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The effect of pressure pulses on isotactic polypropylene crystallization

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ABSTRACT

High hydrostatic pressure pulses, up to 80 MPa, have been imposed for different time and at various temperatures on molten iPP during cooling. The absence of any effect on the crystallization behavior after pressure release and further cooling demonstrates either that no nucleation precursor is produced by this thermo-mechanical history or that the lifetime of pressure-induced precursors is extremely short, as if no crystallization occurs during pressurization. Even when crystals develop during the pressurized stage, when high pressure is released, subsequent crystallization takes place in the same temperature range in which the polymer crystallizes at atmospheric pressure.

Structure and morphology of samples partially crystallized under pressure were investigated. WAXD show that, as expected, the fraction of γ -crystallinity firstly increases with increasing the time under pressure up to impinging of γ -spherulites and then levels off at a constant value. Morphological investigation performed on microtomed samples reveals that the γ -spherulites formed under high pressure exhibit positive birefringence and that their skeleton continues to grow during cooling when pressure is released. On heating, these spherulites melted first, but incompletely: the radial lamellar texture is still present up to relatively high temperature. These features seem to be consistent with the spherulitic architecture described by Lotz: infilling γ -lamellae grow by epitaxy on a skeleton of α -lamellae. Under the adopted experimental conditions, pre-imposed pressure pulses do not promote formation of extra nuclei, while they largely affect the crystal structure and the morphology of melt crystallized isotactic polypropylene.

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1. Introduction

Hydrostatic pressure affects polymer crystallization, both in terms of kinetics and structural features. First of all, high pressure shifts both equilibrium melting and glass transition temperatures to higher values. Consequently, the whole crystallization window is shifted to higher temperatures [1–3]. The pressure shift factor of polyolefines was reported to be of the order of 30 °C/100 MPa [4]. For what concerns the kinetics aspects, it has been reported that, at a given temperature, high pressure accelerates the crystallization process and reduces the Avrami exponent [4]. However, when the crystallization kinetics are compared at a constant undercooling, it has been observed that high pressure slows down the rate of

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crystallization [5], as one should expect as a consequence of the reduced mobility associated to the decrease of free volume. Moreover, Angeloz et al. [6] investigated the nucleation density under different high pressures and found that this characteristic is dictated by the actual undercooling and is independent of the applied pressure. In addition to the influence on the kinetics of development of crystalline order, high hydrostatic pressure has been shown to have a strong effect also on structural and morphological features of the ordered state. For example, under high pressure, HDPE develops a hexagonal phase with extended chain morphology instead of the more stable lamellar orthorhombic modification [7–9]. On the other hand, high pressure crystallization of i-PP leads to formation of the orthorhombic γ -form instead of the most usual α -monoclinic structure [10,11]. Extended-chain morphologies similar to those of HDPE were also found in PET and PA6 crystallized under elevated pressure [12–16].

Due to its important role in the plastic industry, i-PP has been thoroughly investigated, both from scientific and applied point of view, and its rich polymorphism has attracted wide interest since the days it was firstly synthesized. At least four different crystalline structures, namely the α -, β -, γ - and δ -forms, and one mesomorphic phase have been reported for i-PP [17–22]. Under the effect of high pressure, α -, γ - and meso-phase can be obtained, depending on the pressure value, compression rate and cooling rates [8,23–25]. Mostly, i-PP crystallizes in α - and/or γ -phase under high hydrostatic pressure, the higher the pressure, the larger is the fraction of γ -phase. van Drongelen [25] has reported that pressure shifts the development of both α - and γ -polymorphs to a high temperature range, but to a greater extent for the later structure.

Owing to its technological relevance, i-PP is one of the polymers whose crystallization under high pressures has drawn more attention in the past couple of decades. Fulchiron's group [6,26,27] focused on the kinetics aspects by performing crystallization experiments at high pressure under various cooling conditions to simulate polymer solidification and to predict crystallinity development during processing. Rather than to kinetic issues, Phillips et al. [10,11,28,29] tackled the problem of high pressure crystallization from the thermodynamic, structural and morphological point of views. They reported that, for high molecular weight i-PP, the γ -phase starts to form, together with the α -structure, at a pressure of about 50 MPa; and that it becomes dominant at ca. 200 MPa [7]. In another publication [8], they attempted to clarify the reason why the γ -phase is favored at the elevated pressure. According to their results, the γ structure develops at high pressure and low undercooling because of thermodynamic reasons since, in these conditions, its free energy is slightly smaller than that of the α -form. In addition, by performing an in-depth morphological characterization of pure γ -form spherulites obtained under the pressure of 20 MPa and different undercoolings [29], they observed peculiar feather-like spherulites, and ascribed this feature to a self-epitaxy growth mechanism of γ -lamellae.

Our experiments of pressure-induced crystallization stem from the above experimental evidences and tackle a problem which has not been considered in the past. Since, during actual processing (e.g., in injection molding), the molten polymer usually experiences high pressure pulses of short duration, our target is to understand if these pressure pulses have an effect on the kinetics of subsequent crystallization when temperature is decreased below the equilibrium melting point.

In analogy to what it has been ascertained for the polymer crystallization behavior during and after imposition of deviatoric stresses (shear or tension), our aim is to establish if pulses of the hydrostatic stresses lead to formation of nucleation precursors which accelerate subsequent crystallization during cooling. In other terms, we performed experiments aiming at understanding if squeezing the system by high pressure favors the formation of bundles of locally parallel chain segments arranged in a quasi-crystallographic register, i.e. of precursors of crystallization nuclei.

2. Experimental part

2.1. Materials

A commercial highly stereoregular ZN-i-PP homopolymer (Borealis HD601CF) was used. It has a weight average molecular weight (M_w) of 365 kg/mol and a polydispersity index (M_w/M_n) of 5.4. The nominal melting point (DSC at 10 °C/min) is 163.8 °C.

2.2. P-V-T apparatus

A unique dilatometer (IME Technologies) was used; detailed information on this apparatus, that was originally developed in our group, have already been described elsewhere [23,25,41,42]. The actual imposed cooling conditions are expressed in terms of the average cooling rate experienced by the samples in the temperature range in which the polymer solidifies, i.e., between 195 and 130 °C.

The PVT samples are pre-produced with a mini-injection molding machine (Babyplast) in the form of rings with inner and outer diameter of 21 and 22 mm, respectively. For i-PP, this corresponds to a mass of about 76 mg, wall thickness of 0.5 mm and height of 2.5 mm. PVT experiments were carried out according to the procedure schematically shown in Fig. 1.

The sample is initially heated to 220 °C and kept at this temperature for 10 min to erase previous thermal history. During this period the pressure is defined by the weight of the lid (approximately 5 MPa). In the next step, the melt is brought to the target temperature at which the high pressure is imposed (hereafter T_p) and then, after 5 min, required to stabilize the temperature, a high pressure (80 MPa) is applied and held for different times (t_p). Pressure differences are typically realized within 2–5 s. Finally, the pressure is released to 10 MPa and isobaric cooling to room temperature is obtained by blowing

Fig. 1. Schematic representation of the adopted experimental procedure.

compressed air or by natural cooling. The maximum average cooling rate that can be attained with these procedures is about 1 °C/s and 0.15 °C/s respectively. In the experiments, the volume change of the polymer sample is continuously measured, starting from the beginning of cooling.

A somehow different stepwise crystallization procedure was also imposed to obtain samples best suited to investigation of the effect of operational variables on structure and morphology. Details will be described in the following sections.

2.3. X-ray measurements

Wide Angle X-ray Diffraction (WAXD) single-shot experiments were performed at the Dutch-Belgian (DUBBLE) beamline BM26 of the European Synchrotron Radiation Facility (Grenoble, France) using a high resolution Pilatus 1 M detector and a wavelength of $\lambda = 0.1033$ nm. For the convenience of comparing with the traditional WAXD data, the diffraction angle (2θ) has been converted to the ones at wavelength of $\lambda = 0.154$ nm according to Bragg's law: $\lambda = 2d\sin\theta$, with respect to the same d -spacing (d). To calculate the degree of crystallinity, the amorphous halo measured on a quenched low tacticity sample (37% of *mmmm* pentads) with negligible crystallinity has been employed [30]. To extract quantitative data on the phase composition, WAXD patterns were de-convoluted by the method of Murthy and Minor [31] in which the full spectrum is considered as a superposition of a number of reflections originating from different crystal phases. Percentage of individual phases was determined from the area ratio. As it is well documented in the literature, under quiescent crystallization conditions and in absence of particular nucleating agents, monoclinic α -phase, characterized by the reflection at the Bragg distance $d = 4.78$ Å, which corresponds to the diffraction of the $(130)_\alpha$ family of planes, is obtained. Instead, when crystallization occurs under high pressure, the orthorhombic γ -phase, characterized by the diagnostic Bragg distances $d = 0.586$ and 0.438 nm, arising from $(113)_\gamma$ and $(117)_\gamma$ planes, respectively, show up. The other intense diffraction peaks, corresponding to $d = 0.626$, 0.524 , 0.417 and 0.405 nm, are common to both the α - and the γ -phase.

3. Results and discussion

3.1. Dilatometry

In order to probe the role of short pressure pulses on polymer crystallization, experiment were firstly performed in isobaric mode and imposing an average cooling rate of 1 °C/s, see Fig. 2(a). The crystallization temperature T_c was defined as the temperature at which the straight lines fitting the specific volume vs. temperature in the molten state and during crystallization do intersect. By denoting with T_{c1} and T_{c2} the crystallization temperature at low (10 MPa) and high (80 MPa) pressure, respectively, it was found that $T_{c1} = 117$ °C and $T_{c2} = 138$ °C, in perfect agreement with the pressure shift factor of $\alpha_p = (\partial T_m / \partial P) = 0.29$ °C/MPa reported by Zoller and He for i-PP [4]. Accordingly, the nominal melting point of i-PP crystals at 10 and 80 MPa were calculated to be $T_{m1} = 165$ and $T_{m2} = 187$ °C at an heating rate of 10 °C/min. Volume changes on cooling i-PP melt under two different pressures have been drawn in Fig. 2 to emphasize how pressure increase affects the crystallization behavior. In Fig. 2(b) a typical example of a temperature-specific volume curve is shown (in this case for a

Fig. 2. (a) Influence of pressure on i-PP crystallization under isobaric conditions; average cooling rate is 1 °C/min. (b) Example of volume changes on cooling polymer melt under 10 MPa and a high pressure pulse of 80 MPa at 158 °C for 20 min, the zoomed in part in the top left corner represent the volume change under high pressure.

high-pressure pulse of 80 MPa). The polymer melt is submitted to approximately 5 MPa before reaching target T_p of 158 °C and, next, a pressure of 80 MPa has been imposed for 20 min, indicated by (1). Crystallization starts during pressurization, as can be observed from the sharp volume drop (2) and, therefore, on pressure release, the system will not return to the original level. The difference is observed between the curve as expected without the pressure curve (dotted line in Fig. 2(b)) and the curve with a partially crystallized part (4) is due to this crystallization and the difference in applied pressure (5 versus 10 MPa). Another feature worth to point out is the plateau that occurs after pressure release (3). This is due to friction between the moving parts of the dilatometer. On further cooling, after sufficient volume shrinkage, the normal shrinkage behavior is observed again.

3.1.1. Effect of the high pressure pulse temperature

The pressure pulse was first imposed at high temperature, $T_p = 220$ °C, which, according to the reported pressure shift factor $\alpha_p = 0.29$ °C/MPa [4], it is slightly above the estimated equilibrium melting point under the pressure of 80 MPa ($T_{mp}^0 = 218$ °C), when $T_m^0 = 195$ °C was assumed as the equilibrium melting temperature at atmospheric pressure. From the normalized PVT curves displayed in Fig. 3, no detectable shift of the crystallization temperature was observed after pressure release and subsequent standardized cooling. Apparently, the imposed high pressure, even when it is held for a long time (e.g., 20 min), does not affect to any extent the crystallization kinetics. At first glance, this result is unexpected. In the pressurized melt, chain segments feel an environment with a reduced fractional free volume and, therefore, they may tend to adopt to the pressurized state by forming small bundles with locally aligned molecular axes. These embryonic aggregates are expected to need overcoming a reduced free energy barrier to become effective nuclei and, therefore, a faster

Fig. 3. Effect of the temperature at which the pressure pulse is imposed. $P = 80$ MPa; $t_p = 2$ min.

development of crystalline order during the subsequent cooling stage it is expected [43]. Instead, from the PVT curves obtained in our experiments, it is well evident that the volume contraction associated to the phase transition always begins and proceeds in the same temperature range, irrespective of the duration of the pressurized step. This implies that, at variance with what it is observed when the polymer melt is submitted to shear or extensional flow [32,33], crystallization is not affected by the pressure history in the molten state.

Two possible justifications for that can be put forward: (a) no short range order is present in the squeezed macromolecular coils or (b) formation of nucleation precursors by clustering of chain segments, takes place, but these entities instantaneously dissolve as soon as the high pressure is released. In fact, while deviatoric stresses tend to orient chain segments in specific directions and modify the shape of the coils, application of high hydrostatic pressure only leads to a reduction of the radius of gyration of the macromolecular coils without any significant change in the overall chain conformation. In fact, with their neutron scattering experiments on deuterated chains, Guenet and Picot [34] demonstrated that the overall chain conformation does not experience a substantial change during pressurization. Anyhow, small ordered domains, if they exist under high pressure, should have a very short lifetime when pressure is released.

In another series of experiment, pressure (80 MPa) was imposed for a constant time of 2 min at different T_p , in the range $140\text{ °C} \leq T_p \leq 184\text{ °C}$. As it is evident from Fig. 3, the shrinkage of specific volume is fully and immediately recovered upon release of pressure if $T_p \geq 149\text{ °C}$. This implies that, in these conditions, 2 min are neither sufficient to develop any crystallinity nor to leave in the system ordered entities acting as nuclei in the subsequent cooling to room temperature. However, if T_p is lowered to *ca.* 140 °C , which corresponds to the crystallization temperature in the isobaric condition at $P = 80\text{ MPa}$, under the same pressure history the polymer crystallizes to a large extent, as it can be appreciated by the partial recovery of specific volume when pressure is released. It is highlighted that, in this experiment, a further small stepwise contraction takes place at around $110\text{--}120\text{ °C}$, *i.e.*, in the same temperature range in which the specimens pressurized at higher temperature do crystallize.

3.1.2. Effect of time under high pressure

The optimum temperature window to investigate i-PP crystallization by optical microscopy about it is around 30 °C below the nominal melting temperature. Accordingly, to investigate the effect of holding time under high pressure on crystallization kinetics, $T_p = 158\text{ °C}$ was chosen because it satisfies the above criterion when $P = 80\text{ MPa}$ and it is very close to the nominal melting temperature when $P = 10\text{ MPa}$.

From the PVT curves shown in Fig. 4(a), an appreciable drop of v_{sp} is detected during the time the specimen is under the high pressure in quasi-isothermal conditions. This isothermal contraction at a constant pressure corresponds to development of the denser crystalline phase. In fact, the longer is the time the system is held under pressure, the larger is the measured decrease of specific volume. This is also confirmed by the extent of increase of specific volume the system experiences when the pressure is released: the longer has been the time under high pressure, the smaller is the recovery and, in the range of temperature between 120 and 158 °C , the specific volume at low pressure is intermediate between those of the melt and of the crystalline state.

It seems that, from these results, the crystallization behavior under high pressure is understood and the whole phenomenology could be justified on the bases of thermodynamic and kinetic concepts. However, for a final conclusion, still more work needs to be done. When attention is shifted to the further crystallization, which takes place at low pressure during subsequent cooling, an unexpected observation must be made. Completion of crystallization always takes place at *ca.* 115 °C , *i.e.*, in the temperature range corresponding to crystallization of specimens which have never experienced the compression. This implies that the nuclei (and even the crystals) formed at high pressure do not provide effective substrates on which crystallization at low pressure can progress. This implies that the structure of ordered domains formed under high pressure is unable to nucleate the structure which develops at low pressure level during cooling.

In order to rule out the possibility that this unexpected behavior could be sample-specific, all measurements were also performed with another i-PP grade: the HD234CF (Borealis). Data are not reported here because they are identical to those obtained with the i-PP homopolymer HD601CF.

One has to consider that when the sample is cooled relatively fast, the crystallization process is mainly driven by thermal nucleation at high undercooling rather than by the growth of already existing crystals. Using room temperature compressed air as cooling medium, the average cooling rate is around 1.5 °C/s , which, is probably too fast to enable crystallization prevalently dominated by the seeds present in the system when the sample starts to be cooled. Therefore, experiments have been repeated using a lower cooling rate (0.1 °C/s). The results are shown in Fig. 4(b).

From the resulting PVT curves obtained with this slower cooling one observes that, if the holding time under pressure is sufficiently long, alike in previous case some crystallinity develops in the system during the pressurized stage. A clear decrease of specific volume in the temperature range between 140 and 150 °C , which indicates further growth of crystals is now evident, while it could not be appreciated when the sample was cooled faster. Finally, if during the first and second step crystallization was not completed, further crystallization takes place at lower temperature, in the same range of temperature in which the sample is simply submitted to an isobaric cooling.

Apparently, an high cooling rate reduces the amount of crystals originated by the continuously growth of the structure formed at high pressure and leaves more room for crystallization on the thermal nuclei which are progressively formed on decreasing the temperature and which are responsible of the crystallization at around 120 °C . WAXD measurement were employed to investigate the structure of crystals formed in the various stages of the adopted procedure and the results will

Fig. 4. Effect of pressure time on crystallization for cooling rate of (a) 1.5 °C/s and (b) 0.1 °C/s, pressure of 80 MPa imposed at 158 °C.

be shown in next section. The summarized information has been supplied in form of table at [supporting information, see Table S](#).

From the obtained PVT curves it can be deduced that the effect of a high temperature compression stage at 80 MPa on i-PP crystallization kinetics can lead to two different situations depending on the temperature at which the pressure pulse is imposed. When pressure is applied at high temperatures, above the equilibrium melting temperature of the crystals under the specific imposed pressure, or for a short duration, shorter than the induction time for nucleation, no effect at all is observed, even after releasing the pressure and cooling to room temperature. However, using an appropriate low cooling rate, it has been possible to show that the crystalline entities which are formed under high pressure at a suitable temperature continue to grow when pressure is released and the system is cooled, thus partly contributing to the overall development of crystalline order in the final system.

3.2. Crystal structure formed under different pressure levels

The WAXD patterns collected after cooling to room temperature the samples submitted to various compression conditions are shown in Fig. 5. The diagnostic reflection for the identification of the α - and γ -form: $(130)_\alpha$ and $(117)_\gamma$ are identified. Some qualitative information can be directly extracted from the recorded WAXD patterns. It is well evident that the longer the system is held to crystallize under high pressure, the greater is the amount of γ -phase in the final sample. Evidently, provided that the pressurization temperature is sufficiently low to enable structuring, the content of γ -phase arises from the prolonged dwell time under high pressure. To obtain quantitative structural characterization of the solid state, a careful analysis of the acquired WAXD patterns was needed. All collected patterns were deconvoluted according to the procedure suggested by Murthy and Minor [31] and the weight fraction of each phase was computed from the relative

Fig. 5. Room temperature WAXD curves of i-PP samples held under high pressure at 158 °C for different times before cooling and then cooled by (a) compressed air and (b) natural cooling.

area under individual characteristic peaks. Details of the adopted curve fitting procedure have been described by van Erp et al. [25]. An example of the obtained fitting can be found in Fig. S of the supporting information. Composition of the ordered phases as a function of the dwell time under high pressure are summarized in Fig. 6.

From Fig. 6, it can be appreciated that the overall crystallinity in the final state stays constant, at around 80%, for all samples, even if they have experienced different pressure histories. This suggests that, in any of the adopted conditions, the material attains the same level of order. Although the final crystallinity level is relatively high for iPP (in general values around 60–65% are found), we only focus on the relative contributions of the α and γ phase. It must be recalled that, before recording the WAXD patterns, all samples experienced the same thermo-mechanical history: the only difference being in the time (t_p) spent under high pressure at relatively low undercooling. Clearly, the result at $t_p = 0$ refer to a sample which has not been submitted to high pressure. While the final level of crystallinity is the same, the time the polymer is held to crystallize under pressure affects the apportioning of the material between the two main structures (α and γ) of i-PP. When the time under pressure is short, α -form prevails after cooling to room temperature. The fraction of γ -form increases with pressure time only during the first hour, then it stabilizes to a constant value. Taking into account that α -form develops mostly during cooling under released pressure, this result suggests that ca. 1 h is needed to attain the maximum development of order under pressure at T_p . The attained constant level of γ -crystallinity corresponds to the impingement of γ -spherulites, as it has been proved by the optical micrographs presented in the next section.

3.3. Morphology of the samples formed at high pressure

Samples which have experienced different mechanical and thermal histories, were microtomed into slices about 20 μm thick. The direction of sectioning is illustrated in Fig. 7. For optical microscopy observations, the sectioned face lies along the radius, i.e., it is perpendicular to the up and down surfaces of the PVT ring. Instead, for X-ray measurement, the sample was simply cut into small pieces, and the incident direction of X-ray was along the radius.

In Fig. 8 are collected several optical micrographs which were obtained with a Polarized Optical Microscope using a λ -plate inserted along the optical path at 45° respect to the orientation of the crossed polarizer and analyzer. With this optical setting, the sign of the birefringence can be established. Positive spherulites, those in which the refractive index in the radial direction is larger than that in tangential direction, can be recognized by the blue color in the first and third quadrant, whereas negative spherulites have the blue parts in the second and fourth quadrant [35]. The optical micrographs shown in Fig. 8(c) and (g) clearly demonstrate that the birefringence of the inner spherulites, which are formed in the early stage of crystallization, i.e., under the high pressure pulse, is positive. Positive spherulites are also found among the uncompleted spherulites along the wall and as impinged spherulites, in samples submitted to extended pressurization, with pressure time of 20 and 60 min, respectively.

Apparently, under high pressure, spherulites are mostly positive and exhibit clear evidence of radial development. However, another type of morphology can be recognized as well. For example in Fig. 8(g), the morphology in the left-bottom part corresponds to uncorrelated ensembles of birefringent noduli, likely composed of short randomly arranged lamellae. This special morphology has been reported earlier only in case of the presence of γ -crystallinity [7]. Hosier et al. [36] related this morphology to dense arrays of short lamellae in γ -rich i-PP samples.

The correlation between sign of birefringence and spherulitic architecture has been thoroughly discussed by several authors [37–39], who have demonstrated that positive spherulites result when lamellae undergo profuse branching. On the contrary, spherulites with barely branched radial lamellae, exhibit negative birefringence as it can be observed, e.g., in i-PP α -spherulites grown at low undercooling.

Fig. 6. Room temperature crystallinity as a function of dwell time at 158 °C under high pressure of 80 MPa. Open symbols corresponds to the natural cooling (0.1 °C/s), and closed ones to air cooling (1.5 °C/s), respectively.

Fig. 7. Schematic drawing of the samples taken from the PVT rings. Directions of mechanical stresses and of offline measurement are shown. Picture adopted from [23].

Recalling the WAXS results, γ -crystallinity increases with the duration of the pressurization stage and approaches a constant value when high pressure time is long enough. In parallel, the content of α -phase decreases until it reaches a steady value. Therefore, the γ -phase grows at the expenses of the α -phase. By combining WAXS and microscopic results, it can safely be stated that, under high pressure, mainly (or exclusively) γ -phase crystals develop adopting a morphology that, if it is of spherulitic character, it exhibits positive birefringence resulting from profuse branching of the lamellae during their prevalently radial development.

Phillips [29] observed spherulites with positive birefringence in samples crystallized under very high pressure ($P = 200$ MPa) at low undercoolings and assigned this optical properties to self-epitaxy of γ -lamellae associated with feather-like lamellar arrangement inside the spherulitic morphology. However, Lotz and Cheng [40] considered that, as it has been verified in almost all reported observations, the γ -phase can only grow by branching on the α -phase since α -nuclei are much easily generated due to lower energy barrier that must be overcome for the formation of nuclei. Then, according to literature, the sign of birefringence observed in Fig. 8(b), could either be originated from self-epitaxy of γ -lamellae or from γ -branching on α -lamellae.

To better understand the structure formed under high pressure, a step-wise crystallization was performed: PVT rings were cooled at 0.1 °C/s from the melt to 158 °C and crystallized at this temperature under 80 MPa for 40 min. The pressure was then released to 10 MPa and the sample was cooled to $T_c = 130$ °C for 2 h of isothermal crystallization. At the end, the sample was slowly cooled to room temperature, microtomed into slices around 20 μm thick, and then the morphology was investigated by means of polarized optical microscopy as above described.

The sliced film was heated at 1 °C/min, and the changes in the morphology were monitored in-situ. Fig. 9 reports the evolution of morphology during heating, corresponding DSC heating curves at same heating rate are associated. It is clear that the inner spherulites, as well as the transcrystalline layer, melt first and simultaneously. This proves that the structure formed under high pressure is a low melting one, which confirm that the crystallinity developed under high pressure belong to the γ -phase, since it has been well documented by DSC experiments that the melting endotherm of γ -form appears at a temperature that is appreciably lower than that of the α -form. However, a careful inspection of Fig. 9 evidences that the melting of inner spherulites, as demonstrated by the permanence of faint bright radial entities in the black field of the molten part, is uncompleted.

As mentioned above, Lotz and Cheng proposed that γ -phase can only begin to develop as a branch from an α -phase lamella. According to this view, the progress of crystallization in our sequence of steps would be as follows: in the first stage, at high pressure, initial formation of the α -skeleton in the inner spherulites and in the transcrystalline layer. Then, thanks to the high frequency of γ -branching on α -skeletal lamellae, prevailing development of γ -form will take place. Afterward, when pressure is released and temperature is progressively decreased, the remaining part of the sample crystallizes essentially in the more stable α -form.

Another interesting feature can be recognized from both Figs. 8 and 9. After the pressure release, the skeletal α -lamellae continue to grow from those already present in the initially formed spherulites. As pointed out by Lotz, α -lamellae can hardly branch on the γ -ones because, the ab face in γ -form crystals is prerequisite for the α -growth, however, for the γ -phase the fast growth direction is along the c -axis and, therefore, the exposed ab face is small. As a consequence, the frequency of branching of α on γ is expected to be very low. In facts, this kind of structural branching has been reported only one case by Lotz and coworkers [35]. The γ - α branching was observed rather occasionally on the crystallization of thin film. The feature of continuous growth rules out the cross-nucleation, i.e., α -growth by nucleating on the γ -phase.

Fig. 8. Optical micrographs of microtomed samples obtained by fast cooling (upper row) and by slow cooling (bottom row), with pressure time of (a, e) 0 min, (b, f) 20 min, (c, g) 40 min, and (d, h) 60 min. The scalebar at lower right of each image stands for 100 μm .

Fig. 9. Morphological change observed on heating at 1 $^{\circ}\text{C}/\text{min}$ under polarized microscopy. Corresponding points have been indicated on DSC heating curve with same equivalent heating rate.

4. Conclusions

The PVT curves recorded after imposing a short time pressure pulse of 80 MPa has been investigated with the aim of clarifying if the pressure history experienced by the polymer melt during most of the processing technologies has any effect on the kinetics of polymer crystallization. It has been found that when a high pressure pulse is imposed on the molten polymer at high temperature or for a short time, the unperturbed equilibrium molecular conformation restores in very short time after pressure release. Nucleation precursors are not generated under high pressure or, if they form, they disappear instantaneously upon pressure release.

When the pressure of 80 MPa is imposed and held for sufficient time below the melting point, crystallization takes place during the pressurization stage, as indicated by the specific volume drop in the PVT curves. After pressure release, no matter if some crystallization took place during pressurization, it has been seen that subsequent crystallization on cooling begins and proceeds much alike in a system which did not experienced any imposed pressure.

Structural investigation has shown that, provided the temperature does not exceed the melting temperature of the polymer, the fraction of crystals of the γ -polymorph increases when the time in the pressurized state is increased. Initially,

γ -type crystallinity increases linearly with holding time under pressure and then levels off at a limiting value that, in our experiments, corresponds to around 60%.

Morphological investigation of the samples partly crystallized under pressure by means of polarized optical microscopy with inserted λ -plate shows that positive spherulites are formed to a large extent. This observation is consistent with the proposed architecture of the prevalently γ -form spherulites which are expected to be composed of a skeleton of α -lamellae on which highly branched γ -lamellae are nucleated. By coupling morphological and structural results, it can also be deduced that the attainment of a constant value of γ -crystallinity when pressurization lasts longer than 60 min is originated from the impingement of spherulites developed under pressure.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.eurpolymj.2015.07.055>.

References

- [1] P.R. Billingham, D. Tabor, The effect of hydrostatic pressure on the visco-elastic properties of polymers, *Polymer* 12 (2) (1971) 101–118.
- [2] R. Cardinaels, P. Van Puyvelde, P. Moldenaers, Evaluation and comparison of routes to obtain pressure coefficients from high-pressure capillary rheometry data, *Rheol. Acta* 46 (4) (2007) 495–505.
- [3] S.E. Kadijk, B.H.A.A. Vandenbrule, On the pressure dependency of the viscosity of molten polymers, *Polym. Eng. Sci.* 34 (20) (1994) 1535–1546.
- [4] J. He, P. Zoller, Crystallization of polypropylene, nylon-66 and poly(ethylene-terephthalate) at pressures to 200 MPa – kinetics and characterization of products, *J. Polym. Sci. Polym. Phys.* 32 (6) (1994) 1049–1067.
- [5] F. Asmussen, W. Schiwoon, K. Ueberreiter, Kristallisationskinetik von Polymeren, *Kolloid-Zeitsch. Zeitschrift Polym.* 250 (1972) 506–510.
- [6] C. Angeloz, R. Fulchiron, A. Douillard, B. Chabert, R. Fillit, A. Vautrin, et al, Crystallization of isotactic polypropylene under high pressure (gamma phase), *Macromolecules* 33 (11) (2000) 4138–4145.
- [7] D.V. Rees, D.C. Bassett, Origin of extended-chain lamellae in polyethylene, *Nature* 219 (5152) (1968) 368–370.
- [8] D.V. Rees, D.C. Bassett, Crystallization of polyethylene at elevated pressures, *J. Polym. Sci. A – 2: Polym. Phys.* 9 (3) (1971) 385–406.
- [9] B. Wunderlich, T. Arakawa, Polyethylene crystallized from the melt under elevated pressure, *J. Polym. Sci. A: Gen. Pap.* 2 (8) (1964) 3697–3706.
- [10] R.A. Campbell, P.J. Phillips, J.S. Lin, The gamma-phase of high-molecular-weight polypropylene. 1. Morphological aspects, *Polymer* 34 (23) (1993) 4809–4816.
- [11] K. Mezghani, P.J. Phillips, The gamma-phase of high molecular weight isotactic polypropylene: III. The equilibrium melting point and the phase diagram, *Polymer* 39 (16) (1998) 3735–3744.
- [12] S. Rastogi, M. Newman, A. Keller, Pressure-induced amorphization and disordering on cooling in a crystalline polymer, *Nature* 353 (6339) (1991) 55–57.
- [13] A. Siegmund, P.J. Harget, Melting and crystallization of poly(ethylene terephthalate) under pressure, *J. Polym. Sci.: Polym. Phys. Ed.* 18 (11) (1980) 2181–2196.
- [14] S. Gogolewski, A.J. Pennings, Crystallization of polyamides under elevated pressure: 2. Pressure-induced crystallization of nylon-6 (polycapramide) from the melt, *Polymer* 16 (9) (1975) 673–679.
- [15] S. Gogolewski, A.J. Pennings, Crystallization of polyamides under elevated pressure: 5. Pressure-induced crystallization from the melt and annealing of folded-chain crystals of nylon-11, poly(aminoundecaneamide) under pressure, *Polymer* 18 (7) (1977) 660–666.
- [16] J.E. Stamhuis, A.J. Pennings, Crystallization of polyamides under elevated pressure: 6. Pressure-induced crystallization from the melt and annealing of folded-chain crystals of nylon-12, polylauro lactam under pressure, *Polymer* 18 (7) (1977) 667–674.
- [17] G.C.P. Natta, Structures and properties of isotactic polypropylene, *Nuovo Cimento Suppl.* 15 (1960) 40–51.
- [18] S.V. Meille, D.R. Ferro, S. Bruckner, A.J. Lovinger, F.J. Padden, Structure of beta-isotactic polypropylene – a long-standing structural puzzle, *Macromolecules* 27 (9) (1994) 2615–2622.
- [19] B. Lotz, S. Kopp, D. Dorset, An original crystal-structure of polymers with ternary helices, *CR. Acad. Sci. II* 319 (2) (1994) 187–192.
- [20] S. Bruckner, S.V. Meille, Non-parallel chains in crystalline gamma-isotactic polypropylene, *Nature* 340 (6233) (1989) 455–457.
- [21] P. Stagnaro, L. Boragno, M. Canetti, F. Forlini, F. Azzurri, G.C. Alfonso, Crystallization and morphology of the trigonal form in random propene/1-pentene copolymers, *Polymer* 50 (22) (2009) 5242–5249.
- [22] P.B. McAllister, T.J. Carter, R.M. Hinde, Structure of the quenched form of polypropylene, *J. Polym. Sci.: Polym. Phys. Ed.* 16 (1) (1978) 49–57.
- [23] T.B. van Erp, L. Balzano, A.B. Spoelstra, L.E. Govaert, G.W.M. Peters, Quantification of non-isothermal, multi-phase crystallization of isotactic polypropylene: the influence of shear and pressure, *Polymer* 53 (25) (2012) 5896–5908.
- [24] M.Y. Wang, X.R. Liu, C.R. Zhang, D.D. Zhang, Z. He, G. Yang, et al, Compression-rate dependence of solidified structure from melt in isotactic polypropylene, *J. Phys. D: Appl. Phys.* 46 (14) (2013) 145307–145312.
- [25] M. van Dongelen, T.B. van Erp, G.W.M. Peters, Quantification of non-isothermal, multi-phase crystallization of isotactic polypropylene: the influence of cooling rate and pressure, *Polymer* 53 (21) (2012) 4758–4769.
- [26] J.F. Luye, G. Regnier, P. Le Bot, D. Delaunay, R. Fulchiron, PVT measurement methodology for semicrystalline polymers to simulate injection-molding process, *J. Appl. Polym. Sci.* 79 (2) (2001) 302–311.
- [27] R. Fulchiron, E. Koscher, G. Poutot, D. Delaunay, G. Regnier, Analysis of the pressure effect on the crystallization kinetics of polypropylene: dilatometric measurements and thermal gradient modeling, *J. Macromol. Sci., Phys.* B40 (3–4) (2001) 297–314.
- [28] A. Dimeska, P.J. Phillips, High pressure crystallization of random propylene-ethylene copolymers: alpha-gamma phase diagram, *Polymer* 47 (15) (2006) 5445–5456.
- [29] K. Mezghani, P.J. Phillips, The gamma-phase of high molecular weight isotactic polypropylene. 2. The morphology of the gamma-form crystallized at 200 MPa, *Polymer* 38 (23) (1997) 5725–5733.
- [30] F.P.T.J. van der Burgt, S. Rastogi, J.C. Chadwick, B. Rieger, Influence of thermal treatments on the polymorphism in stereoirregular isotactic polypropylene: effect of stereo-defect distribution, *J. Macromol. Sci., Phys.* B41 (4–6) (2002) 1091–1104.
- [31] N.S. Murthy, H. Minor, General procedure for evaluating amorphous scattering and crystallinity from X-ray-diffraction scans of semicrystalline polymers, *Polymer* 31 (6) (1990) 996–1002.

- [32] Y. Hayashi, G. Matsuba, Y.F. Zhao, K. Nishida, T. Kanaya, Precursor of shish-kebab in isotactic polystyrene under shear flow, *Polymer* 50 (9) (2009) 2095–2103.
- [33] G. Kumaraswamy, A.M. Issaian, J.A. Kornfield, Shear-enhanced crystallization in isotactic polypropylene. 1. Correspondence between in situ rheo-optics and ex situ structure determination, *Macromolecules* 32 (22) (1999) 7537–7547.
- [34] J.M. Guenet, C. Picot, Small-angle neutron scattering by semicrystallized chains: evaluation of the mean dimensions, *Polymer* 20 (12) (1979) 1473–1482.
- [35] B. Lotz, S. Graff, C. Straupe, J.C. Wittmann, Single-crystals of gamma-phase isotactic polypropylene – combined diffraction and morphological support for a structure with nonparallel chains, *Polymer* 32 (16) (1991) 2902–2910.
- [36] I.L. Hosier, R.G. Alamo, J.S. Lin, Lamellar morphology of random metallocene propylene copolymers studied by atomic force microscopy, *Polymer* 45 (10) (2004) 3441–3455.
- [37] B. Lotz, J.C. Wittmann, The molecular-origin of lamellar branching in the alpha-(monoclinic) form of isotactic polypropylene, *J. Polym. Sci. Polym. Phys.* 24 (7) (1986) 1541–1558.
- [38] F. Khoury, The spherulitic crystallization of isotactic polypropylene from solution: on the evolution of monoclinic spherulites from dendritic chain-folded crystal precursors, *J. Res. NBS, Sect. A: Phys. Chem.* 70A (1) (1966) 29–61.
- [39] F.L. Binsbergen, B.G.M. de Lange, Morphology of polypropylene crystallized from the melt, *Polymer* 9 (1968) 23–40.
- [40] S.Z.D. Cheng, *Phase Transitions in Polymers*, Elsevier, 2008.
- [41] R. Forstner, G.W.M. Peters, H.E.H. Meijer, A novel dilatometer for PVT measurements of polymers at high cooling – and shear rates, *Int. Polym. Proc.* 24 (2009) 114–121.
- [42] M.H.E. van der Beek, G.W.M. Peters, H.E.H. Meijer, A dilatometer to measure the influence of cooling rate and melt shearing on specific volume, *Int. Polym. Proc.* 20 (2005) 111–120.
- [43] B. Wunderlich, *Macromolecular Physics, Vol 2: Crystal Nucleation, Growth, Annealing*, Academic Press, New York, 1976.