Effects of high pressure on polymers II) crystallization

M. C. M. Cucarella
Escuela de Metalurgia y Ciencia de los Materiales, Universidad Central de Venezuela, Apartado 51717, Caracas 1050 A, Venezuela.

This article reviews the nature of polymeric crystals, its morphology and kinetics of crystallization as well as the effect of pressure upon them. Possible models representing the structure of polymer crystals and theories of crystallization are discussed. The crystallization behavior under pressure of polyethylene, polypropylene, cis- and trans-1,4-polyisoprene, poly(vinylidene fluoride), polychlorotrifluoroethylene, penton, Nylon 6, poly(hexamethylene succinate), poly(ethylene terephthalate), and two copolymers is summarized.

ON THE SCOPE OF THE SURVEY

The purpose of this survey is firstly to introduce the non-specialist to the subject and secondly to give a summary of the work done on crystallization of polymers under pressure, as well as to provide a reasonably extensive, even if by far incomplete, up-to-date references.

The article is concerned with the morphology and kinetics of crystallization of polymers and the effect of pressure upon them.

The published data on crystal growth rate as a function of pressure are discussed and an attempt is made to determine the effect of pressure on particular parameters of the growth rate equations.

The effect of pressure on lamellar thickness and the possible mechanisms of formation of extended-chain type crystals is discussed.

The crystallization under pressure of particular polymers is summarized. Experimental techniques and general descriptions have been omitted. For these conditions and many details that the author cannot cover in this survey the reader is referred to more specialized review articles and original papers.

NATURE OF POLYMERIC CRYSTALS

Polymer crystals are similar to ordinary molecular crystals in that their structure is maintained by van der Waals forces. However, there is a remarkable difference between both types of crystal; while molecular crystals have comparable values for the three dimensions, polymers for very thin crystals (5-20 nm thick). These crystals do not grow in this direction during crystallization. The other two dimensions can grow up to macroscopic size.

Another very important difference is that a non-crystalline phase (10-70 %) is present in a crystallized polymer even if it is held for a very long time at a crystallization temperature, in apparent contradiction with the Gibbs rule.

Possible models representing the structure of polymer crystals are discussed briefly. A much more complete discussion is found in a series of excellent reviews [1-6]. Some of the characteristics of polymeric crystals have been known since the crystalline nature of some polymers was accepted. These crystals are very small, a few tens of nanometres at most. Crystalline polymers retain their high elasticity and pliability, a situation never observed in other crystalline substances. The density and heat of fusion of crystalline polymers show that an amorphous phase is present. This is confirmed by X-ray diffraction patterns [7-9] showing discrete Bragg reflection due to the crystalline region together with halo patterns corresponding to amorphous areas.

Polymers crystallized under non-stress conditions

Under non-stress conditions polymers crystallize in thin platelets generally known as lamellae. The thinnest dimension of these does not grow during crystallization. These lamellae are organized in either a spherulitic or row-nucleated arrays [10-11]. Herrmann and Gerngross [12] proposed a fringed micelle model (Fig. 1) that seemed to account for all the factors mentioned previously. However, this model could not explain the existence of highly crystalline polymers with a crystallinity of 80-90 %. This model also failed to explain the observed size and the mode of development of spherulites [2].

Polyethylene single crystals were obtained, independently, in 1957 by Fischer [13], Keller [14, 15] and Till [16]. Electron diffraction patterns of these crystals confirmed the single crystal structure and gave the orientation of the chains within the crystal. This orientation was perpendicular to the basalplane of the crystal. Since the length of the molecular chains may exceed many times the crystal thickness it was concluded that the molecular chain folds back and forth with a sufficient uniform fold length to result in a smooth crystal. The concept is represented in figure 2.

This chain folding phenomenon has been observed in several organic polymers [5, 17-20], in selenium (inorganic polymer) [21, 22] and in macromolecules of biological interest [23, 26]. While the concept of chain folding is widely accepted, the exact nature of the chain fold is still a matter of controversy. Initially it was suggested [27, 31] that molecular chains were regularly folded, based on the smoothness observed by electron microscopy of the fold plane, the pyramidal nature and the occasional existence of dislocation networks [33].

The study of many properties (density, heat of fusion, degree of crystallization, etc. [34]) leads to the conclusion that 15-20 % of the polymer in single crystals exists in a disordered structure. This disordered region was interpreted by Flory [35] and Fisher [36] to be due to non adjacent re-entry of chains. Figure 3 gives a schematic representation of the random switchboard model.
There also exists a considerable body of experimental evidence, mostly spectroscopic [37--40], neutron scattering [41] and crystallographic [42], consistent with predominantly adjacent re-entrant folding. Some of this evidence has been severely questioned by Mandelkern and co-workers [43] and more recently by Calvert [44] but as yet they have been unable to provide any proof. Several models have been suggested to account for both, apparently contradictory, experimental data.

Zachmann [45] has proposed adjacent re-entry with loose loops in the growth plane (Fig. 4a). Frank [46] suggested non-adjacent re-entry with loose loops and cilia within the growth plane (Fig. 4b). Keller [47] has considered the existence of loose loops and buried folds (Figs. 4c and d), while Sánchez and Di Marzio [48] attribute the disordered contribution to a primary and secondary cilia formation (Fig. 4e).

Hoffmann and Davis [49] have given a quite different interpretation to the phenomenon. They suggest that the amorphous layer is a result of polymer molecules physically adsorbed on a fairly regularly folded surface (Fig. 4f). Although this model accounts for the experimental findings, the real nature of the «amorphous» component in single crystals, is still a matter for discussion. All of these theories have been applied mostly to solution grown crystals, but it has been suggested that similar considerations may be applied to polymers crystallized from the melt.

In this case, however, the real structure of the crystals is even more controversial, especially due to the lack of appropriate techniques. The study of surface replicas [5], fracture surfaces [5] and ultra-microtomed thin sectioning [50, 51] can be questioned due to the distortion that these techniques may produce on the crystal surfaces. Crystallization from the melt in very thin films allows the direct observation of the crystals by transmission electron microscopy [32, 54]. The use of this technique has revealed the existence of single crystals. Diffraction patterns of these crystals showed that the molecular chains had a similar orientation to those within crystals obtained from solution. The kinetics theory of crystallization developed by Lauritzen and Hoffman predicts the observed temperature dependence of the growth rate of the crystals and the observed variation of lamellar thickness with temperature. This theory assumes a chain folded model and supports the idea that crystals obtained from the melt can also be represented by the chain folded model.

The points discussed so far can give the false impression that whenever a polymer exists in a crystalline state the crystals are formed by regularly folded chains. The only possible irregularities would be those produ-
crystallization of trans-polyisoprene by Davies and Ong [57].

These were obtained by crystallizing polyethylene from a blend with a paraffin \( C_{33}H_{66} \) which was later removed with solvent. Phillips and Edwards [56] have given evidence for the existence of the tie-chains in their work on the crystallization of natural rubber in thin films [54, 58-60]. The observations agree with the concept of a row nucleation [61].

Several theories have been developed to interpret the formation of these structures [60-82]. It is possible to obtain the backbone of the «shish-kebab» free from platelets [63, 64]. These fibres were apparently structureless. Later research [65, 66] showed that they have a composite structure.

The chain molecules are parallel to the fibre axis. This fact suggests that the chains might be extended. This assumption is supported by the high melting point and mechanical strength. When a small number of fibres are crystallized from the melt, they act as nuclei for the lamellar crystallization of the whole mass. The lamellae crystallize in the perpendicular direction to the stress due to the fact that the fibres act as nuclei, grow parallel to it. Consequently the whole sample has an oriented structure.

In 1970 Pennings [67] proposed a model consisting of a backbone crystal made up of extended polymer chains to which are attached lamellar crystals containing folded polymer chains. Figure 5 is a schematic representation of it and figure 6 shows the proposed mechanism of its formation.

This model has been questioned by Nagasawa and Shimomura [68] who proposed that the crystals grow first by a screw dislocation mechanism, and are later deformed by the shear stress to form the «shish-kebab» structure.

Polyethylene crystallized from the melt at a pressure of about 5 kbar is similar to non-polymeric crystalline solids in its properties. It is brittle and hard, exceptionally highly crystalline, with no typical polymer properties. The crystals are very broad lamellae (200-500 nm thick on the surface. Unfortunately, for polymers crystallized from the melt, this ideal model seems to be only completely applicable to polyethylene and, perhaps, polypropylene crystals.

Intercrystalline molecular connections are the principal characteristics that distinguish the fringed micellar structure. As will be seen later in this section, these connections between crystals has been observed in several polymers. Furthermore, some polymers can gel [4]. Gelation is a form of solidification that requires the presence of connecting units.

In a polymer with very low crystallinity the «amorphous» area obviously cannot have a completely liquid-like structure, otherwise nothing could stop it from crystallizing. Effects such as non-adjacent re-entry, «cilia» almost as long as the whole molecule, loose and buried loops and molecules belonging to more than one crystal are expected to be highly enhanced in such polymers. Thus, the molecular mobility in the «amorphous region» would be reduced, impeding further crystallization. An intermediate situation between the fringed micelle model and the regularly folded lamellae would be expected. The latter model is approached at high crystallinity.

The conditions of crystallization produce a competition between the two possible structure [4]. The fringed micelle structure is favoured by high concentration of the polymer or, in the extreme case, crystallization from the melt. It is also favoured at high supercoolings, because smaller crystals can be stable. There seems to be a third factor the presence in the molecular chain, of segments that crystallize at different temperatures [4].

Despite the confusion about the structure of the folded surface, the existence of links between lamellae, in a semi-crystalline polymer, is widely accepted. Keith et al. [55] demonstrated the existence of intercrystalline links, in the form of fibrous crystals (3-30 nm thick). These were obtained by crystallizing polyethylene from a blend with a paraffin \( C_{33}H_{66} \) which was later removed with solvent. Phillips and Edwards [56] have given evidence for the existence of the tie-chains in their work on the crystallization of natural rubber in thin films. However, in this case, thick crystalline links were not observed and it is presumed that the links were molecular. A similar effect has been found in the crystallization of trans-polyisoprene by Davies and Ong [57].

Crystals with oriented structures

In industrial processes different conditions, such as crystallization under stress, flow and pressure are frequently applied. Fibrous crystals and extended chain type lamellae are formed under those conditions.

When crystallization of polyethylene is induced during stirring, «shish-kebab» type crystals are formed. Similar kind of crystals have also been observed in the crystallization of stretched thin films [54, 58-60]. The observations agree with the concept of a row nucleation [61].

Fig. 6. Pennings' model for formation of a backbone crystal in a shish kebab, after [67].
nm thick) and are the closest approach to the thermodynamically most stable crystal. Since the thickness of these lamellae is of the same order of magnitude as the molecular chain length, they are known as extended chain lamellae.

The origin of this crystal form is not well understood. The possible mechanisms of formation are discussed later.

Theories of recrystallization

Since thick crystals, formed without folding, are thermodynamically more stable than thin crystals, formed by folded chains, several theories have been developed to explain the prevalence of the latter.

The theories must explain experimental facts, such as dependence of lamellar thickness on crystallization temperature and degree of supercooling, and the thickening effect observed when the crystals are annealed isothermally.

Attempts have been made to explain the phenomenon using two completely different points of view: equilibrium and kinetics. Equilibrium theories [69-77] demonstrate that a region of stability, i.e., a minimum in the free energy, exists for a crystal with a finite thickness \( l \), in addition to the expected minimum at infinite \( l \). The value of \( l \) corresponding to the minimum free energy depends on temperature, in agreement with experimental results. Nevertheless, the depth of the minimum decreases with increasing temperature until it disappears at a certain critical temperature. Consequently, folded chain crystals would not exist, theoretically, above this critical temperature. The formation of folded chain crystals of polyethylene [78] above the predicted critical temperature, 110° C, shows that equilibrium theories fail to describe the crystallization of polymers within certain ranges of temperatures. Another criticism is that the dependence of lamellar thickness on degree of supercooling is not a direct consequence of the theory; only an approximate relationship can be established [78]. Thickening is predicted if crystals are annealed above the critical temperature.

The preceding comments do not imply that equilibrium theories should be discarded or that they are not important.

Kinetic theories are essentially nucleation theories, they consider the formation of the nucleus and its subsequent growth. Several kinetics theories [79-93] and good reviews of them [5, 80, 85, 94] can be found in the literature.

The initial suggestion by Lauritzen and Hoffman [79] of the kinetics theory of the chain folded crystal growth of polymers has had many modifications. It was based on the simplest possible model for chain folding. This model is represented in figure 7. It assumes that the critical secondary or molecular nucleus size is maintained for the rest of the crystal and is expressed by

\[
l_c = \frac{2\tau_c}{\Delta G_m}
\]

Where \( \tau_c \) is the folded surface energy and \( \Delta G_m \) is the bulk free energy of fusion. This change in free energy can be expressed by

\[
\Delta G_m = \Delta H_m - T\Delta S_m
\]

with the usual definitions of \( \Delta G_m \), \( \Delta H_m \) and \( \Delta S_m \). As long as the degree of supercooling is not large, \( \Delta S_m \) can be considered to be temperature independent,

\[
\Delta S_m = \frac{\Delta H_m}{T_m}
\]

Thus eq. (1) can be rewritten

\[
l_c = \frac{2\tau_c}{\Delta H_m - \frac{T_m}{\Delta T}}
\]

Fig. 4. Modes explaining the existence of an amorphous zone: 

- a adjacent re-entry with loose loops in growth plane [46],
- b non-adjacent re-entry with loops in growth plane [46],
- c mostly adjacent re-entry with loose folds [47],
- d mostly adjacent re-entry with some buried folds [47],
- e origin of primary and secondary cilia [48],
- f mostly adjacent re-entry with molecular chains adsorbed on site of the fold surface [49].
Resonable agreement with the experimental variation of lamellar thickness with temperature can be obtained for moderate degrees of supercooling. At large supercoolings, however, a practically constant lamellar thickness is experimentally observed. This behaviour can not be explained by eq. (1). A better approximation is obtained by considering that crystals with a thickness larger than the critical size nucleus will grow to completion. In this case the average lamellar thickness is represented by

\[
<l> = \frac{2\sigma e}{\Delta G_m} + \delta l
\]

where \( \delta l = \frac{kT}{b\sigma} \)

Although this equation gives a better approximation than 1, it does not give a good value for \( \delta l \). Calculated values for polyethylene at 350 K are 1-2 nm while experimental values for the same temperature are about 7 nm. The term \( \delta l \) does not fit experimental values particularly well at high supercoolings. It is predicted that it will tend to infinity when the free energy of fusion approaches \( 2\sigma/a \). This effect, however, has never been observed. Lauritzen and Hoffman [81] in the extension of their theory to high supercoolings, introduced a parameter \( \psi \) in order to overcome this difficulty. This parameter appears as a consequence of assuming that when crystallization there is a weak adsorption of the macromolecules. The growth rate of crystallization as a function of temperature predicted by this theory is in fairly good agreement with experimental results. It can be expressed by

\[
G = G_0 \exp \left[ \frac{U^*/R(T - T_m)}{T_m} \right] \exp \left[ -Kg(T, T_m)l \right]
\]

where Kg can take the values

\[
k_{g(1)} = 4\pi\tau_c b \frac{T_m}{\Delta H_m} k
\]

\[
k_{g(11)} = 2\pi\tau_c b \frac{T_m}{\Delta H_m} k
\]

or some value in between \( k_{g(1)} \) and \( k_{g(11)} \), depending on the mechanism of crystallization.

The first exponential term in equation (7) is a retardation factor due to transport phenomena. The second expresses the effect of the driving force of crystallization on the growth rate. Although partially successful in predicting the variation of lamellar thickness with temperature and growth rate of crystallization, the theory described above is somewhat unrealistic since it ignores any kind of irregularities. It can be considered that the most unrealistic assumption is that the fold length is kept constant.

Frank and Tosi [84] were the first investigators who took into account fluctuations in the crystal stem length and the influence of the crystal substrate. They allowed single fluctuations after nucleation. A nucleus which is too small (\( l < l_c \)) will tend to fluctuate to a larger fold length \( l_c \). A nucleus which is too large (\( l > l_1 \)) will tend to fluctuate to a smaller fold length \( l_c \). The single layer will have an average fold length of \( l_c \). The following layers use the first as a substrate and have an average fold length \( l'_c \) by single fluctuation. This \( l'_c \) will be the observed lamellar thickness. A good agreement between predicted and experimental values is obtained at moderate supercoolings but an infinite value of \( l'_c \) is predicted for high supercoolings AT temperatures near the equilibrium melting point, termination of crystal growth is predicted. Price [88] developed an essentially equilibrium theory based on the Markov chain formalism developed by Mullins [95]. It allows an unlimited number of fluctuations within each layer. The new layer adjusts its fold length to an intermediate value between the fold length of the substrate, \( l_c \), and the new deposited stem. Successive layers are deposited to form the crystals. When two adjacent layers have the same average fold length this value is the final lamellar thickness. The unlimited increase in lamellar thickness predicted by the theories previously described is also calculated by this theory though this point is reached at low supercoolings (Fig. 8). This theory does not present the limitation of a termination of growth at high temperatures. Predicted fluctuations are of the order of 0.1-0.2 nm. Hitherto the most general treatment considering the effect of fluctuations and finite substrate has been developed by Lauritzen and Passaglia [86]. This theory allows for fluctuations at every stage of the crystallization process. It is based on the model shown in figure 9. It differs from the Price theory in that the fluctuations are governed by kinetics rather than by equilibrium conditions.

The predicted curve for lamellar thickness as a function of temperature is shown in figure 8 and can be represented by

\[
l = \frac{2\sigma_{eff} \Delta H_m}{T_m} \frac{T_m}{\Delta T} + \delta l'
\]

where

\[
k_{g(1)} = 4\pi\tau_c b \frac{T_m}{\Delta H_m} k
\]

\[
k_{g(11)} = 2\pi\tau_c b \frac{T_m}{\Delta H_m} k
\]

or some value in between \( k_{g(1)} \) and \( k_{g(11)} \), depending on the mechanism of crystallization.
This equation appears to be identical to 6. The difference between them is in the meaning of $\tau_{\text{eff}}$ and $\tau'$. $\tau_{\text{eff}}$, in the Lauritzen and Hoffman theory, is the fold surface energy of a smooth surface. The value of $\tau_{\text{eff}}$ is calculated from a rough surface with a contribution of extra lateral surfaces. This effective fold surface energy, $\tau_{\text{eff}}$, is strongly dependent on temperature. This theory also predicts a temperature where $\tau'$ tends to infinity. The predicted fluctuations are of the order of $1 \text{ nm}$. Sánchez and DiMarzio [91, 92] include in their model the existence of $c_0$. The most interesting result of this theory is that it predicts the dependence of the nucleation rate on polymer concentration.

Lauritzen, DiMarzio and Passaglia [96, 97] developed a formalism that allows the components to be different chemical species. Obviously it has a great value in the interpretation of crystallization of mixtures or random copolymers [98]. The theory predicts that inclusion of the co-unit impurity is enhanced by any parameter which increases the growth rate of the crystal. It has also been used to study the effects of molecular weight fractionation [93].

All the theories developed so far are based on models of perfect crystals. However, most polymers are expected to have a more complicated structure. A model for a «real» polymer should take into account the interaction between the «amorphous» and crystalline regions and consider the possibility of an irregular surface. This is especially important for polymers with very low crystallinity. Unfortunately the complexity of such a model would make the problem almost insoluble.

Effect of pressure on lamellar thickness

Fracture surfaces of a sample of polyethylene crystallized from the melt around 5 kbar revealed lamellae whose thicknesses were comparable with the typical molecular length [99]. The name of extended chain lamellae was adopted to describe these broad crystals (up to $3 \mu m$) and it has become common usage to identify thick lamellae ($>200 \text{ nm}$) as extended chain type [100] even if they are formed by folded chains.

The existence of such crystals has been explained by either postulating folded chain crystals which have thickened or lamellae that are already thick at the moment of formation. These two possible mechanisms have been a matter of controversy since they were proposed. A different kind of mechanism has been suggested for polyamides. It is described under nylon-6. From observation of the rounding of the ends of the extended chain lamellae [101, 102], narrowing of the lamellae at points of crystal intersections and the increase in lamellar thickness at larger distances from the spherical centres [101], Wunderlich and Melillo [101] concluded that the extended chain crystals grown under such conditions, chain fold initially then extend in a second, solid state process.

Figure 10 shows this process of crystallization into a thin chain folded crystal followed by thickening for polyethylene crystallized under pressure.

The mechanism proposed by Wunderlich and workers suggests no difference between crystallization at atmospheric and high pressure. They consider that thickening, which is kinetically obstructed at atmosp-
heric pressure, is favoured at high pressures probably due to the high temperatures involved in crystallization under pressure.

Annealing experiments carried out at high pressure showed [103, 104] that a thickening process occurred producing extended chain lamellae. Thus thickening can produce extended chain lamellae. This fact does not however, necessarily imply that the crystallization of the extended chain lamellae are formed by this mechanism. The second possibility is that folded chain and extended chain grobths are independent processes. Bassett [105] concluded, from DAT observations, that the latter mechanism allows a simple understanding of the main features. During crystallization of a fraction of molecular weight 50,000 on cooling from the melt at 1 K/min, chain folded crystals were formed at a supercooling of 16 K and extended chain crystals were formed at 12 K [106]. When the two morphologies were concurrent two DTA peaks were detected [105]. Under particular isothermal, isobaric conditions extended chain crystals formed before folded chain material [105]. Thus, both types of crystal must have formed independently. Similar behaviour, using dilatometry, was reported by Maeda and Kanetsuna [107].

The facts seem to shows that there are two independent crystallization processes that can lead to the formation of extended chain crystals. Bassett and Turner [108] postulated the existence of an intermediate phase that would explain the change in kinetic behaviour or polyethylene at high pressure. This phase was discovered by Bassett, Block and Piermarini [109] and has a hexagonal structure. The new phase has a much lower entropy of fusion ($-\frac{1}{2}$) [108] which according to equation (6) allows the formation of much thicker crystals.

---

**Fig. 10.** Formation of extended-chain crystals as a result of thickening, after [10].
The variation of thickness of normal chain folded crystals with pressure is discussed under cis- and trans-1,4-polyisoprenes.

The thickness of a crystal that suffers thickening can be expressed by

$$l_{obs} = \gamma l^*$$  \hspace{1cm} (11)

and, substituting equation 5 into 11

$$l_{obs} = \gamma \left[ \frac{2\tau_e}{\Delta H_m} + \delta l \right]$$  \hspace{1cm} (12)

$$l_{obs} = \gamma \left[ \frac{2\tau_e}{\Delta H_m} \cdot \frac{T_m^o}{\Delta T} + \delta l \right]$$  \hspace{1cm} (13)

Thus the change in lamellar thickness with pressure could be calculated if all the parameters of the equation (13) were known at different pressures.

The variation of $T_m^o$ and $\Delta H_m$ with pressure can be determined, with difficulty, experimentally. The fold surface free energy $\tau_e$ can be expressed by

$$\tau_e = q/2A_o + \tau_{eo}$$  \hspace{1cm} (14)

Where $q$ is the work required to form the fold by bending the polymer chain back upon itself in the appropriate configuration. The term $\tau_{eo}$ is the value that $\tau_e$ would assume if there were no contributions from the energy due to the fold and should have a value similar to $\tau$. $A_o$ is the cross-sectional area of each chain and is equal to $ab$, as shown in figure 11.

The value of $q$ can be calculated from intermolecular and intramolecular potential energy functions [110] or from experimental data of lamellar thickness. These two methods have been found to agree for polyethylene. The work of folding $q$ depends primarily on the chain structure, particularly on the stiffness of the chain itself. The cross-sectional area does not vary considerably with pressure because the crystalline phase is fairly incompressible, consequently the fold surface energy $\tau_e$ is not expected to vary very much with pressure. From the value of $\tau_e$ it is seen that $\tau_{eo}$ is almost negligible for most polymers, therefore eq. (14) can be rewritten as

$$\tau_e = q/2A_o$$  \hspace{1cm} (15)

The parameters in the eq. (13) are either not expected to change very much with pressure or can be expressed in terms of $\Delta H_m$. The value of $\delta l$ in eq. (13) is proportional to $1/\tau$ and, using the empirical relationship [81]

$$\delta l \propto \frac{1}{\Delta H_m}$$  \hspace{1cm} (17)

The theory of lamellar thickening relating to the factor $\gamma$, in eq. (13), predicts [111] a logarithmic increase with time of a magnitude inversely proportional to $\tau^2$, consequently $\gamma$ increases when $\Delta H_m$ decreases.

From the analysis of the parameters in eq. (13) it is obvious that the variation in the enthalpy of fusion with pressure will be of prime importance in the variation of the lamellar thickness. As has been reported before [112] there is not a general tendency for the shape of the curves of $\Delta H_m$ against pressure. For the polymers with falling curves, the magnitudes of the decrease does not seem enough to produce a chain extension as important as in the case of polyethylene. It seems that only the formation of a different phase, with much lower enthalpy of melting, as an intermediary, would allow the formation of extended chain lamellae for all the polymers studied. It should be noticed that the values of $\Delta H_m$ were calculated using the Clausius-Clapeyron equation.

The above arguments explain the existence of very broad lamellae in polyethylene crystallized under pressure. Indeed, since the enthalpy of fusion of the hexagonal phase is about one-fourth that of the normal orthorhombic form the parameters $\delta l$, $\gamma$ and $\Delta H_m$ are all changed so as to increase $l_{obs}$. This might clarify the mechanisms of the formation of extended chain crystals of polyethylene. The initial thickness of the lamellae is given by

$$l^* = \frac{2\tau_e}{\Delta H_m} \cdot \frac{T_m^o}{\Delta T} + \delta l$$  \hspace{1cm} (18)

and consequently for the same degree of supercooling

$$l_{ECPE}^* = l_{FCPE}^*$$  \hspace{1cm} (19)

where FCPE refers to the thin folded chain crystals.
obtained at atmospheric pressure and ECPE to the phase crystallized at high pressure through the mechanisms

orthorhombic phase → hexagonal phase → extended chain crystals

Extended-chain crystals seem then to occur either by thickening of normal folded-chain crystals or to be formed from polymers whose heat of fusion decreases with increasing pressure of polymers which originate a new phase under pressure with a substantially lower heat of fusion.

Effect of pressure on crystal growth rate

The influence that pressure has on the growth are rate of crystallization can be analyzed by studying eq. (7)

\[ G = G_o \exp \left[ - \frac{U^*}{R(T - T_c)} \right] \exp \left[ - \frac{k_g}{T(\Delta T)} f \right] \]

The pre-exponential factor \( G_o \) can be expressed [113] for regimes I and II respectively by

\[ G_o(I) = b(kT/h) \alpha_1 \exp \left( 2ab \sigma_e \Psi/kT \right) \]
\[ G_o(II) = b(kT/h) \alpha_1 \exp \left( ab \sigma_e \Psi/kT \right) \]

Since none of these factors is believed to vary significantly with pressure, the pre-exponential factor \( G_o \) would be expected to be of the same order of magnitude at any pressure.

For very small supercoolings the exponential factor due to transport phenomena has little effect on the formula and, consequently the variation in the growth rate of crystallization is mostly given by the exponential factor

\[ \exp \left[ - \frac{k_g}{T(\Delta T)} f \right] \]

with two expressions for \( k_g \) corresponding to regime I and II respectively

\[ k_g(I) = 4b \sigma_e T_m^0 (\Delta H_m) f \]
\[ k_g(II) = 2b \sigma_e T_m^0 (\Delta H_m) f \]

The parameter \( \sigma_e \), which is proportional to the work of folding, is expected to vary only slightly with pressure and temperature. The lateral surface energy is proportional to the latent heat of fusion eq. (16). Therefore, if pressure does not affect the regime of crystallization, the variation in growth rate at low supercoolings, will be determined mainly by the change in

\[ \frac{T_m^0}{T(T_m^0 - T)} \]

The biggest variation here corresponds to \( (T_m^0 - T) \). The conclusion is that where a polymer is crystallized at a low degree of supercooling the growth rate of crystallization depends mostly on it, as long as the regime of crystallization is not affected by the pressure, i.e., two samples crystallized at the same degree of supercooling, if this were small, would be expected to have comparable crystal growth rates.

When the degree of supercooling increases, the contribution of the exponential factor due to transport phenomena becomes important. Thus the variation of \( U^*/R(T - T_c) \) with pressure will affect the crystal growth rate and particularly the value of the maximum rate.

In this factor the biggest variation is due to \( T_c \), the hypothetical temperature where all motion associated with viscous flow ceases. This temperature is somewhat below the glass transition temperature and to a first approximation can be considered

\[ T_c = T_g - C_2 \]

where \( C_2 \) corresponds to that of the WLF equation [114]. Thus \( T_c \) is expected to vary in the same way with pressure as \( T_g \cdot T_c \), varies, for most polymers, between 15 and 35°C per kbar [115]. \( dT_m^0/dP \) and \( dT_c/dP \) generally increase by different amounts. This difference is the main reason for the change in shape of the crystallization curves when there is not a shift of regime.

Experimental studies of polymer crystallization under pressure

As reported before [112] the melting point of polymers rises greatly with pressure. Thus polymers can be crystallized at much higher temperatures when pressure is applied. The crystallization of several polymers under these conditions of high pressures and temperatures has been studied. Most of the research, however, has been concentrated on polyethylene.

A summary of the most relevant features related to crystallization under pressure is given below.
Polyethylene

$\text{CH}_2-\text{CH}_2$

Crystallizes at atmospheric pressure into chain folded crystals, its unit cell structure is orthorhombic. When it is crystallized under pressure, different morphologies are observed. These morphologies depend on the crystallization conditions and range from spherulitic structures to "cigar-shape" crystals. The most relevant feature is the thickness of the crystals obtained, and this can be greater than 1 μm. Because this thickness is of the same order as the molecular length these crystals are known as extended chain lamellae.

X-ray diffraction studies under pressure demonstrated the existence of a new hexagonal phase. This phase coexists with the orthorhombic phase and the liquid at $220^\circ\text{C}$ and 3.5 kbar (triple point). The orthorhombic phase transforms to the hexagonal phase if the pressure is raised above 3.5 kbar at temperatures just below the melting point. The hexagonal phase formed at high pressure and low supercoolings can be transformed into the orthorhombic phase by lowering the temperature. This phase is considered by some authors to be a necessary intermediary for the formation of the extended chain crystals. Rings corresponding to reflections of a triclinic cell were showed by Marlex type samples crystallized at 4.36 kbar and 5.07 kbar.

Since the thickness of the crystals obtained at high pressure is of the order of molecular length, the influence of molecular weight on crystallization at high pressure has been widely studied. Increase in the number average molecular weight produced crystals with greater average lamellar thicknesses up to molecular weight of about 10,000. A typical distribution is shown in figure 12. From crystallization of polyethylene fractions of narrow molecular weight distribution ($\text{Mn} = 21600, 50100, 280000 \text{ Mw/Mn} = 1.14, 1.14, 1.85$) a range of chain extensions were found rather than just one extension corresponding to the fully extended chain crystals.

### Fig. 12. Molecular weight and crystal size distributions of polyethylene. after [10].
<table>
<thead>
<tr>
<th>Macromolecule</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene CH₂—CH CH₃—</td>
<td>Crystallizes at atmospheric pressure into the monoclinic ( \gamma )-form. A metastable triclinic phase, ( \gamma ), is obtained by crystallization at high pressure (up to 5 kbar). The structure of the new phase was studied by Sauer and Pae, and Kardos et al. using X-ray diffraction. The stability of the ( \gamma )-phase depends on degree of supercooling. When the triclinic ( \gamma )-form is obtained at a high degree of supercooling it transforms into the ( \alpha )-phase. This ( \gamma \rightarrow \alpha ) transformation occurs also by thermal annealing below the melting point of the ( \gamma )-form and it is considered to be a solid state reorganization. The rate of the ( \gamma \rightarrow \alpha ) transformation was found to be a function of temperature.</td>
<td>[154-159]</td>
</tr>
<tr>
<td>Cis-1,4-polyisoprene CH₂—CCH₃—CH—CH₂—</td>
<td>Crystallizes at atmospheric pressure into folded chain lamellae. When thin films of this polymer are crystallized at 4 kbar chain extension up to 3 times the normal is observed. A new phase formed by ellipsoidal crystals was reported in 1972. The variation in lamellar thickness and crystal growth rate, with pressure have been determined up to 3.5 kbar. The major effect of increasing pressure on lamellar thickness appears to be one of increasing the degree of supercooling for crystallization at constant temperature. The maximum growth rate increases with pressure up to 1.5 kbar and there after remains approximately constant up to 3.5 kbar. Estimation of the regime of crystallization suggests a change of mechanism of crystallization when pressure is increased.</td>
<td>[160]</td>
</tr>
<tr>
<td>Trans-1,4-polyisoprene CH₂—CCH₃—CH—CH₂—</td>
<td>Crystallizes at atmospheric pressure into chain folded crystals. There are two concurrent crystallographic forms. The variation of lamellar thickness and crystal growth rate has been studied up to 3.5 kbar. The maximum crystal growth rate decreases continually with pressure for the two obtainable polymorphs. This effect can be explained by the variation of ( T_m ) and ( T_g ) with pressure. Lamellar thickness is dependent on the degree of supercooling for all pressures studied. All the results could be fitted to the Lauritzen and Hoffman equations.</td>
<td>[54]</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride) CH₂—CF₂—</td>
<td>Can be crystallized in at least two crystalline modifications at atmospheric pressure, phase I and phase II. The existence of a new phase formed under pressure was reported in 1968. However, a detailed study of the high pressure crystallized phase indicated that a mixture of phases I and II is present, rather than a new crystalline phase as originally suggested. Recently extended chain lamellae (1500-2000 A) were obtained at pressures higher than 3500 bar.</td>
<td>[166-170]</td>
</tr>
<tr>
<td>Polychlorotrifluoroethylene CClF—CF₂—</td>
<td>Pressures of the order of 1 kbar are sufficient for producing chain extension in this polymer. This polymer produces extended chain crystals (1 ( \mu )m thick) even at atmospheric pressure. These lamellae are arranged in spherulites that present a different branching process from those formed by polyethylene. This morphological difference is shown schematically in figure 13.</td>
<td>[173]</td>
</tr>
</tbody>
</table>

Fig. 13. Schematic representation of two different types of spherulites formed by extended chain lamellae.

a poly(tetrafluoroethylene) and

b polyethylene, after [175].
<table>
<thead>
<tr>
<th>Macromolecule</th>
<th>Description</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penton</td>
<td>A new phase, β-form, is obtained by crystallization above 1.77 kbar. This β-form is metastable below 2 kbar and transforms into the α-form. It is possible to stabilise the β-form by raising the pressure above 2 kbar.</td>
<td>[176]</td>
</tr>
<tr>
<td>Nylon-6 (CH₂)₅CO−NH−</td>
<td>Polyamides crystallized from solution form lamellar crystals, with thickness 5-100 nm. Crystallization from the melt leads to growth of lamellar spherulites of comparable long spacing. Extended chain crystals are obtained when nylon-6 is crystallized under pressure up to 8 kbar. It has been suggested that because of the −CO−NH− groups present in the polymer chain, the mechanism of the extended chain crystallization in polyamides may differ from that proposed for polyethylene. It was shown that the formation of extended chain crystals was accompanied by a chemical reaction which changes the molecular weight and the molecular weight distribution of the fractions. It is believed that under drastic conditions of pressure and temperature transamidation occurs between the CO−NH− groups of broken folds. Figure 14 shows a model for such a mechanism. In A the strained folds of the lamellar crystals are broken. New−CO−NH− bonds are formed by transamidation, between the cut chains. In B the folds in the adjacent lamellae are displaced to each other. Kink bands may be formed. In C, the distance between the CO and NH groups of the exposed folds is too large so they stay unbonded after breaking. Extended chain crystals of nylon-11 and nylon-12 have been obtained by Gogolewski, Stamhuis and Penning. However, the relevant papers have not yet been published.</td>
<td>[5, 177-179] [180-181] [182]</td>
</tr>
<tr>
<td>Poly(hexamethylene succinate)</td>
<td>It has been crystallized under pressure up to 5 kbar. The crystallization rate and the number of nuclei formed were determined as a function of pressure and temperature. It was found that both quantities increase with pressure if the crystallization temperature is the same for all crystallization pressures. However, these quantities decrease with increasing pressure when the crystallization is carried out at a constant degree of supercooling.</td>
<td>[183]</td>
</tr>
<tr>
<td>Poly(ethylene terephthalate)</td>
<td>The lamellar growth kinetics and lamellar thickness at 1 bar were determined as a function of temperature. The parameters $\sigma$, $\sigma_c$ and q were estimated. When crystallized under pressure presents a quite similar behaviour to that observed in pressure crystallized linear polyethylene. Extended-chain and folded-chain lamellae develop, whether simultaneously or in sequence has not yet been determined.</td>
<td>[189] [10] [184]</td>
</tr>
<tr>
<td>Poly(ethylene-propylene) and Poly(ethylene-butene-1)</td>
<td>Crystallizes at atmospheric pressure into a folded chain morphology. A mixture of extended chain and folded-chain crystals was obtained by crystallizing the copolymers at pressures higher than 4.15 kbar. Crystallization rate was found to decrease as a function of pressure.</td>
<td>[185-187]</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENT

The author is specially indebted to Dr. C. K. L. Davies, of Queen Mary College, London, for his stimulating discussions and suggestions.

REFERENCES

42. Bassett, D. C. Phil. Mag., 12 (1965), 907.