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The Texture of Crystalline Polymers: A Brief Review*

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This review of polymer texture subdivides the discussion under chainfolding and then morphology. Subsidiary headings include lamellar thickening, theories of crystallisation, solution as well as melt grown materials and fold surface structure. It closes with consideration of extended chain polymers produced by crystallization either at high pressures or under conditions of flow or stress.

1. Introduction

The properties of polymeric materials and the crystallisation behaviour of polymers are intimately linked with the long chain structure of polymer molecules. Linear molecules consist of large numbers of chemical units, called monomers, joined end to end by covalent bonding. Thus these may be pictured as a chain of atoms (the backbone) with atoms or molecules of various kinds (side groups) attached along it. Molecular lengths vary greatly, being typically 10^3 to 10^5 Å in synthetic polymers while much larger in complex biopolymers. Polymer samples always contain some distribution of chain lengths and thus the molecular weight of a polymer is an average of the molecular weights of all the polymer chains. The number average and weight average molecular weights, $\overline{\mathrm{M}}\mathrm{n}$ and $\overline{\mathrm{M}}\mathrm{w}$ respectively, are commonly used in polymer characterisation. The distribution of molecular lengths, i.e. the polydispersity, is an important characteristic and its relevance to crystallisation and melting behaviour is being increasingly appreciated.

The crystallisation of polymers into an ordered array and the formation of a crystalline lattice requires long molecules to pack neatly together. To achieve this, uniformity of molecules is essential. Thus the nature of the side groups, their stereoregularity along the backbone, and chain branches all affect crystallisation behaviour. As an extreme example, atactic polymers, which have an irregular spatial structure along the molecular chain, are generally unable to crystallise. In contrast, tactic polymers, those with a stereoregular arrangment of side groups, are generally able to form a crystalline lattice since molecular uniformity makes close packing and accommodation of the side groups possible. In view of such considerations, because of its chemical and structural simplicity along with its economic importance, linear polyethylene has been primarily used as a model in polymer crystallisation studies.

The polyethylene molecule may be pictured as a covalently bonded carbon chain, with the angle between successive bonds slightly less than the tetrahedral angle, and hydrogen atoms bonded tetrahedrally to each carbon atom. At sufficiently long chain lengths, other chemical groups at the chain ends may be ignored for the majority of polymer behaviour. Within the polyethylene crystal the molecules form an orthorhomic cell with the *c*-axis in the chain direction and with the molecules in a planar zig-zag conformation [1].

The study of polymer crystallisation has continually been hindered by the inability to observe the structural units of crystalline polymers. However, even before the long chain nature of polymer molecules was recognised, X-ray diffraction of bulk polymers revealed the presence of crystalline units. From the broadening of the diffraction maxima, the crystallite size was estimated to be no more than a few hundred angstroms. In addition, the presence of disordered or amorphous regions could be inferred from the diffuse scatter, while density and heats of fusion measurements gave variable values less than expected from 100% crystalline material. The recognition of the long chain structure of polymer molecules led to a two phase or fringed micelle model of bulk polymers [2]. The structure

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of semi-crystalline bulk polymers was visualised as being composed of crystallites, formed by the alignment of neighbouring chains, embedded in a matrix of amorphous polymer. This amorphous material was composed of entangled molecules threading their way from one crystallite to another and chain ends. Such a mode was partially successful in accounting for polymer behaviour. It was applied to thermodynamic analysis [3] and achieved success in accounting qualitatively for the physical properties of polymers. For instance, the viscoelastic and swelling behaviour could be attributed to the amorphous regions, while the crystallites accounted for the X-ray diffraction patterns, low extensibility and mechanical strength. As the finer morphological features of polymers have become evident, however, the fringed micelle has been shown to be increasingly inadequate. In recent years the concepts of polymer morphology have drastically changed and it is now considered that the basic structural unit of both melt and solution crystallised polymer is the thin lamellar crystal in which the molecules are in a chainfolded configuration.

2. The Concept of Chainfolding in Polymer Crystals

The turning point in the comprehension of polymer crystallisation and polymer morphology stems from the growth of observable crystals of linear polyethylene from dilute solution [4-7]. The earlier work of Storks [8] and that of Schlesinger and Leeper [9] on *trans*-polyisoprene (gutta-percha) had indicated the possibility of obtaining polymer crystals from solution and Storks had surmised that the polymer molecules might fold back upon themselves through the crystallites. At the time these reports did not attract much attention but their significance to polymer crystallisation has now become apparent. Jaccodine, using linear polyethylene, reported the growth of observable rhombus shaped and multilayered lamellar crystal growth spirals from dilute xylene and benzene solution in 1955. However, the molecular orientation within the crystals was not determined. The growth of isolated lamellar crystals of linear polyethylene was independently reported by Till, Keller and Fischer in 1957 [5-7]. Subsequently practically all polymers that have been crystallised from solution have been shown to be able to form thin lamellar crystals, typically 100 Å thick. Examples of lamellar crystals of polyethylene grown from dilute xylene solution are shown in fig.1, while many other examples may be seen in the book by Geil [10].

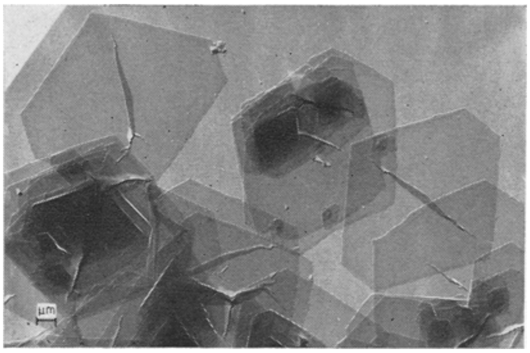

Figure 1 Polyethylene crystals grown from dilute solution in xylene.

The general acceptance of chainfolding during polymer crystallisation originates from the observations on solution grown polyethylene lamellae [6] and subsequently chainfolded growth has been established as a basic and general mechanism of polymer crystallisation, excluding special cases like crystallisation under high pressures, flow or stress. Chainfolding has even been demonstrated in solution grown crystals of complex biopolymers such as D.N.A. [11] and polypeptides [12]. The lamellar thickness of solution grown polymer crystals is typically 100 to 200 Å and the chains are oriented transversely to the lamellar surface. Thus since the chains are much longer than the lamellar thickness, they must fold through 180° at the lamellar surfaces. A simple schematic representation of chainfolding in a polymer lamella is shown by the edge on view in fig. 2.

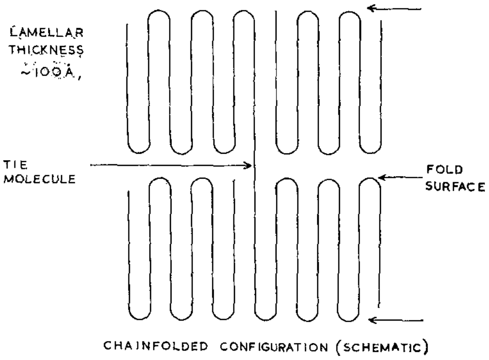

Figure 2 Schematic illustration of chainfolding and related terms (not to scale).

Here the folds are drawn sharp and regular and the fold length uniform. However, this is not necessarily the case as will be discussed later. The straight and aligned chain segments form the orthorhombic lattice, which may be investigated by X-ray and electron diffraction techniques. In polyethylene diamond shaped lamellae (such as shown in fig. 1 but without the truncating faces), the *a* and *b*-axes are in the direction of the long and short diagonals respectively [6].

Chainfolding may be readily deduced in solution grown polymer crystals, but in melt crystallised polymers, because of the inaccessibility of the crystalline units, it is not so readily confirmed. However, it has been shown that the lamellar nature of polymer crystals is not confined to solution crystallisation, but that it is also characteristic of melt crystallised polymer. There are certain differences between melt and solution grown lamellae that will become apparent later but, nevertheless, there is a wide variety of evidence and many similarities between melt and solution crystallisation which confirm chainfolding in melt crystallised polymers.

In an assembly of chainfolded lamellae, such as may be obtained by sedimenting solution grown crystals flat on top of each other, there are periodic fluctuations in electron density associated with the difference in molecular packing at the crystal interior and at the fold surfaces. This gives rise to low angle reflections in X-ray diffraction patterns and in solution grown crystal aggregates the spacings have been related to the crystal thickness, which may be measured separately via the electron microscope [13]. In bulk polymers the interpretation of low angle X-ray diffraction patterns can be a great deal more complicated but still involves lamellar units [14]. Even in the simplest cases there are often two reflections whose spacings are not simply related via Bragg's Law, as would be expected if they were successive orders of the same periodicity [15]. This problem is also demonstrated by the increase in the smaller spacing during isothermal crystallisation while the larger remains constant [17]. At present the origin of these spacings has not been resolved, with some observations indicating that the smaller spacing is appropriate to the lamellar thickness [17], while others have shown correlation with the larger spacing [18, 19]. It has also been suggested that the two spacings originate from distinct crystal morphologies within the bulk polymer [20].

2.1. Variation of Fold Length with Crystallisation Temperature

Any theoretical treatment of polymer crystallisation must not only provide an explanation for chainfolding but must also account for two other major features of polymer crystal growth. One of these is the dependence of fold length upon the crystallisation temperature. Thus the fold length and correspondingly the crystal thickness of polymer crystals, both from solution and melt crystallisation, becomes larger as the crystallisation temperature is increased. This was first observed by low angle X-ray diffraction of solution grown polyethylene crystals [13] and has been demonstrated in bulk polymers both by small angle X-ray diffraction [21] and by electron microscope measurements [17]. In solution crystallisation the effect of crystallisation temperature is readily illustrated by changing its value during growth.The resulting lamellar crystals then contain concentric steps due to changes in crystal thickness [22]. In simpler cases where two thicknesses result, two corresponding sets of low angle spacings are obtained [23]. Using solvents of different solvent power Kawai and Keller [24] have shown that the fold length is not determined by the absolute crystallisation temperature, but that it is in fact dependent upon the degree of supercooling and that it increases for lower supercoolings. A similar conclusion is reached from high pressure studies [25]. The supercooling ΔT, is defined by the equilibrium melting or dissolution temperature, $T_m{}^\circ$ or $T_d{}^\circ$ respectively, minus the crystallisation temperature. This dependence upon the supercooling rather than the absolute crystallisation temperature has important implications for the crystallisation theories as will be discussed later.

The effect of molecular weight on the fold period has been investigated in the case of solution grown polyethylene crystals and found to have a negligible effect [23, 26]. Mandelkern, Fatou and Ohno [27] have reported the effect of molecular weight on the crystallisation rate and concluded that at constant temperature there is a maximum crystallisation rate for a particular molecular weight. Higher and lower molecular weights crystallise more slowly. Similarly, Kawai and Keller [28] have reported the later crystallisation of high molecular weight polyethylene at the edges of solution grown crystals. With low molecular weight polymers, or oligomers, the effect of molecular weight on the fold length is complex and is associated with problems of incorporating chain ends within the crystal lattice. Thus it has been reported that in oligomeric amides and poly(ethylene oxide)s the fold period remains constant above a certain molecular weight [29]. This indicates that chainfolding and incorporation of chain ends within the lattice occurs above a certain molecular length. However, other results on the annealing and crystallisation of low molecular weight poly(ethylene oxide), which have shown integral changes in crystal thickness [30, 31], suggest that the chain ends are at the crystal surface. Further evidence for the exclusion of chain ends from the crystal interior in high molecular weight polyethylene has also been reported from infra-red studies [32]. A solution to this problem, whereby the chain ends of long molecules are likely to be excluded from the lattice and the incorporation of chain ends of short molecules within the crystal is largely determined by the nature of the end group, has been suggested [33].

2.2. Lamellar Thickening

A second and unique property of chainfolded polymer crystals is their ability to increase in thickness and thus fold length when heated above their initial crystallisation temperature. This process is variously called lamellar, solid state or isothermal thickening and in general terms, although much of the lamellar thickening mechanism is not understood, may be considered as a move towards the lowest free energy state of the crystal. Thus by reducing the number of folds and their associated energy, the crystal approaches its optimum state in which the molecules are not folded at all but are in a fully-extended-chain configuration. Under normal circumstances, however, lamellar thickening does not progress to this stage. Solution grown crystals, particularly those of polyethylene, have provided the best opportunities for studying the lamellar thickening process. In the more difficult case of bulk polymers the same fundamental process of lamellar thickening is indicated by comparison with the behaviour of solution grown lamellae. Thus low angle spacings increase in a similar way and a similar dependence of density during annealing is found in bulk and solution grown crystals [34].

The general features of lamellar thickening have been adequately established and various explanations for the phenomena exist. On heating chainfolded crystals at temperatures above their initial crystallisation temperature there is an abrupt irreversible increase in fold length which is associated with a refolding of the molecules [35]. In polyethylene, for example, lamellar thickening typically occurs in the temperature range of 100 to 130°C. At low annealing temperatures an increased tilt of the molecules within certain solution grown polyethylene lamellae and at high annealing temperatures a rotation of the molecules around a particular crystallographic axis has been reported [36]. Apart from these effects the molecular orientation during refolding is maintained. This has been particularly evident in annealed isolated lamellae which develop numerous holes surrounded by thickened regions. The orientation of the *a*, *b* and *c*-axes in these thickened islands is identical and the same as that of the original lamella [35]. The increase in lamellar thickness is larger for higher annealing temperatures and after the initial abrupt increase there is a further slower increase which is proportional to the logarithm of time. This is faster for higher annealing temperatures, but at long times the rate decreases and thickening becomes a slow process. The initial increase in fold length is not amenable to investigation at the lower annealing temperatures, but at higher temperatures X-ray diffraction, density and birefringence measurements show a temporary partial loss of crystalline order during the initial increase in fold length [34]. This is suggestive of some form of melting accompanying the refolding process and it has been suggested that lamellar thickening is merely melting of part of a crystal followed by crystallisation to a larger fold length [38]. Certainly a high degree of chain mobility is required for refolding, however annealing and crystallisation give different results and a variety of evidence suggests that a completely molten phase is not formed during annealing. The term partial melting is often applied to describe the intermediate state. This sometimes means partly molten and sometimes, more correctly, that not all configurational entropies of the melt are adopted Maintained molecular orientation during thickening is often used as evidence against complete melting and Keller [39] cites the particular case of annealed individual lamellae as showing that there has been no full melting of any portion of the crystal. Peterlin [40] uses the fact that the fold length increases uniformly to indicate the same conclusion. Further evidence against complete melting is that the product of annealing depends upon the initial crystal form, i.e. thinner crystals thicken at lower temperatures and reach high fold lengths first [37, 41]. Bair, Salovey and Huseby [42] have concluded that lamellae may thicken without melting, although at high enough temperatures and if allowed enough time, melting and crystallisation may occur.

At molecular level, thickening has generally been envisaged as the formation of a thickening nucleus on the crystal surface and the translation of molecules through the lattice. Reneker [43] has suggested that the molecular translation is by the formation of jogs in the polymer chains. These move along the chains thus translating the whole molecule. Peterlin [44] calculated that such a mechanism would not have the required temperature dependence and proposed the simultaneous displacement of whole chain segments. After incorporating a nucleation term for the additional volume at the crystal surface due to thickening [45], Peterlin obtained an expression with the required logarithmic increase of fold length and temperature dependence of thickening. These models would be expected to be sensitive to molecular length because molecules have to thread through the lattice and Peterlin predicted a rapidly increasing thickening rate for decreasing chain length [46]. However, although shorter chains have been shown to thicken faster the dependence is far less than expected [47]. Furthermore, Keller and Priest [48] concluded that during the annealing of polyethylene lamellae the proportion of chain ends drawn through the lattice is small. Recently, Dreyfus and Keller [49] have proposed that whole molecular loops may refold as a unit; this mechanism would explain their experimental observations of the doubling in the fold period of nylon lamellar crystals. To account for cases where doubling is not observed it is suggested that this mechanism is only applicable when energetically favourable.

Related to the increase in fold length on annealing is the increase in fold length during isothermal crystallisation of polyethylene from the melt [16, 50, 51]; a phenomenon which has important implications for the kinetic theories of chainfolding. By thermodynamic argument the melting point of a chainfolded crystal may be related to its fold length [52], which in conjunction with the predictions of the kinetic theories of chainfolding, leads to the conclusion that polymer crystals should melt near their original crystallisation temperature. Melt crystallised polyethylene, however, generally melts about half way between the crystallisation temperature and its equilibrium melting point [53, 54]. This led to the prediction that the crystals thicken while stored at the crystallisation temperature. Hoffman and Weeks [16] reported the first direct observation of this phenomenon by monitoring the increase in low angle X-ray spacing of polyethylene with crystallisation time, while held at the crystallisation temperature. The interpretation of the low angle X-ray spacings, however, is complicated since of the two observed reflections only the smaller spacing, which Hoffman and Weeks attribute to the fold length, increased with time. Kawai [51] proposed that the long spacing increase was due to fractional crystallisation effects and suggested that the lower molecular weight polymer crystallised later and thus, since this was at a lower supercooling, crystallised to higher fold lengths. Kawai, in contrast to Hoffman and Weeks, obtained less increase in the low angle spacing using fractionated polymer. Hoffman and Weeks, however, obtained no decrease in thickening rate on increasing the temperature to where crystallisation is very slow and concluded that this precludes fractional crystallisation effects. Peterlin [40] has reported that thickening at the crystallisation temperature satisfactorily accounts for the secondary crystallisation effects observed in melt crystallisation.

At atmospheric pressure, therefore, isothermal thickening during melt crystallisation still requires clarification and as mentioned previously has particular relevance to the applicability of the kinetic theories of polymer crystallisation. In solution growth there is no evidence for an appreciable increase in fold length at the crystallisation temperature, either with whole or fractionated polymer [26]. The authors explain the absence of thickening by there being insufficient chain mobility at the lower temperatures required for solution crystallisation.

2.3. Theories of Polymer Crystallisation

Polymer crystal growth, similar to crystal growth in general, may be divided into two stages. Firstly, primary nucleation, i.e. the formation of a stable nucleus whose probability of growth is greater than that of melting or dissolution, and secondly, secondary nucleation and growth upon the primary nucleus. Since the thickness of polymer crystals may be altered by altering the crystallisation temperature [22, 23], it is secondary nucleation processes that determine the fold length. Theories of polymer crystal growth may be divided into two groups, namely the equilibrium and kinetic approaches. The equilibrium theories, proposed initially by Peterlin and Fischer [55] and at present only discussed for polyethylene, do not consider nucleation processes nor directly predict chainfolded crystallisation. Instead they calculate the crystal size in the chain direction corresponding to the lowest free energy state. The free energy density of the crystal is calculated in terms of the surface free energy, which favours a large crystal thickness, and the intra and inter chain forces within the lattice which favour a small crystal thickness. As a function of temperature and crystal thickness, the free energy has two minima with respect to fold length over much of the temperature range of interest. These correspond to the equilibrium crystal thickness at that temperature [56]. One minimum is at a finite fold length while the other occurs at infinite length. With higher temperatures the minimum at the finite fold length becomes shallower and moves to larger fold periods. Above a critical crystallisation temperature, ~ 110°C for polyethylene, only the free energy minimum corresponding to an infinite fold period remains. It is above 110°C that polyethylene crystallises from the melt at a finite fold period. Thus, in this region the equilibrium theories of crystallisation are not considered applicable and the growth appears to be governed by kinetic factors, although they could be applied to solution growth at lower temperatures [40]. A result of the single free energy minimum above ~ 110°C, corresponding to a fully-extended-chain configuration, is that the equilibrium theories predict that polyethylene crystals annealed above this temperature would thicken provided there was sufficient mobility. Thus they would offer a qualitative explanation for lamellar thickening.

In contrast, according to the kinetic theories, chainfolded crystals occur because they have the fastest crystallisation rate and not because they correspond to the equilibrium state. It is explicit in the kinetic theories that the equilibrum crystal thickness is always the fully-extended-chain length [57, 58]. Since the fold length alters with crystallisation temperature, it is independent of the crystal thickness upon which growth occurs and consequently the kinetic theories consider the rate of attachment and subsequent chainfolding of an infinite molecular chain upon a crystal substrate. The fold length which nucleates and propagates first as a stable strip has the fastest crystallisation rate and is considered the most probable for the crystallisation conditions. The preference for a particular fold period may be visualised as competition between the rate of formation of the first fold, which favours a shorter fold length, and the propagation of the chainfolded growth strip. The latter consideration leads to a large fold length because of the energy associated with each fold. These kinetic theories also lead to a partial understanding of lamellar thickening during annealing and isothermal crystallisation as a move away from the kinetically determined fold length towards the equilibrium state or fully-extended-chain configuration of molecules in a crystal.

The early kinetic theories considered that after the first fold was deposited, all additional segments in the same fold plane were rapidly laid down at the same fold period [57], but experiment showed that this was not the case [22]. Later theories, the fluctuation theories, considered the more realistic approach of allowing some fluctuations in the fold periods [59, 60, 61]. The most recent treatment by Lauritzen and Passaglia [61] allows successive fold periods to have any value. A standard deviation of 8 to 14 Å in fold surface roughness results, with the roughness increasing at lower crystallisation temperatures. The theories all arrive at essentially the same expression for the fold length, namely:

$$l = \frac{2\sigma_e Tm^\circ}{\Delta H_f \Delta T} + \delta l \qquad (1)$$

where σ_e is the fold surface free energy, Tm° the equilibrium melting point of an infinite crystal of fully-extended-chain molecules, ΔH_f the heat of fusion, ΔT the supercooling and δl an "extra length" term. This expression shows the observed dependence of fold period on the supercooling, while the form of δl varies between the theories. Most recently Lauritzen and Passaglia predict σ_e and δl to be temperature dependent. The correctness of individual theories is judged by comparison with experiment to determine whether suitable values of the parameters in equation 1 can be obtained. However, there is sufficient leeway in the accepted values for all to have some claim to success.

Both the equilibrium and kinetic theories are compatible with most experimental evidence but there is one qualitative difference which distinguishes them. This is the dependence of fold length upon supercooling predicted by the kinetic theories, rather than the absolute crystallisation temperature as anticipated by the equilibrium approach. This prediction of the kinetic theories has experimental justification [62, 24] and it is becoming increasingly apparent that chainfolding is a consequence of kinetic considerations rather than equilibrium factors. This does not exclude the possibility that the most stable crystal is of a finite thickness under certain conditions, but means that this stage is not achieved during crystallisation since the process is governed by kinetic factors [59].

3. The Morphology of Crystalline Polymers

Solution grown polymer crystals are accessible for direct morphological studies and thus optical and electron microscopy, electron and X-ray diffraction have succeeded in providing much information. By comparison, investigating the morphology of semi-crystalline bulk polymers is complicated by the inaccessibility of representative structural units and the difficulties in studying crystalline aggregates that are representative of the interior of bulk polymers. This problem has generally been approached by making morphological studies on surfaces exposed by fracturing or etching, and by the examination of thin sections of bulk polymer and thin melt crystallisation films. Although these methods have been invaluable, they can reveal the crystal structure under somewhat special circumstances. Thus fracture surfaces may be expected to reveal planes of weakness while etching may be selective in revealing certain morphologies. Further, observations of thin films or free surfaces may not be representative of the interior of bulk polymers because of the altered molecular environment. The understanding of bulk polymer morphology has frequently been assisted by analogy with simple solution grown crystals and a logical approach, which has been useful in providing a link between solution and melt crystallisation, has been the crystallisation of polymers from solution of increasing concentration [63, 64]. The dispersion of bulk polymers by nitric acid degradation is also relevant here since it offers the potential of observing the crystalline lamellar structures [65, 66].

3.1. Solution Grown Polymer Crystals

The morphology and growth of polymer crystals from solution is a very wide topic, with the crystal habit and complexity varying from polymer to polymer and upon the crystallisation conditions. The crystallisation of linear polyethylene has been most extensively investigated and is used here to illustrate the basic facts, although experience has indicated that similar behaviour is widespread among polymers. In general terms the effect of higher concentrations, higher molecular weights or lower crystallisation temperatures is to produce more complex crystals [23]. The basic structural unit, however, even in the most complex crystal aggregates is the thin chainfolded lamella, typically 100 to 200 Å thick, although there are likely to be changes in lamellae with the above factors. For instance, polyethylene crystals from dilute xylene solution, ($\sim 0.01\%$), at 80°C are diamond shaped lamellae with the *a* and *b*-axes in the direction of the long and short diagonals respectively, while at temperatures between 80 and 90°C the crystals become truncated (e.g. fig. 1). At lower crystallisation temperatures growth becomes dendritic and crystals develop multilayer overgrowths. The truncating faces are $\{100\}$ faces and their size increases with higher temperatures [23, 24]. Further, in crystals from poor solvents and in melt crystallisation these are the largest faces. The lateral dimensions of the lamellae are typically upwards of a few microns, with any preparation containing crystals of various sizes and complexity. Regulating the nucleation processes by self seeding results in monolayer crystals of essentially the same size and habit [67] and here observations of individual lamellae, which are ideal for morphological studies, are thus manifestly representative of the crystal population. Such crystal preparations have been of use in crystallisation rate investigations [68].

An important feature of polymer crystals is that they are frequently non-planar and adopt the shape of hollow pyramids or related forms. The non-planarity of the crystals, originally inferred by the formation of cracks and pleats formed by sedimentation, has been confirmed by observing such crystals whilst in suspension [69, 70]. The pyramidal shapes are explained in terms of uniform fold lengths and sufficient regularity of the chainfolding sequence.

Polymer crystal growth is envisaged as the deposition of molecules in a chainfolded configuration along the edge of a layer. In diamond shaped polyethylene lamellae these are the {110} faces. This leads to a subdivision of the crystals into distinct sectors or fold domains, each characterised by a ribbon of folded molecules parallel to the lateral or prism faces [13]. Therefore, in polyethylene diamond shaped crystals there are four sectors defined by the orientation of the fold planes in the ⟨110⟩ directions. In truncated diamond shaped crystals the folding is in crystallographically non-equivalent directions in the {100} and {110} sectors, which makes them structurally different and leads to different thermal stabilities [71]. Equivalent sectors, on the other hand, may be distinguished by different slight distortions of the lattice, due to molecular folds which lie in different crystallographic directions in each sector [71-73]. In hollow pyramidal crystals each sector forms one facet and an important feature is that the molecules are inclined to the basal planes, i.e. the sloping sector faces, while they have a common orientation throughout the crystal. In the simplest case of the non-flat-based hollow pyramid of four {110} sectors the molecules are parallel to the pyramid's axis. In some crystals, the inclinations of the molecules to the basal sector faces and indexing of the basal planes has been achieved by electron and X-ray diffraction and dark field optical and electron microscopy [70]. The molecular orientation within the sloping faces has been explained by a successive staggering of chainfolded ribbons away from the prism faces and by a further staggering along the folded ribbons in sectors whose prism faces are oblique [74, 69, 70]. This staggering of the fold segments arises from the packing requirements of the molecular folds and would be destroyed if the fold lengths were not uniform. Thus this fact, and sectorisation itself which indicates a preferred fold direction, is often used as evidence for some degree of regularity in chainfolding and to deny a completely disordered fold surface structure.

In contrast to the comparatively simple polyethylene monolayer crystals, a wide variety of multilayer crystals of varying complexity is obtained from solutions of increasing concentration. One important feature of the multilayer crystals is that the lamellae are frequently splayed apart. Multilayer crystals are commonly associated with spiral growth and small stacks of spiralling lamellae may develop on monolayer crystal faces. The spiralling lamellae are themselves hollow pyramids and therefore unless they are precisely concentric must be splayed apart. Various origins for such growth, involving an exposed wedge shaped portion of the basal lamellae, have been suggested [74, 75]. More complex multilayer crystals may be entirely composed of roughly concentric spiralling and splayed pyramidal lamellae. These structures and more complicated forms with two multilayer pyramidal crystals joined apex to apex have been directly observed by viewing crystals in suspension [76]. Pyramidal habits and the rotation of successive layers have been explained in terms of a smoothing and regularisation of an initially formed rough fold surface. Thus, the pyramidal shape would not be adopted until after a certain amount of crystallisation [69, 70] and in the case of spiralling layers, the development of the first lamellae into a pyramid might cause successive lamellae to wrap around it as they undergo transformation [77].

With more concentrated solutions a two-dimensional sheaving of the lamellae, which results from less regular splaying, is observed and at high enough concentrations ($\sim 0.3\%$) so called axialites are obtained [63]. These are compact multilayer crystals composed of a large number of lamellae which appear hexagonal in shape when viewed from above. Viewed edge on, they have a pronounced sheaf-like appearance and have a strong birefringence pattern which resembles the characteristic "Maltese Cross" extinction pattern of melt crystallised spherulites. Axialites, as their name implies, represent a two-dimensional splaying of lamellae about an axis whereas in the melt crystallised polymer there is complete three-dimensional sheaving. The transition between the two is effected partly by increasing polymer concentration [63], but the nature of the solvent is also important [64]. Multilayer structures termed hedrites, that are apparently related to axialites have been obtained from several polymers by the slow crystallisation of thin molten films (see for examples, Geil [10]). Thus polymer crystals grown from solution may vary from simple lamellar structures to highly complex and multi-layered formations. In some respects these begin to show some of the features associated with melt crystallisation. The more complicated morphology of melt crystallised polymers and melt crystallisation will now be discussed.

3.2. Melt Crystallised Polymers

The crystallisation of polymers from the melt is typified by the growth of spherulites and even when it is possible to quench polymers to a glassy state, crystallisation to spherulites may result on heating above the glass transition temperature [78, 79]. Although the majority of observations have been made on melt crystallised thin films where the spherulites have a two-dimensional structure, these are generally considered applicable to bulk polymer. Polymer spherulites consist of many crystalline units that have grown radially in three dimensions from a central nucleus or area. In many cases the crystallites appear to be ribbon-like lamellae or fibrils, with widths in the order of 1 μm and thicknesses of 100 to 500 Å. For example, the lamellar structure of polyethylene spherulites in a thin film is illustrated by the surface replica in fig. 3.

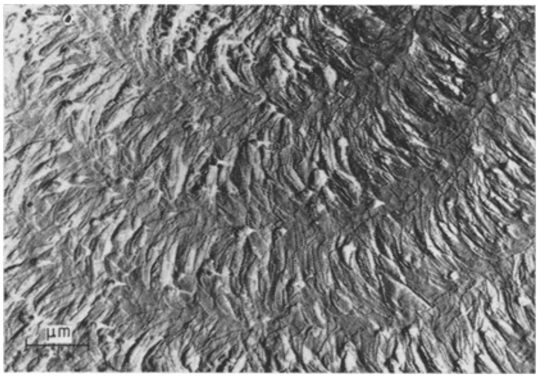

Figure 3 Replica of a free surface revealing lamellae in a "ring" spherulite of polyethylene. Courtesy of D. R. Carder.

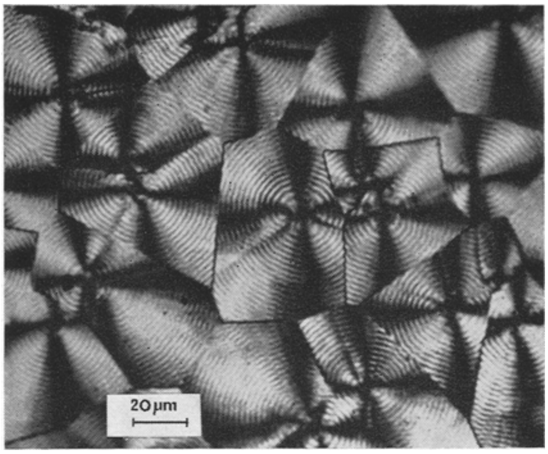

Figure 4 Spherulites in polyethylene photographed between crossed polars showing characteristic extinction effects.

Correspondingly, the dispersion of bulk polyethylene by nitric acid degradation has resulted in lamellar debris [66]. In other spherulites the fibrils may resemble fine threads, with widths approximately the same as their thickness [80].

The crystallographic orientation of fibrils in the radial direction is identical throughout the spherulites and in samples of high ring spacing may be determined by micro X-ray diffraction [81]. In polyethylene, for instance, the *b*-axis is radial and parallel to the fibril axis while the *a* and *c*-axes are tangential [82, 83]. Similarly, in all other polymer spherulites studied to date the chains have been found to be approximately tangential to the radial direction. Chainfolding in melt crystallised lamellae is a logical conclusion from the molecular and lamellar orientations and from analogy with solution crystallisation. During melt crystallisation and similar to crystallisation from concentrated solution, it is possible for molecules to be incorporated into more than one layer [63, 84]. These so called tie molecules bind lamellae together and contribute greatly to the mechanical properties and ductility of bulk polymers.

In the polarising microscope spherulites have a characteristic Maltese Cross extinction pattern, with extinction occurring along radii parallel to the arms of the polariser and analyser. In addition, many polymers also have a concentric ring extinction pattern which is associated with a co-operative twisting of the lamellae (see figs. 3, 4). Under isothermal crystallisation conditions the pitch of the twist is constant though increasing with temperature and is in phase in adjacent regions. Extinction occurs when an optic axis is parallel to the viewing direction and complete optical description of the various extinction features found in spherulites has been made [85-87]. Twisting is also revealed by micrographs such as shown in fig. 3 and twisted lamellar debris has been obtained from dispersed bulk polyethylene [66]. At present, however, the origin of the twisting in the radial fibrils has not been adequately explained.

In the early stages of spherulitic crystallisation a sheaf of fibrillar crystals is often formed, which, by progressive branching of the fibrillar units, develops within a spherical envelope. Continued radial growth along with continued low angle branching, which in general need not be crystallographic is a sufficient mechanism for this feature. Thus a theory of spherulitic crystallisation of polymers must primarily explain the formation of fibre-like crystals and their branching. Keith [64, 75] has investigated the change in crystal habit of polyethylene crystallised from paraffin solutions where, because of the similar chemical structure, the environment of a polyethylene molecule is considered to approach that of the pure polyethylene melt. Changes in crystal habit, from monolayers elongated in the *b*-axis direction to spherulites with ribbon-like lamellae, were obtained. Keith and Padden [86] studied the effect of impurities on the spherulitic crystallisation of several polymers and found that the impurities profoundly affect the spherulite texture. These researches have led to the suggestion of a means of fibrillation during polymer crystallisation based upon the diffusion of impurities in the melt and the segregation of poorly crystallisable material which successfully accounts for a wide range of observations [89, 90]. Briefly, the crystallisation process is considered to be governed by local diffusion in the proximity of the growth face around which there is "non-crystallisable" material such as impurities proper, branched or low molecular weight polymer. Under these conditions the growth face becomes unstable and a cellular growth front with tips of finite size, advancing into the purer melt and rejecting impurities at its sides, is favoured. This process is similar to the cellular crystallisation of metals from impure melts. Here the crystals become broken into parallel cells elongated in the growth direction [91]. The growth of polymer fibrils is controlled by the diffusion of impurities from the growth face and the width of the growth cell is approximately given by $\delta = D/G$, where D is the diffusion coefficient of impurity in the melt and G is the rate at which growing face advances. Thus this approach leads to an explanation for fibrillation during melt crystallisation and on the basis of this theory, a plausible description of low angle branching of the fibrils has also been given.

3.3. The Structure of the Fold Surface

The fold surface structure of polymer lamellar crystals is not directly described by the theories of chainfolding. The equilibrium theories predict only a finite crystal thickness in the chain direction and chainfolding is one way of achieving this. The kinetic theories, on the other hand, assume chainfolding to proceed to the next adjacent site. They may, however, allow for some roughness in the fold surface by introducing fluctuations in the fold length [59, 60, 61]. The nature of the fold surface has not been entirely resolved and experimental evidence indicates two conflicting characters of fold surface structure. A variety of measurements indicates a large amount of disorder and accordingly it is often pictured as an amorphous layer, while morphological observations in particular require a certain regularity at the fold surface. The evidence for order and disorder at the fold surface and the applicability of several models have been discussed in two recent reviews [39, 92].

Polyethylene solution grown lamellae have been used in the majority of investigations and have provided most information about the fold surface structure. Measurements of heats of fusion [93-95] and of density [96-98], along with nuclear magnetic resonance and X-ray investigations [99] all indicate the presence of appreciable disorder within chainfolded lamellae. Density measurements provide the most direct measurement of crystallinity although the reliability of different methods may be disputed. The crystallographic density of polyethylene calculated from unit cell dimensions is 1.000 gm/cc [1] and thus density values less than this indicate either amorphous material or defects within the crystalline lattice. Crystallographic densities have been reported for solution grown polyethylene crystals [100], however most determinations have resulted in lower values of $\sim$ 0.97 to 0.98 gm/cc. The above techniques typically reveal a crystallinity deficiency in the order of 10 to 20%, but do not provide any information about the nature of the amorphous polymer. The continuity of Moiré patterns from superposed monolayers, however, indicates that there is not a large amount of disorder within the lattice itself [96] and there is evidence that chain ends are for the most part excluded from the crystal interior [32]. The majority of the disorder is therefore generally considered to be associated with the fold surfaces. That chemical reactions tend to be confined to these surfaces [101] may be regarded as confirmation of this. A particular case is the relative ease with which the chains may be cut at the fold surface by fuming nitric acid in comparison to the crystal interior [102, 103]. In addition from density and long period measurements of annealed polyethylene crystal mats, it has been concluded that there is a crystallinity deficient layer between the crystalline lamellar cores and that this has a density equivalent to that of an amorphous phase [34, 104].

In contrast, sectorisation and pyramidal habits of polymer crystals clearly require some regularity in fold structure as discussed in section 3.1. Additionally direct evidence for crystallographic order of the folds and a regular fold structure is provided by electron diffraction observations [73] including dislocations at the interface of two superposed but misaligned lamellae [72, 105, 106]. These are interpreted in terms of crystallographic regularity at the fold surface, which will allow in particular circumstances two adjacent fold surfaces to pack together in a crystallographically regular manner with dislocations accommodating slight relative misorientation. Williams *et al* [107] have further indicated the presence of sharp and adjacently re-entrant folds by showing that the molecular weights of polymer obtained from degraded polyethylene crystals correspond to one or two traverses of the lamellae. The possibility of additional looser folds and chain ends at the fold surface, however, was not excluded.

Models for the fold surface structure include the "random switchboard", whereby molecules travel randomly across the fold surface before re-entering the crystal lattice [108]. Following suggestions that the molecular folds were large, loose and irregular the molecular conformation of the chain fold has been treated theoretically [109-113]. Experimental evidence for such a chainfold structure is associated with the phenomenon of interfacial premelting, whereby melting commences at the fold surface and proceeds into the crystal interior at higher temperatures. At present, however, this process is still the topic of debate [114]. Kawai [115] has suggested that the fold surface consists predominantly of uniform and regular folds in adjacent re-entrant positions, which accounts for the observed surface regularity, while a certain amount of disorder is provided by some larger folds and chain ends. The last proposal to be mentioned here is due to Blackadder and Roberts [116], who suggested that experimental evidence is compatible with a uniform fold length and structurally regular re-entrant folds of low density. The surplus volume of the fold surface was accommodated by their being a sloping interface between the crystalline core and fold surface regions, following an earlier suggestion by Frank [117].

3.4. Extended-chain Crystals

In the previous sections the essential features of chainfolded polymer crystallisation have been presented. However, in contrast to these thin lamellar crystals and under special conditions, so called extended-chain crystals which contain few or no chainfolds may be produced. In the following discussion the term fully-extended-chain crystal is reserved for cases where the molecules contain no folds at all and thus the crystal thickness in the chain direction is equivalent to the molecular length. The conditions under which the chain extension of polymer molecules may be increased are of interest not only in providing information about polymeric crystallisation in general and the role of such factors as extended-chain interlamellar connections in particular, but also because so many of the familiar properties of plastics – density, melting point, stiffness (Young's modulus), ductility etc. depend on chainfolding that when there are fewer folds one expects to, and does, find them altered. A suitable fully-extended-chain sample would be significantly changed from normal material. Particularly intriguing is the prospect of attaining in such a crystal the Young's modulus of the covalent carbon–carbon bond (which is a little larger than that of steel) [118]. The intervention of weakly bonded chainfolded surfaces reduces the actual value attained by one or, more usually, two orders of magnitude.

The most studied ways of achieving high molecular extension are crystallisation under conditions of flow and/or stress, which is a general means, and crystallisation from the melt at high pressures, a process apparently peculiar to polyethylene.

3.4.1. Crystallisation under conditions of flow or stress

There is a characteristic morphology associated with polymer crystallised under flow or stress, a condition frequently met, for example, in commercial fibre production, but which has only relatively recently been recognised for what it is. Fig. 5 shows a parallel array of such entities which consist of a central filament overgrown with transverse platelets sharing the same molecular orientation. This appearance is succinctly described by the name "shish-kebab" which is nowadays given to them.

Following the preparation of "shish-kebabs" in model systems [84, 119, 120] and their study notably by nitric acid degradation and gel

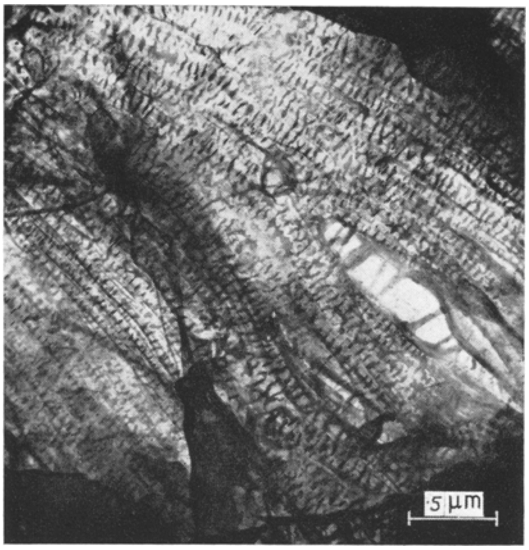

Figure 5 "Shish-kebab" morphology in polyethylene.

permeation chromatography [121, 122] the nature of their morphology has become evident. Broadly speaking, the central thread contains a proportion of relatively highly extended molecules while the lateral platelets are chainfolded. The chain extension and orientation are a function of environmental conditions. They may be imposed by applied tensile stress, which is taken up [121, 123], or molecules may be elongated hydrodynamically. Once a thread has formed then it is obviously capable of nucleating transverse lamellae and at temperatures higher than they would otherwise have formed. In consequence, only a small proportion (a few per cent or less) of a sample may possess the higher chain extensions which played a vital part in its formation.

Of the systems showing "shish-kebab" morphology which have been studied one may, perhaps, single out the crystallisation of rubber [123] and of polyethylene [121] under tension and also the precipitation of polyethylene from stirred solutions. In the last example, the important point has been demonstrated that it is not sufficient merely to elongate molecules, but that conditions of flow must also be such as to keep adjacent ones in register long enough to crystallise [120]. Moreover, the elongation of longer molecules occurs more readily, allowing the technique of stirring to be used successfully as the basis of a novel method of molecular fractionation [119, 124].

Flow-induced crystallisation from the melt is also known. Fast extrusion of molten polymer gives rise to anomalies in viscosity which can occur tens of degrees above the extended-chain melting point. At temperatures below it, however, the same phenomenon can involve polymer solidifying spontaneously in the die giving a product which is highly oriented and has marked chain extension [125, 126].

3.4.2. High pressure crystallisation

The experimental evidence for chainfolding depends upon lamellae being much thinner than molecules are long, but not all crystals satisfy this condition. Anderson [127], studying melt crystallisation of low molecular weight polyethylene at long times and low supercoolings, found three types of layer, one of which had a thickness close to the molecular length. Shortly afterwards, examination of commercial polymer crystallised at pressures above 4 kbar revealed crystals as thick as 3 μm [128], which is in the range expected for fully-extended-chain crystals. These samples show a characteristically striated morphology, as in fig. 6, the striations lying parallel to *c*. In this form, melting points have been raised some 10 to ~ 140°C at 1 bar and densities are 0.99 or more. Moreover, the polymer has become brittle, as befits paraffinic lamellae. Consequently, to serve as a distinction from chainfolded lamellae, the term extended chain crystals has come into general use as a description.

These early observations were interpreted on an either or basis. Lamellae contained molecules

Figure 6 "Extended-chain" lamellae formed by crystallising a fractionated polyethylene ($\bar{M}_n$ = 50,100 $\bar{M}w/\bar{M}n$ = 1.14) from the melt at 4.9 kbar.

which were either chainfolded many times or fully extended. This concept was also in accord with prevailing ideas on the relation of chainfolded to bundlelike nucleation [129]. An alternative explanation was discussed by Peterlin [44, 46] who generalised the logarithmic increase of thickness observed on annealing lamellae at 1 bar and envisaged extended chain lamellae forming by continuous thickening of chainfolded ones.

Of late, experimental evidence has been brought to bear on this point, but the topic remains somewhat controversial. Wunderlich and Melillo [130], investigating the detailed morphology of extended-chain material, observed that spherulitic lamellae increased in thickness as they grew outwards and that despite the large crystal sizes, these were still shorter than the longer molecules present. These findings evolved into a suggestion [131, 132] that extended chain crystals formed at 5 kbar are a result of nucleation at ~ 1000 Å followed by reorganisation to a higher fold length. Molecules shorter than 1000 Å formed fully-extended-chain lamellae, while longer ones gave a range of configurations which included some chainfolding [133].

Rees and Bassett discovered that by annealing 100 Å thick lamellae at between 5 and 10 kbar pressure, it was possible to convert them continuously, with maintained molecular orientation, to high melting layers some thousands of Å thick [134, 135]. Fig. 7 shows the oriented product of such treatment. Much higher thicknesses can be reached at high pressure than is possible at comparable times at low pressure, although at lower annealing temperatures there is little difference between low and high pressure performance [136].

Having shown that chainfolded lamellae could be thickened into the extended-chain region, these authors then searched for direct evidence of thickening during crystallisation from the melt. Using fractionated polymer, it was found that the "extended-chain" thickness was not unique but increased with temperature and time, thereby showing the same trends of behaviour as chainfolded lamellae at 1 bar [41]. This is also in agreement, as far as temperature is concerned, with early work on polytetrafluoroethylene [137]. The large size is established very rapidly, apparently after the passage of a thin growth edge, 1000 Å or less thick.

Latest results [138] support the analogy between melt crystallisation at 1 bar and 5 kbar. In both cases there is a continuous spectrum of thicknesses and their detailed temperature dependence is the same. The apparent dichotomy between chainfolded and extended-chain lamellae thus seems not to exist. Instead, there is the welcome prospect of being able to unify what had been regarded as diverse crystallisation behaviours.

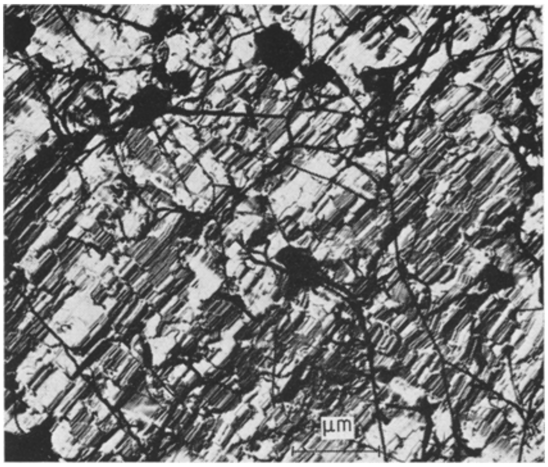

Figure 7 "Extended-chain" lamellae with molecules oriented along the tensile axis produced by annealing at 5 kbar and 247°C for 15 min. The material is Rigidex 2 polyethylene drawn eight times and after treatment has a high melting peak of 141°C at 1 bar. Courtesy of D. R. Carder.

References

1. C. W. BUNN, *Trans. Faraday Soc.* **35** (1939) 1627.
2. K. HERMANN and O. GERNGROSS, *Kautschuk* **8** (1932) 181.
3. P. J. FLORY, "Principles of Polymer Chemistry" (Cornell University Press, 1953).
4. R. JACCODINE, *Nature* **176** (1955) 305.
5. P. H. TILL, *J. Polymer Sci.* **24** (1957) 301.
6. A. KELLER, *Phil. Mag.* **2** (1957) 1171.
7. E. W. FISCHER, *Z. Naturforsch.* **12a** (1957) 753.
8. K. H. STORKS, *J. Amer. Chem. Soc.* **60** (1938) 1753.
9. W. SCHLESINGER and H. M. LEEPER, *J. Polymer Sci.* **11** (1953) 203.
10. P. H. GEIL, "Polymer Single Crystals" (Interscience, 1963).
11. G. GIANNONI, F. J. PADDEN, and H. D. KEITH, *Proc. Nat. Acad. Sci.* **62** (1968) 964.
12. F. J. PADDEN, and H. D. KEITH, *J. Appl. Phys.* **36** (1965) 2987.
13. A. KELLER and A. O'CONNOR, *Disc. Faraday Soc.* **25** (1958) 114.
14. E. W. FISCHER, H. GODDAR, and G. F. SCHMIDT, *Kolloid Z.* **226** (1968) 30.

15. H. HENDUS, *Ergeb. Exakt. Naturw.* **31** (1959) 331.
16. J. D. HOFFMAN and J. J. WEEKS, *J. Chem. Phys.* **42** (1965) 4301.
17. R. G. BROWN and R. K. EBY, *J. Appl. Phys.* **35** (1964) 1164.
18. P. H. GEIL, *J. Polymer Sci.* C **13** (1966) 149.
19. K-H. ILLERS and H. HENDUS, *Kolloid Z.* **218** (1967) 56.
20. F. R. ANDERSON, *J. Appl. Phys.* **35** (1964) 64.
21. L. MANDELKERN, A. S. POSNER, A. F. DIORIO, and D. E. ROBERTS, *J. Appl. Phys.* **32** (1961) 1509.
22. A. KELLER and D. C. BASSETT, *Proc. Roy. Micr. Soc.* **79** (1960) 243.
23. D. C. BASSETT and A. KELLER, *Phil. Mag.* **7** (1962) 1553.
24. T. KAWAI and A. KELLER, *Phil. Mag.* **11** (1965) 1165.
25. B. WUNDERLICH, *J. Polymer Sci.* A **1** (1963) 1245.
26. A. NAKAJIMA and S. HAYASHI, *Kolloid Z.* **225** (1968) 116.
27. L. MANDELKERN, J. G. FATOU, and K. OHNO, *J. Polymer Sci.* B **6** (1968) 615.
28. T. KAWAI and A. KELLER, *J. Polymer Sci.* B **2** (1964) 333.
29. F. J. BALTÁ CALLEJA and A. KELLER, *J. Polymer Sci.* A **2** (1964) 2151, 2171.
30. P. SPEGT and A. E. SKOULIOS, *C.R. Acad. Sci. Paris* **262** (1966) 722.
31. J. P. ARLIE, P. SPEGT, and A. E. SKOULIOS, *Macromol. Chem.* **99** (1966) 160.
32 A. KELLER and D. J. PRIEST, *J. Macromol. Sci. Phys.* B **2** (1968) 479.
33. A. KELLER, *Kolloid Z.* **231** (1969) 603.
34. E. W. FISCHER and G. F. SCHMIDT, *Angew. Chem.* **74** (1962) 551.
35. W. O. STATTON and P. H. GEIL, *J. Appl. Polymer Sci.* **3** (1960) 357.
36. D. C. BASSETT and A. KELLER, *J. Polymer Sci.* **40** (1959) 565.
37. F. J. BALTÁ CALLEJA, D. C. BASSETT, and A. KELLER, *Polymer* **4** (1963) 269.
38. T. KAWAI, *Kolloid Z.* **201** (1965) 104.
39. A. KELLER, *Rep. Prog. Phys.* **31** (1968) 623.
40. A. PETERLIN, *Macromol. Chem.* **74** (1964) 107. (1971).
41. D. V. REES and D. C. BASSETT, *J. Polymer Sci.* **A-2** **9** (1971) 385
42. H. E. BLAIR, R. SALOVEY, and T. W. HUSEBY, *Polymer* **8** (1967) 9.
43. D. H. RENEKER, *J. Polymer Sci.* **59** (1962) 539.
44. A. PETERLIN, *J. Polymer Sci.* B **1** (1963) 279.
45. N. HIRAI, Y. YAMASHITA, T. MITSUHASHI, and Y. TAMURA, *Rep. Res. Lab. Surface Sci. Okayama Univ.* **2** 1 (1961).
46. A. PETERLIN, *Polymer* **6** (1965) 25.
47. M. TAKAYANAGI and F. NAGATOSHI, *Mem. Fac. Eng. Kyushu Univ.* **24** (1965) 33.
48. A. KELLER and D. J. PRIEST, *J. Polymer Sci.* B **8** (1970) 13.
49. P. DREYFUS and A. KELLER, *J. Polymer Sci.* B **8** (1970) 253.
50. T. KAWAI, *Rep. Prog. Polymer Phys. Japan* **10** (1967) 151.
51. T. KAWAI, *Kolloid Z.* **229** (1968) 116.
52. J. D. HOFFMAN and J. J. WEEKS, *J. Chem. Phys.* **37** (1962) 1723.
53. J. D. HOFFMAN, *Soc. Plast. Engin. Trans.* **4** (1964) 315.
54. J. D. HOFFMAN and J. J. WEEKS, *J. Res. Nat. Bar. Std.* **66A** (1961) 13.
55. A. PETERLIN and E. W. FISCHER, *Z. Phys.* **159** (1960) 272.
56. A. PETERLIN, E. W. FISCHER, and C. REINHOLD, *J. Chem. Phys.* **37** (1962) 1403.
57. J. I. LAURITZEN and J. D. HOFFMAN, *J. Res. Nat. Bur. Std. A* **64** (1960) 73.
58. F. P. PRICE, *J. Polymer Sci.* **42** (1960) 49.
59. F. C. FRANK and M. P. TOSI, *Proc. Proy. Soc.* A **263** (1961) 323.
60. F. P. PRICE, *J. Chem. Phys.* **35** (1961) 1884.
61. J. I. LAURITZEN and E. PASSAGLIA, *J. Res. Nat. Bur. Std.* A **71** (1967) 261.
62. B. WUNDERLICH, *J. Polymer Sci.* A **1** (1963) 1245.
63. D. C. BASSETT, A. KELLER, and S. MITSUHASHI, *J. Polymer Sci.* A **1** (1963) 763.
64. H. D. KEITH, *J. Polymer Sci.* A **2** (1964) 4339.
65. R. P. PALMER and A. J. COBBOLD, *Macromol. Chem.* **74** (1964) 174.
66. A. KELLER and S. SAWADA, *Macromol. Chem.* **74** (1964) 190.
67. D. J. BLUNDELL, A. KELLER, and A. J. KOVACS, *J. Polymer Sci.* B **4** (1966) 481.
68. D. J. BLUNDELL and A. KELLER, *J. Polymer Sci.* B **6** (1968) 433.
69. D. C. BASSETT, F. C. FRANK, and A. KELLER, *Phil. Mag.* **8** (1963) 1739.
70. D. C. BASSETT, F. C. FRANK, and A. KELLER, *Phil. Mag.* **8** (1963) 1753.
71. D. C. BASSETT, F. C. FRANK, and A. KELLER, *Nature* **184** (1959) 810.
72. D. C. BASSETT, *Phil. Mag.* **10** (1964) 595.
73. D. C. BASSETT, *Phil. Mag.* **12** (1965) 119.
74. D. C. BASSETT and A. KELLER, *Phil. Mag.* **6** (1961) 345.
75. H. D. KEITH, *J. Appl. Phys.* **35** (1964) 3115.
76. S. MITSUHASHI and A. KELLER, *Polymer* **2** (1961) 109.
77. A. KELLER, *Kolloid Z.* **219** (1967) 118.
78. G. KAMPF, *Kolloid Z.* **172** (1960) 50.
79. R. EPPE, E. W. FISCHER, and H. A. STUART, *J. Polymer Sci.* **39** (1959) 721.
80. F. J. PADDEN and H. D. KEITH, *Bul. Amer. Phys. Soc.* **6** (1961) 153.
81. Y. FUJIWARA, *J. Appl. Polymer Sci.* **4** (1960) 10.
82. A. KELLER, *J. Polymer Sci.* **17** (1955) 351.
83. J-J. POINT, *Bul. Acad. roy. Belg.* **41** (1955) 982.
84. H. D. KEITH, F. J. PADDEN, and R. G. VADIMSKY, *J. Polymer Sci.* A-2 **4** (1966) 267.

85. A. KELLER, *J. Polymer Sci.* **39** (1959) 151.
86. H. D. KEITH and F. J. PADDEN, *J. Polymer Sci.* **39** (1959) 101, 123.
87. F. P. PRICE, *J. Polymer Sci.* **39** (1959) 71.
88. H. D. KEITH and F. J. PADDEN, *J. Appl. Phys.* **34** (1963) 2409.
89. H. D. KEITH and F. J. PADDEN, *J. Appl. Phys.* **35** (1964) 1270.
90. H. D. KEITH and F. J. PADDEN, *J. Appl. Phys.* **35** (1964) 1286.
91. J. W. RUTTER and B. CHALMERS, *Can. J. Phys.* **31** (1953) 15.
92. D. A. BLACKADDER, *J. Macromol. Sci.* C **1** (1967) 297.
93. E. W. FISCHER and G. HINRICHSEN, *Kolloid Z.* **213** (1966) 93.
94. H. HENDUS and K. H. ILLERS, *Kunstoffe* **57** (1967) 193.
95. L. MANDELKERN, J. G. FATOU, R. DENISON, and J. JUSTIN, *J. Polymer Sci.* B **3** (1965) 803.
96. E. W. FISCHER and R. LORENZ, *Kolloid Z.* **189** (1963) 97.
97. G. M. MARTIN and E. PASSAGLIA, *J. Res. Nat. Bur. Std.* A **10** (1966) 221.
98. D. A. BLACKADDER and P. A. LEWELL, *Polymer* **9** (1968) 249.
99. E. W. FISCHER and A. PETERLIN, *Mackromal. Chem.* **74** (1964) 1.
100. T. KAWAI and A. KELLER, *Phil. Mag.* **8** (1963) 1203.
101. D. C. BASSETT, *Polymer* **9** (1964) 457.
102. A. PETERLIN and G. MEINEL, *J. Polymer Sci.* B **3** (1965) 1059.
103. D. J. BLUNDELL, A. KELLER and T. M. CONNER, *J. Polymer Sci.* A-2 **5** (1967) 991.
104. E. W. FISCHER, H. GODDAR, and G. F. SCHMIDT, *J. Polymer Sci.* B **5** (1967) 619.
105. V. F. HOLLAND and P. H. LINDENMEYER, *J. Appl. Phys.* **36** (1965) 3049.
106. D. C. BASSETT, *Phil. Mag.* **17** (1968) 37.
107. T. WILLIAMS, D. J. BLUNDELL, A. KELLER, and I. M. WARD, *J. Polymer Sci.* A-2 **6** (1968) 1613.
108. P. J. FLORY, *J. Amer. Chem. Soc.* **84** (1962) 2857.
109. H. G. ZACHMAN, *Z. Naturf.* **19a** (1964) 1397.
110. H. G. ZACHMAN, *Kolloid Z.* **231** (1969) 504.
111. T. KAWAI, *J. Polymer Sci.* B **2** (1964) 429.
112. T. KAWAI and T. GOTO, *J. Polymer Sci.* A-2 **4** (1966) 521.
113. E. W. FISCHER, *Kolloid Z.* **231** (1969) 458.
114. E. W. FISCHER, *Kolloid Z.* **231** (1969) 499.
115. T. KAWAI, *Mackromol. Chem.* **90** (1966) 288.
116. D. A. BLACKADDER and T. L. ROBERTS, *Makromol. Chem.* **126** (1969) 116.
117. F. C. FRANK, in "Growth and Perfection of Crystals", ed. R. H. Dorenus, B. W. Roberts and D. Turnbull, (Chapman and Hall, London 1958) p. 530.
118. F. C. FRANK, *Proc. Roy. Soc.* A **319** (1970) 127.
119. A. J. PENNINGS and A. M. KIEL, *Kolloid Z.* **205** (1965) 160.
120. A. J. PENNINGS, J. M. A. A. VAN DER MARK, and H. C. BOOIJ, *Kolloid Z.* **236** (1970) 99.
121. A. KELLER and M. J. MACHIN, *J. Macromol. Sci.* B **1** (1967) 41.
122. F. M. WILLMOUTH, A. KELLER, I. M. WARD, and T. WILLIAMS, *J. Polymer Sci.* A-2 **6** (1968) 1627.
123. E. H. ANDREWS, *Proc. Roy. Soc.* A **277** (1964) 562.
124. R. SALOVEY and M. Y. HELLMAN, *J. Polymer Sci.* B **5** (1967) 647.
125. A. K. VAN DER VEGT and P. P. A. SMIT, *Adv. Polymer Sci. Tech.* **26** (1967) 313.
126. R. S. PORTER and J. F. JOHNSON, *Trans. Soc. Rheol.* **11** (1967) 259.
127. F. R. ANDERSON, *J. Polymer Sci.* C **3** (1964) 123.
128. P. H. GEIL, F. R. ANDERSON, B. WUNDERLICH, and T. ARAKAWA, *J. Polymer Sci.* **2** (1964) 3707.
129. J. D. HOFFMAN and J. I. LAURITZEN, *J. Res. Nat. Bur. Std.* A **65** (1961) 297.
130. B. WUNDERLICH and L. MELILLO, *Makromol. Chem.* **118** (1968) 250.
131. R. B. PRIME and B. WUNDERLICH, *J. Polymer Sci.* A-2 **7** (1969) 2073.
132. C. L. GRUNER, B. WUNDERLICH, and R. C. BOPP, *J. Polymer Sci.* A-2 **7** (1969) 2099.
133. R. B. PRIME and B. WUNDERLICH, *J. Polymer Sci.* A-2 **7** (1969) 2061.
134. D. V. REES and D. C. BASSETT, *Nature* **219** (1968) 368.
135. D. V. REES and D. C. BASSETT, *J. Polymer Sci.* B **7** (1969) 273.
136. E. W. FISCHER and H. PUDERBACH, *Kolloid Z.* **235** (1969) 1260.
137. C. W. BUNN, A. J. COBBOLD, and R. P. PALMER, *J. Polymer Sci.* **28** (1958) 365.
138. D. C. BASSETT and J. M. PHILLIPS, *Polymer* (in press).

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