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Polymer crystals

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Abstract

In the twenty years since this subject was last reviewed for this journal by Andrew Keller there has been an almost explosive growth of research in the area of crystallisation of polymers. This growth has been almost exclusively in the area of crystallisation of polymers from the molten state, whereas when Keller wrote his review most of the work was on crystallisation from solution. At that time, the research was conducted exclusively on flexible chain polymers, but during the past ten years or so rigid and semi-rigid crystallisable polymers have been synthesised and become available in large enough quantities for physical measurements to be carried out. Our level of understanding of such systems at this time does not warrant an extensive review, so the major concerns of this area are simply summarised.

The major developments in our understanding of polymer crystals and the kinetics of their formation have been many. It is now established that adjacent re-entry folding of the molecule occurs on crystallisation from solution, but when crystallised from the melt the molecular trajectory approximates a random coil when viewed from a distance. From a closer viewpoint, it appears that adjacent re-entry folding is only one contributor and that any given molecule exits and re-enters several crystals in a manner that is determined by the crystallisation temperature. In addition, it is now accepted that the interface between the crystal and the random melt may be macroscopic in nature. Variously referred to as rigid amorphous phase or interzonal material, the extent of formation of such an intermediate state is strongly dependent on the rigidity of the given polymer molecule.

Our understanding of the kinetics of crystallisation has taken a major step forward through the realisation that three regimes exist, dependent on the relative rates of secondary nucleation and surface spreading. At the time of writing, the third regime is believed to be unique to long chain molecules, whereas the first two regimes have been observed in atomic solids. Although we are now beginning to understand the influence of molecular length and microstructural impurity levels on regime behaviour, our definitive knowledge is still in its formative stages. A further important development is the recognition that the skeletal structure of common superstructural crystalline aggregates, such a spherulites, is determined by a small number of leading or dominant lamellae and that the bulk of the crystallinity develops behind the growth front. Such behaviour had been recognised for many years in low-crystallinity polymers, but is now a recognised feature of growth in common high-crystallinity polymers also.

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1. Introduction

It is now over twenty years since Andrew Keller wrote a review called 'Polymer crystals' (Keller 1968). During the intervening time period, studies of the subject of crystallisation in polymers have experienced intensive growth. This has been largely due to the commercial importance of thermoplastics and to an inherent fascination with the behaviour of long chain molecules. There can be no doubt that a comprehensive review of the crystalline state in macromolecules is no longer possible within the confines of a single review paper. An underlying principle of articles in this journal is that they must provide an introduction to the subject for non-specialists, as well as to comprise an authoritative up-to-date review for scientists actively engaged in the field. In order to achieve these twin objectives it has been necessary to restrict the scope of the review considerably.

In contrast to the earlier review by Keller, which concentrated on the structural aspects of crystals grown from solution, this article will largely consider aspects of the behaviour of crystals grown from the melt. Solution-grown crystals will be considered only where significant advances in our understanding have appeared. In many ways this difference reflects the field itself, in that the vast majority of research over the past twenty years has been on bulk polymers. Several new and powerful techniques have been developed and applied to polymer crystals generating major insights into their behaviour. The important subjects of blends of polymers and crystallisation under the influence of orienting stresses have arisen and are the subject of intense and continuing study. There is not enough space available for these subjects to be reviewed in a manner which does them justice. Both subjects will be introduced only when their behaviour is of relevance to general morphological and kinetic matters. Although they are important subjects, many aspects of their behaviour are controversial and theoretical progress has been slow, making much of the knowledge of their behaviour empirical rather than definitive. The review will concentrate therefore on aspects of the crystallisation behaviour and the structures of the crystalline state of isotropically crystallised polymers. In addition it will consider, primarily, aspects of the crystallisation process which can be quantified and theories tested in a quantitative manner. The review will not attempt to reference all contributions to a given field since this is impossible because of the limited space, but will selectively refer to papers that, in the opinion of the author, best illustrate certain points. No slights to individuals are intended in the exclusion of any publication.

In a subject as difficult as this one, there are many researchers and many schools of thought. Moreover, researchers come from varied backgrounds. Chemists, like myself, chemical engineers and physicists are common, all contributing elements of their respective disciplines. Points of dispute are difficult to resolve because of our collective inability to devise definitive experiments, together with a general lack of co-operation on the part of the molecule to accede to our desires. Many subjects are controversial and have been so since studies of polymer crystals began. Certain viewpoints are held inflexibly and experimental evidence is not sufficiently definitive for one view to receive overwhelming support. Whenever such a controversial subject is reviewed, it is the intention of this author to present all available results in as objective a manner as possible. Undoubtedly, this will upset several researchers who hold definite views on such subjects. For this the author apologises in advance, but prefers to allow the reader to form his or her own conclusions, recognising that no review can be free of the personal preferences of the author.

2. General macromolecular background

Polymers differ from non-covalently bonded materials such as metals, in that on melting, the covalent bonding, which generates the characteristic macromolecular structure, remains intact. The change of state from the solid to the liquid involves only the disruption of secondary bonding forces. Consequently the entropy gain on melting is much less than that of elemental solids, a considerable fraction of the entropy being present in the form of the conformational entropy of the polymer chain. Entropic considerations in the molten state result in the generation of a molecular state of maximum disorder. This state of the molecule is that of a random coil, provided the molecule has a considerable degree of internal flexibility. At the time of Keller's review, this state was the only one studied in an explicit manner. Now, twenty years later it is necessary first to define whether or not a particular molecule is rigid or flexible. This is largely a result of the development and study of a whole new class of polymer molecules that have little or no internal flexibility. It is simply no longer possible to talk about a single class of polymer crystal. At this point it will be informative to consider the relation between the chemical structure of a polymer and the rigidity of the molecule.

2.1. Molecular structure and order

Inherent to the expected modes of behaviour of macromolecules is an extreme dependence on chemical structure. Most important is the flexibility of the polymer backbone. Commonly studied polymers such as polyethylene have a backbone composed entirely of aliphatic units. Base units are most commonly methylenes (CH_2) but slightly more complicated units such as ester and amide groups may also be present. This type of polymer is inherently flexible since the molecule may change its overall shape at ambient temperature if the kinetic energy is adequate to overcome the internal potential energy for rotation about a backbone bond (see figure 1). When side groups replace one or both of the hydrogen atoms of a methylene unit the rotational potential energy diagram is changed and higher kinetic energies are required for the molecule to change its trajectory. In many cases this results in the molecule being flexible only at elevated temperatures. This effect is believed to be directly responsible for the glass transition. Although it is not the intention of the author to review the present state of understanding of the origin of the glassy state, it should be recognised that the mobility of a polymer molecule is directly related to the temperature difference between any chosen temperature and the glass transition temperature.

When inflexible units are incorporated into the polymer backbone, usually in the form of benzene rings, the flexibility of the polymer can be drastically affected. Greatest effects are observed if the benzene ring is attached to other similar groups through the para-positions (see figure 2). In some extreme cases such as poly(paraphenylene) and poly(paraphenylene benzobisthiazole), complete inflexibility is obtained and the molecule is totally rigid. The largest numbers of new polymers generated in recent

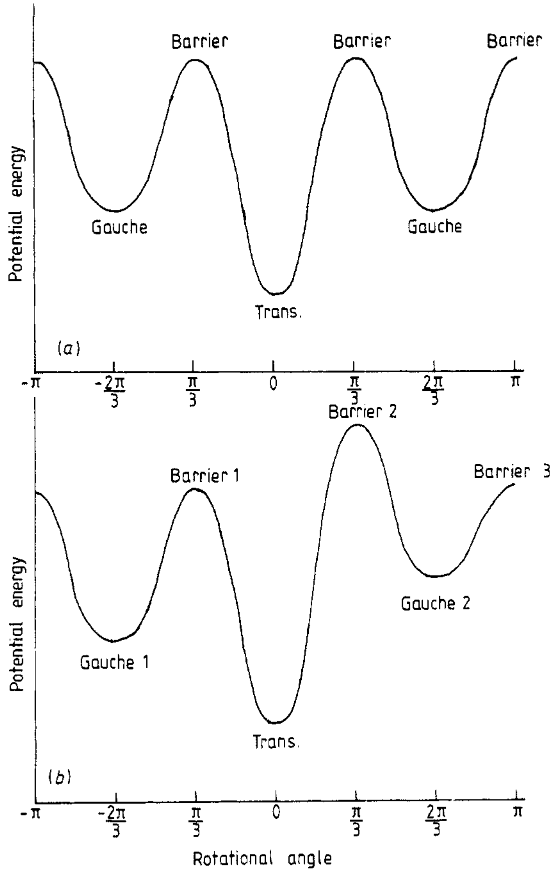

Figure 1. Schematic potential energy diagrams of rotation for (*a*) polyethylene and (*b*) a vinyl polymer.

years are not completely rigid and often are copolymers made up of random sequences of fairly similar semi-rigid units. These molecules have varied levels of internal flexibility, but never enough to permit random coil formation. Their characteristic states are generally described as liquid-crystalline. Some examples are given in figure 2.

Also of significance is the presence of side groups, which are formed whenever a hydrogen is replaced by a chemical grouping. As mentioned above, the flexibility is changed, usually resulting in a stiffer molecule. However, other important effects can be observed. These side groups are not usually added after the polymerisation reaction, but are the result of the polymerisation of a monomer molecule more complex than ethylene. A simple example is poly(vinyl chloride), often known as PVC. Vinyl chloride is simply ethylene with one hydrogen replaced by a chlorine (namely $CH_2{=}CHCl$). On polymerisation the carbons change from being trigonal (sp^2) to being tetragonal (sp^3). It is therefore possible for two isomeric structures to be generated at each alternate carbon atom (see figure 3). This degree of uncertainty, when propagated along the polymer chain, results in three basic chiral forms. There are two ordered forms: isotactic and syndiotactic. In isotacticity the molecule can be envisioned as having all the chlorine atoms pointing to the same side. In syndiotacticity alternate chlorine atoms point to opposite sides of the molecule. All other forms are generally

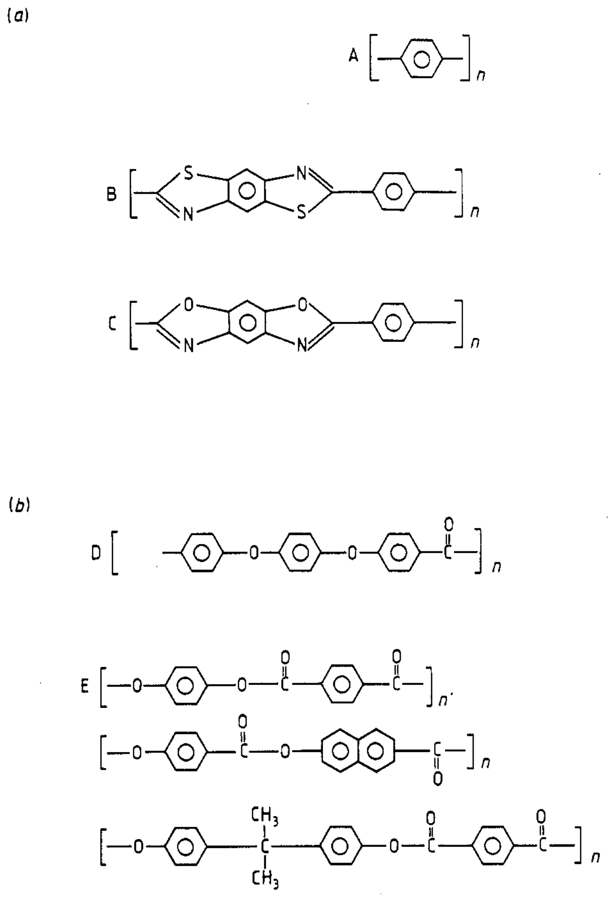

Figure 2. Examples of (*a*) rigid and (*b*) semi-rigid polymer molecules. A, poly(p-phenylene); B, poly(p-phenylene benzobisthiazole); C, poly(p-phenylene benzimidazole); D, poly(ether ether ketone); E, some thermotropic copolyesters.

referred to as atactic and can be regarded as intrinsically disordered since more complex forms of ordering have not been synthesised. Tacticity is important since only the two ordered forms are capable of crystallisation in the conventional sense of the word. Atactic polymers often contain a considerable number of ordered sequences. However, they tend to be fairly short and extensive levels of crystallisation cannot be achieved.

Additional complicating factors arise from the details of the polymerisation process, since invariably several side reactions can occur. The general result is the production of microstructural variations in the chain structure. Since these microstructural defects disrupt the regularity of the chain, they tend to be excluded from the polymer crystal and hence result in the generation of non-crystalline material. Each rejected unit will tend to take a short section of crystallisable chain with it, resulting in amorphous fractions much greater than might be predicted on the basis of the concentration of defect centres. The best known example of this effect is the difference between low-density and high-density polyethylenes. During the polymerisation process, which involves free radicals, the chain end can turn around and react with itself (forming an intermediate in the shape of a six-membered ring) which results in the movement of

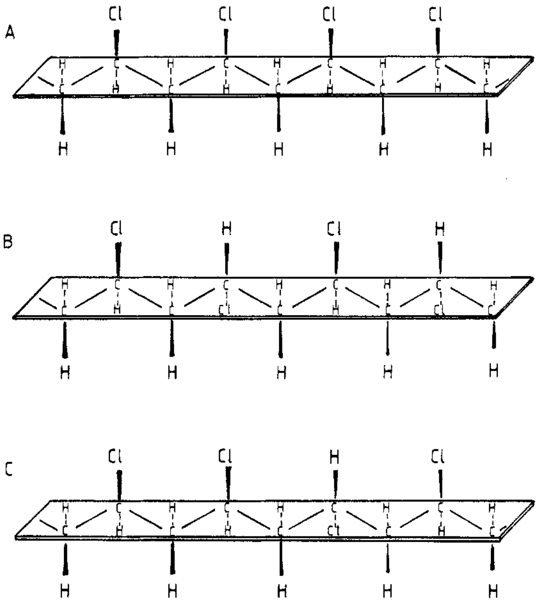

Figure 3. Major tacticity types in poly(vinyl chloride). A, isotactic; B, syndiotactic; C, atactic.

the free radical centre to the carbon atom fifth from the end of the chain. As a result the former end of the chain becomes a butyl branch. This is only one of several types of short chain branching that can occur. In a typical low-density polyethylene there would be fifteen short branches per thousand main chain carbon atoms. The result is a maximum attainable crystalline fraction of about 0.50 whereas for the high-density polyethylene (i.e. unbranched) the value can be as high as 0.90 under normal circumstances. In addition to this short chain branching, long chain branches can be produced when the chain end reacts with a section of chain distant from the end or with another molecule. The amount of long chain branching generated is very low. It has little effect on the crystallisation behaviour except through its influence on the diffusion rates of the polymer chains.

In many of the newer commercial polyethylenes, a different synthetic process is used which does not involve free radicals but involves activated metal oxides as catalysts. Because of this, there are very few naturally occurring branches. Since the branched materials have important commercial uses, short chain branching is normally generated through the use of a comonomer such as hexene or octene thereby producing butyl or hexyl branches respectively. A major complication which is present in these 'linear low-density' polyethylenes is that the branches are preferentially located in the shortest polymer molecules. The polymer therefore behaves as if it were a mixture of linear high molecular weight molecules and branched low molecular weight molecules. On crystallisation these different species tend to fractionate. Although not mentioned previously, it should be recognised that practically all synthetic polymers have present a distribution of molecular weights, being a direct consequence of the mechanisms of polymerisation. The most frequently encountered way of describing the distribution is through the ratio of the second to first moments of the distribution. In 'ideal' systems, this ratio is equal to two. Most commercial systems exhibit values much greater than this. A detailed treatment of this aspect of polymer structure is beyond the scope of this review. Readers are advised to read one of several undergraduate texts for a more thorough treatment (e.g. Billmeyer 1984, Rosen 1982) or to more advanced texts for detailed information (e.g. Lenz 1967, Odian 1970). The subject is important when crystallisation is considered since short molecules are more highly mobile than long molecules; they also have lower melting points. Such considerations have become very important since the original review of Keller and a thorough understanding of polymer crystals and their crystallisation can only be obtained when molecular weight and microstructural defects are considered.

In the discussion so far, only carbon-based polymers have been considered. However it should be recognised that inorganic backbones are also possible. Since atoms other than carbon, sulphur and selenium develop unstable concatenated structures, inorganic polymers invariably alternate the atom concerned with oxygens. Examples are polysiloxanes (or silicones) having alternating silicon and oxygen atoms and poly(phosphazenes) with alternating nitrogen and phosphorus atoms. Molecular structural concerns are usually similar to those of carbon-based polymers with the additional complication that bond angles may not be defined as rigidly.

Briefly alluded to above was the effect of increasing molecular weight on chain mobility and to the consequences which follow when crystallisation behaviour is considered. There are two essential effects. The first and obvious one is that the larger molecules can be expected to move more slowly past one another as they are pulled into the growing crystal. A second and less obvious effect lies in the fact that if the molecules are sufficiently long, the chances of being tightly entangled or even knotted together become significant. When this occurs the crystallisation process will be resisted by rubber-elastic forces. This effect is always present if the molecules have been crosslinked artificially. Such procedures are carried out using radiation or chemical crosslinking agents, the most commonly encountered being peroxides. When crosslinking is carried out, the consequent molecular structure depends greatly on the mode of crosslinking used.

So far little has been said about copolymers. It should be recognised that large fractions of commercially produced polymers are in fact copolymers or terpolymers, although the manufacturers may not say so explicitly. For instance, the term polyolefin is often used to refer to any type of polyethylene, to polypropylene or to copolymers involving either or both of the two. In many cases comonomer units are so different from the homopolymer unit, both in size and shape, that they are excluded from the growing crystals and reside in an expanded amorphous phase. Not only are they rejected but the rejection process takes time and the overall rate of crystallisation is lowered. The majority of copolymers encountered have close-to-random sequencing of the monomer units in the polymer chain. Using special techniques, copolymers can be made in which the different monomer units are encountered as long sequences. Known as block copolymers, these molecules usually have only two or three sequences in total. Since very few polymers form miscible systems, the result is invariably a two-phase material in which the different molecular sections behave as if they were homopolymers.

2.2. *Early views of crystallinity in polymers*

The earliest approaches to crystallinity in polymers were invariably based on x-ray diffraction evidence. Both quiescently crystallised polymers and stress-crystallised polymers were studied. In the latter case the stress orients the molecules, resulting in some molecular sections being straightened out. This straightening produces a decrease in entropy which then makes crystallisation easier. In this review, only quiescent crystallisation will be considered in detail. Diffraction evidence was acquired using both types of crystallisation, oriented crystallisation being generally preferred when unit cells were being determined. As will be seen later, the two types of crystallisation are not intrinsically different, the greatest change lying in the mode of primary nucleation. Diffraction evidence gave not only the unit cell, but also the crystalline fraction (by comparing the intensities of the crystalline and amorphous scattering peaks) and estimates of crystal dimensions (from line broadening analyses and low angle scattering). The result was a picture of polymer crystals 100 Å by 400 Å in size, randomly oriented and comprising about 50% of the material. Since crystalline polymers were able to bear loads and in many ways behaved like reinforced rubber, together with the fact that polymer molecules were generally very much longer than the crystal dimensions, the picture arose of crystals functioning in a similar way to crosslinks. This is the well known 'fringed micelle' model (see figure 4) due to Hermann *et al* (1930). It was not until optical microscopy was carried out that the concept could be questioned. Although first observed in 1926, the existence of major morphological units in the form of spherulites (see figure 5) was generally recognised through work carried out at ICI during the early 1940s (Bunn and Alcock 1945, Bryant 1947).

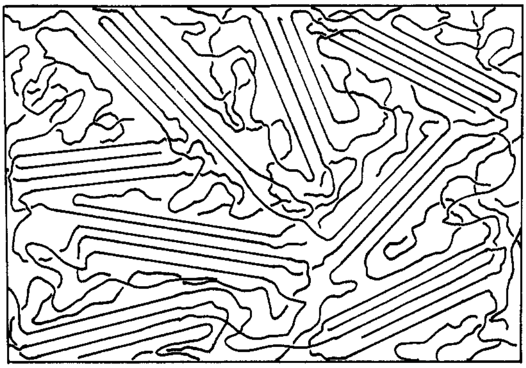

Figure 4. Schematic diagram of the fringed micelle model of polymer crystals.

Although in these early papers, attempts were made to retain the fringed micelle as the basic unit through arranging them in an appropriate manner within the spherulite, it soon became clear that the model was inappropriate. Studies of single crystals in 1938 had shown the crystals to be very thin rhomboid-shaped lamellae. It was the discovery of the form of solution-grown single crystals of polyethylene through electron microscopy studies (Jaccodine 1955, Keller 1957, Till 1957, Fischer 1957) together with electron diffraction evidence that produced the concept of folded chain crystals. The critical information lay in the observation that the molecular backbone was oriented along the thinnest dimension of the crystal and that it could be extended in a continuous manner for no more than 100 Å or so. It was Keller who first suggested that a physical picture of a polymer single crystal in which the molecule folds back on itself in an adjacently re-entered manner would account for the molecular orientation, dimensions, crystallinity and surface packing density. In 1962, Flory showed that no more than one in two emergent molecules in the crystal surface could be Gaussian coils, thereby

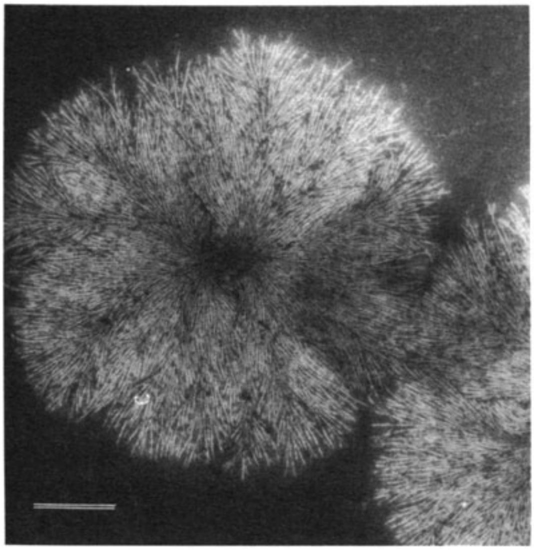

Figure 5. A spherulite growing in a film of *cis*-polyisoprene. The crystal growth has been terminated prior to completion, through reaction of the film with osmium tetraoxide vapour, thereby permitting resolution of the individual lamellar crystals. (Scale bar: 0.5 μm.) First published by Phillips (1983).

ensuring the demise of the fringed micelle concept. A major point of continuing controversy lies in the description of the folded surface as fully adjacently re-entered (also referred to as tightly folded). This concept leads to the idea of ordered surfaces, something quite unique to polymer crystals (Geil 1963). This structure was disputed by Flory (1962) because of the sluggish nature of polymer molecules, an intrinsically disordered 'switchboard' type of folding being preferred. Later this model was modified to incorporate tie-chains, resulting in the 'interzonal' model of Mandelkern.

Although the ordered view of folded chain surfaces was devised for solution-grown single crystals, the approach was extended to melt-grown crystals. This was largely because the dependence of crystal thickness on supercooling was similar in the two preparative methods and it is generally accepted that the relation is determined by the free energy of the folded chain surface. It was, however, always recognised that unless molecules were able to exit the crystal and enter a second crystal, thereby forming tie-molecules, the material would simply behave as a viscous slurry and could not behave in an elastic fashion. For crystallisation from the bulk it was therefore generally recognised that some departures from strictly adjacent re-entry folding had to occur.

The debate on the detailed nature of the folded surface has been long and acrimonious at times (see Krimm and Cheam 1979). It is still not completely resolved, but considerable progress has been made. A major problem has been the lack of definitive experimental probes of the nature of the folded surface. If a strictly adjacent re-entry picture is appropriate, with no tie-molecules and each molecule being incorporated into only a single layer of the crystal, then the shape of the molecule would change drastically on crystallisation. It should change from a random coil, approximating a sphere, to a thin ribbon about 100 Å in width. One of the major advances in the past fifteen years has been the development of a technique which permits the determination of the molecular trajectory, namely neutron scattering. The expression, molecular trajectory, used in this context refers to the trajectory in space of the molecule as deduced from a time-averaging technique.

3. Crystallisation of flexible chain polymers

3.1. *The molecular trajectory*

All the studies that have been conducted on polymers using elastic neutron scattering have taken advantage of the fact that deuterium has a significantly different coherent scattering length than hydrogen (Sadler 1984, Sperling 1984). When a deuterated polymer is dissolved in its hydrogenous equivalent (e.g. $[\text{-CD}_2\text{-CD}_2\text{-}]_n$ in $[\text{-CH}_2\text{-CH}_2\text{-}]_n$), neutrons are scattered in a similar way to light by polymers in solution (Margerison and East 1967, McIntyre and Gornick 1964). The principles of analysis of the data follow the well established methods for light scattering from solutions. The two parameters that can be obtained from neutron scattering data with little difficulty are the molecular weight and the radius of gyration of the molecule. An advantage of neutron scattering over light scattering is that it is not restricted to dilute solutions. Wignall *et al* (1981) showed clearly that the ratio of the weight average radius of gyration to the square root of the weight average molecular weight remained constant up to 50 mol% of deuterated polystyrene in hydrogenated polystyrene.

One of the most important conclusions arising from this technique was that the radius of gyration of a polymer molecule in the melt is identical to its dimensions in a theta-solvent (Flory 1953, Margerison and East 1967). A theta-solvent is a solvent in which the dimensions of the polymer chain are not perturbed by the polymer–solvent interactions, which may cause the molecules to expand or contract dependent on their nature. Such a condition is the equivalent of an ideal solution. This topic had been a subject of controversy for many years. Several scientists had claimed that there was structure to the amorphous phase (Geil 1976) in the form of nodules. Others, including Flory, maintained that a polymer must be its own theta-solvent. The neutron scattering studies proved decisively that the latter was correct (Ballard *et al* 1976).

The extension of neutron scattering studies to crystallisation has produced fascinating results which have caused major changes in our perception of the detailed nature of the folded surface. Most important is the difference in behaviour between solution-grown and melt-grown crystals. Studies of solution-grown single crystals have been quite definitive, whereas many of the conclusions derived from research on melt-grown films are subject to conflicting interpretations. These differences do not arise from experimental variations and inconsistencies, since these are very few, but arise from different approaches to the modelling of neutron scattering curves.

3.1.1. Single crystals. In the case of solution-grown crystals, it is evident that the molecule is present in only one crystal and that it exits and re-enters in a manner which is best described as adjacent re-entry (Spells *et al* 1980). The molecule does not lie down along a single plane but tends to be found on two or three adjacent planes of the same index (see figure 6).

It should be mentioned that in a number of cases the use of infrared spectroscopy in correlative studies supports the above conclusion. (For a general review of the vibrational spectroscopy of long chain molecules the reader is referred to Zerbi (1984).) Such studies have relied on the fact that the motions of deuterated and hydrogenous chains are slightly different. They give rise to different absorption frequencies which

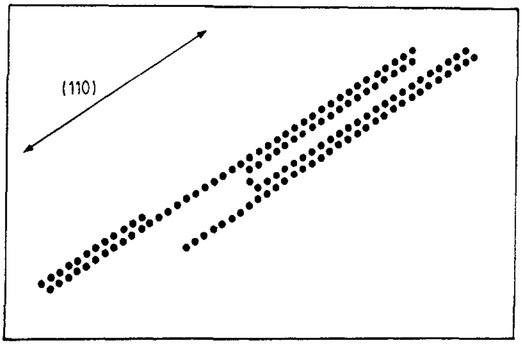

Figure 6. Schematic representation of the trajectory of a molecule in a single crystal of linear polyethylene, as obtained from neutron scattering studies. (After Spells *et al* 1980.)

can easily be distinguished on modern instruments. When a deuterated molecule enters a predominantly hydrogenous crystal, the fine detail of its spectrum will depend on whether or not neighbouring stems are also deuterated. First applied by Krimm's group (Bank and Krimm 1969, 1970, Krimm and Ching 1972, Ching and Krimm 1975a, b), the technique relies on the presence of doublets in the IR spectrum of the deuterated molecule. These bands are a result of two chain stems present in the orthorhombic unit cell not being symmetrically equivalent, both out-of-phase and in-phase vibrations occurring. For instance, if two deuterated stems are adjacent then a doublet will occur; however, if the deuterated stem is adjacent to a hydrogenous stem then only a singlet will occur. The original conclusion that the molecule in solution-grown single crystals is predominantly adjacently re-entered along the (110) plane has been reinforced by more recent studies (Cheam and Krimm 1981, Jing and Krimm 1982a). It has also been concluded that the molecule folds back along the next adjacent (110) plane (Krimm and Cheam 1979). It will be recalled that a similar conclusion was reached from neutron scattering studies (Spells *et al* 1980).

A recent novel morphological technique also provides evidence in favour of ordered fold surfaces characteristic of adjacent re-entry (Wittmann and Lotz 1985). In this technique short polyethylene molecules, produced by evaporation from a hot tungsten filament, deposit on adjacent surfaces. When deposited on single crystals of polyethylene, they condense and crystallise in an ordered fashion and the crystals are oriented along the fold planes. This could not happen if the surface were randomised by a significant amount of non-adjacent re-entry.

It therefore seems to be well established that the molecular trajectory in single crystals is indeed governed by an adjacent re-entry process in which the molecule is folded back along at least two adjacent (110) planes.

3.1.2. Melt-grown crystals. The study of melt-grown crystals yielded undisputed evidence that the radius of gyration of the deuterated molecule decreases by, at most, 10% on incorporation into the crystals. Admittedly, because of segregation problems, the polyethylene specimens studied have been rapidly quenched rather than carefully crystallised. A maximum amount of disorder therefore exists and it is only to be expected that the amount of ordered (i.e. adjacent) re-entry would be minimised. The general recognition that the molecule retains the same approximate shape in the crystallised state that it had in the melt has resulted in a major re-appraisal of the role of secondary nucleation in the generation of detailed surface structure (see section 3.2.1). It is now generally accepted that the original idea of solely adjacent re-entry folding as the means of incorporating a molecule into a crystal is a gross oversimplification. Attempts at defining the detailed molecular trajectory from modelling of neutron scattering curves have been conducted. In principle, it should be possible to analyse the scattering curve at medium and high scattering angles to obtain a picture of how the different stems of the same molecule are positioned relative to one another in the crystal. Although a number of such attempts have been made, there is no consensus on the true situation. Some analyses have predicted that the stems from a given molecule are separated by two stems from another molecule (Yoon and Flory 1981), others have predicted adjacent re-entry. A major problem in some of the modelling studies is that those models that generate non-adjacent re-entry (e.g. Yoon and Flory 1977) do not consider the consequences for surface packing of the emerging stems. As a result, surface densities are generated which are in excess of known values (DiMarzio and Guttman 1980, Guttman *et al* 1981). Put simply, the molecular sections present in the interlamellar space, if folding back on themselves and obeying Gaussian statistics, occupy the same volume as would otherwise be occupied by ordered crystalline stems. Essentially two amorphous sections are occupying the same space as one crystalline stem. Correct levels of amorphous density can therefore only be achieved if a significant fraction of the exiting chains folds back in close proximity to the surface and does so in a tight manner. The maximum possible fraction of non-adjacent re-entry folding was computed by Guttman *et al* (1981) using a 'gambler's ruin' approach. They concluded that for a surface normal to the chain direction, a maximum of one third non-adjacency was possible for amorphous chains, if those chains can be described by Gaussian statistics.

In the case of non-adjacent re-entry, the problem of overcrowding can be alleviated only if the stems are inclined at an angle to the lamellar surface. However some calculations have shown that the maximum known angle of inclination is not sufficient to permit a totally non-adjacently re-entered surface. As a result, the fine detail of the molecular re-entry process has not been defined from neutron scattering studies to date, the data being apparently consistent with several quite different theoretical approaches.

A recent promising approach uses the concept of widely spaced stem clusters (Fischer 1988). The basic approach was first suggested to explain crystallisation kinetic data by Palys and Phillips (1980). Because of multiple nucleation by one molecule on several parts of the same and adjacent crystals, the molecule tends to form clusters of a few stems each which are of course joined by amorphous sections of the same molecule (i.e. tie-chains). The cluster model of Fischer *et al* (1984) recognises that the clusters, being considerably larger scattering entities than single stems, should be detectable in the scattering data in a more accurate and reliable manner. Additionally the approach does not need to make specific assumptions regarding the nature of re-entry. Data are analysed within the Zimm range and an extrapolation is performed. Calculations for polyethylene of molecular weight 4.6×10^4 resulted in an estimate of 2.7 clusters per molecule, the clusters containing an average of 5.2 stems. This analytical technique is obviously new and has not yet been applied by other researchers. Therefore it will be some time before its validity is tested independently.

In infrared studies some clarification of the situation in melt-crystallised systems has proved possible. On the basis of a deconvolution of the CD_2 bending mode contour, which appears as an asymmetric singlet, Jing and Krimm (1982b) concluded that, although the behaviour is at first glance indicative of random re-entry, approximately 30–40% of the re-entry is adjacent along the (110) plane, being composed of no more than three contiguous stems at a time.

The picture emerging of the molecular trajectory in rapidly cooled bulk systems is therefore one of the molecule remaining as a pseudorandom coil in which the molecule enters and re-enters crystals at a myriad of locations and does so in a way which always requires some limited form of adjacent re-entry folding, the remainder of the surface comprising largely tie-molecules, cilia and some non-adjacent re-entry folds.

3.2. The crystal growth process

3.2.1. Secondary nucleation approaches. From the discussion in the previous paragraph, it should be clear that the molecular trajectory found in a polymer crystal is determined by a complicated set of occurrences. First and foremost in importance is the manner in which the molecule is incorporated into the crystal. The key information relevant to a solution to the problem lies in an understanding of the nucleation and growth processes. Any models used must be consistent with crystallisation kinetic data and also the models used to explain kinetics must be consistent with the known facts regarding the molecular trajectory. The earliest approaches to modelling of the growth process (secondary nucleation) were based on the well established models for crystal growth devised for small molecules (Turnbull and Fisher 1949). It was recognised early on that secondary nucleation theory could explain the temperature dependence of the growth rate (Mandelkern 1958, 1964). When the crystallisation of a polymer can be studied over a wide temperature range, the lamellar growth rate shows a bell-shaped dependence on temperature (figure 7) typical of a system in which there is nucleation control at high temperatures and diffusion control at low temperatures. Such a curve can be predicted easily using simple models of the crystallisation process

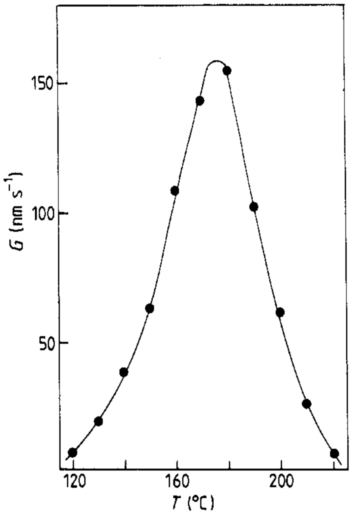

Figure 7. The dependence of the lamellar growth rate on temperature in poly(ethylene terephthalate) at atmospheric pressure determined using laser light scattering. (After Phillips and Tseng 1989.)

which produce the following equation

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

where G is the growth rate at temperature T, G_0 a pre-exponential factor, ΔF^* is the free energy of formation of the critical nucleus and ΔU^* is the activation energy of the elementary jump process. Of considerable importance is the fact that the theories also predict the temperature dependence of the crystal thickness and that it is a direct consequence of the chain folding process.

The most commonly encountered and best-developed theory specific to polymers is that derived by Hoffman and Lauritzen (1961) (see also Hoffman (1964)), which is essentially an adaptation of a theory they derived for crystal growth from solution. Over the years the theory has been adapted and revised several times and shows an amazing resilience. In order for the secondary nucleation equation to be used effectively, it is necessary to have some independent estimation of the activation energy of the elementary jump process. This has always been, and still remains, a fundamental problem. The earliest method used was simply to use the well known Williams-Landel-Ferry (WLF) empirical relation (see for example Billmeyer) which is commonly used to predict the time and temperature dependences of properties such as viscosity, creep, dynamic mechanical behaviour etc, which are strongly dependent on the mobility of the polymer. This relation is well known and calibration constants are available for most common polymers. This approach was first suggested by Hoffman and Weeks (1962) and has been used successfully over the intervening years by many researchers. Its main problem lies in the fact that it is unlikely that the bulk relaxation or flow behaviour of the polymer is the best approach to approximate the mobility of an individual polymer molecule or molecular section. For polymers which crystallise over a short temperature range close to the melting point, such as polyethylene and polypropylene, the actual approach used to estimate this activation energy has little effect on the analysis since the nucleation exponential is dominant (e.g. Tseng and Phillips 1985). Because of this observation, a simplified approach using only one 'universal' constant has been popular (Suzuki and Kovacs 1970, Hoffman *et al* 1976). For polymers which crystallise over wide temperature ranges, such as poly(ethylene terephthalate), polysiloxanes and *cis*-polyisoprene, the approach is inadequate as the mobility exponential controls the behaviour over a large fraction of the crystallisation range. The use of the WLF equation has proved most effective for such situations (e.g. Phillips and Vatansever 1987, Phillips and Tseng 1989).

The problem remains, however, that the molecule must be extracted at high speed from the adjacent molecules with which it is intimately entangled and interwoven, in order for any adjacent re-entry folding to occur. Obviously, molecular mobility, which decreases with temperature in a non-linear manner, will have a strong influence on the interfacial structure generated by the detailed mode of addition of molecules to the crystal. In the case of polyethylene, where the majority of the evidence available favours a strong degree of adjacent re-entry at low supercoolings, it is important for a better approach to the motion of the polymer chains to be found.

A major advance has occurred here in the introduction of approaches to chain mobility based on the concept of reptation (De Gennes 1979, Hoffman 1982, Hoffman and Miller 1988). The introduction of reptation has revolutionised the way of approaching many problems in polymer mobility and is based on the motion of a snake wriggling through a hole. There are many similarities between the snake and a polymer, the most important being the ability of the molecule to move rapidly over large distances without the need for the hole (or the adjacent molecules) to co-operate and adjust their positions. Activation energies for reptation have been estimated for very few polymers and are usually based on the study of self-diffusion of isotopic mixtures (e.g. Klein and Briscoe 1979). This type of analysis has shown, in the case of polyethylene, that reptation rates are adequate for the known rate of addition of molecules to occur through an adjacent re-entry process (Hoffman 1982). The theory has recently been extended to predict molecular weight effects, again in polyethylene (see later and Hoffman and Miller 1988). It should, however, be recognised that reptation is only one of the modes of motion available to polymer molecules. Certainly, it is the fastest mode currently recognised for molecules able to move without significant levels of resistance to motion.

The modes believed to operate have been explored by Lin in a series of recent papers (1984, 1986, 1987a, b). A simple way of envisaging the other motions is to consider once again the snake; if held at both ends it can still wriggle and translate laterally over distances comparable to its length. This motion would be strictly applicable to the motions of a crosslinked polymer. Crystallisation rates change somewhat when light crosslinking is introduced and crystallinities hardly at all, so the ability of the chain to move rapidly, even when crosslinked, is quite high. Additionally, for high molecular weight systems, there exist relatively tight entanglements which strongly resist the ability of the chain to reptate even if the two ends are free, here it is necessary to introduce a probability for chain slippage through an entanglement point. None of these contributory motions and their activation energies have yet been introduced into secondary nucleation theory, although it could be argued because they contribute to the motions characterised empirically by the WLF equation, that they are handled in a second-hand manner when the WLF approach is used.

The most important fundamental revision to secondary nucleation theory was the introduction of regimes in which the formation of a single secondary nucleus need not be the rate-controlling step (Lauritzen and Hoffman 1973, Hoffman *et al* 1976, Hoffman 1983). This is in contrast to the classical theory of secondary nucleation in which the deposition of a single nucleus on a growth face is followed by a rapid lateral spreading process, in order for the crystal to move forward by one unit cell parameter. One of the simplest ways of envisioning regimes is to think of the crystal growth process as being controlled by two competing rates, the first being the deposition of the secondary nucleus and the second being the lateral spreading process. Regime I corresponds to 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 greater than the rate of spreading (see figure 8).

Regimes I and II were first postulated (Hoffman and Lauritzen 1973) on the basis of experimental data obtained for narrow molecular weight fractions of polyethylene (Hoffman *et al* 1975). Intermediate molecular weight fractions were found to exhibit a change in the slope of the growth rate versus temperature curve at a supercooling of about 17 K. In the lower temperature range the slope was about half that observed for the higher temperature range. The regime theory developed by Hoffman and Lauritzen uses the symbols i for the rate of secondary nucleation and g for the rate of lateral spreading. In terms of these variables, the growth rate is proportional to i in regime I and to the square root of ig in regime II. The result of this different dependence is that the free energy term in the nucleation exponential in regime II is a half of that in regime I, thus explaining the change of a factor of two in the slope discussed earlier. It was also observed that low molecular weight fractions exhibited

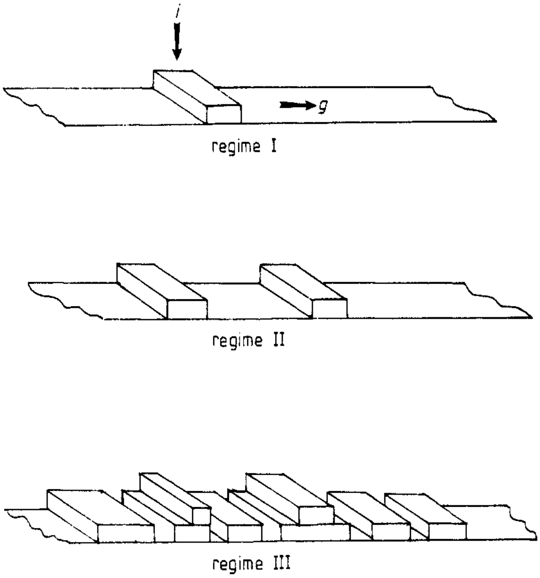

Figure 8. Schematic diagram of the secondary nucleation profiles in the three regimes of crystallisation.

only regime I and that high molecular weight fractions exhibited only regime II. The reasons for these observations have not been explained.

Since no additional polymers were found to exhibit similar behaviour, general acceptance of the idea of regimes was not forthcoming. On the basis of studies of other polymers, Phillips (1979) suggested that there might be a third regime in which the rate of secondary nucleation exceeded the rate of lateral spreading. The theory for regime III was published by Hoffman in 1983 and has received broad acceptance. Since in this case, the rate of secondary nucleation is very fast, the majority of the polymer is deposited through the nucleation process and the rate of crystallisation is again proportional to i. The result is that a second change of slope occurs in the graph of linear growth versus temperature, the slope in regime III being equal to that of regime I. It has been pointed out by Lovinger *et al* (1985) that the regime II to regime III transition is commonly encountered in high polymers, even when they have not been fractionated. Indeed, the general effect of polydispersity is to broaden any regime transition rather than to eliminate it.

In practice the appropriate test for regimes is to plot $\log G + \Delta U^*/kT$ versus $1/T\,\Delta T$ where ΔT is the supercooling. This particular plot factors out the contribution of the elementary jump process to the growth rate and the slope is directly related to the derived expression for ΔF^*, the energy of formation of the critical nucleus, which contains the factor of two referred to earlier. A schematic diagram of the plot expected for a polymer exhibiting all three regimes is shown in figure 9. To date, this type of plot has now been seen experimentally three times. The first observation was in studies of fractions of *cis*-polyisoprene (Phillips and Vatansever 1987) where all three regimes were shown to exist in a fraction of molecular weight 314 000 (figure 10). A fraction of molecular weight 540 000 showed regimes II and III, all higher fractions showing only regime III. All three regimes have recently been observed in poly(3, 3-dimethyl thietane) by Lazcano *et al* (1988) and in poly(ethylene oxide) by Cheng *et al* (1989).

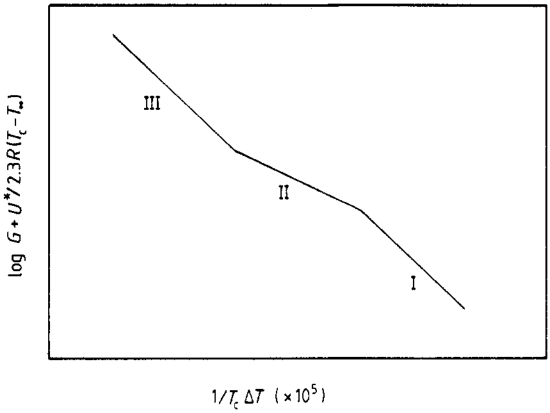

Figure 9. Schematic diagram of a regime plot of linear growth rate data when properly analysed.

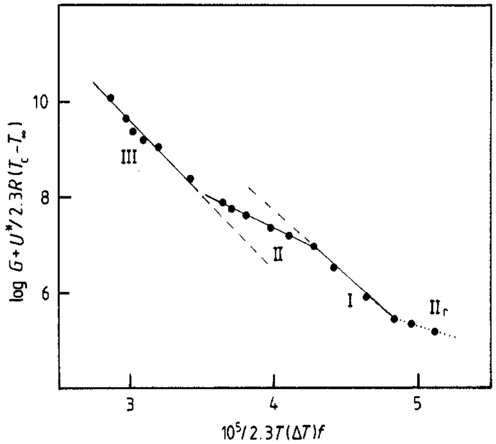

Figure 10. Crystallisation regimes in *cis*-polyisoprene at atmospheric pressure determined from electron microscopy of osmium tetraoxide stained films. All three regimes can be seen, together with a possible reversion to regime II at low supercoolings. (After Phillips and Vatansever 1987.)

The regime I-regime II transition has also been reported to occur in the growth of single crystals of linear polyethylene fractions from dilute solution (Organ and Keller 1986).

Since the location of the regime transitions is controlled by the relative rates of secondary nucleation and surface spreading, any factor which affects either of these rates in different ways will alter the temperature at which any particular transition occurs. Recent studies of crosslinked linear polyethylene have served to demonstrate this fact for two different variables (Phillips and Lambert 1990). If the rate of spreading occurs largely due to adjacent re-entry folding, as assumed by the Hoffman-Lauritzen theory, then it is totally dependent on the ability of the molecule to reptate, since without this particular facility for rapid motion, additional chains would be unable to add at the moving niche at the necessary rate. Elimination of reptation would cause the mechanism to switch to regime III, since the rate of spreading would be significantly impeded. The most effective way to eliminate reptation is to crosslink the polymer.

Alternatively, if the mechanism of surface spreading is addition of stems from neighbouring molecules and a switchboard type of folding occurs, then the rate of surface spreading should be scarcely affected by crosslinking. When such kinetic studies are carried out it is found that the crystallisation does indeed switch to regime III as soon as a network is created (figure 11). Increasing the crosslink network density does not give rise to any other major effects. However, as crosslinking proceeds, the microstructural imperfections incorporated into the chain in the form of branch points give rise to a second effect. The location of branch points within the semicrystalline morphology has been somewhat controversial, but it now seems clear that branch points larger in size than a methyl group are substantially excluded from the polyethylene crystal (e.g. Perez *et al* 1987).

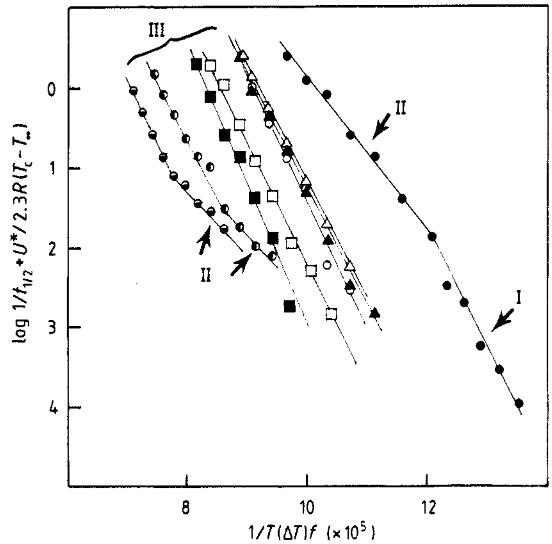

Figure 11. Crystallisation regimes in crosslinked linear polyethylene gels at atmospheric pressure as a function of molecular weight between crosslinks, determined from bulk rates. ●, original uncrosslinked polymer; △, MWX 17 300; ▲, MWX 12 700; ○, MWX 5700; □, MWX 3600; ■, MWX 3100; ◐, MWX 1900 and ◒, MWX 1300. (After Phillips and Lambert 1990.)

In the case being considered, there should be little doubt that the vast majority of the crosslink points are excluded from the crystal. For a polymer molecule to nucleate, a continuous section of defect-free chain is needed which equals or exceeds the length of continuous chain present in the critical, and presumably adjacently re-entered, nucleus. It was shown by Andrews *et al* (1971) that the probability of nucleation can be scaled directly using copolymer sequence theory. The resulting equation contains a proportionality between the logarithm of the linear growth rate (reflecting the rate of secondary nucleation) and the microstructural impurity concentration. This means that the rate of secondary nucleation will be very sensitive to impurity content. For the example under consideration, the impurities are the crosslinks which are rejected from the crystal. Hence, as the crosslink density is increased the rate i will decrease substantially. Ultimately the value of i will approach the value of g, which is already decreased drastically by the elimination of reptation. When these rates approach one another the crystallisation will switch back to regime II. As can be seen for crosslinked linear polyethylene (XLPE) in figure 11 this does indeed occur. The level of microstructural impurities at which regime II reappears is less than the level of branches found in low-density polyethylenes, which normally exhibit regime II alone.

The theory of Andrews *et al*, referred to above, contains an additional prediction. Intrinsic to the analysis is a value for the number of crystallisable units present in a continuous sequence in the critical nucleus. The slope of a plot of the logarithm of linear growth rate at constant temperature versus the mole fraction of non-crystallisable impurity units is just equal to this sequence number less one. Analyses of partially isomerised *cis*-polyisoprene (Andrews *et al* 1971) and of crosslinked linear polyethylene (Phillips and Lambert 1990) both resulted in sequence numbers characteristic of a three stem nucleus containing two adjacent re-entry folds. In both of these cases regime III kinetics were being followed.

Although the theory of regimes as derived by Hoffman *et al* assumes a single stem nucleation event occurring at the end of the molecule, it should be recognised that the phenomenology of regimes is determined by the relative values of two rates and so is independent of the particular model being used. In the case of crosslinked polyethylene there are few chain ends present and nucleation has to occur in the central section of a chain. Similarly, it is known that *cis*-polyisoprene exhibits a high degree of reversible rubber elasticity in the uncrosslinked state, this being due to the presence of tight entanglements which inhibit large scale translation of the molecules. Under these circumstances, it seems reasonable to assume that much of the nucleation will occur in the centres of chains. It is fairly easy to see that a nucleus formed from the centre of a chain in which reptation is highly impeded will take the form of a three stem nucleus (figure 12). The orientation of a section of a chain impinging on a crystalline substrate at an angle will automatically generate two loops, leading to the three stem nucleus. It would also be reasonable to assume that when a molecule is crystallising in regime III, and possibly also in deep regime II, sections of molecule will be nucleating whose ends are already tied down in previously formed secondary nuclei. For such instances a three stem nucleus may be more appropriate. The theory of formation of the three stem nucleus is still in its infancy and no articles have yet appeared in refereed journals.

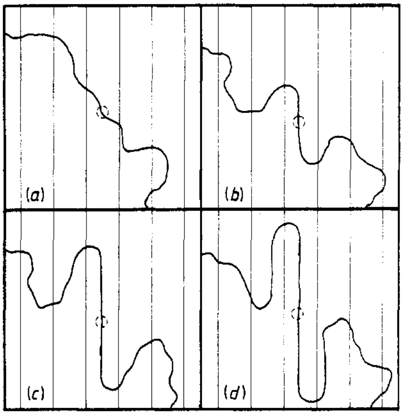

Figure 12. Schematic diagram illustrating the genesis of a three stem nucleus from a randomly oriented confined polymer chain.

The free energy of formation of the critical nucleus can be written in the form

$$\Delta F^* = Nss_e b_0 T_m^0/\mathrm{d}H_f\,\mathrm{d}T$$

where s and s_e are the lateral and fold surface free energies respectively, b_0 the lattice parameter in the growth direction, T_m^0 the equilibrium melting point, $\mathrm{d}H_f$ the latent heat of fusion and $\mathrm{d}T$ the supercooling. The parameter N is equal to four in regimes I and III, but equal to two in regime II. Usually all parameters are known except the surface free energies. A plot such as that shown in figures 9 or 10 permits the product of the surface free energies to be estimated from the slope. Two approaches have been used to obtain the surface free energies independently. One is to estimate the value of s using a version of the Thomas-Stavely relation (1952)

$$s = \mathrm{d}H_f b_0 a$$

where a is a constant often put equal to 0.1 (Hoffman *et al* 1976), a value which seems to be appropriate for non-polar polymers. The value of s_e can then be obtained.

An alternative approach is to estimate the value of s_e from the slope of a graph of the lamellar thickness versus inverse supercooling. The theory of secondary nucleation generates the operating equation as

$$l = 2s_e T_m^0/\mathrm{d}H_f\,\mathrm{d}T.$$

Both approaches work well although both must be used with reservations. In the case of the Thomas-Stavely relation, the value of a is appropriate for polyethylene since the equation was calibrated with data for low molecular weight hydrocarbons, but may not be generally applicable. In the case of the lamellar thickness approach, it has to be recognised that lamellae do thicken after growth and the degree of thickening may be supercooling dependent. Once the value of s_e has been determined it can be used to estimate the amount of excess energy stored in a fold, provided an adjacent re-entry fold is an appropriate assumption, using the equation (Hoffman *et al* 1976)

$$s_e = s + q/A_0$$

where q is the stored energy and A_0 the cross section of a chain in the crystal. For polyethylene such estimates (Hoffman *et al* 1976) are close to theoretical values (Corradini *et al* 1971). Theoretical estimates are not available for many polymers.

In practice, since a polymer invariably is polydisperse, it is strictly necessary to consider the system as being multicomponent. The theory for this more complex situation was presented in a series of papers by DiMarzio and colleagues (Lauritzen *et al* 1967, DiMarzio 1967b, Lauritzen and Passaglia 1967). In the initial paper Lauritzen *et al* (1966) derived the solution to the general problem, which is somewhat analogous to copolymerisation, and then they applied the theory to the straightforward case of crystallisation of a mixture of n-paraffins (Lauritzen *et al* 1967). Not only was the growth rate equation predicted but also the composition of the crystal and the pair distributions. Later the theory was applied to chain-folded polyethylene crystals using the adjacent re-entry assumption. The equations generated were identical to those of the simpler theories (i.e. Lauritzen and Hoffman 1973) provided that the average length of any deposited stem is equal to that of the substrate on which it grows. The standard deviation in thickness of the crystals was found to be of the order of 10 Å; in other words the surface of a crystal may be rough but still adjacently re-entered.

An additional aspect of crystallisation which emerges as a result of this theory is the very important concept of ciliation (DiMarzio 1967a, b). Whenever a single molecule adding to a crystal surface through adjacent re-entry is interrupted by a second molecule which adds at the growth niche, the remaining part of the first molecule will be left dangling i.e. it resembles a hair or cilium. DiMarzio was able to calculate the fraction of ciliated material generated as a function of molecular weight. Cilia can influence the details of subsequent crystallisation and even mechanical properties. For instance, a very long cilium can nucleate on a separate crystal or on the same crystal at a remote distance. Alternatively, any cilium can simply nucleate the layer subsequent to the one in which it is located. Under such circumstances it alters the statistics of secondary nucleation, being a much more likely event than an entirely new nucleation event by a different molecule. Further aspects of ciliation were explored in a series of papers by Sanchez and DiMarzio (1971a, b, 1972).

A more recent extension of the theory of multicomponent systems was an exact estimation of the amount of non-adjacent re-entry present in a long chain paraffin (n-$C_{294}H_{590}$) for crystallisation at a variety of temperatures, both from the melt and from dilute solution. The general equations were first derived (DiMarzio and Passaglia 1987) and then this calculation performed assuming that the system was once folded. They showed that for equilibrium growth at low undercoolings the fraction of cilia was a maximum and that the amounts of adjacent and non-adjacent re-entry were about the same. For high undercoolings the fraction of adjacency increased at the expense of both non-adjacency and ciliation. Because of the size of such modelling studies further extensions of the treatment to larger molecules have not yet been forthcoming.

3.2.2. Alternative approaches. In recent years a completely different approach to lamellar growth was taken by Sadler and co-workers (1984) because of several apparent anomalies between experimental data and the models used in secondary nucleation theories. This new approach used the well known concept for atomic solids involving surface roughening. The original concept arose in a paper by Burton *et al* (1951). Basically, it is possible to enter a regime in which atoms are able to leave the interior of the crystal and sit on the surface. It is obviously a process which should be most prevalent at low supercoolings since it will be an activated process likely to occur with greatest frequency at elevated temperatures, a surface equilibrium state existing. Under these conditions, atoms can associate on the surface without requiring any formal secondary nucleation step.

The presence of crystal growth through roughening and of transitions from roughening to secondary nucleation is now an accepted fact for atomic solids (for example see Jackson 1958, Weeks and Gilmer 1979, Jayaprakesh *et al* 1983). In a series of papers, first involving Sadler and Gilmer (1983), it was suggested that the regime I-regime II transition was in fact a roughening transition. Much of the rationale for this point of view arose because of the observation that polymer crystals rarely contain well developed facets and tend to have curved edges (section 3.5). Such an observation was inconsistent with the basic premises of theories such as the Hoffman-Lauritzen theory since all the theories use a flat growth face. Theoretical simulations of growth under roughening conditions (such as Jayaprakesh *et al* 1983) predict a change in the shape of a faceted crystal to one of ultimate shape in the form of a disc or ellipsoid. Such ellipsoidal crystals do indeed exist in polymers, the reason for their existence requiring explanation.

Sadler and co-workers (1984), using a simulation originally devised for atomic solids, then attempted to develop a theoretical model in which the atoms were joined together in short chains. It was also assumed that once deposited on the surface, a polymeric segment would then be pinned to the surface. This simulation produced crystal growth curves which, at least superficially, mirrored the general dependences known to exist experimentally for polymers. They also predicted a transition from secondary nucleation to roughening which resembled the regime I-regime II transition in polyethylene, but showed a gradual change of slope, not the relatively sharp change predicted by secondary nucleation approaches (Sadler 1986, 1987). A major unresolved shortcoming of the theory was the fact that the chains comprising the model were never connected together and so the relevance of the model to high polymers was never resolved. The unfortunate death of David Sadler in the midst of this new approach has prevented a resolution of the problem being achieved that is to everyone's satisfaction.

Since then, an extended version of the Hoffman-Lauritzen theory (Hoffman and Miller 1989), which introduces the effect of lattice strain on crystal growth, predicts the existence of curved edges, an effect which is already well known in the crystallisation of metals. The theory depends heavily on the recent solution by Mansfield (1988) of the growth of an elliptical front. This approach assumes that the existence of folds produces a strain in the crystal which then influences the energetics of deposition of the next nucleus. In the same theoretical development the authors were able to show why a serrate surface also requires nucleation, an important problem for certain growth faces believed to exist in polymers.

3.2.3. The influence of pressure. Although both temperature and pressure are recognised universally as the two controlling thermodynamic variables in any phase change, the vast majority of research carried out has considered only the temperature variable. In practical moulding operations pressure is an important variable, yet its influence on the structure and properties of the final product is rarely considered. The melting point and the glass transition temperature are strong functions of pressure, increasing by approximately 20 °C kbar^{-1}. Only rarely do the two coefficients have the same value and so increasing pressure can widen or contract the temperature range over which crystallisation occurs. Other parameters of relevance to the crystallisation equation show only a slight dependence on pressure. The fold surface free energy is a different matter. In this case the value is determined in large part by the conformation of the polymer chain present in the form of folds, cilia or tie-molecules. Under appropriate circumstances, the application of pressure during crystallisation may cause the fold to assume a conformation different from that encountered at atmospheric pressure, leading to a change of s_e and hence a change in the growth kinetics.

The first studies of crystal growth at elevated pressures were carried out on polyethylene and considered only morphological effects. Such effects were quite startling, in that the crystals were observed to have thicknesses approaching that of the length of a molecule (Wunderlich and Arakawa 1964). Therefore, research followed which was aimed at understanding this new phenomenon. This aspect of pressure dependence will be discussed in § 3.3.4.

The first extensive study of the influence of pressure on growth kinetics was that of Phillips and Edwards (1975) who studied the lamellar growth kinetics of *cis*-polyisoprene at pressures up to 4 kbar. Results were presented in the form of a contour map of constant linear growth rate on the pressure-temperature field (see figure 13). Data showed that the kinetics were not simply shifted by the changes in melting point and glass temperature, but that also an enhancement of rate occurred over the first one and a half kbar. Appropriate analyses were carried out (Dalal and Phillips 1984) after the pressure dependences of the relevant thermodynamic variables had been

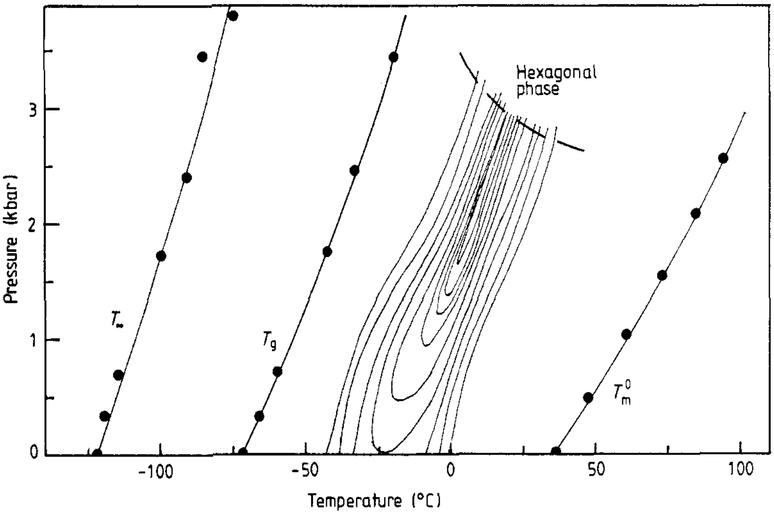

Figure 13. The phase diagram of *cis*-polyisoprene showing the equilibrium melting point, the glass transition temperature, the WLF T_∞ temperature and the lamellar growth rates, presented in contour form. The contour values are (inward) 0.05, 0.1, 0.25, 0.5, 1, 1.5, 2, 2.5 and 3 micrometres per hour. (After Dalal and Phillips 1984.)

determined (Dalal and Phillips 1983a, b). The most important conclusions were (*a*) to a first approximation, secondary nucleation theory could be applied provided the constants used were appropriate for the pressure used and (*b*) the fold surface free energy of *cis*-polyisoprene undergoes a discontinuous increase in the vicinity of 0.75 kbar. This increase is believed to be directly due to more constricted folds of higher energy and lower volume being more stable at the higher pressures due to a compensating $P\Delta V$ term. Additional effects were the occurrence of a new phase at pressures exceeding 3 kbar, which had a hexagonal symmetry, a unique morphology and appeared to be liquid crystalline in nature (Phillips and Edwards 1975).

Similar studies were carried out, but over a more restricted range of conditions, for *trans*-polyisoprene by Davies and Cucarella (1980). In this case it was found that the growth rate decreased with increasing pressure, an effect which was ascribed to the glass transition increasing with pressure at a faster rate than the melting point. The fold surface free energy increased slowly with increasing pressure in contrast to the major increase that occurred in *cis*-polyisoprene.

Studies of the effect of pressure on the radial growth kinetics of linear polyethylene showed that the fold surface free energy remained constant over the first two kbars of pressure (Tseng and Phillips 1985). This behaviour is believed to be due to the fact that a polyethylene fold is already as tight and constricted as possible and that no major changes in conformation are possible at these levels of pressure. In contrast, the fold in *cis*-polyisoprene is believed to contain several monomer units. Studies giving rise to this estimate involved carrying out a chemical reaction at the folds using the double bonds present in a series of polydienes. The average number of monomer units per fold was obtained using carbon-13 NMR. This elegant and inventive technique is the only one devised so far which yields experimental quantification of the length of a fold (Schilling *et al* 1983, 1985, Tischler and Woodward 1986).

It would be expected that three general types of fold energy–pressure dependence should exist. First, the type exemplified by polyethylene occurs when the fold is tight and unable to contract into states of smaller volume and higher energy. The second type would occur for loose folds in which tighter but higher energy conformations are possible, such as in *cis*-polyisoprene. The third type has not yet been observed with any certainty and would correspond to a system composed of Gaussian switchboards. Here it would be expected that the switchboards would change their configuration in a continuous manner as pressure is increased. Such a system should show a small but measurable continuous increase in fold energy with increasing pressure. An additional type of behaviour has been observed, but has not been fully explained.

In the case of poly(ethylene terephthalate) a very large continuous increase of fold energy with pressure has been observed (Phillips and Tseng 1989). The most likely explanation would involve the presence of non-Gaussian chains in the fold surface in appreciable quantities. Such a model would involve the concept of what has been called by Wunderlich a rigid amorphous phase. Basically, because of steric constraints, chains emerging from the surface pass through a transition zone before they regain Gaussian character. The concept is not too different from the interzonal model of Mandelkern referred to earlier. Such a possibility is realistic in the case of poly(ethylene terephthalate) because of the bulky benzene rings found in its main chain. Although the folds occurring at atmospheric pressure are believed to comprise the aliphatic sections of the chain (Koenig and Hannon 1967, Hannon and Koenig 1969), there is no possibility of incorporating benzene rings into adjacent re-entry folds and so the only possible surface structural changes would involve moving to a non-folded situation. Models of the interfacial zone will be discussed in section 3.4.

3.2.4. The influence of molecular weight. Since the earliest studies of polymer crystallisation it has been recognised that the molecular weight is an important variable. Although all of its effects are not completely understood, some advances have been made recently, largely due to the introduction of the concept of reptation. It has long been recognised (Magill 1964) that increasing molecular weight causes a decrease in the rate of crystal growth. It is also known that molecular fractionation can occur, differences in melting point and mobility making major contributions to the effect.

Recent developments have taken two forms. First there is the concept of molecular nucleation, introduced by Wunderlich and Mehta (1974) (see also Mehta and Wunderlich 1975, Cheng *et al* 1988a, b). The basis for the idea rests with the concept of a stable nucleus i.e. as the nucleus grows beyond its critical size it reaches a point at which its energy of formation becomes zero and ultimately negative, hence producing stability. If the molecule is relatively short, it cannot reach the stable nucleus size and hence will have a finite rate of dissolution unless a second molecule lands and is able to help the nucleus achieve a stable size. Therefore, on this basis it is predicted that molecules may fractionate under appropriate conditions. Generally, conditions of slow growth and low supercooling are necessary and believed to apply in practice.

Much of the evidence for separation comes from melting curves where multiple peaks can be observed (Mehta and Wunderlich 1975). Multiple melting peaks can arise for many reasons; however, in all of the experimentation considered here the origin is undoubtedly some form of molecular fractionation. What is in question is the molecular weight of the separating species.

The theoretical approach of Wunderlich and co-workers is totally dependent on adjacent re-entry folding and has been criticised by Glaser and Mandelkern (1988) as unrealistic, in terms of the extent of molecular weight fractionation predicted. In their experiments they blended fractions prior to carefully controlled crystallisation and then performed solvent extraction at temperatures for which isolated crystals of the lower molecular weight fraction would be soluble, if they were present. There have always been problems with the use of solvent extraction techniques since it is possible that partial dissolution of mixed crystals can occur (Mehta and Wunderlich 1975, Dlugosz *et al* 1976, Gedde *et al* 1983). Prior to the recent work of Glaser and Mandelkern (1988) the highest molecular weight believed to separate in polyethylene was 22 000, however, Glaser and Mandelkern claim that their extraction procedure is optimal and that the highest fractionable molecular weight is only 5000.

Recently, the effect of molecular weight on crystallisation rates was predicted by Hoffman and Miller (1988) who introduced molecular weight dependence in the form of the activation energy for reptation. Data on polyethylene fractions were analysed and shown to be consistent with theory if the z-average molecular weight was used, but the rationale for choosing that particular average was not made clear. Cheng *et al* (1989) have recently shown that the equation derived by Cheng, Wunderlich and co-workers for molecular weight dependence can be converted into the equation derived by Hoffman and Miller. It therefore appears that these two groups are now in agreement on this aspect of molecular weight dependence, despite having started from different points of view.

3.3. *The crystal thickness and melting point*

One of the major achievements of secondary nucleation theory is the prediction of the variation of lamellar thickness with supercooling. Polymer crystals, because they are thin, exhibit melting points which depend on the thickness and hence on the crystallisation temperature. It has therefore been necessary to define a special parameter, the equilibrium melting point, which is the temperature at which an infinitely thick crystal will melt. All kinetic analyses are dependent on the accurate estimation of this quantity, which is usually achieved through extrapolation. It should also be recognised that the melting curve of a polymer never resembles the sharp spikes characteristic of atomic or molecular solids. Invariably there is a broad peak, at least 10 °C in width but sometimes as much as 100 °C wide, caused by the variety of crystal thicknesses and perfections generally present.

Therefore, in the case of polymers, that most basic and essential parameter of a crystal, its melting point, is often a matter of very serious debate. The earliest theoretical attempt at predicting the equilibrium melting point is due to Flory and Vrij (1963) and was designed to permit the extrapolation of the melting point of polyethylene from the melting points of linear alkanes, which produce extended chain crystals and can be characterised with precision. The bulk of the data that has been used in extrapolations was compiled by Broadhurst (1962) and the largest molecule has 100 methylene units. Attempts to obtain better extrapolations than the original one of Flory and Vrij (which yielded a value of 145.5 °C) have used fractions obtained by nitric acid etching (Atkinson and Richardson 1969) and additional samples of 120 and 140 methylene units (Heitz *et al* 1972). The analyses of Wunderlich and Czornyj (1977) led to a value of 141.5 °C. These extrapolations and the data used have been criticised by Mandelkern and Stack (1984) who still prefer the value of 146 °C. This difference of 4 °C is important in analyses of polyethylene crystallisation data.

It is generally recognised that as soon as it is formed a crystal tends to thicken, simply because it is a metastable structure and lowers its internal energy by lowering the amount of folded chain surface per unit volume. Until recently it was known that thickening was a relatively rapid process, but the details of how the measurable thickness was achieved were not known.

3.3.1. The estimation of crystal thickness. At this point it is necessary to review the methods by which the crystal thickness can be studied. In the case of single crystals grown from solution, direct measurement is possible (see Keller 1968) but for the bulk polymer all approaches have some assumptions and several pitfalls.

The earliest technique developed and used with some accuracy is small angle x-ray scattering (SAXS) (e.g. Ruland 1977, Kortleve and Vonk 1968, Vonk 1971, Crist 1973, Crist and Morosoff 1973). To a first approximation, it can be stated that at least one intensity maximum is generally observed which can be interpreted using Bragg's law. The distance characteristic of the Bragg maximum reflects a long-range periodicity in the crystalline material, which essentially is determined by the stacking of crystals in a manner which is usually regarded as parallel to a first approximation. Although raw data curves show this maximum, it is best interpreted after carrying out the Lorentz correction. The simplest model used is the parallel stack model which assumes that the characteristic distance, usually referred to as the long period, is a measure of the crystal thickness plus the amorphous thickness. The estimation of the crystal or lamellar thickness is then simply a question of knowing the crystallinity. In practice, the data can be analysed in more complicated fashions, since as mentioned earlier there is always a distribution of thicknesses present. Hence the next step is to use some sort of distribution function for the thickness and to perform curve-fitting operations. Until recently, it was generally assumed that it was the distribution of crystal thicknesses that controlled the scattering behaviour and little attention was paid to changes or variations in the amorphous thickness. So, in general, the simulation of scattering curves should consider three distribution functions, the lamellar thickness function, the amorphous thickness function and the crystallinity function. In practice these are not independent variables and any two can be considered. It appears that there may be misleading interpretations in the literature due to a tendency, especially in the past, to associate any changes in the long period or its distribution with changes in the lamellar thickness.

Another obvious technique is electron microscopy, since no indirect technique, no matter how elaborately analysed, can substitute for direct visualisation. Transmission electron microscopy, however, has its own problems. Generally it is necessary to contend with the fact that electrons interact with all polymers in a destructive manner. It is also not necessarily easy to obtain good imaging and orientation of the crystals. Also, since distances of the order of 100 Å are being considered, it has to be recognised that, given the resolutions normally obtainable with polymers, exact measurements are difficult. The best data appear to have been obtained using staining methods which fix the specimen and at the same time generate contrast between the crystalline and amorphous phases. Two techniques have met with considerable success: they are osmium tetroxide staining of polydienes and chlorosulphonation of polyethylenes. An additional valuable technique is etching of polyolefins using permanganic etching, followed by replication.

Osmium tetroxide staining (Andrews 1962, 1964) exhibits the most versatility since it can be carried out using vapour at reaction rates several orders of magnitude faster than the linear rates of crystal growth. As such it can be used at any time during the crystallisation process, providing the specimen is in the form of a thin film, and so can provide information on variations in morphology as crystal growth proceeds. The principle behind the technique is that the osmium tetroxide vapour penetrates only the amorphous phase and not the crystals. Its major disadvantage is that in general it can only be used with polydienes. The orientation of a lamellar crystal can be discerned in the electron microscope and hence crystal thicknesses obtained can be accurate to within 5 Å (see figure 5). It very clearly gives distributions of crystal thickness with little possibility of major error. Generally, for *cis*-polyisoprene it has been found that distributions are fairly narrow but very dependent on the crystallisation temperature (Phillips and Vatansever 1987). For high supercoolings a fairly narrow distribution is normal, but for low supercoolings a broad distribution with some evidence for bi- or even tri-modal distributions tends to be present.

Chlorosulphonation (Kanig 1973, 1974, 1980) is carried out on already crystallised samples of polyethylene and is often followed by treatment with uranyl acetate (this is only to stabilise the film; contrast is obtained largely from the chlorine atoms). It therefore gives information only on the lamellar thickness distribution after all treatments have ceased and on the state encountered by the stainant at the staining temperature. Specimens need to be thin sectioned for the electron microscope, introducing additional uncertainty into the process. Nevertheless, results have been impressive (see figure 14). Lamellar thicknesses can be measured directly off the screen, if the assumption is made (but rarely stated) that the chlorine has not penetrated the crystal during reaction (Martinez-Salazar *et al* 1984a, b). In contrast to osmium tetroxide, where the penetrating molecule is very large, chlorine penetration is a real possibility which could result in low values of the lamellar thickness. This technique is often used in closely packed structures such as polyethylene to make estimates of the amorphous thickness. To the best knowledge of this author, no attempt has yet been made to evaluate the expansion of the amorphous layers caused by the reaction with the stainant and so estimates of amorphous thicknesses using this approach may be overestimates. Largely pioneered by Voigt-Martin and co-workers (e.g. Voigt-Martin 1985) this technique has demonstrated convincingly that many interpretations of SAXS data in terms of lamellar thickness variations were misinterpretations and that the major variations really occurred in the amorphous thickness. Such data demonstrate for polyethylenes (as osmium tetroxide staining did for *cis*-polyisoprene) that the lamellar thickness distribution is in fact quite narrow.

A relatively new spectroscopic technique which has proved invaluable is Raman scattering using the longitudinal acoustic mode of the polyethylene chain present in

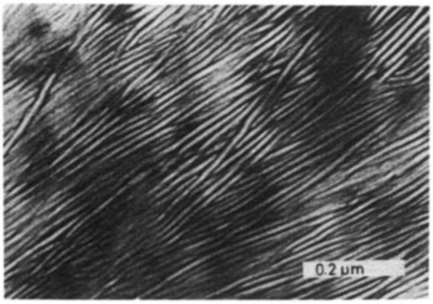

Figure 14. Transmission electron micrograph of a thin section of a polyethylene fraction of molecular weight 11 000, quenched from the melt and stained with chlorosulphonic acid followed by uranyl acetate. (First published by Voigt-Martin and Mandelkern (1984). Photograph supplied by I G Voigt-Martin.)

the crystal. (For an introduction to this general subject the reader is referred to Zerbi 1984.) Commonly known as the LAM mode, the technique permits a quantitative estimation of the length of chain present in the crystal (e.g. Snyder 1982, Strobl 1981, Rabolt and Fanconi 1977, Glotin *et al* 1983, Snyder *et al* 1978, Snyder and Scherer 1980, Martinez-Salazar *et al* 1984a, b). The method relies on a vibration along the length of the chain, sometimes referred to as a concertina mode, in which the frequency is related to the length of elastic chain present, which essentially means the length of extended chain present in the crystal. A common occurrence (e.g. in polyethylene) is that the chain is inclined at an angle to the lamellar surface and hence there may be a significant discrepancy between the value of the lamellar thickness measured by the other techniques listed above and the actual length of molecule present in the crystal. Considerable effort has been expended by Voigt-Martin and co-workers on relating the results obtained using these different measuring techniques. These comparisons have considered the relation between distributions of lamellar thickness and amorphous thickness in a quantitative fashion (Voigt-Martin and Mandelkern 1984, Voigt-Martin *et al* 1989).

3.3.2. The lamellar thickness temperature relation. As was mentioned in the section on secondary nucleation approaches to crystal growth, and also in the earlier review by Keller (1968), one of the earliest successes of nucleation theory was the prediction of the relation between the lamellar thickness and the supercooling. This simple dependence of the crystal thickness on the inverse of the supercooling is a direct result of the fold surface free energy being much larger than the lateral surface free energy. One of the often cited problems with all recent versions of secondary nucleation theory is the problem of the δl catastrophe (Hoffman *et al* 1976). This situation arises because of a small term that is generated during the integration of the thicknesses of critical nuclei in the formulation of the lamellar growth flux equation. Basically, a term in the denominator is negative and supercooling dependent. As supercooling increases the denominator approaches infinity. Attempts at resolving the problem have been most successful when the process by which a molecule adds to the surface is considered to occur in two stages. It proceeds firstly through a deposition which simply adds the molecule to the surface in an adsorbed fashion. Secondly, there is a rearrangement into crystallographic alignment on the surface. In this manner the catastrophe is moved to very high, and probably unattainable, supercoolings. Whether or not this approach is truly satisfactory remains a matter of some debate. As mentioned earlier, several studies have recently shown that the initial lamellar thickness distribution is probably very narrow and that the integration of potential initial crystal thicknesses to infinity may not be appropriate. Much narrower integration limits would also increase the supercooling at which the catastrophe occurs to a very large value. It is however generally accepted that the lamellar thickness-supercooling relation is a smooth function for most polymers. Only under exceptional conditions (see below) is different behaviour encountered. The recent advances in secondary nucleation theory leading to the recognition of the three regimes do not affect this relation. Indeed one of the most telling tests of a proposed regime transition is a smooth lamellar thickness-supercooling relation occurring over the same range of temperature as the regime break. Just such an occurrence was observed in *cis*-polyisoprene.

In certain polymers very special lamellar thickness variations can occur. Generally lamellar thickness varies with temperature as a continuous function, the parameter being inversely proportional to the supercooling. In the case of polyamides, where the crystallographic repeat unit in the chain direction may be the order of 20 Å, a quantisation of lamellar thickness has been observed (Dreyfus and Keller 1970, Dreyfus *et al* 1972) since the repeat distance and the lamellar thickness are of the same order of size.

For relatively short molecules a quantisation may also occur, but caused by the necessity to form a restricted number of adjacent re-entry folds. This effect is exemplified in the data of Kovacs and co-workers on low molecular weight narrow fractions of poly(ethylene oxide) (e.g. Kovacs *et al* 1975). In this case crystals containing one, two and three folds can be grown, as well as extended chain crystals. Poly(ethylene oxide) contains relatively large end groups, which may be partly responsible for stabilising the quantisation. Other polymers of similar molecular length to the poly(ethylene oxides) but having broader distributions of molecular weight (e.g. poly(ε-caprolactone), Phillips *et al* 1987) do not form quantised lamellar thicknesses. The exact mechanisms responsible for the onset of folding in poly(ethylene oxide) and for its detailed and complex behaviour is currently the subject of active debate (Hoffman 1986, Cheng *et al* 1988a).

3.3.3. Lamellar thickening. Since the earliest studies of lamellar thickness, it has been recognised that lamellae thicken very shortly after their formation and that a second thickening process may occur for a long period of time. Definitive studies of the thickening processes are needed largely because of the difficulties inherent in the accurate determination of lamellar thickness distributions. The simplest manifestation of the thickening process can be seen in the dependence of the slope of a graph of melting temperature versus crystallisation temperature, a shallow slope indicating major thickening in the time between crystallisation and melting point determination. Thickening caused by elevating the temperature of a crystal grown at a lower temperature has been the most common method of study. In such studies the measurement of the thickness of a single crystal using electron microscopy of a replica or the use of the Bragg maximum obtained from SAXS has been common. Only during the past ten years or so have there been attempts to look at the change in the distribution of lamellar thicknesses.

Due to the development of synchrotron radiation (Barham *et al* 1985) it has become possible to carry out SAXS studies very rapidly and at rates comparable to the rates of crystal growth. Barham and co-workers were able to show that the long period doubled microseconds after the polyethylene crystals grew. The long period is normally the sum of the lamellar thickness and the amorphous thickness. In fully grown morphologies it can be related to the lamellar thickness through the crystallinity using a simple linear relation. However the meaning of a long period in a system just beginning to grow is not yet clear and so the complete relevance of these fascinating results to our understanding of the crystal growth process has not yet been realised. Should the lamellar thickness be directly related to the long periods measured in these experiments then it will render invalid all of the currently developed secondary nucleation approaches. This is because initial lamellar thicknesses half of those currently measured by other techniques could not possibly produce stable nuclei of reasonable sizes.

There have been few studies of thickening of solution-grown single crystals in contact with solvent and it has been difficult to separate the effects of crystallisation and annealing in the data. Early studies on polyethylene (Holland 1964, Blackadder and Schleinitz 1966) were best interpreted in terms of complete dissolution followed by recrystallisation. Recent studies of the annealing of solution-grown single crystals of nylon-6,6 (Magill *et al* 1981) have generated interesting information. In this study crystals grown at a particular temperature were annealed at a higher temperature whilst in contact with the mother liquor. It was found that the curve of lamellar thickness versus annealing temperature considerably overlapped and smoothly joined the curve of lamellar thickness versus crystallisation temperature. It was suggested that this most unusual effect could mean that there is a maximum lamellar thickness attainable at a given temperature. The authors analysed their x-ray data to support the concept of folds containing acid units, as opposed to amine units. Given the earlier results of Dreyfus and co-workers (1970, 1972) which suggest a quantisation of lamellar thickness in polyamides, it is possible that the effect observed by Magill *et al* is unique to such systems.

Estimation of 'conventional' thickening following crystal growth can easily be achieved using a plot of melting versus crystallisation temperature i.e. the plot that is most easily used for the estimation of the equilibrium melting point. The slope of such a plot yields the thickening coefficient γ, which is usually between one and two. In some cases it is possible to plot both the onset and end of melting temperatures and so obtain initial and longer term thickening coefficients.

It was established early on that raising the temperature of a polymer crystal to a value within its crystallisation range causes an irreversible increase in the thickness to a value close to that which it would have assumed if crystallised at the higher temperature (Statton and Geil 1960). Some recent advances have come from more quantitative analyses of relatively standard data obtained from electron microscopy and SAXS studies. Basic approaches to thickening mechanisms tend to fall into two groups both based on the assumption that a partial melting and recrystallisation are involved: (*a*) selective melting of individual lamellae which differ in stability (Kilian 1969) and (*b*) partial melting is homogeneous and affects all lamellae equally since it occurs due to a thickening of surface layers (Zachmann 1967 or Fischer 1969). A more recent model due to Strobl *et al* (1980) suggests that the essential factor governing the likelihood of thickening at any particular point is the amorphous thickness. The model is a reasonable one based on the interpretation of a combination of SAXS and electron microscopy data. It assumes that the lamellar thickness of a newly growing lamella during annealing is a constant determined by the temperature. Hence only crystals that have sufficient room to grow will do so within the interlamellar space remaining. It does not however recognise that the thickness of a lamella may be influenced by factors other than temperature. There are many molecular variables that will influence behaviour, such as molecular fractionation, internal and external strain as well as microstructural impurities. In the system studied by Strobl *et al*, the polymer was a low-density polyethylene having an unusually high concentration of long chain branches and so the combined effects of molecular entanglements and side branch interference with the crystallisation process may have been underestimated. However, the basic finding from SAXS studies that the increase in long period on annealing is largely caused by an expansion of the amorphous phase thickness has been confirmed for a number of other polyethylenes (Lee 1989).

The rate of lamellar thickening has been measured for only a few systems, the data being often sparse and sometimes ambiguous. Several empirical relations have been derived from SAXS studies. Studies of the change in lamellar thickness distribution with time at the crystallisation temperature have been studied using Raman LAM scattering for a restricted temperature range by Stack *et al* (1982). They showed clearly that, although the most probable thickness increases as had generally been believed, there was also a considerable broadening of the distribution of thicknesses, especially towards higher values. It is therefore an important point to remember that the initial thickness distribution is likely to be very much narrower than that often measured on a fully crystallised sample.

The most thorough theory available is that of Sanchez *et al* (1973, 1974). Some aspects of the theory have been tested on copolymers and, most recently, on poly(ε-caprolactone) (Phillips and Rensch 1989). In the latter study the variation in melting point with crystallisation time was studied, permitting extensive data to be acquired on the rate of thickening during crystallisation. It was found that curves of the ratio of lamellar thickness to extended length versus the logarithm of time obtained at various temperatures could be superposed by horizontal shifts. Estimates of activation energies were made using standard approaches. Some degree of success was also obtained in the superposition of curves for specimens of different molecular weights.

3.3.4. The influence of pressure. The most impressive degrees of thickening achieved have been obtained for linear polyethylene at pressures in excess of 3 kbar by Wunderlich and co-workers (see Geil *et al* 1964 for the first report). Here it was possible for near complete chain extension to be obtained i.e. the crystal thicknesses approached the molecular length (Wunderlich and Davidson 1969, Gruner *et al* 1969, Prime *et al* 1969). In later studies it was realised that complete chain extension could only be achieved for molecules of low and intermediate length. The greatest lamellar thickness achieved was in the vicinity of two micrometres. Molecules longer than that were unable to form their own crystals and hence were present in the crystals of other molecules (see Bassett 1981 or 1985, for a recent review). The mechanism for pressure-induced thickening was debated for some time and was ultimately resolved by high-pressure x-ray studies (Bassett *et al* 1974). It was found that growth at pressures in excess of 3 kbar occurred in a hexagonal phase (Bassett and Turner 1974) and that, because of the much lower heat of fusion, the crystals were much thicker. On transformation from the hexagonal to orthorhombic phases, during release of pressure, more thickening occurred (see figure 15). One additional benefit of this discovery was that the value of the equilibrium melting point could be verified since the crystals were of an effectively ‘infinite’ thickness. At the time that this work was progressing, it was realised that poly(tetrafluoroethylene) (Melillo and Wunderlich 1972, Bassett and Davitt 1974) and poly(chloro trifluoroethylene) were chain extended when crystallised at elevated pressures (Miyamoto *et al* 1972). For some time therefore, it appeared that chain extension was ubiquitous in crystallisation at elevated pressures. Experimentation by Phillips and Edwards (1975) on elevated pressure crystallisation on *cis*-polyisoprene, designed to investigate the thickening mechanism, showed clearly that chain extension did not occur in that polymer. Since that time no additional examples of pressure-induced chain extension have been identified. It is now recognised that the ability of a polymer to thicken to a large extent is controlled by the activation energy of dragging long sections of chain through a polymer crystal and that something as mild as the side chain methyl group of *cis*-polyisoprene inhibits the process.

The crystalline structure of the high-pressure hexagonal phase in polyethylene is very unusual in that the chain is no longer a linear zig-zag. Although this is a higher energy conformation of a single chain, it has a higher entropy than a linear zig-zag chain leading to a $T\Delta S$ term which more than compensates for the $P\Delta V$ expansion term, thus stabilising the crystal. Several polymers, including *cis*-polyisoprene, do form hexagonal high-pressure phases in which the chains have an unusual degree of

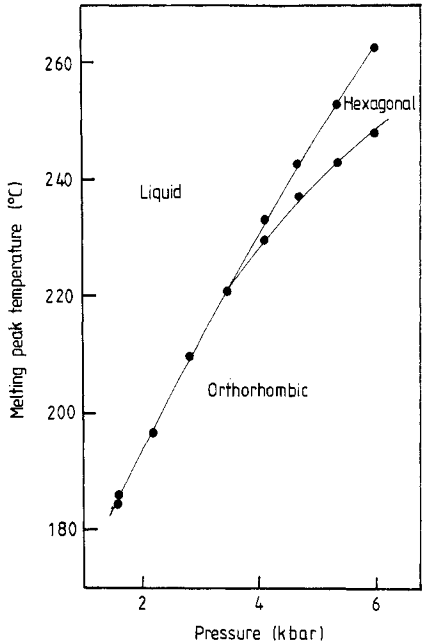

Figure 15. The phase diagram of linear polyethylene obtained from the observed melting points of a specimen previously crystallised at 5 kbar and having a molecular weight of 50 000. (After Bassett and Turner 1974.)

freedom of movement. These phases have been labelled CONDIS crystals by Wunderlich, the acronym standing for conformationally disordered crystals. Such a state of matter is unique to long chain molecular crystals and quite distinct from states such as plastic crystals and liquid crystals (see section 3.8).

3.4. The crystal-amorphous interface

In an earlier section some attention was paid to the nature of chain folding and discussion centred around the subject of whether or not the folding was of an adjacent re-entry form. In recent years the question being considered is what fraction of the folded material is adjacently re-entered. In practice it is possible for sections of several molecules to crystallise close to one another. What then happens to the remaining sections of these molecules? Clearly they are likely to crystallise in other locations—some close, some distant. When they do so they generate tie-molecules which bridge the crystals and are responsible for the occurrence of elasticity. Some of the molecular sections may re-enter the same crystal many times instead of entering other crystals. The amount of each will be determined by many factors, which will include scale parameters such as molecular length, crystal thickness and amorphous thickness.

Other factors such as the crystallisation regime and the internal mobility of the molecule will also be of significance. Clearly there will be a considerable temperature dependence of the detailed surface structure. The modelling of surface structures tends to have relied on the assumption that an emerging chain is Gaussian, although it should be clear that if a chain has to pass through a folded region to enter the amorphous phase then it must be non-Gaussian for part of its traversal. It will have a conformation that is more extended than in a truly random state and hence will be more rigid than a Gaussian chain. Because of this effect, the term rigid amorphous phase was coined by Wunderlich to describe such molecules. Clearly a major factor in the extent of non-Gaussian features will be the inherent flexibility of the molecular chain under consideration. Also of importance will be the level of microstructural defects present in the chain. For instance, rejected short chain branches may be localised near the surface leading to a situation which may be better described as an interfacial zone of finite and measurable thickness. The estimation of these zone thicknesses has been pioneered by Voigt-Martin, Mandelkern and co-workers using a combination of electron microscopy of stained films with other techniques. The study of the volume fractions assignable to this 'phase' has been developed using quantitative thermal analytical approaches by Wunderlich and co-workers.

In a paper published in 1982, Glotin and Mandelkern used a combination of methods of crystallinity measurement to estimate the percentage of material present in the interfacial layer. The method used was, essentially, the development by Strobl and Hagedorn (1978) of an integration method for Raman spectra which defined exactly the proportion of material present in the orthorhombic crystal. One of the isolated bands (1416 cm^{-1}), a CH_2 bending component, is unique to the orthorhombic lattice and can be simply integrated to give the crystallinity when compared to the total intensity of the CH_2 twisting range (which applies to all components regardless of origin). Estimation of the amorphous component has been achieved by using either the 1303 or 1080 cm^{-1} bands. The sum of the crystalline and amorphous fractions, when calculated in this manner, does not equal unity. Glotin and Mandelkern (1982) determined this fraction for a series of linear and copolymerised polyethylenes as a function of method of crystallisation. Their results show that the amount of interfacial phase is extremely small for slowly crystallised linear fractions of low to moderate molecular length, but is appreciable for quenched linear fractions of high molecular weight and for copolymers. The highest amounts postulated for linear, high molecular weight fractions were in the vicinity of 10%, but for quenched copolymers could be as high as 20%. These authors have suggested that the crystallinity determined by heat of fusion measurement corresponds to the actual crystalline fraction and that the crystallinity measured using density is really a sum of the crystalline and interfacial fractions. To date, these ideas and conclusions have not been pursued further by other research groups.

Estimations of the fraction of rigid amorphous phase have been carried out for several polymers by Wunderlich and co-workers, but these have been largely semi-rigid polymers having benzene rings in the backbone. These estimates depend critically on computed heat capacities (for a review of the method see Wunderlich and Cheng 1986, Gaur *et al* 1986, Pan *et al* 1986, Loufakis and Wunderlich 1988). Essentially, a vibration spectrum is computed on the basis of group vibrations and then converted to a heat capacity using the Einstein function, which is generated by use of Debye approximations and a combinatorial equation proposed by Tarasov. The heat capacity is computed as a function of temperature for the liquid and crystalline states and then is subtracted from an experimental curve determined using differential scanning calorimetry. For materials exhibiting a heat capacity at temperatures above the glass transition which is lower than that predicted by the computations, the discrepancy is ascribed to a rigid amorphous fraction (i.e. molecules that are to be found in a partially extended, higher than normal energy state) which melts at a temperature higher than the glass transition. The first polymers for which such calculations proved successful were polypropylene (Grebowicz *et al* 1984) and poly(oxymethylene) (Suzuki and Wunderlich 1985). Three semi-rigid polymers which have been extensively studied using this method are the important high-temperature thermoplastics PEEK (Cheng *et al* 1986), poly(phenylene sulphide) (Cheng *et al* 1987) and poly(butylene terephthalate) (Cheng *et al* 1988b).

3.5. The lamellar profile

3.5.1. Solution-grown crystals. The shapes of polymer crystals have been of interest since single crystals were first made. Indeed, this topic was of major concern in the first review by Keller (1968). Since that time there has been considerable progress especially with regard to crystals grown from the melt. The reader is referred to a review by Khoury and Passaglia (1975) in which considerable attention was paid to the morphology of solution-grown crystals. Since then, there have been a number of important developments, especially in the study of crystals having shapes other than the often quoted lozenge typical of polyethylene. However, the famous polyethylene lozenge and its allied truncated forms have been the subject of an interesting study which attempted to relate the aspect ratio of the crystal to secondary nucleation theory (Passaglia and Khoury 1984). As discussed earlier in this review, secondary nucleation theory in its various forms has successfully described the lamellar thickness and its dependences on such factors as temperature, solvent, molecular weight and concentration, but it had not previously been applied to the lateral dimensions. The aspect ratio of the lozenge is, of course, a constant determined by the unit cell parameters, but for the truncated lozenge there are two different growth faces. These are the {110} faces typical of the lozenge, together with the {200} faces responsible for the truncations. Of course, it was recognised throughout the work that the true growth shape is that of a hollow pyramid and that their calculations applied to the *c* projections of the crystals. In this work, which predated the clear evidence for a regime I-regime II transition in certain solutions by Organ and Keller (1986) and the extension of secondary nucleation theory to the {200} face specifically (Hoffman and Miller 1989), it was assumed that only regime I was operating in the polyethylene solution crystallisation case. The growth rates of the {110} and {200} faces were expressed in terms of secondary nucleation theory. They found that earlier experimental data of Blundell and Keller (1968) and of Valenti and Pedemonte (1972) could be fitted with considerable sensitivity using the ratio of the end surface free energies of the growth faces and the ratio of the lateral surface free energies as two adjustable parameters. Undoubtedly, in due time the approach will be extended further in the light of the new knowledge of the regime transmission and the theoretical development due to Hoffman and Miller. It should also be noted that a simplified version of the theory was derived independently and concurrently by Alfonso *et al* (1982) and published in abstract form.

It is generally recognised that, in the ideal case, the lateral habits reflect the unit cell of the polymer under consideration but may also reflect preferred growth habits. These profiles are generally assumed to take the shape of various polyhedra, however, a number of studies have highlighted the existence of various types of curvature. Many of these advances are related to the development of new techniques, particularly, the scanning transmission electron microscope (Khoury and Bolz 1980) and to the patience and perseverance of a few researchers.

The study of crystals grown at unusually high temperatures has been of considerable interest. Normally, polyethylene crystals are grown from solution at temperatures lower than 95 °C and can be truncated, the degree of truncation increasing with growth temperature. Khoury and Bolz (1980) were able to grow crystals at temperatures in the range 95–115 °C through the use of poor solvents, such as dodecanol and heptyl acetate. The resulting crystals were lenticular and exhibited aspect ratios as high as six (cf 0.67–1.8 for normal and truncated growth). Dark field studies in the STEM (see figure 16) showed that the degree of tilt of the chains in the centre of the crystal was different from that at the long smooth curved edges. Within the centre of the crystal all chains showed the same degree of tilt even on crossing the central sector boundaries. In separate experimentation, using the polymer vapour decoration technique, Wittmann and Lotz (1985) showed that the folds are parallel to the curved growth faces. They were also able to confirm the sectors deduced by Khoury and Bolz, and that the tips of the growing crystals are indeed sharp {110} facets. These two experiments demonstrate the very important principles that curved edges are consistent with regular folding in the conventional sense and that very clear changes in fold orientation occur at sector boundaries in crystals of unconventional shape.

Many interesting studies have been forthcoming on the lamellar profiles of polymers other than polyethylene, grown from solution. Here it will be attempted to review only those that have produced data somewhat novel in nature and have generated or encouraged additional theoretical approaches. The most extensive studies on curved crystals from solution are those of Khoury and Barnes on poly(4-methyl pentene-1) (1972), polyoxymethylene (1974) and of Barnes and Khoury on polychlorotri-

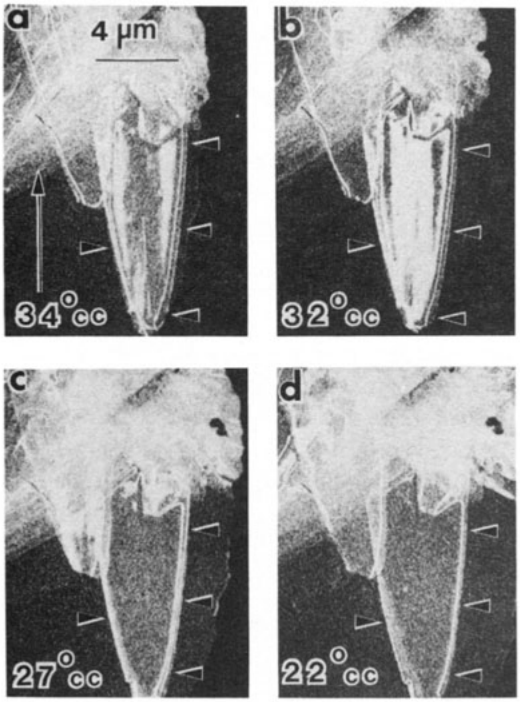

Figure 16. Dark field STEM images of part of a crystal of polyethylene ($M_n = 11\,400$, $M_w = 13\,600$) crystallised from a 0.01% dodecanol solution at 115 °C. Crystals have been tilted counterclockwise by the angles indicated about a tilt axis shown by the arrow. (*a*) and (*b*) illustrate the contrast and, hence, chain axis relative to the surface. Comparison of (*a*) and (*b*) with (*c*) and (*d*) shows that there is a significant difference in orientation between the interior and periphery of the crystal. (First published by Khoury and Bolz 1980, photograph provided by F Khoury.)

fluoroethylene (1974). In all three of these cases it was clearly shown that when crystallised at relatively large supercoolings bowl-shaped crystals occurred. They were observed in solution as well as collected on substrates, in order to demonstrate that they were the original growth shape and not a distortion produced by the drying process.

A remarkable observation is that these polymers do not have similar unit cells nor do they have similar shapes when grown at higher crystallisation temperatures. Another important general observation is that these bowl-shaped crystals grow in multilayered forms. Some of the most striking micrographs of multilayered bowl-shaped crystals, from *trans*-polyisoprene, are to be found in the recently published *Atlas of Polymer Morphology* by Woodward (1989). There does not yet appear to be any generally accepted theory for the formation of this type of crystal, however, it was suggested by Khoury and Barnes that stress generated by the folds was the most likely source. In all of these polymers the folds are likely to be bulky and to generate a surface stress which perhaps could lead to buckling. It should also be recognised that there is no sharp transition from a perfectly faceted regular crystal to these bowl-shaped entities. In fact, there is a wide range of supercooling over which the crystals display a limited amount of curvature, the degree of which tends to increase with supercooling. The 'working model' proposed by Khoury and Barnes incorporates this gradual effect into the general schema.

3.5.2. Melt-grown crystals. Studies of lateral shapes in bulk crystallised polymers are few and far between because of the difficulty of distinguishing the shape of a single lamella from the surrounding crystals, invariably present in the form of a spherulite or axialite (see section 3.6). In some experiments it has been possible to identify the shapes of the growing tips of the lamellae. Several recent studies have considered polyethylene and isotactic polystyrene in some detail (Basset 1984, Keith and Padden 1987c). Except in isolated incidences the overall lamellar shape does not exhibit the regular single crystal profile; often the crystals are ribbon-like with a constant width. The process by which this constant width is attained is simply not understood, although it should be recognised that the recent theoretical developments by Hoffman and Miller (1989) regarding the growth of the {200} face in polyethylene may ultimately lead to some general progress in this area. Most studies of the lamellar profile of melt-grown crystals, therefore, tend to be aimed at generating definitive descriptions of the growth tips and of the overall shape rather than testing any specific theories.

The polymers most easily studied for their lamellar profiles in the bulk are the polydienes which can be studied because of the ability of osmium tetroxide vapour to penetrate thin films rapidly and actually terminate the crystallisation process at an early stage (Andrews 1962, 1964). The most extensive studies of the change in entire lamellar profile in the bulk are those of Vatansever (1987) and Phillips and Vatansever (1987) where the profiles were observed as a function of the operating regime for several molecular weight fractions. It was found that in regimes II and III the profile is essentially that of a ribbon (figure 17), there being no change in the lamellar width with time at a given crystallisation temperature. There is a distribution of lamellar widths at any given crystallisation temperature which is reminiscent of the distribution of lamellar thicknesses. The lamellar width and its distribution increase with increasing crystallisation temperature, the distributions being much narrower in regime III than in regime II. When regime I is entered the constant lamellar width behaviour disappears and leaf-shaped crystals result (figure 18). The change is quite discontinuous. The aggregates are clearly axialitic (see later section on morphogenesis) and have a central

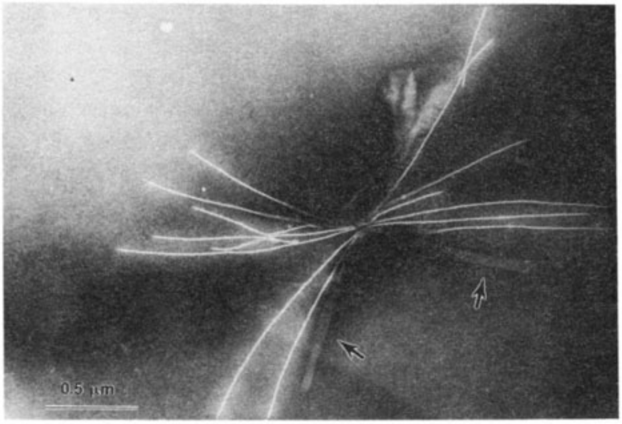

Figure 17. Lamellar growth in *cis*-polyisoprene in regime II at an early stage of the growth of a spherulite showing the ribbon-like lamellar profile (arrows).

Figure 18. Lamellar growth in *cis*-polyisoprene in regime I showing the characteristic leaf-shaped profiles of the lamellae in the 'turned over' orientation.

nucleation site. The crystals are generally ellipsoidal in shape, but appear to have pointed tips where the growth of the major axis occurs.

In what has been said earlier it should be clear that for polyethylene crystals grown from solution the lamellae are hollow pyramids of complex profile, dependent on crystallisation conditions. Studies of the cross-sectional profiles of melt-grown crystals have recently proved possible due to the development of an etching procedure which, when used correctly, can reveal morphological detail (e.g. Olley *et al* 1979). This technique will be discussed in detail in the section on morphogenesis, but it should be stated at this point that it consists of the controlled oxidation of both the crystalline and amorphous phases using a solution of potassium permanganate in concentrated sulphuric acid.

Selected morphological details are revealed because the amorphous phase reacts more rapidly than the crystalline phase. In a series of elegant experiments in which the lamellae were viewed end-on Bassett and co-workers were able to show that for crystallisation at high temperatures (corresponding roughly to regime I growth conditions) the profile was a clear zig-zag which could be related with little difficulty to the pitch of the roofs of the pyramidal single crystals grown from solution (figure 19). This work also provided direct proof that the molecular axis was inclined at a specific angle to the lamellar surface. As the crystallisation temperature was lowered the profile lost its clear facet-like features and became 's-shaped'.

Figure 19. Transmission electron micrograph of a shadowed carbon replica of permanganically etched linear polyethylene showing ridged crystals. The specimen ($M_w = 37\,000$, $M_n = 29\,000$) had been crystallised at 130 °C for 7.5 days followed by 30 min at 125 °C prior to a cold-water quench. (Bassett and Hodge, unpublished work. Photograph supplied by D C Bassett.)

3.6. Morphogenesis of crystalline aggregates

In the bulk phase of a polymer, crystals are practically never encountered as single crystalline entities. In contrast to metals, where a polycrystalline material consists of impinged polyhedra, with each polyhedron being a single crystal, in polymers, which also consist of impinged polyhedra, each polyhedron is itself an aggregate of thousands of ribbon-like crystals arranged in an approximately radial array (figure 5). These species are referred to as spherulites and are the dominant morphological form in bulk crystalline polymers. They are not the only species that can form. In many cases the crystals are not linear but may exhibit some form of twisting. When this occurs the majority of the radiating crystals twist in unison producing what is generally referred to as banding.

In some polymers, usually of relatively low molecular weight and crystallised at low supercoolings, another species generally referred to as axialites can be observed. This species is closer to the single crystals grown from solution in its form than are the spherulites. The crystals tend to be sheet-like, rather than ribbon-like and they do not form a unified and uniformly textured aggregate. When polymer films are crystallised under the influence of an applied stress quite different morphologies are generated. These morphologies have rod-like textures and depend on the level of the applied strain. The major effect of the applied stress is to orient high molecular weight molecules into a state where they condense to form fibrillar nuclei (figure 20). Normal folded chain lamellae then epitaxially crystallise on these nuclei generating textures which are referred to as row-nucleated species, or more commonly 'shish-kebabs'. Our depth of understanding of these different morphological forms is continually changing as investigative techniques are generated. Understandably some features are more difficult to investigate than others and so the depth of presentation of this section of the review will vary according to the subject matter.

3.6.1. Morphogenesis of quiescently crystallized systems. Here the morphologies typified by spherulitic and axialitic growth will be considered. The section will first consider primary nucleation i.e. the nucleation of the aggregates, then the primary growth features of the species and finally the generation of branches, tie-molecules and other such details.

3.6.1.1. Primary nucleation. As in other materials the initial nucleation process is complicated by the presence of small amounts of impurity matter, resulting from contamination during synthesis and may comprise catalyst particles or substrates, metal oxides and other contaminants from the containment vessels or just plain dust picked up during pelletisation, collection and containerisation. It was established at a fairly early stage that the general concepts of heterogeneous and homogeneous nucleation applied to polymers. The terms instantaneous and sporadic nucleation are often preferred since they describe only the time dependence of nucleation and make no presumptions regarding the physical nature of the nucleation event. Nucleation rates and densities are generally studied through interpretation of the Avrami equation or, better still, through direct microscopic observation. Most polymers will show an instantaneous nucleation pattern followed by a period of time-dependent nucleation, which may continue up until impingement or may terminate prior to impingement.

In the case of *cis*-polyisoprene and other diene polymers, the primary nucleation process can be observed with some level of sophistication because of the ability of osmium tetroxide staining to stop the crystallisation process at any stage. When *cis*-polyisoprene has been carefully purified the initiation of crystals can be observed

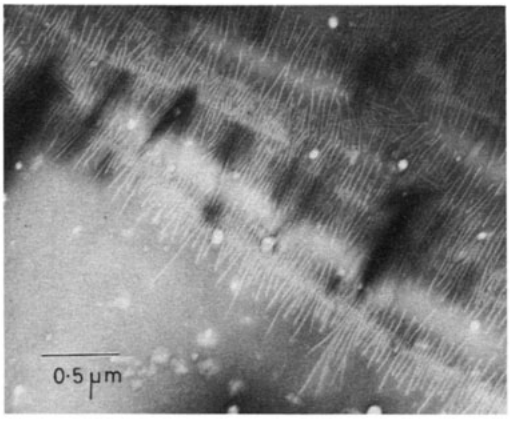

Figure 20. Row-nucleated growth (shish-kebabs) in *cis*-polyisoprene (Edwards and Phillips, unpublished data).

and often it is impossible to detect the presence of any foreign nucleus even when the crystal is only 60 Å thick. In polymers however there is always the possibility of localised melt strain being present because of the long chain nature of the molecules. Sometimes it is possible to identify such an effect because of the alignment of nuclei formed under such circumstances. Generally, a single crystal as the initial nucleation site is a rare occurrence and more commonly a group of three or more crystals of approximately the same length, indicating a common nucleation time, are encountered. It is also possible to encounter shish-kebabs in unstrained films, however the length of the row-nucleus is rarely large enough to generate more than a dozen folded chain crystals.

The subject of nucleating agents has received considerable attention partly due to the commercial importance of these chemicals. For reasons which cannot be explored in this review, certain mechanical properties can be optimised through rapid quenching and/or the generation of very small spherulite sizes. Nucleating agents are usually the easiest way of achieving this objective. Such chemicals are usually aromatic in nature and hence contain benzene rings in their structure. The variety of aromatic chemicals that will serve as effective nucleation agents for a number of polymers is remarkable. Indeed it appeared at one time that the only common feature was the presence of one or more benzene rings. Because of this apparently general functionality and the ability of the chemicals to nucleate polymers with quite different crystal structures, such as polyethylene and polypropylene, Binsbergen (1970, 1977) suggested that they all functioned simply as generators of interfaces for crystal growth with no specific functionality such as epitaxy. This hypothesis was widely accepted until a series of elegant experiments performed by Wittmann and Lotz (1981a, b) and Wittmann *et al* (1983) decisively disproved the hypothesis and showed that epitaxial growth was indeed the mode of nucleation.

Their experimentation involved first growing large thin single crystals of the nucleating agent, primarily anthracene or p-terphenyl, and then growing thin films of the polymer on the flat faces of the single crystals. X-ray diffraction experiments showed that highly oriented films were generated and that the behaviour could be described in terms of a two-dimensional lattice match between the substrate and polyethylene crystals. In the case of the fused ring systems, of which anthracene is the paradigm, the contact plane of the polyethylene with the {001} plane of the substrate is {100}. For the polyphenyls, the contact plane of the polyethylene is the {110} plane. This difference is simply a result of one of the lattice parameters of the polyphenyls being too large for the {100} plane of the polyethylene.

The key to understanding the ubiquity of the nucleating agents is the fact that all the fused ring aromatics are isomorphous in their {001} planes. Similar arguments apply to the polyphenyls. An extension of this behaviour to more than one plane was reported by Parikh and Phillips (1990) for acridine, which is similar in structure to anthracene and has three rings fused in a linear fashion. They found that it was possible to remove film from the side planes of the acridine, whereas for anthracene, film was removed only from the large flat {001} surfaces. It was found that this film was also oriented, but in a different way, from the film removed from the flat surfaces. The sides of the acridine also had lattice spacings determined by benzene ring separations but in this case a better lattice match could be obtained for a different plane of polyethylene.

The conclusions of Wittmann and Lotz had therefore not only been confirmed, but it was shown that each nucleating agent had at least two distinct lattice planes that matched the planes of polyethylene well within acceptable limits for epitaxial growth. The reason for the ability of the nucleating agents to function with both the polyethylene and with polypropylene is that the two polymers also have lattice matches and indeed polyethylene can epitaxially crystallise on polypropylene (Gohil 1985, Lotz and Wittmann 1986b). It was also shown that aliphatic polyesters and polyamides could lattice match with the nucleating agents because of their crystal packings closely resembling that of polyethylene (Wittmann *et al* 1983).

3.6.1.2. The growth of lamellar aggregates. Over the past twenty years there have been important clarifications of the way in which a crystalline aggregate grows and attains its final appearance. These advances have been largely a result of the development of new techniques for uncovering morphological detail together with the introduction of new types of electron microscopes.

It is generally recognised that the following scheme is followed during lamellar crystallisation, namely the spherulite or axialite begins as a group of perhaps three lamellae and as it grows it generates additional lamellae and changes shape. In doing so the crystals splay apart, and do so from the time they are first nucleated. It first takes on the appearance of a sheaf, then, much later, after equatorial filling, it begins to look like a spherulite. Two general classifications of spherulite are possible. For polymers exhibiting crystallinities of 60% or more spherulites are generally densely packed and there tends to be some form of a cooperative growth process, perhaps best illustrated by the periodic twisting in unison of lamellae found in polyethylene. Polymers of lower crystallinity, such as *cis*-polyisoprene and poly(ethylene terephthalate) form much more open spherulites, at least in the early stages of growth, and lamellae appear to be able to grow without regard to the processes being followed by their neighbours.

In comparing different polymers therefore it is necessary to carefully separate features which may be ubiquitous from those which are characteristic of the polymer in question. There is a tendency to regard polyethylene as a paradigm in this respect, but many of the features of its growth are not generally applicable. It should also be noted that polymers of very different habit, such as the orthorhombic polyethylene and the hexagonal isotactic polystyrene are often considered at one and the same time.

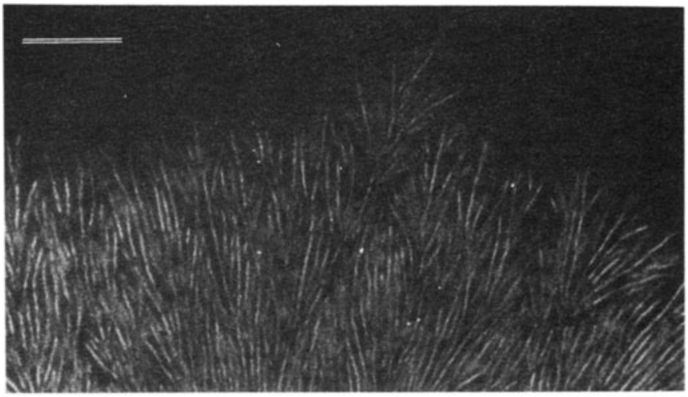

Figure 21. Leading lamellae protruding ahead of the growth front in a beta-spherulite of *cis*-polyisoprene. Due to extensive crystallographic branching, the protuberances are smaller than in spherulites of alpha-crystals of the same polymer. Scale bar 0.2 μm. (Sorenson and Phillips, unpublished data).

In fact there must be significant differences in the ways in which their respective habits change on going from single crystal growth to spherulitic growth.

Two of the staining techniques, osmium tetroxide and chlorosulphonation, have already been mentioned in section 3.3. The chlorosulphonation technique (Kanig 1973, 1974, 1980) treats crystalline polyolefins with chlorosulphonic acid at elevated temperatures for several hours, the reagent reacting with amorphous material. Although osmium tetroxide, when used as a vapour provides the most rapid reaction and the best resolution, its use is restricted to polymers containing reactive double bonds, hydroxyl groups or secondary amines. Ruthenium tetroxide has been shown to react with many other polymers including polystyrene (Trent *et al* 1983) however, it requires several hours for reaction as it is used from solution.

The permanganic etching technique has probably generated more detailed information on the morphology of polyethylene than any other technique. Developed initially by Bassett and co-workers, the technique first used 7% w/w of potassium permanganate in concentrated sulphuric acid at 60 °C for several hours (Olley *et al* 1979). Later this technique was refined to use much lower concentrations at room temperature. A major problem has been the generation of artifacts which sometimes appear to be true morphological features (Naylor and Phillips 1983). The technique has been used most effectively through the use of transmission electron microscopy of carbon replicas. However, when the technique has been used in an optimal fashion, scanning electron microscopy can be used. The most important step in producing good artifact-free films are the washing stages after reaction, which should be carried out in an ultrasonic bath (Naylor and Phillips 1983). Many papers have appeared during the ten years since the technique was first published.

Prior to these recent studies, in which it became possible to view the actual lamellae, models of the morphogenesis process had been based on optical studies. The most widely accepted explanation for the change in growth habit from lozenge in dilute solution to lenticular habit in spherulites was the theory of Keith and Padden (1963, 1964a, b). This theory explained the development of 'fibrous' (i.e. lenticular or ribbon-like) growth to the limited diffusional ability of molecules rejected from the growth process. Based on a well established theory for metals, the approach essentially uses a one-dimensional solution to a three-dimensional problem. Essentially, the accumulation of high concentrations of rejected impurities suppresses the liquidus temperature leading to a supercooling lower than the ideal value. This 'constitutional supercooling' results in a low lateral-growth rate and the development of the lenticular texture. However, recent results of Bassett's group suggest that this theory is incorrect, at least for low supercoolings.

The most definitive conclusion resulting from permanganic etching studies is the recognition of dominant lamellae in the growth process (Bassett *et al* 1979). These are thick lamellae grown from the purest polymer molecules and they grow fastest because of the lack of microstructural defects to impede their growth. They tend to grow in cells and are most noticeable when growth is carried out at low supercoolings, i.e. in regime I. In other words, the first lamellae to grow are not of a narrow ribbon-like shape but are fairly broad and ridged. Undoubtedly, molecular weight fractionation is also occurring in this temperature range, however, the rejection of such species does not appear to generate a narrowing of the width of the dominant lamellae.

Although the evidence is not so strong for crystallisation at higher supercoolings (i.e. within regime II), it does appear that dominant lamellae still occur, but they are no longer ridged or as easily discerned. It is the view of Bassett (1984, for a recent review) that the dominant lamellae control the morphogenetic process, of which the most important parts are the splaying apart and branching of the lamellae. In the light of these results, Keith and Padden (1986, 1987a, b, c) have re-evaluated the effect of impurity diffusion and introduced the effect of reptation into the process. Although the matter is not completely resolved at the present time, it does seem clear that in the growth of unfractionated polymers in regime II, diffusional effects cannot be discounted completely. Attention is currently focused on the early stages of spherulitic growth (Bassett *et al* 1988, Vaughan and Basset 1988).

Although the term 'dominant lamellae' was coined in response to the recent work on polyethylene, it should be recognised that the general features of the Bassett model have been clearly recognised in *cis*-polyisoprene for many years. There are always leading lamellae that protrude into the melt and grow most rapidly (figure 21). The difference between polyethylene and *cis*-polyisoprene has always been in the value of the ultimate crystallinity. What is now clear from the studies of Bassett and co-workers is that leading lamellae occur in both systems and that the growth front of polyethylene is as sporadic as in *cis*-polyisoprene. Such behaviour occurs in all regimes of *cis*-polyisoprene, as has been suggested for polyethylene. There is also evidence from *cis*-polyisoprene which suggests that when branching is prolific, isolated lamellae do protrude into the melt, suggesting that access to easily crystallised material is of consequence (figure 21).

The most intriguing feature of spherulitic growth in polyethylene (i.e. in regime II) is the development of banding (figure 22). These features have been recognised since the earliest optical studies (e.g. Keith and Padden 1959). The general symmetry and periodic change in birefringence led to the suggestion that banding was caused by twisting of the lamellae in unison. Originally thought to have spherical symmetry, the features generally consist of three-dimensional spiral geometries. Permanganic etching permits the study of these structures in a way not possible before.

A new finding is the presence of screw-dislocation-generated branching, which can be seen in bands (figure 22). The micrographs often give the impression that the lamellae are growing linearly and then rapidly change orientation where the screw-generated lamellae can be seen. However, it has been clear for decades from optical studies that the twisting of the lamellae is of a helicoidal form and that the optical and electron microscopic evidence need to be interpreted in a consistent fashion. This rationalisation process is still in progress and the complete picture is not yet clear. From a micrograph, it can be seen that there is indeed a twisting of the lamellae and that the screw-dislocation-generated lamellar stacks have oriented senses (figure 22(*b*)). It is unlikely that the stacks are generated in a continuous manner since there simply is not enough space for such a generation process (Phillips and Sien 1978). In densely packed spherulites such as polyethylene, lamellae can only be generated when the gap between any two lamellae is equal to or greater than the lamellar thickness plus twice the amorphous thickness. Hence for a stack the gap must be equal to this value multiplied by the number of lamellae in the stack. Naturally, this spatial restriction means that stacks cannot be generated continuously but must have a certain minimum periodicity which need not be equal to the band periodicity. In etched surfaces we only see the stacks when the lamellae are in the correct orientation and cannot estimate the number hidden from view between bands.

In less densely packed spherulites such as *cis*-polyisoprene, it is possible to count the frequency of generation of stacks, which in this case may generally comprise one or two daughter lamellae when initially formed, but tend to proliferate later. Such an

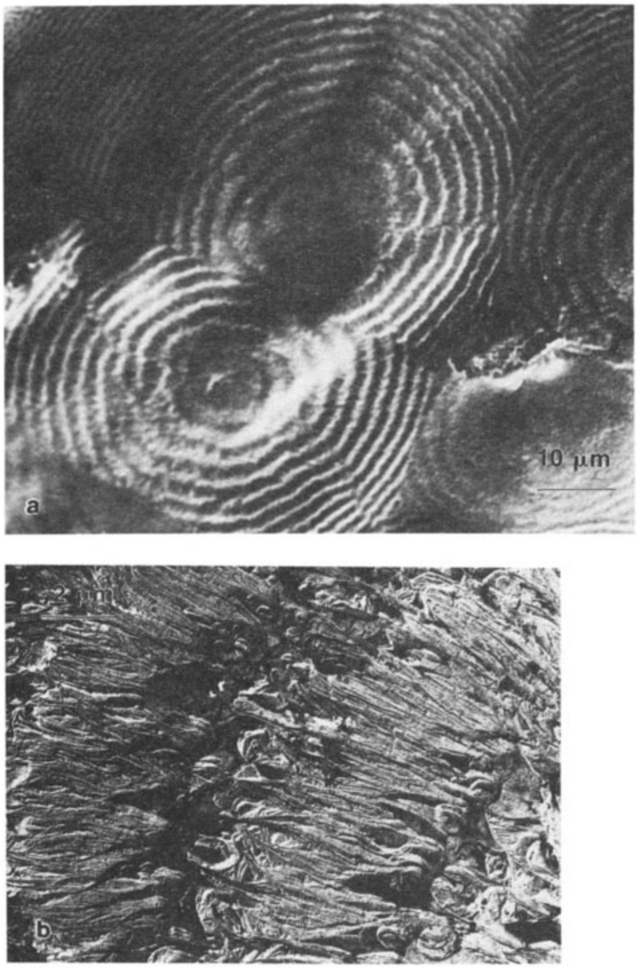

Figure 22. Banding in linear polyethylene as observed using permanganic etching (*a*) SEM photomicrograph of a coated etched surface (Naylor and Phillips, unpublished data), and (*b*) TEM photomicrograph of a chromium shadowed carbon replica of the etched surface (R J Philpot and P J Phillips, unpublished data).

estimate was made by Phillips and Vatansever (1987) and it was found that the regime occurring exerted a major influence on branch generation, the effect being maximised in regime II close to the regime I-II transition (figure 23).

Similar effects can be seen in polyethylene, since only in regime II can the stacks be seen and they have a greater population near the regime I-II transition, however quantification has not yet been reported. Although the presence of screw-dislocated stacks is beyond question, they need not be responsible for the twisting of the lamellae. The most appealing explanation for twisting offered thus far assumes internal stresses present in the folded surfaces (Keith and Padden 1984). These stresses are regarded as due to the natural angle of tilt of the molecular axis in the crystal giving rise to different degrees of disorder in the opposite surfaces. However, it is clear that none of these issues will be settled in a short period of time and it will be several years before all of the re-evaluations are complete and consistent with one another.

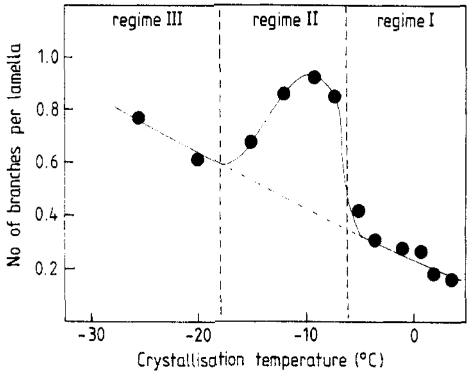

Figure 23. Average number of branches per lamellar crystal in *cis*-polyisoprene as a function of crystallisation temperature for a fraction of molecular weight 313 000. (After Phillips and Vatansever 1987.)

The permanganic etching technique has been applied to many polyolefins, but requires optimisation for the polymer concerned because of the different reactivity of each polymer. For instance, polypropylene is much more reactive than polyethylene and is best etched by a reagent using phosphoric acid rather than sulphuric acid (Bassett and Olley 1984). Polypropylene is a very morphologically complex polymer, showing several different morphologies dependent on crystallisation conditions (Keith and Padden 1959) and a very special form of branching which generates low or even zero birefringence in the spherulites. These branches form approximately normal to the linear growth direction of a lamella and tend to proliferate in certain temperature ranges (Keith and Padden 1973, Khoury 1966, Lovinger 1983, Norton and Keller 1985). It now seems clear that the effect is caused by a specific form of twinning, unique to polypropylene (Lotz and Wittmann 1986a).

One of the major problems in understanding the detailed morphogenetic processes is that each material needs to be investigated in considerable depth at each and every temperature of crystallisation, since there are often significant changes with temperature. Effects are most easily investigated for specimens grown at low supercoolings where the crystals show maximum thickness. It is often very tempting to assume that the growth studied at an isolated temperature or group of temperatures is typical of the entire range of growth temperatures. Some of the detailed aspects of the morphological behaviour of polyethylene, polypropylene and isotactic polystyrene at a limited range of temperatures were discussed by Bassett in a review (1984). It is clear that our knowledge of the subject is growing at a rapid rate, but that the actual wealth of detail present in the micrographs resulting from the permanganic etching technique is in itself an impediment to our interpretations.

3.6.2. Crystallisation under stress. During the last years of the 1960s it was established that crystallisation of polymer films which had been prestrained led to quite different morphologies (see Keller and Machin (1967) for an early general review). It was also discovered that crystallisation in sheared solutions generated complicated morphologies (see Keller and Willmouth 1972 for a review). Since then the subject of crystallisation under stress has received considerable attention. The basic morphological characteristics are established. However, a clear understanding of the physics of the process has not emerged. Since the basic morphological features typical of both melt and solution growth are the same the subject will not be sub-sectioned further in this review. A thorough review of this topic cannot be carried out within the confines of this chapter, however a number of useful reviews do already exist and will be mentioned in the text.

The basic morphological feature which has received greatest attention has been the shish-kebab (figure 20). The major difference between a solution-grown crystal and this species is that it is an oriented aggregate. It is generally accepted that this difference is largely the result of a special nucleation process. First a row-nucleus is produced which takes the form of a crystalline fibre having the molecular axis parallel to its long axis. It is recognised that this fibre is produced from the molecules most likely to be oriented by stress i.e. the longest ones. Secondly, single conventionally folded chain crystals nucleate epitaxially on the fibre and grow laterally in a conventional manner. Although in the early investigations it was thought that the row-nucleus might be an extended chain crystal, it is generally recognised that although it does have a considerable extended chain character it does have some internal folding.

In crystallisation from solution it is now established that the generation of the nucleus requires extentional flow conditions. This corresponds to a situation in which the solution undergoes an acceleration, simple shearing being an insufficient condition (for recent reviews of several important aspects see Zwijnenburg *et al* 1978, McHugh 1982, Keller and Odell 1985). In a special experiment Pope and Keller (1978) were able to produce continuous fibres through the generation of this condition. One ingenious use of knowledge of the effect of crystallisation temperature on folded chain lamellar thickness to optimise the modulus of the fibres was to generate interlocking side growths (Odell *et al* 1978, 1984).

Since the production of oriented fibres is an extremely important industrial process, it was only natural that attention would paid to the exploitation of the principles established. Clearly the greatest strength would be produced through the generation of a fully extended chain fibre with no folded appendages. The closest approach to this ideal has used the idea of pulling the fibres from a gel of high molecular weight polymer (see Lemstra *et al* 1987 for a recent review). Under such conditions there is sufficient resistance to the extraction of the molecule from the gel to produce high orientation, but not so much resistance as to prevent effective disentanglement. A new development has been the introduction of crosslinking of the gels prior to drawing (Hikmet *et al* 1987). Gel-spun fibres have moduli comparable to those of carbon fibres and approach the values expected for a carbon–carbon bond. A detailed description of this process, its evolution and optimisation are beyond the scope of this review.

When a film is strained prior to or during crystallisation, the morphology developed depends greatly on the level of orientation developed at the time nucleation occurs. The general governing scheme was developed by Andrews at an early stage, through studies of osmium tetroxide stained *cis*-polyisoprene (see figure 24). At levels of prestrain less than about 100%, oriented sheaves are produced, since the amount of chain orientation is not sufficient to produce macroscopic row-nuclei. The initial stages of nucleation here comprise groups of three to twelve folded chain crystals all growing normal to the direction of the applied strain. There is never any evidence of the presence of a row-nucleus, however, it should be recognised that there may have been a thin metastable nucleus which melted on crystallisation of the folded chain crystals.

For prestrains between 100 and 400% row-nucleated shish-kebabs are formed, the number of such species per unit volume increasing with the level of strain. The thickness

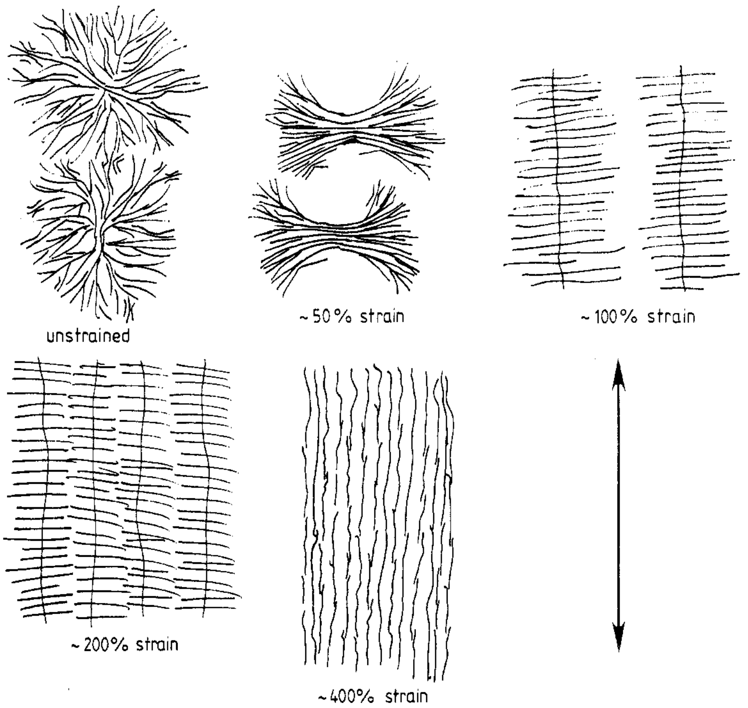

Figure 24. Schematic diagram illustrating the effect of prestrain on nucleation and growth patterns in a high polymer. The arrow represents the direction of applied strain.

of the row-nucleus is below the level of resolution of normal electron microscopes but appears to be 20–40 Å in diameter. When the prestrain approaches 400% only row-nuclei are generated, there being no epitaxial growth of folded chain lamellar appendages. Although this scheme has been known for twenty years there has not yet been any quantification of the nucleation patterns. The crystallisation at 400% strain will be familiar to the reader as the whitening of a natural rubber band when stretched. The study of melt extruded morphologies in polyethylene is more difficult to carry out but has been successfully pursued by Bashir *et al* (1986) using permanganic etching and chlorosulphonation, and also by Adams *et al* (1986) using thin film STEM approaches.

3.7. *Internal mobility of polymer crystals*

It has been recognised for many years that dislocations are present in polymer crystals in large numbers. It has also been recognised from studies of mechanical and dielectric properties (McCrum *et al* 1967) that there is a significant degree of internal motion present in crystals of most polymers. This motion has been most extensively studied in the past through the mechanical and dielectric loss processes that result from its presence. Undoubtedly, the most studied process is the one known as the alpha loss process in polyethylenes (Ashcraft and Boyd 1976, Mansfield and Boyd 1978, Boyd 1984). More recently the use of NMR to study motions in the solid state has led to major advances in our understanding of such features. It is now recognised that there can be present a special type of motion resulting from internal disorder peculiar to long chain molecules.

Condensed states of low molecular weight materials can have restricted degrees of ordering giving rise to mesophase or liquid crystalline states. Alternatively, crystal packing may be achieved, but states may exist in which the molecule can rotate about its axes giving rise to plastic crystals. In long chain molecules there is the possibility of the chain changing its detailed shape or conformation whilst still remaining in crystal register and not rotating. This state has been designated a CONDIS state (i.e. conformationally disordered) and was the subject of a recent review by Wunderlich *et al* (1988). The extent of such behaviour has not yet been established, nor has it been incorporated into theories of secondary nucleation where potential lability of internal crystalline structure could have a major effect on the thermodynamics of the process.

In the past considerable attention has been paid to the likely molecular defects present in a crystal. One of the major problems in handling of dislocations, as normally carried out for FCC metals, for instance calculation of the dislocation energy, lies in the fact that the polyethylene crystal is orthorhombic. Hence it is highly anisotropic and requires the use of anisotropic elasticity theory for explicit solutions (Shadrake and Guiu 1976, 1979). Several approximate models have been proposed. The defects range from the analogues of point defects (Reneker 1962) to dispirations and disclinations (Reneker and Mazur 1988). Much of the work has been aimed at describing the motion of these entities so that activation energies can be generated that are consistent with actual values generated from dielectric studies (Reneker and Mazur 1982, 1985, Ashcraft and Boyd 1976, Mansfield and Boyd 1978). Whereas the Boyd–Mansfield defect appears to give the best fit to experimental data, approaches by Skinner and Woylnes (1980) and Skinner and Park (1984) suggest that a soliton model may also apply. More recently, Zerbi and Longhi (1988) have coined the term twiston to describe the experimentally measurable conformational soliton and have suggested that the term soliton be used for theoretical waves. The major part of the work has been carried out using molecular mechanics approaches which are very slow and use unrealistic amounts of computer time for long chains. Recently, the introduction of molecular dynamics approaches has made it possible for simulations to be carried out on 2000 atom chains in short times and promises to lead to substantial progress in the near future (e.g. Noid *et al* 1988).

Studies of cyclic alkanes having twelve or more carbon atoms in the chain have proved invaluable in the development of understanding disordering transitions in alkane and polyethylene chains. Basically there is a critical temperature at which the ring begins to 'spin' and the carbon atoms begin to interchange. Although infrared and Raman studies have helped in identifying the specific ring conformations, it is magic angle carbon 13 nuclear magnetic resonance that provides the most valuable information (Muller 1985, Muller *et al* 1986, Drottloff *et al* 1987). Essentially, provided the ring is between certain size limits the ringwise reptation mode spinning occurs. However, as the ring becomes larger it begins to approximate polyethylene in that it shows two types of carbon atoms, those in the crystal surface (analogous to folds) and those in the interior. The rotational motion becomes more difficult as this effect occurs, even to the stage where the effect is present only at elevated temperatures, sometimes approaching the melting point. Rotator phase behaviour has been known for many years (Mueller 1932) in n-paraffins, but was never really understood. Ungar (1986) suggested that it was related to the hexagonal phase of polyethylene. It has also been suggested that it is a manifestation of a condis state (Wunderlich and Grebowicz 1984), a view which is essentially identical to that of Ungar.

4. Crystallisation of rigid and semi-rigid polymers

As was mentioned in the previous section, semi-rigid or rigid polymer molecules behave differently from flexible chain molecules. During the past decade or so, considerable attention has been paid to the generation of mesophases in polymers since the relaxation times of liquid crystalline polymers are many times longer than those of molecular liquid crystals, permitting more useful devices to be manufactured. Much of this work has concentrated on designing polymers that would contain mesogens of various types (e.g. see Blumstein 1978, 1985, Ciferri *et al* 1982, White and Onogi 1983 and reviews by Lenz 1985, Jin *et al* 1980, Griffin and Havens 1981, Czer 1979, Wissbrun 1981). Much of the characterisation has utilised differential scanning calorimetry and attention has been paid to the specification of the crystalline structures. Research on detailed morphologies has been relatively scant, partly because the morphologies are difficult to specify and examine. There is a paucity of studies of the kinetics of transformation.

For a listing of the different states identified (largely smectic) the reader is referred to Woodward (1989) where colour photographs are presented permitting the sometimes very subtle differences between states to be identified. For genuine nematic or smectic mesophases many of the morphologies appear to be domain-like structures in which the boundaries are somewhat akin to grain boundaries in metals (e.g. Mackley *et al* 1981, Viney and Windle 1982, Fayolle *et al* 1979, Donald *et al* 1983, Viney *et al* 1985, Noel *et al* 1984, Galli *et al* 1985, Donald and Windle 1984, Mitchell and Windle 1985, Thomas and Wood 1985, Wood and Thomas 1986). As such, it has been necessary to use some of the more subtle approaches of scanning transmission electron microscopy to elucidate features. For specimens solidified under shearing forces, highly oriented fibrillar morphologies are generated, as might be expected for what are essentially linear rigid molecules. Some preliminary studies of the rates of transformation have been carried out for a liquid crystalline polyphosphazene by Kojima and Magill (1985, 1986). Also, some data have been reported by Bhattacharya *et al* (1986) and by Sauer *et al* (1987).

One of the more confusing aspects of the study of what are generally referred to as liquid crystalline polymers arises from the fact that many of these materials are copolymers or terpolymers having no well defined sequential molecular arrangements. If flexible polymers were made in such a way, they simply would be fully amorphous. However, in the case of these semi-rigid systems, partially ordered structures are possible because of the rigidity of the chain (Gutierrez and Blackwell 1984, Blackwell *et al* 1988). If regarded as being similar to a bunch of twigs then it can be seen why some sort of partially ordered structure is possible. Unfortunately, one of the most studied systems (manufactured by Tennessee Eastman) has proved to be more akin to a block-like copolymer having two phases—one nematic and the other being conventional poly(ethylene terephthalate). On the other hand, however, a perfect rigid homopolymer such as polybenzobisthiazole (e.g. Hwang *et al* 1983, Helminiak and Evers 1983), has no known solvent and cannot be melt crystallised. So basic studies of morphology and solidification kinetics cannot be pursued. Some morphological features of the rigid polymer, poly(p-phenylene) have been reported recently (Boudet and Pradere 1984).

Perhaps the most important reason for the study of semi-rigid and rigid polymers is the possibility of producing systems with very high moduli that remain effective at elevated temperatures. It has been recognised from the onset of research in this area that these polymers are easily oriented and much has been written on the achievement of orientation (see earlier citations, especially Wissbrun). The general features of the morphology of fibres produced from liquid crystalline polymers were recently described by two different groups of researchers (Sawyer and Jaffe 1986, Weng *et al* 1986). Essentially, the characteristic feature is a fibrillated morphology that varies somewhat from the surface to the centre of a specimen as might be expected.

One of the reasons for so much interest in liquid crystalline polymers lies in their potential electrical properties, which may be controlled through the use of an electric field during solidification. Recent studies by Stupp and Martin (1985) and by Martin and Stupp (1987) have shown that the orientation of molecules within films can indeed be enhanced by such an approach. They also showed that topology of the confining walls has a significant effect on orientation as also does later annealing.

The best known liquid crystalline polymer is poly(phenylene terephthalamide) or Kevlar, which has considerable use as a fibre (Dobbs *et al* 1977, Warner 1983). At first it was thought that hydrogen bonding between chains played a major part in determining its crystal packing, however, it is now clear that the benzene rings comprising its backbone determine the lateral packing and that to a first approximation secondary bonding considerations can be ignored. This assumption has led to many computer simulations of potential polymers and attempts to predict their transitions and properties prior to manufacture. In other words, the possibility of designing polymers to have specific high-temperature mechanical properties is now being explored. The major problem, of course, is one of generating appropriate methods of synthesis.

5. Concluding remarks

It will be clear to the reader that progress over the past twenty years in this field has been major. Some of the thorniest problems are approaching resolution. Additionally, the development of new investigative techniques and the enhancement of older ones has led to considerable advances in the type and quality of information obtained. The relevance of much of the new data being provided by time-resolved spectroscopic techniques is not yet realised by many of us. Insofar as much of this type of material has not been incorporated into this review, the author apologises and wishes it were otherwise. Many aspects of the crystalline state of macromolecules, such as the electrical properties, could only be mentioned in passing due to the shortness of the review. Despite the progress made recently, including the elimination of some old and dear concepts, there is still a long way to go in understanding even the most elementary concepts of this subject.

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