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Thermal behaviour of homogeneous ethylene-1-octene copolymers and linear polyethylene at high pressures

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Abstract

The thermal behaviour of a linear polyethylene (LPE) and of homogeneous ethylene-1-octene copolymers (2.1, 5.2 and 8.0 mol% of 1-octene) was investigated at high pressures by use of a high-pressure differential scanning colorimetry (DSC). The heating curves of LPE at pressures above 400 MPa reveal a three-peak pattern (peaks denoted by I, II, III at increasing temperature). It reflects the melting of orthorhombic folded chain crystals (I); the melting of extended chain crystals, superposed on the orthorhombic-hexagonal solid–solid transition (II) and the melting of the hexagonal phase (III). Introduction of a small amount of 1-octene results in a similar multiple-peak pattern but with a weakened high-temperature peak. With increasing comonomer content this three-peak pattern evolves over a two-peak pattern (I, II) into a single-peaked endotherm (I).

The influence of the heating rate at elevated pressure as well as the influence of the cooling rate at ambient pressure on the melting behaviour at high pressure are also studied. The data could be fitted well using simple equations making an indicative prediction possible for the crystallisation and melting peak temperatures of homogeneous ethylene-1-octene copolymers as a function of comonomer content and pressure. Besides, the possible occurrence of *extended ethylene sequence crystals* in homogeneous ethylene copolymers, instead of extended chain crystals (both denoted by II) is discussed.

Keywords: Crystallisation; High pressure; Homogeneous ethylene-1-octene copolymers

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1. Introduction

Polyethylenes (PE) are an industrially important class of polymers [1–3]. In addition various types have been used as model substances in the study of the crystallisation and melting behaviour of semi-crystalline polymers. The thermal behaviour and the morphology of various PE's have been frequently studied at atmospheric and elevated pressures (see Huang et al. [4] for an overview). However, results of thermal studies at high pressure (see for instance references in Ref. [5] for DSC studies) performed on homogeneous ethylene-1-alkene copolymers are so far not available in literature. To fill this gap, and in line with our previous results [6–8], the thermal behaviour of three homogeneous ethylene-1-octene copolymers (synthesised by use of a vanadium-based catalyst) has been investigated at elevated pressures. A linear polyethylene (LPE), as produced with the same catalyst system is included in the present study as a reference material. The investigated ethylene-1-octene copolymers are called *homogeneous copolymers* [1,9] because the way in which the comonomer is added during polymerisation can be described by a single set of chain propagation probabilities of (co)monomer incorporation in the chain (P-set). All chains have the same monomer/comonomer ratio and statistically there are no differences within and between the molecules. These materials are of growing interest because they can be produced using metallocene catalysis [10–12] and because of their potential applications, e.g. use as impact modifiers. In contrast to linear low-density and very low-density polyethylenes (LLDPE's and VLDPE's, respectively) [1,13], which are *heterogeneous* with respect to the inter- and intramolecular distribution of the side chain branches, the homogeneous copolymers reported here have a narrow molar mass distribution and a constant comonomer content for all chains while all chains have the same comonomer distribution. This homogeneity makes them very attractive for

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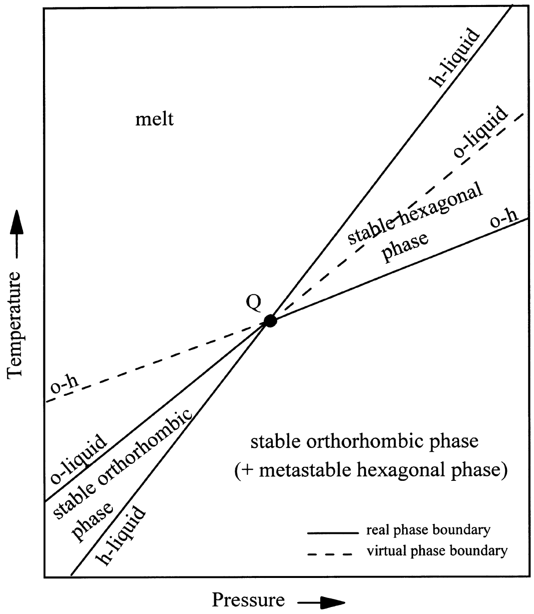

Fig. 1. Schematic *P*–*T* phase diagram of PE including metastable and virtual phase boundaries after Rastogi et al. [29]; triple point (Q) at circa 330 MPa and 220°C.

any fundamental polymer study [2,7,14] and they provide excellent prospects for a more unambiguous interpretation of experimental data of short chain branched polyethylenes. Homogeneity as mentioned, is defined from a polymerisation point of view. Even such "homogeneous" copolymers can (and do [2]) show heterogeneity with respect to crystallisation, melting and morphology. This is caused by the fact that the polymerisation statistics results in an ethylene sequence length *distribution* from which different ethylene sequences can crystallise differently.

In ethylene-1-alkene copolymers every incorporation of a 1-alkene or α-olefin comonomer unit introduces a short chain branch in the polymer chain causing a disruption of the chain regularity. The length of the side chain, which is controlled by the comonomer used, determines whether or not it will be incorporated in the crystal regions. Some consensus exists on the fact that methyl branches are incorporated in crystallites at interstitial positions [15–17], which gives rise to crystal defects. Hexyl branches are not incorporated in the crystal lattice. Longer branches will not be incorporated either, but side chain crystallisation of the branches might occur [18,19].

It is well known that elevating the crystallisation temperature, or annealing above the crystallisation temperature of PE results in thicker folded-chain lamellae of up to ~200 nm. In addition to the higher temperature, if high pressure is applied, crystals can grow as thick as several micrometers [20,21] in the chain axis direction. The induced pressure leads to molecular constraints, which inhibit the orthorhombic-melt transition during heating because the random coil conformation cannot be attained. On the contrary, when increasing the pressure, crystallisation and melting occur at higher temperatures, which leads to larger interchain distances (larger unit cell volume) and a higher chain mobility making the existence of the hexagonal phase, or a CONDIS [22] type of phase, possible. Hence, the chains have the opportunity to organise into extended chain crystals (ECCs) or into much thicker lamellae than usual, involving a decrease of the number of folds. The viewpoint of Wunderlich et al. [23–25] that the polymer molecules transfer from the melt to a folded-chain conformation and further undergo enhanced lamellar thickening and transform into ECC was once commonly accepted. However, Bassett and Turner [26] reported that melting and crystallisation of PE at pressures above ~400 MPa occurred in two stages. They suggested that the intervention of the hexagonal phase [21,26–28] is responsible for the direct formation of ECC by crystallisation from the melt at high pressures. ECCs are formed by crystallisation from the melt into the hexagonal phase, whereas folded chain crystals (FCCs) are formed by crystallisation from the melt into the orthorhombic phase. The studies of Rastogi et al. [29] and Hikosaka et al. [30] together with more precise optical microscopy and X-ray measurements favour the suggestion of Bassett et al. These authors found that, at pressures above 200 MPa, all crystal growth occurs in the hexagonal phase (stable or metastable), and only in this phase. An indicative phase diagram [29] is presented in Fig. 1.

Here, we investigate the thermal behaviour at high pressure of an LPE and three homogeneous ethylene-1-octene copolymers by use of a high-pressure differential scanning calorimeter (HP-DSC) [31]. Because in the literature most of the interpretations and explanations about high-pressure phenomena have been developed for linear and slightly branched polyethylenes [20,21,28–30,32] (LPE and HDPE), there is a need for new data on homogeneous ethylene-1-alkene copolymers with a higher degree of branching. As a start, existing interpretations on LPE and HDPE are applied to the ethylene-1-octene copolymers. As compared to LPE, the hexyl branches hinder the crystallisation process and the chain mobility in the resulting crystallites, generally leading to a lower degree of crystallinity and to smaller and less perfect crystallites. The side branches also limit the thermodynamically favoured chain extension in the crystallites during crystallisation and during annealing in case of the ethylene-1-octene copolymers. At most, chain mobility under high pressure could be high enough to enable chain sequences to extend to lengths comparable to the distance in-between the branching points, limiting the crystal thickness to values comparable to contiguous ethylene sequence lengths. Hence, for ethylene-1-octene copolymers this can lead at most to "extended ethylene sequence crystals (EESCs)" instead of "extended chain crystals (ECCs)" as in the case of polymers without branches (LPE) or with a very few short branches (HDPE). Such EESCs in most cases still will be folded chain crystals with stem lengths comparable to the ethylene sequence lengths present. It has to be realised that the

Table 1
Overview of the investigated (co)polymers and their molecular characteristics

Sample	1-octene content (mole%)	M_w (g/mol)
JW 1114 (LPE)	0.0	52 300
JW 1116	2.1	50 300
JW 1120	5.2	35 600
JW 1121	8.0	42 600

statistical copolymerization gives rise to an ethylene sequence length distribution (ESLD) which in turn leads to broad crystallisation and melting point distributions, reflecting the existence of a crystallite dimension distribution. In these crystallites ethylene sequences of various lengths will be incorporated because the reeling in of sequences will not be perfect [33] due to the kinetics of the crystallisation process.

Besides the influence of pressure, the influence of heating rate, thermal history (given at atmospheric pressure) and comonomer content on the thermal behaviour at elevated pressure has been studied. Studying the effects of pressure on crystallisation, as well as the influence of thermal history, comonomer content, heating rate and annealing, is not only of fundamental importance for our understanding of crystallisation and melting of polymers, but also contributes to basic practical knowledge on final properties of such materials resulting from high-pressure processing conditions (e.g. injection moulding using high pressures).

2. Experimental

2.1. Apparatus

The measurements were performed in a power-compensated high-pressure differential scanning calorimeter (HP-DSC) as constructed by Blankenhorn and Höhne [31]. The DSC cell is developed to work in a temperature range from 20 to 300°C at a maximum pressure of 550 MPa using silicon oil as the pressure medium. The thermal noise is 50–100 μW and the peak detection limit is 5 mJ (i.e. 1 J/g). The samples (5–10 mg) were always hermetically sealed in aluminium crucibles to exclude contact with the pressure medium (silicon oil). They were heated and cooled at different elevated pressures. The cooling rate was −10°C/min and the heating rates varied from 2 to 20°C/min. The temperature and heat of fusion calibrations were done by use of indium and tin [34]. The pressure dependence of the temperature was taken from the literature [35–38] and the pressure dependence of the heat of fusion of indium was used for heat calibration [38]. In addition, a small indium sample was always present in the *reference cell* for “online” calibration control. As a consequence, a crystallisation and melting peak of indium *(of opposite direction: endo and exo, respectively)* is observable in every cooling and heating run, respectively, in the appropriate temperature range. The heating curves were corrected for the heating rate by use of the melting onset of indium, which is omnipresent in the reference cell. Because of the pronounced instrumental curvature in the DSC curves—probably due to small asymmetries between the reference and the sample furnace—neither heat of fusion nor crystallinities were calculated. Reduction of the curvature was tried in vain by the subtraction of a corresponding empty-pan measurement.

2.2. Samples

A linear polyethylene (JW 1114) and three homogeneous ethylene-1-octene copolymers with different comonomer content were investigated. The LPE and the copolymers were synthesised by use of a vanadium-based catalyst [6–8,39]. The comonomer content was tuned by varying the comonomer/ethylene ratio. The investigated copolymers have a 1-octene content of 2.1 (JW 1116), 5.2 (JW1120) and 8.0 mol% (JW 1121). All chains have the same ethylene/1-octene ratio and statistically there are no differences within and between the chains: the comonomer inclusion is “homogeneous”. The molar mass distribution, M_w/M_n, is ~2. Table 1 gives an overview of the investigated polymers and their molecular characteristics.

Before performing the high-pressure DSC-measurements, all the samples (as thin films of circa 0.7 mm thickness) were given the same thermal history at atmospheric pressure: cooling from the melt (200°C) to room temperature at a rate of −10°C/min. From such treated films a small, circular piece of approximately 5–10 mg was cut and put in a DSC pan. In case of JW 1116, the influence of the thermal history was also studied: the cooling conditions at atmospheric pressure were varied from cooling from the melt to room temperature at −1°C/min to quenching from the melt in a CO_2-isopropanol bath (−70°C).

3. Results and discussion

Different research groups observed, in the DTA curves of PE at high pressures, an additional high-temperature endothermic or exothermic peak [29,30,40,41]. In some cases an additional small low-temperature peak appears. According to Prime et al. [23] and Höhne et al. [42] the low-temperature peak is caused to a phase separation related to low molar mass components in the polymer. Hikosaka et al. [40] and Nakafuku et al. [41] assume that, in the case of HDPE, this low-temperature peak—which becomes less pronounced with increasing pressure—results from the melting/crystallisation of orthorhombic folded chain crystals (FCC). Although the actual experimental results of the different research groups are in good agreement, the interpretations offered for the thermal experiments appear to be quite different. Yasuniwa et al. [43] ascribed the high-temperature peak to the melting and crystallisation of an

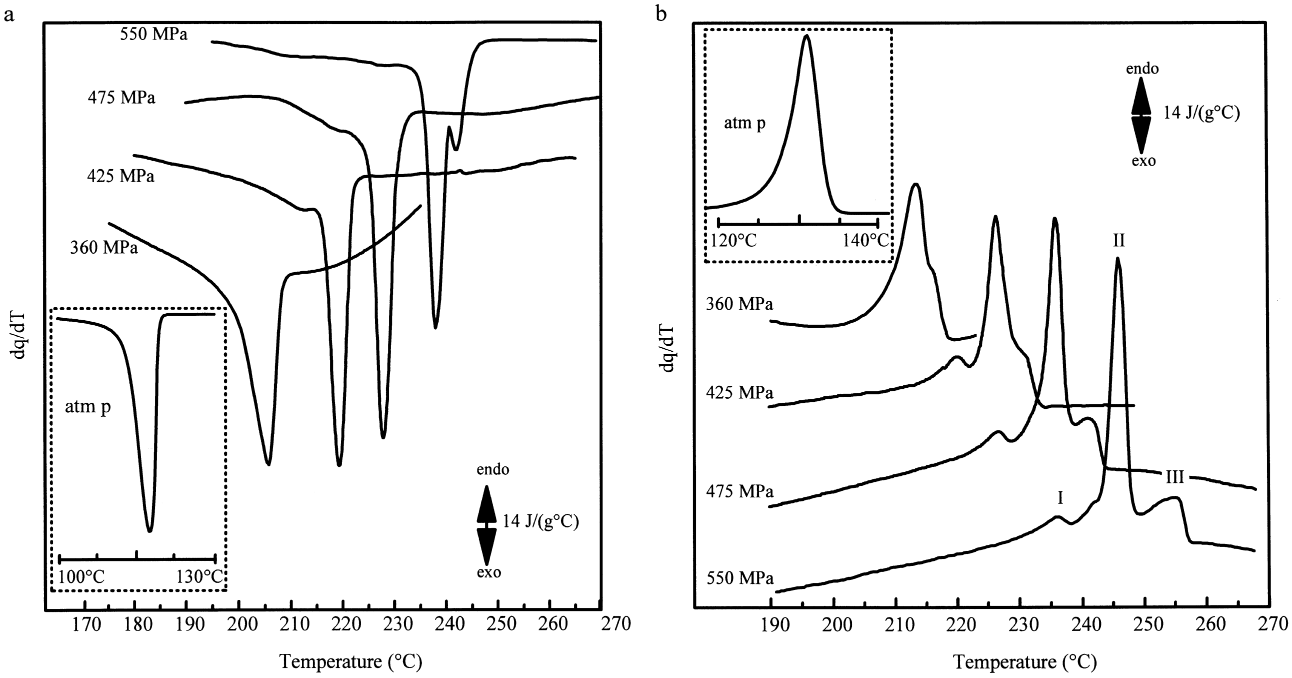

Fig. 2. Cooling (a) and subsequent heating (b) curves of JW 1114 at different pressures, rate: 10°C/min.

unknown structure. In a subsequent paper, using a diamond-anvil cell with an optical microscope, they observed that the growth feature of the unknown structure crystal is similar to that of a liquid crystal. Hence, they presumed that the unknown structure might be a nematic liquid crystal [44]. Maeda et al. [45–47] assume two kinds of ECC with different thermal stability: high ECC (500–800 nm) and ordinary ECC (200–500 nm). They assigned the high- and the somewhat lower-temperature exothermic or endothermic peak to the crystallisation or melting of high ECCs and ordinary ECCs, respectively. Bassett et al. [26] postulated from a number of thermodynamic criteria that a new high-pressure phase may exist between the normal orthorhombic phase and the melt at pressures above ~300 MPa. In 1974, based on the in situ high-pressure X-ray measurements, they suggested the new phase to be a hexagonal one and that the high-temperature peak should reflect the melting/crystallisation of hexagonal structures. This interpretation was supported by Hikosaka et al. [40] and Nakafuku et al. [41]. The large peak at somewhat lower temperature than the hexagonal one is ascribed to the melting of orthorhombic extended chain crystals (ECC) [40,41]. At pressures

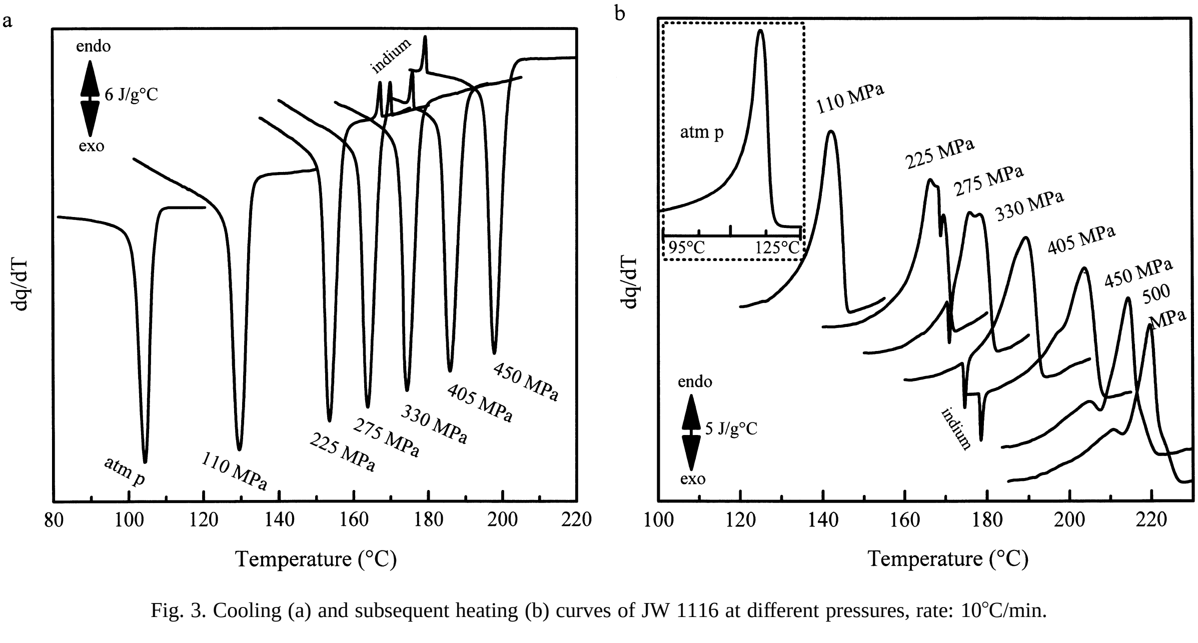

Fig. 3. Cooling (a) and subsequent heating (b) curves of JW 1116 at different pressures, rate: 10°C/min.

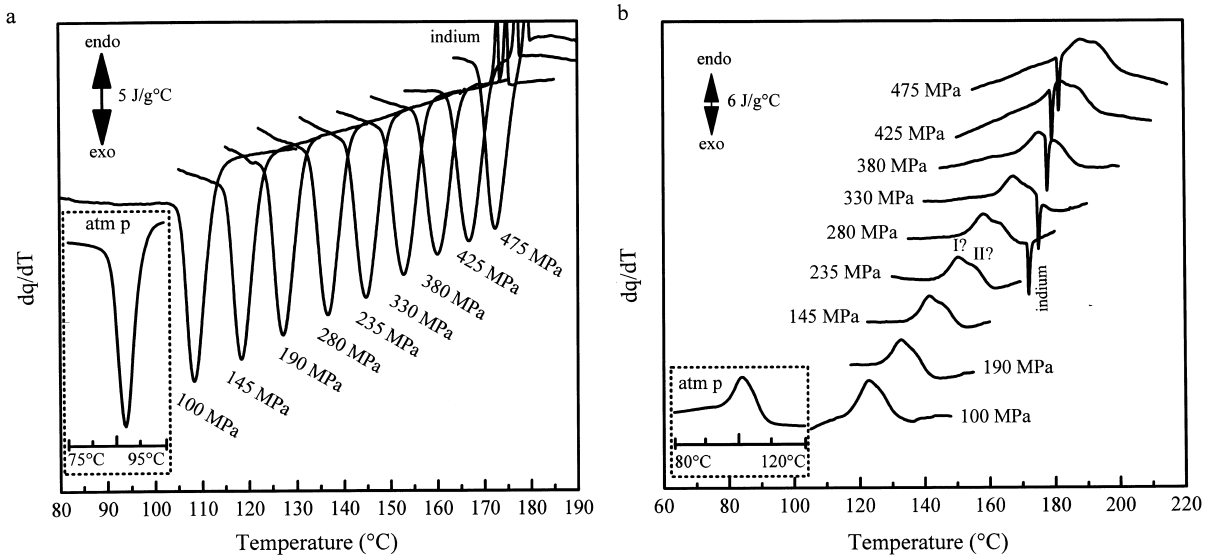

Fig. 4. Cooling (a) and subsequent heating (b) curves of JW 1120 at different pressures, rate: 10°C/min.

above 4 kbar the solid–solid transition between the orthorhombic and hexagonal phase should provide an additional contribution to this peak [40] too.

Here we study the influence of pressure, comonomer content, heating rate and thermal history (at atmospheric pressure) systematically by varying one of these parameters, keeping all other parameters constant.

3.1. Influence of pressure and comonomer content on thermal behaviour

The samples were cooled at −10°C/min and subsequently heated at the same rate at different elevated pressures varying from 550 to 50 MPa in steps of circa 50 MPa. The corresponding exo- and endotherms are shown in Figs. 2–5. In all cases, the DSC-curves shift to higher temperatures with increasing pressure. When pressure is exerted on a (co)polymer sample, its entropy will be decreased resulting in higher crystallisation and melting temperatures.

All exotherms show a major crystallisation peak, while only JW 1114, the linear PE sample, shows at 550 MPa an additional small peak at circa 4°C higher than the main peak. Because of the high chain mobility at high pressure for this LPE, crystallisation via the hexagonal phase into highly extended chain crystals during cooling could be possible. Therefore, the small high-temperature exotherm at 550 MPa is probably due to the transition from the melt into the hexagonal phase, whereas the other peak should—according to Hikosaka et al. [40]—result from the hexagonal → orthorhombic ECC transition. The small

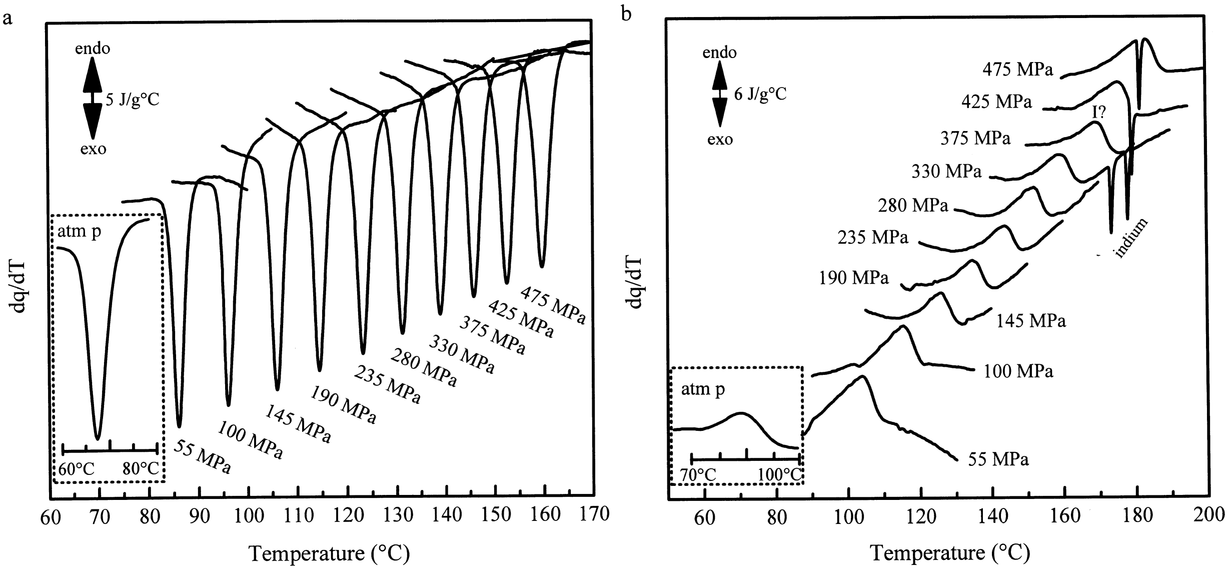

Fig. 5. Cooling (a) and subsequent heating (b) curves of JW 1121 at different pressures, rate: 10°C/min.

peak area of the high-temperature peak compared to the peak area of peak II is thought to be related to the nature of the hexagonal phase. The latter is much closer to the melt with respect to its specific volume and enthalpy than to the orthorhombic form [4,27].

Increasing the pressure leads to a sharper and narrower main peak for JW 1114. An additional small low-temperature peak is present in the cooling curves at 475 and 425 MPa (probably also at 550 MPa), whereas at 360 MPa only one broad exotherm is observed. Based on literature, we assume the low-temperature peak results from the crystallisation from the melt into orthorhombic FCCs. When extrapolating the peak temperatures of this low-temperature peak to lower pressures, one could assume that at 360 MPa this low-temperature peak contributes to the broad exotherm, the broadness of which can be ascribed to the superposition of three transitions in the temperature range of 200–210°C: melt → hexagonal; hexagonal → orthorhombic ECC; and melt → orthorhombic FCC. At 425 and 475 MPa the melt → hexagonal and hexagonal → orthorhombic ECC transitions should both constitute the large exotherm.

In the heating curve at 550 MPa of JW 1114 (Fig. 2(b)) three endothermic peaks are observed: a small low-temperature peak (I), a pronounced major peak (II) at intermediate temperature and a smaller high-temperature peak (III). When lowering the pressure, the peak temperature difference between peak II and peak III becomes smaller and probably coincides at 425 MPa and lower. Similar phenomena were observed by Hikosaka et al. [40]. According to Hikosaka et al. [40] and Rastogi et al. [29], peak I; II; and III should be assigned to the melting of orthorhombic FCCs; to the orthorhombic ECC → hexagonal ECC transition superposed on the melting of orthorhombic ECCs; and to the melting of the hexagonal structures, respectively. The small low-temperature peak I can be detected at pressures above 400 MPa. Below this pressure a broad endotherm is observed probably due to the merging of the different transitions mentioned before. Extrapolations from the peak temperatures to lower pressures support this possible superposition. The presence of the hexagonal phase below 200 MPa can be questioned because of the strong reduction of the mobility of chain segments.

Introduction of a few hexyl branches (JW 1116) results at atmospheric pressure in a decrease of the peak temperatures and also in a peak height decrease and peak broadening; however, at high pressures a change in heating curve pattern is observed. During cooling one single sharp exotherm is observed at all pressures (Fig. 3(a)). On heating (Fig. 3(b)) the typical three-peak pattern is present at pressures above 450 MPa, but the high-temperature peak (III) is very weak and reduced to a small shoulder as compared to LPE. When lowering the pressure the low-temperature peak (I) becomes stronger, resulting in a single peak at 110 MPa, while the high-temperature shoulder decreases and vanishes around 400 MPa (Fig. 3(b)). It is assumed that peak I reflects the melting of FCCs with stem lengths much smaller than the ethylene sequence lengths present, while FCCs with stem lengths comparable with the ethylene sequence length (EESCs) melt in the region of peak II. The increasing peak height of peak I compared to peak II with decreasing pressure then reflects the shift towards folded chain crystals. If one accepts the occurrence of the hexagonal phase in the EO copolymer with only 2.1 mol% 1-octene at high enough pressures (>450 MPa), one could expect an additional contribution to peak II of the orthorhombic EESC → hexagonal phase transition, while peak III should result from the melting of the hexagonal phase. To substantiate these assumptions and interpretations and to evaluate the presence of the hexagonal phase in JW 1116, high-pressure X-ray diffraction measurements are required and planned in future.

Additional introduction of more hexyl branches (5.2 mol% 1-octene, JW 1120) results in a broader exotherm with respect to JW 1116 and JW 1114 at all pressures (Fig. 4). The typical three-peak pattern observed for JW 1114 and JW 1116 on heating changes into double peaked endotherms of lower intensity, again for all pressures. The absence of the hexagonal peak III could be ascribed to the reduced chain mobility caused by the higher branching amount. The reduced peak height results from the lower crystallinity produced at higher branching content. The more (non-crystallisable) side branches are introduced in the main chain, the more the crystallisation process is hindered. Smaller and less perfect crystallites with relatively low thermal stabilities are formed [6–8]. The lower peak temperatures T_m and T_c confirm this interpretation. In the heating curve two partially merged peaks can be detected (Fig. 4(b)). On increasing the pressure the small high-temperature shoulder (II?, same notation as before) evolves into a broad peak of roughly the same size as the original main peak (I?). Both FCCs (I) and EESCs (II) are possibly formed during heating (and/or during cooling) at elevated pressure. On the contrary, the copolymer with the highest comonomer content, JW 1121, reveals a single, narrow exotherm (Fig. 5(a)) and small single peaked endotherm (I?, same notation as before) at all pressures, see Fig. 5(b). For 1-octene contents of 8.0 mol% and higher one can safely assume that the chain mobility is too low to make ethylene sequence extension possible. Moreover, the mobility of the chains is lower because due to the high comonomer content the transitions take place at lower temperatures. One should notice the broadening of the exotherm of JW 1120 compared to JW 1116, whereas JW 1121, on the other hand, reveals a narrower cooling curve compared to JW 1120. The broadening of the exotherm of JW 1120 compared to JW 1116 could be explained by the effect of the comonomer content increase. Branches hinder during crystallisation the selection of ethylene sequences of equal length by reduction of the chain mobility. This results in the formation of less perfect crystallites and in a broader crystallite dimension distribution, as is reflected in the broad cooling curves.

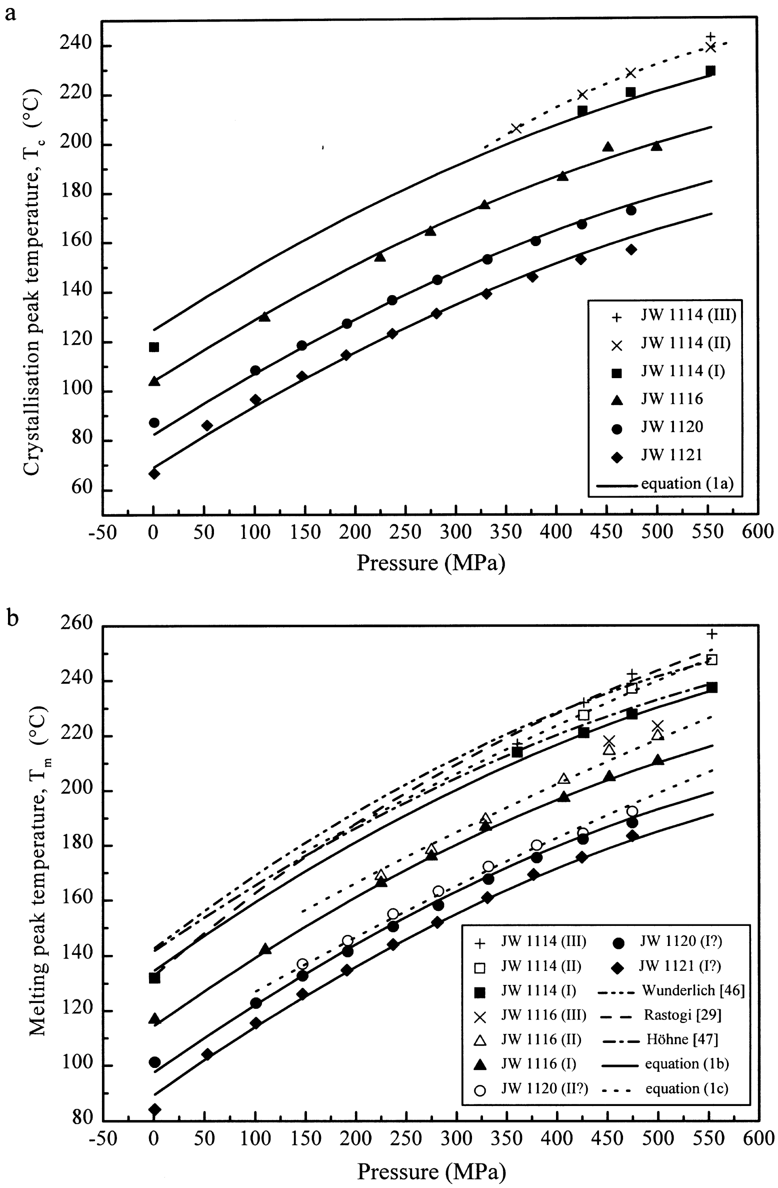

Fig. 6. Crystallisation (a) and melting (b) peak temperatures as a function of pressure of JW 1114, JW 1116, JW 1120 and JW 1121 with the corresponding fitting curves after Equation (1a)–(1c) in Table 2; rate 10°C/min.

The exotherm of JW 1121, in which EESCs can probably not be formed due to the high branching degree, is thought to reflect only the crystallisation into FCCs. The cooling curve of JW 1120, on the other hand, is considered to be the result of the superposition of two peaks (FCCs and EESCs) inducing peak broadening.

In Fig. 6 the crystallisation (T_c) and melting (T_m) peak temperatures (symbols) of the LPE sample and the three homogeneous ethylene-1-octene copolymers are plotted versus pressure. In reality the transition peak of the samples is much broader than for a pure compound; hence, there is a transition range rather than a specific transition temperature. The peak maximum is characteristic for the temperature of the maximum transition rate of the sample. Fig. 6 shows that with increasing pressure T_c and T_m shift to higher temperatures, due to the entropy decrease as already mentioned. This temperature increase is most pronounced at lower pressures and becomes smaller with increasing pressure. The dash–dot–dotted line in Fig. 6(b) represents the fitting curve of the melting temperature of close to equilibrium, extended chain PE crystals after Wunderlich [48, Eq. 28(a)]. The dashed line stands for the pressure dependence of the transition temperature from orthorhombic to hexagonal ECCs of a PE sample after Rastogi et al. [29]. The latter curve reveals a larger slope with respect to the curve after Wunderlich, with fairly good agreement in the values at pressures above 300 MPa. The dash-dotted line represents the pressure dependence of the fusion temperature of an extended chain n-alkane crystal with an infinite number of CH_2-groups. This function was obtained by

Table 2
Parameter values of Eq. 1 for T_c, $T_{m,I}$ and $T_{m,II}$

T_x	$A1$	$A2$	$A3$	$A4$	$A5$	Equation
T_c	39.6704	85.1051	7.4809	0.2615	$1.4\times^{-4}$	1a
$T_{m,I}$	79.5695	54.9261	4.619	0.2615	$1.4\times^{-4}$	1b
$T_{m,II}$	80.8010	66.2104	5.4044	0.2144	$5.7\times^{-5}$	1c

extrapolation of data on the pressure dependence of the fusion temperature (peak maximum temperatures) of different *n*-alkanes (C_{24}–C_{60}) by Höhne et al. [49].

A fitting of the experimental crystallisation peak temperatures (T_c) and melting peak temperatures of peak I ($T_{m,I}$) and peak II ($T_{m,II}$) was performed with pressure and comonomer content as two variables. All three peak temperature sets can be described by a uniform empirical function consisting of a 1-octene dependent exponential part and a pressure dependent quadratic part (see Eq. 1). The corresponding parameter values ($A1$, $A2$,…,$A5$) are given in Table 2.

$$T_x(p, X_8) = A1 + \left(A2\,\exp\left\{\frac{-X_8}{A3}\right\}\right) + A4p - A5p^2 \qquad (1)$$

with T_x in °C, p the pressure in MPa and X_8 the 1-octene content in mole.

The fitted curves are drawn as solid (T_c and $T_{m,I}$) or dotted lines ($T_{m,II}$) in Fig. 6. In case of the LPE-sample the peak maximum of the small low-temperature exotherm was taken for T_c. These empirical equations (with a uniform basic structure) enable to obtain an indicative value of the crystallisation/melting temperature for a homogeneous

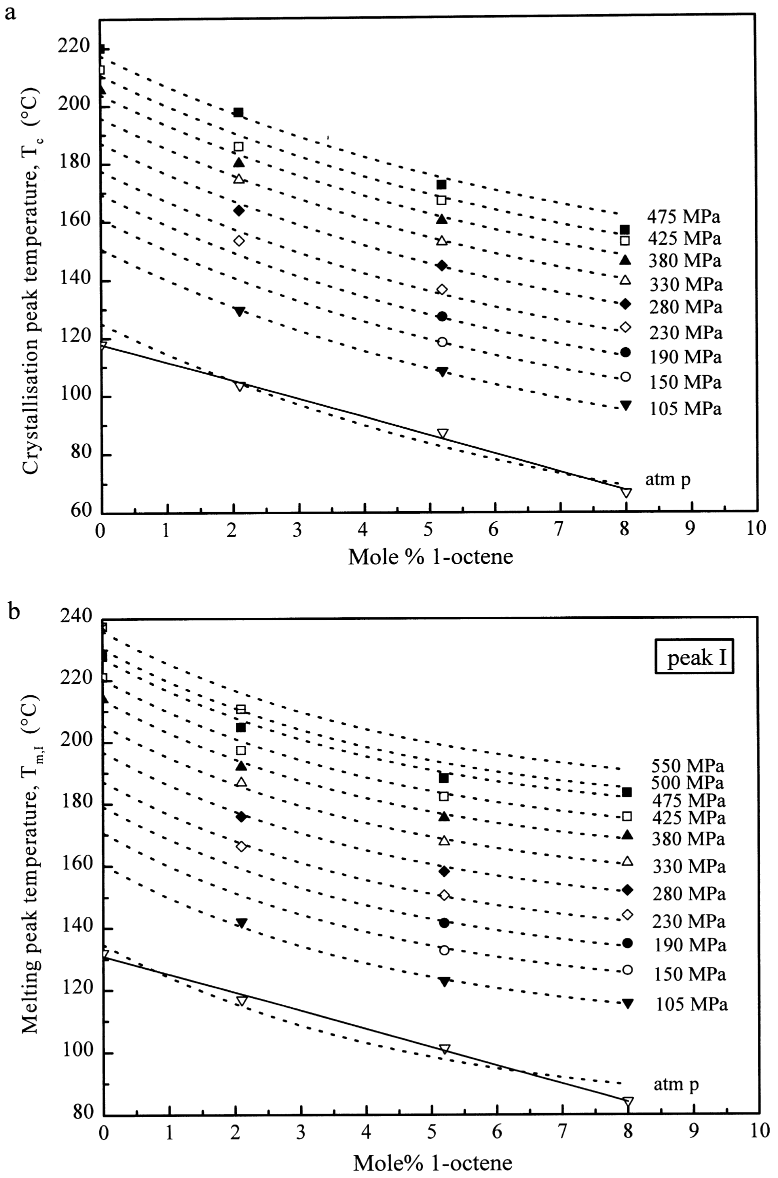

Fig. 7. Crystallisation (a) and melting (b) peak I temperatures as a function of the 1-octene content at different elevated pressures, dotted lines in (a) and (b) represent the corresponding fitting curves after Equations (1a) and (1b), respectively.

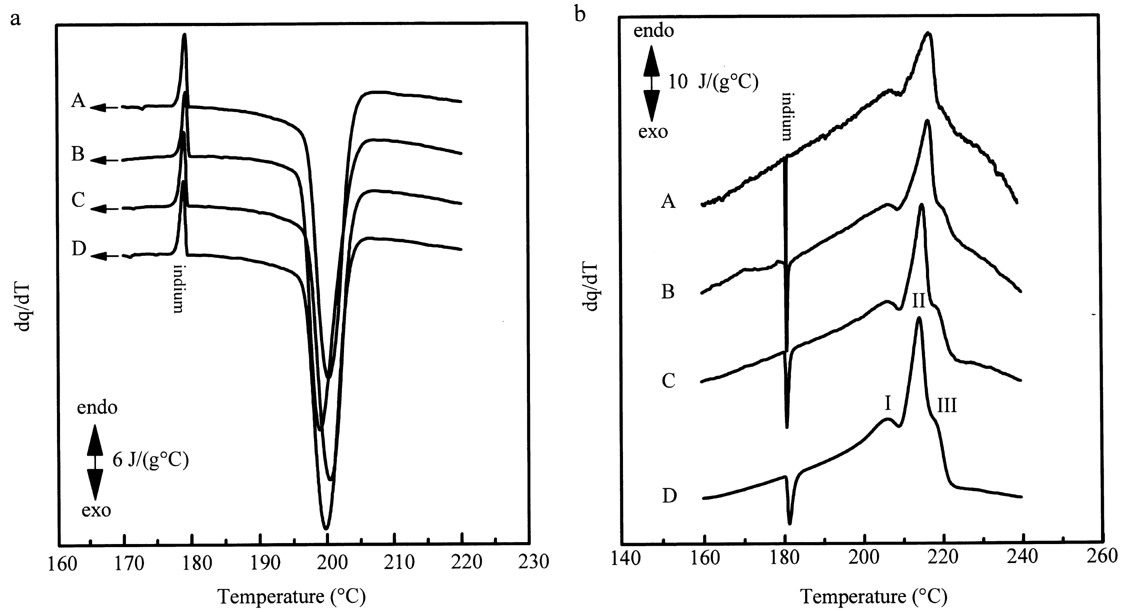

Fig. 8. Cooling curves at −10°/min (a) and subsequent heating curves (b) of JW 1116 at different heating rates: (A) +2°C/min; (B) +5°C/min; (C) +10°C/min; and (D) +20°C/min; pressure 460 MPa.

ethylene copolymer with a given 1-octene content at a certain pressure. One should notice that the pressure dependent part of the fitting function of $T_{m,I}$ is similar to the one of T_c (see Equations 1(a) and 1(b) in Table 2). This implies that T_c and $T_{m,I}$ have a similar behaviour on pressure variation. In the case of $T_{m,I}$ and $T_{m,II}$ the comonomer content dependent part of the fitting function are more or less similar, whereas the differences in the pressure dependent part reflect the slope differences in Fig. 6(b).

It follows from Fig. 6(b) that the pressure dependence of the melting peak temperatures of FCCs ($T_{m,I}$), indicated by the solid curves involving the solid symbols, is independent of the comonomer content, as reflected in the parallel curves. Fair agreement (parallelism) is found in the pressure-dependence of $T_{m,II}$ (open symbols, dotted lines), representing the transition temperature of ECC/EESCs, and the corresponding PE-curve (orthorhomb. → hex. ECC) after Rastogi [29]. The melting temperature curve of extended chain *n*-alkane crystals (dash-dotted line) has a somewhat weaker slope.

Special emphasis should be given to the fact that at elevated pressures the decrease of T_c and T_m with increasing comonomer content is much larger in case of small amounts of 1-octene in comparison with higher amounts, as is illustrated in Fig. 7. At atmospheric pressure, however, T_m and T_c decrease in a nearly linear way as a function of increasing comonomer content. The dotted lines in Fig. 7(a) and (b) are the fitting curves according to Equations. 1(a) and 1(b) in Table 2, respectively. These equations are obviously not applicable at atmospheric pressure, where T_c and $T_{m,I}$ reveal a clear linear relation to the comonomer content. Therefore, a straight line is drawn too.

In conclusion, the high-temperature shoulder, which has been ascribed to the hexagonal phase in case of LPE, seems to be very sensitive to branching of the main chain. Only the copolymer with the lowest comonomer content (JW 1116) and the linear polyethylene sample (JW 1114) reveal a shoulder or peak at high temperature and high pressure. This shoulder/peak only seems to be present when the chain mobility is high enough, i.e. at high pressure, high temperature and low branching content.

3.2. *Influence of heating rate on thermal behaviour at elevated pressure*

For JW 1116 (2.1 mol% 1-octene) multiple peaks are present in the heating runs at the highest pressures, see Fig. 3. Because the cooling curve reveals only one peak, recrystallisation and/or reorganisation during heating are suspected. If so, the multiple peaks should be sensitive to the heating rate, which is why different heating rates were explored. The copolymer was crystallised at 460 MPa by cooling from the melt (270°C) at −10°C/min and subsequent heated under the same pressure at different rates: +2, +5, +10 and +20°C/min.

The cooling curves (same sample and same rate) are shown in Fig. 8(a). The crystallisation peak temperatures are all situated in-between the temperature range of (199.6 ± 0.7)°C, hence within the experimental error. Such observations confirm the good reproducibility of the measurements and hence the reliability of the instrumental performance. The endotherms of JW 1116 taken at different rates at 460 MPa are shown in Fig. 8(b). In all cases a three-peak pattern can be observed, consisting of a small low-temperature peak I (~207°C) and a rather sharp, large peak II (~215–218°C) with a high-temperature shoulder

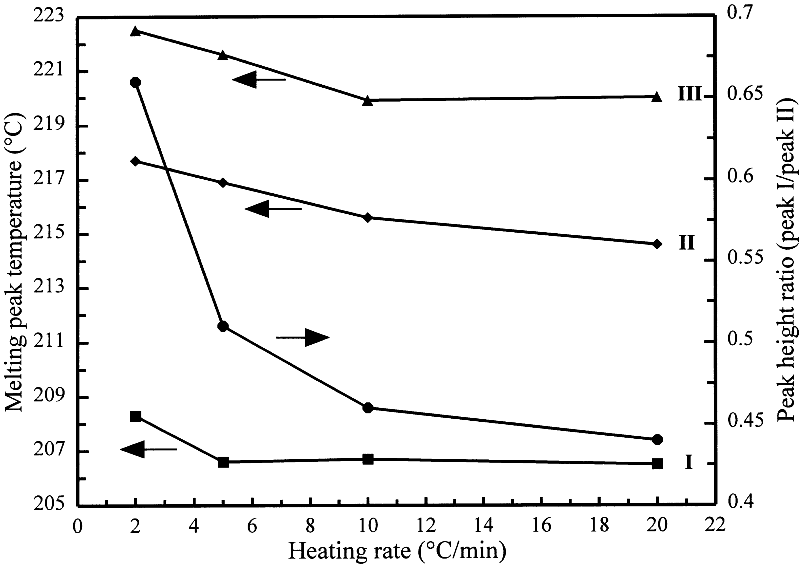

Fig. 9. Peak height ratio of peak I and peak II (right ordinate) and the corresponding melting peak temperatures (left ordinate) as a function of the heating rate (●) ratio peak I/peak II, (■) peak I temperature, (◆) peak II temperature, (▲) peak III temperature; pressure 460 MPa.

III (~220°C). By varying the heating rate from 2 to 20°C/min the position of the low-temperature peak (I) remains nearly constant around 270°C, while the peak temperatures of peak II and peak III (shoulder) slightly decrease (approximately 3°C), as is shown in Fig. 9. The ratios of the low-temperature peak (I) to the larger peak (II), also inserted in Fig. 9, are calculated by drawing a straight baseline through the data points at 160 and 240°C and dividing the peak height (relative to the baseline) of peak I by the peak height of peak II. The peak ratio *decreases* with increasing heating rate, while it should increase in case of recrystallisation. This peak ratio decrease strangely suggests that reorganisation is favoured on increasing heating rate, which is unexpected and quit interesting. The experimental facts that the peak height ratio I/II decreases with heating rate, that only one peak is observed during cooling and that there is no significant difference in the positions of the endotherms taken at +2 and at +20°C/min, suggest that reorganisation of FCCs into EESCs must be a fast process that is induced by the high pressure/high temperature and enhanced by faster heating. In addition, with increasing heating rate the peak height ratio of peak I to peak III decreases, see Fig. 8.

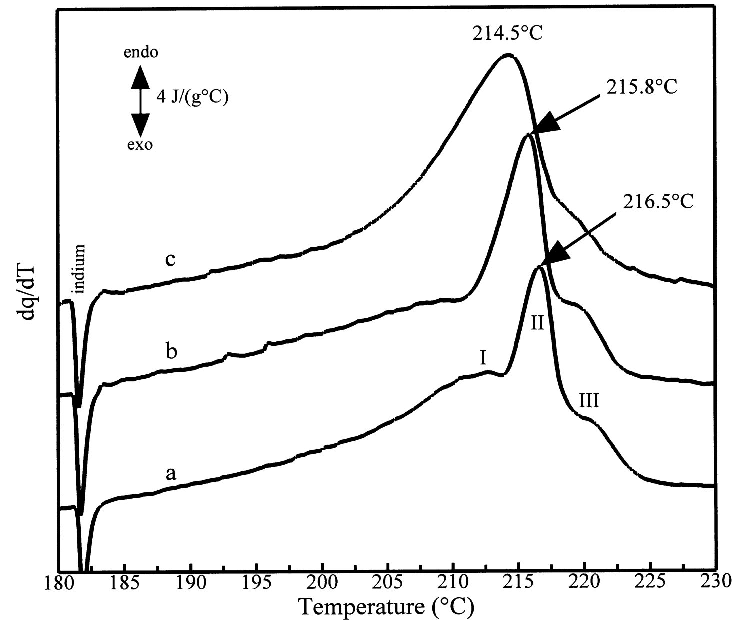

Fig. 10. Heating curves (+10°C/min) at 460 MPa of JW 1116 cooled at different rates at atmospheric pressure: (a) −1°C/min; (b) −10°C/min; and (c) quenched.

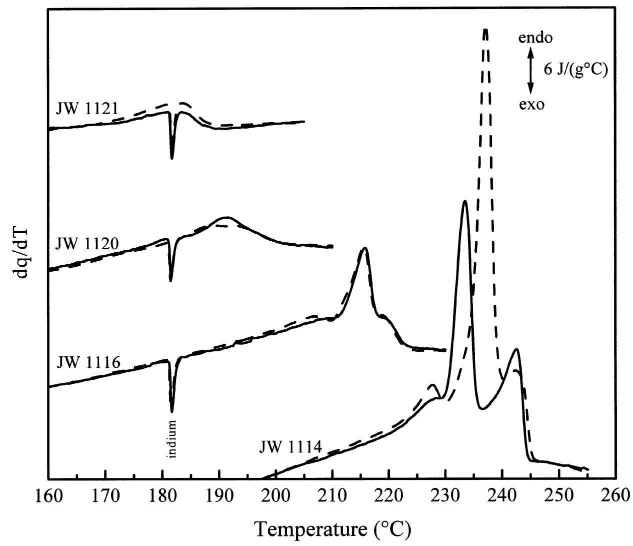

Fig. 11. Heating curves (+10°C/min) at 460 MPa of the samples crystallised at atmospheric pressure (solid line) and crystallised at 460 MPa (dashed line).

At low heating rate the hexagonal phase (peak III) is almost not seen. So, may be, the peculiar reorganisation phenomena are possibly connected to the occurrence of the hexagonal phase.

However, it has to be mentioned that, because of the curvature of the present HP-DSC curves, more quantitative experiments are needed to enable a better determination of the peak height ratios.

In conclusion, concerning the influence of the heating rate on the thermal behaviour of JW 1116 at high pressure, it is concluded that the heating rate has no significant influence on the thermal behaviour—apart from the peak I/peak II ratio—of JW 1116 at high pressure (460 MPa), that recrystallisation in the usual sense can be excluded and that the extension of ethylene sequences during heating is a very fast pressure-induced process, which seems to be favoured by faster heating.

3.3. Influence of cooling rate on thermal behaviour at elevated pressure

To evaluate the kinetic features, one and the same sample, JW 1116, was crystallised at atmospheric pressure by three different cooling procedures: cooled from the melt (200°C) to room temperature at −1°C/min, at −10°C/min and quenched from the melt (200°C) in a CO_2-isopropanol bath of −70°C. After this thermal treatment the sample was submitted to a pressure of 450 MPa at room temperature and subsequently heated at a rate of 10°C/min to 270°C at elevated pressure. The heating runs are shown in Fig. 10. With increasing cooling rate the main peak temperature ($T_{m,II}$) decreases from 216.5 over 215.8 to 214.5°C. The low-temperature peak (I) becomes less pronounced and is not observable any longer for the quenched sample, which may be caused by the broadening of peak II. The high temperature shoulder (III) shifts somewhat to lower temperatures on increasing cooling rate. The quenched sample reveals a much-broadened endotherm, ascribed to cocrystallisation during cooling and reorganisation/recrystallisation effects during heating. Although it is very difficult to estimate the heat of fusion, it seems that the quenched copolymer does not reveal the smallest peak area (lowest crystallinity). The wide range of melting can be understood in the usual way (like in case of measurements at atmospheric pressure): during the very rapid cooling (quenching) the chain segments are captured abruptly in crystallites leading to imperfect and relatively small crystallites which are far from ideal equilibrium crystals. Such crystallites have a strong tendency to recrystallise and reorganise during heating into more perfect and larger crystallites. So, the broad endotherm of the quenched sample might be interpreted as a gradual, continuous reorganisation, melting and recrystallisation under high pressure into thermally more stable crystallites, having a higher perfection. Nevertheless, the reorganisation at elevated pressure seems to be not large enough to enable the quenched material to become more perfect than the slowly cooled material. Such a feature is sometimes observed at atmospheric pressure.

3.4. Samples crystallised at atmospheric pressure

Fig. 11 shows the endotherms (+10°C/min) of the four samples (JW 1114, JW 1116, JW 1120, and JW 1121) crystallised at atmospheric pressure by cooling from the melt at −10°C/min. They were submitted to a pressure of 450 MPa at room temperature and subsequently heated at +10°C/min into the melt. The corresponding heating curves of the samples crystallised at 460 MPa are included in Fig. 11 too for comparison. Beside the shift in peak temperature to lower temperatures and the decreasing peak intensity (lower crystallinity) with increasing comonomer content, one can observe some continuity in the heating pattern when a few hexyl branches are introduced into the polyethylene chains. In case of the samples crystallised at atmospheric pressure, with increasing 1-octene content, the well-pronounced three-peak pattern of the LPE sample evolves over a three-peak pattern with a reduced high-temperature peak III (JW 1116) into a single broad melting peak (JW 1120 and JW 1121). For JW 1121 the indium reference peak is unfortunately overlapping in the melting region.

When the heating curves of the samples crystallised at atmospheric and at high pressure are compared, clear differences only can be observed for JW 1114. The heating curve of the LPE sample crystallised at high pressure reveals a more pronounced low-temperature peak I and a much higher peak II, while the intensity of peak III, seems to be reduced. The peak area (heat of fusion) is obviously much larger too, reflecting the higher crystallinity. The position of peak I and peak III remains constant, while peak II shifts to higher temperatures (ca. 5°C) when JW 1114 is crystallised at high pressure. When JW 1116 is crystallised at high pressure the low-temperature peak is more pronounced compared to the sample crystallised at atmospheric pressure. For JW 1120 and JW 1121 the influence of pressure during crystallisation is rather small. Though not probable, due to the instrumental curvature it cannot be ruled out that the crystallinities of the copolymers are changed by applying pressure.

Further, it has to be noticed that a three-peak pattern is observed for JW 1114 and JW 1116 irrespective of whether crystallisation occurred at ambient or high pressure. This means that the three peaks seen in the samples crystallised at atmospheric pressure is caused by the final high-pressure heating run. This is also confirmed by the absence of a three-peak pattern in the heating curve at atmospheric pressure of a high-pressure crystallised sample.

4. Conclusions

The influence of pressure, comonomer content, heating rate and cooling rate (at atmospheric pressure) on the thermal behaviour of a LPE sample and three homogeneous ethylene-1-octene copolymers of different 1-octene content (2.1, 5.2 and 8.0 mol%) was investigated at different elevated pressures (up to 550 MPa) by use of a high-pressure DSC (HP-DSC).

With increasing pressure the melting and crystallisation regions shift towards higher temperatures due to a decrease in entropy. At high pressure/high temperature the mobility of the polymer chains is drastically increased enabling the chains to organise—probably via the hexagonal phase—into extended chain crystals (ECCs) in case of LPE or, in case of branched copolymers, at most into folded chain crystals with stem lengths comparable to the ethylene sequence lengths, leading to so called extended ethylene sequence crystals (EESCs).

At high pressure and in case of zero or low 1-octene content (0 and 2.1 mol%) a three-peak melting pattern is observed consisting of (probably): a small low-temperature melting peak of FCCs (peak I), a large melting peak of orthorhombic ECCs/EESCs, eventually superposed on the orthorhombic ECC/EESC → hexagonal phase transition (peak II) and a high-temperature melting peak/shoulder of the hexagonal phase (peak III). As the pressure is lowered the hexagonal peak III moves closer to peak II and finally disappears, supporting the absolute necessity of high chain mobility for the occurrence of the hexagonal phase. To evaluate the presence of the hexagonal phase, which might cause the high-temperature shoulder III mentioned, high-pressure X-ray measurements are required and planned in future.

With increasing 1-octene content the three-peak endothermic pattern at high pressure evolves over a broad two-peak pattern (probably only I and II, 5.2 mol% 1-octene) into one broad endotherm (probably only I, 8.0 mol% 1-octene). One can assume that with an increasing amount of hexyl branches the chain mobility becomes much more reduced so that extension of the ethylene sequences and/or the appearance of the high-temperature/high-pressure hexagonal phase is hindered or absent. Therefore, the formation of FCCs with folded ethylene sequences is favoured over ethylene sequence extension.

Further, it is found that at elevated pressures the peak temperature shift to lower temperatures with increasing comonomer content is different compared to atmospheric pressure, where T_c and T_m are linearly related to the comonomer content. The hexyl branches seem to have a stronger influence on crystallisation and melting at high pressure at low branching content and a smaller influence at higher branching content. The crystallisation and melting peak temperatures of the LPE-sample and the three homogeneous ethylene-1-octene copolymers can be described as a function of pressure and comonomer content by use of a uniform basic equation consisting of an exponential and a quadratic part. These empirical equations enable to obtain an indicative value for crystallisation and melting peak temperature for a homogeneous ethylene copolymer with a given 1-octene content at a certain pressure.

Variation of the heating rate at 460 MPa, shows that during heating at high pressure, recrystallisation in the usual sense can be excluded. It appears that the reorganisation of FCCs into EESCs is a very fast pressure-induced process which, surprisingly, is enhanced by higher heating rates, possibly through the hexagonal phase.

Increasing the cooling rate at atmospheric pressure results in a slight shift to lower temperatures and a broadening of the high-pressure (460 MPa) heating curves. The broad endotherm of the quenched copolymer can be ascribed to cocrystallisation during cooling and reorganisation/recrystallisation effects during heating at elevated pressure.

When the heating curves of a sample crystallised at atmospheric pressure and crystallised at high pressure (460 MPa) are compared, the differences become less pronounced with increasing 1-octene content. The peak area of the endotherm of the LPE sample is larger, reflecting the higher crystallinity as obtained during crystallisation at high pressure, while the main peak temperature shifts towards higher temperatures by approximately 5°C. For the systems studied, a three-peak melting pattern seems to be caused by the final high-pressure heating run, since only then three peaks were observed irrespective of whether the sample was crystallised at ambient or elevated pressure, while at atmospheric pressure only one peak is seen.

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