Crystallization of Linear Polyethylene from Melt in Isothermal Compression

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SYNOPSIS

Crystallization and primary nucleation of linear polyethylene has been studied by means of a custom-made miniature pressure apparatus. It has been shown that during isothermal compression of linear polyethylene melt at a constant rate crystallization occurs. In the range of fastest conversion rates the crystallization assumes isobaric character. The level of pressure at which the crystallization occurs increases with the increase of the crystallization temperature and/or with the increase of the compression rate. The crystallization has a spherulitic character up to the highest pressure achieved in the apparatus (approx. 600 MPa). Surprisingly, there are no dependencies of average spherulite size, degree of crystallinity, and lamellae thickness on the pressure and the temperature of crystallization during melt compression, but there is a strong relation to the compression rate. Below 250 MPa and above 300 MPa the crystallization proceeds under pressure, ensuring a constant undercooling. The undercooling for the pressure above 300 MPa is approximately 10°C lower than that for the pressure below 250 MPa. For the pressure 250–300 MPa a change in a primary nucleation and spherulite crystallization has been observed that is connected with the transformation from orthorhombic to pseudohexagonal symmetry of crystals. No noticeable effect of molecular weight of linear polyethylene on crystallization during isothermal melt compression has been observed.

INTRODUCTION

The effect of hydrostatic pressure on crystallization of polymers has been studied for many years. The dependencies of equilibrium melting temperature and morphology of crystallizing aggregates on pressure is now well known.[1] In several cases new crystallographic forms were observed at elevated pressure. At sufficiently high hydrostatic pressure (300 MPa and more), polymer crystals show considerably increased thickness along macromolecular chains. Great attention has been paid to that phenomenon in the past.

Terminology used for crystals formed under pressure varies: before 1972 the term "extended-chain (EC) crystals" was commonly used for the description of lamellae with increased thickness. Based on conformational definition of thickness of lamellae, Wunderlich[2] estimated the lower limit of EC crystals at 2000 Å. Later this definition was considered improper especially in the view of results of investigation of parallel packing of macromolecular chains in uniaxial deformation. Bassett[3] has introduced the term "chain-extended (CE) crystals" for the description of crystallization from the point of view of crystallization mechanism. In the case of polyethylene a melt crystallization at pressure above 300 MPa leads to the formation of hexagonal phase. At reduction of pressure and/or temperature a transition of hexagonal phase to a final orthorhombic symmetry of crystals occurs. The term CE means in that case a series of processes.

Chain-extended crystals in polyethylene were observed for the first time in 1964.[4,5] Chain-extended lamellae formed under pressure of 500 MPa have thickness up to 3 μm, which is comparable with the length of fully extended macromolecules of linear polyethylene.[5] In that form polyethylene is brittle

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and its density reaches 0.994 g/cm^3.[4] Further investigation of morphology of CE lamellae in polyethylene showed, however, that macromolecules are not fully extended. Wunderlich et al.[6,7] demonstrated by comparison of distribution of lamella thickness with weight-averaged molecular weight that only the smallest macromolecules are fully extended in CE crystals of polyethylene while larger ones are still slightly folded. Rees and Bassett[8] found that full chain extension is an exception rather than a rule; conformation of all macromolecules, also the shortest ones, shows folding. There are other similarities between crystals formed under atmospheric and elevated pressures: The temperature dependence of lamellar thickness is identical for atmospheric and elevated above 300 MPa pressure,[9] crystals formed during annealing under low and high pressure.[10] On the basis of these results Bassett[11] concluded that CE lamellae of polyethylene are essentially large-scale copies of chain-folded lamellae formed under atmospheric pressure.

It was found that the lamellar thickness depends on molecular weight, temperature, and pressure of crystallization. Bassett and Turner[12] formulated the following conclusions concerning the lamellar thickness:

1. Increases with the increase of temperature at constant pressure.
2. Increases with the increase of pressure at constant undercooling.
3. Increases with increasing molecular weight in the range from 20,000 to 50,000 g/mol at the same temperature and pressure of crystallization.

Annealing at elevated pressure causes also thickening of lamellae. Hatakeyama et al.[13] obtained CE crystals of linear polyethylene of 50,000 g/mol having thickness of 40 μm during crystallization at 237°C under 480 MPa in 200 h. It means that the thickness of lamellae is not limited by the length of macromolecular chains. It means that chain ends might be embedded inside crystals of thickness several times larger than the extended chain length.[14]

Mechanisms of CE crystallization were extensively studied in the past. Based on morphology observations, it was suggested[6] that macromolecular chain extension is possible by high molecular mobility in crystalline phase during crystallization under pressure. Peterlin[15] assumed that CE lamellae are formed from thin ordinary chain-folded lamellae. Wunderlich et al.[2] suggested that the CE crystallization process consists of two processes: First, chain-folded lamellae are formed with thickness determined by undercooling, and then chains are reorganized to CE conformation at high temperature and pressure. Bassett and Turner[12] showed in differential scanning calorimetry (DSC) that there are two concurrent competitive processes of crystallization of chain-folded and CE lamellae. Under higher pressure CE crystallization becomes dominant. It was suggested that orthorhombic chain-folded lamellae of polyethylene are formed directly from melt while CE crystals of polyethylene result via intermediate hexagonal phase.[12] Hexagonal high-pressure phase was first observed by Bassett and Turner[3] and independently by Yasuniwa et al.[16] According to Bassett et al.[17] CE crystallization of polyethylene above 300 MPa occurs via discontinuous process of transformation of melt to intermediate hexagonal phase, which converts into orthorhombic phase during release of pressure and/or temperature decrease. In that transformation the orientation of a chain axis is preserved, which means that transition from hexagonal to orthorhombic phases occurs via slip along chains in a–b plane of crystallographic unit cell. Critical pressure for this transition is approximately 300 MPa and temperature 235°C.[18]

Maeda et al.[19-21] suggested the existence of different EC crystal forms: Ordinary EC crystals formed at 224°C under 500 MPa having melting point at 237°C, and high melting EC crystals formed at 228°C with a melting point at 244°C. They proposed three ranges of pressure in which the crystallization is significantly different:

1. Up to 200 MPa—polyethylene crystallizes directly from melt into chain-folded lamellae.
2. From 200 to 350 MPa—polyethylene crystallizes into two forms: chain-folded lamellae and EC crystals
3. Above 350 MPa—polyethylene crystallizes into low melting ordinary EC hexagonal crystals.

During pressure release and/or temperature decrease, the transformation to orthorhombic forms occurs: Ordinary orthorhombic EC crystals, high melting orthorhombic EC crystals, and low melting crystals of long folded chains or extended low molecular weight chains.

Based on detailed calorimetric studies, Wunderlich and Grebowicz[22] identified hexagonal EC form in polyethylene as pseudohexagonal conformationally disordered phase—"condis type."

The state of knowledge has been summarized in several reviews.[1,23-25]

It is known that the crystallization of polyethylene under pressure is controlled by primary nucleation since the dominated supermolecular structure are spherulites. In spite of extensive investigations of morphology of polyethylene crystallized under pressure, the habits of primary nucleation of spherulites has not been equally well studied. Besides several fragmentary papers,[26,27] there are no coherent data on primary nucleation of crystallization and spherulite growth rate of polyethylene under elevated pressure. The relative lack of data results from experimental difficulties in following the course of crystallization in heavy and thermally inert high-pressure equipment used. For the purpose of investigation of spherulite nucleation and growth processes, it is required to achieve fast changes and precise recording of the temperature inside the pressure cell, fast application of pressure, possibility to maintain the pressure at certain level, and possibility of recording the specific volume of the sample during pressurization and crystallization. An apparatus with such abilities would deliver instant information on the kinetics of crystallization. The aim of this work was to construct an apparatus for crystallization of polymers under pressures up to 600 MPa possessing the possibilities mentioned. Spherulite nucleation and growth in linear polyethylene was the goal of the studies. Two linear polyethylenes of medium and ultra high molecular weights were chosen for the investigation.

EXPERIMENTAL

Apparatus

Crystallization of polymers was carried out in a custom-made apparatus. The central part of the apparatus is a pressure cell consisting of a miniature 7-mm diameter cylinder with a tightly fitted plunger, brass indium-plated single-use sealings, and two tightly fitted disks. The disks ensure the cylindrical geometry of the samples. Details of the pressure cell are depicted in Figure 1. All elements of the pressure cell are made of high-strength hardened steel. Indium-plated brass sealings make the pressure cell tight up to 600 MPa. It has been determined by weighing the sample before and after application of pressure that the leakage of the polymer melt in the pressure cell beyond brass sealings amounts to 0.001 cm^3 on average. The leakage of the polymer melt was measured in each experiment and considered in the data evaluation. The friction of the plunger against the cylinder walls and sealings never exceeded 300 N. The friction force was measured in each experiment and also considered in the data evaluation.

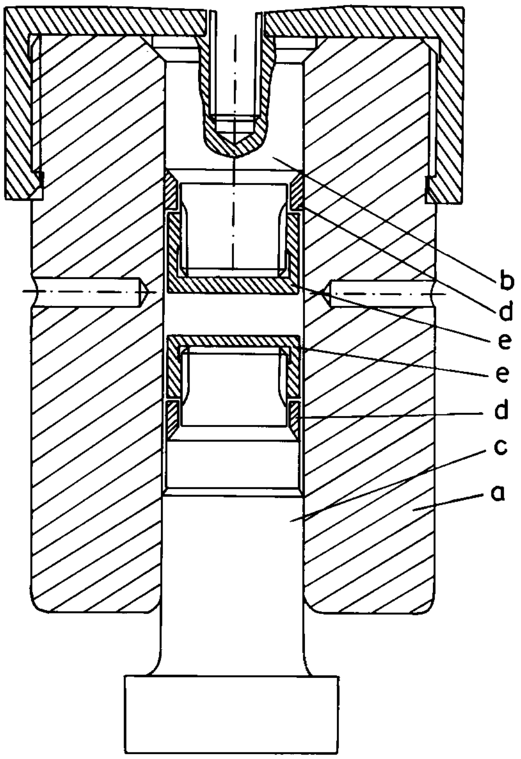

Figure 1 Pressure cell details: (a) pressure cell, (b) upper plunger, (c) lower plunger, (d) indium-plated brass sealings, (e) pads.

The small weight of the pressure cell loaded with a specimen, around 50 g altogether, allows isothermal crystallization of polyethylene even at quite high undercooling because the temperature change can be quickly made.

The use of Instron's tensile testing machine allows compression of the pressure cell to a required pressure with the precision of 0.5 MPa. The determination of the specific volume of the sample is achieved by synchronous measurement of the displacement of the plunger in the pressure cell with the precision of 10 μm. Crosshead speed can be changed from 50 $\mu m/min$ to 50 cm/min.

The temperature inside the pressure cell was controlled by two systems: a rough control with the precision of about 1°C by combination of environmental chamber of the Instron machine and flow of vapors of liquid nitrogen from four concentric tubes directed toward the pressure cell, and a precise control by means of an electric heater wound around the cylinder of the pressure cell and connected to an electronic control unit. The time of thermal response of the system is less than 1.3 min. Data acquisition and evaluation on line was achieved by means of Labmaster Data Acquisition Board by Tecmar and an IBM PC / XT computer.

Samples and Measurements

Commercial linear polyethylene Lupolen 6011L by BASF (density 0.960 g/ cm^3 and melt flow index 5.5 g/ 10 min according to ASTM D 1238-62 T at 190°C and load 2.16 kG) was used. High molecular weight linear polyethylene Lupolen 5261Z by BASF (density 0.952 g/ cm^3 and melt flow index 1.8 g/ 10 min at 190°C and load 21.6 kG) was also used for the purpose of studying the effect of molecular weight on crystallization of polyethylene in isothermal melt compression. Then 0.3-mm samples were compression molded at 190°C under 200 atm and solidified in iced water. Disklike specimens 7 mm in diameter were cut out from compressed films. Two such disks, jointly 0.6 mm thick, were placed in the pressure cell. The weight of samples was determined by weighing the pressure cell before and after placing a sample. The pressure cell was carefully washed in hot toluene before each experiment. The crystallization of polyethylene was studied in the temperature range from 130 to 235°C. In cases of crystallization temperature below 185°C, samples were melt annealed at 185°C for 10 min, and then the required crystallization temperature was reached. In other cases the crystallization temperature was reached without the melt annealing step. Melt annealing at 185°C for 10 min or at the temperature above 185°C for a shorter period of time destroys virtually all self-seeded nuclei of spherulites. After equilibration of the crystallization temperature, the pressure cell was compressed with the Instron tensile testing machine. The displacement of the crosshead and the force acting on the plunger were simultaneously recorded. Before the polymer melt became pressurized, the friction force of the plunger against the sealing was measured. The compression with a constant displacement rate of 0.1 or 0.5 mm/ min was continued until the pressure inside the pressure cell reached 600 MPa. During pressurization the crystallization of the polymer occurs, and for this reason the temperature of the pressure cell was continuously monitored. The pressure was kept at 600 MPa for 10 min and then decreased to 60°C at constant pressure of 600 MPa, and finally the pressure was released and the sample removed from the pressure cell.

Melting of polyethylene crystallized under pressure was also studied by means of pressure release from 600 MPa with a constant crosshead rate of 0.5 mm/ min. The temperature was kept constant at the level of the crystallization temperature. For comparison the crystallization of polyethylene was also conducted in the pressure cell under atmospheric pressure at 126°C.

Mean spherulite size was determined by small-angle light scattering from H_v patterns. He–Ne laser was used as a source of 632.8-nm light. Intensity of scattered light was recorded as a function of radial angle at azimuthal angle of 45° using a goniometer equipped with a photomultiplier. Specimens for small-angle light scattering were prepared by microtoming 50-μm-thick slices from pressure-crystallized samples and immersed in an immersion oil between microscopic glasses. Average size of spherulites in the specimens was determined from Stein's equation[28,29] modified recently for the broadening of maximum of scattered light intensity resulting from size distribution.[30]

Degree of crystallinity and average size of crystallites were estimated on the basis of DSC melting curves using Perkin-Elmer DSC 2a apparatus. Approximately 4-mg samples were cut out from central parts of samples. The scanning rate was 10 K/ min.

RESULTS AND DISCUSSION

A typical dependence of pressure inside the pressure cell on the crosshead displacement is presented in Figure 2. The *P* curve represents compression of a sample while the *R* curve represents the release of pressure with the same crosshead speed. The curves are already corrected for the friction of the plunger against cylinder walls and for the melt leakage beyond sealing rings. Mechanical compliance of the apparatus jointly with the compliance of the tensile testing machine was determined by compression of the empty pressure cell under the same experimental conditions of the temperature and the crosshead speed. That run is also plotted in Figure 2 with a dotted line. The displacement of the plunger in the pressure cell, Δl_p, as a function of the pressure was determined from the dependence:

$$\Delta l_p = \Delta l_{pc} - d_{pc} \tag{1}$$

where Δl_{pc} is the displacement of the crosshead of the tensile testing machine under the pressure, whose value is not corrected for the friction of the plunger, and d_{pc} is the joint deformation of the pressure apparatus and the tensile testing machine under the pressure, whose value is not corrected for the

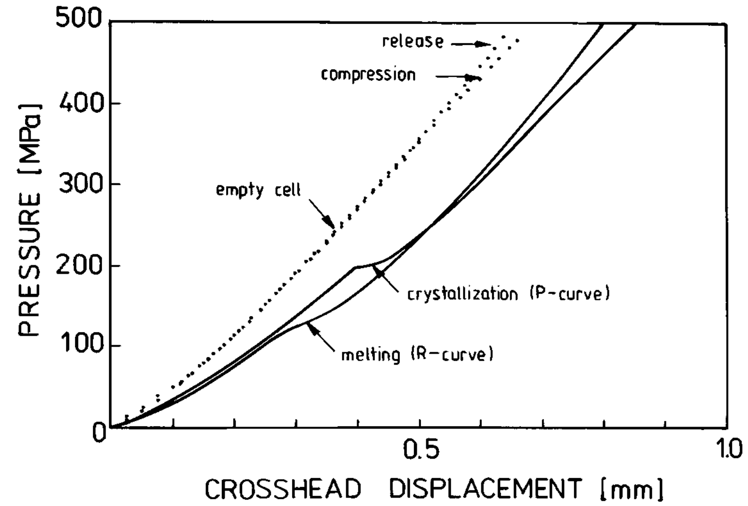

Figure 2 Typical dependence of pressure inside pressure cell on the crosshead displacement for polyethylene crystallized at 169°C during melt compression and melted at 169°C during pressure release. Empty cell runs are also shown.

friction of the plunger. The change of the specific volume of a sample, ΔV_p, in a function of corrected pressure was determined from the formula

$$\Delta V_p = -\frac{\Delta l_p \cdot s}{m_c} \tag{2}$$

where s is the area of the plunger face and m_c is a mass of a sample corrected for the leakage of the melt beyond the sealing rings. It is seen from the curve P in Figure 2 that at a certain pressure the further increase of pressure significantly slows down, although the plunger continuously moves inside the pressure cell with a uniform speed. It is a result of crystallization of the sample associated with the change in its density. In the range of fastest change of the specific volume of the sample, the crystallization is isothermal and almost isobaric in character. In that range the position of the plunger inside the pressure cell determines the degree of conversion of melt into crystalline phase. The shape of the P curve in Figure 2 is characteristic for the crystallization of a polymer due to the increase of the equilibrium melting temperature resulting from the elevated pressure.

The R curve in Figure 2 shows, in a slightly lower range of pressure, similar but broader plateau, which is connected with the increase of the specific volume of the sample during the uniform release of the compression. The increase in the specific volume of the sample is associated with the melting of its crystalline phase. The pressure under which the melting is fastest is always significantly lower than that for crystallization during compression. Such a behavior of a polymer is also characteristic for the crystallization and melting during uniform change of the temperature. The change of the specific volume was correlated with the change in the degree of crystallinity by introducing corrections for the thermal expansion and compressibility. For polyethylene the following was assumed: bulk thermal expansion coefficient of the melt 8.55×10^{-4} cm^3/g K, bulk thermal expansion coefficient of the solidified polymer 3.0×10^{-4} cm^3/g K,[1] bulk modulus 5900 MPa,[31] and modified equation of state according to Spencer and Gilmore:[31]

$$(V_w - v)(P - u) = RT/M_u \tag{3}$$

where $v = 0.88$ cm^3/g, $u = 329$ MPa, and $M_u = 28$ g/mol for polyethylene. After introducing this correction, the volume degree of crystallinity was determined from the formula

$$c = (V_a - V_w)/(V_a - V_c) \tag{4}$$

Typical dependence of the specific volume of crystallizing linear polyethylene sample during compression of melt versus time is presented in Figure 3. It represents a S-shaped curve characteristic for the nucleation-controlled crystallization. The Avrami exponent for that curve is close to 3 as it follows from the analysis by Avrami equation (there is some uncertainty concerning the moment of the

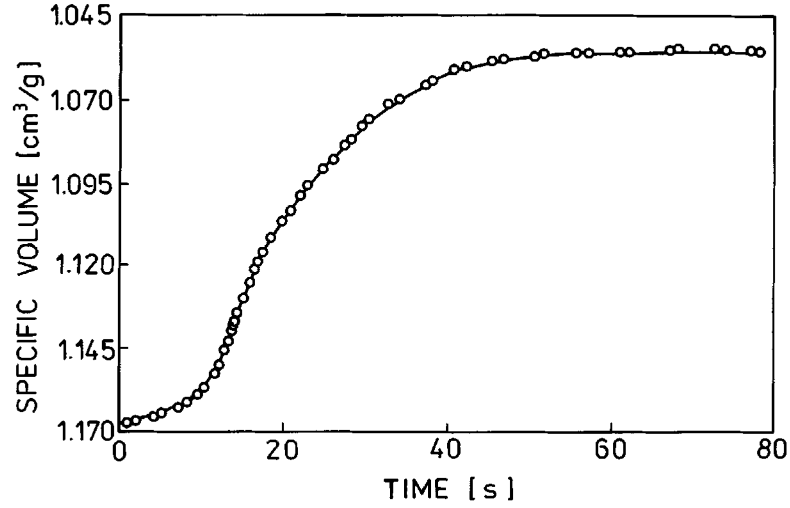

Figure 3 Exemplary dependence of specific volume vs. time obtained for polyethylene crystallized during melt compression at 140°C.

beginning of crystallization). For each measurement the ranges of pressure where the crystallization or melting took place, the pressures where crystallization or melting was fastest, and the pressure, $p_{1/2}$ (more precisely the position of the plunger) at the moment when the conversion degree is 0.5 for both the crystallization and the melting were determined. The pressures, $p_{1/2}$, for crystallization as well as for melting of polyethylene during compression and pressure release as a function of the temperature are presented in Figure 4. In the figure there are also plotted the melting temperature of polyethylene calculated according the formula given in Wunderlich:[32]

$$T_m = 415.7 + 28.1 \cdot P - 1.66 \cdot P^2 \quad (5)$$

and the curve of constant undercooling drawn through experimental points in the lower range of crystallization temperature. It is seen that up to approximately 250 MPa the crystallization occurs under such pressure that ensures constant undercooling at a given compression rate (given crosshead speed). At a crosshead speed of 0.5 mm/min the undercooling reaches 25°C. Above 300 MPa the undercooling during crystallization is also constant, but it is approximately 10°C lower. It is also seen from Figure 4 that the melting of polyethylene during pressure release occurs at a temperature approxi-

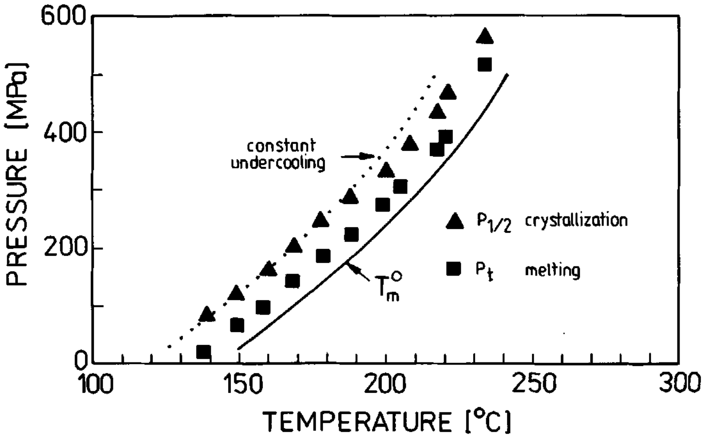

Figure 4 The pressure at the conversion ratio 0.5 plotted vs. crystallization temperature for polyethylene crystallized during melt compression and melted during pressure release with the crosshead speed 0.5 mm/min.

Table I Data for the Crystallization of Linear Polyethylene LUPOLEN 6011L during Isothermal Melt Compression with the Rate 0.5 mm/min

T_c (°C)	P_0 (MPa)	$P_{0.5}$ (MPa)	P_u (MPa)	ΔT (°C)	$t_{0.5}$ (s)	$\langle R \rangle$ (μm)
130	55	61	86	28.1	6.0	8.3
150	122	128	159	25.8	4.6	10.7
165	200	205	233	28.2	4.0	8.2
178	250	258	288	26.0	4.2	9.7
195	308	320	343	20.5	4.4	10.4
205	358	364	375	17.8	3.0	9.7
214	394	410	425	15.9	4.25	—
225	496	510	532	17.7	4.6	—

T_c = crystallization temperature, P_0 = pressure at the beginning of crystallization, $P_{0.5}$ = pressure at the conversion ratio 0.5, P_u = pressure at the end of crystallization, ΔT = undercooling, $t_{0.5}$ = half-time of crystallization, and $\langle R \rangle$ = average spherulite radius determined from small-angle light scattering.

mately 6°C lower than the equilibrium temperature. The extrapolation to the atmospheric pressure gives the crystallization and melting temperatures 115°C and 134°C, respectively, which are rather correct.

Table I summarizes the parameters for the crystallization during melt compression and average spherulite size. The data on spherulite sizes for polyethylene samples crystallized above 350 MPa are difficult to obtain by means of sectioning of bulk samples because the samples are very brittle, and sections and sectioned material contain large number of microcracks and fissures after the first stroke of the sectioning knife. From Table I it follows that the average spherulite size does not depend on the temperature and pressure of crystallization during isothermal melt compression up to 300 MPa. Table II presents the exemplary data for crystallization of polyethylene during isothermal melt compression at two different compression rates and two different temperatures of crystallization. It follows that the undercooling as well as the average spherulite size changes during the change of the compression rate. At the same compression rate, but at different crystallization temperatures, the undercooling as well as the average spherulite size remain constant. Table III shows the data obtained from DSC for polyethylene samples crystallized at two different crystallization temperatures during isothermal melt compression with two different compression rates. The degree of crystallinity was determined assuming the heat of fusion of polyethylene crystals $\Delta h_f = 293$ J / g.[32] Average thickness of lamellae was calculated from the volume distribution of lamellae thickness, which was determined from the contributions to the melting thermal effect of crystallites melting at temperatures from the range from the beginning to the end of crystallization. The thickness of lamellae melting at a certain temperature was calculated from the empirical formula from Wunderlich:[32]

$$T_m = 414.2\left(1 - \frac{6.27}{L}\right) \pm 0.8\ \mathrm{K} \qquad (6)$$

where the thickness of lamellae are expressed in angstroms. From Table III it follows that the temperature has no direct effect on the crystallinity of the samples crystallized during isothermal melt compression nor on the average thickness of lamellae; the decisive factor is the compression rate.

The character of changes of the specific volume

Table II Undercooling at Maximum Crystallization Rate and Average Spherulite Radius in Linear Polyethylene (LUPOLEN 6011 L) Crystallized during Isothermal Melt Compression

T_c (°C)	V_p (mm/min)	P_c (MPa)	$\langle R \rangle$ (μm)	T (°C)
126	0.0	1 atm	17.3	—
	0.1	20	12.5	22.2
		34	10.1	26.1
	0.5	33	10.0	25.8
140	0.1	70	12.3	21.6
		77	10.0	23.4
	0.5	76	9.8	23.1

T_c = temperature of crystallization, V_p = crosshead speed, P_c = pressure at maximum crystallization rate, $\langle R \rangle$ = average spherulite radius as determined by small-angle light scattering, and ΔT = undercooling as determined from the Eq. (5).

Table III Exemplary Data for Linear Polyethylene Crystallized during Melt Compression with Two Different Compression Rates at Two Different Temperatures Obtained by DSC Measurements

T_c (°C)	V_p (mm/min)	T_m (°C)	L (A)	X_c
126	0.1	135.0 ± 0.1	320 ± 1	0.76 ± 0.01
	0.5	133.6 ± 0.3	285 ± 5	0.70 ± 0.01
140	0.1	134.9 ± 0.1	328 ± 5	0.76 ± 0.01
	0.5	133.7 ± 0.1	280 ± 5	0.71 ± 0.01

T_c = crystallization temperature, V_p = crosshead speed, T_m = peak melting temperature, L = lamellae thickness as obtained from T_m and melting peak width, and X_c = degree of crystallinity calculated from heat of melting.

of polyethylene during isothermal melt compression indicate that the crystallization begins after a certain pressure is reached. The following are the most important features observed:

1. Quasi-isobaric character of crystallization in the region of maximal conversion rates.
2. Characteristic for spherulitic crystallization shape of the dependencies of the degree of crystallinity and changes of the specific volume versus time.
3. The decrease of the average spherulite size in comparison with the sample crystallized at isothermal condition under atmospheric pressure (see Table II).
4. Increase of the pressure under which the crystallization occurs with the increase of the temperature and with the increase of the compression rate (see Table III)
5. No temperature and pressure dependencies of the average spherulite size in samples crystallized by melt compression with the same compression rate.
6. No temperature and pressure dependencies of the degree of crystallinity and the thickness of lamellae in samples crystallized by melt compression with the same compression rate.
7. Half time of crystallization is independent of the temperature and pressure of crystallization during crystallization by melt compression with the same compression rate.
8. The decrease of the degree of crystallinity and the average thickness of lamellae with the increase of compression rate (see Table III).
9. The decrease of the average spherulite size with the increase of the compression rate (see Table II).
10. Up to 250 MPa (see Figs. 2 and 3 and Table I) the crystallization occurs at constant undercooling (around 25°C).
11. Above 300 MPa undercooling is also constant except that it is approximately 10°C lower.
12. The melting of samples during pressure release in isothermal conditions occurs at the temperature approximately 6°C below equilibrium melting point. Extrapolation to ambient pressure gives the temperature of melting of polyethylene as 134°C.

These results indicate that above 300 MPa there is a change in the kinetics of primary and secondary nucleations of linear polyethylene. The density of primary nuclei remains almost constant to the pressure of at least 360 MPa. No data on spherulite number were obtained for samples crystallized under higher pressure, as mentioned earlier. The same density of primary nuclei in a sample crystallized under 360 MPa requires 10°C lower undercooling than that for samples crystallized under 250 MPa.

The data for crystallization of linear polyethylene obtained in a droplet experiment[33] indicates that primary nucleation is of a heterogeneous character even at 50°C below the equilibrium melting point. The number of heterogeneous nuclei slightly increases with increasing undercooling. At undercooling of approximately 30°C the number of heterogeneous nuclei saturates. Homogeneous nucleation begins at temperatures 50°C below equilibrium melting point (in Ref. 33 at 56°C below equilibrium melting point). It is commonly accepted to describe the nucleation intensity by Turnbull–Fisher equation (see e.g., Ref. 1):

$$I = (NkT/h)\exp[-(\Delta G^* + \Delta G)/kT] \quad (7)$$

where N is the number of crystallizable elements in volume unit, ΔG^* is the enthalpy change for the formation of critical sized nuclei, ΔG is the free enthalpy of activation of diffusion, T is the temperature of crystallization, and k and h are Boltzmann and

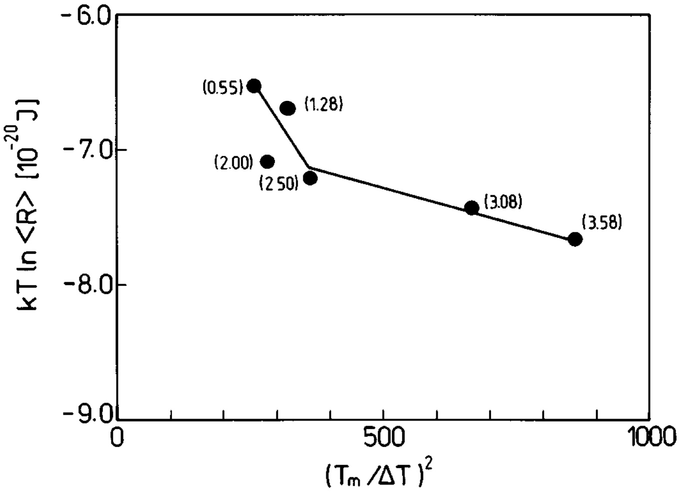

Figure 5 The dependence of $kT\ln\langle R\rangle$ on $[T_m/(T_m - T)]^2$.

Planck constants, respectively. In the case of heterogeneous nucleation ΔG^* can be approximated with

$$\Delta G^* = 16\Delta\sigma\,\sigma\sigma_e T_m^2/[\Delta h_f(T_m - T)]^2 \quad (8)$$

where σ and σ_e are free surface energies of a crystal parallel and transverse to macromolecular chains, respectively, $\Delta\sigma$ is a parameter characterizing the surface-free energies of the interfaces—melt, crystal, and nucleating species—T_m is the equilibrium melting temperature and Δh_f is the change in free enthalpy. After substitution of Eq. (8) into Eq. (7) and some transformation, one can obtain a formula describing the average spherulite size, $\langle R\rangle$:

$$kT\ln\langle R\rangle \sim \Delta G + (16\Delta\sigma\,\sigma\sigma_e/\Delta h_f)[T_m/(T_m - T)]^2 \quad (9)$$

In Figure 5 the plot of $kT\ln\langle R\rangle$ versus $\langle T_m/(T_m - T)\rangle^2$ based on the data from Table I is presented. In Figure 5 the equilibrium melting temperature was assumed under the pressure of the beginning of crystallization since it is expected that most of heterogeneous nuclei become active in earlier stages of crystallization. The annotations are the pressures at which the crystallization occurs. It is seen that the plot can be approximated with two straight lines with a higher slope for pressure below 250 MPa and with a lower slope for higher pressure. The ratio of slopes is around 8:1. This result suggests two possibilities:

1. Under pressure of 250 MPa a drastic change of surface-free energies and/or a change of enthalpy of fusion, Δh_f, occur that are connected with the change in mechanism of nucleation or with the change of crystallographic form.
2. There are changes in nuclei shapes or kinetic elements of macromolecular chains taking part in nucleation. The description of free enthalpy of nuclei formation by Eq. (8) becomes inadequate.

In view of the data for the half time of crystallization from Table I, it is obvious that also the spherulite

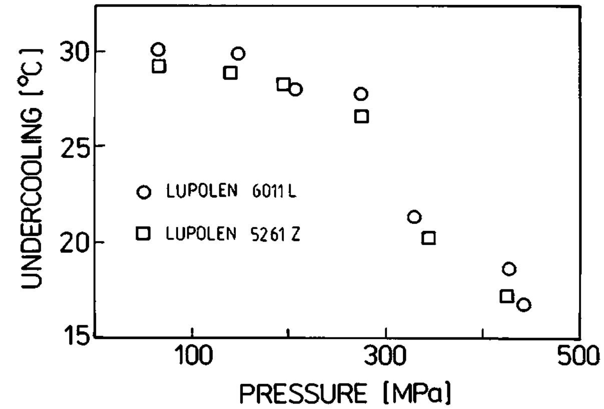

Figure 6 The dependence of undercooling determined by using Eq. (5) on the pressure at the fastest crystallization rate for two different linear polyethylenes melt compressed with the rate 0.5 mm/min.

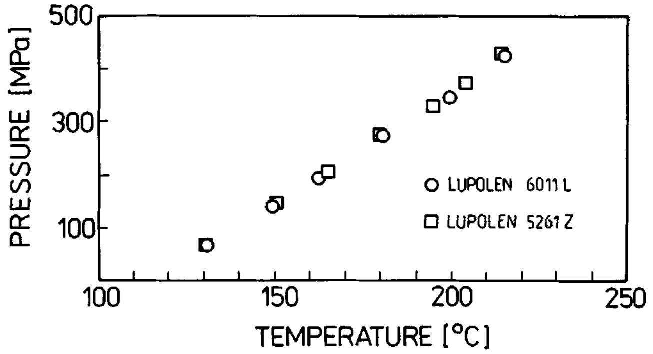

Figure 7 The dependence of the pressure at the fastest crystallization rate vs. temperature for two linear polyethylenes compressed with the rate 0.5 mm/min.

growth rate undergoes a drastic change; the half time of crystallization remains constant far above 350 MPa while the undercooling changes from 25 to 15°C. Under atmospheric pressure such change of undercooling would cause a change of growth rate by several times (see e.g., Ref. 34). The change in spherulite growth rate is a result of a significant lowering of the energy barrier for secondary nucleation.

There is a coincidence of pressures under which a new pseudohexagonal phase arises, and changes in the kinetics of primary and secondary nucleations are observed. Hence, it is very likely that the changes in primary and secondary nucleations are caused by the formation of this new pseudohexagonal phase of a "condis" type. The phase diagram of linear polyethylene was determined on the basis of calorimetric studies in Ref. 29. At a given pressure the equilibrium melting temperature for pseudohexagonal phase is always lower than that for orthorhombic phase. It indicates that pseudohexagonal phase is less thermally stable, i.e., possess higher free energy than orthorhombic phase. Hence, crystallites of pseudohexagonal phase are characterized by much faster growth rate.[23] The changes in the crystallization behavior of linear polyethylene, which follow from the differences in free energies, equilibrium melting temperatures, and spherulite growth rates between the two crystallographic phases, are best illustrated in Figure 6. Figure 6 plots the dependence of undercooling on the pressure under which the crystallization reaches the maximum rate. It is seen that under pressure below 250 MPa the undercooling is within the range 25–30°C. Above MPa a sudden decrease of the undercooling is observed. Such a larger change of undercooling, essential for crystallization with the rate allowing for volume compensation as determined by the compression rate, indicates a drastic change in the crystallization mechanism.

The crystallization experiments during isothermal melt compression were repeated for samples of very high molecular weight linear polyethylene (Lupolen 5261Z). The obtained data are also plotted in Figure 6. No significant difference between the data for the two polyethylenes can be noticed. In Figure 7 the pressure under which the crystallization reaches the maximum rate is plotted versus temperature of crystallization for the two polyethylenes. Also on this graph no significant difference in the crystallization behavior between medium (LUPOLEN 6011L) and high (LUPOLEN 5261Z) molecular weight linear polyethylenes is seen. It follows then that the molecular weight does not affect significantly the thermodynamic and kinetic conditions of crystallization during isothermal melt compression. The influence of molecular weight should be expected if the crystallization during isothermal melt compression involves displacements of large segments of macromolecular chains.[35] High molecular weight makes such displacements more difficult. The experimental results indicate, however, that the displacements of large segments of macromolecules are not crucial for the crystallization of linear polyethylene during isothermal melt compression.

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