Morphological features and mechanisms of crystallization*

J. J. Point

Université de Mons-Hainaut, B-7000 Mons, Belgium

(Received 30 April 1991; revised 9 September 1991; accepted 23 September 1991)

Crystallization of polygonal polyethylene (PE) crystals (lozenge, diamond-shaped or with rectangular 2 0 0 sectors) is well accounted for by the Seto and Frank theory (SF theory). Crystallization of polyethylene with rounded crystal habit can be explained, according to Sadler, by the study of a two-dimensional lattice model with addition and removal of small square units (Sa approach). In such an approach, the outline of the crystal is rough. It is not reasonable to explain the growth of polygonal crystals by the Sa approach and nor can the SF theory justify the shape of curved crystals. We have used, therefore, the equation of Point and Villers, which generalizes and mediates between these two approaches. This equation reproduces accurately the observed morphology and simultaneously furnishes the values of three important physical parameters (the kinetic length, the mean rate of spreading of a nucleus and the reflection coefficient of a step at the end of a substrate). It gives an insight into the structure of the crystals.

(Keywords: crystallization; morphology; polyethylene; crystal growth)

INTRODUCTION

Limiting the scope of this paper to a discussion on the morphology of polyethylene (PE) crystals, my aim here is to indicate the way forward for a better understanding of the structure of these crystals and of the various mechanisms of their growth.

As noted by Keller, in a famous review[1], direct visual observation has a persuasiveness stronger than perhaps any other mode of information. Comparison of the outlines of PE lamellae grown from xylene solution, and of PE crystals grown from the melt, has an exceptionally strong appeal for the validity of *both* the theory of nucleation-controlled growth by Seto and Frank[2] (SF theory) and the model used by Sadler[3] to justify the existence of rough surfaces (Sa approach). In this model, no details of the crystal outline can, for a significant duration, be identified as a nucleus – the use of the adjective 'rough' may be confusing because the same term is used with a precise (and different) meaning in the theory of 'roughening transition'. As shown more than twenty years ago by Takamizawa *et al.*[4], the shapes of PE single crystals may be continuously changed from one extreme case (mode of growth) to the other. Without denying the disparities between the two modes of growth, I thus intend to show how the unified approach of Point and Villers generalizes and mediates between the nucleation (SF) and rough surface (Sa) approaches.

The aim of this present paper being morphology, I do not wish to review the large amount of experimental evidence[1] that, with all its many interesting features, lends support to the original model of Keller[5] for solution-grown crystals. We also retain, but we do not discuss at this stage, the *fact* that for the same molecular weight the radius of gyration of a PE molecule is lower in solution-grown than in melt-grown crystals. Despite the fact that as shown by Bassett[6] the melt-grown crystals display some regularity, it is thus unlikely that in these crystals the amount of adjacent chain re-entry is large. These considerations reinforce the feeling gained from morphological observations: both the SF and Sa approaches are justified in appropriate but different situations.

NUCLEATION-CONTROLLED GROWTH OF PE CRYSTALS

The growth (*Figure 1*) from an irregularly shaped nucleus of a polygonal crystal suspended in a dilute solution of PE in xylene has a strong appeal for use of the theory of two-dimensional crystal growth controlled by secondary nucleation. There is a near general agreement on this view; but as concerns the so-called 'régime' of growth, various research groups contradict each other. I therefore have to review briefly this classical subject, by scrutinizing the dependence of growth rate G first on the crystal size and then on the crystallization temperature (a much more delicate problem).

According to the SF theory, secondary nuclei are initiated on the edge of the lamella at a rate i (events per unit time and per unit length) and spread on the substrate with a rate g (expressed in unit length per unit time). The most clear and quantitative criterion to distinguish between the aforementioned view and that of Sadler is to study the dependence of the growth rate on the length of a crystal edge. In the Sa approach this growth rate is invariable and therefore nearly *polygonal* crystals must grow with constant shape. It is concluded from this remark that the Sa approach cannot justify the shape of

---

*Paper presented at 'Polymer Physics', 3–5 April 1991, Bristol, UK

0032-3861/92/122469-06

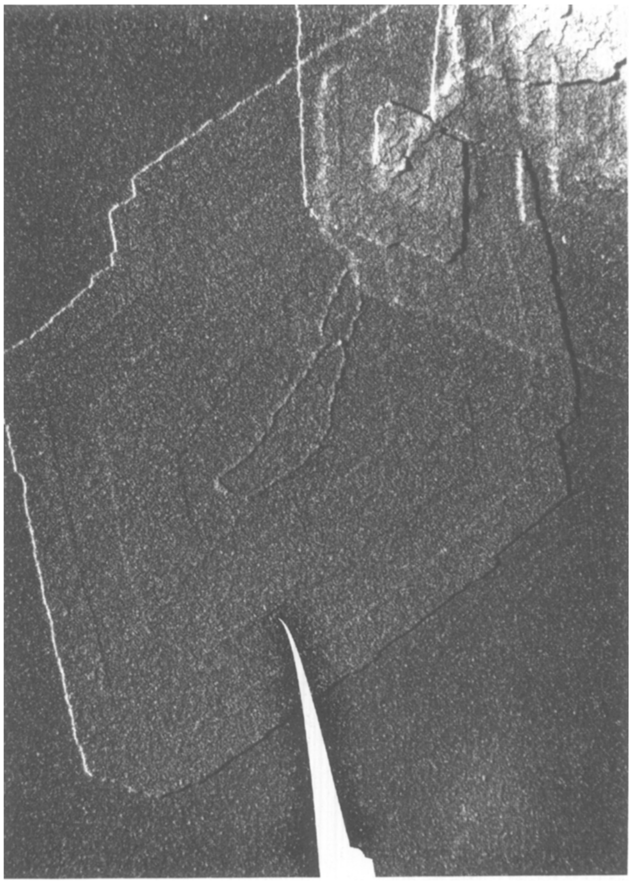

Figure 1 PE crystal grown from dilute solution of PE in xylene. The irregularly shaped nucleus is obtained by partial melting of a crystal. Note the isohypse decoration

PE crystals with rectangular 2 0 0 sectors (*Figure 2*). According to SF theory, if the length of the substrate is of the same order of magnitude as the kinetic length[7] $L_k = \sqrt{(2g/i)}$, which is the mean distance between successive left (or right) steps, the growth rate increases with the length of the substrate to reach an asymptotic value for a sufficiently large substrate length. If we imagine a 2 0 0 facet the length of which is of the order of magnitude of $L_{k,200}$ comprised between two large (with respect to $L_{k,110}$) 1 1 0 facets, then its size remains equal to L^* where L^* is the length such that:

$$G_{200}(L^*) = G_{110} \cos \varphi$$

This was predicted by our group[8] and observed by us[9] and by Toda[10], and gives one of the most definitive arguments in favour of the SF theory. More subtle morphological arguments are reviewed elsewhere[8].

Let us now turn to the study of the thermal dependence of G. Frank has proposed[11] to look at the quantity $\partial \log G/\partial T$, to see if it is a linear function of ΔT^{α}, where the exponent α is either $+1$, -1, -2, -3, depending upon the mode of growth. This criterion is excellent when one deals with crystallization of atomic crystals, for which the range of interest in supercooling is a small fraction of a kelvin. In the case of polymer crystallization, the temperature range of crystallization is usually large, such that ΔT^{α} is not the sole factor to consider in the expression of the thermal dependence of $\log G$ and as such the criterion becomes quite uncertain. An example of some concern at the moment is the existence of régime I–II transitions. If, for some obscure and bewildering reason, the length L of the substrate is assumed to be independent of the crystal size and temperature, and further if this length L is smaller than L_k, then the growth rate is given by $G = bLi$ (b being the thickness of a nucleus). This is known as crystallization in régime I (which differs from the mononucleation régime of SF). If, on the contrary, numerous nuclei are simultaneously growing on the substrate then $G = b\sqrt{(2gi)}$. This is known as crystallization in régime II (a new appellation for the polynucleation régime of SF). When crystallization proceeds from the melt it is customary to consider a Williams–Landel–Ferry (WLF) factor $\exp[-U^*/R(T-T^*)]$, which is an additional factor introduced in the expression of G. For a one-dimensional nucleus $1/T\Delta T$ is proportional to a term $\log i$. Therefore, if the WLF factor is representative of the effect on $\log G$ of the thermal dependence of the mobility of molecules, and if, in the studied range of temperature of crystallization, the other physical parameters involved (for instance in the standard theory of nucleation and with universally adopted notations, U^*, L_p, σ, σ_e, g, Δs_f) are constant or if their variations cancel each other out, then on a graph of $\log G + U^*/R(T-T^*)$ *versus* $1/T\Delta T$ straight segments are predicted and the ratio of their slopes is 2. When this is actually observed it is customary to say that 'a régime I–régime II transition' is observed.

A priori (but this remark does not *a priori* disqualify the premise of régime transition), that all the conditions just enumerated are simultaneously satisfied would seem an amazing coincidence. However, before taking the observation of 'a régime I–régime II transition' as a proof of *all* the involved assumptions, it seems necessary to proceed to some cross-examination. In this respect, and

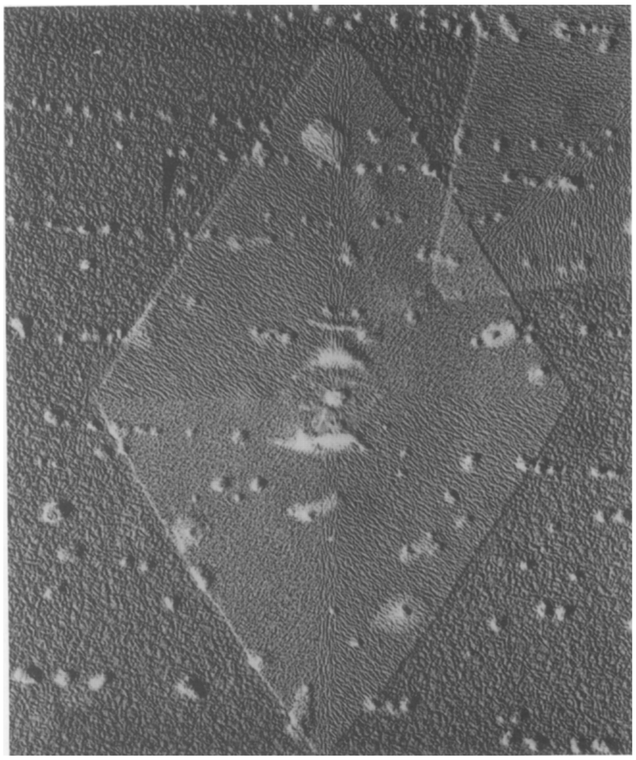

Figure 2 PE crystal with rectangular 2 0 0 sectors. Decoration according to Lotz and Wittman

as concerns PE, please note:

(a) that to justify the thermal dependence of the lamellar thickness Hoffman *et al.*[12] assume that the value of σ_e depends on the temperature (and have taken values going from 90 to 135 mJ m^{-2});

(b) that Toda[13] has definitely shown that in a particular case g depends noticeably on T_c;

(c) that from the study of Organ and Keller[14] it may be concluded that in common solvents the growth of 2 0 0 facets of PE crystals proceeds usually in the hypothetical régime I and that according to Toda[15] it proceeds in régime II. (In the framework of the standard theory this implies a difference of a factor of 2 on the estimation of the work for chain folding.)

We conclude from this review (our group have given elsewhere[16,25] a more detailed analysis of the concept of régime I–régime II transition) that morphological evidence indicates that the growth of polygonal PE crystals from solution such as xylene, octane,... is nucleation-controlled and proceeds either in mono-nucleation or polynucleation régime depending on the size of the crystal facets. From direct morphological evidence, L_k may be as large as 50 nm (for instance).

THEORIES OF CRYSTALLIZATION AND MORPHOLOGY OF PE CRYSTALS GROWN FROM THE MELT

In this section by using successively the SF and the Sa approaches, we analyse the shape of PE crystals grown from the melt by Labaig[17] and Bassett[18]. The shape of these crystals is that of a laurel leaf, or, using a more precise botanical term, these crystals are lanceolated (*Figure 3*). In a few cases[17,18] it may be that, in addition to two '2 0 0 curved facets', the 1 1 0 facets are still discernible. Actually, I have observed very small 1 1 0 facets in two of the micrographs that I have studied (more than a hundred were looked at). Denote by B/A the elongation ratio of the crystals and by θ the angle between the '2 0 0 facets' at the crystal tips. Note that when θ is greater than 67.2° (for instance for PE of $MW = 50\,900$ at crystallization temperatures lower than 129.5°C) these 1 1 0 facets must certainly be absent. Otherwise the crystal would have four straight facets and six (or four) curved facets (a case never observed). I analyse now the shape of these crystals in the framework of existing theories of nucleation-controlled growth.

The Mansfield approach

According to Mansfield[19], which uses the Frank and Seto theory, a crystal may be 'limited by a section of an ellipse'. From the (exact) equation given by Mansfield (equation (44) of ref. 20), it does not appear clearly either than the centre of this ellipse is the centre of the crystal or that the size and shape of this ellipse do not depend of the rate h of the moving boundaries. Roughly speaking, the 2 0 0 facets of a melt-grown PE crystal may be thought of as arcs of *two different ellipses* (if we neglect the increase of the radius of curvature of these facets when we go from the centre to the tips of the crystal). The shape of these lanceolated crystals cannot be accounted for by the equation of a *single* Mansfield's ellipse written as:

$$y = b\sqrt{(2git)}\sqrt{[1 - (x/gt)^2]}$$

(a much clearer expression than that given by Mansfield).

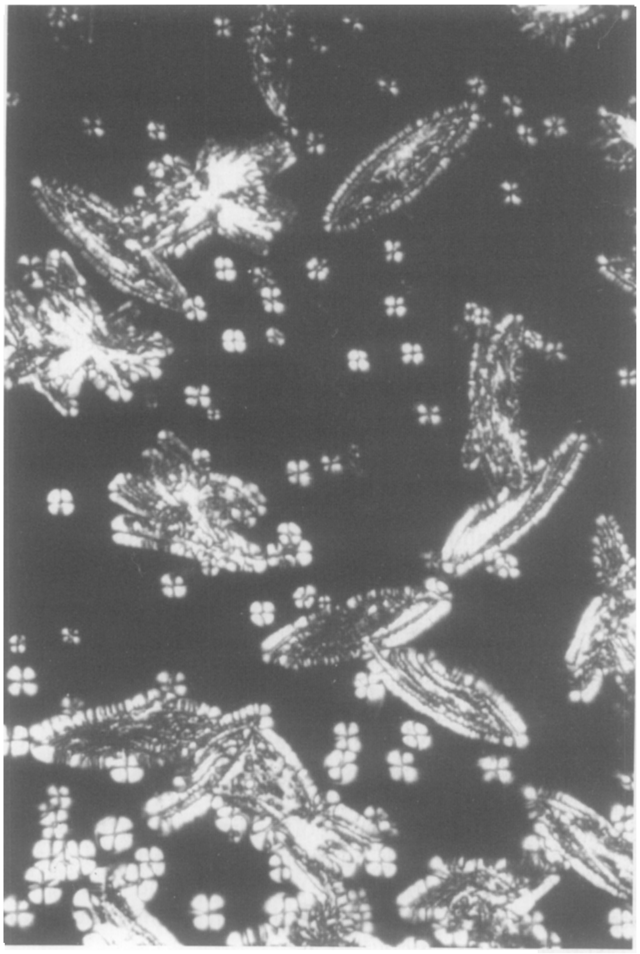

Figure 3 PE crystal grown from the melt. Micrography by Labaig[25]. (Courtesy of B. Lotz)

The Toda approach

According to a calculation given by Toda[21] the shape of a lanceolated crystal may be approximated by a curve made up by parts of a Mansfield's ellipse completed by four straight segments tangent to the ellipse. This must be taken into consideration despite the fact that the outline of a lanceolated crystal near its tips cannot in every case be assumed to be made up of straight segments. Note, however, that Toda[21] using oligomeric PE has observed such a type of crystals.

In his calculation, Toda uses the Frank and Seto theory. This implies that the mean distance L_k between successive left (or right) steps must be large with respect to the width of a stem a. Otherwise, no detail of the crystal outline can be identified, for a significant duration, as a nucleus. To verify if this *necessary* (for the validity of the approach) condition (see the last part of Frank's paper[2]) is actually satisfied, we may also calculate L_k/b (b being nearly equal to a).

This last ratio is given in Toda's model by:

$$L_k/b = 2\sqrt{[(B/A)^2 - \cot^2(\theta/2)]}$$

We give in *Table 1* the *experimental* values of this parameter obtained from the data of Labaig on PE of $M_w = 50\,900$. In most cases it appears that L_k/b is probably too small for adequate application of the SF theory of nucleation-controlled growth and we cannot retain Toda's approach because of this obvious internal contradiction.

Table 1 Estimation of L_k/b from the model of Toda. The data used are those on PE of $M_w = 50900$ and $M_w/M_n = 1.09$ grown from the melt

T_e (°C)	127.0^5	128.7	129.2	129.5	130.0^5	130.0^5	131.0^5
B/A	1.755	2.14	3.06	4.49	5.88	9.02	12.4
$\theta/2$ (deg)	90	87	43	23	16	9	6.4
L_k/b	3.5	4.3	5.7	7.6	9.4	13.2	17.3

The Hoffman and Miller approach

According to Hoffman and Miller[22] (HM), the growth of a crystal is powered by the attachment of molecules on 1 1 0 facets. I do not wish to comment on this claim, because I have not observed such facets. It remains to be explained as to what occurs on the 2 0 0 facets. This was done by HM. I have two short comments on this work:

(1) As just shown, the value of L_k is too small for an application of the SF theory.

(2) HM describe a model for attachment of a molecule on 2 0 0 sectors and obtain from an (erroneous) calculation values for the mean thickness l and the growth rate G_{200} of such sectors. In fact, because the attachment of the first stem results in a decrease of the free energy of the crystal, there is no nucleation barrier and the 'δl catastrophe' is expected. Following the (curious) approach of HM, we note that the ratio of the rate constants for the attachment of the first and further stems is $e^{q/kT}$. Therefore, the number N of nuclei of length l does not depend (in régime) either on the number of stems they contain or on their length l. Thus the mean crystal thickness calculated as:

$$\int_{l_{\min}}^{\infty} lN\,\mathrm{d}l \bigg/ \int_{l_{\min}}^{\infty} N\,\mathrm{d}l$$

diverges to infinity. If the (unrealistic) assumption of régime is not retained, the HM calculation is not valid for various reasons, and in particular because the lower boundary for integration must be 0.

Conclusion

Because L_k is experimentally found to be small, the SF theory of nucleation-controlled growth cannot (regardless of the particular approach adopted) be applied. Moreover, these particular approaches do not reproduce accurately the observed shapes. We can use Sadler's model of a rough surface growth where we can represent a crystal on a regular square lattice, and assume that the growth is due to the addition or removal of small square units with solid-on-solid (SOS) restriction. Sadler[3] has performed very interesting simulations on such models (however, using periodic boundary conditions). However valuable computer simulations of this type may be, some specific assumptions about the value of the rate constants were implied. For this reason, it is difficult to reach general conclusions from such work. Moreover, it is also of interest to find some evidence for the possibility of a continuous transition between the two modes of growth. Therefore, in the next section an analysis of experimental data (by using the equation of Point and Villers, which covers both mechanisms of crystallization and generalizes the SF and Sa approaches) is further discussed in detail.

ANALYSIS OF CRYSTAL SHAPE FROM A UNIFIED POINT OF VIEW

The SF and Sa approaches are similar in many ways. In both, the substrate exhibits steps and growth proceeds by the addition of units (respectively irreversible and reversible in the SF and Sa models).

Both models were designed to explain the growth of atomic crystals and they must be improved when extended to polymer crystal growth. In polymer crystallization the encounter of two opposite steps does not necessarily imply their annihilation. The two cilia may create a new pair of steps (at the instant of such encounter). The cilia of a nucleus that reaches the right (left) end of the substrate may create a left (right) step or be involved in the lengthening of the substrate.

Glossing over the mathematical details (given elsewhere[23,24]), introduction of the various ingredients into the theory leads to a new model, which encompasses both modes of growth.

The equation giving the shape $y = y(x, t)$ of the outline of the crystal is obtained by introducing an auxiliary variable Y and is:

$$\frac{\partial^2 Y}{\partial t^2} = 2ig\alpha Y + g^2 \frac{\partial^2 Y}{\partial x^2} \qquad \text{where } y = \frac{b}{\alpha} \ln Y$$

Here g is the *mean* rate of step drift, i is the initiation rate in the nucleation approach or the net rate of attachment of a unit at a site 0 in the rough surface model, and α is the mean efficiency of the annihilation of two steps on their encounter and has a value between 0 and 1.

The boundary conditions are:

$$x = ht \qquad l/r = (h - g)/(h + g) = \beta$$

$$x = -ht \qquad r/l = (h - g)/(h + g) = \beta$$

In other words, instead of assuming (as Frank, Mansfield and Toda did) that at the right end of the substrate the density of a left step is zero, we have introduced the notion that when a molecule reaches this extremity of the substrate it has a probability of folding back and of attaching itself to the substrate. This corresponds to the creation of a left step and we denote by $\beta = l/r$ the coefficient of reflection of a step at the end of the substrate. If the coefficient of reflection is 0 we get the generally used boundary conditions:

$l = 0$ $(r = 0)$ at the right (left) end of the substrate

The introduction of the idea of reflecting boundary conditions is not an additional and arbitrary complication. This concept is necessary because it has been demonstrated[24] that, when absorbing boundary conditions are used, the crystal cannot exhibit the shape of a laurel leaf. Solutions of that equation which depend upon the boundary and initial conditions have been given[23,24] and reproduce well the various observed shapes.

We have now to use these results to derive from the works of Labaig and Bassett physical information concerning the mode of growth.

EXPERIMENTAL DATA OBTAINED FROM THE ANALYSIS OF THE ACTUAL SHAPES FOUND IN PE CRYSTALS

Depending upon the values used for the physical parameters, the equations just given describe either rough surface growth when the mean distance between the steps:

$$L_k = \sqrt{(2g/i)}\alpha$$

is not large with respect to the width of a single stem, or they describe nucleation-controlled growth otherwise.

Moreover, the shape of the crystal depends strongly upon g, i and on the reflection coefficient β. For instance, the rate h of displacement of the tips of the crystal is related to β and is given by $h = g(1 + \beta)/(1 - \beta)$.

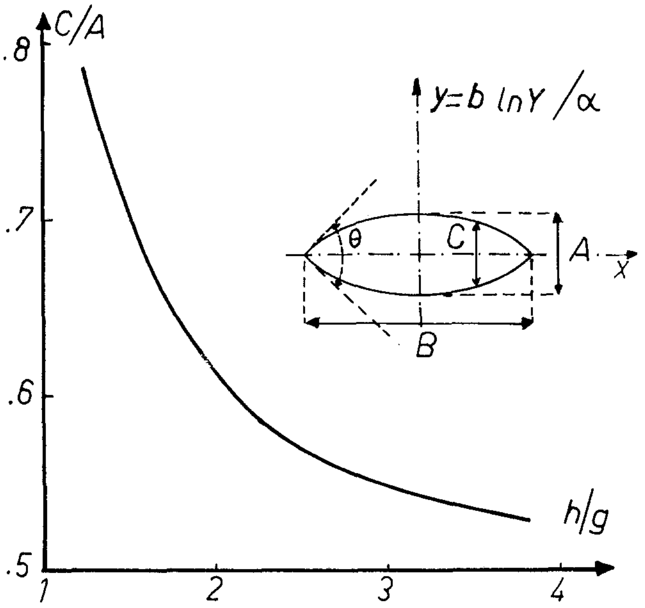

Figure 4 Dependence of C/A on h/g. (Courtesy of D. Villers)

Table 2 Estimations of L_k/b, g and β for melt-crystallized PE (from the model of Point and Villers)

(a) Data of Labaig: PE of $M_w = 50\,900$, $M_w/M_n = 1.0$, y

T_c (°C)	B/A	C/A	L_k/b	log [g (μm s^{-1})]	β
127.0^5	1.755	0.81	3.1	−1.83	0.07
128.7	2.14	0.78	3.5	−2.64	0.10
129.2	3.06	0.73	4.4	−3.02	0.15
129.5	4.49	0.66	5.4	−3.30	0.25
130.0^5	5.88	0.63	5.9	−3.84	0.33
130.5	9.02	0.58	7.7	−4.33	0.40
131.0^5	12.4	0.56	9.2	−4.99	0.46

(b) Data of Labaig: PE of $M_w = 8400$, $M_w/M_n = 1.1$, $125 < T_c$ (°C) < 128.3

$5.86 < L_k/b < 7.3$ $0.27 < \beta < 0.37$

(c) Data of Basset:

$L_k/b \simeq 7$ $\beta \simeq 0.13$

In reality, lanceolated crystals grown (either from solutions in poor solvents or from the melt) have various elongation ratios and their outlines are more or less curved. To characterize this curvature, we have measured the ratio of A to C where $C = y(ht/2, t)$ is the halfwidth of the crystal at mid-length. *Figure 4* gives, from theory, the dependence of C/A on h/g. Conversely we can calculate g from the measurable values of h and C/A.

In conclusion, the experimental determinations of the crystal shape and growth rate allow the evaluations of L_k, g and β. Typical values for these quantities derived from the data of Labaig and Bassett are given in *Table 2*. Four main conclusions emerge from this table.

(a) The mechanism of crystallization of PE from the melt follows a rough surface growth (or is at the borderline between this mode of growth and nucleation-controlled growth).

(b) The mean rate g of drift of steps varies dramatically with T_c and therefore the growth rate depends on both i and g. Therefore, the thermal dependence of G does not allow the estimation of the thermal dependence of i and as such cannot be used in the estimation of the nucleation barrier. (The calculation of Kg does *not* give the value $\sigma\sigma_e$).

(c) The coefficient of reflection of the steps at the ends of the substrate is noticeably different from zero.

(d) Because of the low value of L_k, an individual molecule is shared between numerous nuclei, and it is not surprising that its radius of gyration is noticeably larger than that of a single sheet, constituted by an adjacently folded molecule.

GENERAL CONCLUSIONS

Direct morphological observations provide an insight into the mechanism of crystallization and the structure of PE crystals. The mode of growth may be continuously changed (for instance, in the case of growth from PE in octanol solutions) from nucleation-controlled to rough surface growth. These views seem to explain (at least partially) why the radius of gyration of an individual molecule is larger in melt crystallization than in solution-crystallized lamellae.

The equation of Point and Villers allows the calculation of important physical parameters (L_k, g, β). The shape of lanceolated crystals is accurately reproduced. It still remains to explain the shape of more exotic crystals; this may be possible because the solutions of a Klein–Gordon equation depend on both the initial and boundary conditions.

All these conclusions were obtained by assuming that the molecule attaches to the crystal one stem after another. It is also possible to consider the simultaneous deposition of a bundle of stems. But theoretical development in this direction is still in its infancy.

ACKNOWLEDGEMENTS

J. J. Labaig, B. Lotz and J. C. Wittman provided me with the original photographs of J. J. Labaig[17] used throughout this work. They are gratefully acknowledged. We are also indebted to D. Villers, who did the calculations of the dependence on C/A of h/g. This work was partly supported by the FNRS (Fonds National de la Recherche Scientifique, Belgique).

REFERENCES

1 Keller, A. *Disc. Faraday Soc.* 1979, **68**, 145
2 Frank, F. C. *J. Cryst. Growth* 1974, **22**, 233
Seto, T. *Rep. Prog. Polym. Phys. Jpn* 1964, **1**, 67
3 Sadler, D. M. *Polymer* 1987, **28**, 1441; *J. Chem. Phys.* 1987, **87**, 1711
4 Takamizawa, K., Urabe, Y. and Hara, T. *Rep. Prog. Polym. Phys. Jpn* 1969, **12**, 179
5 Keller, A. *Phil. Mag.* 1957, **2**, 1171
6 Bassett, D. C., Olley, R. H. and Al Raheil, A. M. *Polymer* 1988, **29**, 1539
7 Point, J. J. and Dosière, M. *Polymer* 1989, **30**, 2292
8 Colet, M. C., Point, J. J. and Dosière, M. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 1183
9 Point, J. J., Colet, M. C. and Dosière, M. in 'Morphology of Polymers' (Ed. B. Sedlacek), de Gruyter, Berlin, 1986, p. 153
10 Toda, A. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 1721
11 Frank, F. C. 'Growth and Perfection of Crystals', Proc. Int. Conf. on Crystal Growth, Cooperstown, Wiley, New York, pp. 496–7
12 Hoffman, J. D., Davis, G. T. and Lauritzen, J. J. 'Treatise on Solid State Chemistry' (Ed. N. B. Hannay), Vol. 3, Plenum, New York, 1975, pp. 497, 614
13 Toda, A., Miyaji, H. and Kiho, H. *Polymer* 1986, **27**, 1505
14 Organ, S. J. and Keller, A. J. *J. Polym. Sci., Polym. Phys. Edn.* 1986, **24**, 2319
15 Toda, A., Kiho, H., Miyaji, H. and Asai, K. *J. Phys. Soc. Jpn* 1985, **24**, 1411
16 Point, J. J. and Colet, M. C. *Ann. Chim. Fr.* 1990, **15**, 221
17 Labaig, J. J. *PhD Thesis* Strasbourg, 1978
18 Bassett, D. C., Olley, R. H. and Raheil, I. A. M. *Polymer* 1988, **29**, 1539
19 Mansfield, M. L. *Polym. Commun.* 1990, **31**, 285
20 Mansfield, M. L. *Polymer* 1988, **29**, 1755
21 Toda, A. *Polymer* 1991, **32**, 771
22 Hoffman, J. D. and Miller, R. L. *Macromolecules* 1989, **22**, 3038
23 Point, J. J. and Villers, D. *Polymer* in press
24 Point, J. J. and Villers, D. *J. Cryst. Growth* in press
25 Point, J. J., Colet, M. C. and Dosière, M. *J. Polym. Sci., Polym. Phys. Edn.* 1990, **28**, 1275