Growth regimes and the time development of lateral habits in polyethylene crystals

Elio Passaglia and E. A. DiMarzio
Institute for Materials Science and Engineering, National Bureau of Standards, Gaithersburg, MD 20899, USA
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On the assumption that in regime I the growth rate of the lateral face of a lamellar crystal is proportional to the length of the face, and that in regime II the growth rate is independent of the length of the face, the time development of the size and aspect ratio of a polyethylene lamellar crystal is calculated. The aspect ratio is defined as the ratio of the length of the crystal in the ***b*** crystallographic direction to that in the ***a*** direction. It is assumed that steady state growth obtains, i.e. the solution concentration is constant. When both {110} and (200) faces are in regime I, the dimensions of the crystal increase exponentially in time, and lozenge shape (i.e. a crystal bounded by {110} faces) cannot be obtained under experimentally realizable conditions. When one of the faces is in regime I and the other in regime II, novel time dependencies of the crystal size and shape are derived, none of which has heretofore been observed. Despite the fact that the experimental conditions have never been realized in growth from solution, the now well-known fact that in regime I the growth rate is not proportional to the length of the growing face is re-established. Some new ways by which this assumption might be removed are suggested, and qualitative values for the upper bound for the 'substrate length' over which growth takes place from a nucleation event are discussed.

(Keywords: crystal growth; crystal habits; non-linear growth; lateral habits; aspect ratio)

INTRODUCTION

It is now well established that polymer crystals can grow in three regimes, generally denoted as I, II and III[1–3]. These regimes are distinguished by the dependence of the growth rate on undercooling, with the dependence in regimes I and II being equal and higher than in regime II. Briefly, in regime I the growth rate is considered to be nucleation controlled. In this regime in the idealized case, a nucleus is formed randomly at any point on the growing face and then a strip immediately grows and adds a layer on the face. In regime II, multiple nuclei are formed on the face and the growth rate is proportional to the geometric mean of the nucleation rate and the strip growth rate[4]. In regime III nucleation becomes so rapid that nuclei are formed even on partially grown strips, and hence the growth rate is again proportional to the nucleation rate. In this case the crystal–liquid interface is rough.

Perhaps the most interesting of these regimes is regime I, for in the idealized case growth would not be linear with time[1,4,5]. This comes about because the probability of forming a nucleus is proportional to the length of the lateral face of the growing crystal. The prediction of the maximum length of the face is one of the (probably improper) uses of the well known Lauritzen '*Z* test'[5]. Except possibly for the case of spherulites, where it can be argued that the length of the growing faces ({110} in polyethylene) remains constant since the lateral (200) faces do not grow or grow only very slowly because of fractionation or impurity segregation[6] or other factors, the length of the growing faces of the crystal must necessarily increase as the crystal size increases, and hence the growth rate would increase with time. This is particularly evident for monolayer crystals grown from solution when the crystal has high enough symmetry (higher than orthorhombic) so that the growing faces are crystallograpically the same. But, as will be seen below, this is also the case for polyethylene although in that case the situation is more complex, since the faces are crystallographically distinct, and need not all be in regime I.

Since linear growth is generally observed in crystals grown from solution[7–9] it has been argued that some 'persistence length' or 'nucleation length'[1,10] exists in the crystal. Once nucleation occurs, strip growth would take place only to the end of this length. It has been shown that crystals with sides longer than this length will grow linearly in time[10]. Only crystals with edges shorter than this length will show non-linear growth. Lauritzen[5] used the term 'substrate length' for this length, and we shall henceforth use the same term. There is one other situation that would ensure that the growth rate in regime I would be independent of the length of the crystal face. This would be the situation in which nucleation occurs at least preferentially at some unique position on the face of the crystal, possibly the corners. In such a situation, the rate of nucleation would clearly be independent of the length of the growth face, and hence questions of the effect of the length of the face on growth rates would be obviated. Possible mechanisms for preferential growth at the corners of crystals will be addressed in the discussion section.

To our knowledge, the only evidence that has been adduced to show that in regime I the growth rate is not proportional to the length of the lateral face is the linear growth rate. In this paper, we shall show that the time and temperature dependence of the lateral habits of polyethylene crystals provides even stronger evidence. The analysis of the temperature dependence of the lateral

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habits of such crystals has recently been shown to be a sensitive means of determining relative values of surface energies for the growing edges and of assessing various aspects of the kinetic theory of polymer crystallization[11]. In that paper it was assumed that the substrate length was not the length of the lateral face, and hence the growth rate was taken to be independent of the crystal size. In this paper we shall remove this assumption. Moreover, since in polyethylene the growing faces are crystallographically distinct, the possibility arises that one of the faces may grow in regime I and the other in regime II. We do not consider regime III, since the possibility of having one face in regime I and the other in regime III is highly unlikely. Moreover, in regime III, the growth is not dependent on the length of the crystal face. Hence, the mixed regime II–regime III case is equivalent to the previous treatment[11]. We investigate all the resultant possibilities and derive interesting, unusual, and heretofore unreported results for the time development of the lateral habits. First we present a rather formal exploration of the consequences of assuming that the substrate length is the length of the face growing in regime I. After this we discuss the possibilities of the experimental observation of the results we derive.

ANALYTICAL DEVELOPMENT

We show in *Figure 1* the *c*-axis projection of a polyethylene crystal in the form of a truncated lozenge. In polyethylene crystals, (010) faces are not seen. We assume, therefore, that if in the process of growth incipient (010) faces appear, they immediately grow out of the crystal. Clearly, in such a crystal, either the {110} or (200) faces, or both, can grown in regime I or II. Of the resulting four cases, the one in which both faces are in regime II (which is analytically the same as when both are in regime I but the growth rate is independent of their length) has been exhaustively treated previously[11]. We are therefore left with three cases to consider:

(1) Both the {110} and (200) faces are in regime I; (2) the {110} faces are in regime I and the (200) faces are in regime II; (3) the {110} faces are in regime II and the (200) are in regime I.

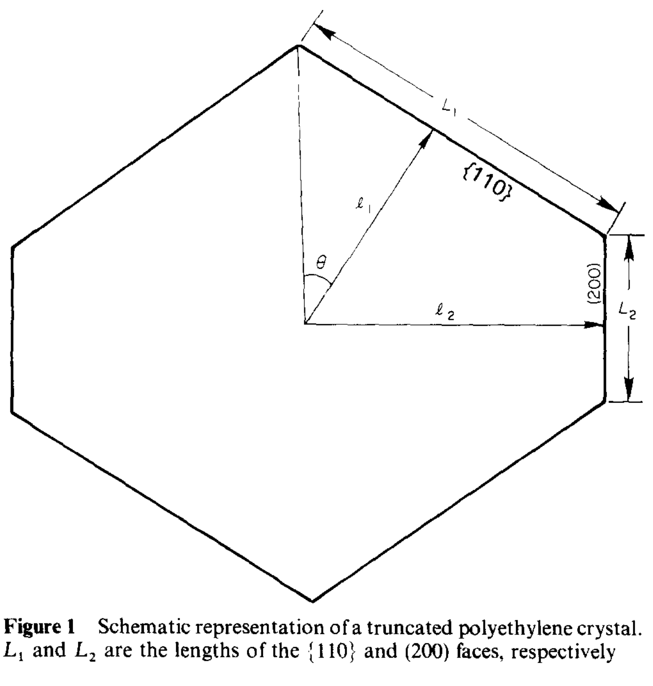

Figure 1 Schematic representation of a truncated polyethylene crystal. L_1 and L_2 are the lengths of the {110} and (200) faces, respectively

It is clear that the growth of a layer on say {110} increases the length of the adjacent (200) face by one unit and conversely. Hence, we have coupled growth rates when at least one of the faces is in regime I, which includes all of the cases considered.

From the figure, we define L_1 and L_2 to be the lengths of the {110} and (220) faces, respectively. Similarly, l_1 and l_2 are distances from the centre of the crystal to L_1 and L_2, respectively. Our main problem is to compute the time dependence of l_1 and l_2, and the aspect ratio, $\boldsymbol{r}$, which is the ratio of the length of the crystal in the ***b*** crystallographic direction to its length in the ***a*** direction[11]. This is an easily measured experimental quantity[15,16] and is a sensitive measure of the ratio of the growth rate of the {110} and (200) faces[11]. It is given by

$$r = l_1/(l_2 \cos\theta) \tag{1}$$

For the lozenge, in which $L_2 = 0$, the aspect ratio has a minimum value denoted by r_l, and is given by

$$r_l = b/a = \tan\theta \cong 0.66 \tag{2}$$

It is also clear that

$$L_1 = l_2/\cos\theta \tag{3}$$

and

$$L_2 = 2l_1/(\cos\theta - 2l_2 \tan\theta) \tag{4}$$

With these preliminaries we are ready to write the differential equations for the growth of the crystal.

Case (1), both {110} and (200) in regime I

In this case, with our assumption that the growth rate is proportional to the length of the growing face we have

$$\mathrm{d}l_1/\mathrm{d}t = L_1 G_1^{\mathrm{I}} \tag{5a}$$

$$\mathrm{d}l^2/\mathrm{d}t = L_2 G_2^{\mathrm{I}} \tag{5b}$$

in which G_1^{I} and G_2^{I} are the rate coefficients given by the kinetic theory of polymer crystallization and include all transport terms, etc.[11]. In particular, they are functions of the concentration[1,11], which we take to be constant. This will be discussed more fully in the discussion section. It is also to be noted that our rate coefficients are dimensionally different from those customarily employed in regime I, for we have specifically kept the lengths L_1 and L_2 as variables. Finally, we have allowed for the fact that the surface energies for growth along {110} and (200) may be different. It was previously shown[11] that this had to be the case in order to obtain a lozenge and the proper temperature dependence of the aspect ratio when both growing faces are in regime II or in regime I, when the growth rate is independent of the length of the growing face.

It is to be noted that equations (5) are generalizations to two dimensions of the situation that obtains in the growth of whiskers from the vapour[12–14]. In that case, the mathematical (but not physical) role of the length of the growing face is taken by the average diffusion distance of adsorbed atoms on the lateral surfaces of the whisker. For whisker lengths shorter than this length, the growth of the whisker is proportional to its length, which therefore varies exponentially with time for growth and dissolution[13,14]. For whiskers longer than this distance, the growth rate is constant, and the length increases linearly with time.

Using equations (3) and (4) we obtain

$$\frac{dl_1}{dt}=\frac{l_2G_1^{\mathrm{I}}}{\cos\theta} \tag{6}$$

$$\frac{dl_2}{dt}=\frac{2l_1G_2^{\mathrm{I}}}{\cos\theta}-\frac{2l_2G_2^{\mathrm{I}}}{\tan\theta} \tag{7}$$

These two simultaneous equations are easily solved. We obtain

$$l_1=A^+e^{\lambda^+t}+A^-e^{\lambda^-t} \tag{8}$$

and

$$l_2=\frac{2A^+G_2^{\mathrm{I}}e^{\lambda^+t}}{\alpha+\beta}+\frac{2A^-G_2^{\mathrm{I}}e^{\lambda^-t}}{\alpha-\beta} \tag{9}$$

where A^+ and A^- are constants to be determined from the initial conditions (l_1° and l_2°), λ^+ and λ^- are given by

$$\lambda^\pm=-G_2^{\mathrm{I}}\tan\theta\pm\left[(G_2^{\mathrm{I}})^2\tan^2\theta+\frac{G_1^{\mathrm{I}}G_2^{\mathrm{I}}}{\cos\theta}\right]^{1/2} \tag{10}$$

and α and β are given by

$$\alpha=G_2^{\mathrm{I}}\sin\theta \tag{11}$$

and

$$\beta=[(G_2^{\mathrm{I}})^2\sin^2\theta+2G_1^{\mathrm{I}}G_2^{\mathrm{I}}]^{1/2} \tag{12}$$

We note that λ^+ is positive and λ^- is negative, and the crystal size from equations (8) and (9) shows the expected exponential dependence on time.

It is worthwhile investigating the value of the time constants $\lambda^\pm$. Taking $G_1^{\mathrm{I}}=G_2^{\mathrm{I}}=G^{\mathrm{I}}$, which is sufficient for the present purposes, we see from equation (10) that λ^+ and λ^- are proportional to G^{I}. Now, it is notoriously difficult to calculate absolute values of the rate coefficients. However, to obtain a rough estimate of the values of $\lambda^\pm$ we have used customary expressions and values of the constants for them[1,11]. In this manner in the range of undercoolings of 20–30°C we obtain values for G^{I} of $10^{-6}\ \mathrm{s}^{-1}$ to $50\ \mathrm{s}^{-1}$, with the value depending strongly on the value of ϕ, the parameter that assigns the free energy of fusion to the forward and backward reactions[1,11,17]. The values of $\phi=1$ are approximately 10^3 times the values of $\phi=0$. Then, $\lambda^+\sim0.7G$ and $\lambda^-\sim-2G^{\mathrm{I}}$, and the negative exponential dies out at about three times the rate that the positive one grows.

In principle, we should now solve for A^+ and A^- from the initial conditions. In this case, this is not necessary for our purposes, and it is sufficient to calculate the aspect ratio $\boldsymbol{r}$ from equation (1). When the negative exponential transient has died out, we obtain

$$r=\tfrac{1}{2}[r_l+(r_l^2+2G_1^{\mathrm{I}}/G_2^{\mathrm{I}}\cos^2\theta)^{1/2}] \tag{13}$$

This is the expected result. For any given values of the rate coefficients G_1^{I} and G_2^{I}, the crystal attains a steady state shape.

The shapes, however, are not in accord with experiments. In particular, the lozenge shape $r=r_l$ is obtained only when the ratio of the growth coefficients is zero. Depending on the surfaces energies associated with G_1 and G_2 this can strictly occur only at zero undercooling or at zero temperature and hence is not possible.

The sensitivity of this result, however, needs to be checked. It was previously shown[11] that the behaviour with temperature of the ratio G_1/G_2 is critically dependent on the quantity

$$\Delta=\frac{a(\sigma\sigma_e)^{200}}{2d_{110}(\sigma\sigma_e)^{110}}-1 \tag{14}$$

where a is length of the crystallographic $\boldsymbol{a}$ axis, d_{100} is the (110) spacing, σ and σ_e are the lateral and end surface energies, respectively, and the superscripts refer to the growth face. We recall that experiments uniformly show that the aspect ratio increases as the temperature increases[11,15,16,18,19]. If $\Delta>0$, then the ratio G_1/G_2 increases with temperature (decreasing undercooling), and so does the aspect ratio calculated from equation (13). If on the other hand $\Delta<0$, then the calculated aspect ratio can decrease with temperature, contrary to all experiments. This leads to the condition that to obtain the proper temperature dependence of the axial ratio

$$\frac{(\sigma\sigma_e)^{200}}{(\sigma\sigma_e)^{110}}>\frac{2d_{110}}{a}\cong1.09 \tag{15}$$

However, even with highly unrealistic values of the ratio $(\sigma\sigma_e^{200}/(\sigma\sigma_e)^{110}$, lozenges are not obtained at any reasonable temperature from equation (1). For example, with $(\sigma\sigma_e)^{200}/(\sigma\sigma_e)^{110}=1.5$ and other parameters as used previously[11], the calculated aspect ratios at undercoolings of 20°C and 110°C are 134 and 3, respectively. With $(\sigma\sigma_e)^{200}/(\sigma\sigma_e)^{110}=1.101$, the values obtained are 1.24 and 1.14 at the same undercoolings.

Thus we conclude that both on the basis of the exponential growth and that both lozenges and the proper temperature dependence of the axial ratio cannot be obtained at attainable temperatures, the assumption that in regime I the growth rate depends upon the length of the face leads to results that are even qualitatively contrary to experiment.

We next consider the first of our mixed regime cases.

Case 2: {110} in regime I and (200) in regime II

In this particular case, the governing equations are

$$\frac{dl_1}{dt}=\frac{l_2G_1^{\mathrm{I}}}{\cos\theta} \tag{16}$$

$$\frac{dl_2}{dt}=G_2^{\mathrm{II}} \tag{17}$$

where the superscripts denote the growth regime. It should be noted that the rate coefficients are dimensionally different. These equations have the solution

$$l_1=G_1^{\mathrm{I}}G_2^{\mathrm{II}}t^2/(2\cos\theta)+G_1^{\mathrm{I}}l_2^\circ t/\cos\theta+l_1^\circ \tag{18}$$

and

$$l_2=G_2^{\mathrm{II}}t+l_2^\circ \tag{19}$$

where l_1° and l_2° are the initial lengths. It can be seen that this gives the remarkable results that l_1, or equivalently the length of the crystal in the **b** direction, increases quadratically with time. Equally remarkable is the behaviour of the aspect ratio. This is given by

$$r=\frac{G_1^{\mathrm{I}}G_2^{\mathrm{II}}t^2+2G_1^{\mathrm{I}}l_2^\circ t+2l_2^\circ\cos\theta}{2\cos^2\theta(G_2^{\mathrm{II}}t+l_2^\circ)} \qquad (20)$$

It is easy to show that the axial ratio goes through a minimum. This occurs at positive real time provided that

$$G_2^{\mathrm{II}}/G_1^{\mathrm{I}}>l_2^\circ/r_0\cos^2\theta \qquad (21)$$

where r_0 is the aspect ratio of the seed crystals. To see if this condition could be met under reasonable experimental conditions, approximate calculations were made using equal surface free energies for G_1^{I} and G_2^{II}. Since these two faces are in different growth regimes, differences in surface free energies for the two faces are relatively unimportant. Customary values of the surface free energies were used[1]. As in the previous case, the value of ϕ is very important in the results. Thus, for $\phi=0$, the values of $G_2^{\mathrm{II}}/G_1^{\mathrm{I}}$ at undercoolings of 10°C and 20°C are 15 cm and 7.8×10^{-3} cm, respectively, while for $\phi=1$, the values under the same conditions are 2×10^{-2} cm and 10^{-5} cm. (Recall that G_1^{I} has the dimensions of time^{-1}, while G_2^{II} has the dimensions of length time^{-1}.) The values for $\phi=1/2$ are intermediate. It is thus seen that the condition in equation (21) would formally apply for most initial sized crystals if $\phi=0$, but only for smaller crystals of high aspect ratio if $\phi=1$. The matter is, however, complicated by the fact that for regime II to apply, the crystal face must be larger than a minimum size[5], which implies a minimum size for the (200) face in this case. The question will be addressed more fully in the discussion section.

It is seen from equation (21) that a minimum occurs if the seed crystal is long and thin (high r_0 and low l_2°). The origin of the minimum is then easy to understand. For such a crystal, the growth rate normal to the {110} faces is small since these faces are in regime I and L_1 is small. The constant and relatively large initial growth rates of the (200) faces then causes these faces to begin to 'grow out' of the crystal, increasing the length of the {110} faces, and decreasing the value of r. After reaching a minimum value (which may be r_l), the aspect ratio begins to increase. Finally, for long times, as may be seen from equation (20), the interesting result that the aspect ratio increases linearly with time is obtained.

$$r=G_1^{\mathrm{I}}t/2\cos^2\theta \qquad (22)$$

There is one case that superficially resembles this one, and that is the case of spherulite growth. In that case, the aspect ratio of the spherulite lamellae appears to increase as the spherulite grows. However, experiments unambiguously show that the radial dimension, which is of course in the **b** direction in polyethylene, increases linearly with time, contrary to the quadratic dependence predicted in the present case. In the spherulite case, the (200) faces appear not to grow or grow only very slowly because of molecular weight fractionation[6] or steric or other factors. What this does is essentially uncouple the growth on the {110} and (200) faces, giving rise to a linear growth rate of the {110} faces and hence along the **b** direction, even though in that case growth {110} may be in regime I and the length of the growing face may be the substrate length. Indeed, inspection of equations (18) and (20) show that as G_2^{II} approaches zero, both l_1 and r become linear in time, which is the spherulite case. In solution, we know of no experiments which indicate that the **b** dimension of the crystal increases quadratically with time and the axial ratio increases linearly.

Calculations show, however, that only under very restricted conditions will the linear increase of r with time be manifested before the {110} face has grown so large that it will be in regime II. It could be observed with initial crystals of high aspect ratios at relatively high undercoolings, but these are details that will not be pursued.

Case 3: {110} in regime II and (200) in regime I

In this final case the pertinent equations are

$$\frac{\mathrm{d}l_1}{\mathrm{d}t}=G_1^{\mathrm{II}} \qquad (23)$$

and

$$\frac{\mathrm{d}l_2}{\mathrm{d}t}=\frac{2l_1G_2^{\mathrm{I}}}{\cos\theta}-2l_2G_2^{\mathrm{I}}\tan\theta \qquad (24)$$

The solutions to these are

$$l_1=G_1^{\mathrm{II}}t+l_1^\circ \qquad (25)$$

and

$$l_2=\frac{G_1^{\mathrm{II}}t}{\sin\theta}+A\exp[-2G_2^{\mathrm{I}}r_lt]+(l_1^\circ-G_1^{\mathrm{II}}/2r_lG_2^{\mathrm{I}})\sin\theta \qquad (26)$$

where l_1° and l_2° are the respective lengths of the initial seed crystal and

$$A=l_2^\circ-(l_1^\circ-G_1^{\mathrm{II}}/2r_lG_2^{\mathrm{I}})/\sin\theta \qquad (27)$$

The aspect ratio is given by

$$r=\frac{r_lG_1^{\mathrm{II}}t+r_ll_1^\circ}{Ar_l\cos\theta\exp[-2G_2^{\mathrm{I}}r_lt]+G_1^{\mathrm{II}}t+(l_1^\circ-G_1^{\mathrm{II}}/2r_lG_2^{\mathrm{I}})} \qquad (28)$$

These equations predict an interesting behaviour. It is seen from equation (25) that l_1 increases linearly with time. Equation (26) shows that after an initial exponential transient, l_2 also increases linearly with time, and from equation (28) for very long times, r approaches r_l. This occurs independently of the values of the rate coefficients and hence of the temperature of growth of the crystal, and of the initial conditions. Hence this mode of growth predicts the interesting and remarkable result that the lozenge is always the ultimate shape.

A routine but tedious investigation that will not be presented here leads to the following results:

(1) $\mathrm{d}l_2/\mathrm{d}t$ is always positive, as is, of course, $\mathrm{d}l_1/\mathrm{d}t$.

(2) The ultimate length of the (200) face is

$$\lim_{t\to\infty}L_2=G_1^{\mathrm{II}}/\sin\theta G_2^{\mathrm{I}} \qquad (29)$$

(3) If the initial length of the (200) face is smaller than this, L_2 increases with time, and conversely. If the initial length of the (200) face is just equal to the ultimate length, then the length is constant in time and leads to the interesting relation

$$L_2^\circ G_2^{\mathrm{I}} = G_1^{\mathrm{II}}/\sin\theta \tag{30}$$

which says that the condition of constant length for the growing (200) face is achieved when the growth rate normal to this face ($L_2^\circ G_2^{\mathrm{I}}$) is just equal to the projection on this direction, of the growth rate normal to the {110} face (G_1^{II}).

(4) There is a maximum in $\boldsymbol{r}$ as a function of time provided that

$$2l_1^\circ[r_0 - r_l] < G_1^{\mathrm{II}}/G_2^{\mathrm{I}} \tag{31}$$

which can be written

$$r_0 L_2^\circ < G_1^{\mathrm{II}}/G_2^{\mathrm{I}} \tag{32}$$

These equations are related to equation (29) and express the fact that in order for there to be a maximum in $\boldsymbol{r}$, the initial length of the (200) face (L_2°) must initially increase, but the length normal to this surface (l_2) must not increase as rapidly. This is easiest to visualize if the initial shape is a lozenge. In that case $r_0 = r_l$ and equation (31) is clearly satisfied. As the edges of the lozenge grow, (200) faces are developed, and the axial ratio increases. This proceeds until the (200) faces have grown so large that the rate of growth normal to them exceeds the projection along the $\boldsymbol{b}$ axis of the rate of growth normal to {110}, which is constant because {110} is growing in regime II. The (200) faces then begin to 'grow out' of the crystal in relative terms, and the axial ratio begins to decrease. It ultimately approaches r_l, from whence it began, while the length of the (200) faces approaches that given in equation (29).

DISCUSSION

On the assumption that in regime I the substrate length is the length of the growing crystal face, we have derived a number of interesting and unexpected results for both the time development of the lateral habits of isolated polyethylene crystals and for their ultimate axial ratios. Experiments so far have not reported any of the results we have derived, but the experimental situation has never been the ideal one that we have invoked. Hence we need to discuss what would be necessary in experiments to observe the results that we have derived, even assuming our basic assumption is tenable.

There are three principal factors that enter into the experimental observation of the derived results. These are constancy of concentration, size and shape of seed crystal, and the time constants involved. Concentration is important in all three cases and we discuss it first. Then we discuss each of our cases separately.

Since our development applies to isolated crystals we are principally concerned with crystallization from solution. Our development, however, assumes that the rate coefficients are independent of time. These coefficients contain explicitly a factor which is a function of the concentration[1,11,20]. Hence, our development applies to an experimental situation in which the concentration is kept constant. Such arrangements have been used to study the growth kinetics of n-paraffin crystals[21], but we know of no similar experiments for polymer crystal growth. What effect this might have on the experimental results will be discussed in the individual cases.

Case 1

This case, in which all the growing surfaces are in regime I, is the easiest to realize. Indeed, in the customary self-seeding experiments, where the seed crystal is very small, our Case 1 would seem inevitably to apply at least in the early stages of growth. Use of the Z test[5,11] indicates that such crystals are well in regime I. This application of the test, of course, is also based on the assumption that the substrate length is the length of the growing face, but this seems appropriate for such very small crystals.

Growth rates linear with time are always reported for crystals grown from solution[7,8,22,23], and it has been deduced from this that the length of the growing face is not the substrate length[1]. There are, however, two other factors that should be kept in mind. If, in fact, the growth is exponential, as we have derived, then the decreasing solution concentration might compensate for this to give an apparent linearity. Experiments in which the solution concentration is kept constant, and the crystals are sampled while still very small would be needed to demonstrate the existence of exponential growth. These experiments are very difficult but could serve to give some idea of the magnitude of the substrate length.

The exponential growth is, of course, linear for times short compared with the reciprocal of the λ's in our Case 1 development above. However, it is easy to show, and is also physically obvious, that this applies to the very early stages of growth when the seed crystal has not changed appreciably in size. For crystals much beyond this size, exponential growth would be manifested.

The other important fact is that in Case 1, lozenges are never predicted. Lozenges are, of course, commonly observed experimentally. What the effect of changing solution concentration would have on the ultimate shape attained is hard to decide, but we rather feel that the development of lozenges, more than the liner growth rate, is evidence that the substrate length is some physical length smaller than the length of the growing face. Regime I kinetics appear to hold while the crystal habit is a lozenge[1], although 'mixed mode' growth (a combination of regime I and II) has been reported and discussed theoretically[22–24]. A lozenge can, of course, be formed in regime I provided that the substrate length is shorter than the length of the growth face and multiple nucleation does not occur on the substrate length. It thus becomes important to investigate the relative lengths of the substrate and the growth face at the regime I–II transition. From the early calculations of Lauritzen[5], at the lowest temperatures for polyethylene, the minimum value of the substrate length for multiple nucleation (regime II) to occur is 20–140 μm, although lower values may be calculated[11]. Hoffman[26] has calculated values ranging from 15 to 3000 nm for the substrate length at the regime I–II transition for crystallization from the melt, depending on the values of several parameters, particularly the melting point of the extended chain crystal. More recently, from the analysis of experimental results on growth from the melt, Hoffman[26] has concluded that this length is approximately 800 nm. Yet lozenges smaller than this, and linear growth rates have been reported[23,27]. Clearly, this is an area for further investigation, but our analysis would indicate that the substrate length is smaller—perhaps considerably smaller—than this value.

The existence of a substrate length which is small compared with the length of the growing face is not the only mechanism that can be considered to make the growth rate in regime I independent of the length of the growing face. Any mechanism in which nucleation occurs at a unique location (or locations) on the crystal face will also make the growth rate independent of the length of the face. Such unique locations are obviously provided by the corners of the crystal. That nucleation occurs at corners under at least same conditions has been shown by Moyer and Ochs[29], Keith[30] and Khoury and Barnes[31]. For these cases it is likely that diffusion of either material or heat was significant in the rate controlling step. However, even for cases in which the growth is nucleation controlled, nucleation can occur at the corners. Thus, Frank[28], in a discussion of the growth of snow crystals, which grow by a nucleation process, comes to the conclusion that nucleation occurs preferentially at the corners because the supersaturation is slightly higher there than at locations along the growing face. Moreover, as the growth step proceeds down the face, nucleation is inhibited for a distance of a few micrometers (in the case of snow) from the growing step because the supersaturation is reduced over that distance. The result is that nucleation occurs '...at almost regular time intervals at almost the same place successively'.

In an attempt to determine if a similar process could apply to the case of polymer crystals, rough calculations were carried out for both heat and mass flow assuming a crystal growth rate of one step s^{-1}, which corresponds approximately to $1.4\,\mu\mathrm{m\,h}^{-1}$, which is in the range in which growth rate experiments in solution are carried out. Under these conditions, calculation of the rate of heat diffusion at the crystal edge gives diffusion times that are much shorter than the average time between successive deposition of strips. This means that at this growth rate, nucleation does not occur during the time that there is variable supersaturation along the strip. A similar conclusion holds for diffusion of the (centre of mass of) polymer molecules up to the growing strip. At sufficiently rapid growth rates, of course, diffusion becomes important, and hence preferential nucleation occurs at the corners.

However, the above two processes do not exhaust all the possibilities for providing preferential nucleation at the corners. Another interesting possibility arises if it is assumed that nucleation requires a certain critical number, n, of monomer units to exist simultaneously at a spot on the strip. Now, it is well known that there is decrease in the density of segments near a non-adsorbing impenetrable surface. This decrease in density near the surface arises from the large reduction in the number of configurations available to a polymer near a surface[32]. The region near a corner has less interference and less of a density defect than an equally sized region near the centre of the strip. It is clear that the probability of n segments being at some location on the surface varies as the nth power of some function whose value depends upon whether the location is at the centre or the corner. Hence, the probabilities for occupation at corner and centre positions will vary. If n is sufficiently large these probabilities can result in preferential nucleation at the corners. This mechanism will be more thoroughly treated in a subsequent publication.

Case II

In this case we have the $\{110\}$ faces in regime I and the (200) faces in regime II. Bearing in mind as previously discussed that the minimum substrate length for regime II to occur is probably from less than one to some tens of micrometres, this case cannot apply to the customary self-seeding experiments. It would appear to apply most closely to the high aspect ratio crystals reported by Keith[19] and Khoury and Bolz[18]. Growth rate experiments have not been conducted on these crystals, and while the aspect ratios have been determined, this was not carried out as a function of time under conditions of constant solution concentration. As a result we can only say that the proper experiments to check the results predicted here have not been performed.

Case III

This case is similar to the preceding one, but the situation is reversed. In this case, the $\{110\}$ faces are in regime II, while the (200) faces are in regime I. Clearly, the simplest experimental situation would be for the seed crystal to be a large lozenge, with lateral edges larger (perhaps substantially larger) than one micrometre. Beginning with such a large lozenge, it should be possible to begin to see the development of (200) faces as discussed above. Such a situation is normally encountered during growth rate experiments from solution[23]. To see whether the predicted effects are observable, we recall from equation (29) that the ultimate size of (200) is $G_1^{\mathrm{II}}/G_2^{\mathrm{I}}\sin\theta$. Calculations show that at an undercooling of 20 to 25 degrees, this length varies from 0.1 to 2000 μm, depending on the value of ϕ chosen for the calculations. Thus the development of such faces from a lozenge growing in regime II should be visible. If, however, the substrate length were small (say less than 0.1 μm), then such faces would quickly grow larger than this, and, while still in regime I, the growth rate would no longer be proportional to the length of the face. Then the previously published analysis[11] would apply with the net result that the ultimate size of this face would be of the order of the substrate length. If this were small enough, the crystal would look substantially like a lozenge. Since this is the experimental situation, it appears that the substrate length, at least on the (200) faces, is substantially less than 1 μm.

CONCLUSIONS

On the assumption that in regime I, the growth on a crystal face occurs by sporadic nucleation anywhere on that face followed by rapid completion of a new layer on the face, we have calculated the dependence on time of the growth rate normal to the faces of isolated polyethylene crystals, as well as the time dependence of the aspect ratio of the crystals. In these calculations, the concentration of the solution from which the crystal grows has been assumed to be constant. None of the effects predicted by these calculations has been observed, but generally the required experimental conditions have not been precisely those needed to demonstrate the effects. However, in two cases—when both the $\{110\}$ and (200) faces are both in regime I, and when the $\{110\}$ faces are in regime I and the (200) faces are in regime II—the customary experimental conditions approximate to those required. From these results it can be concluded that in regime I the substrate length over which growth proceeds before stopping is much smaller than presently derived values[25], at least for the (200) face, or else that nucleation can occur at specific sites on the faces, very likely at the corner. It is also possible, of course, that the kinetic theory of polymer crystal growth may require some modification.

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