unity. Henceforth we shall use equation (7) in the analysis, i.e., it will be assumed that ΔG is principally entropic.

Critical size of defect as calculated from surface nucleation theory

We now wish to establish the size of the omega defect of critical size. This is readily done with the help of results of surface nucleation theory.

In chain-folded crystallization the initial lamellar thickness l_g^* is determined by the flux $S(l)$ across the barrier corresponding to the successive acts of primary nucleation and substrate completion. Thus[7,9]

$$l_g^* = \frac{1}{l_u}\int_{2\sigma_e/(\Delta f)}^{\infty} lS(l)\mathrm{d}l \Big/ \frac{1}{l_u}\int_{2\sigma_e/(\Delta f)}^{\infty} S(l)\mathrm{d}l \qquad (9a)$$

$$= 2\sigma_e/(\Delta f) + \delta$$

$$= 2\sigma_e T_m/(\Delta h_f)(\Delta T) + \delta$$

where to an approximation sufficient for illustrative purposes[7,9] (see *Footnote 3* below)

$$\delta \simeq kT/b_0\sigma \qquad (9b)$$

In the above expressions, k is Boltzmann's constant, l_u the length of a monomer unit, σ_e the fold surface free energy, σ the lateral surface free energy, and Δf the thermodynamic driving force for crystallization, $\Delta h_f(\Delta T)/T_m$, where Δh_f is the heat of fusion, ΔT the undercooling, and T_m the equilibrium melting temperature appropriate to the molecular weight under consideration. Results based on more exact expressions for δ will be discussed later.

The lower integration limit of $l = 2\sigma_e/(\Delta f)$ in equation (9) corresponds to the lamellar thickness of a crystal that is just on the borderline of metastability and instability, i.e., an infinitesimal decrease in thickness would cause it to melt[7]. A lamella of this thickness cannot accomplish substrate completion. However one of thickness $l_g^* = 2\sigma_e/(\Delta f) + \delta$ has the correct mean rate of passage over the barrier including substrate completion, and after passage over the nucleation barrier it achieves thermodynamic stability[4,7,9]. It follows that if an amorphous and inherently uncrystallizable patch of diameter δ as given by equation (9b) occurs on the substrate (see *Figure 3*) the substrate completion will be interrupted for the lifetime of the defect (see *Footnote 4*).

It is possible to show in a more explicit way that the substrate stopping effect of the amorphous omega defect is related to the δ of nucleation theory. The substrate completion rate, g, for a substrate with stems of normal length $l_g^* = 2\sigma_e/(\Delta f) + \delta$ is readily shown to be proportional to[4]

$$e^{-q/kT}\left\{1 - e^{-a_0 b_0 \delta(\Delta f)/kT}\right\} \qquad (10)$$

where q is the work of chain folding. Now in the immediate vicinity of the defect of critical size that covers the length δ on the substrate, there will be a few stems in the new layer whose length is close or equal to $2\sigma_e/(\Delta f)$, so that $\delta \approx 0$ for these stems. From equation (10), this gives $g \approx 0$ in the vicinity of the defect of critical size. This minimal requirement for the cessation of growth of the new layer could be strengthened by multiplying δ in equations (11) and (12) to be given shortly by a factor γ that is slightly greater than unity. This will lead to a considerable row of stems near the defect shorter than $2\sigma_e/(\Delta f)$ where $\delta \leqslant 0$, which leads to a minimum in a plot[4] of $\Delta\phi$ *versus* v at the defect corresponding to $L = a_0 v$, and which thereby ensures that substrate completion has an even higher probability than before of being interrupted by the defect. (v is the number of stems on the substrate.) We have felt it unnecessary to introduce $\gamma > 1$ in a preliminary treatment, other than to mention it. It is possible to suggest other mechanisms by which an omega defect could cause cessation of substrate growth, e.g., a build-up of strain energy resulting from distortions in the stems in the new layer in contact with the defect, but the one given above involving δ seems most appropriate in the present situation. This permits us, after the selection of a suitable geometry, to estimate the number of chain units involved in the omega defect of critical size. Below we utilize two different geometries to arrive at this estimate.

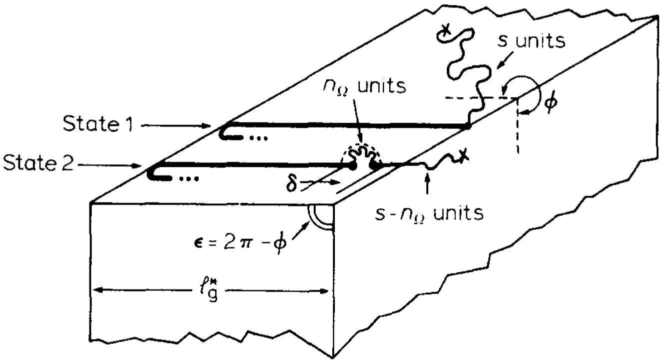

Figure 3 Model for calculating partition functions for an emergent cilium and an omega defect leading to theoretical estimate of net entropy of formation of the defect. The omega defect shown is formed from part of an emergent cilium (state 1) by drawing n_Ω units from it on to the substrate (state 2). The defect can also be generated from an interlamellar link or loose loop (not shown). The defect of critical size covers a length δ of a stem on the substrate

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Footnote 3. Somewhat more accurate formulae for δ that include the effect of undercooling are given in refs. 7 and 9. At $\Delta T_t = 16.5°\mathrm{C}$ ($T = 402.2$ K), δ ranges from 10.18 Å–12.62 Å depending on ψ, which is to be compared with $\delta = 11.14$ Å computed with equation (9). This leads to no important difference in n_Ω and the resultant ΔS. However, theories that include fluctuations of stem length about l_g^* give larger values of δ at $\Delta T = 16.5°\mathrm{C}$ than equation (9), ~20 Å being typical for $\sigma = 12\ \mathrm{erg\,cm^{-2}}$ (see ref. 20).

Footnote 4. The stems of length $2\sigma_e/(\Delta f)$ or less that are put down in the new substrate layer in the vicinity of the defect on the underlying layer are not to be regarded as having niches of the usual type that invite further deposition—the growth of the new substrate layer is in effect blocked for the lifetime of the defect of critical size.

Hemispherical defect. Here it is assumed that the amorphous omega defect at the substrate edge is hemispherical (*Figure 3*). The number of chain units required to form a hemisphere that covers a length δ of a stem on the substrate is

$$n_\Omega = (\pi/12)\delta^3/a_0b_0l_u = 15.1 \text{ –CH}_2\text{– units (hemisphere)} \qquad (11)$$

where $a_0b_0l_u$ is the volume of a $-CH_2-$ unit, which is 2.40×10^{-23} cm^3 for polyethylene. The value of δ at 402.2 K is 11.14×10^{-8} cm for polyethylene as calculated with $b_0 = 4.15\times10^{-8}$ cm and $\sigma = 12$ erg cm^{-2}. This leads to the numerical value for n_Ω given in equation (11).

Disc-shaped defect. If it is assumed that the 'amorphous' defect is rather more two-dimensional in character, and lies mostly as a flattened random walk (see *Footnote 5* below) of thickness $\sim b_0$ near the edge of the surface of the substrate, the number of chain units in the omega defect becomes

$$n_\Omega \simeq (\pi/4)\delta^2/a_0l_u = 16.9 \text{ –CH}_2\text{– units (disc)} \qquad (12)$$

where $\delta = 11.14\times10^{-8}$ cm, $a_0 = 4.55\times10^{-8}$ cm and $l_u = 1.27\times10^{-8}$ cm for polyethylene.

It is evident from the above calculations that the omega defect of critical size is rather small in polyethylene, being comprised of perhaps 15 to 17 chain units for the case where δ is given by equation (10)[20]. It is also clear that the results are not highly sensitive to the geometry of the defect. In the preliminary theoretical estimates of ΔS to follow we shall use $n_\Omega \simeq 15$.

Theoretical estimates of the entropy of formation of the omega defect

Below we give estimates of the upper and lower bounds of the entropy of formation ΔS of the omega defect of critical size. This can be done because we now have an estimate, based on nucleation theory, of the number of chain units in the defect of critical size, and also partition functions for the relevant structures through the work of DiMarzio[10] on doubly-pinned chains on a plane surface, and the work of Lauritzen and DiMarzio[11] on a cilium attached at one point to a crystal edge such that it has an angle of sweep ϕ as depicted in *Figure 3*.

We begin by considering a cilium containing s chain units attached to a lamellar edge as shown in *Figure 3*, where the sweep angle of the cilium is ϕ radians. This is state 1, and represents a cilium on the edge of the substrate as in *Figure 2*, case (i), prior to the formation of the omega defect. The partition function for this initial state (state 1) is[11]

$$Q_1 = Z^s/s^{\pi/2\phi} \qquad (13a)$$

where Z is the partition function per chain unit. Now if n_Ω chain units are pulled on to the surface of the substrate near the edge, the cilium is shortened to $s-n_\Omega$ units, and these n_Ω units are used to form a doubly-pinned omega structure on a plane as in state 2, *Figure 3*, the total partition function for the system (omega defect + shortened cilium), (state 2), becomes

$$Q_2 = \frac{Z^{n_\Omega}}{n_\Omega^{5/2}} \cdot \frac{Z^{s-n_\Omega}}{(s-n_\Omega)^{\pi/2\phi}} \qquad (13b)$$

Here the factor $Z^{n_\Omega}/n_\Omega^{5/2}$ is the partition function of the doubly-pinned[10] set of n_Ω units that comprise the omega defect, which is three-dimensional but confined to one side of a plane. The other factor is the partition function of the slightly shortened remanent cilium.

The net entropy of formation for the case of a very long cilium where $s \gg n_\Omega$, which represents the upper bound for ΔS, comes to (see *Footnote 6*)

$$\Delta S = R\ln(Q_2/Q_1) = -\frac{5}{2}R\ln n_\Omega = -13.5 \text{ cal mol}^{-1}\text{ deg}^{-1} \qquad (14)$$

(three-dimensional defect, long initial cilium)

for $n_\Omega = 15$. Notice that this result is independent of the sweep angle ϕ of the cilium. In the above, as we shall do henceforth, we have subtracted the entropy of the standard state $n_\Omega R\ln Z$.

The lower bound of ΔS refers to the case where the initial cilium is short, and contains just n_Ω chain units. Then the partition function for state 1 is

$$Q_1 = Z^{n_\Omega}/n_\Omega^{\pi/2\phi} \qquad (15a)$$

When this short cilium is completely pulled in to form an omega defect consisting of n_Ω units on the substrate, the partition function becomes

$$Q_2 = Z^{n_\Omega}/n_\Omega^{5/2} \qquad (15b)$$

with the result that

$$\Delta S = -\left(\frac{5}{2} - \frac{\pi}{2\phi}\right)R\ln n_\Omega \qquad (15c)$$

(three-dimensional defect, short initial cilium)

Observe that ΔS now depends on the sweep angle ϕ of the initial cilium. In the case of an angle of sweep of 270° ($\phi = 3\pi/2$), corresponding to $\varepsilon = 90°$ as defined in *Figure 3*, and using $n_\Omega = 15$ as before, we arrive at a reasonable lower bound

$$\Delta S = -\left(\frac{5}{2} - \frac{1}{3}\right)R\ln 15 = -11.7 \text{ cal mol}^{-1}\text{ deg}^{-1} \qquad (16)$$

Footnote 5. Some justification for introducing a two-dimensional model is to be found in the fact that low molecular weight species tend to be rejected at the growth front, with the result that, even for fractions, crystallization from the melt can on occasion be considered as occurring locally from something approaching a concentrated solution. In such a situation, physical adsorption of the omega loop on the substrate to a more or less flattened state is not to be omitted from consideration as a limiting case.

Footnote 6. In making these illustrative calculations of ΔS, we have omitted a factor x_0 that divides n_Ω to convert it to the correct number of statistical segments, viz, $\Delta S = fR\ln(n_\Omega/x_0)$. The quantity x_0 does *not* correspond to the number of chain units in the 'statistical segment' that is commonly employed to describe chain dimensions. In early lattice theories (e.g. Flory[20a]), x_0 is given by $(z-1)/e$, where z is the coordination number of the liquid 'lattice'. Taking $z = 4$, which seems appropriate to the n-alkane case, one gets $x_0 = 1.10$. A more detailed treatment (Gibbs–DiMarzio[20b]), which includes weighting factors E_{gauche}/kT, gives $x_0 = 0.98$ for $z = 4$, and 1.65 for $z = 6$ with $E_{gauche}/kT \approx 1$.

The corresponding calculations for the case where the cilium is replaced by a long interlamellar link, or long loop that re-enters the same lamella, are not given here. It suffices to point out that the results are similar to equation (14) above because of the overriding effect of the factor $n_\Omega^{5/2}$ in Q_2, which is associated with the 'double-pinning' effect arising from the formation of the defect on the substrate.

It follows from the foregoing that, insofar as we may regard the defect as three-dimensional and rely on equation (10) for δ to give a reasonable n_Ω by way of equation (11), the entropy of formation of an omega defect of critical size is of the form $-\Delta S = fR \ln n_\Omega$, where $n_\Omega \sim 15$ and $13/6 \leqslant f \leqslant 5/2$ or $2.166 \leqslant f \leqslant 2.500$, giving $-\Delta S$ as 11.7–13.5 cal mol^{-1} deg^{-1}. Notice that these theoretical values bracket the experimental estimate given in equation (8) of $-\Delta S_{\text{expt}} = 12.6$ cal mol^{-1} deg^{-1}. Physically, the entropy of the system is lower after the omega defect has formed, since what is done in generating it is in the main equivalent to the conversion of a set of n_Ω once-pinned units to an equal number of twice-pinned units, which significantly reduces the number of configurations.

The calculations given above are considered to be approximately valid for highly flexible chains, but deviations must be expected for chains with large inflexible sections in the repeat unit, even though flexible units permitting chain-folding are present between them (see Discussion).

From a comparison of equations (15) and (16), it is seen that omega defects will tend to form from the shorter cilia, since ΔS is slightly smaller in this instance. It is also clear from equation (15c) that if the substrate is tilted from the perpendicular to the fold plane, i.e. if ε in *Figure 3* differs from 90°, the defects formed from short cilia will tend to occur preferentially on the edge that has the smaller ϕ and thus where $\varepsilon > 90°$. An increase of ε above 90° lowers ΔS, and thereby increases the probability of defect formation; the other edge, where $\varepsilon < 90°$, will have a lower density of omega defects. In situations where $\varepsilon \neq 90°$, the larger population of defects near the edge where $\varepsilon > 90°$ will tend to control L. The dependence of ΔS on ϕ has a number of other interesting consequences, among them that crystallographically different facets can have a different value of L.

To complete the picture we observe first that the extension of nucleation theory allowing fluctuations of stem length about l_g^* given by Lauritzen and Passaglia[20] yields δ values that are somewhat larger than that given by equation (10), which leads to increased values of n_Ω by equations (11) and (12). For a σ of 12 erg cm^{-2}, δ for the fluctuation theory comes to about 20 Å $= 20 \times 10^{-8}$ cm as estimated at $\Delta T_t = 16.5$°C[20]. The resulting n_Ω values are shown in *Table 1*. Second, we note that if we use the disc-like model to calculate n_Ω, we must (at least as an approximation) calculate ΔS with a partition function for the defect on the substrate that corresponds to a doubly-pinned two-dimensional random walk on a plane that is blocked on one side. The blocking effect results from the close approach of a new layer on the substrate to the two-dimensional defect. In this case the partition function of state 2 (cilium + defect) is

$$Q_2 = \frac{Z^{n_\Omega}}{n_\Omega^2} \cdot \frac{Z^{(s-n_\Omega)}}{(s-n_\Omega)^{\pi/2\phi}} \tag{17}$$

which in the case of a long initial cilium leads to

$$\Delta S = -2R \ln n_\Omega \tag{18}$$

(two-dimensional defect, long initial cilium)

corresponding to $f = 2$.

Slightly smaller ΔS values exhibiting a dependence on ϕ of the type given in equation (15c) are obtained for the two-dimensional defect if a short initial cilium is assumed. In this situation, $\Delta S = -[2 - (\pi/2\phi)]R \ln n_\Omega$.

By taking the above factors into account, we have calculated theoretical values for the net entropy of formation of the omega defect for polyethylene for the various permutations of the models and recorded them in *Table 1*. Estimates of L derived from these ΔS values using equation (7) are also given in *Table 1*.

It is seen from *Table 1* that most of the calculations give reasonable values of ΔS that in turn lead to L values that are well within an order of magnitude of the experimentally estimated substrate length. Any value of L that is within a factor of five of 0.77 μm will predict the regime I→II transition temperature T_t to within better than 2°C with a Lauritzen 'Z' *versus* ΔT plot[4]. Only one of the choices, the hemispherical defect with the δ from fluctuation theory, seems considerably out of line with experiment, and even this is mitigated if x_0 is taken as 1.65, corresponding to $z = 6$ (see *Table 1*).

We do not at this juncture choose a specific defect geometry or method of calculating δ. Instead we note that the results given in *Table 1* are quite sufficient, as they stand, to show that under a rather broad set of conditions the omega defect is feasible from an energetic stand-point. It is evident from the calculations that, under the assumptions that the free energy of formation is principally entropic in character, local equilibrium is established, and that the 'stabilized' defect has a long lifetime, the omega defect model for the origin of L in a number of its manifestations has a reasonable claim to reality for melt-crystallized polyethylene fractions $M_z \sim 2.5 \times 10^4$ to $\sim 2 \times 10^5$.

It would appear that, under appropriate circumstances, equilibrium or quasi-equilibrium surface roughening with subsequent stabilization can in fact produce amorphous defects of sufficient size, frequency, and lifetime so as to interrupt the substrate completion process in a manner that gives rise to a persistence length of the order of the observed value of L as determined from growth rate data. The theory gives surprisingly good results even in its simplest form. In retrospect, we see that we could have taken the mean value of ΔS from equations (14) and (15), which is -12.6 cal mol^{-1} deg^{-1} based on $n_\Omega = 15$ from the simplest approximation for δ, taken f_a to be 1/3, and made the *a priori* calculation with equation (7) that L is 0.77 μm, which is identical to the experimental[4] 'kinetic' value. Undoubtedly this degree of accord between theory and experiment is partly fortuitous, but it does imply that the theory can be useful even in its simplest form. This may be a helpful guide in future applications of a preliminary character, especially in view of the fact that the calculation of δ from fluctuation theory is not a trivial pursuit. One could of course maintain that the omission of the enthalpic contribution to ΔG oversimplifies the problem, and further that there are uncertainties in δ, x_0 and the defect geometry. Despite these shortcomings, we see no compelling reason to doubt on energetic grounds our

Table 1 Comparison of experimental and theoretical entropy of formation of omega defect for polyethylene[a]

1. Hemispherical defect

Value of δ	n_Ω by equation (11)	Calculated entropy of formation[b] (3-d doubly-pinned random coil above infinite plane) $\Delta S = -fR\ln n_\Omega$	Predicted value of L by equation (7) with calc. ΔS
$\delta = kT/b_0\sigma = 11.14 \times 10^{-8}$ cm by equation (10)	15.1	-13.5 e.u. for $f=5/2$ (long cilium) -11.7 e.u. for $f=5/2-1/3$ (short cilium)	1.22 μm 0.49 μm
$\delta \simeq 20 \times 10^{-8}$ cm from fluctuation theory[20]	87.4	(-22.2 e.u.) for $f=5/2$ (long cilium)	-

2. Disc-like defect

Value of δ	n_Ω by equation (12)	Calculated entropy of formation[b] (2-d doubly-pinned random walk on plane blocked on one side) $\Delta S = -fR\ln n_\Omega$	Predicted value of L by equation (7) with calc. ΔS
$\delta = kT/b_0\sigma = 11.14 \times 10^{-8}$ cm by equation (10)	16.9	-11.2 e.u. for $f=2$ (long cilium) -9.36 e.u. for $f=2-1/3$ (short cilium)	0.38 μm 0.15 μm
$\delta \cong 20 \times 10^{-8}$ cm from fluctuation theory[20]	54.5	-15.9 e.u. for $f=2$ (long cilium) -13.2 e.u. for $f=2-1/3$ (short cilium)	4.0 μm 1.05 μm

3. Experimental values of L and ΔS

		$\Delta S_{\text{expt.}} = 12.6 \pm 1.5$ e.u.	$L_{\text{expt}} \cong 0.77\ \mu$m

[a] The notation 'e.u.' means cal mol^{-1} deg^{-1}. Results are for $T = 402.2$ K, $b_0 = 4.15 \times 10^{-8}$ cm, $\sigma = 12$ erg cm^{-2}, and $f_a = 1/3$. The value of ϕ was set at 270° for the short cilium calculations.

[b] The calculated entropy and L values are for the case $\Delta S = -fR\ln(n_\Omega/x_0)$ with $x_0 = 1$. As noted in the text, this is appropriate to the case where the coordination number z is four. In the case where z is taken to be six, $x_0 \simeq 1.65$, and the ΔS values are correspondingly reduced. This has the general effect of causing the ΔS values associated with the fluctuation theory δ to agree better than before with $\Delta S_{\text{expt.}}$; in this case ΔS(hemisphere) for $f = 5/2 - 1/3$ comes to -17.1 e.u., and ΔS(disc) is -13.9 e.u. for $f=2$ and -11.6 e.u. for $f = 2 - 1/3$.

overall conclusion that the omega defect is very likely the entity that inhibits substrate completion and creates a persistence length L in melt-crystallized polyethylene fractions.

Energetics of defects by drawing chain-folds into the surface

It remains to be shown that the free energy of formation of an omega defect that is created by pulling a sharp adjacent re-entry chain fold in toward the centre of the substrate and exposing some σ surface is quite large. This is shown as case (v) in *Figure 2*. In order to form an omega defect with n_Ω units, it is necessary in this instance to introduce what amounts to a double row vacancy on the surface of length $l_u n_\Omega/2$. The free energy required to expose the new σ surface is

$$\Delta G_{\text{surface vacancy}} = \sigma l_u n_\Omega (a_0 + b_0) \tag{19}$$

where σ is the lateral surface free energy, a_0 the stem width, and b_0 the layer thickness. With $\sigma = 12$ erg cm^{-2}, $a_0 = 4.55 = 10^{-8}$ cm, $b_0 = 4.15 \times 10^{-8}$ cm and $n_\Omega = 15$, this comes to $\sim 2.0 \times 10^{-13}$ erg per double row vacancy or 2880 cal mol^{-1}. To this free energy one must add an entropy of formation of the amorphous loop itself of $\sim 2.5\,R\ln n_\Omega$, giving at 402.2 K an estimated free energy of formation of $2880 + 402.2 \times 13.5$ or 8310 cal mol^{-1}, which is significantly larger than the observed value of ΔG_{expt} of ~ 5063 cal mol^{-1} as given by equation (6). (Considerably larger $\Delta G_{\text{surface vacancy}}$ values arise if the n_Ω from the fluctuation theory δ calculations given in *Table 1* are used in equation (19)). Thus, while the process described is not forbidden, it is clearly not favoured on energetic grounds. Similar high free energies of formation are indicated for all of the 'tight' fold structures. This supports our hypothesis that it is the 'mistakes' in the chain-folding process (i.e., cilia, loose loops and inter-lamellar links) that most readily permit the formation of the omega defect. The 'mistakes' noted are a natural part of the 'variable cluster' model of chain folding[3,12,13].

Temperature dependence of L

Starting with equation (7) and recalling that $\Delta S/R$ is of the form $-f\ln n_\Omega$, it is readily found for the n_Ω for the hemispherical model given in equation (11) that

$$L = (a_0/f_a)\exp\{f\ln[(\pi/12)(kT/b_0\sigma)^3/a_0 b_0 l_u]\} \tag{20a}$$

where f for the three-dimensional defect is between 2.1666 and 2.5000 as we have shown. By adjusting the value of f to 2.3351 to give the observed L of 0.77 μm $= 7.7 \times 10^{-5}$ cm at 402.2 K, one obtains with $f_a = 1/3$ the expression

$$L(\text{cm}) = 1.265 \times 10^{-7}\exp\{2.3351\ln[2.3209 \times 10^{-7}T^3]\} \tag{20b}$$

for melt-crystallized polyethylene fractions. The predicted variation with L is plotted in *Figure 4*, and is seen to be quite small. The disc-shaped omega defect model leads to an even smaller increase of L with rising temperature (not shown).

Defect lifetimes and the range of applicability of the treatment

Having seen that the treatment seems at least initially successful in the case of polyethylene fractions, it is instructive to examine the basis of equation (5) more carefully. This requires a derivation of $L = a_0/P_\Omega$, and a more detailed consideration of the defect lifetimes τ_d and

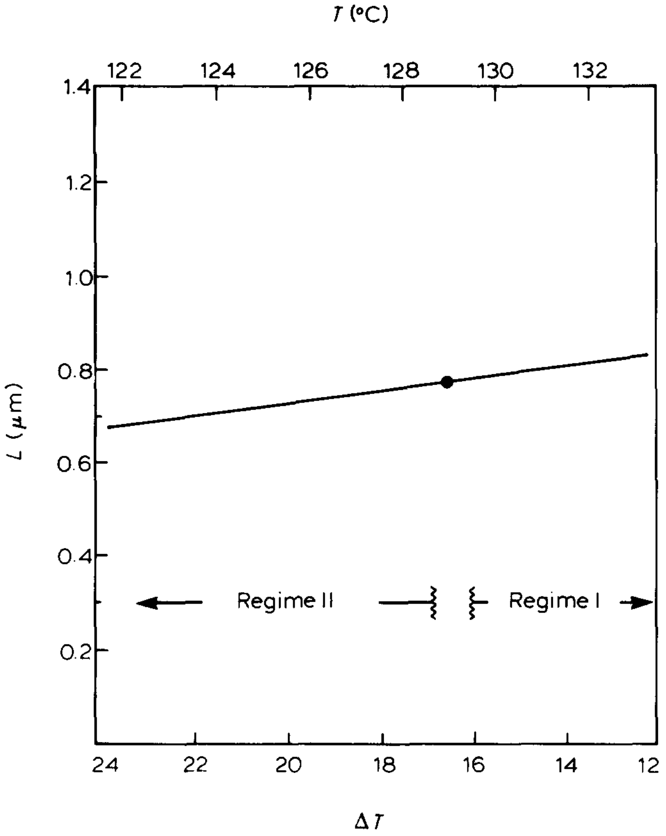

Figure 4 Substrate length L as a function of undercooling for melt-crystallized polyethylene fractions according to equation (20b). Temperature scale at top of graph applies only to high molecular weight fractions where melting point closely approaches $T_m^\circ(\infty)$. (●): is the estimated experimental value[4] of L at $\Delta T_t = 16.5°C$

τ_d^*. From this one can gain a clearer view of the range of applicability of the theory and the requirements for the appearance of a regime I→II transision.

Derivation of $L = a_0/P_\Omega$ *and the relationship to the lifetime of the 'stopping' defect.* If P_Ω is the probability of a 'stopping' defect per unit width (a_0 = unit width), the probability of a 'stopping' defect occurring and then being followed by a sequence of x stems of width a_0 with no stopping defects is $P_x = P_\Omega(1-P_\Omega)^x$. It follows that

$$\bar{x} = \frac{\sum\limits_{x=0}^{\infty} x P_\Omega (1-P_\Omega)^x}{\sum\limits_{x=0}^{\infty} P_\Omega (1-P_\Omega)^x} = \frac{1-P_\Omega}{P_\Omega} \qquad (21a)$$

which gives

$$\langle L \rangle = a_0 \bar{x} = a_0(1-P_\Omega)/P_\Omega \qquad (21b)$$

or

$$L = \langle L \rangle = a_0/P_\Omega \qquad (21c)$$

for the situation where P_Ω is much less than unity, which will always be the case in this treatment.

The above derivation of L depends specifically on the assumption that

$$\tau_d^*(\text{'stabilized' defect}) \gg \tau_s \qquad (22)$$

i.e., that the lifetime τ_d^* of the 'stopping' defect is long compared with the time τ_s required for substrate completion, or, in the more general case, the residence time of the substrate between surface nucleation acts. This is required to establish a fixed mean value of L, which is vital to the prediction of a I→II transition. If τ_d^* were comparable with or shorter than τ_s, the defects of critical size would stop substrate growth only for a short time, and the effective value of L would become very large.

The magnitude of τ_s at any temperature in regime I is in general given by the relation

$$\tau_s = 1/iL \qquad (23)$$

where i is the surface nucleation rate in stems s^{-1} cm^{-1}. The τ_s in equation (23) is actually the mean residence time of one layer of substrate of length L, and correctly includes the waiting time between surface nucleation acts; at the I→II transition temperature this expression is also equivalent to the mean substrate completion time (see *Footnote* 7 below), $L/2g$, where g is the substrate completion rate in cm s^{-1}.

It is of interest to mention the actual time scale involved. It is known[4] that at a specified undercooling i varies with $\sim M^{-1}$. A precise expression for i together with values of the relevant parameters for polyethylene have been given in a previous paper[4], and from this and equation (23) it is readily found that τ_s at the I→II transition ($T_t = 402.2$ K) is $1.385 \times 10^{-5} n$ s, where n is the number of $-CH_2-$ units in the chain. This comes to $\tau_s = 2.4 \times 10^{-2}$ s for $M = 2.5 \times 10^4$ and 0.19 s for $M = 2 \times 10^5$ (M = molecular weight). The value of τ_s rapidly becomes larger as the crystallization temperature is raised above T_t. In order for the regime I→II transition to have appeared in the polyethylene fractions, the lifetime τ_d^* of the 'impinged' or 'stabilized' omega defect that stopped the substrate completion process after a traverse of length L must have been substantially longer than the figures just quoted.

We now examine the approximate magnitude of the free energy of activation barrier W^* that is required to impede the backward reaction of the 'impinged' or 'stabilized' defect of critical size such that the condition $\tau_d^* \gg \tau_s$ will hold near the I→II transition at 402.2 K in melt-crystallized polyethylene. In what follows we assume that the 'free' defect barrier was W prior to impingement by the new layer. For purposes of illustration we adopt the 'surface reptation' model. Here some of the chain segments in the overlayer will cover the units underneath that were formerly undergoing the more rapid surface reptation process in the 'free' defect (*Figure 3*). This will tend to increase the free energy of activation of the defect regression process to W^*, since the 'reptation' is no longer taking place on a free surface. Thus we must expect $W^* > W$. Then we may write the approximate expression

$$\tau_d^*(\text{'stabilized' defect}) \simeq A n_r^* \exp(W^*/RT) \qquad (24)$$

where n_r^* is the number of chain units in the now covered or partly covered portion of stem between the edge of the

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Footnote 7. At the I→II transition, $\tau_s = 1/iL = L/2g$, which leads to $iL^2/4g = 1/2$. This is the value of the Lauritzen 'Z' parameter at the transition[4]. (Recall that the 'Z' parameter is defined[6] as $iL^2/4g$, and that regime I is in effect for $Z \leq 0.1$ and regime II for $Z \geq 1$.) The 'Z' parameter defined here is not to be confused with the partition function per chain unit employed in 'Theoretical estimates of the entropy of formation of the omega defect'.

defect and the lamellar edge. It is then found with $A = h/kT \sim 10^{-13}$ s, $n_r^* = 20$, that a W^* of 24.8 kcal mol^{-1} or larger will give a τ_d^* that is 1 min or longer, which is much greater than the longest τ_s in the transition region ($\tau_s \sim 0.19$ s). (In the above, h is Planck's constant.) Accordingly, equation (22) is satisfied under these conditions and equation (21c) thereby provides a valid definition of L. Such a free energy of activation for τ_d^* does not strike us as unreasonable for what amounts to a solid-state chain translation process, as opposed to the less encumbered surface reptation effect with barrier W operating for τ_d. (For comparison we note that the activation energy of reptation in the melt[4] is ~ 5.5 kcal mol^{-1}.) A parallel argument giving a similar W^* can be made for the 'inchworm' model of defect regression. Either way, the possibility exists that an impinged defect of critical size can in effect be 'complexed' by the overlayer and thereby stabilized. It is apparent from the experiments that the condition $\tau_d^* \gg \tau_s$ is met in the case of the melt-crystallized fractions up to $M_z \sim 2 \times 10^5$.

Attainment of the equilibrium distribution of defects. It is mentioned earlier that one of the conditions that would permit the attainment of the equilibrium distribution of omega defects of critical size is

$$\tau_d(\text{'free' defect}) \lesssim \tau_s \tag{25}$$

(Conformance with this expression is required only if the 'kinetic' distribution is not initially rather close to the equilibrium set.) By a treatment parallel to that shown in equation (24) it is readily found that τ_d is comparable with τ_s at the I→II transition for the melt-crystallized polyethylene fractions of interest when W in

$$\tau_d(\text{'free' defect}) \simeq A n_r \exp(W/RT) \tag{26}$$

is ~ 18.6 to ~ 20.2 kcal mol^{-1}. Since τ_d can be somewhat less than τ_s, we would judge that W could be as low as *circa* 16 kcal mol^{-1}, corresponding to $\tau_d \sim 10^{-3}$ s. Given the range of W values just cited, and accepting the concept that the stabilization effect subsequently gives $\tau_d^* \gg \tau_s$, it then follows that $L = a_0/P_\Omega$ is a valid approximation for the mean substrate length near the I→II transition in polyethylene. The occurrence of slow lamellar thickening near the I→II transition may be indicative that the molecular motions required to allow equation (25) to be operative in creating the equilibrium distribution are present to a sufficient degree. Observe that the stabilization effect that converts τ_d to τ_d^* on impingement involves an increase of only ~ 4.2 to 8.8 kcal mol^{-1} in W to attain the value $W^* \simeq 24.8$ kcal mol^{-1}. However, the allowable estimated range of W is still rather narrow, and in some cases it may be necessary to fall back on the concept that the 'kinetic' distribution is similar to the equilibrium one. If the latter applies, we can have $\tau_d \sim \tau_d^* \gg \tau_s$ at the outset, and there is no need to conform to equation (25) in order for P_Ω in equation (4) or the definition of L as a_0/P_Ω given in equation (21c) to be reasonable approximations.

An interesting alternative expression for the mean substrate length arises from assuming that $\tau_d \ll \tau_s$ and $\tau_d^* \gg \tau_s$. The first relation ensures an equilibrium defect distribution, and the second ensures that the defects of critical size stop substrate growth. However, in the limit $\tau_d \ll \tau_s$ where $\tau_d \rightarrow \tau_d^*$ on impingement, the relation $L = a_0/P_\Omega$ does not apply because the now very rapidly forming and regressing 'free' defects ('flickering' defects) promptly become stopping agents by the stabilization-by-impingement mechanism well before this L is attained. In this limit, the mean substrate length is given by

$$L_\tau = g\tau_d \tag{27}$$

Here g is the (free) substrate completion velocity[4]. This expression gives a value of L_τ that is considerably smaller than that observed in polyethylene, and which depends inversely on the molecular weight because g has such a dependence[4]. Since neither of these predictions corresponds to the experimental results, we have emphasized the formulation based on $L = a_0/P_\Omega$ in the body of the paper.

The foregoing brings up the question of whether in the process of substrate completion it is reasonable to suppose that the 'kinetic' distribution of omega defects can be similar to the equilibrium one. In their interesting treatment of the cilium length distribution in the substrate completion process, Sanchez and DiMarzio[21] showed that this distribution was very similar when considered from either the kinetic or equilibrium viewpoints (see Section II-B of their article). We would judge from the general nature of their argument that the same result might well hold for the rather closely related process of omega defect formation, especially at low undercoolings, i.e., high crystallization temperatures. In the discussion to follow we shall usually rely on the relationship expressed in equation (25) to ensure the presence of the equilibrium distribution of omega defects of critical size. However, we shall at the same time bear in mind that the 'kinetic' distribution may resemble the equilibrium set even at the beginning so that any molecular motions that occur on the surface allow a close approach to the required equilibrium distribution.

Effects resulting from failure to meet provisos. It is evident that one cannot always expect adherence to the provisos that (a) the equilibrium distribution of omega defects, or a good approximation to it, is present and (b) the lifetime τ_d^* of the 'stabilized' defects is considerably longer than the mean residence time of the substrate nucleation and completion process ($\tau_d^* \gg \tau_s$). Therefore it is appropriate to indicate in at least broad terms what will likely occur if these provisos are not met. This will set the stage for some of the comments to follow in the Discussion, where certain experimental results are discussed.

In the event that the equilibrium defect distribution is present but the omega defects of critical size are too short-lived so that equation (22) is not fulfilled, the mean value of 'L' will increase with time. In the limiting case, this will lead to very large effective substrate lengths that will invite copious multiple nucleation and therefore give regime II kinetics over a considerable range of temperature ((·····) *Figure 1*). In intermediate situations, one must expect 'mixed' regime I and II behaviour with no clear-cut I→II transition effect. Failure to meet the condition $\tau_d^* \gg \tau_s$ may well occur in many polymers with the result that a clear-cut regime I→II transition may not be a particularly common occurrence.

Recalling that τ_s is directly proportional to the molecular weight, it is seen that regime I→II transitions may occur at low molecular weights where $\tau_d^* \gg \tau_s$ but give way to 'mixed' I and II or regime II behaviour at higher molecular weights because of the increase in τ_s and the concommitant inability of the defects to stop substrate growth. Examples of where this may be occurring will be cited in the Discussion. Notice also that because τ_s varies as i^{-1} as in equation (23), and recalling that i falls off rapidly with increasing temperature, it is probable that the condition $\tau_d^* \gg \tau_s$ will fail at some temperature well above a regime I→II transition. This would cause a tendency for a gradual reversion to mixed regime I and II or even regime II kinetics above the I→II transition. No clear example of this is currently known, but its occurrence is to be anticipated.

If the 'kinetic' defect distribution is quite different to the equilibrium one, which is most apt to occur at low crystallization temperatures, and if the 'kinetic' distribution is 'frozen in' by an absence of the requisite molecular motions allowing formation and regression of the 'free' defects, one can expect a broad range of essentially static 'L' values. (The lack of sufficient mobility on the free surface may be signalled by the absence of any isothermal thickening.) It is to be anticipated that such a broad distribution of static 'L' values will lead at best to a diffuse regime I→II phenomenon that is in effect 'mixed' regime I and II in character. We shall shortly cite an example where this apparently occurs.

It is evident from the treatment of the relaxation time effects given above that rather special conditions must be met in order for a definite mean value of L to appear, this condition being a natural prerequisite for the occurrence of a clear-cut-regime I→II transition. The failure to fulfill the conditions $\tau_d^* \gg \tau_s$ and $\tau_d \lesssim \tau_s$ (or otherwise to have the equilibrium distribution of defects be present) will generally lead to the absence of regime I and its replacement by regime II or 'mixed' regime I and II behaviour. Nevertheless the I→II transition effect has already been observed in fractions of two polymers during melt crystallization, and it is considered reasonable to comment further on the subject in the discussion to follow.

DISCUSSION

The treatment given here traces the origin of the substrate length L back to a thermally-induced roughening of the substrate of equilibrium or quasi-equilibrium origin. This 'roughness' consists of occasional amorphous defects that inhibit substrate completion. The critical size of the amorphous omega defect that inhibits the substrate completion process is determined by surface nucleation theory, and the fraction of active stems is determined by the gambler's ruin limitation on non-adjacent re-entry. This is a very interesting case in that surface roughness inhibits rather than promotes crystallization.

The validity of the proposed model depends largely on how credibly it explains the known behaviour of L at the regime I→II transition in the first instance, and to what degree the free energy of formation of the omega defect obtained from experiment can be independently justified in the second. In the previous section it was shown under the assumption that the free energy of formation was mostly entropic in character that the energetics of the model appear to be justified by simple statistical mechanical considerations for melt-crystallized polyethylene fractions, and we accordingly need not pursue this point further. Below we concentrate on the remaining issues. A number of properties of L and the I→II transition have been noted in a previous publication[4], and we shall take these up one by one and discuss them in terms of the proposed theory. The treatment applies only when certain provisos are met, and an effort is made to highlight these, since they provide insights into the conditions under which regime I→II transitions might be either present or absent.

As pointed out previously[4], the current rarity of the observation of I→II transitions may be related partly to the fact that they evidently occur only in fractions, and then only at quite high crystallization temperatures where growth rates are often very slow and thus extremely inconvenient to measure. Subsequently we shall discuss why a relatively sharp (see *Footnote 8*) I→II growth rate transition is expected only in fractions. We shall also deal further with the circumstances under which a I→II transition might not occur even in a sharp fraction in certain cases. The effect of molecular weight is also considered, as are issues related to morphology.

The theoretical approach suggested here provides a quite general vehicle for understanding the appearance (or alternatively the failure to appear) of regime I→II transitions in melt-crystallized fractions. Three requirements are that (1) the chain be flexible enough to form a small amorphous defect at the edge of the substrate, (2) that a reasonable approximation to the equilibrium defect concentration be present prior to the formation of a new layer, and (3) that the 'impinged' or 'stabilized' defect of critical size have a long lifetime. Then a definite mean value of L can develop, leading under appropriate conditions to a I→II transition. Regime I→II transitions have been found in a number of melt-crystallized polyethylene fractions[1], and in a low molecular weight melt-crystallized fraction of poly(L-lactic acid)[22].

Chains with alternating stiff and flexible chain units. The stipulation above concerning chain flexibility requires comment. We would have reservations about applying the theory to polymers where the monomer units were long and rigid, and only the links between them flexible. It is well known that some such polymers can form chain-folded crystals because of the flexible linkages[7]. However, because of the relatively large volume per monomer unit, n_Ω by equation (11) could become so small as to be meaningless, in which case one could not assume that the free energy of formation was mainly entropic and employ expressions such as equations (14) or (16) to estimate ΔS. Actually we would expect a large enthalpic contribution to the free energy of formation of a 'stopping' defect in such a situation. Accordingly, we would anticipate quite large values of L and correspondingly small values of ΔT_t in such materials, with the result that it is probable that only regimes II and III will ordinarily be seen in them even in fractions.

Comparison of regime behaviour in melt- and solution-crystallized polyethylene. We consider now a case where clear-cut regime I→II transitions occur in crystallization from the melt at relatively high growth temperatures, but fail to appear in fractions of similar molecular weight crystallized from dilute solution at significantly lower

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Footnote 8. By 'relatively sharp' we mean that the I→II transition is essentially completed in a temperature range of about 1.5 to 2°C. This implies that the Lauritzen 'Z' parameter $iL^2/4g$ changes from 1 to 0.1 in this interval (see Figure 3 of ref. 4).

absolute growth temperatures. This occurs for polyethylene. The data for melt-crystallized polyethylene fractions strongly resembles the solid line (———) in *Figure 1*, i.e., all three regimes are clearly represented[1,3]. The failure of a definite regime to appear in the low temperature dilute solution case will be represented as a possible example of where, because of the lower temperature, the 'kinetic' defect distribution is both 'frozen in' and significantly different from the equilibrium omega defect distribution. Recall that in such a situation 'mixed' regime I and II behaviour is predicted. We mention that there is considerable evidence for the presence of some slow isothermal thickening in melt-crystallized polyethylene near the I→II transition at ~402.2 K[23-26], but no evidence for such thickening for the solution-grown crystals where the absolute growth temperature is substantially lower (typically ~360 to ~364 K for xylene; see below).

Cooper and Manley[27] have published growth rate data on polyethylene fractions crystallizing isothermally as single crystals from xylene from 86.6°C to 90.7°C or ~360 to ~364 K. With $T_d^\circ = 114.2°\mathrm{C}$, this corresponds to an undercooling range of 23.5–27.6°C. One might have expected regime II growth at this large undercooling. (Recall that T_t was ~129°C = ~402 K and $\Delta T_t \sim 16.5°\mathrm{C}$ for melt-crystallized polyethylene.) However, pure regime II growth was not found, and no clear-cut regime transition was evident. Some definite curvature appropriate to the presence of a diffuse I→II transition was clearly observed for the lower molecular weight fractions in plots of $\ln G$ *versus* $1/T(\Delta T)$; furthermore the $\sigma\sigma_e$ values obtained from the slopes of such plots for all of the fractions using 'mixed' regime I and II kinetics conformed most closely to the $\sigma\sigma_e$ from melt-crystallized fractions[27]. Because isothermal thickening is absent in single crystals at the relatively low crystallization temperatures quoted, the surface mobility is probably highly restricted, and thus not conducive to allowing changes in the defect distribution. Then if the 'kinetic' distribution corresponds to a broad range of frozen in 'L' values, we would expect no clear-cut I→II transition, and would anticipate that 'mixed' regime I and II kinetics might occur instead. This appears to correspond to the observations (see *Footnote* 9).

Attention is now directed toward a more detailed discussion of melt-crystallized polymer, with emphasis on polyethylene.

Temperature-dependence of L *and transition sharpness.* As we have shown in *Figure 4*, the variation with temperature of L for melt-crystallized polyethylene fractions is predicted to be quite small. This is important, since, assuming all other provisos are met, it permits the regime I→II transition to be relatively sharp on a plot of $\ln G + Q^*/RT$ *versus* $1/T(\Delta T)$ or as described by the Lauritzen 'Z' *versus* ΔT plot[4,6]. This accords with what is known from experiments concerning the sharpness of the I→II transition in certain melt-crystallized fractions[1,22]. There are no experimental data on the variation of L with temperature; L is known from kinetic data only at the I→II transition temperature[4]. We would note that a tendency for L to increase more rapidly with increasing crystallization temperature than is depicted in *Figure 4* may result from τ_s as given by equation (23) becoming very long owing to the higher temperature so that the new substrate layers begin to get past the defects.

Effect of molecular weight. The experimental data on polyethylene show that for five melt-crystallized fractions in the range of $M_z = 26\,500$ to $M_z = 203\,600$ ΔT_t is $16.5 \pm 0.4°\mathrm{C}$, i.e., the undercooling at which the transition occurs is not strongly dependent on molecular weight[2,4]. This in turn implies that L is not strongly dependent on molecular weight[4] in the range noted; the variation is certainly not greater than $L \propto M^{\pm 1/2}$. The theoretical treatment given here would predict a molecular weight dependence of L only insofar as f_a and ΔS in equation (17) changed with molecular weight so long as equations (22) and (25) held. We do not foresee these changes as being large in the molecular weight range indicated, so that theory appears to be consistent with experiment in regard to the approximate constancy of L with changing molecular weight in melt-crystallized polyethylene. It is evident that in the molecular weight range indicated the conditions $\tau_d^* \gg \tau_s$ and $\tau_d \lesssim \tau_s$ are met. The presence of some slow isothermal thickening is consistent with $\tau_d \lesssim \tau_s$, and it is clear from the constant value of L that 'stopping' defects where $\tau_d^* \gg \tau_s$ are very likely present.

As was remarked previously, an increase in molecular weight will cause a corresponding increase in τ_s since this quantity is proportional to M. This could lead to a failure to meet the condition $\tau_d^* \gg \tau_s$ at a certain molecular weight. In such a case, a regime I→II transition would be seen below this molecular weight, but only regime II or 'mixed' regime I and II above it. This explains why only the low molecular weight fraction of poly(L-lactic acid)[22] exhibited a I→II transition. All the higher fractions exhibited only regime II. Polyethylene fractions show a somewhat similar effect beginning at about $M_z \simeq 2 \times 10^5$. Below this molecular weight they show distinct I→II transitions but well above it they exhibit no clear-cut I→II effect but only 'mixed' I and II behaviour[1].

Absence of relatively sharp I→II transition in specimens with broad molecular weight distribution. Experimental evidence is clear on the point that the regime I→II transition in melt-crystallized polyethylene is quite distinct in the narrow fractions up to $M_z \sim 2 \times 10^5$, but very diffuse in polymer with a broad molecular weight distribution that contains considerable low molecular weight material[1]. As stated earlier, ΔT_t and thus L did not exhibit any major change in the molecular weight range $M_z = 26\,500$ to $M_z = 203\,600$[2,4]. Nothing in the theory as expressed in equation (7) suggests any major change in L down to moderately low molecular weights. Accordingly, we shall advance the principal explanation for the diffuseness of I→II transition in broad molecular weight distribution specimens in terms of an approximately constant L. The key here is that the I→II transition for fixed L occurs at a constant undercooling ΔT_t and *not* at a constant temperature; the transition temperature T_t falls with decreasing molecular weight because the corresponding T_m falls. When a whole polymer sample containing some low molecular weight material that melts well

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Footnote 9. Recent studies by S. Organ show a change of slope at $\Delta T \sim 20°\mathrm{C}$ ($T_X \simeq 114.3°\mathrm{C}$) of ~2.0 in a plot of log G *versus* $1/T(\Delta T)$ for a polyethylene fraction crystallized from a dilute solution of n-octadecane; this system has a T_d° and range of growth temperatures well above that for xylene (private communication, Prof. A. Keller, Bristol University). This effect evidently has at least the general characteristics expected for a I→II transition, and is consistent with the higher growth temperature allowing attainment of the equilibrium distribution.

below the equilibrium melting temperature $T_m^\circ(\infty)$ is isothermally crystallized, the I→II transition for the low molecular weight portion will occur at a lower T_t than for the higher molecular weight components. This will smear out the I→II transition over a range of many degrees of isothermal crystallization temperatures. Thus, the presence of low molecular weight material that melts well below the 'infinite crystal' melting point $T_m^\circ(\infty)$ is the probable major cause of the unsharp regime I→II transition in specimens with a very broad distribution of molecular weight. We remark here that the concept of segregation of molecules of different molecular weight by crystallization underlies the above explanation. The II→III transition can be rendered diffuse in broad fractions by a similar mechanism.

The above discussion makes it clear that one may expect to see definite I→II regime transitions during crystallization from the melt mainly in good fractions of flexible-chain polymers where the initial narrow molecular weight distribution is not broadened by degradation of the specimens during either the initial melting step or the long residence times that are required to obtain growth rates above T_t. Other conditions required for the existence of a stable mean value of L and thence the appearance of a I→II transition have already been mentioned, and are not repeated here.

Morphological aspects: Locally rough versus *molecularly smooth growth faces.* The concept of L is required to assure lineal growth in regime I, and to explain the presence of a distinct regime I→II transition when such transitions are seen experimentally[4]. One consequence of this is that if a relatively sharp I→II transition is seen in growth rate experiments, one must expect a molecularly flat region of approximately the length of L on the leading edge of the lamella or crystal in regime I in the immediate vicinity of the transition temperature. While it is difficult to prove smoothness on such a scale, it is of interest that in the case of degradation fragments from isothermally melt-crystallized polyethylene, Keller and Sawada[28] noticed 110 faces of $\sim 1\ \mu$m in length that appeared to be quite straight. Note also that the 110 facets were similar in magnitude to the kinetically determined value of $L \sim 0.77\ \mu$m for this polymer[4]. Meanwhile, it was shown in other work that the growth in regime I was lineal, i.e., the growth velocity was constant as a function of time and spherulite (or axialite) radius up to the point of crystal impingement[1]. In these respects, the theory of regime I growth is at least seemingly intact, and consistent with the theory of L presented here. There is no requirement of smoothness or perfectly straight edges on a molecular scale in regime II, or in regime III, where multiple nucleation occurs in each case[3]. Here a locally rough surface with lineal growth properties is predicted.

We view the situation regarding L and the nature of the growth front to be quite different in the case where the 'kinetic' distribution differs significantly from the equilibrium set, and where this broad set of 'L' values is frozen in. In such situations one cannot expect a fixed mean value of L to develop, with the result that no distinct I→II transition will appear, and 'mixed' I and II growth kinetics will likely obtain. Though the evidence is in a sense circumstantial, this appears to be the case for polyethylene crystals formed in dilute xylene solution at moderately low growth temperatures as we had noted. Concurrently, because of the presumed 'mixed' regime I and II character, we see no requirement in this situation that long and completely straight facets of length L must occur as for strict regime I crystallization, nor do we see any difficulty explaining lineal growth. In normal situations, the growth faces will have a relatively straight overall appearance, but will possess some local roughness on a molecular scale because of the regime II component. These remarks apply as well to the case where regime II or 'mixed' regime I and II behaviour is caused by the failure of the system to adhere to the conditions $\tau_d^* \gg \tau_s$ because the lifetime of the defects is too short, thus allowing 'L' to become quite large. Here again the growth face will be locally rough.

The recognition that the properties of defects, including their free energy of formation and lifetime, affects L, and thence regime behaviour, modifies the frequently propounded generalization that nucleation theory must always lead to perfectly faceted crystals in the limit of slow growth. We have mentioned at various places in this paper the basic reasons for the frequent occurrence of regime II or 'mixed' I and II growth up to high temperatures where growth is slow and τ_s very long, and further appreciate that the appearance of a regime I→II transition is probably more the exception than the rule because of the rather stringent provisos that must be met to have pure regime I occur. Accordingly, we see the possibility, within the confines of surface nucleation theory as modified by the effect of substrate-inhibiting defects with their accompanying lifetime dependent properties, of many instances of the persistence of locally rough 'facets' up to high growth temperatures that correspond at least in the practical sense to the limit of slow growth. It is only at growth temperatures *just above* an authenticated regime I→II transition (or when the Lauritzen 'Z' test clearly shows that regime I behaviour occurs) that one must expect long, straight and molecularly smooth growth facets of the order of L. At crystallization temperatures somewhat higher than the I→II transition, it is commonly to be expected that the substrate will begin to go past the defects because of their finite lifetime, with the result that regime II character with some local surface roughness will again be introduced.

Aspect ratio and regime behaviour. Passaglia and Khoury[29] have explained in terms of differing growth rates stemming from different $\sigma_{e(110)}$ and $\sigma_{e(200)}$ values the tendency for polyethylene single crystals to exhibit only $\{110\}$ type (relatively straight) faces at low solution growth temperatures, and both $\{110\}$ and $\{200\}$ type faces, also of a relatively straight character, at intermediate growth temperatures. Further, the fact that $\sigma_{e(200)} > \sigma_{e(110)}$, which gives the required faster growth on the $\{110\}$ faces, was justified on fundamental grounds. This work goes a long way toward explaining the previously puzzling b-axis orientation and the large aspect ratios found at even higher crystallization temperatures (see *Footnote 10*). It is noteworthy that their explanation

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Footnote 10. As the limit of high growth temperatures is approached, it is commonly to be expected that one type of 'facet' will grow considerably faster than the others, with the result that lath-like structures will appear. The fastest growing facet will have the lowest work of chain folding[29]. In some cases the sides of these 'laths' may be decorated with more slowly developing layers whose chain folds are parallel to the direction of maximum growth, but these may be subdued or absent if the work of chain folding q_{parallel} is too high to allow significant substrate completion (see equation (10)).

maintains its general validity quite independent of the regime assumed in the analysis. Hence the occurrence of 'mixed' regime I and II growth, if actually present for xylene solutions as we suggested earlier, would not alter their basic conclusions. We regard that it is entirely possible that, because of the presence of regime II component, the relatively straight growth faces mentioned above were not smooth on a molecular level.

SUMMARY AND CONCLUSIONS

Omega defect model for L *and the regime I→II transition.* The omega defect model, arising as it does from nucleation theory on the one hand, and simple equilibrium statistical mechanical considerations and the gambler's ruin limitation on the other, provides a plausible origin (subject to specific provisos) for the existence of a definite substrate length L that can in turn lead to a regime I→II transition in polymer crystallization with chain folding. The omega defect itself, which creates a persistence length L by inhibiting substrate completion, is formed most efficiently from structures such as cilia and loose loops that are 'mistakes' in the otherwise regular chain folding process.

In brief, the theory gives

$$L = a_0/P_\Omega = (a_0/f_a)e^{-\Delta S/R}$$

where

$$\Delta S = -fR\ln n_\Omega$$

In these expressions

L = substrate length, i.e., mean distance (persistence length) between omega defects on substrate

P_Ω = equilibrium probability of formation of omega defect for stem of width a_0

f_a = fraction of stems on substrate susceptible to ready formation of defect, i.e., fraction of non-adjacent reentries (cilia, loops, interlamellar links) characteristic of 'variable cluster' model as estimated from the 'gambler's ruin' calculation

ΔS = net entropy of formation of omega defect

f = numerical factor between about 1.667 and 2.5 that depends on shape assumed for defect and length assumed for initial cilium; the value of f can also depend on ϕ, the angle of sweep of the initial cilium, if the latter is relatively short

n_Ω = number of chain segments in omega defect of critical size, i.e., one that covers a length of stem δ on the substrate; the magnitude of δ is determined from surface nucleation theory and is $kT/b_0\sigma$ in the simplest approximation.

The theory is applicable only to cases such as melt-crystallized polyethylene fractions where there is reason to suppose that the equilibrium distribution of 'free' omega defects of critical size is present and where the lifetime of the 'impinged' defects is considerably greater (probably through the impairment by the overlayer of the defect regression process) than the residence time associated with substrate nucleation and growth ($\tau_d^* \gg \tau_s$). Here the theory seems successful even in predicting L on an *a priori* basis, the required entropy of formation being estimated by straightforward statistical mechanical procedures for a defect whose critical size was estimated from nucleation theory (*Table 1*). This is tantamount to a quite accurate prediction of the regime I→II transition temperature. The theory gives estimates of the variation of L with temperature and molecular weight, and these appear to be consistent with the limited information that is available. In particular, the predicted variation of L with temperature is small, so that the regime I→II transition can in favourable circumstances be rather sharp, as is observed in fractions of melt-crystallized polyethylene and poly(L-lactic acid). It is pointed out why a diffuse I→II transition is commonly to be expected in a specimen with a broad molecular weight distribution even when a relatively sharp transition is seen in a corresponding fraction. This accords with the observations on melt-crystallized polyethylene. The theory appears to be consistent with the rather sparse amount of information that is available concerning the dimensions and morphology of the growth tip in melt-crystallized polyethylene. It is noted that in the situation where the local equilibrium distribution of omega defects at the edge of the substrate is not attained, the I→II transition may be either absent or diffuse. This apparently occurs in the crystallization of polyethylene single crystals from dilute xylene solution at relatively low temperatures where at best only a diffuse I→II regime transition is implied by the data, and where (unlike the melt-crystallized case) the total absence of isothermal thickening implies a low mobility and the possibility of a 'frozen in' kinetic defect distribution. (In an appropriate solvent, growth occurs at higher temperatures, and the I→II transition then appears, as has been noted in footnote 9.) It is also mentioned that if the lifetime of the 'impinged' or 'stabilized' defect τ_d^* is too short relative to the residence time of the substrate, τ_s, the I→II transition will be absent and will be replaced by regime II or 'mixed' I and II behaviour (*Figure 1*). This can occur with increasing molecular weight, and explains the absence of distinct I→II transitions in the higher molecular weight fractions of poly(L-lactic acid) and polyethylene. Other conditions that must be met for a relatively sharp I→II transition to appear are that (a) the chain shall be flexible in the sense mentioned in the text and (b) the polymer must be a fraction that maintains its narrow molecular weight distribution during thermal cycling and the long residence time at the crystallization temperature.

In summary, the treatment given seems capable of explaining and organizing much of the information that is available concerning the magnitude and behaviour of the substrate length L and the corresponding regime I→II transition effect.

The regime II→III transition. It is considered useful to put the regime I→II transition in perspective with the regime II→III transition that has recently been predicted and shown to occur[3]. Because of the somewhat special conditions that are required to lead to clear-cut regime I→II transitions, one gains the impression that future investigations may reveal that they are not particularly common. The regime II→III transition effect is not encumbered by provisos of the type involving τ_d and τ_d^* in their special relation to τ_s mentioned for the I→II transition, though the II→III effect, like the I→II, will certainly be seen most clearly in fractions. The II→III effect is simply a result of the niche separation on the substrate approaching to within a factor of three or so of the molecular width a_0 because of the very high surface nucleation rate at sufficiently large undercoolings[3]. In many systems this can hardly be avoided, and the II→III transition should be observable in a fraction unless it is obscured because it occurs below the maximum in the growth rate where transport effects dominate. Thus we would anticipate that the most frequently encountered situation in the broad realm of crystallizable polymers that exhibit chain folding would correspond to a II→III transition being found in fractions well below the melting point, with regime II (or sometimes 'mixed' I and II) behaviour prevailing at all higher temperatures where growth rate measurements without degradation are feasible (see *Footnote 11* and dotted line in *Figure 1*). Thus locally rough 'facets' should be common even at the highest practicable crystallization temperatures in many polymers in contrast to the customary prediction of perfect facets. In the probably less frequent cases where the appropriate conditions are met, the I→II transition will be found above the II→III transition. Perfect facets of length L are predicted only just at or slightly above the I→II transition. With the properties of defects considered, including their equilibrium free energy of formation and lifetime, nucleation theory now deals with all these cases.

Relationship to the 'variable cluster' model. It is worth emphasizing that the present treatment of the substrate length L is based on an overall scheme of molecular morphology applicable to melt-crystallized lamellar systems with chain folding called the 'variable cluster' model[3,11,12] that has proved highly successful in a number of applications.

Some of the key features of the variable cluster model, such as a significant fraction of adjacent and near-adjacent re-entry, some non-adjacent re-entries back into the lamella of origin with an intervening random coil structure, and a few random-coil interlamellar links, are depicted in a highly schematic fashion in *Figure 2*. The degree of 'tight' folding is quite high, and conforms to equation (3); in the case of quench-crystallized polyethylene, the degree of 'tight' folding is ≈ 0.6 to ≈ 0.66, depending on the local angle of tilt. This degree of 'tight' folding is fully consistent with the well-documented existence of a definite lamellar structure. Yet because of the random coil connections between the 'tight' chain-folded clusters, an amorphous phase of thickness l_a is present, and the radius of gyration of a given chain, which participates in several clusters, averages out to a liquid-like value[13] that varies as $M^{1/2}$ (M = molecular weight). The latter is consistent with the neutron scattering results[12,31]. Thus the 'variable cluster' model combines the high degree of adjacency or very near adjacency compatible with the presence of well-defined lamellar structures on the one hand, and the presence of an amorphous phase and a liquid-like radius of gyration (see *Footnote 12*) on the other[3,12,13].

In the present paper we began with the 'variable cluster' model and exploited the 'mistakes' in the regular folding process characteristic of it to uncover the nature of the molecular situations that facilitate the formation of the omega defect. At the same time we employed the 'gambler's ruin' limitation on non-adjacent re-entry to quantify the fraction of active sites for the formation of the defect. In this sense, the present treatment is part of a larger and more comprehensive picture.

It is significant in the above connection that Keith and Padden have recently given a treatment of the origin of lamellar twist in spherulites that has a similar foundation[32]. They began with what was in essence a 'variable cluster' model for the situation where the growth front was tilted, i.e., the case $\varepsilon \neq 90°$ in *Figure 3*. They let the tilted growth front accept a few too many random coil structures preferentially on one edge, which led to a (small) violation of the 'gambler's ruin' limitation on non-adjacent re-entry that differed in intensity on the two large lamellar surfaces proper (see *Footnote 13*). This led in turn to asymmetric surface stresses that were relieved by twist. Thus the 'gambler's ruin' restriction, as expressed by equation (3), was satisfied to a sufficient degree in the twisted lamella.

Recent calculations have shown that a thin (≈ 10 Å) semi-ordered interfacial layer[16] must occur in the amorphous material just outside the fold zone in a 'variable cluster' type model. This further improves the model (without altering the deductions from equation (3) concerning the degree of 'tight' folding) and doubtless will be important in dealing with certain physical effects.

It follows from the sum of the foregoing that the 'variable cluster' model of chain folding is centrally departure for future developments concerning the prediction and understanding of the properties of lamellar semicrystalline polymers. Here we have shown that the 'variable cluster' model of chain folding is centrally important to understanding the origin and properties of the substrate length L and the corresponding regime transitions in such systems.

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Footnote 11. In a recent paper, Lovinger, Davis and Padden[30] have commented on the paucity of the number of polymers that exhibit I→II transitions. Poly(*p*-phenylene sulphide), which they studied in detail, exhibited a II→III transition but not a I→II transition. This is a rather typical result in the sense that the II→III effect is more commonly found than the I→II effect. As we have noted, polymers with long stiff segments, though flexible at the intervening joints, are not apt to be able to form omega defects, which tends to preclude a I→II transition. This is probably the cause for the absence of the I→II effect in poly(*p*-phenylene sulphide).

Footnote 12. It is an error to assume generally that a liquid-like radius of gyration in a semicrystalline lamellar system means that random re-entry prevails; as is evident from equation (3), fully random re-entry ($p_{tf}=0$) is only possible for $\theta \simeq 70°$. No polymer systems are known where such a large angle of tilt occurs, so it is clear that a random re-entry model cannot be regarded as a general description of the molecular morphology in semicrystalline lamellar polymers.

Footnote 13. The restriction on the degree of non-adjacency at the crystal edge is less stringent than that imposed by the 'gambler's ruin' expression, equation (3), which refers to the allowed degree of non-adjacency on an infinite plane[14]. Also, the prevailing degree of non-adjacency allowed at the crystal edge depends on the angle of attack. Accordingly, asymmetric surface stresses build up well behind the growth front resulting from the different degrees of excess of random coil structures on either side of the lamella.

butions, brought to light the importance of the defect lifetimes. The useful comments of Dr Peter Barham of Bristol are also acknowledged. Thanks are due to Prof Robert Zwanzig of the University of Maryland for a most helpful discussion concerning the properties of rapidly 'flickering' defects; Prof Marc Mansfield of the same university kindly provided helpful comments and review. This research was supported by grant DMR 84-03358 of the Polymers Program of the National Science Foundation.

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