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Polymorphism in polymers; its implications for polymer crystallisation

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The aim of this article is to extend the earlier reported observations on the role of transient metastable phases in polymer crystallisation in relation with the initial crystal size. In this article experimental evidence is provided to bridge the gap between single crystal formation in the melt at elevated pressure and temperatures vs. crystallisation at atmospheric pressure using polyethylene as a model substance. During transformation from the hexagonal to the orthorhombic phase it is shown that in the process of growth, a crystal goes through thermodynamically stable and metastable states before transformation to the orthorhombic phase occurs. The crystal growth, on transformation to the thermodynamically stable orthorhombic phase, has been followed with the help of *in-situ* optical microscopy and transmission electron microscopy. The observations are that the newly transformed crystal acts as a nucleation centre for many new crystals starting in the hexagonal phase. It is also noticed that with increasing supercooling multilayering dominates. Subsequently, the distinction between primary and secondary thickening has been made and its morphological consequences will be discussed. In its wider generality, the experimental findings indicate that in polyethylene at atmospheric pressure crystallisation occurs via the hexagonal phase. When extended to atmospheric pressure, the morphological features give further insight into spherulite formation. The observations have been extended to other polymers such as nylon, paraffins, poly-di-alkyl siloxanes, trans-1,4 polybutadiene etc. The proposed viewpoint on the crystal size influence in phase transition has been extended to polymer processing as will be illustrated briefly for the case of processing of the intractable polymer ultra-high-molecular-weight polyethylene (UHMW-PE). © *2000 Kluwer Academic Publishers*

1. Introduction

Crystallisation of polymers has been a widely studied subject and still is an important topic in view of several different models describing the complex crystallisation behaviour of long chain molecules. In the case of synthetic polymers, the first concepts of crystallisation were based on very extensive crystallisation studies performed on solution-grown single crystals where crystallisation proceeds in very dilute systems (<0.01 wt. %). The long flexible chains crystallised from solution form platelet (lamellar) single crystals. Since the thickness of these lamellar crystals is much smaller than the length of a fully extended chain, it was proposed by Keller [1] and Fischer [2] in 1957 that chains fold back and forth, forming folded chain lamellar crystals. Detailed studies demonstrated that the crystallisation temperature, viz. the degree of supercooling, plays a prominent role in determining the lamellar thickness of solution-crystallised single crystals. It was also found that the lateral habit of single crystals is dependent on the crystallisation temperature [3]. Moreover the melting temperature of single crystals is strongly dependent on the lamellar thickness, mainly due to the small crystal size in the chain direction, viz. the fold length, related to the relatively large surface area compared with the volume of the crystals [4, 5].

Detailed studies have been performed concerning crystallisation from dilute solutions involving narrow molecular weight fractions. Based on these studies, it was proposed that polymer crystallisation is a nucleation controlled process. Classical, well-established theories on crystallisation (surface nucleation) for low molar mass substances were adopted for describing polymer crystallisation [4, 5]. Together with thermodynamic parameters such as supercooling, kinetic features concerning surface nucleation were included to understand the experimental observations. Several theories were proposed, for example by Frank & Tosi [4], followed by Hoffman and co-workers [5], and later by the late David Sadler [6]. The proposed theories took into account the crystal growth process after the formation of critical nuclei. However, the origin of nucleation in polymers is still a matter of debate [7], both for quiescent and notably for oriented polymer systems.

With the help of detailed Transmission Electron Microscopy, the formation of terraces in polymer crystallisation has been observed frequently [8]. The proposed screw dislocation for crystal growth in general, proposed by Frank, was used to explain such intriguing morphological features [9]. Similar to the constrained lattice, which results in dislocations in inorganic crystals, it is the surface of lamellar crystals which causes dislocations in polymers.

The studies and theories/modelling, mentioned above were based on experimental studies of solution-crystallized polymers, notably linear polyethylenes. Crystallisation from the melt is a much more complex phenomenon. The polymer chains in the melt are highly entangled and folding of chains during the nucleation and crystallisation process is hindered. However, current models invoke reeling-in of chains from the melt on the crystal surface which is in fact a disentangling process from a virtual tube based on the concept of reptation [10].

Crystallisation from the polymer melt results in the formation of spherical crystal aggregates, the so-called spherulites, notably at isothermal crystallisation at low supercoolings. The origin of spherulitic growth including nucleation, the growth of sheaf like structures in the beginning and subsequent branching and the development of spherical crystal aggregates is still not very well understood, despite many studies [11].

To bridge the gap between single crystal growth (crystallisation from dilute solutions) and growth into spherulitic structures (crystallisation from the melt), crystallisation studies on linear polyethylenes at elevated pressures and temperatures are of utmost importance since *single crystals can be grown directly in the melt* and their growth can be studied *in-situ* and can be compared with the nucleation and growth of spherulites at ambient pressures.

In the past, many experiments have been performed [12–15] concerning *in-situ* observation of single crystal growth at elevated pressures and temperatures using PE as a model substance. It appeared that crystal growth initially proceeded via the hexagonal phase and, moreover, that a metastable hexagonal phase could be observed at early stages of crystal growth within the thermodynamically stable orthorhombic phase [16]. The observation that a thermodynamic stable state is reached via a metastable state of matter is not unique for polymers nor a novel issue. Already in 1897 Ostwald made this observation in the case of freezing of liquids.

In this article we will provide experimental evidence to bridge the gap between single crystal formation at elevated pressures and temperatures and crystallisation at atmospheric pressure. The main aim of this paper will be to investigate metastability in polymer systems and its influence on crystallisation at atmospheric pressure. After addressing some salient findings on crystallisation from the mesophase we will proceed with new experimental findings on the fate of the crystal after transformation from the metastable back to its thermodynamic stable state. Subsequently, the distinction between primary and secondary thickening will be made and its morphological consequences will be discussed. Finally, we will address the phenomenon of size dependent phase stability and its significance in improving the processability of the ultra high molecular weight polyethylene (UHMW-PE) powder.

Generalisation to the proposed viewpoints in the crystallisation behaviour, especially the issue of metastability, will be made by giving examples of polymers other than polyethylene, such as trans-1,4-poly butadiene, poly-di-alkyl siloxanes, nylons, polyethylene) terephthalate and paraffins.

2. Experimental section

2.1. Materials

Two types of sharp fractionated polyethylene were obtained from the National Bureau of Standards, U.S.A. The two fractions are: sample 1, NIST-SRM1483 having $M_w = 32000$, $M_w/M_n = 1.1$ and sample 2, NIST-SRM1484 having $M_w = 120000$, $M_w/M_n = 1.2$. Trans-1,4-polybutadiene was synthesised in our laboratory [17]. UHMW-PE nascent powder, specially synthesised for our studies, possesses a molecular weight of 3.5×10^6 and $M_w/M_n = 5.6$. Solution crystallised films of UHMW-PE have been prepared from 1% Xylene solutions via a route well documented in literature [18].

2.2. High pressure cell

In this work a piston-cylinder type of pressure cell similar to the one used by Hikosaka [19] has been used. A sample is sandwiched in between two diamond windows which enable in-situ observation by light microscopy, Raman spectroscopy and X-ray diffraction. The pressure on the sample is generated hydrostatically by precise movement of two pistons, provided by pressure-regulated flow of nitrogen gas.

2.3. Polarising optical microscopy

Polarising optical micrographs have been taken *in-situ* during crystallisation of polyethylene under elevated pressures and temperatures. In our previous studies it has been shown that when crystallising the polyethylene at elevated pressures and temperatures, the crystals emerge and grow as isolated “cigar”-shaped birefringent entities. Such uniform objects have been shown to be in the hexagonal phase. At a certain stage of growth, the shape of the crystal changes into a blotchy structure with reduced birefringence which indicates the transformation from the hexagonal into the orthorhombic phase [12, 13, 20].

2.4. Wide angle X-ray scattering

In situ X-ray experiments were performed using monochromatic X-rays of wavelength 0.0798 nm and a high flux using beamline ID11-BL2 on the European Synchrotron Facilities in Grenoble. The lower wavelength was required to avoid the X-ray absorption from the diamond windows. Each diffraction pattern was recorded for 15 s on a two dimensional CCD detector. Using the FIT2D program of Dr. Hammersly (ESRF), 2D X-ray patterns were transformed into one dimensional patterns by performing an integration along the azimuthal angle.

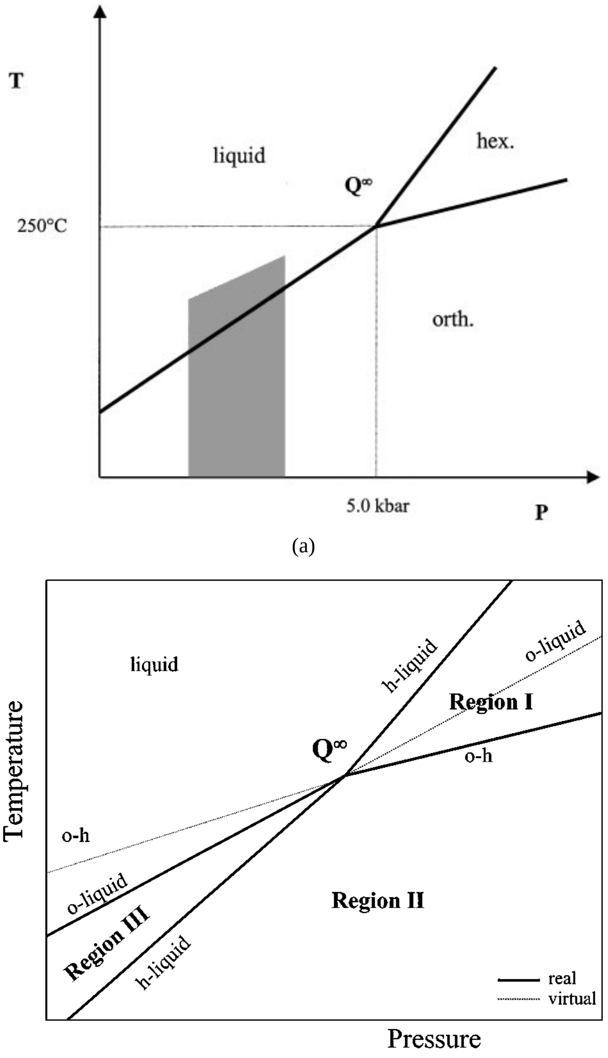
3. Results and discussion

Before proceeding with our most recent observations, it is essential to recapitulate some of the salient findings which have been published in the past and which form the basis for the present discussion.

3.1. Polyethylene – a summary of previously reported results on crystallisation of single crystals in polyethylene melts

With the help of *in-situ* optical microscopy at the requisite pressure and temperature, it has been shown that crystallisation of a linear sharp fractionated polyethylene proceeds via the hexagonal phase, even in the thermodynamically stable orthorhombic region of the pressure-temperature phase diagram (see Fig. 1a). It was shown that the birefringent entities observed at 45° to the polarised light, are crystals growing from the melt under isobaric and isothermal conditions. It was also possible to make a distinction between the hexagonal and orthorhombic phases, optically. Compared to the crystals in the orthorhombic phase, the crystals in the hexagonal phase possessed smooth and well defined boundaries. Thus, the phase transition could be followed *in-situ* as a sudden change in birefringence. From a series of experiments under isobaric and isothermal conditions within the thermodynamically stable region of the orthorhombic phase, the following conclusions were made.

1. Crystallisation always occurs initially via the hexagonal phase [12, 13].
2. After a certain crystallisation time, crystals initially in the hexagonal phase transform into the orthorhombic phase [12, 13].
3. Once a crystal is transformed, further crystal growth is arrested, at least within the experimental time [12, 13] of several hours.
4. The residence time for a crystal in the hexagonal phase is dependent on the supercooling and pressure at which an experiment is performed [14].
5. Below the equilibrium triple point (Q^{∞}), under isobaric and isothermal conditions, after a certain crystallisation time two different populations of crystals can be observed – one in the hexagonal phase which continues to grow and the other one which has transformed into the orthorhombic phase, and stops growing. On heating the sample, the crystals in the hexagonal phase melt at a lower temperature in comparison with the ones which are in the orthorhombic phase (see Fig. 1b). The melting behaviour is contradictory to the observations above the triple point (Q^{∞}) – i.e. the melting of an orthorhombic crystal occurs via its transformation to the hexagonal phase. Thus, above the triple point, crystals in the hexagonal phase possess a higher melting temperature [12, 13].



(a)

(b)

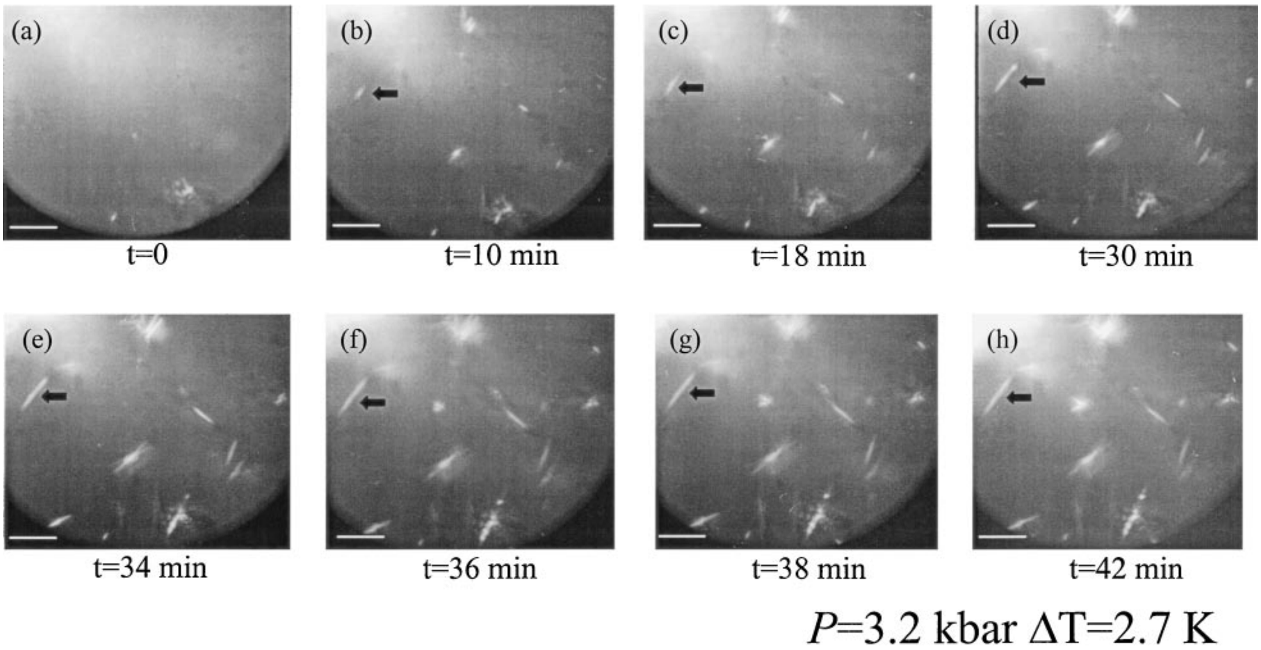
Figure 1 (a) Schematic pressure-temperature phase diagram of polyethylene. Q^{∞}, the equilibrium triple point (from ref. [16]) is the intersection of orthorhombic to hexagonal, hexagonal to liquid, and orthorhombic to liquid transition lines. The shaded region in the figure is the p-T region where experiments have been performed in this work. P = pressure, T = Temperature. (b) Schematic p-T phase diagram according to reference [12]. The diagram includes metastable (——) and virtual boundaries (······) between the hexagonal and orthorhombic phase as well as the liquid. Q^{∞} is the equilibrium triple point. Regions I, II, III are defined in ref. [12].

6. The difference in the melting temperature of the orthorhombic and the hexagonal phase increases with decreasing pressure, below the triple point [12].
7. With a series of such experiments, a more general pressure-temperature phase diagram was proposed (Fig. 1b) with three different supercoolings defined below the equilibrium triple point – first a virtual transition line from orthorhombic to hexagonal, second from orthorhombic to liquid and the third from hexagonal to liquid [13].
8. Three different regions were defined in the proposed schematic phase diagram (Fig. 1b). A Region III below the equilibrium triple point Q^{∞}, bounded in between the hexagonal-liquid (h-liquid) and orthorhombic-liquid (o-liquid) in the phase diagram was defined as a region for no crystal growth [12, 13], see also below.

3.2. Experimental observations on a crystal after its transformation from the metastable hexagonal phase into the thermodynamically stable orthorhombic phase

In this paper we will extend the earlier observations, summarised above, by discussing the effect supercooling has on the phase transition as well as crystal growth after the phase transition from the hexagonal to the orthorhombic phase.

In a series of composite figures (Fig. 2–5) taken at a fixed pressure of 3.2 kbar and at different supercoolings ($\Delta T = 2.7$ K in Fig. 2; $\Delta T = 4.7$ K in Fig. 3; $\Delta T = 5.7$ K in Fig. 4; $\Delta T = 6.7$ K in Fig. 5), relative to the melting temperature of the hexagonal phase, the following observations can be made. Taking the criteria for optical distinction between the hexagonal (marked by $\rightarrow$) and the orthorhombic phase (marked by $\Rightarrow$) it can be stated that independent of the supercooling, crystallisation always starts in the hexagonal

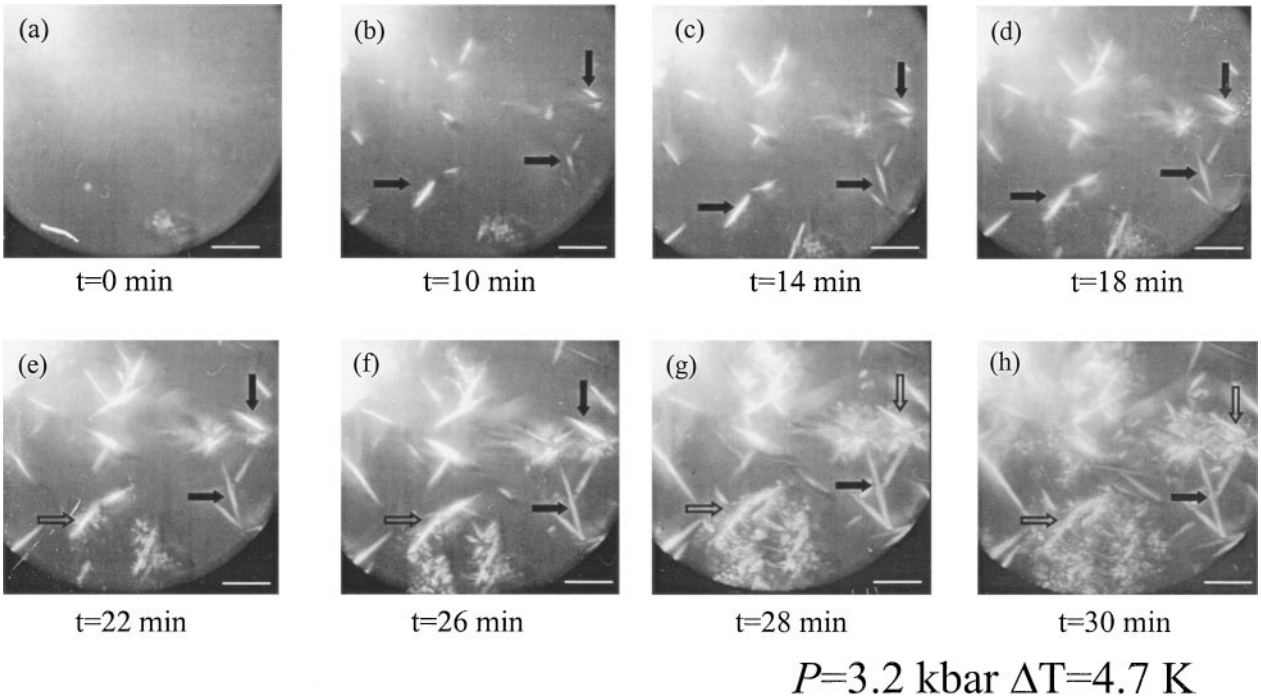


t=0 t=10 min t=18 min t=30 min

t=34 min t=36 min t=38 min t=42 min

P=3.2 kbar ΔT=2.7 K

Figure 2 *In-situ* optical micrographs of the sharp fractionated polyethylene (NIST SRM1483, $M_w = 32000$) during isobaric and isothermal crystallisation at $P = 3.2$ kbar and $(\Delta T)_{\text{orth}} = 2.7$ K. The bold arrows ($\rightarrow$) denote the hexagonal crystals. It can be observed that within the experimental time no transformation from the hexagonal to the orthorhombic phase took place at low supercoolings. Scale bar 50 μm.



t=0 min t=10 min t=14 min t=18 min

t=22 min t=26 min t=28 min t=30 min

P=3.2 kbar ΔT=4.7 K

Figure 3 *In-situ* optical micrographs of sharp fractionated polyethylene (NIST SRM1483, $M_w = 32000$) during isobaric and isothermal crystallisation at $P = 3.2$ kbar and $(\Delta T)_{\text{orth}} = 4.7$ K. The bold arrows ($\rightarrow$) denote the hexagonal crystals while the open ones ($\Rightarrow$) indicate the orthorhombic crystals. Scale bar 50 μm.

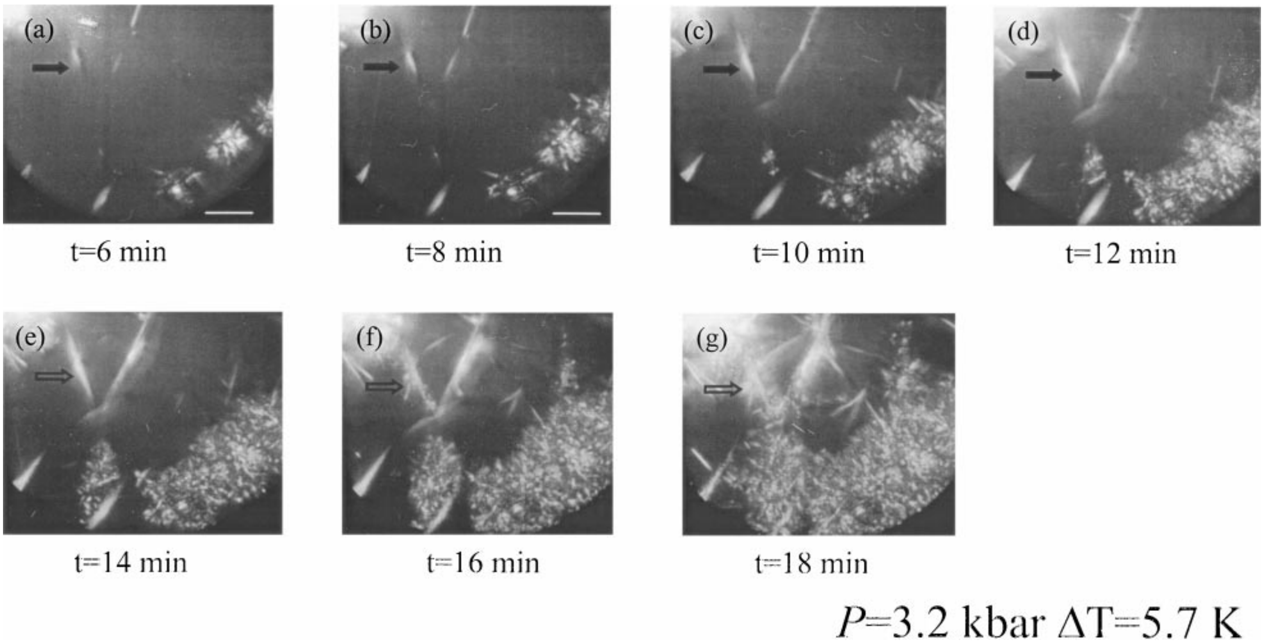


Figure 4 *In-situ* optical micrographs of sharp fractionated polyethylene (NIST SRM1483, $M_w = 32000$) during isobaric and isothermal crystallisation at $P = 3.2$ kbar and $(\Delta T)_{\text{orth}} = 5.7$ K. The bold arrows (→) denote the hexagonal crystals while the open ones (⇒) indicate the orthorhombic crystals. Scale bar 50 μm.

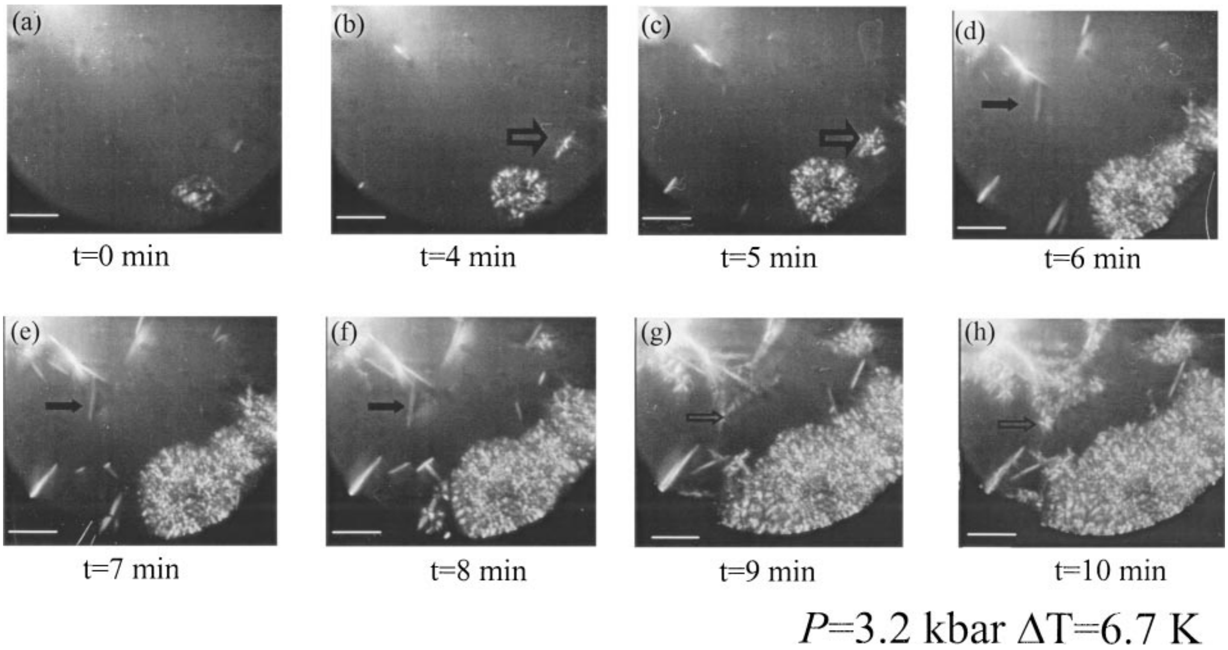


Figure 5 *In-situ* optical micrographs of sharp fractionated polyethylene (NIST SRM1483, $M_w = 32000$) during isobaric and isothermal crystallisation at $P = 3.2$ kbar and $(\Delta T)_{\text{orth}} = 6.7$ K. The bold arrows (→) denote the hexagonal crystals while the open ones (⇒) indicate the orthorhombic crystals. Scale bar 50 μm.

phase. The crystals in the hexagonal phase, observed as birefringent entities, possess chains running perpendicular to the lateral growth direction, and continue to grow. Once the transformation from the hexagonal to the orthorhombic phase occurs, viewed as a sudden change in birefringence, further crystal growth is arrested. The issue of arrest in crystal growth will be given quantitatively in Fig. 8. From the series of optical micrographs it is obvious that with increasing supercooling the residence time for a crystal in the hexagonal phase decreases. The quantitative values on the residence time for the hexagonal phase has been provided elsewhere [14]. Further, it has to be noted that when a crystal transforms into the orthorhombic phase, many crystals grow around the transformed crystal and after a certain time the overall growth of the multicrystal cluster becomes spherical in nature. This is clearly more evident for higher supercoolings like 5.7 and 6.7 K in Figs 4 and 5.

The crystal that has transformed from the hexagonal to the orthorhombic phase appears to become blotchy (or block like). Many crystals seem to grow on the thus transformed crystal. It appears that the just transformed crystal acts as a nucleating centre for other new crystals

(Figs 3e–h, 4e–g, 5b–h). It has to be noted that the crystals growing on the substrate of the transformed hexagonal-orthorhombic crystals are in the *hexagonal phase* [12]. *In-situ* polarising optical microscopy, involving multistage temperature cycling below the equilibrium triple point, revealed that those branched lamellae possess a hexagonal structure, at least initially [12]. During the multistage temperature cycling, under isobaric conditions, it is observed that the new crystals formed on the basal surface of the just transformed crystal from the hexagonal to the orthorhombic phase, melted at the same temperature with the other hexagonal crystals. But crystals in the orthorhombic phase melted at a higher temperature. Further, it has been noticed that unlike the orthorhombic crystals, which do not grow laterally, the new hexagonal crystals continue to grow. Moreover when the sample is left to anneal above the melting temperature of the hexagonal phase (Region III in Fig. 1) no crystal growth is observed. This phenomenon will be explained in detail later in this article. Since the hexagonal to orthorhombic transition is a solid-solid phase transformation and is a nucleation controlled process, the hexagonal crystals growing on the orthorhombic substrate are much easier to transform into the thermodynamically stable orthorhombic phase because nucleus for the transformation already exists. Fig. 6 shows the Transmission Electron Micrograph of isolated single crystals surrounded by lamellae spread perpendicular to its basal surface, thus confirming the high nucleation activity of the once transformed single crystal.

On the other hand, the crystals which did not transform into the orthorhombic phase continue to grow and no other crystals can be observed in their vicinity (for example see Fig. 3g and h). It seems that these crystals are pulling chains from the melt during the growth process. At this instant it need to be mentioned that the single crystals of polyethylene have a tapered morphology, suggesting that in the very initial stages of crystallisation chains are folded [12, 13, 27]. Due to the enhanced chain mobility within the hexagonal phase, which arises from a more open lattice and thus weak Van der Waals interaction between the neighbouring chains, refolding to longer fold lengths is facilitated which leads to full chain extension, a thermodynamic requirement in polymer crystallisation. This implies that the crystals in the hexagonal phase grow simultaneously along the lateral and the thickening direction. To fill in the cavities, as generated during crystal growth, mainly because of simultaneous thickening, more material is needed to be pulled from the surface of the growing crystal. This may be an explanation for the absence of new crystal formation in the vicinity of the growing crystal [9, 14, 22].

3.3. Multilayering: Primary and secondary thickening

A crystal, in the hexagonal phase, can also stop growing because of morphological reasons. For example, growth in the lateral direction may get restricted because of impingement with another crystal, growing in the melt. The crystal growth along the thickness direction may also stop because of multilayering – i.e. the growth of crystals on top of each other, due to a screw dislocation. A series of electron micrographs summarised in Fig. 7, suggests that with increased supercooling, at a fixed pressure, multilayering becomes more and more prominent, even when a crystal is in the hexagonal phase. These observations suggest that with increasing supercooling, as the growth rate increases laterally, and along the thickening direction, screw dislocations also become prominent. It is also noticable that once a crystal transforms from the hexagonal to the orthorhombic phase, several crystals grow on top of the transformed crystal without the uniform registration of the newly formed crystals, ultimately leading to spherical like growth of crystal aggregates (Figs 4 and 5). A combination of the multilayering and the spherical like growth of crystal aggregates gives an insight into the initial stages of spherulitic formation. In Fig. 7b,

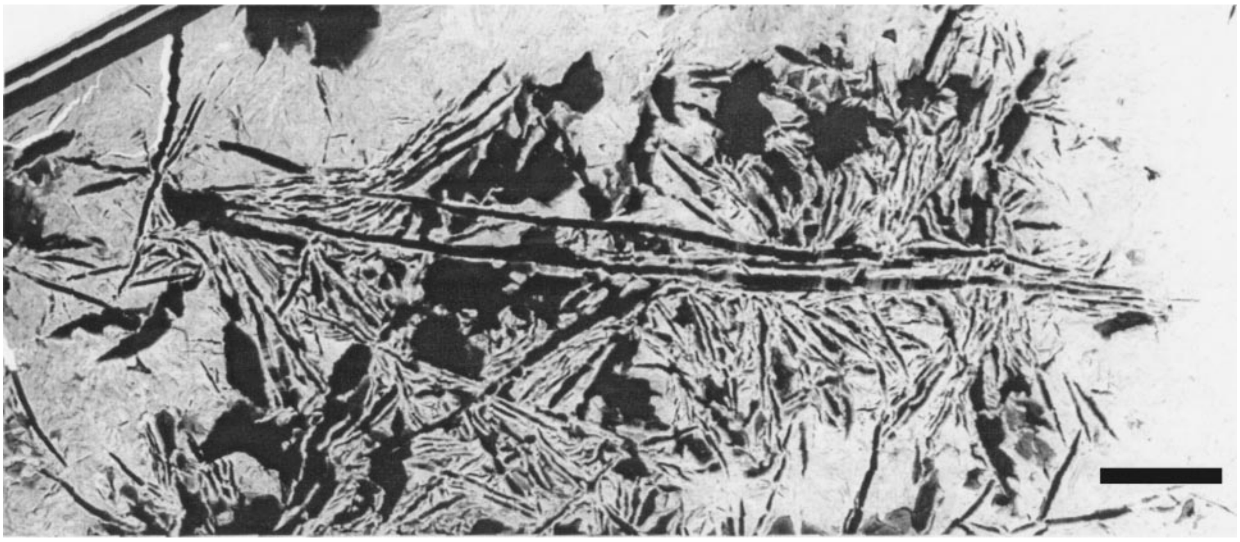


Figure 6 Transmission electron micrograph showing single crystals grown at 3.1 kbar and $(\Delta T)_{\text{hex}} = 4.5$ K surrounded by lamellae perpendicular to the basal surface. The spread lamellae crystallised after the transformation of the single crystals from the hexagonal to the orthorhombic phase. Scale bar is 3.5 μm.

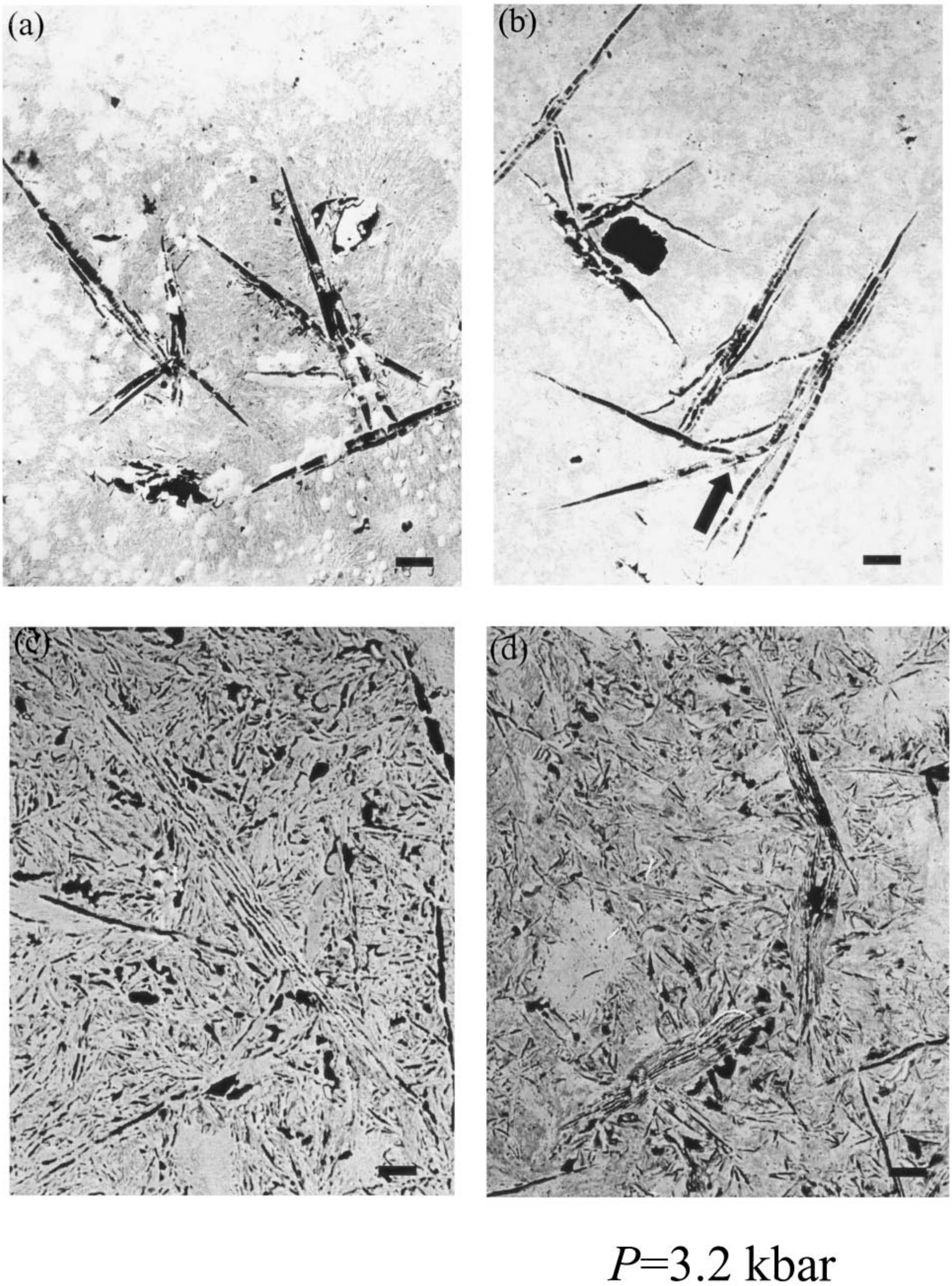


Figure 7 Transmission electron micrograph showing multilayering at different supercoolings and constant pressure of 3.2 kbar. (a) $(\Delta T) = 4$ K, (b) $(\Delta T) = 4$ K; bending of the crystals is marked by →, (c) $(\Delta T) = 8$ K, (d) $(\Delta T) = 10$ K. It is to be noticed that the overall shape of the multilayered crystals as viewed edge-on has resemblance with the crystals observed by optical microscopy (as birefringent entities, when viewed edge-on) when growing in the hexagonal phase. Scale bar is 1 μm.

the crystal marked by the arrow shows how a lamella bends when it comes into contact with another crystal (as viewed edge-on). This indicates the flexibility of crystal growth in the hexagonal phase.

The thickening growth in an isolated single crystal corresponds to primary thickening. Once crystals are multi-layered, lying on top of each other, further thickening requires penetration of chains within the adjacent crystals. The process of further thickening in the solid state is usually referred to as secondary thickening. This is feasible only when the chains within the crystals adjacent to each other are in regular registration, thus facilitating further lamellae thickening in the preferred morphology only, i.e. the morphology having regular chain registraton with adjacent crystals. An extensive study performed by Hikosaka *et al.* [14, 15] showed that both the primary thickening and the lateral thickening have the same energy barrier to overcome for crystal growth.

At a fixed pressure, as the residence time for the crystals in the hexagonal phase decreases exponentially with increase in supercooling, the average lamellar thickness also shows an exponential decay [14]. These results strongly suggest that the primary lamellar thickness is dependent on the crystals residence time in the hexagonal phase. Fig. 8, shows variation in the crystal length with crystallisation time for different supercoolings at constant pressure. The slope of the curve (in Fig. 8) at a fixed degree of supercooling and a fixed pressure represents the crystal growth rate. It is to be noted that with an increase in supercooling, the crystal growth rate increases. Since in the hexagonal phase crystal growth occurs simultaneously along the lateral and the thickening direction, the growth rate can be measured from a series of electron micrographs showing isolated single crystals. A detailed description of the methods used to quantitatively determine values for the lateral and thickening growth rates is provided elsewhere [12, 14]. Table I shows numerical values for such observations. Thus giving an insight into chain mobility along the *c*-axis in the hexagonal phase. From Fig. 8 it is evident that once a crystal transforms into the orthorhombic phase, crystal growth stops, at least in the lateral direction. The residence time for crystals in the hexagonal phase decreases with increase in supercooling.

From the results summarised above in Sections 3.1 to 3.3 important implications for polymer crystallisation can be drawn and these will be discussed in the following two sections.

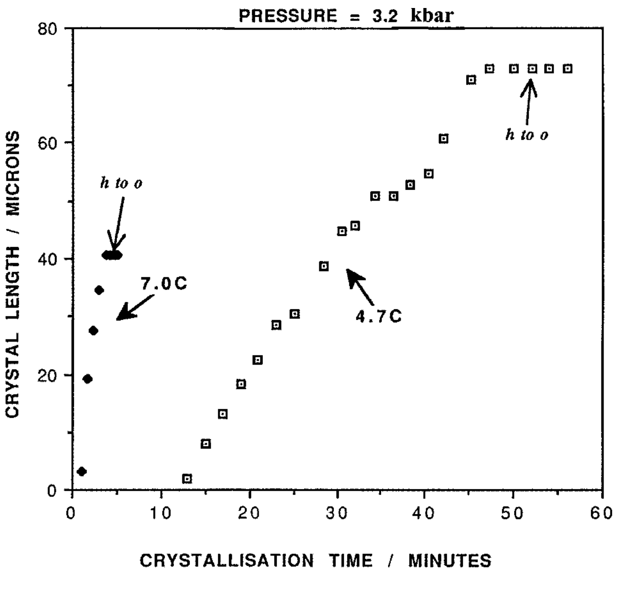


Figure 8 Variation of crystal length with crystallisation time for two different supercoolings, $(\Delta T)_{\text{hex}} = 4.7$ K and $(\Delta T)_{\text{hex}} = 7.0$ K, at 3.2 kbar.

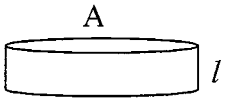
TABLE I

$(\Delta T)_{\text{hex}}$ (°C)	Pressure = 3.2 kbar *lateral growth rate* (nm/sec)	*thickening rate* (nm/sec)
4.0	21.8	0.8
6.0	112.5	5.2
8.0	317.0	26.4
10.0	652.0	37.2–55.8

3.4. Size influence in phase transformation: Stable, metastable and transient states of a phase

In this section we will address the issue of metastability of the hexagonal phase below the equilibrium triple point. From the unique tapered morphology of the single crystals, it was concluded that at the early stages of crystallisation, due to kinetic reasons, chains are in the folded state [12]. As a crystal grows, chains slide along the *c*-axis to thicken the crystal. When the experiments are performed in Region II (Fig. 1), i.e. within the thermodynamic stability region for the orthorhombic phase, a crystal initially in the hexagonal phase transforms into the thermodynamically stable orthorhombic phase. These observations strongly suggest a third parameter, i.e. the crystal size in the pressure-temperature phase diagram. The experimental observations can be expressed mathematically.

In general, to a first approximation, the Gibbs Free energy of a crystalline phase having a surface area A and thickness l can be expressed for the orthorhombic (G_{o}) and the hexagonal (G_{h}) phase by the following expressions:



$$G_{\text{o}} \cong (H_{\text{o}} - TS_{\text{o}}) + 2\sigma_{\text{o}}A \quad (1)$$

$$G_{\text{h}} \cong (H_{\text{h}} - TS_{\text{h}}) + 2\sigma_{\text{h}}A \quad (2)$$

Where, H and S are enthalpy and entropy for the specific phases, respectively and σ the end surface free energy.

The difference in Gibbs Free energy between the orthorhombic and the hexagonal phase in polyethylene can be expressed as:

$$\begin{aligned}\Delta G &= G_{\text{o}} - G_{\text{h}}\\ &= [-(H_{\text{h}} - H_{\text{o}}) + T(S_{\text{h}} - S_{\text{o}})] - 2(\sigma_{\text{h}} - \sigma_{\text{o}})A\end{aligned}$$

The orthorhombic phase will be thermodynamically stable when $\Delta G < 0$.

At the transition temperature $T^{\infty}_{\text{h}\to\text{o}}$ of a crystal having infinite thickness, $\Delta G^{\infty}_{\text{h}\to\text{o}} = 0$ and

$$H_{\text{o}} - T^{\infty}_{\text{h}\to\text{o}}S_{\text{o}} = H_{\text{h}} - T^{\infty}_{\text{h}\to\text{o}}S_{\text{h}}$$

Therefore,

$$S_{\mathrm{h}} - S_{\mathrm{o}} = \frac{(H_{\mathrm{h}} - H_{\mathrm{o}})}{T^{\infty}_{\mathrm{h}\to\mathrm{o}}}$$

Thus,

$$\Delta G = \left[-(\Delta H)_{\mathrm{h}\to\mathrm{o}} \frac{(\Delta T)_{\mathrm{h}\to\mathrm{o}}}{T^{\infty}_{\mathrm{h}\to\mathrm{o}}} + 2(-\Delta\sigma)A \right] \quad (3)$$

Making an assumption that the volume for both the hexagonal and the orthorhombic phase is the same, to the first approximation the Gibbs free energy per unit volume can be expressed as

$$\Delta g = \frac{\Delta G}{V} = \left[-(\Delta h)_{\mathrm{h}\to\mathrm{o}} \frac{(\Delta T)_{\mathrm{h}\to\mathrm{o}}}{T_{\mathrm{h}\to\mathrm{o}}} + \frac{2(-\Delta\sigma)}{l} \right] \quad (4)$$

where Δh is the enthalpy per unit volume and $(\Delta h)_{\mathrm{h}\to\mathrm{o}} = h_{\mathrm{h}} - h_{\mathrm{o}} > 0$ because the transition is endothermic in nature as observed by high pressure DSC [23]; $(\Delta T)_{\mathrm{h}\to\mathrm{o}} = T_{\mathrm{h}\to\mathrm{o}} - T > 0$, is a supercooling defined from the equilibrium transition temperature $T^{\infty}_{\mathrm{h}\to\mathrm{o}}$ for the infinite crystal size; and $(-\Delta\sigma) = \sigma_{\mathrm{o}} - \sigma_{\mathrm{h}} > 0$ is the change in the end surface free energy for the hexagonal to the orthorhombic transition, as has been discussed earlier [21].

At a critical thickness of the crystal $l = l_{\mathrm{cr}}$, $\Delta g = 0$. For $l > l_{\mathrm{cr}}$, Δg becomes negative, thus a crystal initially in the thermodynamically stable hexagonal phase will be no longer stable and the transformation from the hexagonal to the orthorhombic phase will become possible.

Further thickening in the metastable hexagonal phase will solely be a consequence of kinetics, rather than of thermodynamics.

In our case from Equation 4 we can derive the following expression:

$$T_{\mathrm{h}\to\mathrm{o}} = T^{\infty}_{\mathrm{t}} \cdot \left[1 - \left(\frac{2(-\Delta\sigma)}{l(\Delta h)_{\mathrm{h}\to\mathrm{o}}} \right) \right] \quad (5)$$

since solid to solid transformation from the hexagonal to the orthorhombic phase is a nucleation controlled process. The rate of nuclei formation for the orthorhombic phase within the hexagonal crystal can be expressed as

$$r_{\mathrm{h}\to\mathrm{o}} = \frac{kT}{h} \exp\left(\frac{-\Delta G}{k(\Delta T)_{\mathrm{h}\to\mathrm{o}}} \right); \quad (6)$$

where ΔG is the nucleation barrier.

Once a nucleus is formed a metastable crystal is in a transient state. The transition time of the transient hexagonal phase into the thermodynamically stable orthorhombic phase can be expressed by the formation of the nucleus and its propagation from its origin to the overall crystal.

From the given mathematical expressions, it is evident that a crystal initially in a hexagonal phase passes through four different states before the transformation to the thermodynamically stable orthorhombic phase is reached:

(a) thermodynamically stable region for the hexagonal phase i.e. below $l < l_{\mathrm{critical}}$

(b) metastable region for the hexagonal phase; though a crystal is thermodynamically unstable further thickening is a kinetic process i.e. $l > l_{\mathrm{critical}}$, before a nucleus for the transformation is formed

(c) since the solid-solid phase transition is a nucleation controlled process, the residence time for a crystal to stay in the metastable hexagonal phase depends on the nucleation barrier which the crystal has to overcome to go in the thermodynamically stable orthorhombic phase.

(d) once a nucleus for the orthorhombic phase is formed, the time required for a crystal to stay in the hexagonal phase (i.e. in its transient state) depends on the propagation time of the nucleus over the whole crystal.

An intriguing possibility, having implications in condensed matter in general, arises when phase size is taken into consideration in the phase diagram. A similar hypothesis for the size dependence has been invoked in the past for the stability of different phases in pure substances. It is well established that for an infinite sphere (or crystal), an equilibrium triple point Q^{∞} can be defined as an intersection of three planes i.e. solid-vapour plane, liquid-solid plane and vapour-liquid plane in the pressure-temperature phase diagram. For a finite sphere (or crystal), the triple point lies below the equilibrium triple point in the pressure-temperature phase diagram [24].

In combination with the thermodynamic concepts laid out in the paragraph above, when an issue of metastability during crystallisation is invoked, Ostwald in 1897 stated that the thermodynamic stable state is reached through a metastable state of a matter, via a phase which grows faster [25]. For example on cooling from vapour, the first nucleus appears to be liquid even though the temperature may be well below the freezing point of the liquid. Ostwald's stage rule states that the phase transformation will always start with the phase (polymorph) which is stable down to the smallest size, irrespective of whether this is stable or metastable when fully grown. In the case where the phase transformation is nucleation controlled, a connection between the kinetic and thermodynamic considerations can be readily established.

When considering polymers a unique feature of varying size dependence with crystal growth in terms of thermodynamic stability arises, i.e. the crystal size increases with crystallisation time as shown above for polyethylene. This leads to an unique phenomenon in polymers, that a phase which is initially thermodynamically stable may no longer be stable after crystal growth, therefore passing through a metastable state before a thermodynamically stable phase intervenes. The latter will be a nucleation controlled phenomenon.

Similar hexagonal phases with enhanced chain mobility are present in trans-1,4 polybutadiene at atmospheric pressure, thus making the experimentation more convenient [26, 17, 27]. The monoclinic to the hexagonal phase transition is observed on heating at atmospheric pressure. The equilibrium phase transition temperature from the monoclinic to the hexagonal phase, for the infinite lamellae thickness, is found to be approximately 80°C [26]. Like polyethylene, crystallisation within the thermodynamically stable hexagonal phase leads to the formation of lamellae several hundred nanometers thick, of the extended or nearly extended chain type [27]. Lamellar thickness was found to increase by several tens of nanometers in solution-crystallised mats, having an initial lamellae thickness of 10.4 nm, immediately upon heating above the monoclinic to hexagonal transition temperature [27]. For these finite crystals having thickness of 10.4 nm, the monoclinic to hexagonal phase transformation occurs at 68°C. In addition, a unique phenomenon of isothermal phase reversal in the solution-crystallised mats was observed on annealing just above the transition temperature. That is, on annealing just above the monoclinic to hexagonal transition temperature at 68°C (which is below the equilibrium transition temperature of 80°C for the monoclinic to hexagonal transition) the crystals transformed initially to the hexagonal phase and subsequently back into the thermodynamically stable monoclinic phase, as shown by *in-situ* WAXS results presented in Fig. 9. On heating again the transformed crystals in the monoclinic phase transform back into the hexagonal phase before melting occurs. These observations when combined with SAXS strongly supported the above viewpoint that crystal size depends upon the phase transition [27].

Thanks to the synchrotron radiation facility at Grenoble, it has been possible to observe the phenomenon of isothermal phase reversal in polyethylene at the elevated pressures and temperatures even for inaccessible experimental conditions. For our studies, solution-crystallised films of Ultra High Molecular Weight Polyethylene were prepared and used as a model system because of the well-defined regularly stacked lamellae having a thickness of 12.5 nm [18]. The film was placed between two diamonds in the piston cylinder type pressure cell of Hikosaka [19]. The cell was mounted in a high-resolution powder diffraction beamline, ID11/BL2 (ESRF, Grenoble). The following routes, shown schematically in Fig. 10, were used for the *in-situ* pressure-temperature experiments [28].

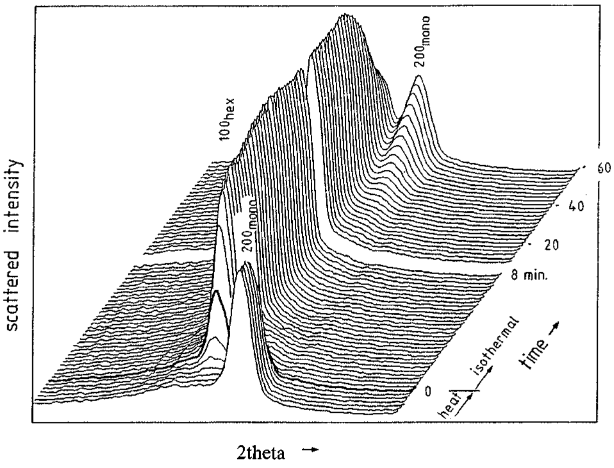


Figure 9 Wide angle X-ray diffraction experiment showing isothermal phase reversal. The monoclinic $(200)_{mon}$ and the hexagonal $(100)_{hex}$ reflections can be seen. The single crystal mats are heated at 3°C/min to 68.5°C and after that the temperature was kept constant. In the beginning the monoclinic to the hexagonal phase can be observed and subsequently the reverse from the hexagonal to the monoclinic phase occurs upon annealing.

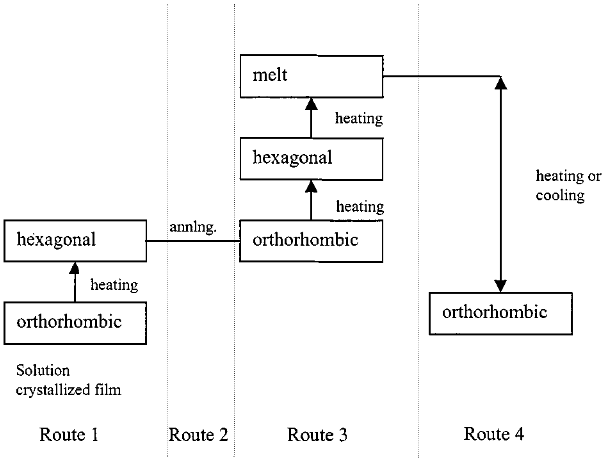


Figure 10 Schematic drawing of the experimental routes adopted in the *in-situ* X-ray study of the solution crystallised UHMW-PE at constant pressure of 1.6 kbar, i.e. below the equilibrium triple point.

Route 1. Isobaric heating (Fig. 11a): The solution-crystallised UHMW-PE sample was heated at a fixed pressure of 1.6 kbar. The X-ray diffraction pattern at lower temperatures shows the characteristic orthorhombic (110) and (200) reflections . Upon heating, the (100) reflection of the hexagonal phase appears at approximately 195°C, next to the (110) reflection of the orthorhombic phase. Note that the pressure of 1.6 kbar is far below the pressure corresponding to the triple point [15] and the hexagonal phase is observed within the region of the thermodynamically stable orthorhombic phase.

Route 2. Isothermal and isobaric annealing (Fig. 11b): Upon annealing at 204°C at a pressure of 1.6 kbar (route 2 in Fig. 10), the (100) reflection of the hexagonal phase disappears again, after approximately 5 minutes, whereas the orthorhombic reflections gain in intensity.

Route 3. Isobaric heating (Fig. 11c): During isobaric heating at a rate of 2°C/min (route 3 in Fig. 10), the hexagonal phase re-appears and before final melting at 220°C, the characteristic (100) reflection of the hexagonal phase gains intensity at the expense of the (110) and (200) reflections of the orthorhombic phase.

Route 4. Isobaric cooling (Fig. 11d): Upon cooling from the melt at the same constant pressure of 1.6 kbar, only the orthorhombic phase is visible on crystallisation. If the sample is heated once again to the melting temperature, the hexagonal phase is no longer observed (route 4 as shown in Fig. 10).

From this set of experiments, it can be concluded that the melting of the lamellar crystals of approximately 12 nm (initial) thickness proceeds via the hexagonal phase much below the equilibrium triple point

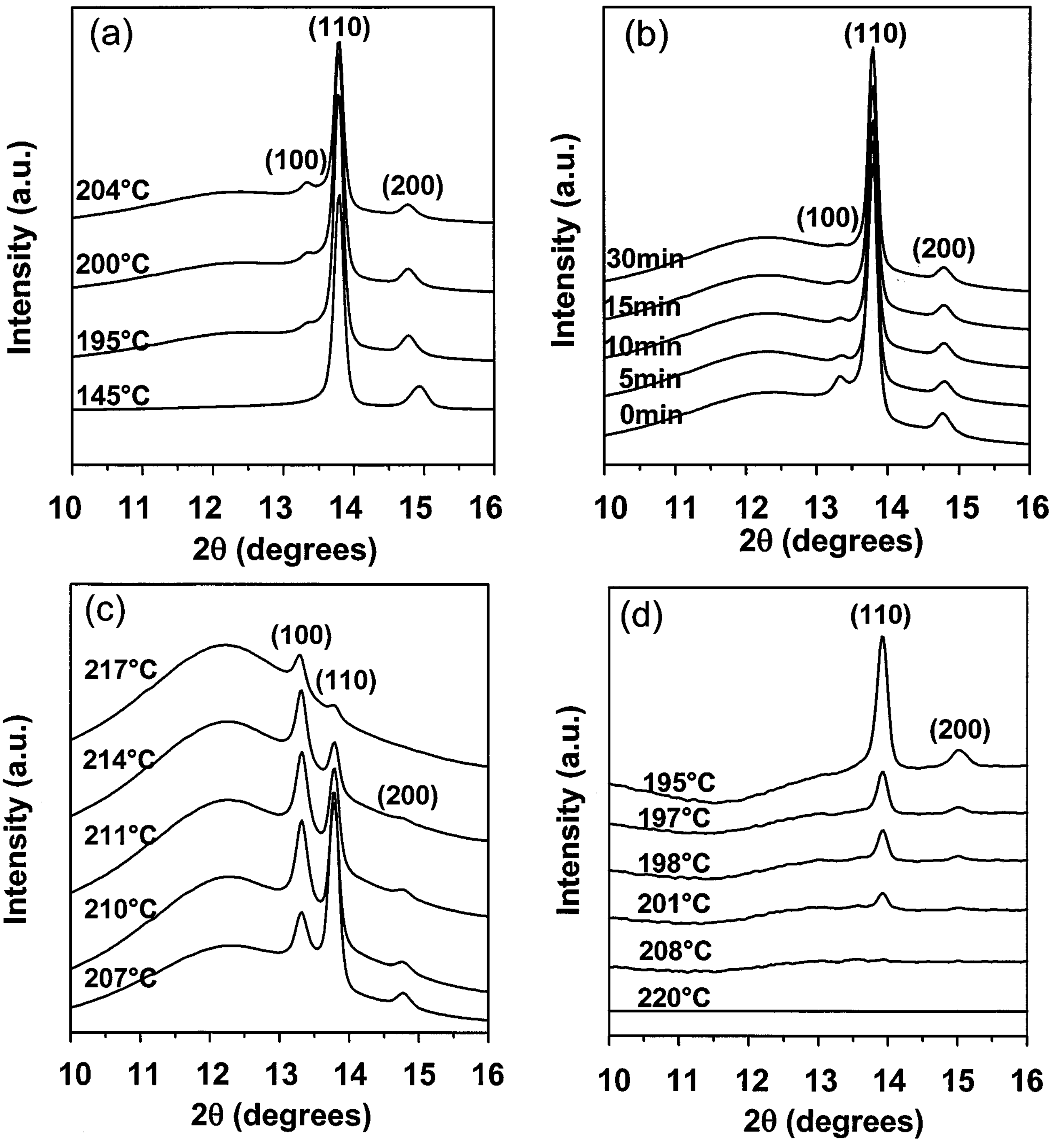


Figure 11 X-ray diffractogram of solution-crystallised UHMW-PE at fixed pressure of 1.6 kbar. (a) Next to the (110) and (200) reflections typical for the orthorhombic unit cell of polyethylene, incoming of the hexagonal (100) reflection with increasing temeperature at constant pressure can be observed. (b) The disappearance of the hexagonal (100) reflection during isothermal and isobaric annealing. The orthorhombic (110) and (200) reflections gain the intensity. (c) The melting of the crystals via the hexagonal phase can be observed, similar to the melting behaviour anticipated above the triple point. (d) The crystallisation from the melt directly ino the orthorhombic phase can be observed; to observe the very initial stage of crystallisation, each diffraction pattern is subtracted from the diffuse melt spectrum.

and within the region of the thermodynamically stable orthorhombic phase. After complete melting and upon re-crystallisation from the melt, the appearance of the hexagonal phase could not be observed again. During heating and annealing of solution-crystallized samples, the thickness of the lamellar crystals increases, especially in the mobile hexagonal phase [29, 30, 31, 13, 12] with the result that crystals initially in the hexagonal phase transform first into a transient metastable hexagonal phase and subsequently back to the thermodynamically stable orthorhombic phase. The appearance and disappearance of the hexagonal phase during heating and annealing at pressures below the equilibrium triple point can be related to the initial lamellar thickness. Crystallisation from the melt usually leads to much thicker lamellar crystals, compared to solution-crystallized samples, and consequently no crystals in the hexagonal phase are observed on cooling at the same pressure and temperature [32].

These observations have been confirmed and further strengthened by performing the same set of the experiments on irradiated solution crystallised films. It was discussed above, that in polymers because of the chain mobility along the *c*-axis the crystal size can alter, unlike with other materials. However, the chain mobility along the *c*-axis can be suppressed by crosslinking the amorphous zone between the lamellae by irradiation. If the irradiation dose is sufficiently high the lamellae thickening process can be completely suppressed. With the help of Small Angle X-ray Scattering it has been shown that the crystal thickening can be fully suppressed on irradiating the solution crystallised films of UHMW-PE by 2000 kGy. Unlike in the unirradiated solution crystallised films of UHMW-PE, crosslinking of the amorphous region can inhibit lamellar thickening even in the hexagonal phase. Therefore, it would be anticipated that even below the equilibrium triple point, once the transformation from the orthorhombic to the hexagonal phase occurs, no phase reversal from the hexagonal to the orthorhombic phase during annealing under isobaric and isothermal conditions could be observed [28]. Moreover, on heating, the irradiated crystals not only transform into the hexagonal phase but also melt via the hexagonal phase at pressures below the equilibrium triple point. The observed melting behaviour is very similar to the one anticipated above the triple point, thus confirming the thermodynamic stability of the hexagonal phase for the small crystals in the thermodynamic stable region of the orthorhombic phase for crystals having infinite lamellar thickness.

To summarise, with a series of experiments on polyethylene and polybutadiene, described above, it has come up strongly that on considering the effect of phase size on the phase diagram an intriguing possibility has arisen. These results suggest that the true thermodynamic stability conditions can invert with size. Specifically, for a polyethylene crystal that is small enough, the hexagonal phase can be the thermodynamically stable phase, even in the pressure-temperature regime where orthorhombic is the thermodynamically stable phase for an infinite crystal-size, as shown in Fig. 12 by dashed lines, having its triple point Q located below Q^{∞}. When this is the case, true metastability need not be involved to account for the observation of a metastable phase appearing first. In fact, here the metastable phase in its very small dimensions, will be the thermodynamically stable phase with an inversion of phase stability on growth, i.e. Q moves towards Q^{∞} with thickening of lamellae. These observations are in accordance with the mathematical expressions provided earlier in this section.

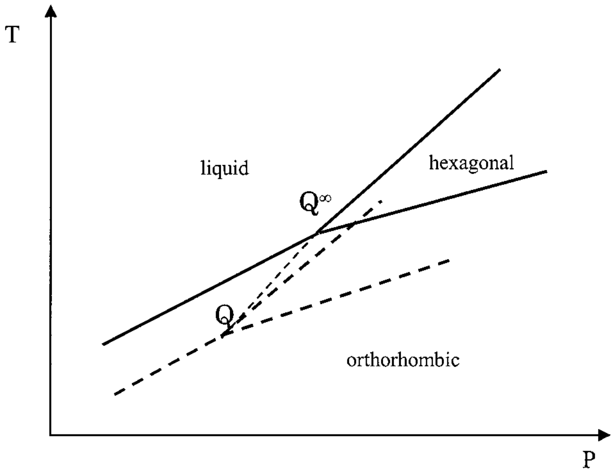


Figure 12 Schematic drawing of the shift of the triple point from Q^{∞} to Q due to the small initial lamellar thickness. Full lines represent the equilibrium phase diagram for the infinite size crystals with Q^{∞} being its equilibrium triple point. Dashed lines represent shifted phase diagram due to the reduced crystal with Q being its triple point. T = temperature, P = pressure.

Further, a Gibbs Free Energy phase diagram can be provided for the experimental observations on the isothermal phase reversal in unirradiated and irradiated UHMW-PE solution crystallised films.

The melting point of lamellar crystals with average thickness l is given by the well-known melting-point depression relationship [33]:

$$T_{\mathrm{m}} = T_{\mathrm{m}}^{\infty}\left[1 - \left(\frac{2\sigma_{\mathrm{e}}}{(l \cdot \Delta H)}\right)\right] \tag{7}$$

As shown in Hoffman-Weeks equation [33], the observed melting point (T_{m}) is dependent on the thickness l, i.e. if l approaches infinity, T_{m} approaches T_{m}^{∞}, the equilibrium melting temperature. σ_{e} is the end surface free energy of the crystals.

The ratio $\sigma_{\mathrm{e}}/\Delta H$ for orthorhombic crystals is greater than for hexagonal crystals [21]:

$$\left(\frac{\sigma_{\mathrm{e}}}{\Delta H}\right)_{\text{orth.}} = 3.5\left(\frac{\sigma_{\mathrm{e}}}{\Delta H}\right)_{\text{hex.}} \tag{8}$$

This implies that for a folded-chain crystal of the same average lamellar thickness l the difference $(T_{\mathrm{m}}^{\infty} - T_{\mathrm{m}})$ is larger for the orthorhombic crystals than for the hexagonal ones. Equivalently, the Gibbs free energy for a lamellar crystal with thickness l is closer to the equilibrium Gibbs free energy G^{∞} in the case of a hexagonal crystal structure. Based on these experimental facts, the Gibbs free energy diagram in Fig. 13, could be constructed to account for the experiments described in Fig. 11. For the sake of simplicity, the Gibbs free energy functions in Fig. 13 are drawn as straight lines, which is in fact an oversimplification but not an essential requirement for the present discussion.

In Fig. 13, the Gibbs free energy at pressure P as a function of temperature T is shown for orthorhombic and hexagonal crystals. Below the equilibrium triple-point, the Gibbs free energy of a perfect (extended-chain) orthorhombic crystal, G_{orth}^{∞}, is lower than that of a perfect (extended-chain) hexagonal crystal, G_{hex}^{∞}. The Gibbs free energy of the folded-chain crystals is higher due to the contribution of the surface free energies. Assuming for the present discussion that the free energy curves for the folded-chain crystals are parallel with the free energy of the extended-chain crystals and taking into account, as discussed above, that for a given lamellar thickness l the free energy is closer to equilibrium for hexagonal crystals, the various curves in Fig. 13 become self explanatory.

If an orthorhombic folded-chain crystal with thickness l, discontinuous line in Fig. 13, is heated at a constant pressure P, the corresponding free energy curve crosses the free energy curves of hexagonal folded-chain crystals. At the crossing point A_1, the crystal

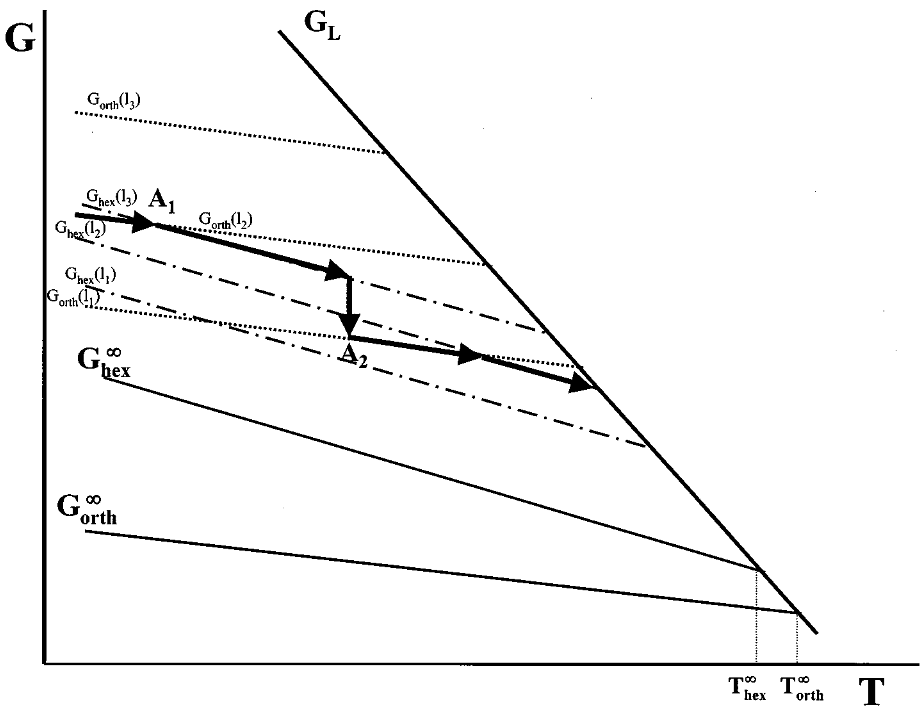


Figure 13 A thermodynamic explanation for the experimental observations made during heating and annealing at the pressure of 1.6 kbar (i.e. below the equilibrium triple point). Black bold lines are equilibrium free energy lines for extended chain orthorhombic and hexagonal crystals, (·········) are the free energy lines for folded-chain orthorhombic crystals possessing different thickness $l_1 > l_2 > l_3$, (–·–·–·–·–·–) are the free energy lines for folded-chain hexagonal crystals possessing different thickness $l_1 > l_2 > l_3$. G = Gibbs free energy, T = temperature.

can transform from an orthorhombic into a hexagonal crystal structure since the decrease in free energy with increasing temperature, $(\mathrm{d}G/\mathrm{d}T)$, is faster in the case of hexagonal crystals. This situation is encountered during isobaric heating (see Fig. 6a). Upon annealing at temperature T, Fig. 6b, the hexagonal crystals thicken in order to decrease the Gibbs free energy towards the equilibrium value. However, during annealing and thickening at temperature T, the driving force $(G^{\infty}_{\mathrm{hex}} - G_{\mathrm{hex}})$ becomes smaller and the thickening process slows down and finally is arrested, for example at point A_2. The driving force $(G^{\infty}_{\mathrm{orth}} - G_{\mathrm{orth}})$ at temperature T and point A_2 is higher than $(G^{\infty}_{\mathrm{hex}} - G_{\mathrm{hex}})$ and, consequently, the crystal could transform back into the orthorhombic crystal structure. Upon further heating, Fig. 11c, once again, the Gibbs free energy curve corresponding to the orthorhombic crystals crosses many times the Gibbs free energy curves of hexagonal folded-chain crystals. Consequently a transformation from orthorhombic into hexagonal crystals can appear again before the final melting into the liquid phase.

In the case of irradiated samples thickening during heating and annealing is hindered by the crosslinks present in the amorphous region of the lamellar morphology. Nevertheless, the transformation from the orthorhombic into the hexagonal phase during heating at pressures below the equilibrium triple point will occur at the crosspoint $A1$ (Fig. 13) because decrease of Free energy with increase in temperature is faster for the hexagonal crystals than for the orthorhombic ones. However, during isothermal and isobaric annealing, thickening in the mobile phase is arrested and melting proceeds via the same line corresponding to the free energy of the hexagonal folded chain crystals having thickness l_3 for the hexagonal crystal. Due to the absence of lamellar thickening the triple point of the P-T phase diagram stays "arrested" at the lower values of pressure and temperature (position Q^{∞} in Fig. 12), implying that the shift in the triple point is related to the crystal size.

The authors hasten to add that the above explanation refers only to thermodynamic parameters. The rate of transformation from the orthorhombic into the hexagonal crystals and vice versa, however, is dependent on kinetic barriers between the two crystal structures as stated in the thermodynamical section discussed above. The transformation from the orthorhombic into the hexagonal crystal structure involves nucleation and growth [15] and consequently, the occurrence of a metastable hexagonal phase and the rate of transformation from orthorhombic into the hexagonal crystal structure and vice versa, is system dependent and will depend upon parameters like the initial morphology such as crystal thickness, molar mass and pressure. In fact, preliminary experiments on other solution-crystallized polyethylene samples, for example a fractionated sample kindly provided by the National Institute of Standard Technology, possessing a M_{w} of 32 kg·mole^{-1} and a molecular weight dispersion of 1.11, showed that a metastable hexagonal phase appeared at even lower pressures, for example as low as 1 kbar.

3.5. Implications to crystallisation at atmospheric pressure

The observations summarised above, together with the Region III in the proposed schematic pressure-temperature phase diagram (Fig. 1b) raises further implications in our understanding of crystallisation at atmospheric pressure. Our observations have been that, even below the equilibrium triple point, crystallisation always proceeds via the phase which grows fastest even if it is not a thermodynamically stable phase, obeying Ostwald's stage rule. In the proposed schematic phase diagram in Fig. 1b, region III is defined as the region between the melting temperature of the hexagonal and the orthorhombic crystals within, the pressure-temperature phase diagram.

Below the equilibrium triple point in the pressure-temperature phase diagram, melting of the crystals that have transformed from the hexagonal to the orthorhombic phase occurs directly without transformation; an observation in contradiction to the anticipated melting behaviour above the triple point. The difference between the melting temperature for the orthorhombic and the hexagonal crystals increases with the decreasing pressure. Thus below the equilibrium triple point a crystallisation temperature can be defined by at least two supercoolings, one from the melting temperature of the hexagonal phase and the other from the orthorhombic phase. Since the difference between the melting temperatures for the orthorhombic and the hexagonal phase increases with decreasing pressure and the melting temperature for the orthorhombic phase is higher than the hexagonal phase, the supercooling defined from the orthorhombic phase is always higher than the one defined from the hexagonal phase. Fig. 14 shows the opening of region III with decreasing pressure for two different sharp fractionated molecular weights of polyethylene synthesised at the laboratory scale, obtained from NIST. The data point shown in the phase diagram has been obtained by *in-situ* melting of the single crystals (extended chain as confirmed later by electron microscsopy) under isobaric conditions [13]. Since the melting points for the hexagonal and the orthorhombic crystals, within the pressure-temperature region explored so far, falls along the straight line an estimation of the difference in the melting temperatures versus pressure can be made. The estimated value for the difference in the melting temperatures of the extended chain crystals (as confirmed by Transmission Electron Microscopy) of the orthorhombic and the hexagonal phase against decreasing pressure amounts to 4.375 K/kbar. The value of 4.375 K/kbar extends from the experimentally measured triple point of approximately 3.5 kbar for NIST SRM1483 ($M_w = 32000$, $M_w/M_n = 1.11$). On extrapolating the value from the measured triple point to atmospheric pressure the difference between the melting temperatures for the extended chain crystals of the hexagonal and the orthorhombic phase amounts to approximately 15 K. If we consider the extension of our viewpoint on Region III (defined as no crystal growth region) to atmospheric pressure we are forced to the suggestion that at least 15 K supercooling from the equilibrium melting temperature of the orthorhombic crystals would be required for crystallisation to occur. It means that if we consider the equilibrium melting temperature of polyethylene to be 145°C, the minimum temperature required for crystallisation would be 130°C.

Crystallisation in the hexagonal phase requires much lower supercooling (like 1 K) in comparison with the orthorhombic phase. For crystallisation in the hexagonal phase the supercooling is defined from the melting temperature of the hexagonal crystals. The lower supercooling for the hexagonal crystals is justified because of the much lower end surface free energy desired for the crystallisation to occur in the hexagonal phase. On considering the extrapolation of "no growth region III"

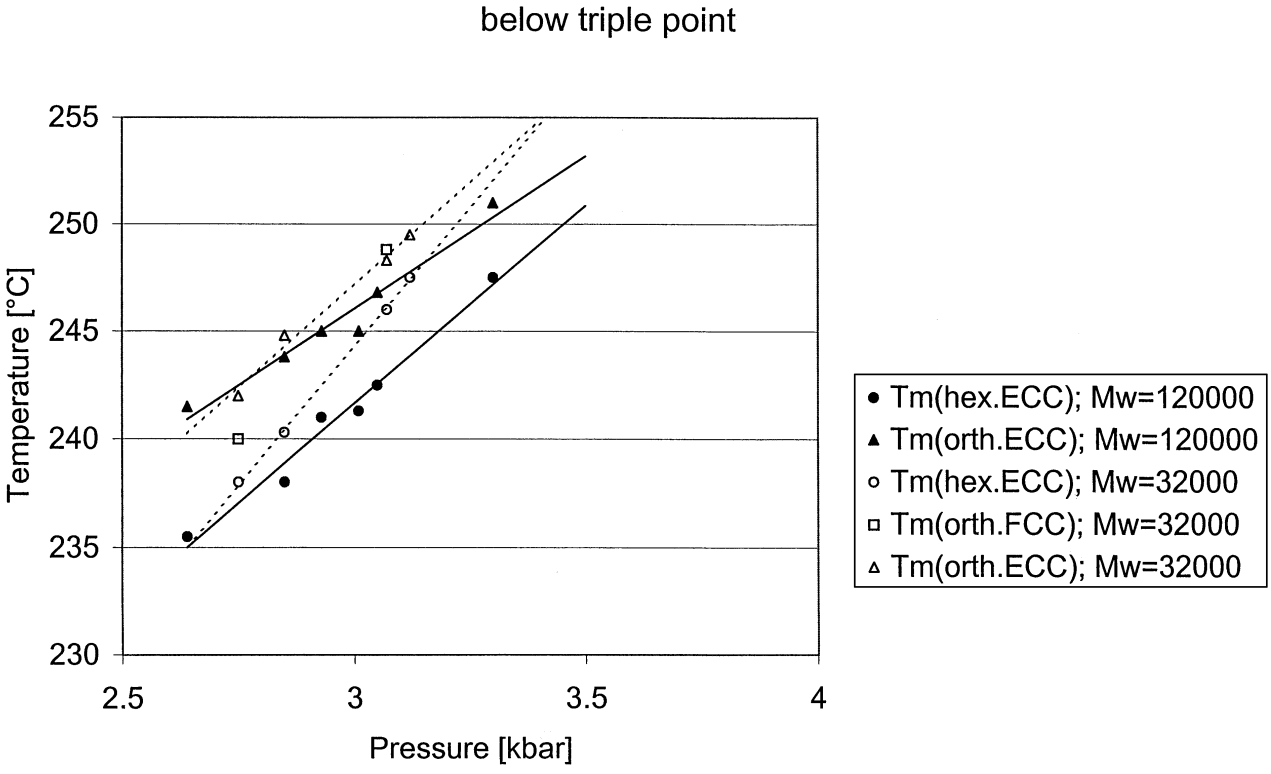


Figure 14 Pressure-temperature phase diagram for two different sharp fractionated polyethylenes (NIST SRM 1483, $M_w = 32000$, $M_w/M_n = 1.11$ and NIST SRM 1484, $M_w = 120000$, $M_w/M_n = 1.2$) obtained by *in-situ* melting of the single crystals at the isobaric conditions.

to atmospheric pressure the melting temperature of the hexagonal phase would be in the vicinity of 130°C, for infinite crystals in an unconstrained bulk.

On considering the following experimental facts the possibility of crystallisation starting via the hexagonal phase at atmospheric pressure can not be ignored. (a) The residence time of crystals in the hexagonal phase decreases with decreasing pressure, (b) a transformed crystal from the hexagonal to the orthorhombic phase acts as nucleation centre for the other crystals, (c) a low energy barrier is required for crystallisation to occur in the hexagonal phase, (d) the crystal on transformation to the thermodynamically stable orthorhombic phase favours the growth of other crystals in the hexagonal phase, ultimately leading to formation of spherulitic morphology (as discussed earlier) and, (e) the hexagonal phase leads to a unique tapered morphology at elevated pressures. Evidence in single crystals for such a unique tapered morphology has been reported at atmospheric pressure also [34].

Recently, in paraffins like hexadecane it has been reported that crystallisation always proceeds via a transient metastable rotator phase before transformation into the thermodynamically stable triclinic phase sets in. Sirota and co-workers [35] have reported these findings for the first time, showing the influence of a metastable phase in crystallisation of paraffins independent of even or odd number of carbon atoms. The observations with paraffins strongly support the above stated hypothesis, especially in polyethylene.

Similar observations on the influence of the mesophase in the early stage of crystallisation have been made for nylons [36], poly-di-alkyl siloxanes [37] and trans-1,4-polybutadiene [27].

Referring to a series of observations on polymers and paraffins we have tried to strengthen the viewpoint that polymer crystallisation from the melt can often proceed via a transient phase which grows faster and has a lower nucleation barrier due to low surface energy in comparison to a thermodynamically stable phase. Several other examples are also known in a range of inorganic and organic materials where a material crystallises via a metastable phase when cooled from the melt. In such a class of inorganic or organic materials a metastable phase may remain stable indefinitely and for very large undercoolings. However, if a nucleus is formed a metastable phase is transient in nature and is bound to transform into the thermodynamically stable phase. In polymers, where a folded-chain crystal is not a thermodynamic stable entity, it is forced to thicken, to minimise its surface free energy. In this process, a crystal which possess small dimensions has a stable phase, when grown, may no longer be a stable phase [38]. In this respect polymers fall into a unique class of materials.

It is important to mention at this point that our views are limited to polymer crystallisation from the melt. We do not have any evidence for crystallisation starting via a transient (or metastable) phase during growth of a crystal from solution. In that respect the existing theories of Hoffman and Weeks, Sadler-Gilmer for polymer crystallisation should hold well and good for crystallisation from solution. However, in melt crystallisation where a transient phase can play a prominent role in the early stages of crystallisation, a theory proposed by Hikosaka [31] can be easily extended for the purpose.

3.6. An application of enhanced chain mobility in the transient phase of ultra high molecular weight polyethylene

The observation of the hexagonal phase below the equilibrium phase diagram could be of great significance, mainly due to the enhanced chain mobility within this phase. Considering the feature of enhanced chain mobility within the hexagonal phase, processing of polyethylene via this phase could become feasible within an experimentally accessible pressure and temperature range, in particular for ultra-high molecular weight polyethylenes (UHMW-PEs). UHMW-PE powder is considered to be intractable via conventional processing routes for polymers due to the excessively high melt-viscosity. Polymer melts are highly viscous and the viscosity strongly increases with increasing molar mass, given by [39]:

$$\log \eta_o = C + 3.4 \log M_w \tag{9}$$

Equation 9 is a universal relationship, where η_o is the zero-shear viscosity, C is a constant depending on the polymer architecture and M_w is the weight-average molar mass. Similar to viscosity, the reptation time is also strongly dependent on the molecular mass, given by the mathematical expression [40]:

$$\tau_r \propto M^{3.4} \tag{10}$$

Thus with increasing molar mass the reptation of the chain from one point to the other becomes increasingly difficult for high molar mass melts. Consequently products based on UHMW-PE, usually processed by compression-moulding, possess fusion defects within the bulk material usually referred to as grain boundaries.

On the other hand, mechanical and physical properties of polymeric materials are also highly dependent on the molar mass. In this respect, UHMW-PE is a well-known type of polyethylene possessing excellent mechanical properties such as wear and friction characteristics compared with any other polymer material. Due to this reason UHMW-PE is selected as the material of choice in high-performance products such as hip- and knee-joint prostheses. In both types of artificial joints, a UHMW-PE part is used as an interface between human body and metal component of the artificial joint. However, the limited lifetime of the artificial joints is related to the failure within the UHMW-PE component. Improper fusion of the UHMW-PE particles is considered as an important issue in extending the lifetime of the artificial joints.

Fig. 14a and b show the optical micrographs (using phase contrast technique) of thin sections cryo-cut from as-recieved and used (for 7 years) UHMW-PE hip cups respectively. Grain boundaries related to the original UHMW-PE powder particles can be observed in both

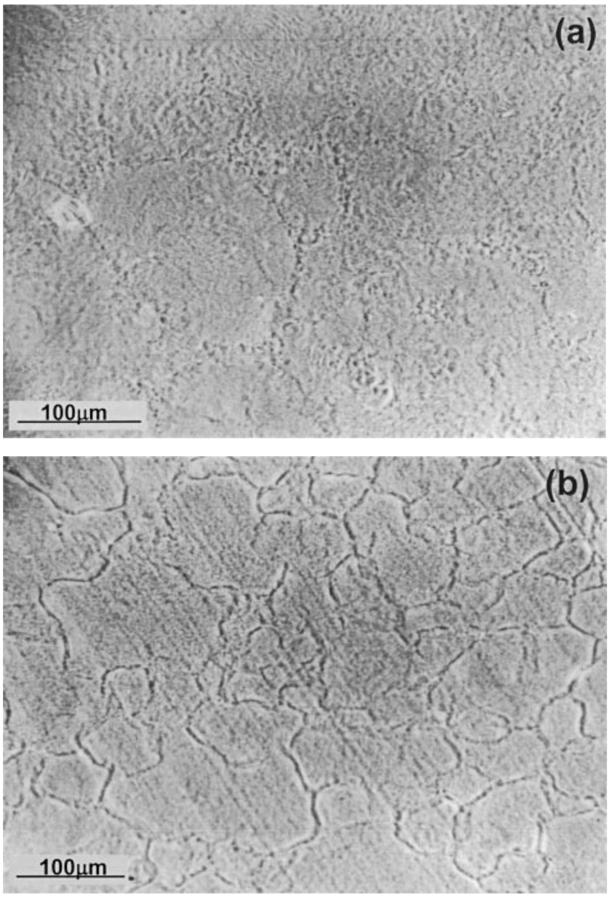


Figure 15 (a and b) Optical micrographs of thin sections of new and used (7 years in the active patient) hip cups respectively. Thin sections of approximately 5 μm thickness were prepared by cryo sectioning the samples of the hip cups. Scale bar: 100 μm.

hip-cups though it is much more pronounced in the used UHMW-PE cup, Fig. 15. Similar grain boundaries are seen in the UHMW-PE inlays used in knee-joint prostheses where it has been well documented that cracks propagate through the improperly fused grains causing delamination [41].

From the series of studies reported above, it has emerged that in the pressure-temperature phase diagram of polyethylene the presence of the hexagonal phase is strongly dependent on initial crystal size. Ongoing research activity in our group suggests that during polymerisation at relatively low temperatures (lower than the dissolution temperature) small metastable folded chain crystals of UHMW-PE can be obtained directly on the catalyst surface. The obtained "nascent morphology" of the folded chain crystals exhibits the hexagonal phase even at pressures of 1 kbar [28]. Taking this into account a novel route has been developed to process grain boundary free products of UHMW-PE. The optical micrographs of fully grain boundary free materials are shown in Fig. 16.

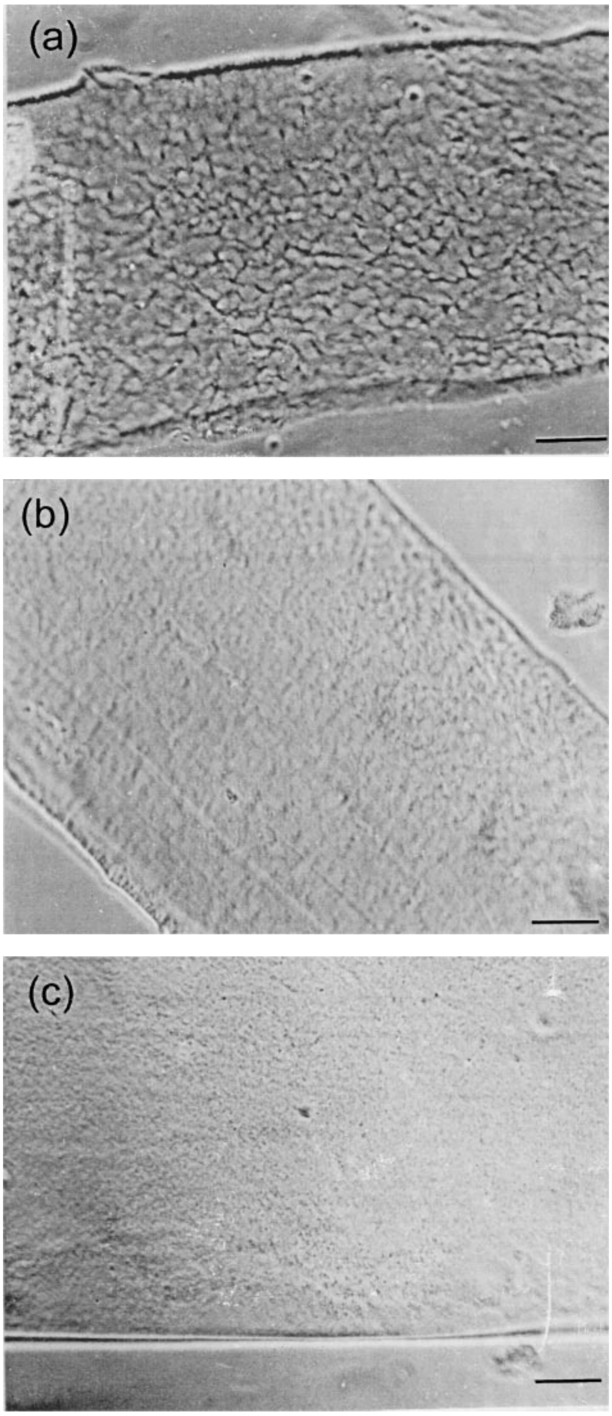


Figure 16 Optical micrographs of thin sections of compression-moulded nascent UHMW-PE. (a) The compression moulded nascent UHMW-PE at 0.8 kbar, heated to 205°C before being cooled to room temperature. (b) The compression moulded nascent UHMW-PE at 1.0 kbar, heated to 205°C before being cooled to room temperature. (c) The compression moulded nascent UHMW-PE at 1.2 kbar, heated 220°C before being cooled to room temperature. Scale bar: 50 μm.

Since crystal formation is a process for chain disentanglement, because of the enhanced chain mobility along the *c*-axis in the hexagonal phase, the phase has been also used to disentangle chains in UHMW-PE. At this stage it is important to mention that the sintering of UHMW-PE powder particles is a combination of a chain disentanglement process and crystal size finally achieved before melting – a requirement to increase the radius of gyration on melting, especially at the interface of the powder particles. This is a desired condition to overcome the problem of "grain boundary" in UHMW-PE. Ward and co-workers have also shown that the hexagonal phase can be used for disentanglement of chains in UHMW-PE.

If the polymerisation temperature is lower than the crystallisation temperature, a growing chain on the catalyst surface will immediately crystallise and fold, leading to disentangled chains. In this respect the disentangled nascent morphology also favours the sintering of UHMW-PE.

4. Conclusions

From the experimental observations reported in this article and elsewhere, it has emerged that in polyethylene even in the thermodynamic stability region for the orthorhombic phase crystallisation always starts via the hexagonal phase. The crystal growth occurs simultaneously in the lateral and the thickening direction. In this article it has been shown experimentally and mathematically that a crystal initially in the stable hexagonal phase, will be no longer thermodynamically stable when fully grown. The crystal, in the thermodynamically metastable state, continues to grow untill a nucleus for the orthorhombic phase is formed. Once the nucleation barrier is overcome, the nucleus thus formed spreads over the whole crystal and further crystal growth is arrested. The residence time for the crystals in the hexagonal phase decreases with decreasing pressure and increasing supercooling.

The growth of a polyethylene crystal after its transformation from the hexagonal to the orthorhombic phase has been followed. The experimental observations are that a crystal transformed in the thermodynamically stable orthorhombic phase promotes the nucleation of many crystals. At the initial stage of crystallisation, the newly formed crystals, formed on the basal plane of an orthorhombic crystal, are in the hexagonal phase. However, for the same pressure-temperature, an isolated crystal growing in the hexagonal phase, stays in the metastable state for a longer time when compared with a crystal growing in the hexagonal phase on the surface of the transformed orthorhombic crystal. This is because in the latter a nucleus required for the transformation from the hexagonal to the orthorhombic phase already exists. These observations further strengthen the hypothesis that solid-solid transformation from the hexagonal to the orthorhombic phase is a nucleation-controlled phenomenon. Further, from a series of optical micrographs, it is evident, that no crystals are formed in the vicinity of a crystal growing within the hexagonal phase.

The issues of primary thickening and secondary thickening have been also invoked. From a series of electron micrographs presented in this article, it can be concluded that with increasing supercooling, at a fixed pressure, regular stacking of crystals becomes prominent, as viewed edge-on. These observations strongly suggest that dislocation formation on the surface of the growing crystal is much easier to form at the higher supercoolings.

The observations like multilayering in the hexagonal phase and the overgrowth of crystals on the newly transformed crystal in the orthorhombic phase, considered in the wider generality, can give further insight in the formation of axialites at low supercoolings and spherulite formation at the higher supercooling at the atmospheric pressure.

The experimental observations summarised in this article have relevance to polymer crystallisation in general, especially on crystallising from the melt. In this article, Figure 1b, it has been proposed that the Region III (i.e. no growth region) in the pressure-temperature phase diagram for polyethylene can be extended to atmospheric pressure. Region III has been defined as the region lying between the melting temperature for the hexagonal phase and the orthorhombic phase below the triple point. A simple calculation provided in the article shows that the extension of the Region III to atmospheric pressure, accounts for 15°C difference in the melting temperature for the hexagonal and the orthorhombic crystals. On considering the no growth region at atmospheric pressure and the experimental observations that crystallisation always starts in the hexagonal phase, suggests that at least 15°C supercooling will be required for the crystallisation to occur at atmospheric pressure. It is to be noted that the supercooling here is defined from the equilibrium melting temperature for the orthorhombic crystals (145°C). The proposed viewpoint is in agreement with the well accepted experimental observations.

With the series of experiments we have stated that the crystallisation in polyethylene, from the melt, should occur via a phase which grows faster though it may not be thermodynamically stable when fully grown. At this point it needs to be mentioned that the end surface free energy and the minimum thickness required for crystallisation to occur in the hexagonal phase is lower than the orthorhombic phase. Therefore, because of both thermodynamic and kinetic reasons, the formation of the nucleus in the hexagonal phase will be relatively easier than in the orthorhombic phase.

The observations on polyethylene have been extended to other polymers like nylons, trans-1,4 polybutadiene, paraffins, poly-di-alkyl siloxanes, polyesters etc. where observations similar to those with polyethylene have been reported. The fundamental basis laidout in the article, especially the issue of phase reversal with crystal size, has been extended for applications like sintering of ultra high molecular weight polyethylene. Recently, Andrew Keller and Stephen Cheng together [42] have published a review article expressing their views on the metastable phases of polymers, having implications in the condensed matter physics.

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