Ethylene−1-Octene Copolymers at Elevated Pressure−Temperature. 1. Order−Disorder Transition

S. Vanden Eynde,[†] S. Rastogi,*,[‡] V. B. F. Mathot,[†] and H. Reynaers[†]

Katholieke Universiteit Leuven, Departement Scheikunde, Laboratorium voor Macromoleculaire Structuurchemie, Celestijnenlaan 200F, B-3001 Heverlee, Belgium, and Eindhoven Polymer Laboratories/The Dutch Polymer Institute, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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ABSTRACT: Homogeneous ethylene−1-octene copolymers of 5.0 and 8.0 mol % 1-octene content lose their crystalline order and become seemingly "amorphous-like" during isothermal pressure increase to 370 MPa at room temperature, as investigated by in-situ wide-angle X-ray scattering. The disordering in the crystalline lattice of the orthorhombic unit cell is likely to be caused either by destruction of the initial (orthorhombic) crystalline structure or by breaking up of crystallites in very small entities, which escape detection, by WAXD. On cooling from 190 °C at high pressure (∼370 MPa), crystallization into the orthorhombic phase starts at 163 °C. On further cooling a sudden densification of the orthorhombic unit cell takes place at approximately 70 °C, and simultaneously a new reflection appears which can be assigned to the hexagonal phase. This phenomenon is indicative for the occurrence of a pressure-induced sequence length separation, probably leading to two crystallite populations: orthorhombic crystals, relatively large and well developed, and hexagonal structures, possibly built up of small ethylene sequences containing hexyl branches. Further, experimental observations are that both "amorphization" and the pressure-induced sequence length separation strongly depend on the pressure, being absent at a pressure of 195 MPa. The present high-pressure X-ray results correspond well with comparable DSC results obtained recently.

1. Introduction

The crystallization and melting behavior and the morphology of various polyethylenes have been frequently studied at ambient and elevated pressures (see Huang et al.[1] for an overview). However, it is not known how the crystallographic structure of homogeneous ethylene−1-alkene copolymers is influenced when such copolymers are subjected to pressure−temperature ramps. Studies on crystallization and melting of homogeneous copolymers of ethylene with propylene, 1-butene, and 1-octene by differential scanning calorimetry (DSC) have been reported recently.[2,3] Moreover, a comprehensive DSC study involving high-pressure DSC measurements was performed on homogeneous ethylene−1-octene (EO) copolymers with low comonomer contents (≤8 mol % 1-octene).[4] In this work, we report the results of time-resolved, high-pressure wide-angle X-ray diffraction (HP-WAXD) measurements performed on the same ethylene−1-octene samples.

The short branches in homogeneous ethylene−1-alkene copolymers, as the ones discussed here, give rise to an ethylene sequence length distribution (ESLD), which has a major influence on the crystallization behavior.[5,6] Considering the polymerization conditions and a homogeneous catalyst used for the synthesis, the samples have a distribution of octene units along the chains which is homogeneous with regard to the statistics.[5] The morphology of the investigated samples at ambient pressure shows lamellae organized in spherulites.[7,8]

During cooling at ambient pressure, crystallization of sequences of comparable length is favored because of thermodynamic reasons,[9−11] while side branches containing six carbon atoms are rejected from the crystal core. However, in reality, sequences differing in length will cocrystallize because the diffusion of equal-length sequences to the same crystal growth front is hindered by the long-chain nature of the molecules. Moreover, once the longest sequences have crystallized, diffusion of shorter sequences to appropriate crystal fronts is frustrated increasingly. Nevertheless, even a rough selection of sequences as described from the ESLD leads to a *crystallization temperature distribution* and thus a *distribution in the crystallite dimensions*. The latter is reflected in the crystallization *range* in DSC cooling curves (see Figure 1a). For thermodynamic reasons, these crystallites with different dimensions will melt at different temperatures during heating, resulting in a *melting temperature distribution*. This results into a broad melting peak in DSC heating curves (see Figure 1b).

Since packing of the chains within the crystal is strongly hindered because of the short-chain branches, physical parameters like degree of crystallinity, the density at room temperature, the (temperature-dependent) properties of the material, etc. (see Figure 1),[2,3,6] are strongly influenced. Increasing comonomer content strongly influences the thermal behavior as is seen from the changes in the shape, position, and size of the crystallization and melting peaks in DSC curves. With increasing 1-octene content, the DSC curves during cooling and heating become broader, corresponding to broader crystallite distributions. There is also a shift to lower temperatures, reflecting smaller and less perfect crystallites. The reduced DSC peak area is due to the lower crystallinity at higher comonomer content.

These physical features, strongly influenced by increasing comonomer content, can be explained as a

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[†] Katholieke Universiteit Leuven.
[‡] Eindhoven University of Technology.
* To whom correspondence should be addressed.

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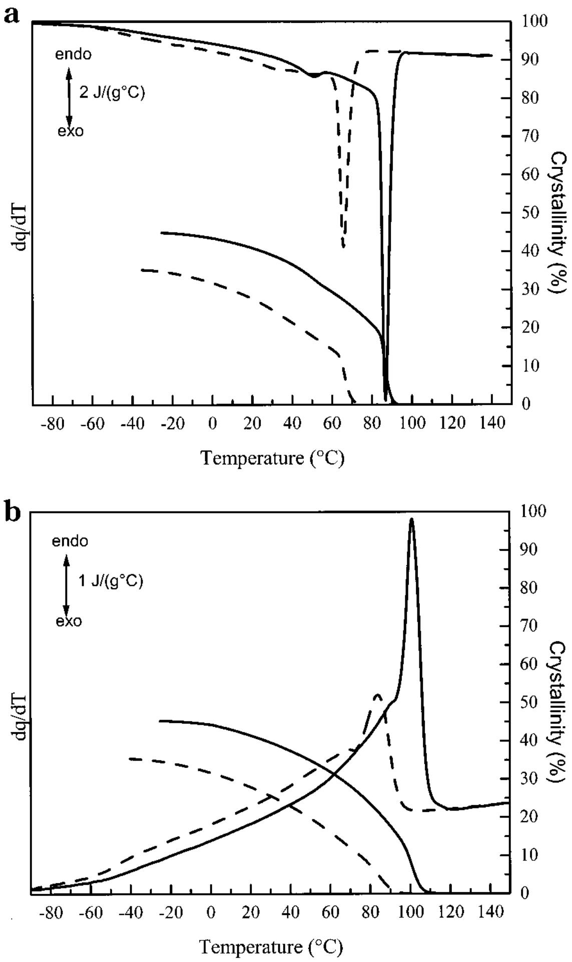

Figure 1. DSC curves and corresponding enthalpy-based crystallinities during cooling at 10 °C/min (a) and subsequent heating at the same rate (b) of two different homogeneous ethylene−1-octene copolymers with 5.2 mol % (JW1120, solid line) and 8.0 mol % (JW1121, dashed line) 1-octene.

result of decreasing length of crystallizable ethylene sequences with the increasing amount of branches. Moreover, chain mobility decreases with decreasing melting temperature; i.e., the decreasing temperature strongly influences the rate at which segments of the same length are sorted[9−11] out for crystallization. This further results in the formation of smaller, less perfect and less stable crystallites with increasing comonomer content.[5,12]

The small exotherm at lower temperature, often observed in ethylene-based polymers, has tentatively been ascribed to homogeneous nucleation.[13] On the basis of temperature-modulated DSC (TMDSC) measurements on an ethylene−1-octene sample, formation of—at least—two different types of crystals, lamellae and fringed-micellar crystals, have been proposed by Wunderlich.[14] In these experiments, the relatively sharp high-temperature part of the melting peak was assigned to the melting of lamellae (largely irreversible melting), while the broad lower-temperature endothermic region (reversible melting) was assigned to melting of crystals having fringed-micellar structures. The presence of different morphologies, even within one and the same homogeneous copolymer, cannot be excluded.[5]

Crystallization and melting behavior of the copolymers can be strongly influenced when a sample is subjected to high $p-T$. Usually the melting point increases with pressure, thus increasing the crystallization temperature. This facilitates crystallization into more perfect and larger crystals because of the high chain mobility provided with the increasing crystallization temperature. Especially in linear polyethylene, in addition to increase in melting temperature, incoming of a new phase (hexagonal) at the elevated pressures and temperatures further enhances the chain mobility.

Considering the general criterion in polyethylene, it is feasible that the ethylene sequence sorting procedure will be much more efficient because of the higher mobility provided due to increase in the melting temperature with pressure or incoming of a new phase.

In addition, it cannot be ruled out that at high $p-T$ chain segments containing isolated side chains, which are likely to be excluded from the orthorhombic crystalline phase at ambient pressure, might be able to crystallize during cooling. These side chains will probably crystallize in a more open and expanded crystal structure such as the hexagonal form. In copolymers of polyethylene the hexagonal phase has been reported recently by Androsch et al.[15] These authors suggest a three-phase model for isotropic and elongated homogeneous ethylene−1-octene copolymers consisting of an amorphous phase, an orthorhombic crystal structure, and a hexagonal mesophase that probably accommodates hexyl branches. In contrast to linear polyethylene, where the hexagonal phase is not stable at room temperature, the presence of the side chains in ethylene copolymers could stabilize the hexagonal form at low temperatures.

In this and forthcoming papers crystallization of ethylene−octene copolymers and resulting crystal structures are investigated in real time at elevated pressures and temperatures using HP-WAXD. In this paper a particular sample (JW1121, 8.0 mol % of 1-octene) was selected for investigation because it contains a significant amount of side branches, thus facilitating investigation of the effect of side branches on crystal structure.

2. Experimental Section

Materials. The measurements were performed on a homogeneous ethylene−1-octene copolymer with a comonomer content of 8.0 mol % (code: JW 1121, M_w = 31 000 g/mol). Some remarks are also made on JW1120 (5.2 mol % of 1-octene, M_w = 34 000 g/mol). The sample was synthesized with the help of a vanadium-based catalyst.[17,18] The comonomer content was tuned by varying the 1-octene/ethylene ratio. 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".[5]

Before placing the sample in the high-pressure cell, it was heated to 200 °C and was left at that temperature for 5 min. The sample was subsequently cooled from the melt to room temperature (RT) at 10 °C/min at atmospheric pressure.

Equipment. The time-resolved WAXD measurements at elevated pressures were performed at the beamline ID11-BL2 at the European Synchrotron Radiation Facility (E.S.R.F.), Grenoble, France. The high-pressure cell used is similar to the one designed by Hikosaka and Seto.[19] The maximum attainable pressure is 400 MPa, and the temperature can be varied between room temperature and 300 °C. A 0.4 mm thick sample is placed between two diamond windows, each of 1 mm thickness, surrounded by Teflon spacer rings. The use of diamond windows enables to perform in-situ X-ray studies. Monochromatic X-rays of wavelength 0.714 Å and high flux were used to minimize X-ray absorption by the windows. Pressure on the sample is generated three-dimensionally by the movement of two pistons activated by pressure-regulated nitrogen gas. A constant pressure is maintained during any

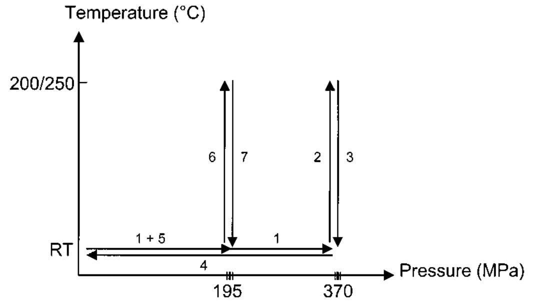

Figure 2. Experimental procedure, the paths along which the experiments have been performed at two different pressures like 370 and 195 MPa.

volume change occurring due to crystallization or melting because of the smooth motion of the pistons.

The sample was subjected to an approximate pressure of 370 MPa (or 195 MPa) at room temperature (25 °C), before it was heated to 200 °C at the same pressure. The heating rate for all experiments reported in this paper was 4 °C/min. After reaching the requisite temperature, the sample was subsequently cooled to room temperature at the same pressure at the rate of 4 °C/min. The experimental procedure is schematically illustrated in Figure 2.

Each diffraction pattern was recorded for 30 s on a two-dimensional Princeton CCD detector. The data were corrected for curvature of the detector using the diffraction pattern of a specific calibration grid placed in the X-ray beam. The circle coordinates of strong reflections were used to determine the correct beam center. The two-dimensional patterns were transformed into one-dimensional plots by performing integration along the azimuthal angle using the FIT2D program provided by Dr. A. Hammersley of ESRF.

3. Results and Discussion

3.1. Pressure-Induced "Amorphization or Disordering" during Isothermal Pressure Increase at RT to 370 MPa. The diffraction patterns of JW 1121 recorded in situ during increasing pressure at room temperature to a maximum value of 370 MPa are shown in Figure 3. At low pressure the diffraction pattern consists of crystalline orthorhombic 110 and 200 reflections and a pronounced shear-induced[20] monoclinic reflection ($2\theta \approx 8.7°$) originating due to internal shear generated within the sample during compression. In the process of increasing pressure 370 MPa at room temperature, an unexpected behavior is observed: the copolymer, semicrystalline at ambient conditions, progressively loses its crystalline order and appears to become an "amorphous-like" feature. Analogous results we found for a less copolymerized sample JW1120, with 5.2 mol % of octene. It resembles "pressure-induced amorphization" behavior as reported earlier[21–23] in the case of another polymer, poly(4-methylpentene-1). The intensities of the orthorhombic 110 ($2\theta \approx 9.3°$) and 200 ($2\theta \approx 10.4°$) reflections gradually fade away on pressure increase and vanish around 155 MPa. The monoclinic reflection shifts to higher angles as a result of compression and decreases continuously in intensity. This experimental finding in the copolymer is in disagreement with the reported findings on linear polyethylene; for example, see Figure 3 in ref 24. The experimental observations on the linear polyethylene have been that no disordering or amorphization occurs with increasing pressure at room temperature (25 °C). In the linear polyethylene, with increasing pressure an orthorhombic to monoclinic transition occurs, but no shift in the monoclinic reflection is observed.

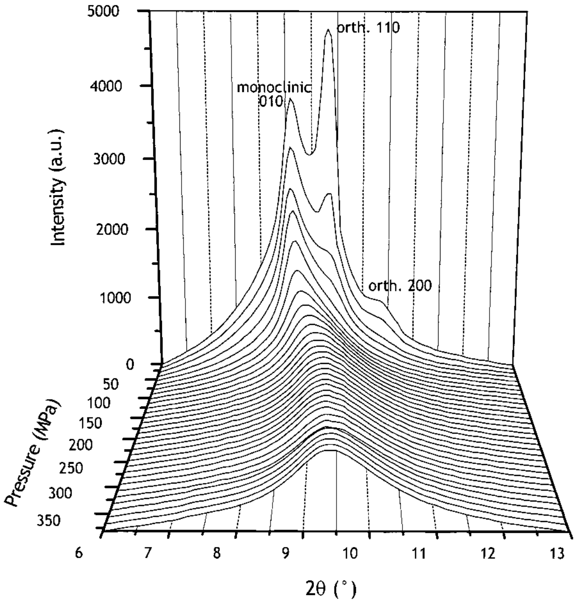

Figure 3. Wide-angle X-ray diffraction patterns recorded in situ during isothermal pressure increase at 28 °C of the sample JW1121 (8.0 mol % 1-octene), from 5 to 380 MPa i.e., along path 1 as shown in Figure 2. The wavelength used for the experiment is 0. 714 Å. Each diffraction pattern represents integrated intensity along the azimuthal angle. The d values at 5 MPa for the three strong reflections are 4.70, 4.34, and 3.94 Å. Considering the position and intensity of these reflections, the diffraction peak at 4.7 Å is assigned to the 010 monoclinic reflection, and the peaks at 4.34 and 3.94 Å are assigned to the 110 and 200 reflections for the orthorhombic phase. Compared to the reflections for linear polyethylene in the orthorhombic phase, where $d_{110} = 4.1$ Å and $d_{200} = 3.7$ Å, the assigned 110 and 200 reflections for the copolymer have higher d values. Relatively speaking, the position of the assigned monoclinic reflection is in close agreement to that for the linear polyethylene (i.e., $d_{010} = 4.6$ Å).

These results show conclusively that because of the presence of hexyl branches, the applied pressure leads to disorder within the crystalline structure, i.e., converting the crystals into an amorphous-like state. An alternative explanation could be that, on applying pressure, the relatively large orthorhombic crystallites are broken up into smaller entities, resulting in very weak and broadened reflections, which might lie under the amorphous halo and therefore escape detection by X-rays. The latter hypothesis could in principle be checked by high-pressure SAXS measurements, as the invariant is extremely sensitive to the presence or changes in small amounts of crystalline material.[3] At this stage it could be mentioned that preliminary results strongly indicate complete loss in the invariant (or overall integrated intensity) with increasing pressure. This would be the subject of the forthcoming paper.

It is found that on subsequent release of pressure at room temperature the orthorhombic and monoclinic reflections reappear. However, on pressure release the 110 and 200 reflections are much less pronounced while the underlying amorphous scattering increases, with respect to the amorphous scattering of the sample at the beginning of the experiment, before increasing pressure. In case there is complete amorphization during pressure increase, such reappearance would mean crystallization during pressure release. However, in the case of existing small entities, a kind of healing of these entities in combination with crystallization is expected to take place.

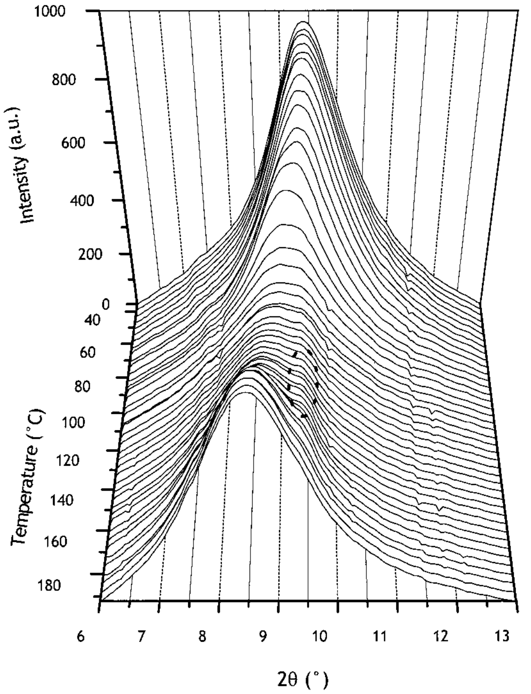

Figure 4. A series of wide-angle X-ray diffraction patterns recorded during heating, at a fixed pressure of 370 MPa, at a rate of 4 °C/min from 35 to 192 °C, i.e., along path 2 in Figure 2. The encircled area in the figure constitutes very weak 110 and 200 reflections for the orthorhombic phase. The wavelength used for the experiment is 0.714 Å.

Pressure-induced "amorphization" was also observed in poly(4-methyl-pentene-1) by Rastogi et al.[21−23] Upon increasing pressure beyond a threshold, this polymer, semicrystalline at ambient conditions, loses its crystalline order isothermally and becomes reversibly "amorphous" in two widely separated temperature regimes (around 20 and 200 °C), the transformation occurring via a liquid-crystalline state. Amorphization under pressure has also been observed in other loosely packed materials such as ice,[25,26] silica,[27] and $AlPO_4$.[28−30] The underlying common feature between the polymer and the inorganic materials is that the crystals possess loose packing. In view of this, a possibility of the existence of a loose crystalline structure, because of the hexyl branches, cannot be ignored in the present case. We will return to this point more conclusively later in this paper.

3.2. Subsequent Heating at 370 MPa. After reaching the "amorphous-like" state by pressurizing the sample at room temperature, when the sample is subsequently heated from room temperature to 192 °C at the fixed pressure of 370 MPa at a heating rate of 4 °C/min, the following observations were made. Very weak peaks that can be assigned as 110 and 200 reflections for the orthorhombic phase are found to appear in the temperature range 140−180 °C. Simultaneously, the "amorphous" halo moves to lower angles (see Figure 4). At temperatures above 180 °C, the 110 and 200 reflections of the orthorhombic phase disappear; i.e., melting occurs without any intervention of a new phase. This experimental observation is in contradiction with the anticipated intervention of the hexagonal phase in linear polyethylene at these pressures and temperatures. Our experimental observations in copolymers are in agreement with the recently reported morphological findings by Bassett et al.[31] But it is to be noted that the overall profile of the WAXD patterns for the melt is still asymmetrical in nature.

Whether the orthorhombic crystalline reflection develops during heating or becomes just visible because of the shift of the "amorphous halo" to the lower angles on heating is not evident from these experiments. The orthorhombic 110 reflection is extremely weak in intensity, suggesting low crystallinity even at these pressures and temperatures. Such could be a result of very few or small and/or imperfect crystallites that are either present from the beginning (before heating) or formed during the heating process at fixed pressure.

In terms of melting temperature of 180 °C at 370 MPa, a fair agreement is found with the end melting point observed in HP-DSC,[4] which is 175 °C at ca. 380 MPa. At this point it need to be mentioned that in HP-DSC on heating isobarically at 380 MPa no exotherm was observed. The absence of an exotherm favors the hypothesis that the amorphous-like state obviated on increasing pressure at room temperature is not equivalent to the melt at high temperatures. To gain a better insight into the structure of the amorphous-like state, high-pressure Raman spectroscopy studies are in progress and will be the subject of the following paper.

The concomitant shift of the amorphous halo to lower angles observed for JW 1121 is ascribed to the thermal expansion of the amorphous state during temperature increase.

3.3. "Pressure-Induced Sequence Length Separation" during Cooling at 370 MPa. During subsequent cooling of JW 1121 at 4 °C/min from the melt (190 °C) at a fixed pressure of 370 MPa, crystallization into the orthorhombic phase is observed at 163 °C (see Figure 5a,b). The crystallization temperature is roughly in agreement with $T_c^{onset} = 155$ °C as observed by HP-DSC[4] at 10 °C/min for the same pressure. When the sample is left to cool further, within a small temperature interval of ~5 °C, around 70 °C, the orthorhombic 110 reflection ($2\theta_{110} \approx 9.55°$; $d_{110} = 4.32$ Å) and 200 reflection ($2\theta_{200} \approx 10.55°$; $d_{200} = 3.88$ Å) abruptly shift to higher angles. Now the new position of the two orthorhombic reflections 110 and 200 is at $2\theta_{110} \approx 9.94°$ ($d_{110} = 4.15$ Å) and $2\theta_{200} \approx 11.20°$ ($d_{200} = 3.65$ Å), respectively. With the abrupt shift, intensity of the two reflections also decreases. Simultaneously, a new reflection appears at $2\theta \approx 9.34°$ (4.42 Å).

The new position of the orthorhombic 110 and 200 reflections for the coploymer is in good agreement with the Bragg *d* values assigned for these reflections in the case of linear polyethylene, having the unit cell dimensions $a = 7.41$ Å, $b = 4.94$ Å, and $c = 2.55$ Å.

The position of the new reflection at $2\theta \approx 9.34°$ (4.42 Å) lies between the monoclinic 010 ($d_{010} = 4.7$ Å) and the 110 ($d_{110} = 4.15$ Å) reflection for the orthorhombic phase. In terms of the Bragg *d* value, the position of this reflection is relatively larger than the 100 reflection for the hexagonal packing in linear polyethylene. In linear polyethylene for the hexagonal unit cell $a = b = 4.91$ Å, the Bragg $d_{100} = 4.22$ Å. Considering the position of the new reflection (4.42 Å), closer to the 100 reflection for the hexagonal phase than the monoclinic, and the higher symmetry for the hexagonal packing, the new reflection has been assigned as the 100 reflection for the hexagonal phase. Because of the flexibility in packing of the chains in the hexagonal phase, the hexagonal phase here may be also termed the pseudohexagonal phase or columnar hexagonal phase[32] or condis phase.[33]

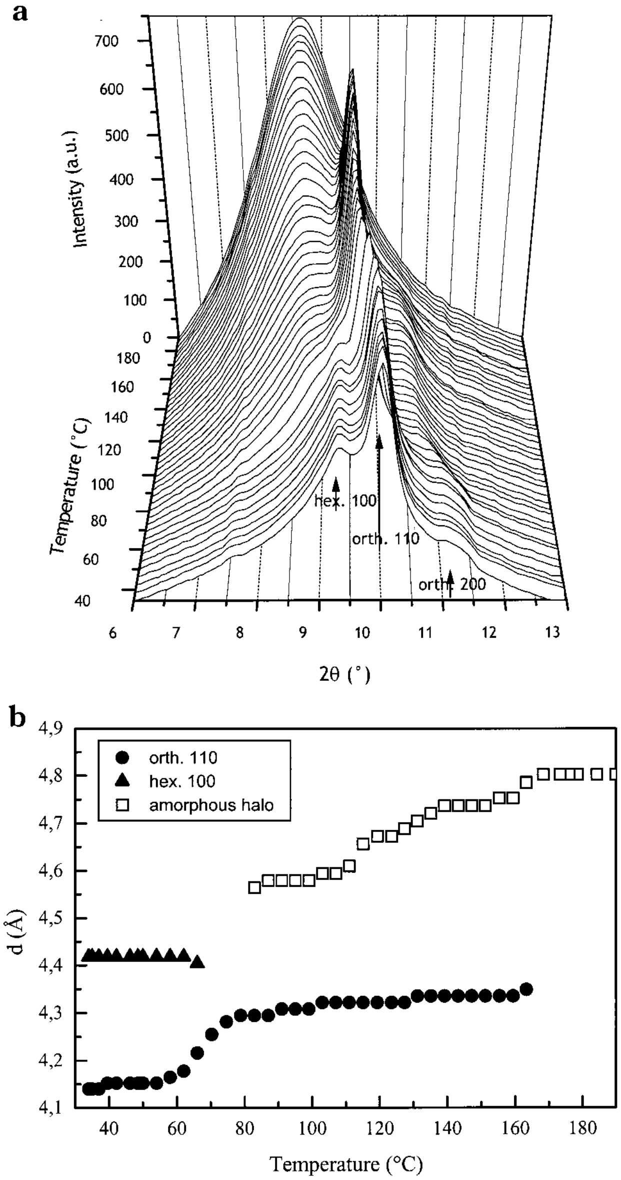

Figure 5. (a) A series of X-ray diffraction patterns recorded in situ during cooling from 190 to 34 °C at a rate of −4 °C/min, at a fixed pressure of 370 MPa, along path 3 in Figure 2. Two reflections, one strong and the other weak, appear around 160 °C. These reflections strengthen with cooling. Considering their relative intensities and position, these reflections have been assigned as 110 and 200 for the orthorhombic phase. On further cooling, around 70 °C a sudden shift in the two reflections is noticed with the simultaneous appearance of a new reflection. Together with the appearance of the new reflection, the intensity of the 110 and 200 reflections also decreases. Since the position of the new reflection is in between the monoclinic (010) and the orthorhombic (110) reflections, the new reflection is assigned as 100 reflection for the hexagonal packing. The wavelength used for the experiment is 0. 714 Å. (b) Quantitative values representing changes in the *d* values with decreasing temperature at a fixed pressure. The sudden shift in the orthorhombic 110 reflection from 4.32 to 4.15 Å, along with the simultaneous appearance of the hexagonal reflection at 4.42 Å, is apparent from this figure. The new *d* value for the orthorhombic 110 reflection (4.15 Å) for the copolymer is in agreement with the linear polyethylene (4.1 Å). Whereas in comparison to the linear polyethylene (4.22 Å), the De Bragg *d* value for the hexagonal reflection is relatively higher for the copolymer (4.42 Å).

The sharp shifts in the d_{110} and d_{200} spacings to smaller values (Figure 5), on cooling from the melt at the elevated pressure, point to a sudden densification in the packing of the chains in the orthorhombic unit cell. The sudden densification of the unit cell shows that at the higher temperatures the unit cell was relatively more open than the one observed for linear polyethylene. Relatively loose packing of the chains in the unit cell can be attributed to the overall influence the hexyl branches have in packing of the ethylene sequence lengths. The loose packing of the unit cell at high temperature mainly may arise due to the incorporation of a few carbon atoms of hexyl branches within the crystal. While on cooling, as the unit cell shrinks, the hexyl branches can no longer be accommodated within the orthorhombic lattice, and they form a kind of separate loose packing, that is, a columnar or condis or pseudohexagonal phase. Alternatively, the contraction of the orthorhombic unit cell could result from the relaxation of severe forces within the crystal induced by the crystallization of some part of the ethylene sequences involving hexyl branches, rejected earlier from the crystallites. Such hexyl branches remain in the amorphous regions, probably at the crystal surface, until a sufficiently high undercooling is reached, enabling these hexyl branches to crystallize under pressure. To be able to accommodate some part of the ethylene chain sequences together with the hexyl branches in a crystal, less dense molecular packing is needed, which is realized by favoring the hexagonal phase. Both hypotheses, one involving a solid-state transition from orthorhombic to hexagonal and the other postulating an additional phase transition from the amorphous state into the crystalline state, however, do not exclude one another, as they both imply a “pressure-induced separation according to sequence lengths”.

To gain further insight into the feasibility of the hypothesis given, it is essential to evaluate overall intensities during the sudden shrinkage in the lattice with the incoming of the new reflection. Such evaluation shows that the sums of the integrated intensities for the 110 and 200 reflections of the orthorhombic phase and for the 100 reflection of the hexagonal phase remain constant before and after the sudden shift occurs at 70 °C, i.e., even before and after appearance of the 100 reflection. From these experimental observations it appears that the hypothesis associated with the solid−solid state transition is more viable.

The simultaneous appearance of the hexagonal peak with the shift in the orthorhombic reflections, and no change in the sum of the integrated intensities, strongly suggest that the two simultaneous occurring phenomena result from the crystallization and densification of two different parts of the same crystal: one originating from crystallization of previously partially included hexyl branches in the crystal and the other from the concomitant densification of the existing orthorhombic unit cell. Also, the copolymer JW1120, mentioned earlier, shows analogous results.

3.4. Pressure Release at RT from 370 MPa to Atmospheric Pressure. The 2-dimensional diffraction patterns of JW 1121 obtained during subsequent pressure release from 370 to 1 MPa at 28 °C are shown in Figure 6a. Pressure release from 270 to 225 MPa results in the disappearance of the hexagonal phase. Simultaneously, with the disappearance of the phase the orthorhombic reflections shift back to the lower angles i.e., higher *d* values ($d_{110} = 4.39$ Å and $d_{200} = 3.97$ Å), as illustrated in Figure 6b. These observations strongly suggest that even at room temperature, due to the hexyl

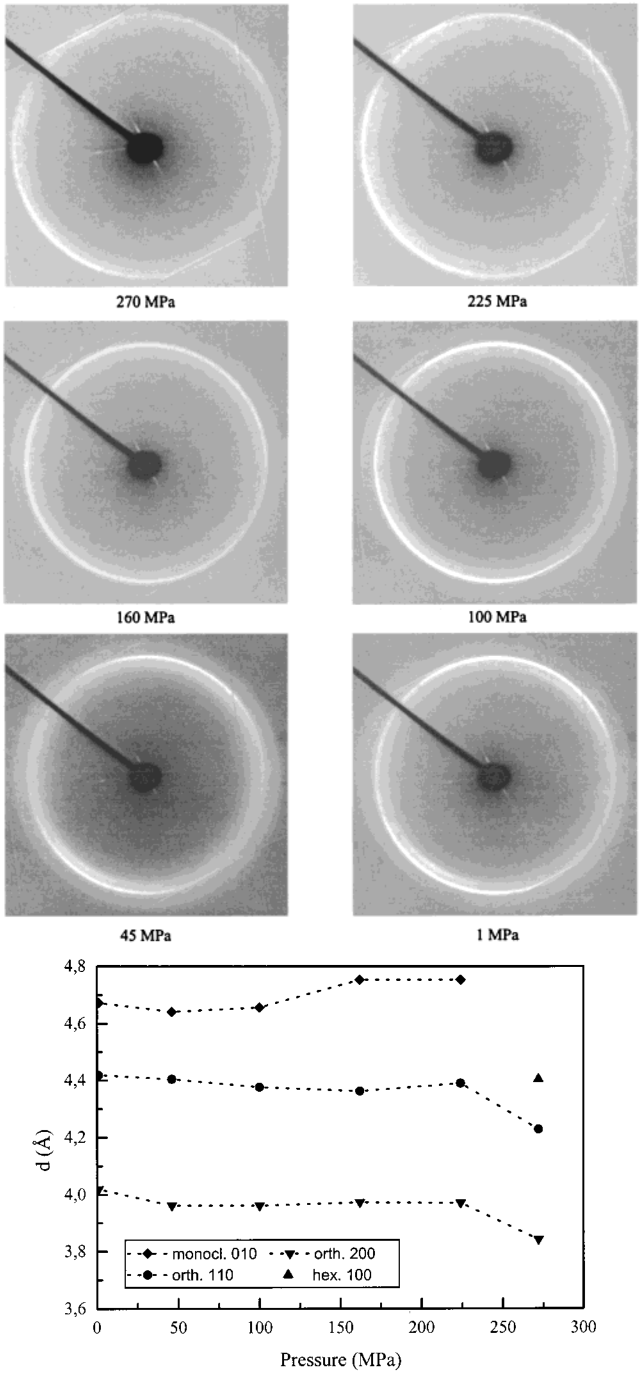

Figure 6. (a, upper) A series of two-dimenional X-ray diffraction patterns recorded during isothermal pressure release from 270 to 1 MPa at 28 °C, along path 4 in Figure 2. Lines with inverse intensity, which appear like arcs, originate from the diamond windows and can be used as an internal calibrant to evaluate position of the reflections. (b, lower) Changes in the *d* values with releasing pressure at 28 °C are represented in this figure. Below 250 MPa, while the hexagonal reflection diminishes, simultaneously a sudden shift in the 110 and 200 reflections occurs. With the disappearance of the hexagonal reflection a relatively broad reflection that sharpens with decreasing pressure appears at approximately 4.75 Å. The position of this reflection at atmospheric pressure (4.64 Å) is in good agreement with the 010 monoclinic reflection assigned for the linear polyethylene (4.58 Å), whereas the positions of the 110 and 200 reflections for the orthorhombic phase in the copolymer, i.e., 4.0 and 4.4 Å, respectively, are relatively larger compared to that for the linear polyethylene. On comparison with the starting point in Figure 3, it is evident that the *d* values of the three reflections before and after the pressure cycle are in good agreement.

branches, the crystals in the orthorhombic phase are relatively loosely packed. The loose packing of chains within the crystal causes these crystals to be sensitive to pressure. In this case it appears that decreasing pressure or heating have similar effects on a sample. This indicates that low temperature and high pressure are both simultaneously required to obtain the presumed "fractionation" according to ethylene sequence lengths. Upon further pressure release, an incoming monoclinic reflection (at $d_{010} = 4.7$ Å) intensifies (now the appearance of the monoclinic reflection is solely due to the internal stresses the material develops during crystallization), and finally, at 1 MPa a diffraction pattern similar to the one before pressure increase is observed. The orthorhombic reflections, on the other hand, are somewhat more pronounced, indicating a higher crystallinity obtained by the high-pressure cycle as compared to the starting conditions. Some small orientation effects can be seen in the two-dimensional diffraction patterns.

The positions of the d_{110} and d_{200} reflections for the orthorhombic phase, as observed after releasing the pressure, are the same before the sample was subjected to the pressure cycle. These observations strongly suggest that even after the cycle at room temperature and atmospheric pressure, due to the hexyl branches, chains in the orthorhombic phase are relatively loosely packed compared to linear polyethylene.

As stated above, not much difference in the X-ray diffraction patterns is observed in the sample before and after the pressure cycle. To gain insight into any morphological differences that may be present between the sample crystallized at atmospheric pressure and elevated pressure (370 MPa) and the role of pressure in crystallization, a series of experiments have been performed along path 5 to 7 as defined in Figure 2. What follows are the experimental observations along path 5 to 7.

3.5. Influence of Pressure in Chain Segregation and Crystallization at 195 MPa. It is well documented that when linear polyethylene is crystallized at the elevated pressure−temperature, the usual orthorhombic phase gives way to the hexagonal phase.[34] In the pressure−temperature phase diagram of linear polyethylene, the intersection point between the orthorhombic to hexagonal, hexagonal to liquid, and orthorhombic to liquid transition line is defined as the triple point.[34] Above the triple point melting of the orthorhombic crystals occur via the hexagonal phase, whereas below the triple point melting occurs directly via the orthorhombic phase. Under normal circumstances the triple point exists at 360 MPa, 230 °C in the pressure−temperature phase diagram. Formation of the extended chain crystals is attributed to the high chain mobility associated with the hexagonal phase above the triple point. It has been also reported that crystallization at the elevated pressure−temperature leads to segregation of chains.[35] The driving force for the segregation can be inter- or intramolecular differences.[36]

Our observations by WAXS on the copolymer suggest an absence of the anticipated hexagonal phase even at pressures as high as 370 MPa. Nevertheless, similar to linear polyethylene, copolymer segregation of chains occurs on crystallization at 370 MPa, most likely because of the relatively high crystallization temperature, compared to atmospheric pressure. However, when the same polymer is crystallized at relatively lower

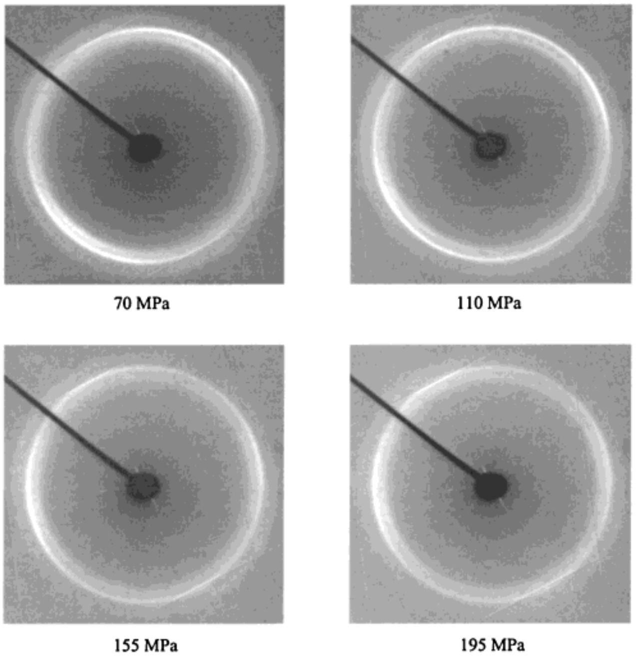

Figure 7. 2D X-ray diffraction patterns, recorded in situ during pressure increase at 28 °C from 70 to 195 MPa, along path 5 in Figure 2. The starting sample was the same pressure crystallized sample at 370 MPa, along path 1−4 in Figure 2. Unlike Figure 3, during pressure increase, no noticeable changes in the X-ray diffraction patterns have been observed. Three reflections observed at 195 MPa correspond to (010) reflection for the monoclinic phase and (110), (200) reflections for the orthorhombic phase.

pressures like 195 MPa, the experimental observations have been different.

Figure 7 shows a series of X-ray diffraction patterns recorded on the sample, which has gone through the high-pressure cycle following path 1 to 4 in Figure 2. When the sample crystallized at high pressure is subjected to a maximum pressure of 195 MPa, at room temperature, the sample did not show disordering with increasing pressure. When compared with the sample crystallized at atmospheric pressure (Figure 3), the observed phenomenon is rather different. A comparison of Figures 3 and 7 strongly suggests that the morphology of the sample crystallized at atmospheric pressure is considerably different from the sample crystallized at high pressures like 370 MPa. Figure 7 shows that at 195 MPa and room temperature (25 °C) three reflections attributed to the orthorhombic and the monoclinic phase exist.

Figure 8a shows a series of X-ray diffraction patterns recorded in situ during heating at fixed pressure of 195 MPa, along path 6 in Figure 2. Since no disordering was observed during compression at 28 °C, the observed peaks at the start of the heating run are clearly distinguishable and have been assigned to the monoclinic and orthorhombic phases. Upon heating, the monoclinic phase melts (or transforms to the orthorhombic phase) at 80 °C, followed by melting of the orthorhombic crystals at 150 °C, as shown in Figure 8b. The latter is more or less in agreement with $T_m^{end} = 140$ °C obtained in HP-DSC[4] at 190 MPa. The shift of the amorphous halo to lower angles results from thermal expansion.

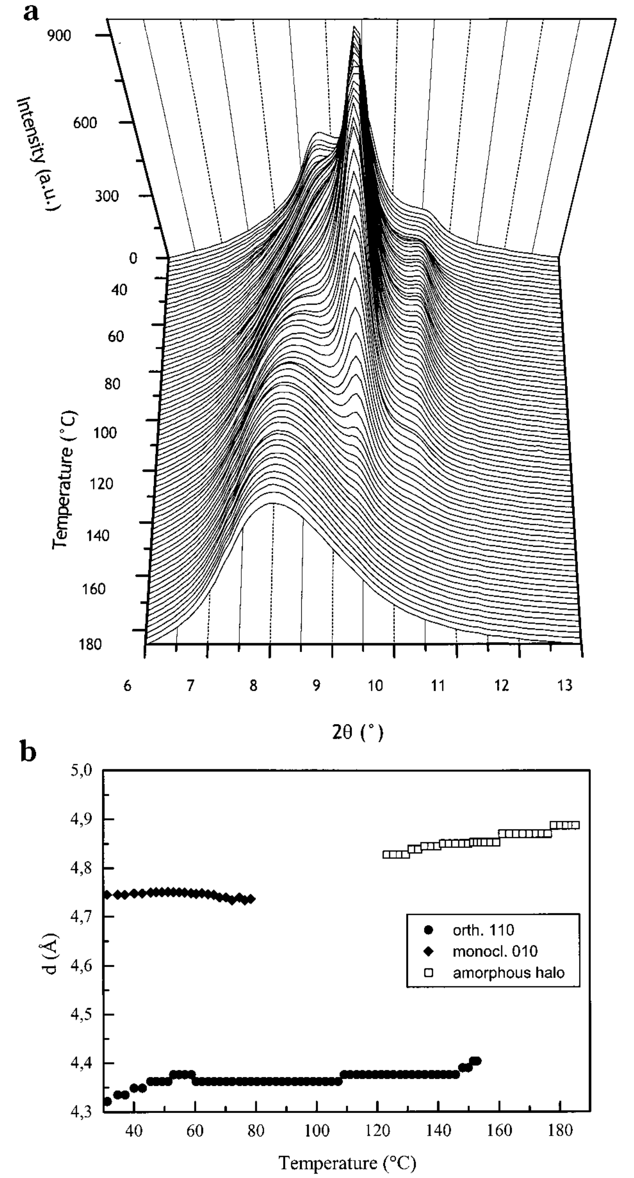

Figure 8. (a) Integrated diffraction patterns recorded in situ on increasing temperature from 31 to 185 °C, at a heating rate of 4 °C/min, at a fixed pressure of 195 MPa. Three reflections observed at d values of 4.74, 4.32, and 3.94 Å correspond to (010) reflection for the monoclinic phase and (110) and (200) reflections for the orthorhombic phase, respectively. The quantitative changes in these reflections have been summarized in (b). The wavelength used for the experiment is 0. 714 Å. (b) Quantitative changes in the d values on heating from 31 to 185 °C, at a heating rate of 4 °C/min, at a fixed pressure of 195 MPa, i.e., along path 6 in Figure 2. The monoclinic reflection disappears around 80 °C. No major shifts in the reflections have been observed.

On cooling at 4 °C/min from 184 to 40 °C at 195 MPa, crystallization of the orthorhombic phase starts at 130 °C, while the monoclinic reflection appears at 46 °C and strengthens on cooling further, as is shown in Figure 9a,b. In contrast to the cooling run at 370 MPa, no shift in the orthorhombic reflections to the higher angles is observed. Probably, the applied pressure (195 MPa) is not sufficiently high to enable the occurrence of a "pressure-induced sequence length separation". Fair agreement is found with $T_c^{onset} = 125$ °C observed in HP-DSC[4] at 190 MPa. Because of the thermal contraction of the material during cooling, the amorphous halo shifts to higher angles. When the pressure is released at 28 °C from 195 to 15 MPa, the orthorhombic 110 and 200 reflections become more pronounced, as shown in Figure 10, while the intensity of the monoclinic reflection decreases.

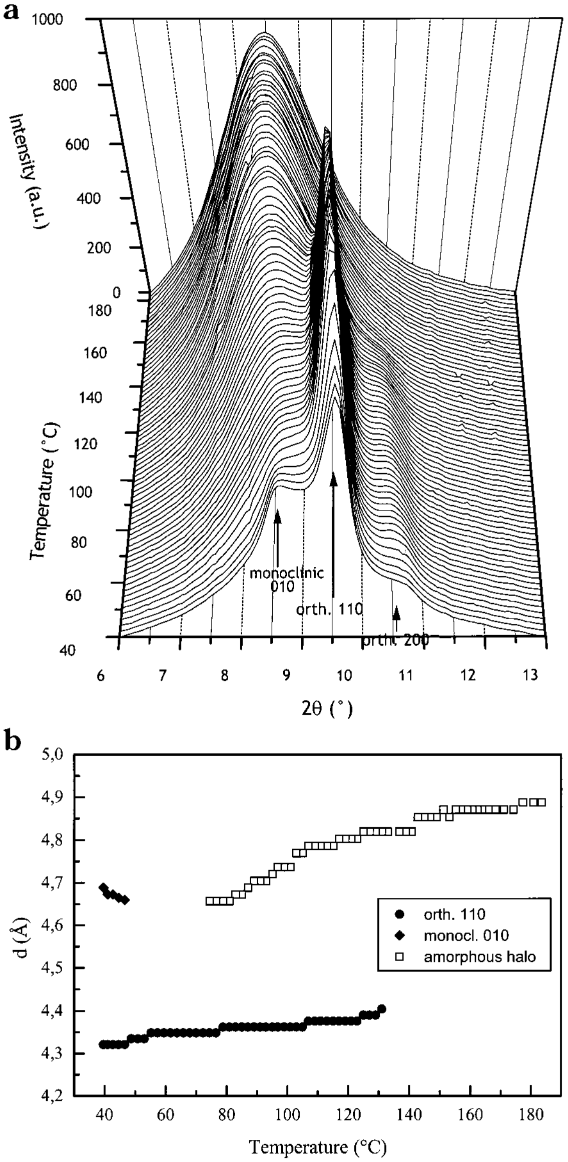

Figure 9. (a) Integrated diffraction patterns recorded in-situ on decreasing temperature from 184 to 31 °C, at a cooling rate of −4 °C/min, at a fixed pressure of 195 MPa. That is along path 7 in Figure 2. First the 110 and 200 reflections assigned to the orthorhombic packing of the chains appear. On cooling further, a new reflection at 4.65 Å appears. The new reflection shifts to 4.7 Å on further cooling. Considering its position, this reflection has been assigned as the 010 reflection for the monoclinic phase. Unlike in Figure 5, no shift in the orthorhombic reflections is noticed with the incoming of the new monoclinic reflection. But some drop in the intensity of the 110 and 200 reflections with the incoming of the monoclinic reflection is evident from this figure. The drop in the intensity suggests that the part of the crystal that was in the orthorhombic phase has transformed into the monoclinic phase on cooling. The wavelength used for the experiment is 0. 714 Å. (b) Quantitative changes in the *d* values, as observed in (a), i.e., on cooling along path 7 in the Figure 2.

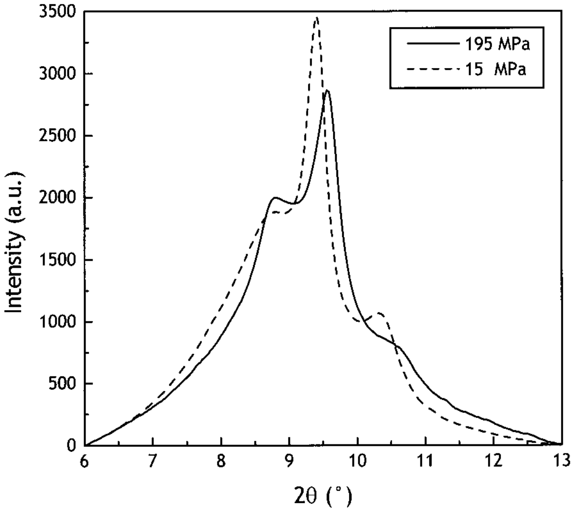

Figure 10. Integrated patterns recorded at 28 °C of the sample crystallized along path 7 (Figure 2) at 195 MPa and on pressure release to 15 MPa. Compared to the sample crystallized at 370 MPa (Figure 6b), a considerable shift in the 110 and 200 reflections for the orthorhombic phase can be noticed. This comparison shows conclusively the influence of pressure on crystallization of the copolymer. The wavelength used for the experiment is 0.714 Å.

4. Conclusions

Crystallization and the resulting crystal structures of a homogeneous ethylene−1-octene copolymer with comonomer contents of 8.0 mol % (JW 1121) are investigated at elevated pressures (up to 380 MPa) using real-time, high-pressure wide-angle X-ray diffraction (HP-WAXD). A copolymer (JW 1120) with 5.0 mol % octene shows similar behavior. The semicrystalline copolymer becomes seemingly “amorphous-like”, according to WAXD, at room temperature upon increasing pressure isothermally. A similar phenomenon—in contrast with results for linear polyethylene—was observed earlier for poly(4-methyl-pentene-1) by Rastogi et al.[21−23] In polyethylene copolymers, possibly, the applied stress destroys the orthorhombic crystals and converts them into an “amorphous-like” state.

Besides the peculiar “disordering” phenomenon, high pressure induces a separation according to sequence lengths. It is found that the orthorhombic reflections 110 and 200 abruptly shift to higher angles and decrease in intensity at ~70 °C, in a 5 °C range, during isobaric cooling from the melt at 370−380 MPa, while simultaneously a hexagonal reflection appears. Two explanations are proposed for these observations.

A first possible explanation is that an expanded unit cell, at high temperature and pressure, enables ethylene sequences containing hexyl branches to be partially included within the crystal. This causes the relatively large orthorhombic spacings, as observed. The suggested inclusion at high pressures probably occurs near or at the lamellar surface in the orthorhombic crystal lattice.[37] At lower temperatures, these hexyl chain sequences can no longer be accommodated and are rejected, leaving relatively more perfect orthorhombic crystals giving rise to smaller spacings. Facilitated by the high pressure, the rejected hexyl-containing chain sequences might be accommodated in a hexagonal structure.

A second possibility is the crystallization of short, hexyl-containing sequences at the crystal surfaces, at low temperatures and high pressures. The crystallization relaxes the severe forces within the crystal, leading to a sharp densification of the orthorhombic unit cell of the crystal.

The sketched “pressure-induced sequence length separation” generates two populations of crystallites having different thermal stabilities: one involving relatively large and perfect orthorhombic crystals and the other one consisting of small and distorted structures resulting from the crystallization of short-chain sequences containing hexyl branches. A comparison of the WAXD patterns of the sample that has been subjected to the pressure cycle with the sample that has been crystallized at atmospheric pressure shows that the position of 110 and 200 reflections is the same. This agreement in the *d* values strongly suggests that though at the atmospheric pressure the hexyl branches may not be accommodated within the crystalline lattice, they strongly influence packing of the ethylene sequences in the orthorhombic unit cell. Isothermal pressure increase to 195 MPa does not lead to an “amorphous-like” state or to “pressure-induced sequence length separation”.

The hypothesis presented in this paper has been further strengthened with the help of WAXS, SAXS, and Raman spectroscopy on a range of copolymers with varying concentration of hexyl, butyl, and propyl branches. All investigated polymers have been synthesized using the same catalyst. Results obtained from these studies would be the subject of second paper in this series.

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