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The Size Factor in Phase Transitions: Its Role in Polymer Crystal Formation and Wider Implications [and Discussion]

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The size factor in phase transitions: its role in polymer crystal formation and wider implications†

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It is shown that under specifiable circumstances stabilities of competing phases can invert with size: specifically, that a phase which is metastable when of infinite size can become the stable one when of sufficiently small dimensions. It follows that phase development, crystal growth in particular, may start in a phase variant which becomes metastable when the new phase is fully developed. If it stays in this form Ostwald's rule of stages will seem to be obeyed, if it transforms into the phase of ultimate stability the past history of phase development becomes obliterated. In the special instance of flexible polymers, polyethylene in particular, there can be thickening growth while in the metastable 'mobile' phase (hexagonal phase in polyethylene), hence residence within this phase will determine the lamellar thickness, consequently also the final texture of the crystallizing material. Based on these considerations the two so far essentially disconnected areas of chain folded and extended chain type crystallization can be visualised within a unified frame work with new, broadened perspectives for the whole subject of polymer crystallization. In addition, the scheme creates a junction between thermodynamic (stability) and kinetic (rates) aspects of phase transitions in wider generality.

1. Introduction

(a) General

The theme of this paper is the formation of crystals. While specifically it will be concerned with polymers, and within polymers with flexible, periodically regular chains, as exemplified by polyethylene (PE), the most widely used model substance, the issues arising should be of consequence for crystallization and beyond, for phase transformations in general.

The specific focus will be on the situation where, in the course of transformation from an isotropic phase (melt or solution) to the crystal there is a choice

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(or competition) between two or more phase variants. The latter could comprise different polymorphic crystal structures or mesomorphic, including liquid crystal, states. Of course, all eligible anisotropic phase variants must be stable (i.e. possess lower free energy) with respect to the isotropic state, but in general, they cannot all be stable with respect to each other. It follows, that unless we are on a phase line in the phase diagram all but one of the alternative phase variants will need to be metastable. It has emerged lately (Rastogi *et al.* 1991; Hikosaka *et al.* 1992) that such metastable phases have important parts to play in polymer crystallization, and will be central to this paper.

One reason for the frequent appearance of metastable phases in polymer crystallization lies in the fact that polymers require substantial supercooling in order to crystallize at practically observable rates. When cooling so far below the stability limit of the stablest phase we may enter the existence régime of other phase variants of lower ultimate stability within the appropriate phase diagram. These would then appear as metastable phases instead, or in competition with the phase of ultimate stability. In fact by general experience, in such a situation these metastable phases are the first to appear and thus can become dominant features of the overall phase behaviour. This common experience has found expression long ago in Ostwald's rule of stages, which states that a transformation from one stable phase to another will proceed via stages of metastable phases whenever such metastable phases exist (see Keller *et al.* 1993). This 'rule', together with the underlying empirical experience, will receive some rational justification by the argumentation to be developed below and to be referred to (even if, due to space restrictions only in utmost brevity) at the end of this paper.

While, by the foregoings, the prominence of metastable phases is a general feature in phase behaviour it can acquire special significance in polymer crystallization because it can have conspicuous consequences for the structure and properties of the resulting polymeric materials. Of the rich canvas, presently in the process of unfolding, there is space here to lay out only one class of effects. This relates to the issue of folded versus extended chain type crystallization, and this as exemplified by polyethylene (PE), in what we feel is a central issue for polymer crystallization.

(*b*) *Background and scope*

As familiar, PE normally crystallizes in the form of lamellae containing the chains in a folded conformation (figure 1).

This we term 'mainstream crystallization' . As a principal feature, such crystals only grow laterally at unaltered constant thickness, where the latter corresponds to the fold length, with the crystal itself having the usual orthorhombic (o) crystal structure. However, PE can be obtained also in a chain extended form (figure 2) when crystallized under the rather special condition of suitably high hydrostatic pressure (see Wunderlich & Melillo 1967) to be termed here 'speciality stream crystallization'. It has been established that the requirement for the latter is crystallization in a hexagonal (h) crystal form for which pressure can open up an appropriate stable h phase régime in the pressure (P) temperature (T) phase diagram (figure 3) (Bassett 1982).

In this h phase the chains are sufficiently mobile to chain extend from their initially folded conformation, which for kinetic reasons is the primary form in which the chains attach themselves to the growing crystal. In fact, by latest emphasis

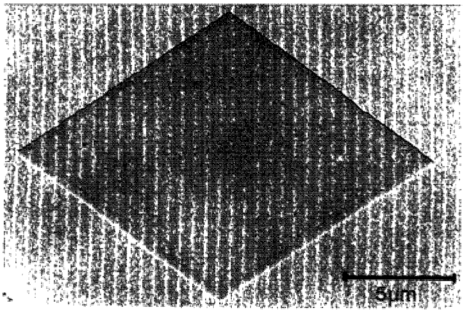

Figure 1. A monolayer single crystal of polyethylene as crystallized from solution containing the chain molecules in a folded configuration. Here the crystal grows with constant thickness which here is about 10 nm. Electron micrograph.

Figure 2. Cross-sectional view of extended-chain type crystals of polyethylene while growing in the hexagonal phase at 3.2 kbar pressure. Where in isolation, thickening growth proceeds unimpeded concurrently with lateral growth, while in the hexagonal phase, giving rise to wedge shaped profile. Electron micrograph. Scale bar is 3.5μm. (Hikosaka *et al.* 1992, by permission of Marcel Dekker.)

crystals in this 'mobile' h phase grow simultaneously in the lateral and thickness direction the resulting thicknesses successively comprising the dimensions corresponding to folded, extended and multiples of extended chains (Hikosaka *et al.* 1993). All these stages can be present in one and the same crystal when growing in isolation, the cross-sections displaying wedge shapes as in figure 2. (Note this increase in thickness is here genuine primary growth in the thickness direction which we term 'thickening growth'. This is distinct from most previously considered 'lamellar thickenings' which usually correspond to rearrangements within

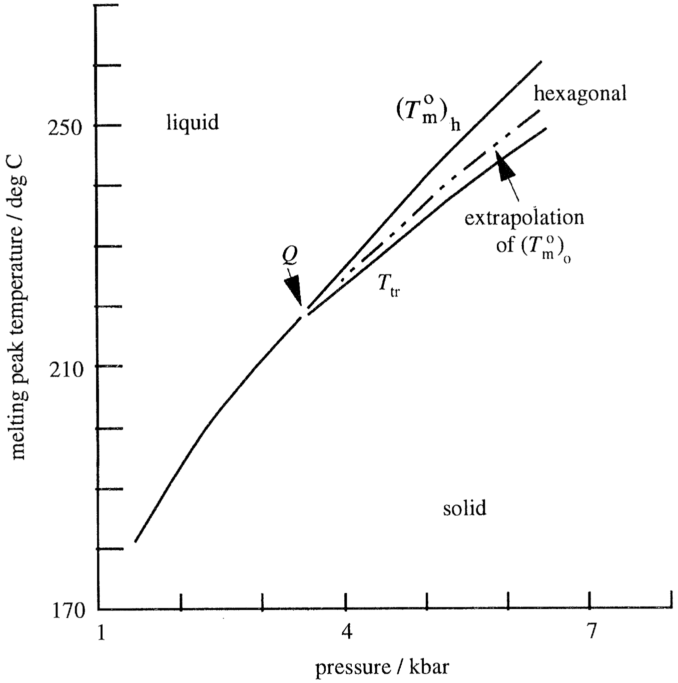

Figure 3. P–T phase diagram of polyehtylene displaying the appearance of a hexagonal (h) phase beyond the triple point (Q). $(T^{\circ}_{\mathrm{m}})_{\mathrm{o}}$, $(T^{\circ}_{\mathrm{m}})_{\mathrm{h}}$ are the melting points of the orthorhombic (o) and hexagonal (h), phases and T_{tr} the o→h transition, all pertaining to infinite phase size. (After Bassett & Turner 1974.)

already crystallized material thus corresponding to secondary crystallization, the two processes namely 'thickening growth' and 'lamellar thickening' being fundamentally different.)

As known from previous works by Bassett & Turner (1974) the h phase and the associated mode of crystal growth can occur also in the o phase régime in which the h phase is thus metastable. To this our own recent work adds the new important information, that, at least not far from the triple point in the P–T phase diagram (figure 3) – investigated in detail – this metastable h phase can be the dominant, in fact even the only mode of crystallization. At some stage the crystals growing in this (here) metastable h phase are observed to transform into the stable o variant when all growth, both lateral and thickening growth stops, or at least slows down drastically (Rastogi *et al.* 1991; Hikosaka *et al.* 1992). While other mechanisms for propagating the crystal laterally are seen to set in, the layer thickness remains confined to that pertaining to the h→o transformation. This has the important implication of a new, hitherto unsuspected cause of the limited, fixed lamellar thickness, which is the principal characteristics of the 'main stream' crystallization. To note: through this new recognition the characteristic lamellar thickness would establish itself while the crystal is in the 'mobile' h phase which, except for the h stability régime defined in the P–T phase diagram (figure 3), is usually metastable. It follows that the existence of the metastable phase, and residence time within this metastable phase during which the lamellar crystal can grow in the thickness direction, would determine the final texture of the material. Thus through the intermediary of a metastable phase there is the prospect of bringing the so far largely disconnected 'main' and 'speciality streams' of polymer crystallization under a unifying umbrella.

When comparing the relative stabilities of alternative phase variants a further factor needs to be taken count of, namely the relative size of the phases, in the present instance that of the o and h crystals. This arises from the fact that for small dimensions the phase stability is also size dependent and this size dependence will, in general, be different for different phase variants. It is to this aspect that we shall give attention in what follows. As will hopefully emerge, these deliberations will not only lead to new possibilities in polymer crystallization but will also throw new light on the role and meaning of metastable phases, should help to account for their frequent dominance and with it for Ostwald's rule of stages.

2. Size dependent phase stability

The lowering of phase (crystal) stability with decreasing size, manifest by melting (or dissolution) temperature depression, is in total generality expressed by the Gibbs–Thomson relation, which for thin lamellar crystals reduces to the equation due to Hoffman & Weeks (1965):

$$T_{\mathrm{m}} = T_{\mathrm{m}}^{\circ}(1 - 2\sigma_{\mathrm{e}}/l\Delta H). \tag{2.1}$$

Here T_{m} is the melting point of lamellar crystal of thickness l, T_{m}° is the melting point for $l = \infty$, σ_{e} is the free energy of basal surface, ΔH is the heat of fusion (per unit volume).

Note that (2.1) applies both to the o and h phases (and also to the o→h transformation temperature T_{tr}), i.e. each of these will be depressed on decreasing l but to different extents pending on the parameters involved. More precisely, the appropriate T_{m} (or T_{tr}) will be a linear function with a negative slope in a plot of T_{m} (or T_{tr}) against $1/l$. Here the slope is the appropriate $2\sigma_{\mathrm{e}}/\Delta H$ (or the appropriate difference values for the o→h transformation) and the intercept along the T axis the appropriate T_{m}° (or T_{tr}°), the value for $l = \infty$, i.e. the true equilibrium melting (or transformation) temperature. Now for PE at atmospheric P, where h is metastable $(T_{\mathrm{m}}^{\circ})_{\mathrm{h}} < (T_{\mathrm{m}}^{\circ})_{\mathrm{o}} < (T_{\mathrm{tr}}^{\circ})$. (Here T_{tr}° is virtual, hence unrealizable.) Thus the possibility arises that the $(T_{\mathrm{m}})_{\mathrm{h}}$ against $1/l$ and $(T_{\mathrm{m}})_{\mathrm{o}}$ against $1/l$ lines will intersect in which case the T_{tr} against $1/l$ line will also intersect, the intersection of the three lines being at the same point (Q) in the T against $1/l$ plane (figure 4) (treating a three-component system as a superposition of two two-component ones with one component common to both, an approximation which should not affect the qualitative message we intend to convey).

From (2.1) the condition of intersection is clearly

$$(\sigma_{\mathrm{e}}/\Delta H)_{\mathrm{h}} < (\sigma_{\mathrm{e}}/\Delta H)_{\mathrm{o}}. \tag{2.2}$$

In figure 4 the bold lines, including dashed and dotted, represent the demarcation lines corresponding to stable phases as a function of $1/l$, hence phase size. We shall denote such a representation 'phase stability diagram' (reserving the notion 'phase diagram' for infinite phase size as customary in thermodynamics).

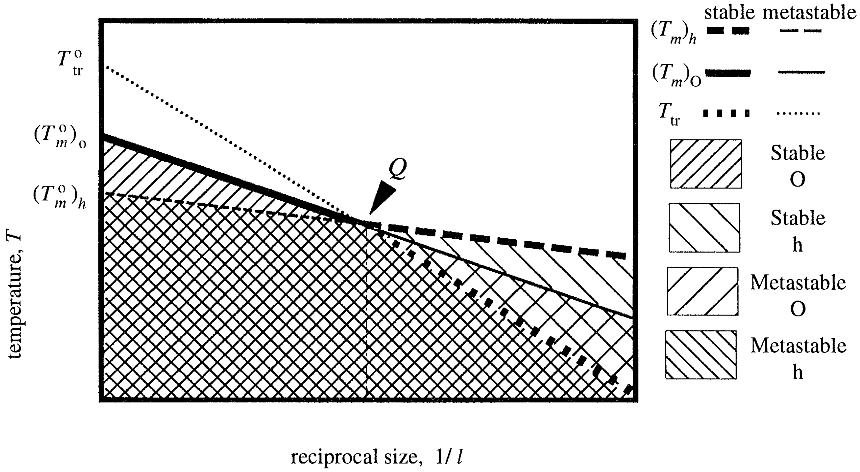

Figure 4. Temperature (T) against reciprocal size ($1/l$) 'phase stability' diagram, displaying phase stability inversion with size. Subscripts refer to phases in polyethylene (o, orthorhombic; h, hexagonal; tr, h→o transition). Bold lines (continuous, dashed and dotted) delineate the 'stable' phase régimes including the triple point (Q). For complete key to lines and shadings see insert.

In addition to the bold lines for stable phases we have their metastable and virtual (weak line) extensions with their customary significance in true equilibrium phase diagrams.

It will be apparent from a phase stability diagram such as figure 4 that the stability of the h and o phases (or in general metastable and stable phases) can invert with size, i.e. a phase which is metastable for infinite size could become the stable one for sufficiently small size, which in our case of PE would mean that the h phase would be stable for lamellae which are sufficiently thin (even at atmospheric pressure). The limit of stability is defined by the 'triple' point Q, i.e. by the temperature T_Q and size l_Q. Clearly, the above phase inversion relies on the condition that inequality (2.2) holds. Quantitative analysis shows that this should in fact be so for the case of PE (Keller *et al.* 1993). More far ranging considerations imply that inequality (2.2) is in fact quite general, even if not a strict necessity, in fact it is implicit in Ostwald's rule of stages. It follows that size dependent phase stability inversions are expected to play a significant part in phase transitions in general and in polymer crystallization in particular.

3. Crystal growth: new possibilities

We proceed to treat crystal growth (or in broadest generality phase growth) in terms of a phase stability diagram such as figure 4. Consider figure 5*a*.

Here isothermal growth is represented by horizontal arrows pointing towards $1/l = 0$, i.e. infinite size, chosen to lie in the two principal temperature regions, one above, the other below T_Q, denoted by A and B respectively. In both cases, while in the liquid (L) stability region, the new phase entity is transient until the size ($1/l$), corresponding to a phase line at a specified T, is reached. At this point the new phase (crystal) will become stable and capable of continuing growth. As seen, in region A it passes straight into the region of ultimate stability. There is a subdivision within A, according to whether the metastable phase (h in PE)

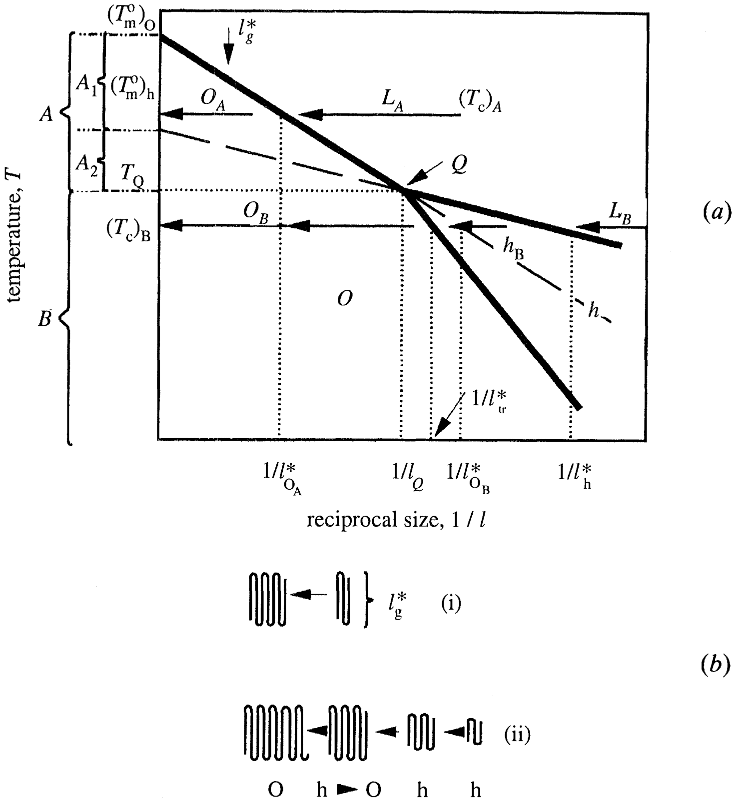

Figure 5. (*a*) Phase growth in terms of a 'phase stability' diagram as figure 6 with notation referring to crystal forms (h and o) in PE with L standing for the melt (liquid). The two sets of horizontal arrows, pointing towards $1/l = 0$, denote isothermal growth pathways at the two selected (crystallization) temperatures (T_c), here chosen to be in the two temperature régimes A and B. (*b*) Schematic representation of chain folded polymer crystal growth (for the example of PE): (i) region A leading to lamellae of a specific restricted thickness (l_g), in which they continue to grow laterally through direct growth in phase o; (ii) region B where crystals arise in the h phase and develop by simultaneous lateral and thickening growth with the latter stopping (or slowing down) on h→o transformation and/or impingement (up to the stage of impingement crystals will be wedge shaped; not represented in sketch).

can exist (here as intrinsically metastable, A_2) or not (A_1), a point not to be enlarged upon at this place. In region B, the first crystal appears in a form (h in PE) which is only stable within a limited size range at and beyond its genesis, but is metastable for larger dimensions (as is the h phase in PE). It continues to grow in this phase until reaching the size $1/l_{tr}^*$) representing the boundary between the two phase régimes in T–$1/l$ space. After traversing this boundary two possibilities arise: (i) the crystal stays in the form of its inception, hence becomes metastable and remains so in the final product, or (ii) transforms into the phase of ultimate stability somewhere between l_{tr}^* and $l = \infty$ in the course of its growth. In case (i) Ostwalds rule of stages will appear to be obeyed, while in case (ii) the previous history of phase development, i.e. that the crystals started life in a different phase, will be obliterated (except for our polymers where the texture at the stage of transformation remains preserved; see below).

In order to apply the above to chain folded crystallization in polymers (here PE) we take l, the phase stability determining dimension, as the lamellar thickness. Within region A the first crystal to appear will be in the o phase, and growth will proceed only up to a limited l, (l^*_{g}), from whereon further growth will only be in the lateral direction with this constant l (figure 5*b*(i)). This mode of growth embraces the entire presently known and accepted body of material on chain folded polymer crystallization. In region B growth will start in a different phase (h in PE) with a minimum stable lamellar thickness, which will increase in the course of continuing lamellar thickening growth (figure 5b(ii)), which it can do readily in view of the high chain mobility in this phase. Beyond a certain value of l, within the newly attained o stability régime, h→o transformation will take place when, within the much less mobile o phase, the phase of ultimate stability, further growth will slow down or, particularly in the case of thickening growth, will practically come to a halt. The process just outlined is a new possibility not envisaged before. It has two salient consequences.

First, it would practically lock in the thickness at which h→o transformation has taken place thus imparting the characteristic thin lamellar feature to polymer crystals formed from flexible chains. Secondly, it would provide a new, alternative explanation for the commonly observed limited lamellar thickness, the principal characteristics of polymer crystallization, with potentially far reaching consequences.

4. The P–T–$1/l$ phase stability diagram and its consequences

Next we consider the connection between the T–$1/l$ phase stability diagrams of figures 4 and 5 applying to situations where the h phase (focusing on the case of PE) is metastable at infinite size, hence metastable in the sense of a usual phase diagram, and the P–T phase diagram of figure 3, which apply to infinite size, and reveals a truly stable h régime at elevated pressures. This can be provided by a three-dimensional P–T–$1/l$ phase stability diagram such as figure 6.

Here, as seen, there is a continuous volume of stable h phase in P–T–$1/l$ space which should be the complete description of the system involved, with a 'triple line' (readily calculable (Keller *et al.* 1993) forming the lower boundary of the h stability régime. Crystal growth can be represented in the same way as in figure 5. For the most usual case of isobaric growth we need to take sections with $P =$ const. and explore isothermal phase development, as done in the preceding section, following horizontal arrows along $1/l$. There will be a major distinction as to whether $P > P_Q$ or $P < P_Q$ ($P_Q \equiv P$ at triple point for $l = \infty$).

1. Section at $P > P_Q$. Here we shall have a stable h phase interval even for infinite l. Thus for a range of crystallization temperatures the crystals will appear in the h phase (as before) but now will stay in this phase as a stable phase up to macroscopic size (l_∞). For our polymer this means that it starts as a chain folded crystal in the mobile h phase and will grow by thickening growth to increasing thicknesses up to full chain extension and beyond, until terminated by impingement on other growing crystals. This is the customary experience in high pressure crystallization of polyethylene (Bassett 1982).

2. Sections at $P < P_Q$. Here the general form of the T, $1/l$ section will be as in figures 4, 5. For P close to P_Q there will be a small A region which, however,

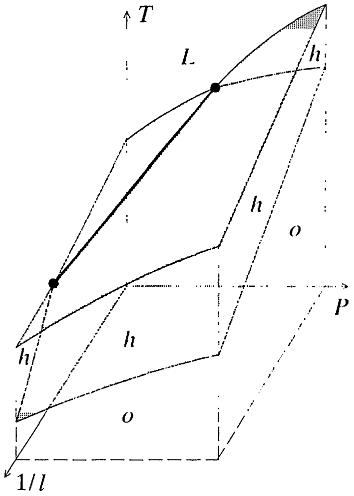

Figure 6. Combined P–T–$1/l$ 'phase stability' diagram. This, in case of PE, would create continuity between the pressure and (restricted) size generated mobile h phase. Isobaric crystal growth can here be represented as in figure 5a) for any T–$1/l$ section at a chosen constant P (including atmospheric pressure). (Keller 1993; by permission of Kluwer Academic Publishers.)

will become larger for sections at increasingly lower P; correspondingly, T_Q will be shifting to increasingly lower temperatures as compared with T_{m}, and so will region B.

At this point we invoke some kinetic considerations. When region A is small we are close to $(T_{\mathrm{m}}^{\circ})_{\mathrm{o}}$ throughout region A, hence at small supercoolings. Consequently, crystallization will be slow, in fact for a sufficiently narrow A region it may become unrealizable in practise. In such a situation crystallization, if it is to take place, will need to be in region B, hence in the case of PE in the h form alone. On the other hand if region A is very wide, region B will lie far below $(T_{\mathrm{m}}^{\circ})_{\mathrm{o}}$. To reach region B the system will need to be cooled through region A first, when depending on rate conditions, the system may crystallize in the phase of ultimate stability before it reaches T_Q. In this situation region B would become kinetically inaccessible. Referring to PE, in such a case the h phase will play no part in crystallization.

5. Applicability to polyethylene

The above scheme follows directly from basic thermodynamics and relies only on the validity of the Gibbs–Thomson equation. In that case, if inequality (2.2) applies, the rest follows. How far a given system conforms to the scheme depends on the input parameters, i.e. (T_{m}°), ΔH and σ_e for the two phases involved which have to be assessed numerically in each case.

For polyethylene, the most widely studied model system, the two phases are o and h. Here the situation as under (1) in the preceding section (i.e. for $P > P_Q$), is well established and has been the starting point for the present considerations. The main issue is whether considerations for case (2) (i.e. for $P < P_Q$) also apply, in particular, whether there is any mode B crystallization under the most widely

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studied circumstance at atmospheric pressure. If so, much of our present thinking would need to be reconsidered and past results re-evaluated.

The first question which arises is whether phase stability diagrams such as figures 4, 5 apply at atmospheric pressure, i.e. whether a 'triple point' temperature T_Q, hence region B, exists at all. If the answer is 'yes' the second question is the value of T_Q itself.

Computations involving a systematic variation of input parameters (Keller *et al.* 1993) have shown that for all input values which were within the limit of plausibility, a T_Q, hence region B, does exist, and further that T_Q is in the range , or just above the range, where PE crystallizes at measurable rates from the melt at atmospheric pressure (122–130 °C). It follows that PE, as normally crystallized, could well do so in mode B, or at least mode B may compete with mode A, an issue calling for further attention. However, for crystallization from solution (at atmospheric pressure) T_Q is much lower, at around room temperature. It follows that here, by the above argument, region B is kinetically inaccessible, hence crystallization should proceed by mode A, as in fact has always been envisaged in the past. The origin of the difference between the melt and solution case is readily envisaged. Namely, it can be shown from simple free energy considerations, that not only is $T_{\rm m}$ lowered when going from melt to solution (melting becomes dissolution), but in addition, the intervals between the melting (dissolution) temperatures of polymorphic phases widens, thus widening region A with a consequent depressing of region B.

In fact at the time of writing important experimental evidence has emerged in support of the scheme here presented. By X-ray evidence (using a synchrotron source) a distinct new phase régime could be identified in PE just below the melting point in the case of the thinnest crystals available (solution grown with $l = 14.5$ nm). This new phase did not appear for the thicker crystals with $l = 23$ nm where the usual o crystals passed over directly into the melt on heating. The above is consistent with the newly found phase régime being (small) size limited as specified by the area denoted as 'stable h' in figure 4. The new phase itself was manifest through the abrupt disappearance of all except the 1 1 0 reflexion of the o phase. A single reflexion in that spacing range is at least consistent with it being 'the' hexagonal phase. Most significantly, its appearance was found to be accompanied by pronounced lamellar thickening consistent with it being a 'mobile' mesophase in accord with the main theme of this paper.

6. Connections with kinetics

The first and most general connection with kinetics arises from the meaning of the phase stability diagrams themselves. Namely, the phase lines in the T–$1/l$ diagrams represent the size at which a particular phase can be stable at a given T, which in fact is the size of the critical nucleus (l^*). Thus, when crossing a phase line along one of the arrows in figure 5 we are in fact traversing the size of the corresponding l^*, hence surpassing the principal activation barrier in the kinetics of crystal (or in general phase) growth. The connection between the purely thermodynamic considerations implicit in phase stability diagrams and that of the kinetics of the phase transformation will therefore be apparent in all cases where nucleation is the rate determining step. This is always the case for the emergence of the new phase (primary nucleation), but will also apply to the growth of the new phase on condition that the growth is controlled by the free energies of interfacial attachment (limited by surface nucleation and/or entropic barriers).

There is a further important sequel to the connection between thermodynamic considerations, as arising from the preceding phase stability diagrams, and the kinetics of the phase transformation, as arising from nucleation as the rate controlling step. For sake of brevity here only the conclusion can be quoted from our more comprehensive publication (Keller *et al.* 1993) and a preceding preview (Keller 1993). Accordingly, in the case of competing phase variants (e.g. polymorphs in crystal growth) the phase which appears and develops first will be the one which is stable down to the smallest size (implicit in the phase stability diagrams), and that this same phase variant will, in addition, develop fastest. As out of two or more phase variants in general only one can be stable, with the rest being metastable (as referred to infinite size), it follows that the above assertion also embodies the kinetic competition between stable and metastable phases and, specifically, the long standing general experience that metastable phases usually evolve faster than the stable ones. It can be shown that this also leads to a combined kinetics–thermodynamics based justification of Ostwald's rule of stages within the appropriate, quantitatively definable boundaries where the stage rule can be expected to hold.

7. Limitations of the treatment

It will have become apparent that the argumentation presented in this paper should have relevance to the wider sphere of phase transformations in general, in addition to its potential consequences for the specific subject of polymer crystallization. In all cases it relies on the validity of the Thomson–Gibbs equation. The lowest size to which this equation still applies is an issue of present topicality in condensed matter physics (Buffat & Borel 1979) and is beyond the scope of this paper which, as presented, sets no lowest size limit. Nevertheless, within the range of general applicability of (2.1) some limiting considerations arise.

We may consider the above issue in two stages:

(i) While retaining equation (2.1) as formulated for lamellae we scrutinize the appropriateness of the use of a single constant for σ_e referring to the basal surface. Clearly, as l increases, at some stage the type of the basal surface will change from one corresponding to folded into one with extended chain characteristics with the associated change in σ_e (in addition to much smaller changes with temperature within one and the same surface type). The above will have no effect on the conceptional aspects of our argument but will affect the actual numerical values according to whether the h→o transformation occurs in the folded or extended régime of thickening growth.

(ii) When the developing crystal is still small laterally the lamellar approximation itself will not yet hold, in which case l and σ will correspond to mean values of size and surface free energies respectively. As lateral growth is very much faster than thickening growth (Hikosaka *et al.* 1993) this will only have an effect (namely alter the actual numerical values and the slope in figures 4 and 5) at or immediately after primary nucleus formation, a stage the crystal will soon outgrow, beyond which l becomes the lamellar thickness and σ_e the surface free energy as throughout the preceding discussions. Clearly, the initial stage just indicated is an issue on its own requiring separate attention. If, however, lateral growth is frustrated, say by impingement due excessive nucleation density, this lamellar growth stage may not be reached with significant consequences for the present scheme. This is a situation which could be relevant for crystallizations at very high supercoolings.

References

Bassett, D. C. 1982 The crystallization of polyethylene at high pressures. In *Developments in crystalline polymers* (ed. D. C. Bassett), pp. 115–151. London and New Jersey: Applied Science.

Bassett, D. C. & Turner, B. 1974 On the phenomenology of chain extended crystallization in polyethylene. *Phil. Mag.* **29**, 925–955.

Buffat, Ph. & Borel, J. P. 1976 Size effect on the melting of gold particles. *Phys. Rev.* A **13**, 13–2298.

Hikosaka, M., Amano, K., Rastogi, S. & Keller, A. 1993 Lamellar thickening growth of an isolated extended chain single crystal of PE. In *Crystallization of polymers* (ed. M. Dosière), pp. 331–336. NATO ASI series vol. 405. Dordrecht, Boston and London: Kluwer.

Hikosaka, M. Rastogi, S., Keller, A. & Kawabata, H. 1992 Investigations on the crystallization of polyethylene under high pressure. *J. Macromol. Sci. Phys.* B **31**, 87–131.

Hoffman, J. D. & Weeks, J. J. 1965 Melting process and the equilibrium melting temperature of polychlotrifluoroethylene. *J. Res. natn. Bur. Stand.* A **66**, 13–28

Keller, A. 1968 Polymer crystals. *Rep. Prog. Phys.* **31**, 623–704.

Keller, A. 1993 A unifying scheme for polymer crystallization. In *Crystallization of polymers* (ed. M. Dosière), pp. 1–16 NATO ASI Series vol. 405. Dordrecht, Boston and London: Kluwer.

Keller, A., Hikosaka, M., Rastogi, S., Toda, A., Barham, P. J. & Goldbeck-Wood, G. 1993 An approach to the formation and growth of new phases with application to polymer crystallization. *J. Mater. Sci.* (In the press.)

Rastogi, S., Hikosaka, M., Kawabata, H. & Keller, A. 1991 Role of mobile phases in the crystallization of polyethylene. *Macromolecules* **24**, 6384–6391.

Wunderlich, B. & Melillo, L. 1968 Morphology and growth of extended chain crystals of polyehtylene. *Makromol. Chem.* **118**, 250–264.

Discussion

A. H. Windle (*University of Cambridge, U.K.*) In alloys of aluminium containing a few percent copper, there is a particular example of the Ostwald stage rule in which precipitates of an intermetallic compound are seen to move through a sequence of different crystal structures and compositions as they nucleate and grow. The precipitates, having structures which are intrinsically less stable than the equilibrium one, are examples of mesophases; although metallurgists don't call them that. These precipitates are of technological importance in that they are hardening the component used in most high strength aluminium alloys. The standard explanation for the occurrence of non-equilibrium crystal structures when the precipitates are small, is that the interface energy is a dominating factor because of the large surface/volume ratio. Hence, the crystal structure which will appear is that for which the sum of the volumetric and surface free energies is a minimum. In other words, it can be a structure that is less stable than the equilibrium Cu Al_2 precipitate in volumetric terms, but will occur in a small precipitate if its interface energy is lower than that of Cu Al_2 by a sufficient amount.

The principle of the stabilization of mesophases for small crystal sizes is a general one. Another example of crystalline mesophases is seen in a well-known thermotropic liquid crystalline system, that based on random copolymers of hydroxy benzoic and hydroxy naphthoic acids (the Vectra series of polymers). In this case a mesophase, which has a pseudo hexagonal crystal structure and is seen at high temperatures at ambient pressures in both of the parent homopolymers, is stabilized in thin, sequence segregated crystals which form in the random copolymer. The chain packing in the mesophase appears to be the same density as that of the liquid crystalline phase to which it is intimately connected, indeed the densities are so similar that it is impossible to obtain any discrete small angle X-ray peaks corresponding to the long period. The strain energy associated with the interface is thus minimal. By comparison, the 'stable' orthorhombic phase is some 5% more dense, and thus could only form with considerable strain energy at the crystal surfaces across which there is chain continuity to the liquid crystalline phase. The mesophase crystal thus appears to be stabilised because of its lower interface strain. Annealing below the melting point enables it to transform slowly to the equilibrium othorhombic structure, a process that can be followed by the appearance of small angle diffraction peaks. However, in this case the transformation does not appear to be triggered by an increase in crystal thickness in the growth direction, as is seen in polyethylene. Instead, it is possible that the mismatch strain is relieved by the segregation of chain ends to the interface.

Thus, in relation to the mesophase in polyethylene stabilized at ambient pressures for small crystallite thicknesses, one might look for a distinctly lower fold surface energy as its raison d'etre. Is there independent experimental evidence for this lower surface energy, or is it possible to calculate it?

A. KELLER. I was interested to hear of examples of the basic phenomenon in question also in areas of other materials. This gives confidence in the broeder generality of the theme I was presenting. Of course it is ultimately the low surface free energy that is responsible for preference of metastable phases whether due to actual stability inversion (with consequences for rates) or whether by rate considerations alone. In polymer crystals the focus of attention is on the fold surface. A calculation, due to M. Hikosaka, of the relative fold surface free energies of the two competing phases (orthorhambic and hexagonal) in polyethylene is contained (as Appendix III) in our joint comprehensive paper.

E. L. THOMAS (*University of Bristol, U.K.*). In your description of the thickening of polyethylene crystals you focused on the role of the axial chain mobility within the crystal. Please comment on how constraints outside the crystal, for example entanglements, tie molecules, etc., affect the chain mobility.

A. KELLER. I made no attempt to quantify the axial chain mobility for the purposes of this presentation. Such quantification is contained by the theoretical papers of M. Hikosaka, quoted in the paper. But even that is for the intrinsic mobility of the chain within the crystal without external constraints. Nevertheless ignoring such constraints, at least for rearrangement within the crystal, may not be too much of an approximation. Namely, by all evidence on refolding such rearrangement occurs by localized movements of fold stems without involving chain portions totally outside the body of the crystal where constraints are likely to be located. All this is of course for chain portions in the crystal already: arrival on new chains and their attachment of course is bound to be affected, but this is outside the scope at this stage.

D. C. Bassett (*University of Cambridge, U.K.*). We have recently found that a new type of polyethylene does not form the hexagonal phase at 9.4 GPa but is constrained to crystallize as very thin lamellae and, therefore, directly into the orthohombic phase. This material has 9.6 butyl groups per 1000 C atoms and was synthesised using a metallocene or single-site catalyst. It is believed that the branches are place regularly along the chain, a claim with which our results are consistent.

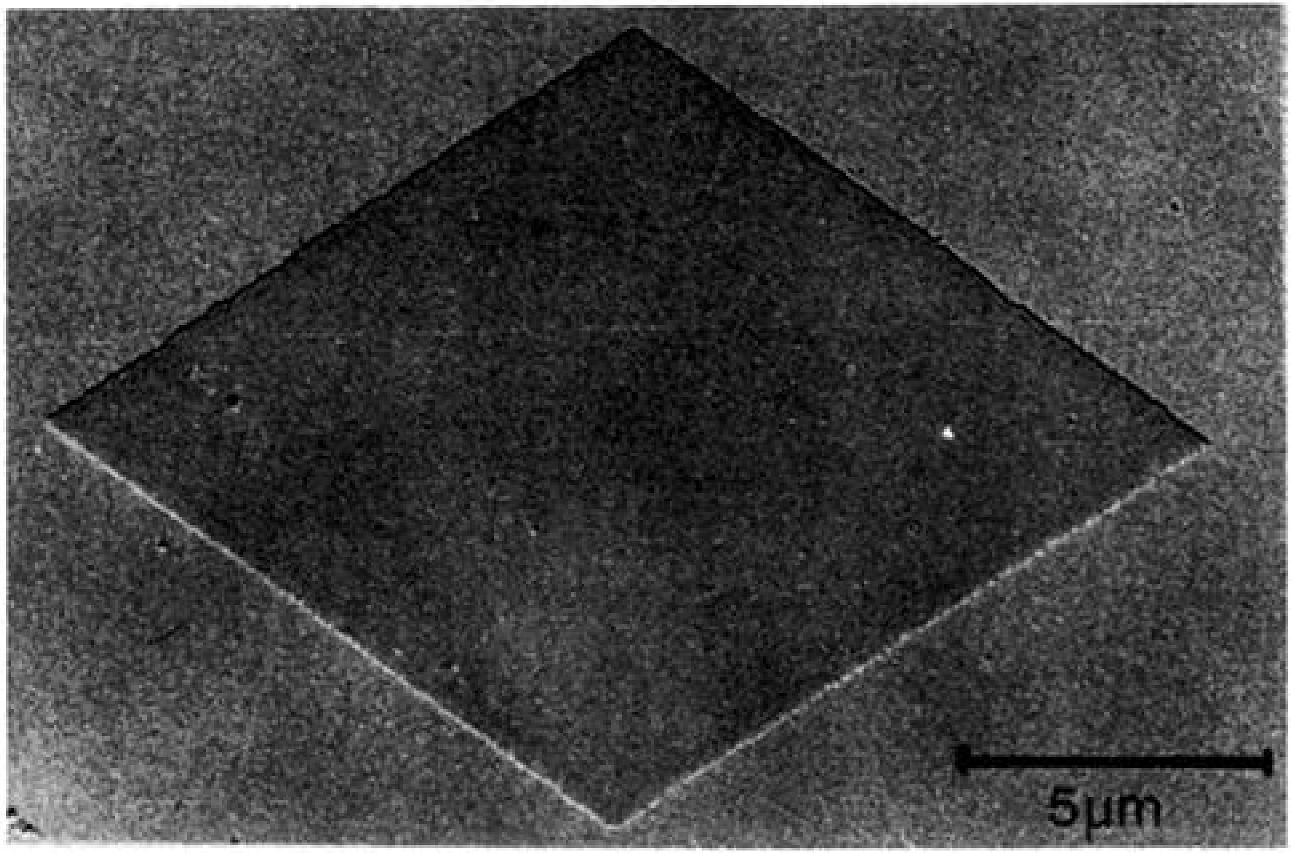
Of major interest is that the peak (atmospheric) melting point of this polymer, 117 °C, is the same both before and after crystallization at 0.5 GPa. Moreover, despite unambiguous evidence of recrystallization at 0.5 GPa, its morphology then consists entirely of banded spherulites; previously shown to indicate direction formation of the orthorhombic phase from the melt (Bassett & Turner, *Phil. Mag.* **29**, 285–307 (1974)). This behaviour is unprecedented in our experience and is in marked contrast to that of a random copolymer with the same average butyl branch content (but synthesised by Ziegla–Natta catalysis) treated identically. For this random copolymer, high pressure crystallization produces, in accordance with previous experience, multiple populations of lamellae, the thickest of which had crystallized directly into the hexagonal phase, the remainder sequentially directly into the orthorhombic phase. This is attested by a multiply peaked atmospheric melting endotherm, with the highest peaks substantially above that of the starting material and a mixed morphology in the sense of Bassett & Turner (*Phil. Mag.* **29**, 285–307 (1974)).

These different behaviours stem from the exclusion of butyl groups from lamellae and reflect the differing distributions of branches in the two copolymers. A regular distribution would place each branch 104 C atoms apart, i.e. 130 Å, a value which agrees with the 25 K of melting point depression and also thicknesses resolved in the electron microscope for the metallocene-synthesized polymer but is much too low for direct crystallization into the hexagonal phase. This follows because a lamella must always have crystallized below its melting point. The data of Bassett & Turner (*Phil. Mag.* **29**, 925–955 (1974)) show that the changeover from hexagonal to orthorhombic crystallization occurs at *ca.* 15 K of supercooling with respect to the hexagonal/melt transition). For the regular copolymer, crystallization would be expected at around twice this figure or more and must, therefore, be directly into the orthorhombic phase. On the other hand, in the random copolymer, the longest inter-branch lengths will allow crystallization at lower supercoolings and directly into the hexagonal phase followed for moderate and shorter branch separations by a sequence of lamellae crystallizing directly into the orthorhombic phase, in agreement with the observed morphologies and melting points.

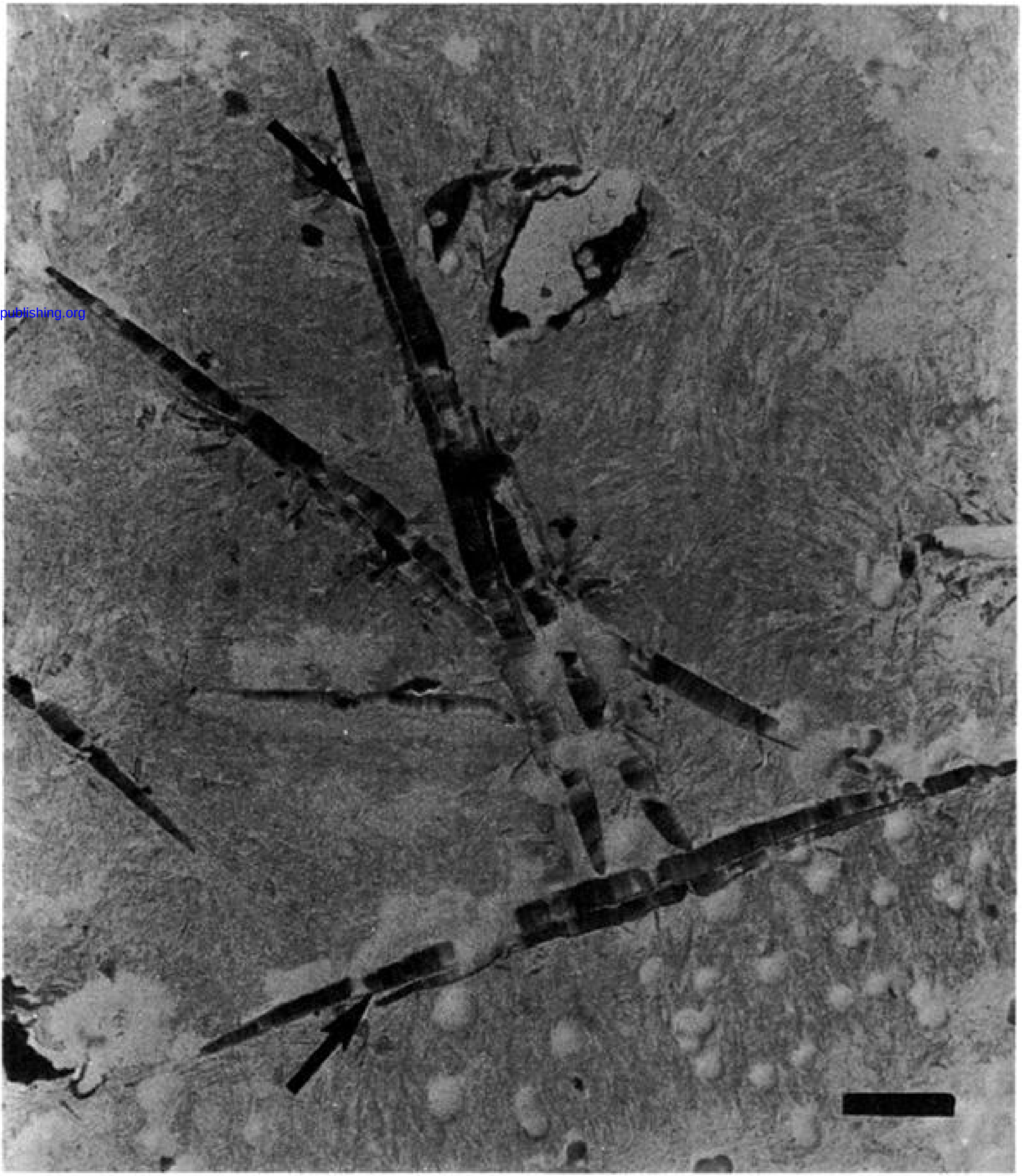
This explanation is akin to that given by Bassett & Turner (*Phil. Mag.* **29**, 925–955 (1974)) which also accounted for their extensive data (Bassett & Turner

Phil. Mag. **29**, 285–307 (1974)) showing the conditions below the triple point at which crystallization of the hexagonal phase gave way to that of the orthorhombic. Moreover the emphasis on kinetics is especially appropriate for polymers which show particularly clearly that those lamellae which form are those which grow fastest, not those which are most stable. Although the stability criteria implicit in the combination of the Gibbs–Thomson equation and the polyethylene phase diagram is explicit, it will still be the case that those crystals which occur will be those which grow fastest. Data in the two papers cited show the conditions when hexagonal crystallization of polyethylene gives way to the orthorhombic in practice.

A. KELLER. I was interested to hear of the experiments with the new polyethylene having strictly regularly spaced butyl groups at closely 100 C atoms along the chain. The stability determining 'size' of the crystals is not necessarily the thickness of a layer. It happens that in a conventional polyethylene crystal, where the layers splay apart and thus have identities of their own, the layer thickness is the stability determining factor. However, in a usual alkane, say $C_{32}H_{66}$, the basic layer thickness comprising the extended chain does not represent the crystal size but the lattice period; the true crystal size in the thickness direction is very much larger and comprises many such layers and in fact may cease to be a stability determining factor. The new polyethylene may well represent a similar situation. Namely, the layers may be so regularly stacked that they do not define the crystal dimension but the crystallographic identity period. In that case my argument would not hold, at least in the form presented. As a reminder: we three (i.e. Professor Frank, Professor Bassett and myself) went through the same argumentation relating even to ordinary polyethylene as early as 1964, namely whether the layer thickness represents the crystal thickness or instead, a crystallographic repeat period, an issue which deserves to be recalled in the present context.



igure 1. A monolayer single crystal of polyethylene as crystallized from solution containing the hain molecules in a folded configuration. Here the crystal grows with constant thickness which ere is about 10 nm. Electron micrograph.



igure 2. Cross-sectional view of extended-chain type crystals of polyethylene while growing the hexagonal phase at 3.2 kbar pressure. Where in isolation, thickening growth proceeds nimpeded concurrently with lateral growth, while in the hexagonal phase, giving rise to wedge aped profile. Electron micrograph. Scale bar is 3.5μm. (Hikosaka *et al.* 1992, by permission of arcel Dekker.)