Long-chain branched polypropylene: crystallization under high pressure and polymorphic composition

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Abstract

High-pressure crystallization and resulting polymorphic composition of long-chain branched polypropylene (LCB-PP) were studied and compared with common linear isotactic polypropylene (PP). Commercially available LCB-PP and PP with similar melt flow indexes were crystallized under several high pressures (20, 40, 80, 120 and 160 MPa) at constant cooling rate 5 °C min^{-1}. Structure of crystallized samples was evaluated via wide-angle X-ray scattering, differential scanning calorimetry and scanning electron microscopy. It was shown that under low pressure LCB-PP crystallizes at higher crystallization temperature than PP due to its higher nucleating density. The opposite situation is observed at high pressures (120 and 160 MPa): crystallization temperature of PP exceeds that of LCB-PP as a negative effect of branching is pronounced. Polymorphic analysis proved that LCB-PP tends to crystallize into orthorhombic γ-form. This crystalline form becomes to be dominant at 40 MPa, and LCB-PP samples crystallized at 120 and 160 MPa contain solely γ-form. On the other hand, no pure γ-form sample was prepared from PP in this study, although positive effect of pressure on its formation is observed. Thermodynamic stability of LCB-PP crystalline structure is systematically lower compared to PP. With pronounced crystallization pressure, the melting peak broadens and finally splits, indicating the presence of dominant amount of γ-form in LCB-PP. In comparison with PP, crystallites in LCB-PP structure are considerably smaller due to lower crystal growth rate and higher nucleating density.

Keywords Crystallization under high pressure · Long-chain branched polypropylene · Polymorphism · Thermal properties

Introduction

Isotactic polypropylene is one of the most widely used commercial polymers due to its beneficial behaviour such as high melting point, low density, good chemical resistance, advantageous mechanical properties and, finally, low cost.

Nevertheless, isotactic polypropylene prepared using Ziegler–Natta or metallocene catalysts usually possesses a linear chain structure and a narrow molecular weight distribution. This leads to a number of problems in melt processing. Isotactic polypropylene manifests low elongational viscosity, low melt strength and almost no strain hardening behaviour in the melt state, which makes it difficult to process with predominant elongational flow, such as thermoforming, blow moulding, foaming and extrusion coating. As a result, linear isotactic polypropylene (PP) has been excluded from some

end-use applications. Thus, the preparation and research of high melt strength polypropylene is very important industrially [1, 2].

The introduction of long-chain branches onto the polypropylene backbone is one of the most effective methods for increasing its melt strength. The industry uses two main methods for preparing long-chain branched polypropylene (LCB-PP). The first is electron beam irradiation of PP in solid state [3, 4], and the second is post-reactor chemical modification of PP using peroxides in melt state [5, 6]. LCB-PP prepared by these methods has complex branch structures and a wide molecular weight distribution. Besides them several other preparation techniques have been reported [e.g. 7–11]

Long-chain branches incorporated onto PP backbone can improve its melt processing properties, including melt strength, strain hardening and shear thinning, which leads to the broadening of end-uses and processing methods of PP [12, 13]. LCB-PP is thought to exhibit different helical conformations and crystallites due to the specific chain structure [2]. It has been shown that LCB-PP crystallizes generally

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faster than common PP, which can be explained by self-seeding effect of chain branches. Thus, increased nucleation density accelerates the overall crystallization rate [14–16].

In terms of polymorphic composition, LCB-PP has a higher tendency to crystallize into orthorhombic γ-form alongside α-form [2, 14, 17]. This crystalline form of PP possesses different thermomechanical behaviour than monoclinic α-form predominantly occurring in melt crystallized PP [1, 2, 18, 19]. Commonly, γ-form polymorph origins in PP by crystallization of stereoblock copolymers or random copolymers with small amounts of ethylene or butene-1 comonomers [15]. Indeed, an analogy in γ-form formation in random copolymers and LCB-PP could be taken into account. The γ-form content strongly increases with chain irregularity [20]; branching points in LCB-PP backbone act as disturbing elements that lead to stronger tendency to crystallize into γ-form.

The γ-form formation is also favoured by crystallization of PP under elevated pressure [21]. Several authors reported the effect of heterogeneous nucleation on crystallization of PP under high pressure and resulting morphology [22–24], using both α- and β-nucleating agents. The competition between the effect of nucleating agent and effect of high pressure on crystallization of PP was observed. As for LCB-PP the situation may be different due to high nucleation density (as in nucleated PP) and increased tendency to crystallize into γ-form.

The purpose of the present paper is to describe and explain crystallization behaviour of commercial LCB-PP under elevated pressure. Except the process of crystallization, morphology and thermal properties of prepared samples is also studied. This work should open a new perspective on the crystallization of LCB-PP and at the same time provide practical guidelines for optimizing the processing technology.

Experimental

Material and specimen preparations

Two commercially available polypropylenes, both supplied by Borealis Company Vienna, Austria, were used. The first was a Daploy WB130HMS long-chain branched polypropylene (LCB-PP) prepared by radical-driven monomer grafting. The second material was a HC600TF linear polypropylene homopolymer (PP). Both materials have similar processing properties represented by identical value of melt flow rate (230 °C, 2.16 kg, ISO 1133) of 2.8 g 10 min^{-1}.

Samples were prepared using a pvT100 high-pressure device manufactured by SWO Polymertechnik GmbH, Krefeld, Germany. Polymer pellets of mass of approx. 0.7 g were inserted into a measurement cylinder and heated to 220 °C at a heating rate 80 °C min^{-1}. The cylinder was then closed by the piston which enables to control the crystallization pressure and monitor the sample dimension. Subsequent crystallization proceeded during cooling from 220 to 50 °C at a cooling rate 5 °C min^{-1} and several constant pressures (20, 40, 80, 120 and 160 MPa). During the crystallization process, temperature, time and piston position were recorded.

Rectangular specimens of approx. $8 \times 15 \times 2$ mm^3 for wide-angle X-ray scattering (WAXS) were taken from the centre of crystallized cylindrical samples using a Leica RM2255 rotary microtome supplied by Leica Microsystems.

Scanning electron microscopy (SEM) was performed on specimens prepared from centre of crystallized samples. Surface of specimens was etched for 60 min in 1% solution of $KMnO_4$ in H_3PO_4 (85%).

The slices (approx. 7 mg) were microtomed from centre of crystallized samples, put into aluminium pans and analysed using differential scanning calorimetry (DSC).

Analysing methods

Wide-angle X-ray scattering analysis was performed with a X'Pert Pro MPD (Multi-Purposed Diffractometer) from PANalytical company. This diffractometer is equipped with CuKα in reflection mode and nickel filter of thickness 0.2 mm. Radial scans of intensity vs. diffraction angle 2Θ were recorded in the range of 7° to 30° by steps of 0.026°. Crystallinity X_c was determined as a ratio of the integral intensities diffracted by a crystalline part (I_c) and total integral intensities (I):

$$X_C = \frac{I_C}{I} 100 \tag{1}$$

Relative content of γ-form (G) in the γ/α crystalline system was calculated according to Pae:

$$G = \frac{H_\gamma}{H_{\alpha 3} + H_\gamma} 100 \tag{2}$$

where H_γ is the intensity of (117) γ-reflection and $H_{\alpha 3}$ is the intensity of (130) α-reflection [25].

For the purpose of crystallization studies, a PerkinElmer Pyris 1 differential scanning calorimeter was used. Prepared samples were heated from 50 up to 190 °C at a heating rate 10 °C min^{-1}.

In order to study morphology of the crystallized samples, a Vega-II LMU scanning electron microscope, Tescan Company USA, was employed.
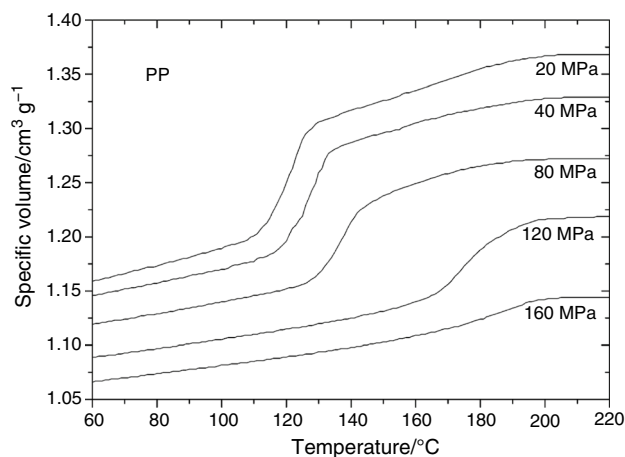
Fig. 1 The dependence of specific volume on temperature of PP crystallized at various pressures
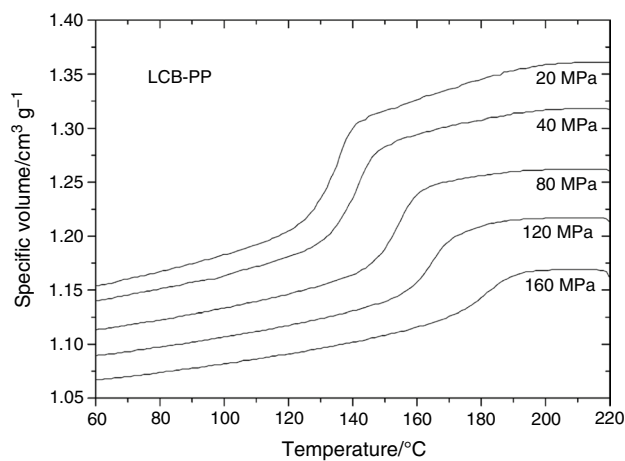
Fig. 2 The dependence of specific volume on temperature of LCB-PP crystallized at various pressures

Table 1 Crystallization temperatures (T_c) of PP and LCB-PP crystallized at various pressures

Pressure/MPa	PP T_c/°C	LCB-PP T_c/°C
20	123	136
40	126	142
80	137	155
120	172	165
160	193	181

Fig. 3 Crystallization temperatures of PP and LCB-PP crystallized at various pressures
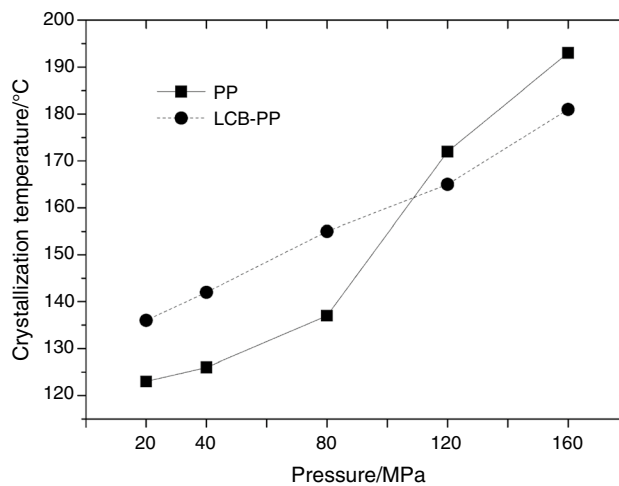
Results and discussion

Crystallization of PP and LCB-PP was performed in a high-pressure chamber allowing simultaneous control of pressure and temperature and recording of specific volume. Five constant pressures (20, 40, 80, 120 and 160 MPa) were applied varying from 20 to 160 MPa. Curves of typical sigmoidal crystallization curve of each material obtained by pvT100, i.e. dependence of specific volume as a function of temperature at constant pressure, are shown in Figs. 1 and 2. Crystallization temperature was calculated from dilatometric data as a curve flex point, and its values are summarized in Table 1 and depicted in Fig. 3.

The results show that crystallization temperature rises with the pressure for both used materials; however, the effect is more pronounced in PP (see Fig. 3):

crystallization temperature increased for 70 °C (versus 45 °C in LCB-PP) by increasing the crystallization pressure from 20 to 160 MPa. As compared to PP, LCB-PP has higher T_c up to crystallization pressure 80 MPa. Then, at pressure 120 and 160 MPa, the T_c of PP exceeds those of LCB-PP. A higher crystallization temperature of LCB-PP at low pressure has been already assigned to long-chain branches which can have self-seeding effect and thus speed the overall crystallization [1]. The reason of faster crystallization could be also ascribed to gel content which arises from the radical-driven synthesis process using peroxides. During these reactions, besides long-chain branches formation, also chain scission and cross-linking can occur. Even local cross-linking (gel) could lower melt entropy and serve as nuclei during crystallization. On the other hand, long-chain branches act as defects in the polymer chains and decrease the crystal growth rate. This phenomenon can be observed at high crystallization pressure (120 and 160 MPa) manifesting itself by slower crystallization of LCB-PP than that of PP.

To observe a polymorphic composition of crystallized samples, wide-angle X-ray scattering was employed. The corresponding WAXS patterns are shown in Figs. 4 and 5.
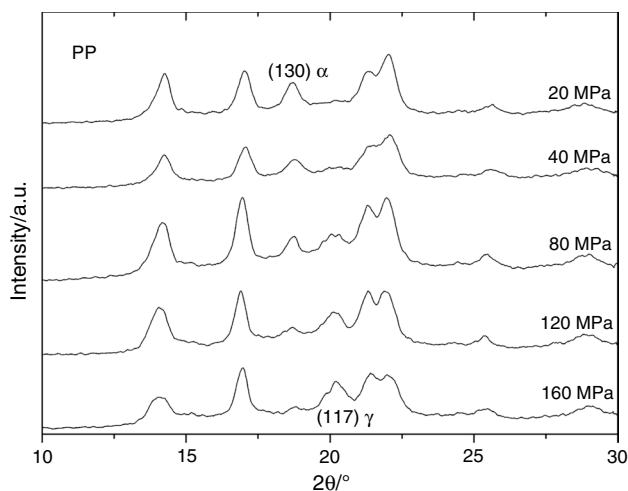
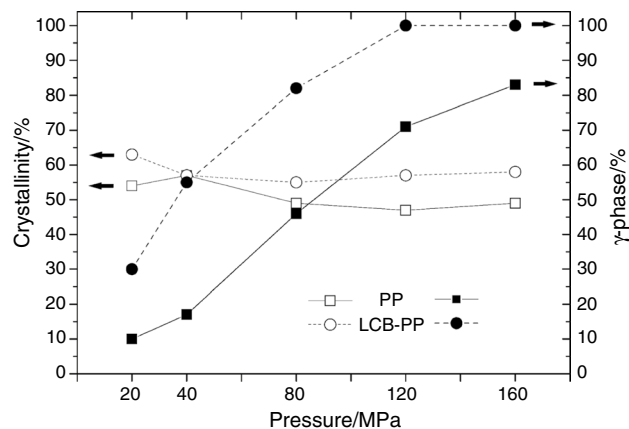**Fig. 4** Diffractograms of PP samples crystallized at various pressures
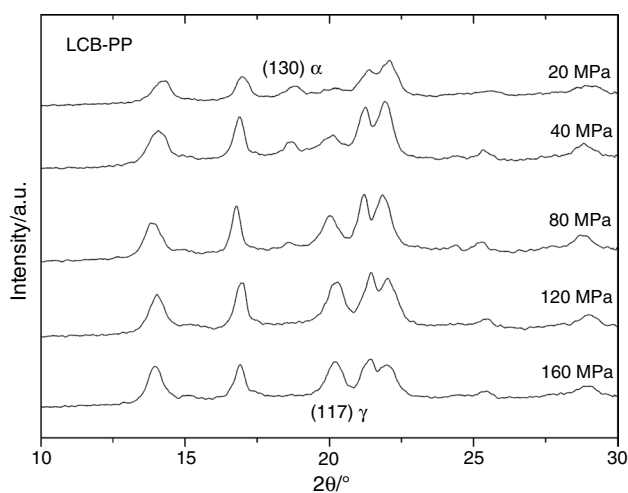
Fig. 5 Diffractograms of LCB-PP samples crystallized at various pressures

Table 2 Crystallinity (X_c) and relative content of γ-form (*G*) of PP and LCB-PP crystallized at various pressures

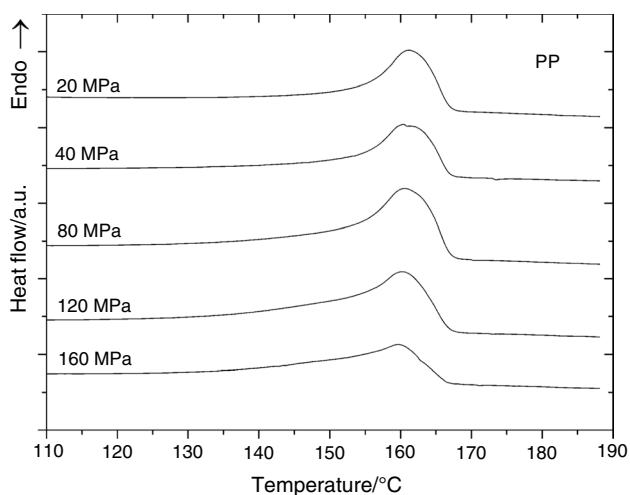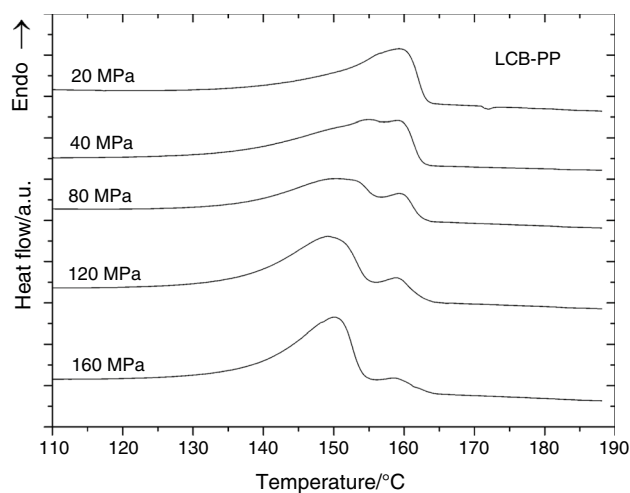| Pressure/MPa	PP		LCB-PP	
	X_c/%	*G*/%	X_c/%	*G*/%
20	54	10	63	30
40	57	17	57	55
80	49	46	55	82
120	47	71	57	100
160	49	83	58	100

Fig. 6 Crystallinity and relative content of γ-form of PP and LCB-PP crystallized at various pressures

in Figs. 4 and 5, (117) reflection of γ-form becomes distinct with increasing pressure. From diffraction patterns crystallinity (Eq. 1) and relative content of γ-form (Eq. 2) were calculated and are shown in Table 2.

The γ-form content increases with increasing pressure in both used materials. However, the relative content of the γ-form is systematically higher in all LCB-PP samples crystallized under various pressures, as can be seen in Fig. 6. Moreover, at pressures 120 and 160 MPa, only crystalline γ-form was detected. The shape of both curves is similar, and individual values are only shifted to each other. Thus, it could be expected that even PP can crystallize solely into γ-form, however, at pressures significantly higher than needed in LCB-PP. This observation is in agreement with Mezghani and Philips [31]. On the other hand, the crystallization behaviour of LCB-PP and its polymorphic composition is not yet fully understood. In general, the crystallization of LCB-PP can be compared with crystallization of PP containing comonomer. The disturbance of regular chain leads to promoted formation

It is evident that the high-pressure crystallized materials consist of α- and γ-forms, while β-form is not manifested. Actually, to achieve a considerable amount of β-form usually an introduction of β-nucleating agents is needed [26–29]. Typical reflections for α-form of iPP are observed at 2Θ = 14.2°, 17° and 18.8° corresponding to (110), (040) and (130). However, diffraction curve for γ-form is quite similar and most of the reflections for both phases are located at the same positions. The only difference can be found in 2Θ range of 18-21°, where two well-separated diffraction peaks of (130) plane of α-form and (117) plane of γ-form (2Θ = 20.5°) can be found [30]. As can be seen

Fig. 7 DSC heating curves of PP crystallized at various pressures


Fig. 8 DSC heating curves of LCB-PP crystallized at various pressures

of γ-form [2, 14, 17, 32]. The papers published [e.g. 20, 33–35] indicate that the molecular structure of branches plays an important role. Very short isotactic sequences (branches) cause crystallization to the γ-form, while long regular isotactic sequences (branches) usually crystallize only to the α-form. In this work, both effect—pressure and chain disturbance—on γ-form formation has been proved.

Differential scanning calorimetry was employed for measurements of melting curves of samples crystallized under high pressure. DSC curves are shown in Figs. 7 and 8. It can be seen that the melting peak broadens with increasing pressure applied during crystallization. This observation correlates with the formation of γ-form at high pressures. γ-Form of PP has lower melting temperature which results in melting onset at lower temperature of samples containing both α- and γ-forms. In the case of LCB-PP, the broad peak splits into two individual peaks, indicating separate melting of the two crystalline forms. Indeed, this material contains systematically higher amount of γ-form (see Fig. 6) as compared to PP. However, double melting peak can be found even in samples crystallized at 120 and 160 MPa, although solely γ-form is detected by WAXS. This phenomenon can be ascribed to transformation of metastable γ-form into α-form upon heating.

Figure 9 shows the evolution of melting temperature as a function of crystallization pressure. Values of melting temperature were taken as a maximum of melting DSC curve (in the case of double melting peak, both values are indicated
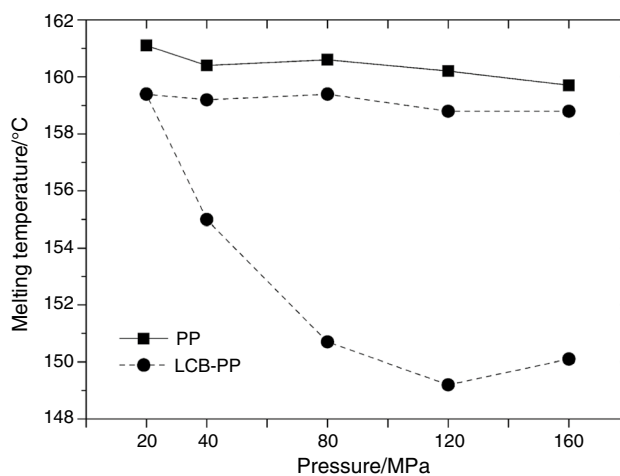

Fig. 9 The evolution of melting temperature of PP and LCB-PP crystallized at various pressures

in the graph). In all cases, PP possesses higher melting temperature as compared to LCB-PP. Because the melting point is related to the thickness of the lamellae [36], it can be suggested that PP contains thicker and more perfect lamellae, while LCB-PP is formed by thin crystallites with a number of defects, which is in agreement with Auriemma et al. [37]. The decrease of melting temperature with rising pressure, observed in both materials, correlates with acceleration in overall crystallization rate.

To observe a higher structural level of the morphology, namely the detailed spherulite structure, scanning electron
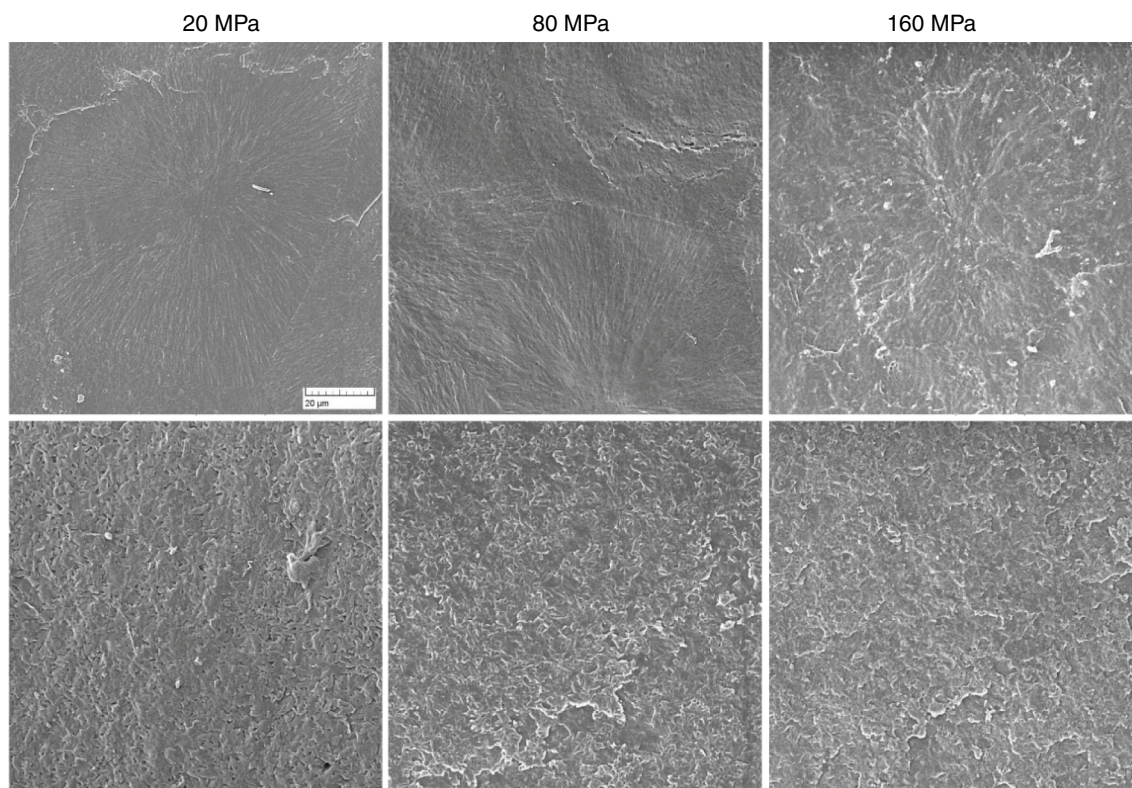
Fig. 10 SEM morphology of PP (up) and LCB-PP (down) samples crystallized at 20, 80 and 160 MPa

microscopy was employed. Figure 10 shows the fracture surfaces of PP and LCB-PP where distinct differences between the structure of materials crystallized under 20, 80 and 160 MPa can be seen. Morphology of PP crystallized at 20 and 80 MPa consists of spherulites with distinct boundaries. According to WAXS measurements, PP crystallized at these pressures contains predominantly α-form. On the other hand, relatively rough fracture surface and indistinguishable spherulite boundaries of PP crystallized at 160 MPa indicate dominating γ-form in crystalline portion. Entirely different scenario is manifested by LCB-PP—distinctly rough fracture surface does not show spherulitic structure. Such structure results from a high nucleating density, enhanced formation of γ-form and reduced grow rate of crystallites in LCB-PP [17]. It has been reported that LCB-PP consists of aggregates with incorporated nuclei from which the arrays grow up. The arrays contain probably radial (mother) lamellae which seem to be overgrown epitaxially [18].

Conclusions

The effect of both the long-chain branching and a high pressure on crystallization behaviour and structure of PP is studied in this work. Pressure–volume–temperature technique was used for a high-pressure crystallization (20, 40, 80, 120 and 160 MPa) at constant cooling rate of 5 °C min^{-1} of linear and long-chain branched polypropylene. The results show that under low pressure LCB-PP crystallizes easily than PP due to higher nucleating density arising from molecular structure. The opposite situation is observed at high pressures (120 and 160 MPa): negative effect of long-chain branches on regularity of backbone manifests itself in lower crystal growth rate of LCB-PP and overall faster crystallization of PP.

As for polymorphic composition the results show that prepared samples consist of α- and γ-forms, while β-form is not present. γ-Form content increases with rising pressure in both PP and LCB-PP. LCB-PP can easily crystallize into γ-form and reaches 100% at pressure 120 and 160 MPa.

Differential scanning calorimetry shows that the melting peak broadens and even splits in LCB-PP with increasing crystallization pressure, which reflects the presence of γ-form. PP possesses systematically higher values of melting temperature as compared to LCB-PP.

Scanning electron microscopy shows that the structure of PP consists of spherulites; however, their boundaries can be clearly distinguished only at low crystallization pressure. On the contrary, morphology of LCB-PP does not show typical spherulitic structure and the crystallites are significantly smaller.

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