

CHAPTER 18

Spherulitic Crystallization in Macromolecules

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1. Introduction

Since the earliest studies of crystallization, spherulitic growth has been recognized. Well-known are the geological specimens which are eagerly purchased by tourists in desert places like Arizona, where "rock roses" and pyritic "suns" (imported from Illinois!) [1, 2] are found in large numbers in souvenir shops (fig. 1). Approximately spherical polycrystalline entities are also known to metallurgists, e.g. in cast iron. However, spherulites par excellence are usually encountered in organic materials, especially in macromolecules, both synthetic and natural. Indeed, the paradigm of bulk macromolecular morphology is the spherulite [3]. Because of its special importance in controlling the physical and mechanical properties of semi-crystalline thermoplastics, it is in macromolecules that the study of spherulitic growth has become paramount. Much of our understanding of the details of spherulitic crystallization comes from studies of these man-made materials. Spherulites can also be encountered in natural polymers, such as DNA and other polypeptides (fig. 2). For an excellent descriptive review on the phenomenon of spherulites and optical behavior the paper by Morse and Donnay [4] is strongly recommended.

As can be seen in figs. 1 and 2, spherulites are approximately radial arrays of long thin crystals (lamellae), the first crystals having been nucleated at a central point. However, in order for the fully formed disc or sphere to be generated it is essential that new crystals be continuously nucleated as the radius increases. From the earliest studies of spherulites [2] it has been recognized that there are two essential forms of spherulite. The first is that already described, of tight radial arrays of crystals (fig. 1a). The second is represented in fig. 1b and is a less compact form in which interstices between the crystals are filled with some other materials. In the case of macromolecules this form corresponds closest to what are known as *axialites*. It has also been recognized for a long time that spherulites are not dendritic in nature as they are not usually generated by crystallographic branching. In the majority of cases the branching process is non-crystallographic. There can be exceptions where crystallographic branching occurs as a contributory process. An understanding of spherulitic growth requires that the three basic processes of initial nucleation, crystal growth and continuous crystal generation be understood separately. Furthermore, the reasons why crystals that are initially growing parallel to one another should splay apart and grow in a nonparallel fashion need to be determined.

In addition, a fundamental question which needs to be answered in most cases is why the spherulite forms in the first place, instead of a single grain growing in the conventional manner to generate a polycrystalline material. Early speculations on the reasons for the formation of mineral spherulites (such as lithoidal rhyolite) were based on their being encountered in obsidian, or other glasses, and it was suggested that the diffusion of vapours into the glass caused the crystallization to occur [5]. Such explanations, of course, were not based on scientific studies of the process and now that such studies are possible, but difficult, interpretations have changed [6]. In the cases of inorganic materials, whether mineral or metallic, the basic reasons may vary from one material to another [7]. In many cases the primary cause lies with chemical impurities and the demonstration of that source for some materials has been quite graphic (see, e.g.

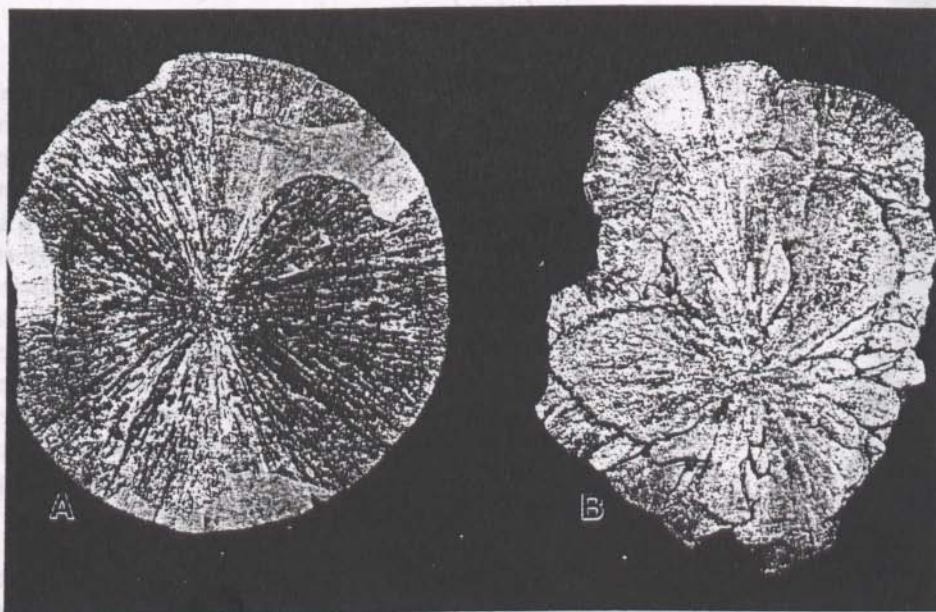


Fig. 1. The two basic types of aggregation found in spherulites, illustrated using pyritic suns. (a) Tight arrays of narrow radial lamellae; (b) open arrays of wide lamellae.

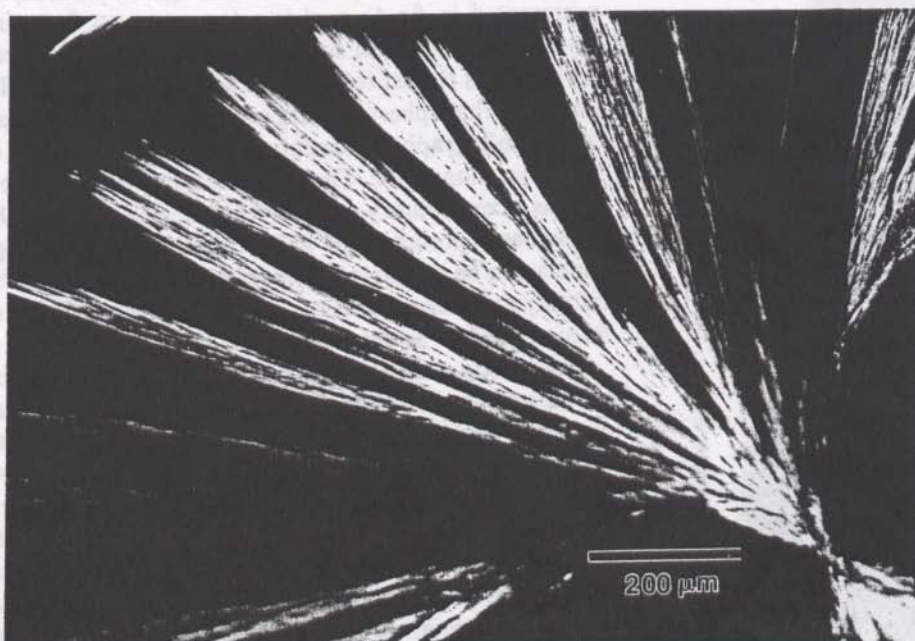


Fig. 2. Spherulitic growth of DNA from the gel state [119].

[8]). Indeed, it has generally been assumed that impurities need to be present to generate spherulites, and that indeed their formation may be induced by the addition of impurities [9]. It now seems clear that the presence of heterogeneous nuclei play a critical role in the generation of spherulitic and related textures in minerals [10]. However, one study of spherulites in antimony concluded that stress was necessary to the nucleation of groups of crystals, rather than single crystals or conventional polycrystals [11]. These authors also showed that nucleation involved the presence of a hole, an occurrence that is well established in polymer thin films [12], but not essential for spherulitic formation in macromolecules. In the case of graphite spherulites in cast irons and related alloys, it was suggested that spherulites could only form when sulphur was absent [13]. In this case stress was also invoked as a mechanism to generate the folded fan-like crystals which were found to compose the spherulite. So it does need to be recognized that the reasons for the occurrence of spherulites may vary considerably from material to material.

When macromolecules and hydrocarbons are considered, intensive studies using polarized microscopy of the growing spherulites have made it a little easier to obtain quantitative definitive data that stand up to the test of theory. Macromolecules and similar shorter molecules do have the unique common feature that the lamellar crystals which make up the spherulite are a natural form of the crystal caused by *inherent limitations in the molecules* themselves. Any real understanding of the phenomenon, as in all cases of crystal growth, comes from observation of the growth kinetics of the individual crystals and the development of models that predict all aspects of the observed behavior, including the crystal shape, the growth faces, the rates of linear growth and the dependence of all these parameters on temperature and pressure. Why lamellar crystals of macromolecules should be found in a spherulitic aggregate is another matter. The early explanations, which held up for over two decades [14, 15] invoked the effect of impurity concentrations on diffusion. This very sound theory was based on constitutional supercooling (see [16], for a review) which had been derived for metallic systems. Expressed very simply it comes down to the suppression of melting point by impurities, or in other words the very well known principle from physical chemistry of the depression of freezing point in mixtures. However, the advent of new methods of preparation for electron microscopy (see, e.g. [3, 17]) has shown that although diffusion of impurities is undoubtedly a factor in the generation of spherulitic textures, it does not account for the detailed mode of formation of a spherulite. It is somewhat ironic that a well-developed theory based on solid scientific logic should be proven not to apply to polymers at a time when it has been found to apply well to minerals [6, 7, 18]. However, there can be little doubt that when impurities are present in a material, and of sufficient concentration at the growth front, then the Keith and Padden theory is perfectly appropriate.

In this chapter the general phenomenology of bulk spherulitic growth will be discussed first, together with an analysis of the bulk growth kinetics, including nucleation and growth processes. Then the actual form of the individual crystals that comprise the spherulite will be discussed and the reasons for the known dependences. This will be followed by an analysis of the growth kinetics and the models which account best for the behavior. The mechanisms by which new, or "daughter" crystals are

generated will then be considered in the context of the spherulitic morphogenesis. Throughout, the emphasis will be on the crystals formed by synthetic macromolecules and how the behavior is influenced by the molecular structure and by the length of the molecule.

Many of the concepts that apply, and are understood best, simply do not translate to the non-macromolecular world of elemental and inorganic substances. The reason for this is simple, the atoms that make up macromolecules are joined together to form *strings which survive the melting process*. Hence, unlike the metallic and mineral systems, the generation of a crystal involves the rearrangement of the pre-formed strings to form the crystalline state. Naturally, this process is much more complicated than that of packing together spheres or sphere-like objects. The string has its own characteristics, which can range from wire-like stiffness to rope-like flexibility to wet spaghetti-like tangled mattedness. Additionally, the strings can have both short or long branches, or even may be joined together into one continuous three-dimensional grid [19, 20]. Each string may have a chemical microstructure which varies along its length in a highly ordered or a random fashion, all determined by the details of the process by which it was synthesized. Despite this richness of diversity the basic concepts of nucleation and growth apply ubiquitously to all systems. Of paramount importance to the commonality of behavior is the presence of the lamellar crystal and the manner in which the molecule adds to the crystal.

A first glance at any table of the unit cells formed by polymers tends to generate a phobia for all things polymeric because of the complexity and diversity of the structures generated. However, it should be recognized from the outset that the complexity is a result of the rules of crystallography. In fact polymer crystals have a remarkably uniform method of general packing, which when understood, by even the novice, cures the phobia. The simplest way to envision a polymer crystal is to recognize that each chain has a lowest-energy form, which is normally only attained in the crystal. These lowest-energy forms invariably generate cylindrical shapes, which then pack together laterally to form the crystal. Of course, this is an oversimplification since the actual chain shape will also be influenced by the lateral packing, however, in most cases this is a very useful concept.

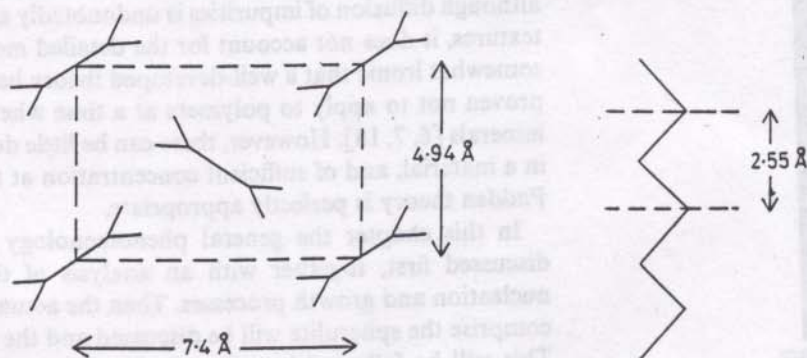


Fig. 3. The orthorhombic unit cell of polyethylene.

Polymer chains tend to form their own stable conformations (or shapes) determined by the energetics of rotation about the chain backbone atoms. The most intensively studied system is the highly flexible chain, polyethylene, in which the chains first form an extended structure, usually referred to as a linear zig-zag (see later). The extended forms then pack together laterally, parallel to one another, giving an orthorhombic unit cell (fig. 3). The other general form of chain shape is the helix, which again gives rise to an approximately cylindrical shape for the chain. Again the cylinders pack together efficiently to form the crystal. Unless mentioned otherwise, it should be assumed that polymers generally form crystals in which the chains are stacked parallel to one another and that the approximate shape of the units that pack together laterally is cylindrical.

2. Bulk crystallization behavior

The measurement of bulk changes can be followed by any method which accurately responds to the changes occurring in any fundamental property, such as volume or heat capacity. The earlier studies generally used some dilatometric method to measure volume changes [21]. However, dilatometry is a laborious technique and more utilitarian methods are now available. Two techniques are popular at the present time: (a) transmitted polarized light intensity [22, 23]; and (b) the most commonly used technique, differential scanning calorimetry (DSC) [24], which essentially measures the energy released by the crystallization process as a function of time (fig. 4a). When such data are plotted as a fraction of the crystallinity achieved at completion of the crystallization process versus the logarithm of time, characteristic sigmoidal curves are obtained (fig. 4b).

In most experimentation it is usual to study the bulk growth rate under isothermal conditions and to repeat the experiment for the widest range of supercoolings over which accurate data can be obtained. Data may also be obtained as a function of both pressure and temperature for the case of transmitted light intensity studies [25].

2.1. Avrami analyses

Experimental data are usually analyzed first using the Avrami equation [26]:

$$\ln(1 - X_c) = kt^n, \quad (1)$$

where X_c is the volumetric crystallinity, t the time and n is known as the Avrami exponent. k is simply a scaling constant which contains information on the individual rates of nucleation and linear growth. This generalized equation results from several models of the crystallization process that utilize combinations of the type of nucleation process with the shape of the growing entity. The use of instantaneous (heterogeneous) nucleation or sporadic (homogeneous) nucleation gives different time dependencies because of the time dependence of the sporadic process. Similarly, the assumptions of a disc or a sphere as the growing entity give different powers of time dependence because of the different dimensionalities of the objects. All the versions of the model use the concept of expanding wavefronts governed by a Poisson distribution of nucleation

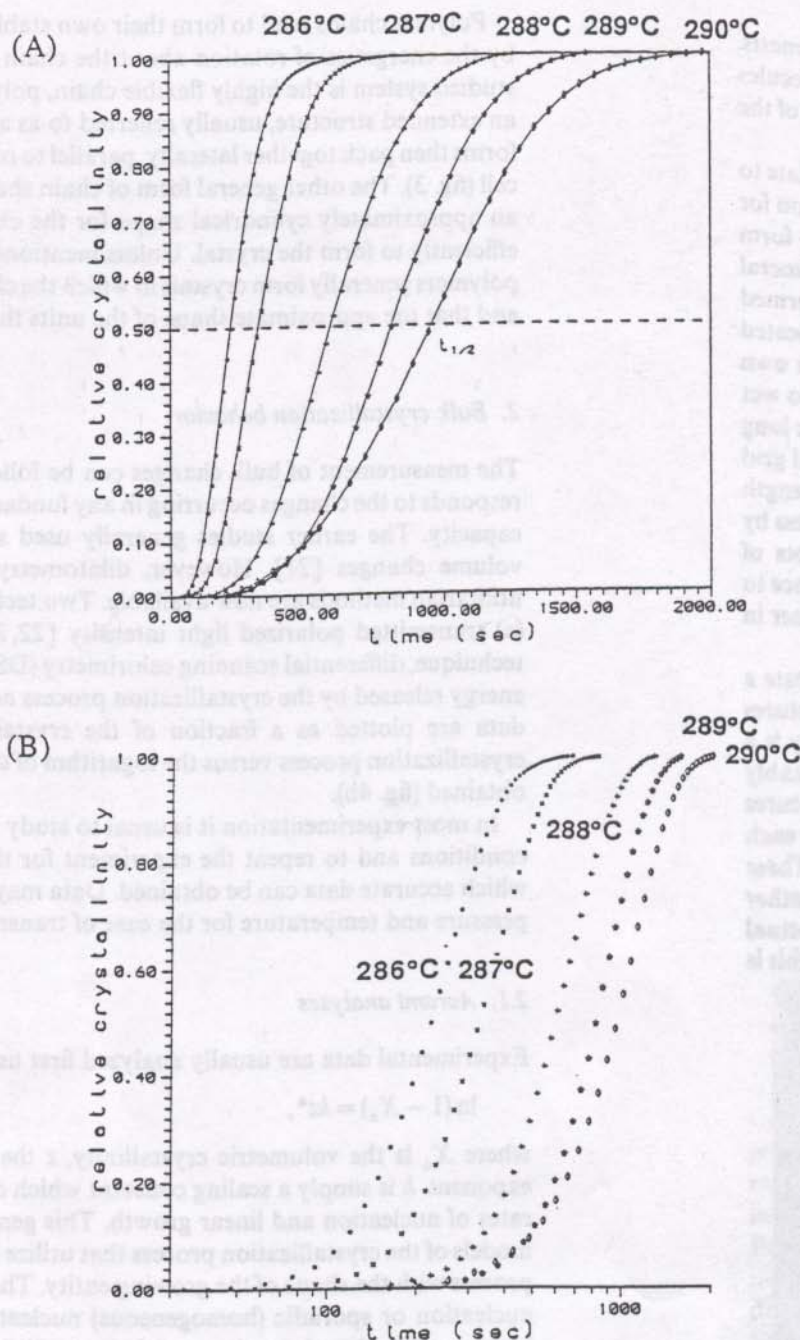


Fig. 4. (a) Fractional crystallinity versus time, obtained as the energy released in a DSC experiment, during the conversion of a polymer liquid crystal from the nematic to the crystalline state [27]. (b) Fractional crystallinity versus logarithm of crystallization time for the data of (a) [27].

sites. Since all of the models use integral growth processes, rather than a mixture of the possible growth processes, the volumetric growth rate always depends on an integral power of time. The values of the time exponent (usually referred to as the Avrami exponent) and the combinations of nucleation type and growth morphology giving rise to those values are summarized for principal types in table 1.

Although, very simple in approach, this type of analysis was for many years the only way of obtaining an estimate of the morphology occurring in a system. For opaque systems and for systems in which the morphological units are too small to be seen in an optical microscope, it still remains a valuable tool.

One example is that of fig. 4, a liquid crystalline macromolecule which forms crystals from its nematic liquid crystalline state with no change of the morphology being

Table 1
Avrami exponents and morphologies

| Morphology | Instantaneous | Sporadic |
|------------|---------------|----------|
| disc | 2 | 3 |
| sphere | 3 | 4 |
| rod | 1 | 2 |
| sheaf | 5 | 6 |

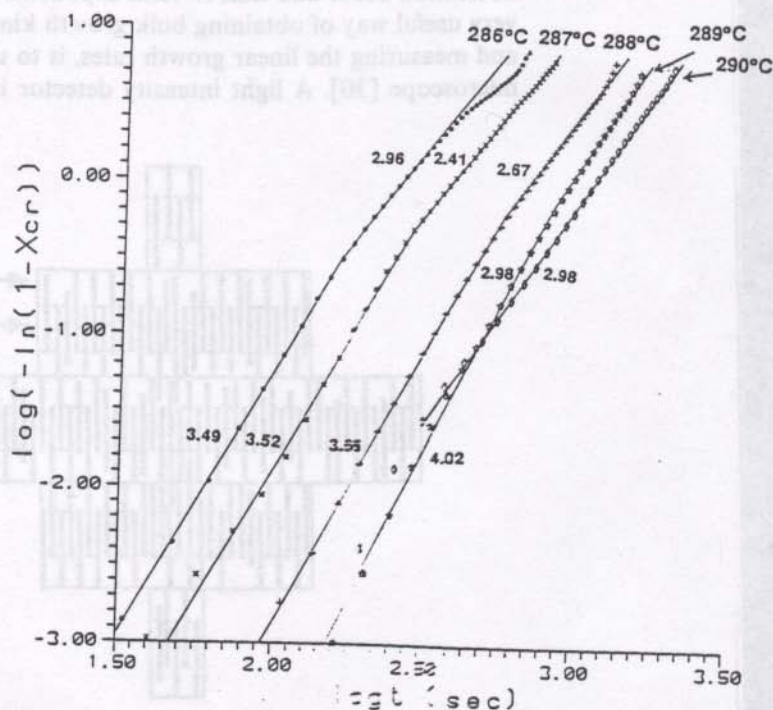


Fig. 5. Avrami plots of the data of fig. 4 [27].

apparent in the optical microscope [27, 28]. The typical Avrami curve is shown in fig. 5, again for this liquid crystalline polymer. As can be seen, the Avrami exponent (the slope) lies between 3.5 and 4.0. Hence, its morphology approximates a sphere with considerable disc-like character (it being a fair assumption that the nucleation process is homogeneous for this unusual substance). The values were surprising, since the process is one of condensation of pre-aligned rods into a crystalline form, and disc-like crystals were expected. The data resulted in the formulation of a model which assumes that one disc can easily nucleate others on its upper and lower faces, because of molecules protruding from the surfaces (fig. 6). The model generated values of the Avrami exponent which correlated well with the experimental values and also explained other types of data.

Because transmission optical microscopy of many substances permits the observation of the nucleation of crystals and the quantitative study of the associated growth rates, the use of the Avrami analysis has decreased significantly. However, in industrial solidification processes, unlike in basic physics, it is important to know the time it will take for a given process to be completed. Because of this fact, studies of bulk transformations, using especially DSC, are a very popular analytical tool in processing applications. Whereas, in basic studies it is important to carry out a study isothermally, in commercial operations the processes occurring are dynamic, so modelling of processes using the Avrami approach are of importance [29].

In general, it should be recognized that a mixture of instantaneous and sporadic nucleation occur and that Avrami exponents should be non-integral. Additionally, a very useful way of obtaining bulk growth kinetics, whilst at the same time observing and measuring the linear growth rates, is to use a trinocular eyepiece in a polarizing microscope [30]. A light intensity detector is set in the monocular to monitor the

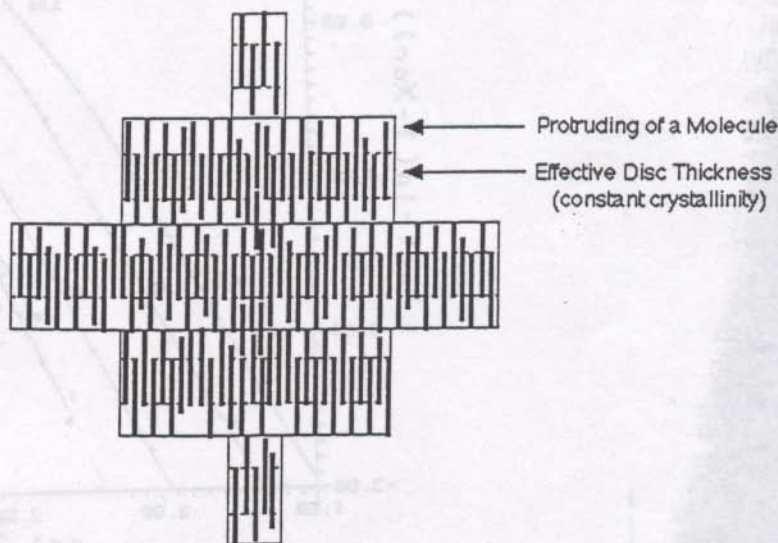


Fig. 6. Model for the growth morphology of the crystalline state of a liquid crystalline polymer [27].

increase in polarized light intensity as the crystallization progresses. In this case, as in any experiment using thin films on microscope slides, the spherulites may indeed simply occur as discs because of lateral size constraints. This fact has been allowed for in studies of bulk growth using this approach, Avrami exponents being approximately 1.0 less than they would be for true bulk studies.

The Avrami equation, as derived, considers the material ahead of the growth front to be liquid and the material behind it to be crystalline. In practice, the latter condition does not occur in any macromolecular material. The spherulites contain both *amorphous and crystalline material* at the completion of the solidification process. Many macromolecular materials are only 30% crystalline, and the highest observed crystallinities under most circumstances are in the range 80–90%. In practice, this seemingly insurmountable complication is easily handled by defining the reference “completely crystalline material” as being the “*completely spherulitic material*”. This procedure permits the estimation of the initial slope, as in fig. 5, and hence the Avrami exponent appropriate to the growth of the spherulites prior to impingement. There is always an additional complication in the form of crystallization within the spherulites behind the growth front. Hence a material composed of fully impinged spherulites, which when viewed through a microscope would resemble a polycrystalline metal, continues to crystallize and hence densify. This process, usually referred to as *secondary crystallization*, is responsible for the second lower slope observable in fig. 4. (In the case of the liquid crystal the mechanism is different from that of flexible macromolecules and believed to be the incorporation of the protruding parts of the molecules into the crystal by a thickening process.)

2.2. Half-time analyses

The Avrami analyses give indications of the morphologies being developed and of the nucleation processes occurring, but they give no analysis of the actual growth rates of the crystals. A simple approach which can be used to give broad estimates of relative growth rates that is especially useful for a variable temperature study is to use the concept of half-time. Any basic growth curve, such as those shown in fig. 4b, can be converted into a rate study by taking the reciprocal of the time it takes for the process to be half complete. If such data are plotted versus reciprocal supercooling, a linear relation occurs for instantaneous nucleation, whereas a linear relation will be found when plotted versus the reciprocal of the square of the supercooling if sporadic nucleation results [31]. Much more in-depth analyses of the crystal growth process can also be carried out using this approach as will be seen later.

2.3. Nucleating agents

Commercial polymers often contain additives to enhance the rate of crystallization and so reduce the processing time during molding. This practice is especially prevalent in the higher-temperature plastics such as PET and PEEK. For many years it was thought that such agents functioned simply through providing heterogeneous surfaces

on which crystals could nucleate, despite the fact that there were significant variations in the effectiveness of many of these additives. The reasons for this belief lay in the observation that many different nucleating agents of widely differing crystal structures could nucleate many polymers which also had widely differing crystal structures. Known as the Binsbergen hypothesis [32,33], this concept was proven totally erroneous in a series of elegant experiments by Wittmann and co-workers [34–36].

They were able to demonstrate that the effective nucleating agents functioned through epitaxy! The key to obtaining a true understanding was the recognition that all the agents contained benzene rings in their chemical structures. These could occur as single or fused rings or as polyphenyls. In all cases there is a set of lattice spacings in their crystals determined by the stacking periodicity of the ringed structures, which is essentially a constant. All polyphenyls also have a constant stacking periodicity, but it is different from that for the single and fused ring systems. Many polymers fall into two general classes of crystal packing. First, there is the polyethylene type already discussed. The lateral packing distances of chains of aliphatic polyamides, polyesters and other polymers are essentially those of polyethylene. Lotz and Wittmann were able to demonstrate that some of the lateral packing lattice parameters of polyethylene matched those of the aromatic stacking lattice parameters of the nucleating agents. In all cases considered there existed the two lattice matches needed for these orthorhombic crystals that were well within the 13% tolerance limits needed for epitaxy. They also clearly demonstrated experimentally that polyethylene could be grown epitaxially on large single crystals of chosen aromatic molecules. It was later shown that more than one set of lattice matches functions in practice for polyethylene [37].

The second general type of polymer crystal is that exemplified by polypropylene in which the equilibrium chain structure is a 3:1 helix [this convention gives the number of chemical repeat units (in this case 3) found in a given number of turns of the helix (in this case 1)]. The chain helices then pack together laterally to form the crystal. It was also demonstrated by Lotz and Wittmann [38] that polyethylene and polypropylene have an effective epitaxial relationship, polyethylene growing on polypropylene because of its lower melting point. So an epitaxial match between polypropylene and the nucleating agents was a given. The concept has also been extended to polymers containing benzene rings in the main chain such as PEEK and PET, it having been demonstrated that the stacking of rings in these polymers generates epitaxial relations between them, nucleating agents and the commoner aliphatic polymers such as the polyethylene and polypropylene already mentioned [39].

The most effective nucleating agents known are generally referred to as *clarifiers* [40] since their nucleating ability is so great that the size of the resultant spherulites is so small that the haze or opacity of crystalline polymers, which is a direct result of light scattering by these optically anisotropic spheres (see later), is essentially eliminated. These clarifiers are based on sorbitol derivatives and are known to form single string-like crystals only about 10 nm in diameter [41,42]. A small amount of the material produces a dense web of these crystalline strings with a very high surface-to-volume ratio. The web appears to function as an epitaxial agent for polymers perhaps because of the six-membered rings of the sorbitol, or because of the benzene rings attached to them, forming stacks.

3. The lamellar crystal

For certain macromolecules it is possible to observe the individual crystals that form the spherulitic aggregates and even to observe the nucleation process. The greatest degree of resolution has been possible for certain polymers known as polydienes. These materials contain reactive double bonds in the main chain of the polymer and can be reacted with osmium tetroxide vapour. The reaction is rapid if the polymer is in the form of a thin film (i.e. 80 nm thick) and occurs in 10–15 s. The gas penetrates all of the amorphous material and none of the crystalline material. It adds onto the double bond, thereby generating electron-dense amorphous regions, which can be observed with high levels of resolution in a transmission electron microscope (fig. 7). Since the crystals tend to be of the order of 10 nm thick, transmission electron microscopy is the only way of

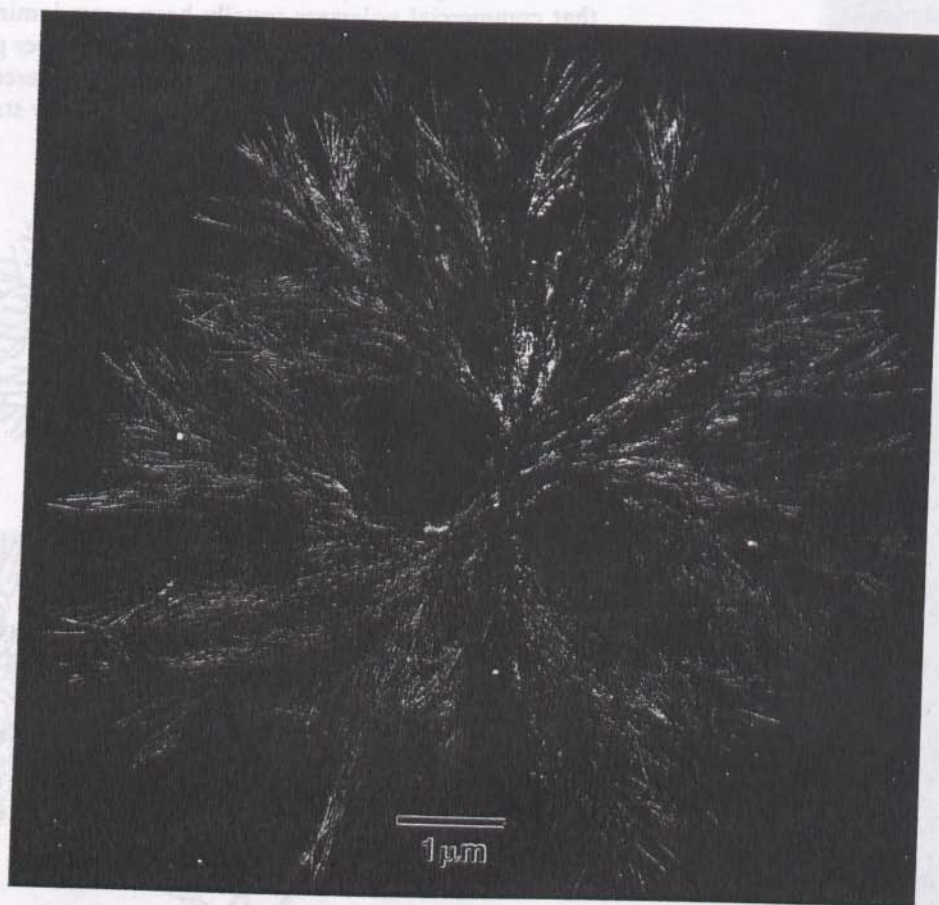


Fig. 7. Lamellar crystals in a spherulite of a film of cis-polyisoprene stained using osmium tetroxide (crystallized at -12°C).

conducting a high-resolution study of such crystals. This technique was first used by Andrews [12, 43] to directly visualize the lamellar crystals formed in bulk polymer.

The technique has an added advantage in that the sections of chain to which the osmium tetroxide have added are no longer mobile and cannot crystallize. It therefore stops the crystallization process permitting the earliest stages of growth to be observed in a specimen [44]. Schematics are shown in fig. 8 of the centers of spherulites shortly after nucleation. In the schematic A an example is shown of heterogeneous nucleation where several of the lamellar crystals have nucleated on a heterogeneous impurity. The schematic B shows the most commonly observed nucleation process in highly purified material, in which no heterogeneous objects can be observed in the centers of the crystals. Generally regarded as a form of homogeneous nucleation, this form gives rise to spherulitic textures which are quite different from those generated from obviously heterogeneous nuclei. The aggregates grow as *sheaves* (fig. 9) and late in their growth process take on the characteristic spherulitic texture (fig. 7). Those species growing from a heterogeneous nucleus always have a spherulitic appearance. It should be noted that commercial polymers usually have a predominantly heterogeneous nucleation process because of the high levels of dust and other particles present from processing operations. However, if properly cleaned and filtered from dilute solutions they will also give rise to the sheaf-like textures in the early stages of growth.

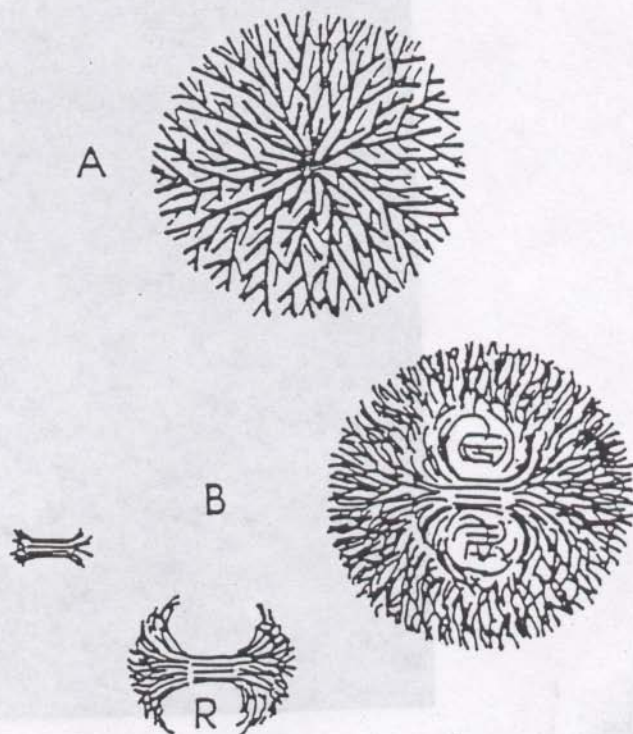


Fig. 8. Schematics of (a) heterogeneous and (b) homogeneous nucleation in a high polymer.

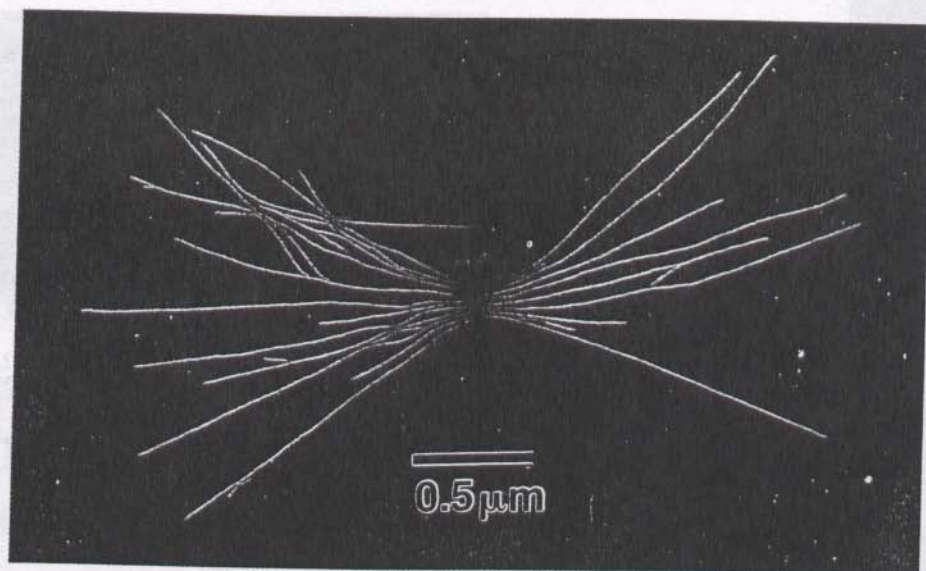


Fig. 9. Sheaf-like growth characteristic of the early stages of spherulitic growth in polymers (cis-polyisoprene crystallized at -9.2°C).

In the pictures shown of cis-polyisoprene occasional crystals can be observed having a wide profile and of intermediate contrast. These are the same crystals but in a different orientation from normal. In fact the crystals of cis-polyisoprene are *ribbon-like* in shape. Dependent on the growth regime (see later) they may also grow with a wider *leaf-shaped* profile [45]. Under such circumstances the aggregates consist of stacks of leaves which have all nucleated at about the same time at the center of the approximately elliptical leaf. However, the crystals are not directly superposable on each other as would be expected of crystalline stacks grown on a screw dislocation (fig. 10).

In the case of ribbon-like crystals the growth face can be seen directly in micrographs (fig. 11) and is flat, corresponding to the (010) plane. For the leaf-shaped crystals there is not a well-defined growth plane visible. The tips of the crystals do appear to be pointed in shape and the growth face may be the (110) plane. It should be noted that in these two types of crystal the growth direction is the same and is the [100] direction of the crystal.

When other polymers are considered, the general phenomenology often corresponds to that of cis-polyisoprene. The most commonly studied polymer is linear polyethylene. It is from solutions of this polymer that the first in-depth studies of single crystals of a polymer were conducted [46–48]. These crystals were rhombus-shaped and very thin (fig. 12). They were nicely faceted and the growth faces could be identified easily as predominantly {110}. Later studies showed that they were actually *hollow pyramids*, which had collapsed to give the flat rhomboid crystals during specimen collection [49].

When directly studied using electron diffraction it was clear that the polymer molecules were oriented with their axes across the smallest dimension, i.e. the crystal thickness. This was directly contrary to intuition, which would lead one to assume that the molecules would be oriented along one of the major dimensions of the crystal,

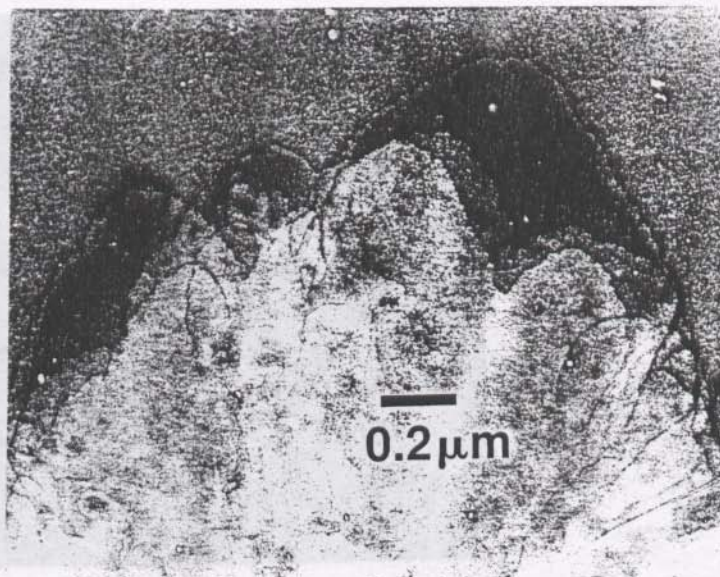


Fig. 10. Leaf-like crystals growing in axialites of cis-polyisoprene.

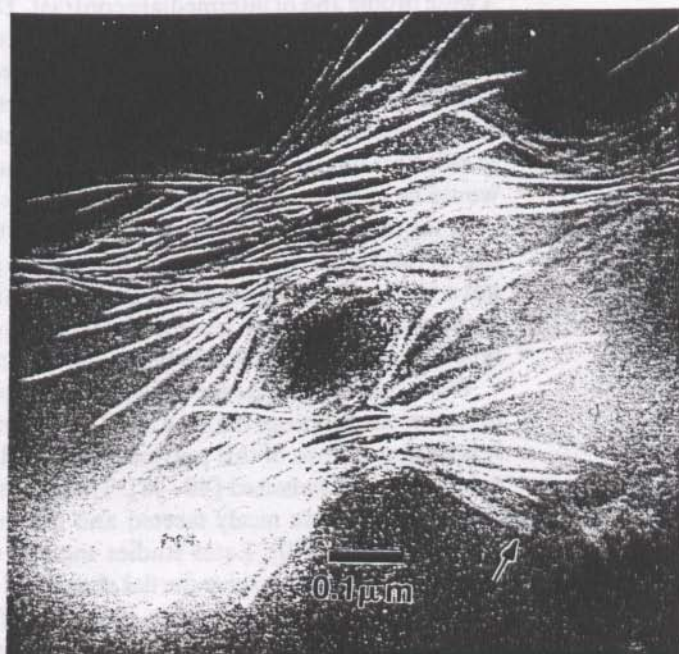


Fig. 11. Ribbon-like crystal growth in spherulites of cis-polyisoprene showing the (010) growth face (arrow).

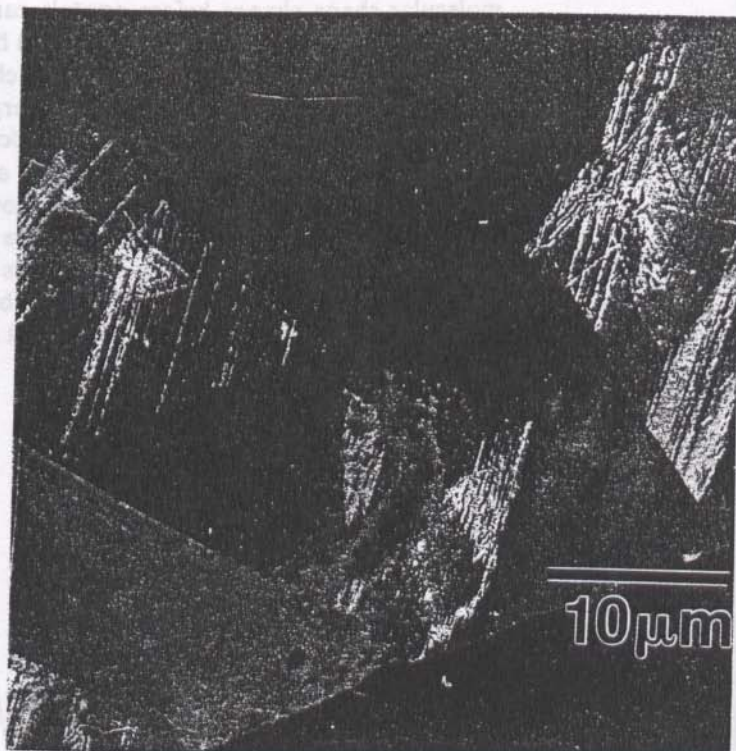


Fig. 12. Single crystals of polyethylene grown from dilute solution. Dark-field TEM using (110) and (200) rings. (Photomicrograph supplied by J.R. White).

indeed the molecular length is about the same size as the edge lengths of typical crystals. This simple and irrefutable piece of evidence led to one of the greatest controversies in macromolecular science. *Simply, the length of the molecule is many times greater than the thickness of the crystal.* For example, a typical polyethylene molecule of molecular weight 100 000 is about one micron in length yet its crystals are only one hundredth of that value in thickness. Since the crystals were about 90% crystalline, it was obvious that the molecule had to fold back and forth re-entering the crystal many times. The nature of the folding has been the controversy.

Crystals of linear hydrocarbons have the same molecular structure as polyethylene but are much shorter in length. Typical molecules are 3–10 nm long. As such, the lengths of the longest ones are similar to the crystal thicknesses of polyethylene crystals. They have been studied for many years and much of the initial understanding of polyethylene crystallization came from knowledge of their behavior. Lamellar crystals are formed which have the same crystal structure as polyethylene crystals [50, 51]. They differ from polyethylene in that the molecular length and the crystal thickness are the same. Hence they are *extended-chain* crystals.

Here it will be necessary to diverge from the general narrative in order to acquaint the general reader with the basic nature of polymer molecules and the necessity for a

molecular shape change before crystals can be formed. The majority of synthetic macromolecules are flexible in nature. This flexibility is a direct result of the ability of individual links, or groups of links, in the chain to rotate into three major positions (fig. 13). For polyethylene the increase in energy between the *trans* and *gauche* positions is only 800 cal/mol and hence changes can occur easily at room temperature or above. The molecule hence exists in the form of a random coil, whose properties can be modelled using Gaussian statistics. It does however have a lowest-energy configuration which corresponds to every bond being in the *trans* state (fig. 13). Such a chain is known as the all-*trans* or *linear zig-zag* chain. It is this lowest-energy shape which must be achieved to make crystalline packing possible. Crystallization in long-chain systems therefore includes as an essential component the achievement of the lowest-energy state

Polymer crystals

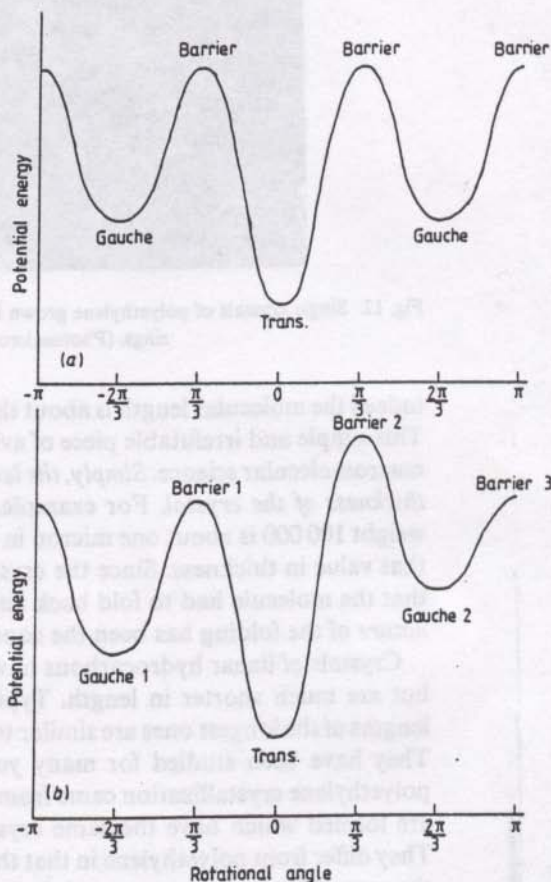


Fig. 13. Schematic potential energy diagrams for (a) polyethylene and (b) a vinyl polymer (first published in [3]).

of the isolated chains. This is a very slow process as it requires cooperation from all units present in the chain and also those other molecules with which the crystallizing molecule is intimately entangled. For a more extensive basic discussion of this subject the reader is referred to Boyd and Phillips [20].

Similar considerations apply to the shorter hydrocarbon systems, however, their shorter length precludes the major problems associated with chain entanglements, and full extension is readily achieved. They do comprise a valuable corroborative tool for the understanding of polyethylene crystallization, as they possess all the same features, but without the complication of chain folding. Studies of their crystal growth have provided values of surface free energies and other parameters for use in analyses of polyethylene crystal growth [52]. In all of the cases considered so far, the polymer chains in their extended linear zig-zag form *stack parallel to one another* like rods to form their crystals. The packings are simply achieved by obtaining the tightest lateral packing of the non-circular cross-section rods. In practice, this results most commonly in the form of an orthorhombic crystal (fig. 3). At elevated temperatures where the rods can rotate and twist, the orthorhombic structure adjusts and approaches a hexagonal state.

When crystallization from the bulk polymer is considered, most of the behavior characteristic of dilute solution growth is retained, with the exception that isolated single crystals cannot occur. This is an essential result of the entangled nature of these long-chain molecules, since it is possible for any given molecule to crystallize in *several crystals at the same time*. The most essential characteristic that is retained is the dependence of the lamellar (crystal) thickness on temperature. The crystal thickness is in fact controlled by thermodynamic variables and is a constant at any temperature. It

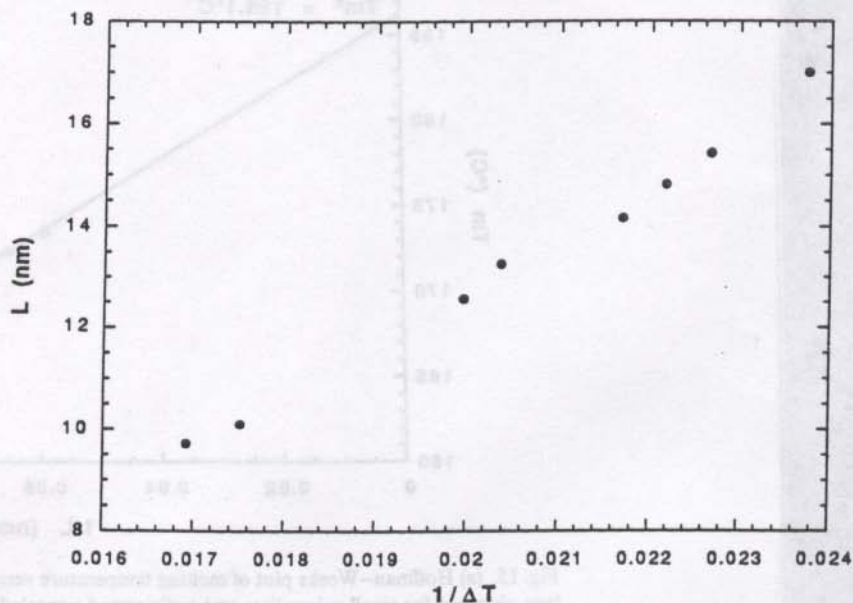


Fig. 14. Variation of crystal thickness with reciprocal supercooling for polypropylene.

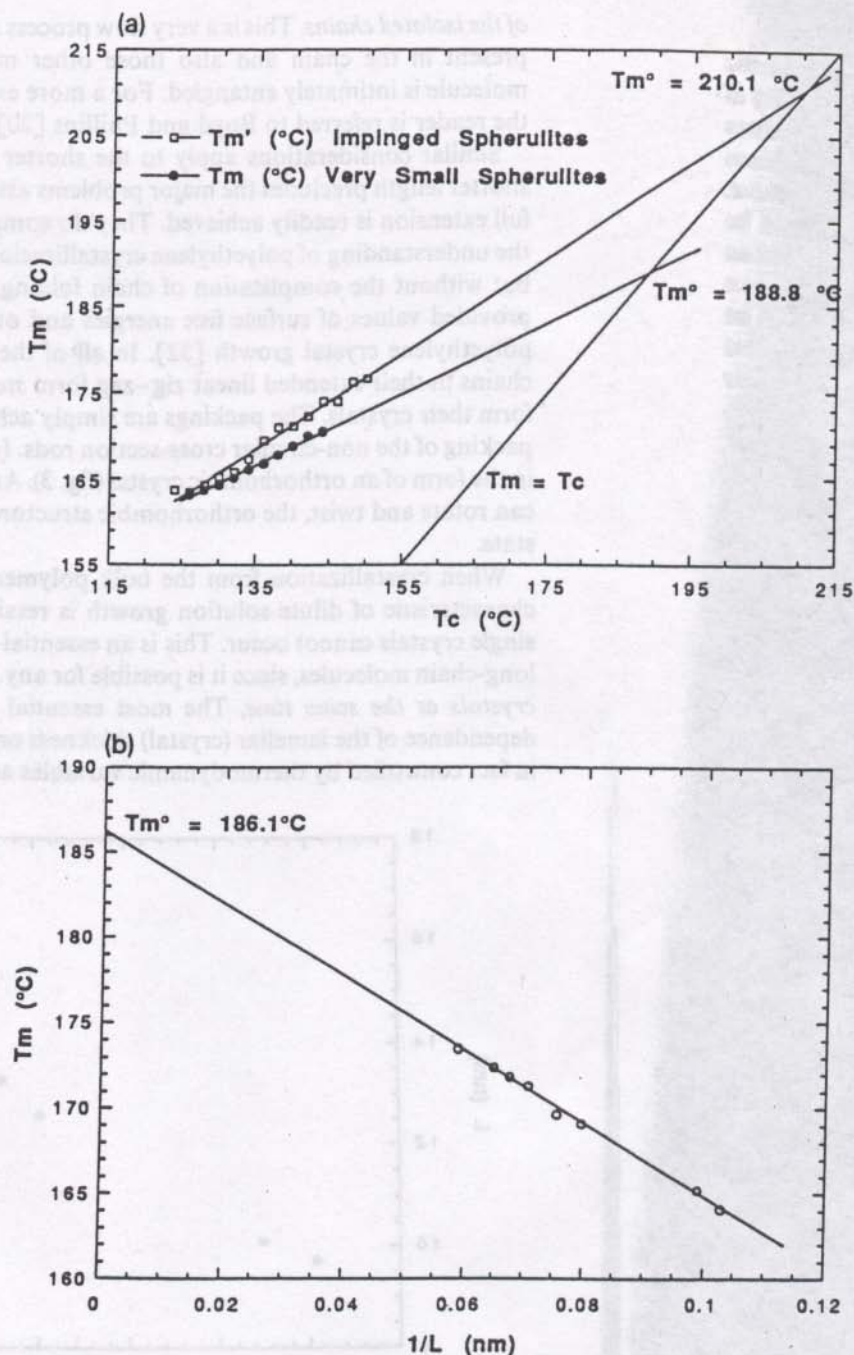


Fig. 15. (a) Hoffman-Weeks plot of melting temperature versus crystallization temperature of polypropylene obtained for small spherulites and well-formed annealed spherulites (Mezghani and Phillips, unpublished data). (b) Melting temperature versus reciprocal lamellar thickness of polypropylene [54].

does not vary with time of crystallization, unlike some other crystal dimensions. The dependence is a simple one, namely the reciprocal of the supercooling (fig. 14). Because of the thinness of the crystals the melting point is a function of crystal thickness and, hence, also a function of the supercooling. This leads to the well-known Hoffman-Weeks plot of melting point versus crystallization temperature (fig. 15) which can be used with caution to estimate the thickness-free or *equilibrium melting point* of the polymer [53]. This task is achieved by extrapolating the $T_M - T_C$ straight line relation to $T_M = T_C$. It does incorporate several assumptions regarding the annealing behavior of the crystals as a function of temperature and has been misused. The accurate extrapolation of this type of curve requires a knowledge of the crystal thickening behavior of the polymer. It has generally been assumed that the behavior reported for polyethylene applies to all systems. It is characterized by an increase in lamellar thickness which is greatest for the thinnest crystals and results in a lower slope for the Hoffman-Weeks plot than would be obtained without significant thickening having occurred. In this case the extrapolation always leads to about the same value. It has recently been demonstrated that polypropylene exhibits a quite different behavior (fig. 15a). In this case it is the crystals produced at lowest supercoolings (i.e. the thicker crystals) that are able to thicken most. Enhanced thickening therefore leads to an erroneously high estimate of the equilibrium melting point and studies have to be conducted using specimens produced at very short crystallization times [54].

In reality the only definitive method of obtaining an estimate of the equilibrium melting point is to perform an extrapolation to infinite thickness of a plot of melting point versus reciprocal lamellar thickness (fig. 15b). It can be seen that the estimate of the T_M value from thickness studies correlates well with that obtained from the Hoffman-Weeks plot for small spherulites.

Appropriate points to consider at this time are the driving force for the thickening process and the true state of an equilibrium crystal. Undoubtedly, the lamellar crystals described are not equilibrium structures, since they are of finite size and only part of the molecule is in the crystalline state. The equilibrium crystal form must be the *fully-extended-chain crystal* characteristic of the hydrocarbons. All lamellae must tend to increase the length of extended chain present and this can only be done by thickening. Hence as a crystal is heated it will tend to thicken. For the purposes of characterization it is fortunate that the thickening process is slow and it is possible to carry out melting studies without appreciable thickening occurring if the rate of heating is high enough. An additional factor always present is the low thermal conductivity of polymer crystals which can cause superheating to occur and hence the acquisition of inaccurately high melting points for a different reason.

The ability of a crystal to thicken is controlled by the detailed manner of re-entry of the molecules into the crystal and its neighbours. Before it is possible to proceed further it will be necessary to explore that problem in detail.

3.1. The molecular trajectory

There are only two methods available for the determination of the shape attained by the molecule in the bulk state. Both involve the "dyeing" of the molecule through

replacement of hydrogen atoms by deuterium atoms. Once this change has been made, infra-red spectroscopy [55, 56] and neutron scattering [57] can be carried out. A blend is then made of the deuterated polymer with the hydrogenated (i.e. regular) polymer and, provided there is no segregation into isotopic species during crystallization, the deuterated polymer can be regarded as an indicator of general molecular behavior.

In the case of infra-red spectroscopy (FTIR) it is possible to study changes in spectra produced by changes in the nearest-neighbor interactions. So such a study may provide proof as to whether or not adjacent chains in a crystal are from the same molecule. As will be seen later, this microscopic scale view of the detailed molecular placement is extremely important in understanding the manner in which a molecule adds to a growing crystal.

Elastic neutron scattering studies take advantage of the fact that deuterium has a much larger scattering cross-section than hydrogen. The scattering of neutrons by the deuterium is much greater than by hydrogen and so the blend behaves as if the deuterated molecule were dissolved in a transparent solvent. Indeed the manner of the scattering and the molecular analyses that follow are directly derived from the well-known scattering of light by polymer molecules in an organic solvent [20, 58]. Two parameters extractable from the data are the molecular weight and the radius of gyration of the molecule. From the earliest studies it became apparent that the radius of gyration of the molecule in the crystalline state remained close to its value in the randomly coiled melt. The obvious conclusion to be drawn is that the molecule crystallizes substantially in place without any major change of shape.

This result was substantially different from the result obtained from studies of solution-grown single crystals where it was clear that the molecule is segregated into two or three adjacent growth planes of the crystal (in the case of polyethylene that corresponded to the (110) [59]). Hence although the lamellar crystals grown from the melt and from dilute solution show similar thickness dependences on supercooling the detailed molecular placements in the two forms are quite different. Such observations led to several attempts being made at regenerating the scattering intensity curves using computer simulations of different models. Some of the modelling studies were ultimately shown to be seriously flawed after considerable debate [60–62]. None of the models generated is sufficiently definitive for a molecular scale picture to be developed on the scale of chain adjacency. However, the broader scale picture of the molecular chain retaining essentially spherical overall shape is undisputed.

The use of FTIR has not resolved the problem either for melt-grown systems, although data for solution-grown crystals strongly support the interpretations of the neutron scattering data and indeed pre-dated those studies [55, 56]. It is possible to move towards a more detailed picture from studies of the crystallization kinetics since any model proposed must be consistent with and capable of explaining the growth behavior in a kinetic sense and not simply a morphological sense. In order to discuss further the detailed molecular trajectory it is necessary to consider the ways in which the molecule may re-enter the crystal and/or enter an adjacent crystal whilst maintaining its molecular integrity. It is also important to come to some conclusions regarding the conditions under which various types of re-entry would be predicted to predominate.

3.2. The nature of the molecular re-entry process

Many studies have been conducted using neutron scattering, especially on polyethylene. In all cases of bulk crystallization, because of isotopic segregation problems, they have been conducted on crystals produced by rapid quenching [57]. Therefore, they have contained the greatest amount of disorder that can be generated in the system. The retention of the approximately spherical molecular shape should not therefore constitute a major surprise. Prior to these studies the preponderance of experimental evidence was in favor of a molecular trajectory similar to that believed to be present in single crystals. This picture is generally referred to as the adjacent re-entry model (fig. 16) since it assumes that the molecule folds regularly along the growth plane in an adjacent manner [47, 49]. Clearly, this precise picture is inconsistent with the neutron scattering evidence. The predominant alternative model assumes total non-adjacency of re-entry and is usually referred to as the switchboard model [63] (fig. 17). It is now recognized by most researchers that this model generates an unacceptably high density in the crystal surface when the emerging chains are regarded as Gaussian at the crystal interface.

Another model is the interzonal model (fig. 18) which assumes a total lack of adjacency, but combines non-Gaussian chains in the vicinity of the surface with

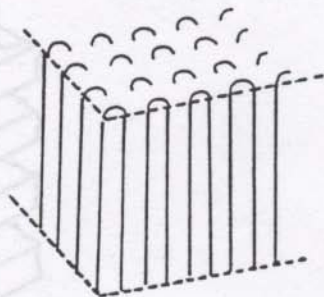


Fig. 16. The adjacent re-entry model of molecular re-entry.

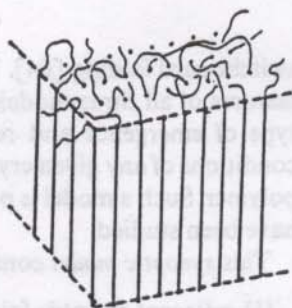


Fig. 17. The switchboard, or non-adjacent re-entry, model of molecular re-entry.

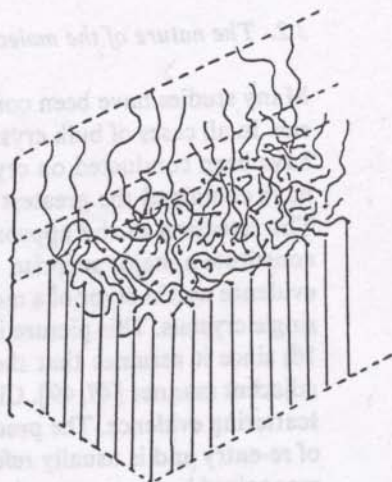


Fig. 18. The interzonal model of molecular re-entry.

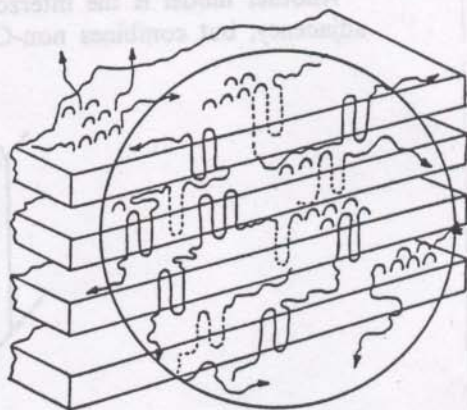


Fig. 19. The synoptic, or comprehensive, model of molecular re-entry. The circle represents the radius of gyration of a typical high-molecular-weight polymer.

switchboard folding [64]. The picture which is closest to the truth would incorporate features of all three models, but would recognize that the frequency with which each type of emergence and re-entry occurs would depend very much on the detailed conditions of any given crystallization experiment and on the chemical structure of the polymer. Such a model is presented in fig. 19 and is believed to apply to all systems that have been studied.

This *synoptic model* combines the following essential features:

- (1) adjacent re-entry folds;
- (2) non-adjacent re-entry folds, which

- (a) re-enter along the same growth face a few stems away, dependent on internal chain stiffness,
- or
- (b) re-enter on a subsequent growth face parallel to the first, dependent on chain stiffness;
- (3) emergent non-Gaussian chains which
 - (a) remain in the amorphous phase, or
 - (b) re-enter at a distant location, or
 - (c) re-enter only in other crystals, having in each case gone through a Gaussian form some distance away from the crystal surface.

Clearly, solution-grown single crystals are composed of predominantly type 1 with some type 2b re-entry. Melt-grown crystals produced at low supercoolings of a flexible polymer such as polyethylene would be expected to contain predominantly type 1 with some type 2a, 2b, 3a, 3c and smaller amounts of the other forms. When grown at high supercoolings, lesser amounts of type 1 would be expected as would larger amounts of types 2 and 3.

The semi-rigid backbone polymers, such as PEEK and others containing aromatic rings in their main chains are incapable of adjacent reentry as they cannot turn through 360° within the distance available and hence can only re-enter the crystal several chain stems away from the point of emergence. They will therefore contain predominantly types 2a, 2b, 3a and 3c.

Very rigid systems, such as the liquid crystalline polymer referred to earlier cannot fold at all and their crystal surfaces will contain only types 3a and 3c.

It is, of course, the flexible systems that have received greatest attention, and it is there that major variations in relative proportions of the different types of surface features can occur, dependent on the crystallization conditions employed. For the semi-rigid systems variations in the proportions of the different types there can also be expected, again dependent on preparation conditions. For these latter materials the term "rigid amorphous phase" was coined to describe the region near the surface where the chains are non-Gaussian and hence have a degree of rigidity that is higher than the equilibrium conformation would dictate [65, 66].

Chains can also have branches on them and this feature also influences the character of the surface. Branches such as butyl and hexyl are commonly found in low-density and linear low-density polyethylenes (readers unfamiliar with this terminology are referred to Phillips [3], or to Boyd and Phillips [20] for a discussion). Such groups cannot be incorporated into the crystal structure because of their size and are rejected to the surfaces. The chain section to which they are attached must either be incorporated into a fold or remain in the amorphous phase. However, incorporation of the branches into the folds in large numbers may cause packing problems and reduce the number of tight adjacent re-entry folds. One possibility is to make the fold into a loop or to cause non-adjacent re-entry. These possibilities themselves put more material into the interface and it must expand in thickness, hence many of the ideas incorporated into the interzonal model become operative.

Any fold, whether adjacent re-entry or not, must attain its own lowest energy state. In the case of an adjacent re-entry fold in polyethylene this was shown to require five main

chain bonds. For this fold shape to be achieved it was necessary for several bonds to be in the higher-energy gauche configuration and hence, by its very nature, a fold has energy in excess of a molecular section of equal length in the crystal. It was recently demonstrated in simulations that the incorporation of a branch into the fold changes the conformation of the fold and hence the amount of *excess energy* stored in it. Such details of the fold structure have a major bearing on the crystallization process since the excess energy stored in a fold contributes to the surface free energy of the crystal and also to the *surface free energy of the critical nucleus*. Hence, what appear to be minor details of the molecular trajectory are in fact of major fundamental importance in the formulation of any theory of crystal growth. It is the folded surface of the lamellar crystals that is directly responsible for the thinness of the crystals and hence for the spherulitic habit.

4. The crystal growth process

The theory of crystal growth must account for the thickness behavior of the crystals in addition to the growth habits, temperature dependence and other features that are common to all materials. It must recognize that growth does not occur at the highest-energy surface, unlike in other materials, and that the crystal thickness is essentially constant with time of crystallization. It must also recognize the possible presence of all of the potential surface features of the crystals and how they will influence the growth process.

The general phenomenology of supercooling dependence of linear growth rates and of the lamellar thickness has been incorporated from the beginning [67,68]. Indeed, they can be incorporated without recourse to the detailed structure of the surface. The simple fact that the folded surfaces, regardless of their detailed structures, will have a much higher surface free energy than the lateral surfaces of the crystals explains the behavior. All successful approaches are based on the secondary nucleation approach of Turnbull and Fisher [69], adapted for the chain molecule.

Other approaches are, of course, possible, such as the surface roughening model originally proposed by Burton et al. [70] and later applied to polymeric systems [71–73]. Although this model does indeed apply to many elemental systems the basic concept of atoms being able to jump out of the uppermost crystal layer to sit on the surface, simply does not transfer across to macromolecular systems. Entire sections of a chain would have to jump out and the activation energy required would be prohibitively high for it to occur with any reasonable frequency. It most certainly is possible, and indeed highly probable, that chain sections are sitting on the surface and mobile (see later). Since they are not jumping out of the crystal to do so, the basic concept of a low-activation-energy surface defect model as the controlling process is not applicable. The necessity for the atoms to be permanently connected together in the form of long strings effectively eliminates the possibility of applying conventional atomic mobility statistics to a macromolecular problem. It is a surface adsorption process, followed by the rearrangement of the chain into a partially extended form, that is generally recognized as the initial step in the addition of a flexible polymer molecule to a crystal.

It still remains to be seen if a version of roughening theory applicable to polymers can be developed and tested.

The version of secondary nucleation theory most commonly used is that originated by Hoffman and Lauritzen in 1961 [74], modified several times to incorporate complicating factors that were omitted from the original version for simplicity. The current version [75] incorporates an essential feature missing from all earlier versions, namely the change of shape of the molecule. The most fundamental of all aspects of polymer structure, the conformation of the molecule and the statistical entropy associated with it, now a part of crystallization theory, provides major new insights into polymer crystallization. Of considerable significance is the unification of secondary nucleation theory for polymers with classical physical chemistry of polymer molecules [76].

Secondary nucleation theory of polymers has always embodied the fundamental concept that the critical nucleus must be formed by condensation of stems of approximately equal length on the substrate crystal (fig. 20). In this respect it is very different from classical nucleation theory applied to elemental systems. The freedom of action of individual molecules or atoms is not present, and is a general consequence of the fact that indissoluble strings of atoms are considered. It is this aspect that partially unites the application of the theory to polymers with the application to hydrocarbon chains.

For the first chain to deposit there is an energy penalty of

$$\Delta\Phi = 2abl\sigma + abl\Delta G_c, \quad (2)$$

if it deposits in crystallographic register, which is very unlikely in the case of flexible chain molecules. a , b and l are the dimensions of the nucleus as shown in fig. 20. σ is the

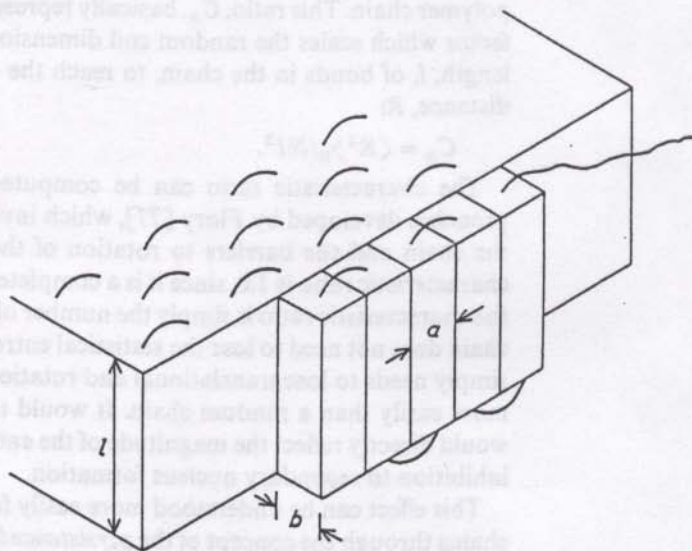


Fig. 20. Stem deposition model of secondary nucleation.

lateral surface free energy and ΔG_f the volumetric free energy of fusion. For non-crystallographic register the energy penalty will be at least as high, if not greater due to the extra length of chain adsorbed on the surface.

In practice, chains do not adsorb on the surface in register, they must rearrange their shape on the surface in order to achieve register. This means that the free energy of fusion is released in two steps, whereas the lateral free energy penalty is incurred immediately on adsorption. It is necessary for the process to be separated into two steps, as shown in eq. (3). Sections of the chain that attain crystallographic register release free energy of fusion which partially compensates for the lateral free energy penalty of eq. (3a). At some later stage the stem attains complete crystallographic register, this second stage being handled by the second expression [eq. (3b)]. The symbol Ψ is used to denote the fraction of the free energy of fusion released during the adsorption step. During the formal derivation of the theory it automatically apportions the activation energy of the Eyring-Kauzman equation into its forward and backward reaction components.

$$\Delta\Phi_1 = 2abl\sigma + \Psi abl\Delta G_f, \quad (3a)$$

$$\Delta\Phi_2 = (1 - \Psi)abl\Delta G_f. \quad (3b)$$

The lateral free energy penalty of eq. (3) in fact does not simply represent a lateral free-energy term as traditionally represented. Attainment of deposition on the surface requires the loss of a major fraction of the entropy of the chain and it is implicitly incorporated into the value of the surface free energy, σ . So, in the case of polymers the surface free energy, σ , represents more than simply the mismatched bonding at an interface. It is the most recent adaptation of the Lauritzen-Hoffman theory that *explicitly* relates σ to the change in shape of the polymer chain. This approach writes σ as equal to a constant multiplied by the reciprocal of the *characteristic ratio* of the polymer chain. This ratio, C_N , basically represents the stiffness of the polymer chain as a factor which scales the random coil dimensions, calculated using the number, N , and length, l , of bonds in the chain, to reach the dimension of the real chain, end-to-end distance, R :

$$C_N = \langle R^2 \rangle_0 / Nl^2. \quad (4)$$

The characteristic ratio can be computed with reasonable accuracy, using approaches developed by Flory [77], which involve details of the molecular structure of the chain and the barriers to rotation of the chain. For an ideal flexible chain the characteristic ratio is 1.0, since it is a completely random coil. For the totally stiff chain the characteristic ratio is simply the number of bonds in the chain. Clearly, a totally stiff chain does not need to lose the statistical entropy that must be lost by a random coil. It simply needs to lose translational and rotational entropy and should crystallize much more easily than a random chain. It would therefore be expected that the value of σ would directly reflect the magnitude of the entropy loss required, since it represents the inhibition to secondary nucleus formation.

This effect can be understood more easily for semi-rigid, as opposed to totally rigid, chains through the concept of the *persistence length*, which is related to the characteristic ratio. It basically represents the minimum length of chain needed for a given

polymer to develop a coil-like nature. In such a case it might be expected that if the lamellar thickness under a specific crystallization condition were approximately equal to the persistence length that crystallization would be easy because of small loss of statistical entropy needed for incorporation of a persistence length in the crystal.

For flexible chain polymers such as polyethylene, however, the persistence length is about the size of the bond and no unusual effects would be expected. Equation (2) can be used in a continuous manner, as in classical secondary nucleation theory to predict the size of the critical nucleus. In the case of a polymer it has been assumed that the chain is added one stem at a time and so the only dimensional variable is the length of the chain in the first stem. It is this dimension which therefore becomes constant as a function of time. It does, however, vary with temperature, or more accurately supercooling, and the final equation [52] predicts the experimental behavior.

$$l = 2\sigma_e T_m^0 / \Delta H_f \Delta T + \delta l, \quad (5)$$

where σ_e is the free energy of the folded surface. In practice, the value of l produced from the equation is not immediately identifiable with the measured value of the lamellar thickness. This occurs because there exists in most cases a thickening process which appears shortly after deposition of the stem as the crystal reduces its total free energy. However, the equation can be used accurately to describe the experimental behavior if a thickening coefficient is included in the equation.

Complete development of the theory requires the generation of a series of equations for the forward and backward steps of each stem addition. This is then followed by the formulation of a flux equation from which an equation for the rate of deposition of critical first stems, and hence, the rate of linear growth can be predicted. In the early versions of this theory it was assumed, as in classical nucleation theory, that the deposition of the first stem was the rate-controlling step. This assumption made it possible to generate the equation.

$$G = G_0 \exp(-\Delta F^*/kT) \exp(-\Delta U^*/kT), \quad (6)$$

where G is the linear growth rate, G_0 the pre-exponential factor, ΔF^* the free energy of formation of the critical nucleus and ΔU^* the activation energy of the elementary jump process. For the classical case the value of ΔF^* is given by

$$\Delta F^* = 4\sigma\sigma_e T_m^0 / \Delta H_f \Delta T. \quad (7)$$

The theory therefore predicted the dependence of lamellar thickness and of linear growth rate on supercooling, the most important experimental dependences.

The most important fundamental revision to be made to the theory until recently was the introduction of regimes in which the formation of a single critical nucleus need not be the rate-controlling step [78, 52, 79]. One of the simplest ways to envision regimes to think of the crystal growth process as being controlled by two competing rates, the first being the deposition of the critical nucleus (i.e. first stem) and the second being the subsequent surface spreading process (i.e. second and other stems). Regime I consists of the classical picture in which the spreading rate is much greater than the nucleation rate. Regime II occurs when the two rates are comparable, and regime III when the rate of nucleation is much greater than the rate of spreading (see fig. 21).

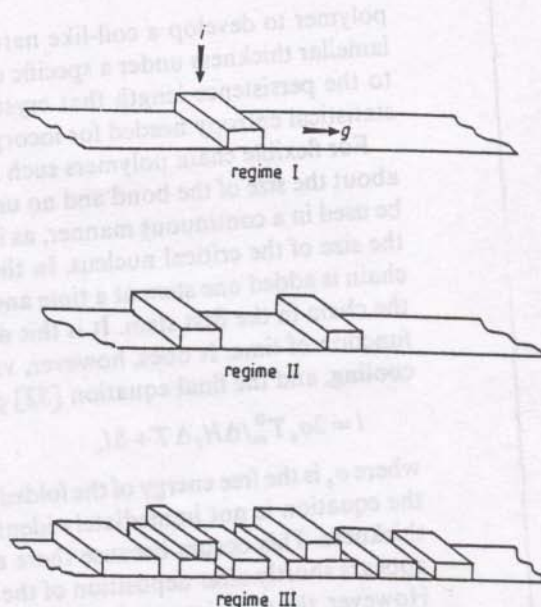


Fig. 21. Schematic diagram of secondary nucleation profiles in the three regimes of polymer crystallization (first published in [3]).

The original experiments which spurred this development were reported by Hoffman et al. in 1975 [80] and were carried out on polyethylenes having very narrow molecular weight distributions. Intermediate molecular weight fractions were found to exhibit a change of slope in the growth rate versus temperature curve at a supercooling of 17 K. The slope in the lower temperature range studied was about a half of that for the upper temperature range. Regime theory, as published by Lauritzen and Hoffman in 1973 [78], uses the symbols i for the rate of secondary nucleation and g for the rate of lateral spreading. The theory predicts that in regime II, where the two rates are comparable, that the linear growth rate is proportional to the square root of the product ig . The immediate result of this assumption is that the free-energy term, ΔF^* , in regime II is a half of that in regime I, explaining the observed change of slope. The observed regime behavior is strongly dependent on molecular weight. Low-molecular-weight fractions crystallized exclusively in regime I and high-molecular-weight fractions exclusively in regime II. Although not yet understood in detail, the difference in behavior as a function of molecular weight is undoubtedly related to ability of the molecule to translate across the crystal-amorphous interface, since higher-molecular-weight molecules are unable to move as rapidly as low-molecular-weight molecules.

Following studies on polymers other than polyethylene, Phillips [81] in 1979 suggested that there might be a third regime occurring at even lower supercoolings than the second regime. This third regime would require that the rate of nucleation would exceed the rate of spreading. The theory for regime III was formulated by Hoffman and published in 1983 [79]. The concept of three regimes has received broad acceptance and it is now recognized that the commonly encountered regimes are regime II and

regime III. The classical approach, regime I, is rarely encountered [82]. It is also important to recognize that regime transitions can be observed in unfractionated polymers, and indeed most of the reported studies use unfractionated systems. The effect of polydispersity is to broaden the transitions and they can usually be identified with care in the analyses.

In practical terms, the most appropriate test for regimes is to plot eq. (8) in the form $\log G + \Delta U^*/kT$ versus $1/T\Delta T$ where ΔT is the supercooling. The major problem encountered with this approach is the need to factor out the effect of the elementary jump process, represented as ΔU^* . It is preferable for some form of independent estimate of this parameter to be available. The most useful is to use the Williams-Landel-Ferry (WLF) relation, which is well established and for which calibration constants are available for many systems. Originally suggested by Hoffman and Weeks [53], the approach has been found to work well. Its major problem is that it is an empirical relation usually derived from studies of relaxation or of viscous flow. Bulk studies may not provide an appropriate estimate of the behavior of a section of crystallizing chain. However, since in many cases it appears that the large-scale mobility of the chain, including the effects of entanglements, may be an important controlling variable, the WLF equation may be adventitiously quite appropriate. For polymers which crystallize over a narrow range of temperatures close to the melting point, the ΔU^* factor has little influence on the analyses [25] and the way ΔU^* is treated is not critical. Because of this observation a simplified approach using one "universal" value has been popular for those systems [83, 52]. For polymers having a wide crystallization range, this approach is inadequate and the WLF equation using the values of the constants for the polymer being investigated has proved to be the most reliable method (see, e.g. [23, 45]).

The essential problem facing theorists is that the molecule must be extracted from the entangled melt at high speed and sufficiently fast not to inhibit the very rapid surface spreading process. The process does not require that the entire molecule translate as a whole, but that it be reeled in from one end, or perhaps from the middle. The introduction of the concept of reptation by De Gennes [84] has been of assistance. This different approach to polymer mobility assumes that the molecule has to snake its way through a "hole" defined by its neighbours without their behavior being significantly modified. Experimental values for the activation energy of such a process are hard to come by and are available for very few polymers. Hence, the continuing need for some sort of reliable semi-empirical approach. A value for the activation energy of reptation has been obtained for polyethylene, using studies of self-diffusion in isotopic mixtures [85]. A major achievement of the introduction of this approach to crystallization was the demonstration by Hoffman [86] that the value of the rate of reptation in polyethylene was just adequate for the rate of spreading to occur at its known rate, whereas estimates of the rate of translation of the entire molecule were inadequate by orders of magnitude.

A major problem arising from the lack of real knowledge of the correct method of handling the mobility exponential is the possibility of "generating" a regime transition where none exists. The reverse is also possible, in that a single regime can disappear in performing the plot. The latter had occurred several times prior to the recognition of

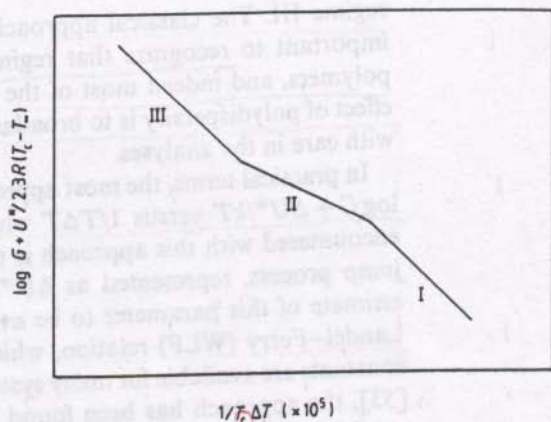


Fig. 22. Schematic diagram of a regime plot of linear growth rate data (first published in [3]).

the existence of regimes, where the objective was to produce a single slope line through appropriate choice of ΔU^* [87]. The true test of regime theory is the existence of all three regimes in a given polymer, since no amount of inappropriate curve fitting can generate the expected two changes of slope (fig. 22). The first such incontrovertible study was for studies of cis-polyisoprene [45] (fig. 23), where all three regimes were observed in a polymer of molecular weight 314 000. Higher molecular weights showed either a combination of regimes II and III or regime III alone. These results confirmed the conclusions regarding the molecular weight dependence of the regime I–regime II transition obtained from polyethylene studies and demonstrated the molecular weight dependence of the regime II–regime III transition. All three transitions have now been reported for an additional three polymers [88–90].

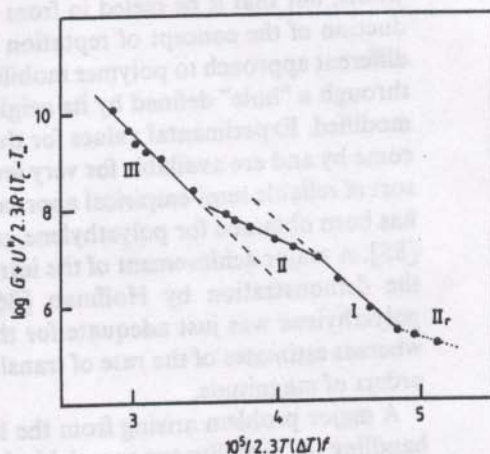


Fig. 23. Crystallization regimes in cis-polyisoprene determined from transmission electron microscopy of osmium tetroxide stained films (first published in [45]).

It is important at this point to discuss the influence of regime on the detailed structure of the fold surface and on mechanical properties. Regime I corresponds to type 1 folds almost exclusively, i.e. adjacent re-entry, which is possible because of the reptation of the relatively short molecules which normally give rise to this regime. Any one molecule lies almost exclusively within a single lamella, its ends being either buried in the surface or dangling from the surface as cilia. There are therefore very few molecules which add to two or more crystals concurrently and hence bridge the amorphous phase. The material therefore consists of crystals suspended in a highly viscous fluid (the amorphous phase). Such materials are usually of the highest crystallinities possible, ca. 80%. It is well known that such materials have very poor mechanical properties and usually fail in a brittle manner at low stresses [91].

Regime II crystallization will give rise to many molecules which bridge the gaps between crystals. This occurs largely because the effective diameter of a random coil molecule of medium to high molecular weight is several times the lamellar thickness. As demonstrated by neutron scattering, this diameter is approximately retained during crystallization. The chains can be envisioned as crystallizing in many crystals concurrently and also at many sites in each lamella being formed. Adjacent re-entry folding is probably restricted to less than ten contiguous stems, dependent on crystallization temperature. The large concentration of tie-molecules generated by the process form effective mechanical links between the crystals, the material failing by the plastic deformation processes for which polymers are well-known.

In regime III the detailed surface structure is more difficult to predict. The situation is similar to that of regime II with the exception that the number of chain sections depositing as secondary nuclei is much greater. There are limits to the concentration of emerging non-folded chains that can exist in a surface because of packing constraints [62, 63]. Such limitations have been estimated on the assumption that the chains are Gaussian immediately on emergence. It seems likely that the chains will be non-Gaussian on emergence and become Gaussian some distance from the crystal, as suggested in Mandelkern's interzonal model [64] and in Wunderlich's rigid amorphous phase model [65, 66]. Such structures correspond to type 3 chains of the synoptic model given earlier. It has been well known for generations to plastics fabricators that the best mechanical properties are obtained when crystalline thermoplastics are quench-crystallized. Hence they are trying to crystallize the polymers in regime III or deep regime II in order to maximize the number of tie-molecules present.

There is a misconception prevalent with regard to this effect. It is often thought that brittleness is a result of too large a spherulite size, whereas it is really the conditions necessary to generate a large spherulite that are those that produce regime I crystallization, with its paucity of tie-molecules. Additionally, at such high crystallization temperatures in some polymers impurities tend to be effectively segregated to the spherulite boundaries, intensifying the brittleness problem.

4.1. *The influence of molecular structure*

In the above discussion it was mentioned a number of times that the molecular weight of the polymer was of significance in influencing regime behavior. Recognizing that the

regime transitions are determined by the relative values of the rate of secondary nucleation and the rate of surface spreading, it should be possible to change the transition temperatures through appropriate changes of variables that might influence one rate more than the other. It is here that the synthetic chemistry can be used in a very useful manner. The major principles are still being elucidated; however, several important relations have already been demonstrated.

The first clear demonstration of the influence of structure on regimes was demonstrated by crosslinking polyethylene [92]. First, it was predicted that crosslinking should eliminate reptation as a mechanism for transfer of the molecule from the amorphous to the crystalline state. As such, it should significantly reduce the rate of spreading, g , and switch the regime from I or II to III. This was seen to occur clearly (fig. 24). This effect would be expected to be unique to crosslinking. A second effect observed should also be seen in random copolymers, but requires more explanation.

When a polymer chain contains a defect (e.g. comonomer units, branches or isomers) which cannot be incorporated into the crystal, the exclusion process slows down the rate of secondary nucleation. This is largely because the first stem that deposits as the critical nucleus requires a finite number of crystallizable units in a continuous uninterrupted sequence. There is therefore a limited probability of locating the appropriate string needed and this probability has to be incorporated into the theory. This was first done by Andrews et al. [93] and applied to isomerized cis-polyisoprene. The theory predicts that the logarithm of the rate of secondary nucleation should depend on the mole fraction of chain impurities in an inverse fashion. Hence a few

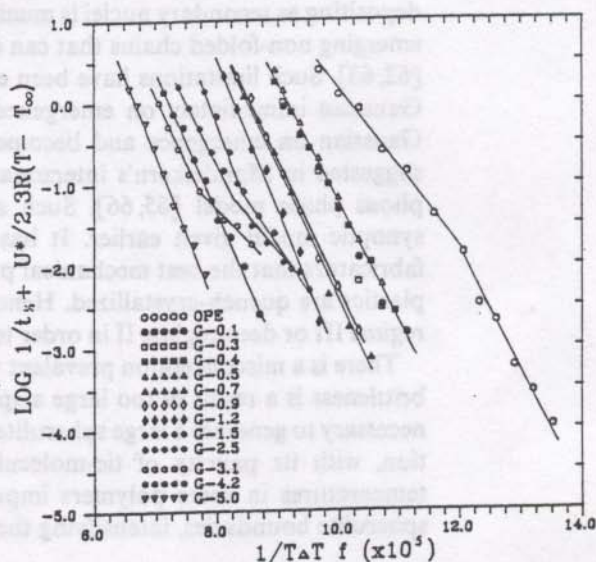


Fig. 24. Crystallization regimes in crosslinked linear polyethylene as a function of the molecular weight between crosslinks (MWX), determined from bulk growth rates. G-0.1: MWX 17 300; G-0.3: MWX 12 700; G-0.4: MWX 9400; G-0.5: MWX 5700; G-0.7: MWX 4500; G-0.9: MWX 3600; G-1.2: MWX 3100; G-1.5: MWX 2200; G-2.5: MWX 1900; G-3.1: MWX 1300; G-4.2: MWX 960 and G-4.5: MWX 560 [94].

percent of chain defects cause the rate of linear growth to drop by orders of magnitude. The Andrews theory of course pre-dated regime theory by several years. As the degree of crosslinking is increased the rate of secondary nucleation, i , must decrease and ultimately must become comparable to the rate of spreading, g , and the regime III induced by the first crosslinks must revert to regime II. This effect is demonstrated in fig. 24.

The second effect, that of a reducing rate of secondary nucleation, is to be expected of all polymers containing chain defects, including copolymers. Hence copolymers such as branched polyethylenes, where the branch is excluded from the crystal, are expected to have regime transitions different from those of linear polyethylene and dependent on the level of branching. Such effects have recently been studied for cross-fractionated polyethylenes (i.e. they have been fractionated according to molecular weight and then according to branching frequency). The effect is quite clear for relatively low-molecular-weight fractions (i.e. those that show a regime I–regime II transition). As the level of branching increases the regime I–regime II transition temperature translates to successively lower temperatures (fig. 25). In the case of higher-molecular-weight fractions, where only regime II is observed for the linear polymer, a regime II–regime III transition is induced for high levels of branching [94].

All recent versions of secondary nucleation theory start the first stem at a chain end and then reel in additional stems in one direction along the growth face. The Andrews theory contains as one of its predictions that the number of crystallizable units in a critical nucleus can be calculated from the slope of a plot of the logarithm of growth rate at a given temperature versus the defect content. When this calculation was performed for cis-polyisoprene it was found that the number corresponded not to a single stem but to three stems. A similar conclusion was reached in the aforementioned studies of

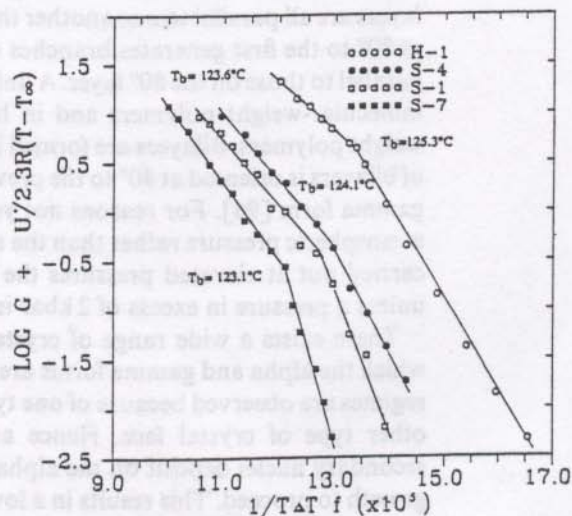


Fig. 25. Crystallization regimes in polyethylene fractions of molecular weight 20000 as a function of hexyl branch content per 1000 C atoms. H-1: linear; S-4: 8.8/1000; S-1: 16.7/1000 and S-7: 20.7/1000 [94].

crosslinked polyethylene. In both cases free ends are not easily available. In the case of *cis*-polyisoprene this is because of its high molecular weight giving rise to "permanent" entanglements, and in the case of crosslinked polyethylene due to the crosslinks having eliminated chain ends. Hence, it was postulated that the three-stem nucleus is a natural consequence when there are major constraints on chain mobility [92].

There is, however, an additional major change that can be generated by increasing the chain defect content. This effect was seen first in the crosslinked polyethylenes [94]. The Andrews theory assumes that the basic tenets of secondary nucleation theory remain in effect when the chain defects are present. One of the major tenets is that embodied in eq. (4), namely that the lamellar thickness is determined by the supercooling. In the cases under consideration currently, this corresponds to the combined length of three stems and the folds linking them together. There is a point reached, as defect level is increased, where the total length required at a given temperature of crystallization by eq. (4) simply is not attainable. The maximum length achievable under such circumstances corresponds to the average separation of chain defects, which is less than the total length required by the three-stem nucleus. The system therefore reverts to a single-stem nucleus with a lamellar thickness determined by the chain microstructure. This results in a switch to regime III as there is a higher probability of finding these less stable structures than there is of finding the preferred three-stem nuclei. This type of behavior is to be expected in all copolymer systems containing excluded units.

There is another type of effect involving the polymer structure in a more subtle fashion. As mentioned earlier, polypropylene forms a 3:1 helix and these helices pack together to form the crystal. Because the methyl side groups of the polymer stick out from the helical cylinder there exists a helical groove in the surface of the cylinder. This unique geometry (fig. 26) makes it possible for additional helices to lay down at an angle of 80° to the helices in the layer below [95,96]. When the chains in successive layers are all parallel to one another the common α crystal results. A layer of chains at 80° to the first generates branches of α if the chains in succeeding layers are all parallel to those on the 80° layer. A unique situation occurs in the crystallization of low-molecular-weight polymers and in high-pressure crystallization of high-molecular-weight polymers. Bilayers are formed involving parallel chains, but each succeeding set of bilayers is oriented at 80° to the previous one. This results in a new type of crystal, the γ form [96]. For reasons not yet understood, the α form is encountered at atmospheric pressure rather than the more dense γ form. When crystallization is carried out at elevated pressures the γ form starts to form, but does not dominate unless a pressure in excess of 2 kbar is used.

There exists a wide range of crystallization pressures (from 1 bar to 2 kbar) over which the α and γ forms are generated concurrently. Here unusual effects on regimes are observed because of one type of secondary nucleus trying to deposit on the other type of crystal face. Hence at low pressures of crystallization the γ secondary nuclei deposit on the α growth face and have to be removed for α growth to proceed. This results in a lowering of the rate of secondary nucleation, *i*, and hence a movement from the normal regime II-regime III system found at atmospheric pressure to a regime I-regime II system. At higher pressures where the γ crystals

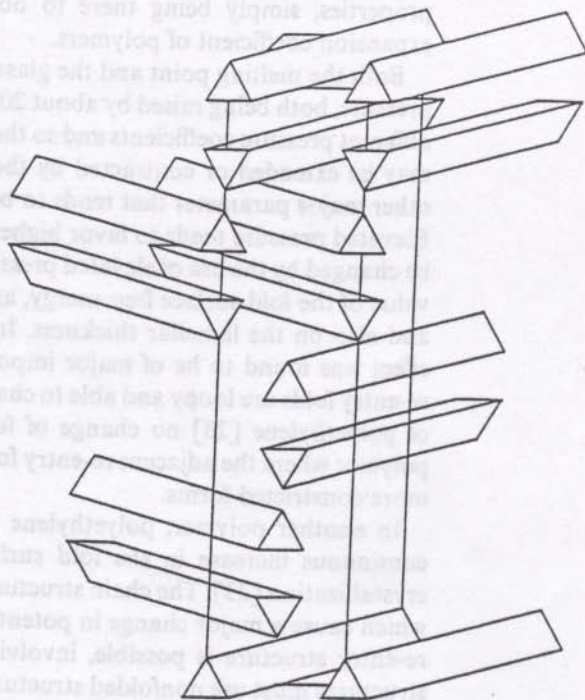


Fig. 26. Chain packing in a gamma crystal of polypropylene [30].

are growing, an analogous effect occurs and a regime I–regime II gamma system is observed. At even higher pressures, where only gamma occurs, a regime II–regime III system is found. The two forms have similar values of stem lengths and fold surface free energies at equivalent supercoolings. This tends to indicate that the differences between the two forms are somewhat analogous to the well-known differences between bcc and hcp crystals, namely different stacking sequences between essentially identical layers [30, 97, 98].

This unusual behavior of polypropylene is the only known example of two competing crystalline forms poisoning each others growth surfaces with alien secondary nuclei and is a direct result of the molecular structure of polypropylene.

4.2. The influence of pressure

The majority of the research carried out on spherulitic growth has considered temperature alone as the variable. Less than one percent of the effort has considered both primary thermodynamic variables, pressure and temperature. Pressure is routinely used in plastics moulding operations and in many cases the pressures used do cause significant changes in growth behavior, an excellent example being that of polypropylene given above. Yet pressure is not used as an active variable in the control of

properties, simply being there to obviate problems caused by the large thermal expansion coefficient of polymers.

Both the melting point and the glass transition temperature are strong functions of pressure, both being raised by about 20°C per kbar. Generally the two parameters have different pressure coefficients and so the temperature range available for crystallization may be extended or contracted by the imposition of an elevated pressure. The only other major parameter that tends to be influenced by pressure is the folded structure. Elevated pressure tends to favor higher-density forms and so fold conformations may be changed by the use of elevated pressures. This in turn will have a major effect on the value of the fold surface free energy, and hence on the rates of growth of the lamellae and also on the lamellar thickness. In the case of *cis*-polyisoprene [87, 99, 100] this effect was found to be of major importance, it being a polymer where the adjacent re-entry folds are loopy and able to change conformation easily. In an analogous study of polyethylene [25] no change of fold surface free energy could be found in this polymer where the adjacent re-entry folds are tight and relatively incapable of forming more constricted forms.

In another polymer, polyethylene terephthalate, there was found to be a major continuous increase in the fold surface free energy with applied pressure during crystallization [23]. The chain structure of PET contains phenyl rings in the backbone which cause a major change in potential folded structures. Only one type of adjacent re-entry structure is possible, involving the aliphatic groupings. Any other surface structures must use nonfolded structures such as tie-chains or non-Gaussian cilia. It is possible that the studies of PET at elevated pressures have involved the pressure

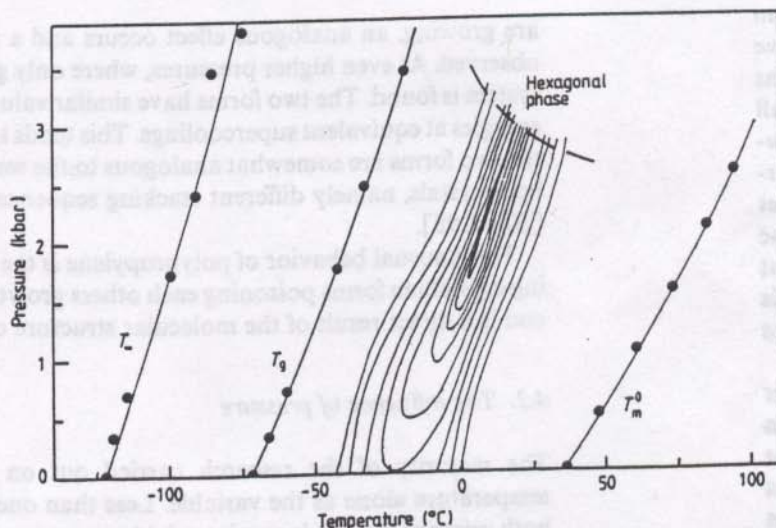


Fig. 27. The phase diagram of *cis*-polyisoprene showing the equilibrium melting point, glass transition temperature, WLF T_{00} temperature, and the lamellar growth rates in contour form. The contour values are (inward) 0.05, 0.1, 0.25, 0.5, 1, 1.5, 2, 2.5 and 3 microns per hour (first published in [99]).

dependence of the conformations of non-Gaussian chains, but theoretical approaches are not available to test such a hypothesis.

Polymers which can be crystallized over a complete range of temperatures from the glass transition to the melting point are expected to show combined phase-kinetic diagrams such as those of *cis*-polyisoprene (fig. 27). There are four basic forms of fold surface-pressure dependence to be expected:

- (1) insensitivity due to tight adjacent re-entry folding,
- (2) step changes due to loose adjacent re-entry folding,
- (3) small continuous increase due to switchboard folding,
- (4) large continuous or discontinuous increase due to nonfolded forms.

Only type 3 has not yet been observed in experimentation.

There is an additional effect which was once thought to be general, but is now known to be restricted to a small number of polymers that crystallize in regime I where continuous adjacent re-entry folding occurs and where activation energies for "snaking" through the crystal are relatively low. This is the formation of chain-extended crystals in which the lamellar thicknesses approach those characteristic of the fully extended chain [101-104]. The effect is only seen in molecules of low and intermediate length.

In the case of polyethylene it has been established that the mechanism for the formation of these unusual species involves first the growth of hexagonal crystals, followed by their transformation to the orthorhombic form [105,106]. Thickening occurred in two stages: first, the lower heat of fusion of the hexagonal phase causes thicker crystals to form; second, during the transformation more thickening can occur. It should be recalled that when crystallization of orthorhombic polyethylene occurs at very low supercoolings at atmospheric pressure (i.e. in regime I), crystals as thick as 50 nm are easily produced. Only two additional polymers exhibit major chain extension, poly(tetrafluoroethylene) and poly(chlorotrifluoroethylene).

5. Spherulitic morphogenesis

The mechanisms whereby the lamellar crystals generate spherulitic textures will now be considered. It has to be recognized at the outset that lamellae are single crystals and differ only from those large species grown from solution in size, degree of faceting and in the mix of fold surface structures present. The equations given earlier that describe the relation between lamellar thickness and temperature and between crystal growth rate and temperature apply to all conditions. In metals the differences between single-crystal growth and polycrystalline growth are largely due to changes in primary nucleation. In macromolecules many of the differences are endemic to their length and entangled nature. Placing macromolecules in solution serves to isolate the molecules and mitigates complications due to their long-chain nature. A graphic example of this effect is the ability to draw out the macromolecules from a gel in such a way that the molecules crystallize from an essentially fully extended form to generate fibers which have a modulus approaching that of a carbon-carbon bond [107].

One important, but poorly understood, aspect of spherulitic generation is the effect of molecular variables on the lamellar width. Although the lamellar thickness has been studied quantitatively for many years (see [3]) and so also has the lamellar length through spherulitic growth, the lamellar width is a much more elusive quantity. Its study requires some form of electron microscopy combined with some form of specimen orientation. It also requires that the lamellae be relatively loosely packed so that individual crystal shapes can be discerned. Sometimes it is possible to discern the width if some crystals at the growth front protrude into the melt. It is generally accepted that the width increases with crystallization temperature, but the detailed dependence is not understood in general.

In the case of *cis*-polyisoprene, because of the afore-mentioned ability of osmium tetroxide to terminate the crystallization process at will, it was possible to observe clearly that there was a major change in the width dependence on temperature at the regime I–regime II transition temperature [108,45]. In both regimes III and II the

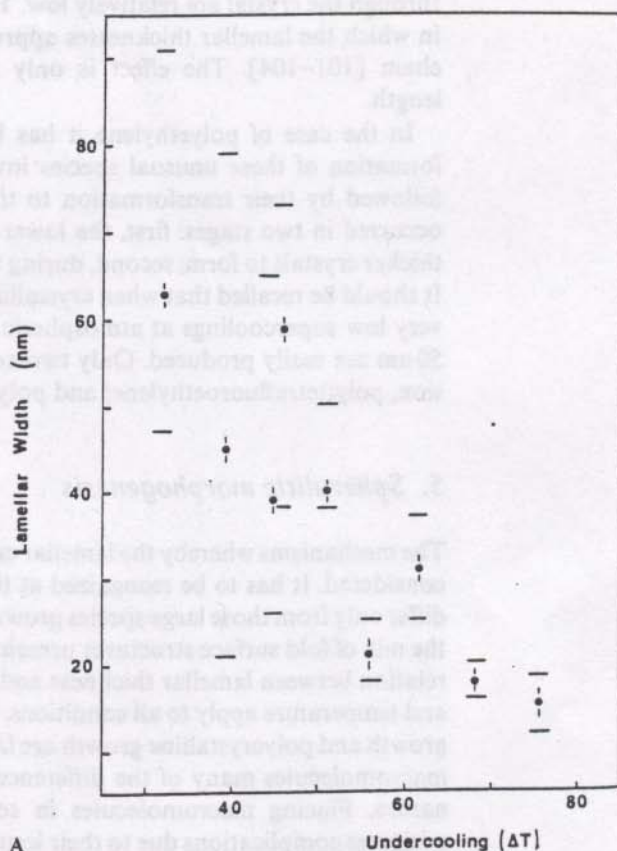
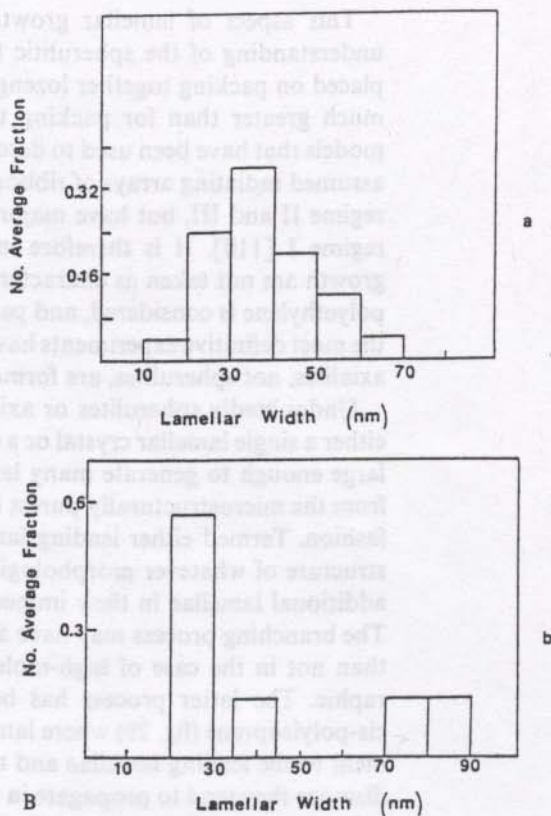


Fig. 28. (A) Distribution of lamellar widths in a fraction of *cis*-polyisoprene of molecular weight 313 000, and (B) dependence of lamellar width on supercooling at (a) -20°C and (b) -0.6°C (molecular weight 543 000) [108].



(Fig. 28 cont'd)

crystal grew as a ribbon of constant width. Although there was a distribution of widths present (fig. 28a) the peak width clearly was inversely proportional to supercooling in a similar way to lamellar thickness (fig. 28b). In regime I leaf-shaped crystals resulted (fig. 17) and the constant width relation disappeared. In polyethylene and some other highly crystalline polymers the shapes of the dominant lamellae appear to be leaf-shaped in both regimes I and II (personal communication from D.C. Bassett). The ribbon-like lamellae observed in regimes II and III in *cis*-polyisoprene and other low-crystallinity polymers may be characteristic of only polymers where for some reason or other the lamellae are separated by large amounts of inherently non-crystallizable material. It may be a direct result of the very long molecules, long-chain branches or even gels present in such systems.

In other polymers studied, researchers have of necessity considered the shapes present at the growth tips. It has also been necessary to carry out the studies at low supercoolings in order to obtain reasonable descriptions, and so studies of polyethylene have been primarily in the regime I region. They have tended to confirm a wide lamellar profile of approximately leaf-shaped entities, often with relatively well-defined growth tips.

This aspect of lamellar growth is very important to the generation of a real understanding of the spherulitic formation process, simply because the constraints placed on packing together lozenge or leaf-shaped crystals into a spherical entity are much greater than for packing together ribbon-like crystals. The most successful models that have been used to describe the light scattering [109] from spherulites have assumed radiating arrays of ribbons and are very effective for polymers crystallized in regime II and III, but have major problems when applied to polyethylene grown in regime I [110]. It is therefore important that features defined for one regime of growth are not taken as characteristic of all conditions. This is very important when polyethylene is considered, and perhaps taken as the paradigm for all polymers, since the most definitive experiments have been made at low supercoolings in regime I, where axialites, not spherulites, are formed.

Undoubtedly spherulites or axialites in the vast majority of polymers begin from either a single lamellar crystal or a cluster of such lamellae, unless a particulate nucleus large enough to generate many lamellae is operative. The initial lamellae are grown from the microstructurally purest molecules present and they tend to grow in a linear fashion. Termed either leading lamellae or dominant lamellae, they form the superstructure of whatever morphological species is being formed. They tend to generate additional lamellae in their immediate vicinity, presumably by a branching process. The branching process may have a crystallographic contribution to it, but more often than not in the case of high-molecular-weight polymers, it may be non-crystallographic. The latter process has been demonstrated to occur in polymers such as *cis*-polyisoprene (fig. 29) where lamellar branches are seen to have no physical attachment to the leading lamellae and to splay away shortly after formation. After a short distance they tend to propagate in the same radial fashion as the first lamellae created.

In the early stages of growth the morphological units do not have a spherulitic appearance, but are sheaves. In the case of axialites, where the lamellae are very wide,

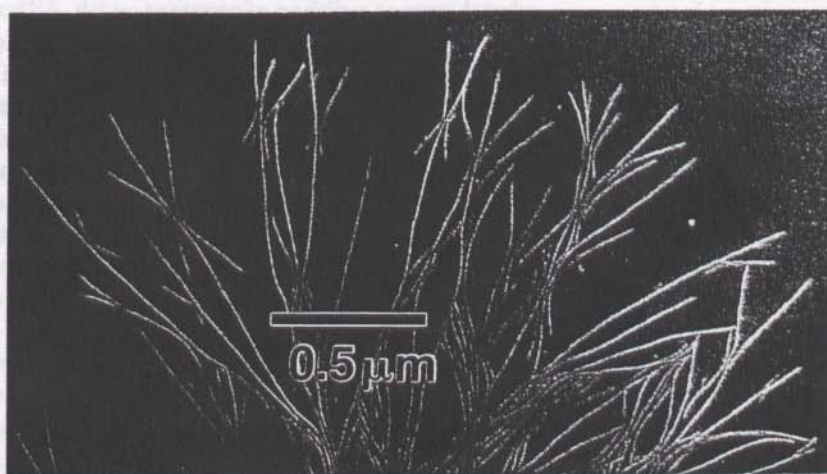


Fig. 29. Non-crystallographic branching in *cis*-polyisoprene crystallized at -15°C .

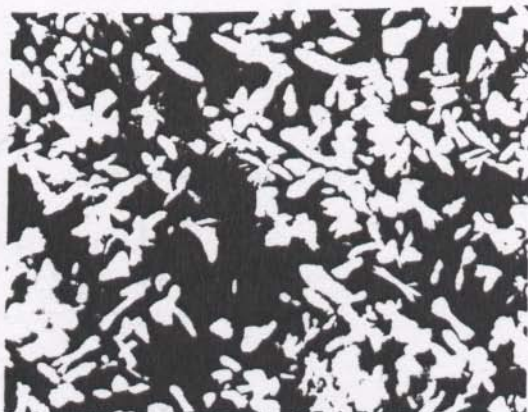


Fig. 30. Axialites growing in a branched fraction of polyethylene of molecular weight 35700 and 15.5 hexyl branches per 1000 C atoms [94].

the growing entities appear as single, or more often as double, propellers (fig. 30) in an optical microscope. In the case of polyethylene grown in regime I, the dominant lamellae tend to grow in cells and are very wide and ridged (see [17] for a review). The ridges are a reflection in the melt of the tendency of the solution-grown single crystals [111] to form hollow pyramids and ridged pyramids (fig. 31). The chain stem is inclined to the surface of the fold surface in these ridged crystals at an angle consistent with that in single-crystal growth. The ridging disappears when lower temperatures of crystallization consistent with regime II are used.

There can be little doubt that the leading lamellae are formed from the microstructurally purest molecules and they have a higher probability of secondary nucleation



Fig. 31. Ridged crystals in linear polyethylene (photograph supplied by D.C. Bassett; first published in [3]).

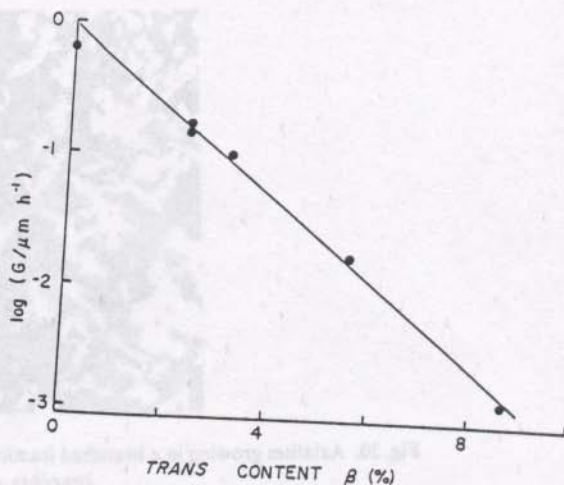


Fig. 32. The growth rate of cis-polyisoprene lamellae at -26°C as a function of microstructural impurity content (first published in [120]).

than do microstructurally impure molecules. The research referred to earlier, in which the effect of branches and of comonomers was considered, predicts that this must be the case. It has been recognized for many years that impure molecules are rejected at the growth face and crystallize later. The reason did not become clear until Andrews et al. [93] clearly demonstrated that this rejection was due to their lower probability of secondary nucleation (fig. 32) and was a logarithmic dependence on impurity content. Although the effects of chain impurity content on crystallization are now beginning to be understood in terms of probability of rejection and of regimes for narrow fractions, the details of blending of fractions together defines the ultimate events and are only now being investigated.

The recognition of the presence of leading lamellae and their control over the spherulitic superstructure and the growth front has emphasized the lack of understanding that exists with regard to subsequent events. Prior to this realization it had been generally assumed that the branching was sufficiently rapid for the newer crystals to be growing at the front. It is now recognized that a large amount of the crystallization occurs behind the growth front and the degree of retardation will depend on the polymer. In the case of axialites in polyethylene, the filling in between cells of the leading lamellae may not take place until the temperature is lowered. In the case of spherulitic growth in polyethylene in regime II many of the branched crystals growing from relatively pure microstructurally defective molecules may be only slightly behind the growth front of the dominant lamellae and impossible to resolve optically. In the case of PEEK the secondary crystallization can be seen as a second spherulitic growth front emanating from the center of the spherulite due to an unusually severe retardation of the branching processes [112].

It has to be recognized from fig. 32 that in any system there will be a whole range of molecules of differing levels of microstructural impurity and molecular weight that simply will crystallize on different time scales at a given isothermal condition. The

conditions, both environmental and molecular, that are needed to convert axialitic growth into spherulitic growth are simply not understood in any detail. It involves a change of lamellar shape from leaf to ribbon, probably the infilling taking place as ribbons. It is known [95] that the tendency to form axialites initially is controlled by molecular weight and temperature alone in fractions and not by impurity levels. However, high molecular weights combined with high levels of branching ensure spherulitic textures.

A still poorly understood feature of spherulitic growth in polyethylene is the formation of banding. This feature has been recognized from the earliest studies using optical microscopy (see, e.g. [14]). Early interpretations involved a regular helicoidal twisting of the lamellae as they radiated outwards and there is no doubt that such an explanation is absolutely consistent with polarized microscopy. It is a feature that is associated with regime II growth. More recent studies using permanganic etching and

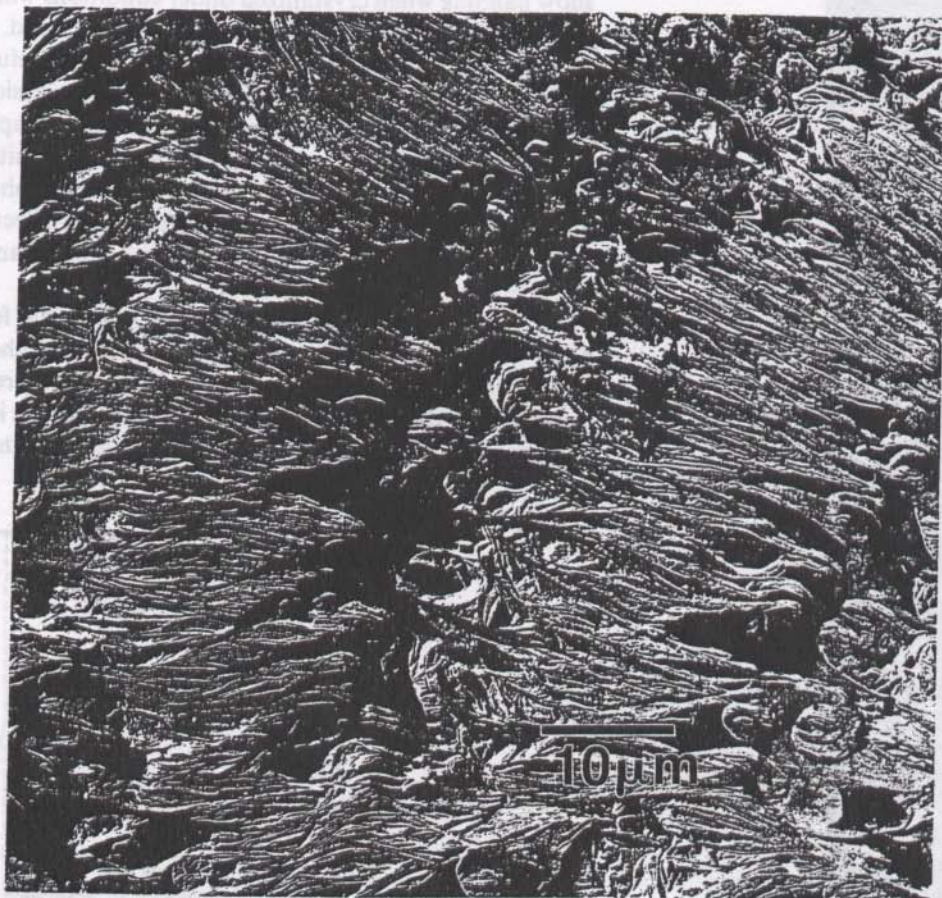


Fig. 33. Banding in linear polyethylene in a TEM photograph of a chromium shadowed permanganically etched surface (first published in [3]).

chlorosulphonation show that individual lamellae do not twist continuously (see [17] for a review), but that the regular banding is the result of an aggregate effect. Permanganic etching studies suggest that screw-dislocation-generated branching is an integral feature of regular banding (fig. 33). Such a mechanism generates six to twelve new crystals in a stack each time it functions. Under such circumstances the new lamellae will rapidly outweigh their progenitors and will follow very closely behind the original lamellae as they grow. It is also clear from micrographs such as that in fig. 33 that twisting of the lamellae remains an integral part of the process. It is possible that the new stacks are generated whenever there is space generated by the radial growth process for their generation [113]. Why such a process should generate so many crystals at one time rather than simply one or two at a time has not been established.

It has also been demonstrated [94] that banding is rarely present in crossfractionated specimens of polyethylenes. Materials which had been subjected to fractionation for both branching and molecular weight in two separate consecutive treatments did not show banding when crystallized under conditions which generated spherulites. Indeed, the spherulites formed were very poorly developed. However, specimens which had only been subjected to TREF (temperature rising elution fractionation), which essentially separates largely by branching, formed classical spherulites. The complicated molecular features which control the generation of spherulites and also the generation of banding in bulk unfractionated materials are quite poorly understood. It is something of an anachronism that the best known morphological unit manifest by macromolecules is generated most easily and most perfectly by polymers showing a wide range of molecular weights combined with a wide range of chemically microstructural imperfections.

In less densely packed spherulites it is possible for the number of branch stacks being generated by screw dislocations, or some other process, to be estimated. The results for *cis*-polyisoprene are shown in fig. 34, where it can be seen that the process is controlled by the regime operating. In this case there is a discontinuous jump as regime II is entered by lowering the temperature and that the maximum generation is

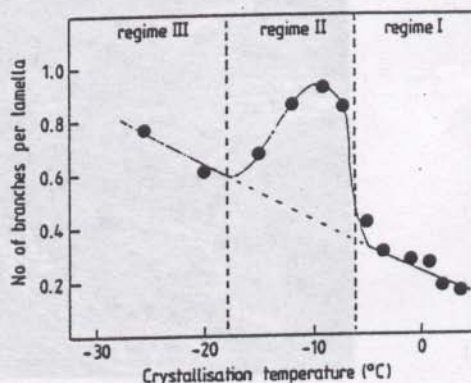


Fig. 34. Average number of branches per lamellar crystal in *cis*-polyisoprene as a function of crystallization temperature for a fraction of molecular weight 313 000 (first published in [45]).

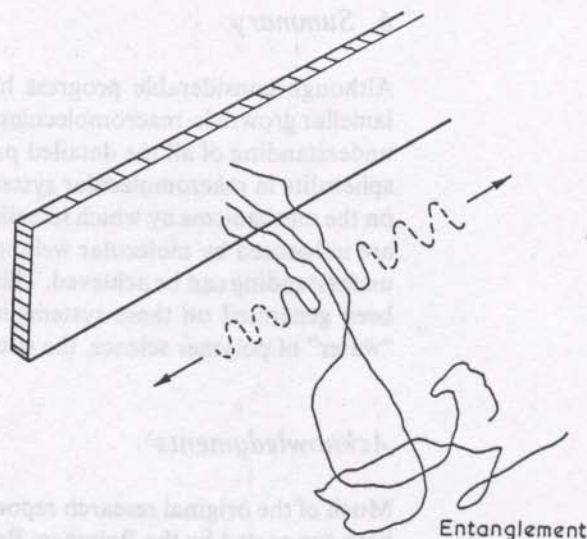


Fig. 35. Early view of the mechanism of non-crystallographic branching in a high polymer (first published in [121]).

somehow associated with the regime change. Since regime II occurs when multiple nucleation becomes prevalent it seems reasonable to speculate that the occurrence is related to the formation of tie-molecules and to stress being generated at the crystal-amorphous interface by tie-chain extension. An early view of the process is depicted in fig. 35 but it does not involve the initiation of screw-dislocation-type growth. Whether or not such a type of stress generation could produce a screw dislocation and the growth that can be generated by it remains to be explored theoretically.

It should also be noted that, although lamellae have been referred to as ribbons or leaves throughout, they are not necessarily planar entities. A glance at any of the micrographs of *cis*-polyisoprene used in this chapter shows that they tend to bend and curve, especially near the sites of their inception. This comment is true of the leaf-shaped lamellae found in axialites. Clearly, for a leaf-shape to be curved the object itself must have some overall convex or concave shape. The existence of such "bowl-shaped" lamellae has been investigated in some detail for a small number of polymers largely by Khoury and Barnes [114-116]. Although circumstances leading to their formation have been well documented the detailed explanations for the behavior have not yet been resolved. It is unlikely that they are quirks, since similar objects in the form of multilayered aggregates have been seen in several systems (see, e.g. [115]). Additionally, it is worth noting that solution-grown single crystals of polyethylene are generally reported as hollow pyramids, but that in the early work of Bassett [111, 118] it was noted that a substantial number of double-cupped crystals were found.

6. Summary

Although considerable progress has been made in understanding the essentials of lamellar growth in macromolecules, as a community we are well away from a complete understanding of all the detailed processes that lead to the generation of the classical spherulite in macromolecular systems. It is clear that much additional work is needed on the mechanisms by which lamellae branch and splay apart, and how these processes are influenced by molecular weight and molecular microstructure, before any overall understanding can be achieved. This is despite the volume of excellent research that has been generated on these systems in the past forty years. Even for polyethylene, the "water" of polymer science, the situation is far from being resolved.

Acknowledgments

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