Roughness of growth faces of polymer crystals: Evidence from morphology and implications for growth mechanisms and types of folding

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(*Received* 6 *October* 1982; *revised* 18 *January* 1983)

It is proposed that the growth faces of lamellar polymer crystals can have an equilibrium roughness (or crenellation). This can explain why some polymer crystals show no evidence of faceting. Support for this idea comes from the extensive theoretical developments on the nature of crystal surfaces. The characteristic habits of polyethylene are analysed in terms of a roughness which, on the {110} faces, increases progressively over a temperature range of about 100°C. At a temperature near 110°C the roughness becomes sufficient for there to be no free energy penalty for arbitrary crystal shapes (e.g. rounded) compared with one bounded by {110} faces. Above this temperature of crystallization most of the habits which are observed are leaf-shaped, with an apex along ⟨010⟩. Below 110°C {110} facets (or microfacets) are normally seen. There is no positive evidence that faces approximately parallel to (100) planes, observed for crystallization temperatures in the range 80°–110°C, are ever other than rough. The relative rates of growth on the {110} compared with the (100) increase with temperature, since {110} faces predominate at low but not high temperatures of crystallization. These changes are attributed to the increase in roughness with temperature on the {110} faces. The existence of surface disorder (roughness) requires that the binding energy between units in the crystal is comparable with kT. Hence this unit is probably several monomer units of polyethylene (rather than, for example, a complete stem which contains a hundred or more monomers). There is therefore a surface lattice on the growth faces with twenty or more units in the direction perpendicular to the lamellae. Monte Carlo calculations are cited for lattices of 20 by 50 units. These show that a cooperative increase in surface roughness with temperature and a transition between faceted and non-faceted growth can be expected for lattices of such limited extents. No explicit allowance has been made as yet for the consequences of the units being linked into chains and, for that reason, not being able to arrive or leave the surface independently. It is noted that changes in the alkane lattice with temperature indicate a possible evolution in binding energy, and in mobility, and hence may influence surface roughness. Theories of crystallization in polymers have normally assumed a growth surface which is molecularly smooth in equilibrium, and have emphasised nucleation events. Since this paper shows that the equilibrium structure may often be rough, it may be necessary to re-examine the basis of these theories. A brief review is included of the experimental evidence for surface nucleation events: nucleation may be a more important barrier at low temperatures than at high. The type of folding will be influenced by equilibrium roughness just as it will be by kinetic roughness, and some comparisons are made with neutron scattering results on this topic. The degree of adjacent folding is higher in the faceted regime as expected. Brief comments are made on the applicability of this idea to polymers other than polyethylene.

Keywords Polymer crystals; roughening transitions; crystallization theories; surface structure; growth faces; facets; morphology; polyethylene; habits; folding; lamellae; bond energies; alkane crystal lattice

INTRODUCTION

Mechanisms of crystallization fall into three categories; of these only one (secondary nucleation) is normally considered in the theories of polymer crystallization. The purpose of this paper is to point out that another mechanism, that of continuous growth on to rough growth faces, ought to be seriously considered.

The pioneering work of Burton, Cabrera and Frank[1] showed that the equilibrium structure of the surface could be either molecularly smooth or rough, depending on the bond energies compared with kT, and that there should be a transition between the two structures. It was calculated that if new layers were to nucleate on to a smooth surface, then the growth rates at low supercoolings would be much too small compared with experiment. If, however, growth steps were to exist on an otherwise smooth surface as a result of screw dislocations, much faster growth would result since the secondary nucleation step would no longer be necessary. Later work showed that rough surface growth ('continuous growth'), secondary nucleation, and dislocation spiral growth could all exist depending on the material and the crystallization conditions. I will concentrate on the distinction which can be made between the first two of these mechanisms.

0032-3861/83/111401-09$03.00

ROUGHENING TRANSITIONS

Order disorder phenomena in two dimensions, as can be expected on crystal surfaces, have been extensively studied, especially from the theoretical point of view (see reviews in refs. 2–5). Some of the conclusions will be listed.

It is usual to consider a square surface lattice on to which rigid atoms or molecules, nearly cubes or spheres in shape, can be added or subtracted. It is customary to associate an energy ε with each bond which is broken, and to neglect interactions other than with nearest neighbours. This model neglects the fact that both the enthalpy and entropy associated with a unit will depend in more complex ways on its position (whether in the bulk of the crystal, in the surface region, in the outermost monolayer, or at a corner position on the surface). This is particularly so for molecular rather than atomic units, since there is the variability of structure internal to the units as well as more ways in which the units can be packed.

If the crystal is two-dimensional an analytical calculation shows that the surface is always rough or crenellated, though the number of re-entrant corners or niches is very small if ε_1 is large compared with kT. ε_1 is the energy of the bonds parallel to the surface. The surface is normally considered to be parallel to a close-packed plane, even though a highly roughened surface could adopt a different orientation (see below). For this simplified situation a roughness parameter r is defined as the number of bonds parallel to the surface which are broken as a fraction of the number of surface lattice sites. The increase in surface energy per surface lattice site as a result of roughening is given by $r\varepsilon_1/2$. The surface of a three dimensional crystal is fundamentally different from that of a two dimensional crystal, since the roughening becomes a cooperative process. If any closed loop on the surface is followed, then the total number of steps away from the crystal must equal the number towards the crystal; there is no equivalent of this restriction in the case of a one dimensional structure at the edge of a two dimensional crystal. There is an extensive literature on the problem of predicting roughness in the three dimensional case. All the treatments agree that the surface for $kT/\varepsilon_1 \lesssim 0.4$ is smooth apart from isolated adsorbed units (or isolated surface vacancies). Above a temperature T_a the roughness starts to increase, and at T greater than about 1.2 T_a (where $r \approx 1$) it increases very steeply. The exact functional form of this increase depends on the model which is used but, except when the roughness is arbitrarily restricted to a finite number of surface planes, the roughness will continue to increase indefinitely with T. *Figure 1* shows a small selection of r *versus* kT/ε_1 plots[2]. There has been extensive discussion of how a transition temperature T_R should be defined, and whether such a temperature exists (see ref. 4 for example). For the present purposes, I shall be concerned with the loss of long range correlations along the surface. At low kT/ε_1, one can calculate the probability of site occupation averaged over surface layers, and along the surface normal this will fall rapidly from near unity to near zero. However, as soon as kT/ε_1 is sufficiently large, long range correlations along the surface will be lost, and in this sense the surface becomes delocalized. It has been shown[6] that the thickness of the surface region containing the interface diverges for $kT/\varepsilon_1 \gtrsim 0.63$, and this temperature can be used to define a T_R value. Equivalent information was obtained using Monte Carlo methods for an array of 20 × 40 sites[7]. At low kT/ε_1, tilting the surface can only be done by introducing a surface step, and hence by increasing the surface energy. At $T=0$ this energy is simply $20\varepsilon_1$. At T_R, however, the surface energy increment for tilting decreases very quickly with T and becomes zero. It was inferred that for an infinite surface there would be a discontinuity in the surface energy increment at T_R. There will be no energy (or free energy) penalty for tilted surfaces above T_R, and definite facets will disappear at equilibrium. The fact that results were obtained on a surface only twenty units wide is very useful in the polymer case, since the crystal lamellae are so thin (see below).

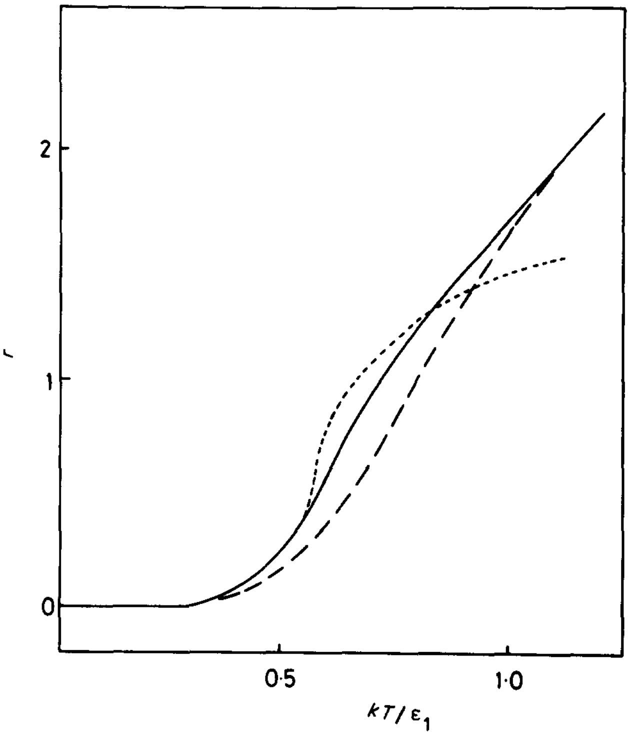


Figure 1 Plots of roughness r (the number of unmade bonds parallel to the surface which are broken per site on the two dimensional (square) surface lattice) *versus* kT/ε_1, where ε_1 is the bond energy parallel to the surface. Adapted from Figure 22 of ref. 2, the diagram shows results of calculations using: double layer Ising model[1,2] (dotted line), multilayer mean field model which assumes an averaged environment for each unit[8] (broken line) and Monte Carlo methods[2] for a face of finite size (solid line). $kT_R/\varepsilon_1 \simeq 0.6$

A calculation of the situation with finite supercooling $\Delta\mu$ was made by Temkin[8], who found that a static solution (i.e. one with no finite advance of a (100) crystal plane) was only possible for restricted values of $\Delta\mu$ and kT/ε. $\Delta\mu$ is the difference in chemical potential. For some values of kT/ε_1, it is possible to have a metastable static situation when $\Delta\mu \simeq 0$, but for this no longer to exist when $\Delta\mu$ increases. This is intuitively reasonable, since if $\Delta\mu$ increases it is to be expected that a surface at a temperature not far below T_R will be able to grow without the nucleation event which is necessary for smaller $\Delta\mu$.

Theoretical studies of kinetic effects are at a less advanced stage than the calculations briefly reviewed so far. Cahn proposed a criterion for nucleation or continuous growth which suggested that nucleation growth could occur even when the interface is diffuse rather than sharp (this is described and applied in ref. 9). Temkin[10] extended his mean field calculation to the case of steady growth rather than equilibrium. Again, this showed that in some cases increasing $\Delta\mu$ beyond a certain critical value can change a surface from being nearly smooth to one which is rough and which advances continuously. The mean field approach assumes an equal and averaged environment for each unit in a given surface layer. This restriction was removed by the application of other methods[11] and it was found that the surfaces were rougher during growth (finite $\Delta\mu$) than when the surface is in equilibrium ($\Delta\mu \simeq 0$), i.e. kinetic as well as equilibrium roughness is predicted.

The clearest illustration of the ideas discussed so far is possible when the crystals are able to equilibrate, e.g. for ^{4}He[12] and gold[13]. For ^{4}He[12] the entropy of melting is negligible, and crystallization at any desired speed can be induced over a range of temperatures by changing the pressure. At 1.08K and 0.85K two crystallographic faces have been found to have roughening transitions. Below the transitions the crystal has facets following low index planes as expected for 'smooth' surfaces. At higher temperatures the surface is rounded and determined by gravity only. It has also been observed that the habit is not the same during growth (Lipson, private communication); at temperatures between transitions of two different facets the crystals can grow in a totally faceted form, and only equilibrate to a curved form when the growth has stopped. This is also true of gold[13]. If some faces are rough and others not, the former will crystallize faster until the only faces remaining are the smooth ones.

Few crystals can equilibrate to the degree that the entire habit can be transformed with no net rate of crystallization. Even so, many features of crystal habits were explained successfully on the basis that below or above T_R the surface will be nearly smooth or rough respectively[14]. The habits which result will then reflect the mode of crystallization: either by nucleation or dislocation growth, or by continuous growth. The former gives faceted habits, the latter does not, and most crystallizable materials fall into these categories. There are also borderline cases: the two morphologies can occur at different temperatures of growth for the same material[15,16]. For C_2Cl_6 it was suggested[15] that the transition spanned the temperature range of 95°–105°C.

Rough surfaces could lead to any one of a large number of curved morphologies. In order to explain the occurrence of any particular one, it would be necessary to specify kinetic factors such as diffusion of heat and matter. Irrespective of these detailed questions however, the existence of a curviture which is observed in the electron microscope is explained most directly by a molecularly rough growth surface, even though it is possible to construct curvature on a macroscopic scale by the existence of a zig-zag surface consisting of a sequence of 'microfacets'.

For polyethylene, faceted habits are observed at low temperatures of crystallization and rounded habits at high temperatures (see below). This is the basis of the case for considering rough growth faces in polymers which will be described in more detail below.

CRYSTAL HABITS IN POLYETHYLENE

The dominant feature of polymer crystals is of course their lamellar habit, with molecules passing many times through the depth of the lamella[17].

Unlike most materials, polymers can be crystallized over a range of temperature: for example polyethylene is commonly crystallized in the temperature range 70°–130°C (343–403K). Although the proportional change in T over this range is relatively modest, it is still worth looking for changes in habit as the result of changes in surface roughness.

For temperatures of growth of 70°–90°C from xylene, faceted crystals are seen in general though microfacets are promoted by fast crystallization, high concentration, and high molecular weight. For crystallization at or below 70°–75°C the characteristic crystals have four {110} facets. As the temperature of crystallization is raised in the range up to 90°C, the apexes in the a directions become truncated by (100) facets of increasing length[18], the trend being towards an equilateral shape. For solution growth for a range of solvents with higher dissolution temperatures than xylene, the trend of increased (100) facets is continued as the crystallization temperature is increased. In many cases the (100) faces are visibly rounded[18–21] (see *Figure 2(a)*, courtesy of S. Organ). In fact there is no definite evidence that these faces are ever truly straight and hence they are probably only nominally (100) facets. The {110} faces become curved at about 110°–115°C (this is just discernible in *Figure 2(a)*) and are absent at higher temperatures. The first reports of systematically curved habits (for paraffinic solvents[22]) were of the high temperature type with no {110} faces. The only apexes remaining are along b, and the crystals then have the appearance of leaves. For paraffinic solvents, the transition from straight to curved edges is at about 100°C. More recently, similar leaf morphologies have also been seen for crystallization from the liquid polymer[23], where the crystallization temperatures are in the range 120°–129°C. The work of Labaig is unusual since observations were made during crystallization, with the crystals still in a liquid medium. The most clear cut case of growth from the melt which is at least partly faceted, is for the polymer/air interface of droplets crystallized well below 100°C[24]. Under these conditions the speed of crystallization has been estimated as greater than $2\,\mathrm{m\,s^{-1}}$. Conventional ideas on polymer crystallization would predict that these would be the least likely conditions for faceted growth.

This review cannot of course be exhaustive, in particular considering the experimental difficulties in observing free crystal edges for bulk crystallization (normally no significant volumes of polyethylene remain uncrystallized). Degradation fragments suggesting {110} facets[25] have been observed, and more recently a similar observation has been reported by Bassett and Hodge (ref. 26 notes Figure numbers). Again, I have observed curved crystals grown at crystallization temperatures from xylene near room temperature[27]: however they are not seen when well defined fractions are used and appear to be correlated with the presence of paraffinic material (molecular weights less than about 1000).

At the risk of a certain oversimplification, then, there is a good case for a general scheme with facets at low temperatures and rounded habits at high, in the sequence shown schematically in *Figure 2(b)*. The precise value of the temperatures at which the habit changes can be affected by the choice of solvents, and molecular weight. It should also be emphasized that it is difficult to differentiate experimentally faces which are straight from those that have a high radius of curvature (see (iii) and (iv) in *Figure 2(b)*).

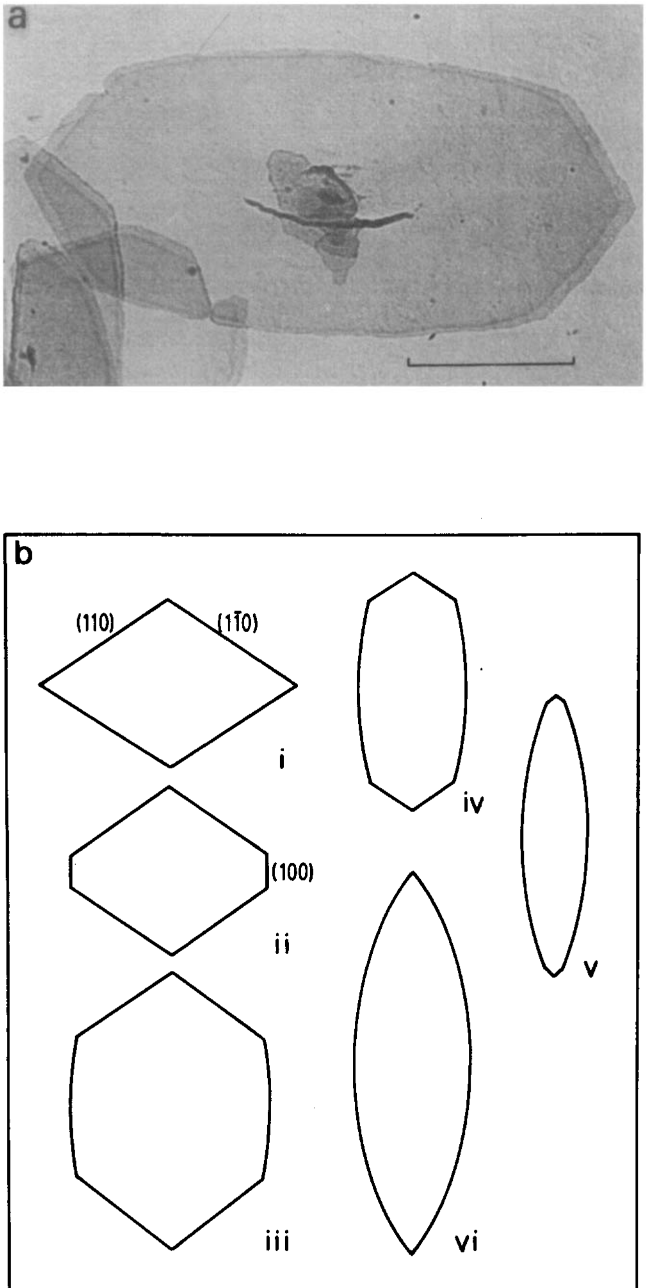


Figure 2 Outline shapes of polyethylene lamellar crystals. (a) Micrograph of a crystal grown from a 0.05% solution of Rigidex 50 in tetradecanol at 110.3°C (courtesy of S. Organ). The distinct rim of the crystal is probably caused by fractionation by molecular weight. (b) Schematic description of the various outlines which have been observed (not to scale). For a given molecular weight of polymer and solvent, the sequence of habits as temperature of crystallization is increased is always (i) → (vi). References which give the details of growth conditions are: (i) and (ii), (18); (iii) (iv) and (v) (20) and (21); (vi) (22) and (23). The unit cell of polyethylene, with the conventional representation of the planar zig zag, is shown with the same orientation in the inset. Examples of (110) (1$\bar{1}$0) and (100) faces are labelled

EQUILIBRIUM SURFACE ROUGHNESS OF POLYMER CRYSTALS

The curvature of crystal edges, when it is observed, cannot be explained by a sequence of low index facets unless these are short enough not to be seen in the microscope (less than 100–200 Å). The natural interpretation is roughness on a molecular scale. Irregular habits of polymer crystals (and possibly molecular roughness) can be induced by kinetic factors, as remarked above in connection with microfacets. However, the roughness of leaf crystals is quite distinct from this, since a high temperature of crystallization, not a high speed of crystallization, is usually the deciding circumstance. A thermodynamic driving force for roughness, arising from a surface entropy term, must be present.

The enthalpy of melting or dissolution per molecule is very high indeed for polymers, which might seem a good reason to dismiss consideration of rough growth surfaces. However, it is only rarely the case (e.g. globular proteins crystallized from solution) that the individual unit added to the crystal is likely to be a complete molecule. For synthetic polymers where chain folded crystallization into lamellae is the general rule, the individual unit is either one stem or a small part of a stem. So a surface roughness should be considered which corresponds to *Figures 3(a)* (one stem as one unit) or to a structure such as in *Figures 3(b)* and *(c)* (parts of a stem as one unit).

In order to substantiate this idea it is necessary to consider two principal questions: whether values of kT/ε_1 are in the correct range, and whether the temperature dependence of the crystal habit can be explained in a straightforward way.

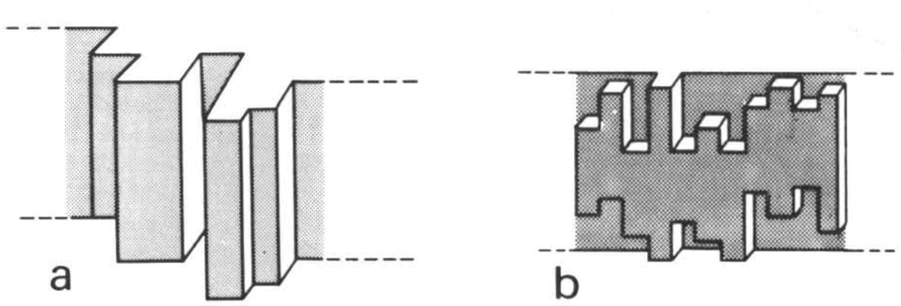
Types of surface roughness and magnitudes of ε_1

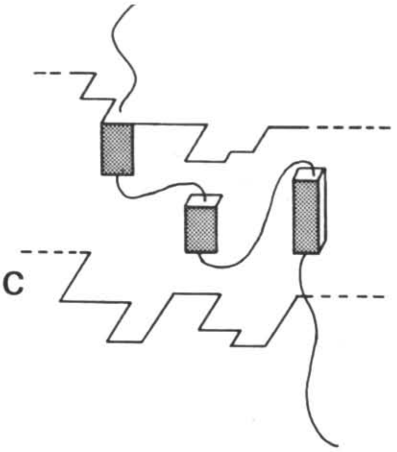
It is customary to estimate ε_1 from the enthalpy of transition, on the basis that only nearest neighbour interactions need to be considered (see above). This is 1 kcal mol^{-1} of CH$_2$ [28]. For flexible molecules there is the further complication that a significant part ΔH_i of the energy changes may be due to intramolecular changes. The three methods used below suggest that roughly half the enthalpy of melting is intermolecular (ΔH_e), and this estimate is more than adequate for the present purposes.

σ, the lateral surface free energy, has been taken[29] to be 14 erg cm^{-2} which leads to ΔH_e of 0.46 kcal mol^{-1}.

The isomeric state model for the liquid gives ΔH_i of 0.25 or 0.34 kcal mol^{-1} (from a Boltzman distribution of *trans/gauche* bonds based on energy differences between the two states of 0.5 kcal mol^{-1} [30] or 1 kcal mol^{-1} [31] respectively).

There are several calculations of lattice packing energies (see refs. 32–36 for example). Unfortunately they do not use the molten state as a reference, as is necessary for the present purposes. Very crudely, this can be done by separating the melting into two steps: firstly a change to a hypothetical hexagonally packed structure (all *trans* conformation) with the density of the melt, and secondly to the true melt. ΔH_e is then calculated from the first of these to be 0.65 kcal mol^{-1}, using the attractive energy terms only, and an analytic formula for Van der Waals attraction: Energy $= -1240/d^5$ kcal mol^{-1} [34]. The interstem distance d is higher along $\langle 010 \rangle$ than $\langle 110 \rangle$, so that ε is smaller: with the above simplification the magnitude of the former energy should be about 1.6 times lower than the latter. A much more detailed analysis has also shown





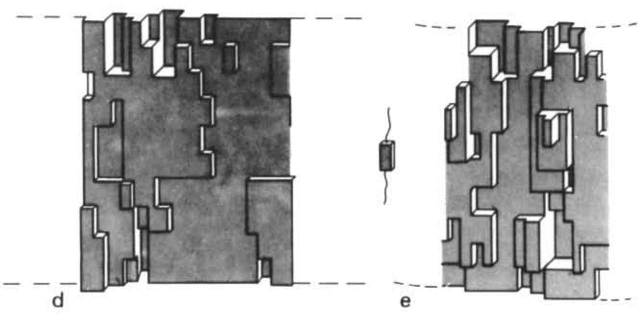


Figure 3 Schematic representations of three of the different types of roughness which might be possible on the growth surface of a lamellar crystal. (a) Stems either present or absent. (b) A single layer model with varying stem lengths. (c) A multi-level model with each unit corresponding to a short length of chain. (d) and (e) Sketches taken from preliminary simulation studies of surface roughness, following the methods in ref. 2, with the difference that at the top and bottom edges the boundary conditions corresponded to free surfaces. The lattice was 50 units wide and 10 high (only a small width is illustrated), with cyclic boundary conditions linking the left to the right hand edges. Equal ε_1 values were taken in the two directions, with kT/ε_1 of 0.5 for (d) and $0.65 \simeq T_R$ (for (e)). No account is taken of chain continuity (see text). The purpose of (d) and (e) is to give an idea of the actual magnitudes of roughness involved, and the properties are not identical in detail to the lattice studied previously[2,7]. Note the incipient 'rounding off' in (d) and (e) due to preferential removal of units from top and bottom edges

differences in bond energies along $\langle 010\rangle$ and $\langle 110\rangle$[35]. Although omitting the repulsive energy terms is a drastic simplification, it has been shown that agreement between prediction and experiment for the orthorhombic to hexagonal (rotator) phase can be achieved, and in this case the changes in attractive energy terms are much more significant than the repulsive[33]. Furthermore, it is not practicable to calculate the repulsive terms for the melt. For solution crystallization ε_1 should be related to the enthalpy of dissolution; for xylene it is approximately equal to the enthalpy of fusion[54].

Hence ΔH_e is about 0.5 kcal mol^{-1} (or higher), kT/ε_1 4.5. The consequences of different ε_1 values for (100) and $\{110\}$ faces are discussed further below.

In order to verify that kT/ε_1 is about 0.6 as expected if changes in roughness are to occur, the number n of CH_2 groups in the basic unit of crystallization is required: if, as in model (a) (*Figure 3*), this is a complete stem n is 100–200, but a 'flexible unit'[37] as indicated in (c) could correspond to n of about 6. If for the present the packing in the (001) plane is taken to be hexagonal, we have

$$\varepsilon \simeq 2n\Delta H_e/6$$

Hence $kT/\varepsilon_1 \simeq 0.045-0.02$ for *Figure 3*(*a*), and $kT/\varepsilon_1 \simeq 0.7$ for model (c). Although model (a) would be the simplest from the point of view of making predictions, the roughness would always be low (one niche every 30μ–30m). What is more, ε_1 would increase with lamellar thickness, which does not agree with the observation that lamellae are thicker for the higher temperature of crystallization. It is just this last situation where the habits are rounded and the surface is proposed to be rough. Model (b) is open to the same objection since the probability of a stem in the outermost layer being absent is also very small. With the degree of roughness shown in (b) the lamellae would in fact be faceted.

It is worth mentioning in parenthesis that the structure 3(b), corresponding to roughening of the lamellar corners is the one which can most nearly approach a 'smooth surface'. The surface monolayer can be considered as a two dimensional crystal either side of which corresponds to a one dimensional surface. The corresponding theory can be used to find the equilibrium roughness of these surfaces and hence the fluctuations in the lengths of the stems. As this system is considered to be two dimensional, there is no well defined transition temperature and the roughness is finite at all temperatures. The values for the roughness, using the estimates for kT/ε_1, for polyethylene, are similar whether one takes the basic unit to be one or six monomer (CH_2) groups, and correspond to a root mean square displacement of 13 monomers. This gives a total depth on the surface which is rough considerably in excess of 26 monomers.

Existing theories for two dimensional crystal surfaces can be applied to the structure in *Figure 3*(*c*) with the very drastic simplification of ignoring connectivity between crystallizing units (e.g. between groups of six monomers). There is an obvious problem with *Figure 3*(*c*) that a very tangled structure will be created which will only lead with difficulty to an ordered crystal. It should be borne in mind however that simulations of surfaces on atomic crystals[3] show a very high degree of mobility, so that there will be considerable opportunity for chain rearrangements. *Figure 3*(*d*) shows results of computer simulations for lamellar crystals at about T_R ($kT/\varepsilon_1 = 0.65$) and 3(e) for $kT/\varepsilon_1 = 0.5$.

Interpretation of habits

Any shape of crystal can be related to a polar plot of inverse growth rate[38]. A discussion of the general consequences of such an approach is given, though not a quantitative application of the method. Suppose a number of stable facets can exist, and all surfaces with other orientations are rough. The rate of growth on to the latter will be relatively high, and as long as there are sufficient faceted surfaces to make a closed figure, the rough surfaces will 'grow out' leaving facets only (cf. gold and ^{4}He). In the present case this could apply to habit (i) (*Figure 2*(*b*)). If, as another example, the polar plot was featureless apart from a maximum in the growth rate in a symmetry direction (which was sufficiently well developed) the resultant habit would have an apex along that direction but would otherwise have curved faces with no special features. This could apply to habit (vi). The sequence of habits (i) to (vi) means that the relative rate of growth on to $\{110\}$ faces is progressively increasing until, (habit (vi)), it is much more than along such directions as $\langle 010\rangle$. Over the same sequence of habits, (100) faces are either short (habit (ii)) or have distinct curvature (habit (iii)). $\{110\}$ faces can be straight (i) and (ii) but acquire a significant degree of curvature (*Figure 2*(*a*)). The simplest interpretation of these changes is to presume that (100) faces are always rough, whereas $\{110\}$ are fairly smooth at low temperatures and acquire roughness as the temperature is increased.

Changes in roughness with temperature

Is the change in roughness of the $\{110\}$ faces due to a change in the equilibrium molecular structure of the surfaces, and in particular can the onset of curvature on $\{110\}$ be explained in this way? In order to achieve a curvature which does not imply a large departure from equilibrium it is necessary for the free energy of a step which reaches across the surface to be comparable with kT, (see the section on roughening transitions). It can be conceived that at high r values, steps which can cross the lamellae can be created from rearrangements of existing edge sites, without incurring additional surface energy. The step free energy can be calculated from energy *versus* kT/ε_1 plots[68] for steps 20 units wide[7]. The step free energy falls by about ε_1 over 40°C ($T_R \simeq 390$K), so that the step probability will increase as a consequence. The free energy fall should be faster than this since the Monte Carlo method underestimates the cooperativity for the onset of roughness (see above for the limitations of simple nearest neighbour bonding). More detailed work is necessary to analyse the onset of curvature on $\{110\}$ faces as the temperature approaches that where $\{110\}$ faces are no longer seen. An increase in curvature over about 40°C or less, up to that which could give a few degrees tilt, would not seem to be inconsistent with either the observations or the predictions.

Even when the number of edge sites is too small to lead to curvature, there will still be an effect on crystallization rate. If T_R is taken to be 390K, the highest temperature T_a for a face which is smooth (in the sense of having only adsorbed and desorbed units) could be as low as 250K. Between T_a and T_R there will be an accelerating rate of increase of r with T which would explain most if not all the observed increase in growth rate of $\{110\}$ faces compared with (100).

Effects of the nature of the polyethylene lattice

In order to correlate the theoretical predictions with observations on polyethylene, it is necessary to consider the differences between the usual simple cubic lattice of most theories with the actual lattice. The surface lattice on both growth faces is rectangular rather than cubic, and the rectangular lattice in each plane is displaced with respect to the one underneath. The effect of the displacement will be assumed not to be important. Some results for different energies for niche creation in two directions have been given (see Figure 19 of ref. 1). The higher energy is the more important in determining the onset of roughening (i.e. the roughening is at a higher temperature than would be given by an average bond energy).

Is a difference in the roughnesses between (100) and $\{110\}$ faces unreasonable in view of what is known of the bond energies in the alkane lattice ε_{hkl}? (The subscripts indicate the direction of the bond.) Only those bonds whose numbers change when edge sites are created need be considered, which include bonds along $\langle 110\rangle$ on the $\{110\}$ faces and along $\langle 010\rangle$ on the (100). It may be possible, once a more detailed model for the roughening has been proposed, to calculate a free energy associated with the interruption of a stem. This will include entropic effects due to partial attachment of chains. Each growth face contains two classes of edge site, one occurring with incomplete stem attachment, the other with unmade bonds of energy ε_{110} or ε_{010}. If the energy for interrupting a stem were to be much larger than either ε_{110} or ε_{010}, then a two dimensional roughening could be controlled by that energy for both growth faces. It will be presumed in what follows that the energy for stem interruption is not large compared with ε_{110} or ε_{010}: indeed this presumption has in effect already been made since, if it were very large, the roughening would approximate to the one dimensional model (*Figure 3*(*a*)). (This neglects the possible effect of changing stem lengths: the structures in *Figure 3*(*a*) and 3(*b*) both have the same number of stem ends.) It has already been indicated that ε_{110} and ε_{010} will be different. This is in agreement with higher roughness on (100) faces.

A change in the equilibrium roughening seems to be sufficient to explain the observed changes in habit with temperature. However, it is possible that kinetic factors may provide alternative explanations, especially since the temperature range where habit changes are most pronounced is also the one where mobility in the lattice increases significantly. Kinetic smoothing effects are conceivable, whereby the destruction of edge sites is faster than their creation, even though there is no precedent for this.

Finally, it is possible that changes in ε_1 may contribute (as well as T) to those in kT/ε_1 and hence to the temperature dependence of the roughening. The alkane lattice is known to have a number of polymorphic forms, and surface effects[35] may induce changes in the surfaces which are not apparent in the bulk.

CONSEQUENCES ON TYPES OF FOLDING

The most natural way to explain why 'adjacently re-entrant' folding would predominate is to suppose that the first stem of a molecule to attach incurs much more surface energy than the subsequent ones. A partially attached molecule will be a good candidate to supply the second stem and hence give an adjacently re-entrant fold. However, if there were plentiful edge sites on the crystal edge, a new molecule could attach with consecutive stems along its length being separated on the edge. This has been considered for kinetic roughing, of the type in *Figure 3(a)*, Regime III[39]. Attachment with widely separated stems would be disfavoured not because of the growth kinetics but because space would be overfilled in the fold surface region[40,41]. This factor alone is not however sufficient to impose adjacent re-entry. This is because, at least in principle, the existence of a transition layer on the lamellar (fold) surfaces can alleviate the crowding so as to permit consecutive stems to be separated by a small multiple of the nearest neighbour distance[42].

The consequences of growth surface roughness on types of folding are apparent in the recent results using the small-angle neutron scattering technique. For crystallization at 70°C from xylene solution there is now consensus that the stems from a molecule are in rows[43–45] with recent work suggesting about 75% adjacent re-entry along the rows[46]. For crystallization from the melt, the folding is more random[43–45]. Several models exist in the literature, which differ widely in the way they are described. However, a common feature to several[47,41,48] is a grouping of stems which are relatively compact, together with a large and more random separation between one group of stems and the others in the molecule. Within the group, or 'subunit', the folding can be described as 'nearby re-entrant'[47] a terminology intended to convey the idea of folds with stem separations up to a few lattice spacings.

We now see that when curved growth faces are either observed directly or inferred to be present, adjacent re-entry does not predominate, but when faceted crystals are found it does. This is exactly what would be expected for a difference in roughness between the growth surfaces of melt and solution grown crystals. For the latter the 25% of folds which are not adjacent could be explained by the finite degree of roughening at temperatures between T_a and T_R (see *Figure 3(d)*): this could lead to independent attachments along the growth face.

Continuous rather than 'nucleated' growth increases the time available for laying down a stem compared with previous estimates[45]. This is relevant to whether molecules are 'frozen in' during crystallization[44].

KINETIC THEORIES OF CRYSTALLIZATION

A criterion which is sometimes used for distinguishing different mechanisms of growth is the dependence of growth rate on supercooling ΔT: for 'continuous' growth on to rough surfaces it is normally predicted to be linear, whereas for a 'nucleation' type of growth it is of an exponential type[2]. For polymers the growth rate is found to be proportional to $\exp(-K/(T\Delta T))$ where K is some constant (e.g. ref. 29). It is possible however that the growth rate dependence may be explained without the existence of nucleation events as envisaged hitherto.

The first theory to predict the lamellar thickness and growth rates in a successful way[49] was based on a model whereby the equilibrium structure of the growth face was implicitly assumed to be smooth, and stems were added sequentially to make a secondary nucleus. The free energy of the new layer at each stage of formation was calculated from the bulk free energy change and the free energies for creation of additional surface area. The rate at which thermodynamically stable nuclei are created is calculated as a function of stem length, and a length is calculated which is an average weighted according to growth rates. The crystallization rate was calculated directly from the rate of formation of nuclei, on the premise that the 'filling in' of a new layer is much faster and has little influence. Later versions of the theory allowed the second[50] and subsequent[51] stems to fluctuate in length, and show that a steady state lamellar thickness establishes itself. Recently the partial attachment of stems[50] has been considered in detail[37]. Other modes of crystallization have now been proposed (Regime II[52] and Regime III[39]) which are not solely nucleation controlled, in the sense that filling in is no longer neglected and new secondary nuclei form before the 'niches' created from previous ones have grown out. Regime III, the extreme situation, corresponds to a steady state density of niches of about 1/3, this ratio being deduced from the criterion that at least three stems from the same molecule must be added nearby on the growth surface so as to avoid overcrowding in the (fold) surface layer.

In all Regimes which have been proposed, I (solely nucleation controlled) II and III growth rates are of the exponential type. This is a consequence of stages in the crystallization process which have high free energy, associated with the attachment of stems to otherwise smooth faces. However, it has already been discussed (in relation to the quantity ψ, pages 562 of ref. 29 and 660 of ref. 53) that high free energy intermediate steps may occur for other reasons such as the existence of an adsorbed layer. If this is so it may not be necessary to have complete stem attachment to a smooth face in order to explain the exponential type growth rates: the existence of alternative high free energy intermediate steps may suffice. The laying down of even a part of a macromolecule must be a complex process, and it is not unreasonable that entropically disfavoured states are involved as intermediates. It may however be necessary to restrict the type of such steps so that their free energy depends on supercooling in a suitable way (P. J. Barham, personal communication). Whatever the detailed form of a calculation of growth rates, it is to be expected that the change in roughness with temperature will affect the predicted growth rates and their temperature dependence. This effect will be most noticeable around T_R (*Figure 1*) and hence will involve the growth regime which has been associated with Regime II crystallization[29].

There may be another significant difference between existing theories and one which would incorporate roughness of an approximately equilibrium type. The former incorporates as an essential feature a significant fall in free energy of the system during crystallization, and this has several consequences. For example, the ratio of the rates of attachment to the rates of detachment of complete stems during 'filling in' are high (typically 10–300 for crystallization from xylene, using formulae and values for quantities in ref. 29). Again, the lamellar thickness l is predicted to be larger than l_m (the minimum value of l) by a quantity δl (about 14 Å at low supercoolings[29]). The minimum value of l corresponds to the (bulk) free energy driving force being balanced by the fold surface free energy, and to the crystals being in that sense 'in equilibrium' with the solution or melt. Even though any growth mechanism must involve at least some finite decrease in free energy for the crystallization to proceed at a finite rate, growth on to a rough surface may involve less decrease than the 'filling in' process which would follow from nucleation. The rates of attachments and detachments of the basic unit of crystallization (see *Figure 3*(*c*)–(*e*)) must be comparable for a near 'equilibrium' roughness to be established. It is possible that in addition the ratio of the rates for complete stems may be nearer unity than in a nucleation mechanism of growth. Similarly, δl may be smaller. (Any model with δl values which are not large will give the observed proportionality $l \sim \Delta T^{-1}$, since this is contained in l_m.) Dissolution experiments for solution grown crystals could in principle test the existence of the quantity δl. The dissolution temperature T_s where the crystals dissolve very quickly is indeed several degrees above the crystallization temperature T_x, as expected for δl values in the range of 14 Å. However, even in the temperature range between T_x and T_s there is a finite rate of crystal dissolution[54] (followed by recrystallization into thicker crystals). The most straightforward interpretation of this behaviour is that the crystals are superheated below the temperature which is normally considered to be the 'dissolution temperature'. This in turn would mean that δl is small. These experiments were in a crystallization range corresponding to crystal types (i) and (ii), i.e. where facets are found but where the surface may still be rough (*Figure 3*(*d*)). In summary, the dissolution behaviour can give useful information on these questions, though it would be premature to attempt any definite conclusions. After isothermal crystallization of a polydisperse polymer from solution, some low molecular weight material remains in solution, and the details of this fractionation effect appear to be consistent with an 'equilibrium' partition between crystal and solution[55]. These observations may also be relevant to the question of how to distinguish between a nucleation and other possible mechanisms.

Finally, in connection with crystallization theories, there is important evidence to be derived from the morphology of twins, since nucleation controlled growth is known[56,57] to produce twins with enhanced growth rates along the direction where a reentrant corner exists on the crystal (this provides a nucleation site). Twins which grow with inconstant shape, as a result of this phenomenon, have been observed in crystallization from solution[57–60]. The temperatures of growth, when these were clearly established, were 64°C or less, and the molecular weights 10000 or less.

This implies that Regime I type crystallization may exist, but at very much lower temperatures than proposed previously. Twins grown at higher temperatures and from higher molecular weights[61] do not show the effects of enhanced growth in the direction of the reentrant edge, and hence growth is probably not solely nucleation controlled in these cases.

REFOLDING

It has long been recognized that about 110°C marks the lower temperature at which refolding can occur in the dried state[62]. It is possible that this process, which requires the creation of new surfaces, will occur more readily above T_R where surface *free* energy is lower.

APPLICATION TO POLYMERS OTHER THAN POLYETHYLENE

There is not scope to pursue this extensively here—the habits of crystals, grown from solution alone, of 50 different polymers have been listed[63]. Some rather speculative comments will be made about the following examples.

Lath morphology is the consequence of growth rates on one pair of (parallel) faces being very much slower than on the others. (For polyethylene by contrast the more slowly growing faces at lower temperatures, $\{110\}$, are not all parallel.) Two important polymers, polypropylene[64] and nylons[65] are known to crystallize in laths with, in both cases, the long dimensions along $\langle 010 \rangle$. (Lath crystals of polypropylene have the monoclinic unit cell modification, and the usual unit cell for nylons is triclinic.) Polypropylene also exhibits other complex habits. For both smooth and rough surfaces, the high relative rates of growth on to (010) faces indicates low relative ε_{100} values. For nylons this is entirely reasonable since hydrogen bonds are not involved. If, as in nylons, $\varepsilon_{100} << \varepsilon_{010}$ it is not unreasonable that one set of planes (the (100)) will be smooth and the other (the (010)) rough, since the melting point will be controlled by some average of ε_{100} and ε_{010}. In fact, these two sets of planes are visibly smooth and rough respectively even on the scale of the microscope. This may help to clarify the possible modes of folding: for laths of polypropylene the folds are parallel to $\langle 010 \rangle$ (the growth direction)[64], which is much more readily understandable for rough than for smooth growth faces.

The case of polyethylene oxide is interesting since extensive morphological work has been done, and it is known that the crystal faces are sometimes straight and sometimes curved[66]. A sequence of habits with temperature of crystallization has been closely correlated with discontinuities in curves of growth rate and lamellar thickness with temperature. An important difference compared with polyethylene is that the straight facets when they do exist are not all parallel to separations between nearest neighbour stems.

CONCLUSIONS

It is proposed that the growth surfaces of polymer crystals can be rough on the basis of the type of morphological evidence which has been used for non-polymer crystals. Some of the consequences of this idea are explored.

The progressive change in habit as crystallization temperature of polyethylene is raised can be explained by the (100) faces being rougher than $\{110\}$, and by an increase in equilibrium roughness with temperature on the $\{110\}$ faces. Roughness when it is large enough leads to curved habits, since steps can then be continuous across the depth of the growth face. It can be shown that the onset of curvature occurs over a narrow range of temperature even when the roughness itself varies relatively gradually with temperature. The changes in roughness may also be at least partly kinetic in origin. Roughness also increases relative rates of crystallization, which explains the increase with temperature in the proportion of the crystals grown *via* the (100) faces, as the roughness on the $\{110\}$ increases.

The roughening involves the interruption of stems as well as their complete absence.

Neutron scattering measurements on folding in polyethylene correspond to both the faceted (solution growth) regime and unfaceted (melt growth). The folding is different in these two regimes, as would be expected since the mechanism of crystallization will be different. Contrary to general expectations higher temperatures promote rough growth surfaces and more irregular folding.

Kinetic theories of crystallization of polymers require re-examination in order to take account of roughness, and a discussion is included of how this may be done. Evidence for surface nucleation events are reviewed, and it is more likely that they are more important at *low* temperatures than at high temperatures.

Several polymers other than polyethylene show promise of providing other applications of this idea.

Note added in proof

There is no explicit calculation of the lamellar thickness l in this paper, but it is clear that any model will be able to explain the proportionality $l \sim \Delta T^{-1}$ as long as δl can be shown not to be greater than a small proportion of l_m. A computer simulation has shown this to be possible for rough faces as long as kinetic barriers are included for the addition of units to one set of planes (to be published). The kinetic barriers could have several origins, including that against adding new units to the fold surfaces.

ACKNOWLEDGEMENTS

I wish to thank gratefully many colleagues with whom I have had useful and encouraging discussions. In particular I wish to mention Sir Charles Frank whose detailed comments on more than one version of this manuscript were extremely valuable, Dr B. Gyorffy, Professor A. Keller, Dr R. Evans, Dr P. J. Barham (all of the University of Bristol, Physics Department), Professor J. J. Point (University of Mons) and Dr S. G. Lipson (Haifa Institute of Technology). I wish to acknowledge Drs B. Lotz and Wittmann in connection with the importance of twins.

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