

Journal of Thermal Analysis and Calorimetry

Long chain branched polypropylene: Crystallization under high pressure and polymorphic composition

--Manuscript Draft--

Manuscript Number:	JTAC-D-18-02553R2
Full Title:	Long chain branched polypropylene: Crystallization under high pressure and polymorphic composition
Article Type:	Research Paper
Corresponding Author:	Jana Navratilova Univerzita Tomase Bati ve Zline CZECH REPUBLIC
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Univerzita Tomase Bati ve Zline
Corresponding Author's Secondary Institution:	
First Author:	Jana Navratilova
First Author Secondary Information:	
Order of Authors:	Jana Navratilova Lenka Gajzlerova Lukas Kovar Roman Cermak
Order of Authors Secondary Information:	
Funding Information:	
Abstract:	<p>High pressure crystallization and resulting polymorphic composition of long chain branched polypropylene (LCB-PP) was 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 $5\text{ }^{\circ}\text{C min}^{-1}$. 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 contains 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 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.</p>
Response to Reviewers:	<p>Dear editor, according to your recommendation, we have reduced the similarities in the manuscript text. I have also corrected the title to Long chain branched polypropylene: Crystallization under high pressure and polymorphic composition.</p> <p>We hope that you will find the revised manuscript suitable for publication in Journal of thermal analysis and calorimetry.</p>

Best regards,

Jana Navratilova
Faculty of Technology
Tomas Bata University in Zlin
e-mail: j1navratilova@utb.cz

List of revision

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No: JTAC-D-18-02553

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Long chain branched polypropylene: Crystallization under high pressure and polymorphic composition

Jana Navratilova*, Lenka Gajzlerova, Lukas Kovar, Roman Cermak

Tomas Bata University in Zlin, Faculty of Technology, Vavreckova 275, 760 01 Zlin, Czech Republic

*Corresponding author, e-mail: j1navratilova@utb.cz, phone: +420 57 603 1384

ABSTRACT: High pressure crystallization and resulting polymorphic composition of long chain branched polypropylene (LCB-PP) was 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 contains 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 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

1. 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. 7–12].

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 [13, 14]. 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 faster than common PP, which can be explained by self-seeding effect of chain branches. Thus, increased nucleation density accelerates the overall crystallization rate [15–17].

In terms of polymorphic composition, LCB-PP has a higher tendency to crystallize into orthorhombic γ -form alongside α -form [2, 15, 18]. This crystalline form of PP possesses different thermomechanical behaviour than monoclinic α -form predominantly occurring in melt crystallized PP [1, 2, 19, 20]. Commonly, γ -form polymorph origins in PP by crystallization of stereoblock copolymers or random copolymers with small amounts of ethylene or butene-1 comonomers [16]. 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 [23]; 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 [24].

Several authors reported the effect of heterogeneous nucleation on crystallization of PP under high pressure and resulting morphology [21, 22, 25], 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.

2. Experimental

2.1. 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. 8x15x2 mm³ 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).

2.2. 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 $\text{CuK}\alpha$ 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):

$$X_c = \frac{I_c}{I} 100 \quad (1)$$

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

$$G = \frac{H_\gamma}{H_{\alpha 3} + H_\gamma} 100 \quad (2)$$

where H_γ is the intensity of (117) γ -reflection and $H_{\alpha 3}$ is the intensity of (130) α -reflection [26].

For the purpose of crystallization studies, a Perkin-Elmer 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.

3. 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 on temperature at constant pressure are shown in Fig. 1 and Fig. 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.

1 The results show that crystallization temperature rises with the pressure for both used
2 materials, however, the effect is more pronounced in PP (see Fig. 3): crystallization
3 temperature increased for 70 °C (versus 45 °C in LCB-PP) by increasing the crystallization
4 pressure from 20 to 160 MPa. As compared to PP, LCB-PP has higher T_c up to crystallization
5 pressure 80 MPa. Then, at pressure 120 and 160 MPa, the T_c of PP exceed those of LCB-PP.
6 A higher crystallization temperature of LCB-PP at low pressure has been already assigned to
7 long chain branches which can have self-seeding effect and thus speed the overall
8 crystallization [1]. The reason of faster crystallization could be also ascribed to gel content
9 which arises from the radical-driven synthesis process using peroxides. During these
10 reactions, besides long chain branches formation, also chain scission and crosslinking can
11 occur. Even local crosslinking (gel) could lower melt entropy and serve as nuclei during
12 crystallization. On the other hand, long chain branches act as defects in the polymer chains
13 and decrease the crystal growth rate. This phenomenon can be observed at high crystallization
14 pressure (120 and 160 MPa) manifesting itself by slower crystallization of LCB-PP than that
15 of PP.
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17 To observe a polymorphic composition of crystallized samples, wide angle X-ray scattering
18 was employed. The corresponding WAXS patterns are shown in Fig. 4 and Fig. 5. It is
19 evident that the high pressure crystallized materials consist of α - and γ -forms, while β -form is
20 not manifested. Actually, to achieve a considerable amount of β -form usually an introduction
21 of β -nucleating agents is needed [27–30]. Typical reflections for α -form of iPP are observed
22 at $2\Theta=14.2^\circ$, 17° and 18.8° corresponding to (110), (040) and (130). However, diffraction
23 curve for γ -form is quite similar and most of the reflections for both phases are located at the
24 same positions. The only difference can be found in 2Θ range of $18\text{--}21^\circ$, where two well-
25 separated diffraction peaks of (130) plane of α -form and (117) plane of γ -form ($2\Theta=20.5^\circ$)
26 can be found [31]. As can be seen in Fig. 4 and Fig. 5, (117) reflection of γ -form becomes
27 distinct with increasing pressure. From diffraction patterns crystallinity (equation 1) and
28 relative content of γ -form (equation 2) were calculated and are shown in Table 2.
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30 The γ -form content increases with increasing pressure in both used materials. However, the
31 relative content of the γ -form is systematically higher in all LCB-PP samples crystallized
32 under various pressures, as can be seen in Fig. 6. Moreover, at pressures 120 and 160 MPa,
33 only crystalline γ -form was detected. The shape of both curves is similar and individual
34 values are only shifted to each other. Thus, it could be expected that even PP can crystallize
35 solely into γ -form, however, at pressures significantly higher than needed in LCB-PP. This
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1 observation is in agreement with Mezghani and Philips [32]. On the other hand, the
2 crystallization behaviour of LCB-PP and its polymorphic composition is not yet fully
3 understood. In general, the crystallization of LCB-PP can be compared with crystallization of
4 PP containing comonomer. The disturbance of regular chain leads to promoted formation of γ -
5 form [2, 15, 18, 33]. The papers published [e.g. 34–37] indicate that the molecular structure of
6 branches plays an important role. Very short isotactic sequences (branches) cause
7 crystallization to the γ -form, while long regular isotactic sequences (branches) usually
8 crystallize only to the α -form. In this work, both effect – pressure and chain disturbance – on
9 γ -form formation has been proved.

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

21 Fig. 9 shows the evolution of melting temperature as a function of crystallization pressure.
22 Values of melting temperature were taken as a maximum of melting DSC curve (in the case
23 of double melting peak, both values are indicated in the graph). In all cases, PP possesses
24 higher melting temperature as compared to LCB-PP. Because the melting point is related to
25 the thickness of the lamellae [38], it can be suggested that PP contains thicker and more
26 perfect lamellae, while LCB-PP is formed by thin crystallites with a number of defects, which
27 is in agreement with Auriemma et al. [39]. The decrease of melting temperature with rising
28 pressure, observed in both materials, correlates with acceleration in overall crystallization
29 rate.

30 To observe a higher structural level of the morphology, namely the detailed spherulite
31 structure, scanning electron microscopy was employed. Fig. 10 shows the fracture surfaces of
32 PP and LCB-PP where distinct differences between the structure of materials crystallized
33 under 20, 80 and 160 MPa can be seen. Morphology of PP crystallized at 20 and 80 MPa
34 consists of spherulites with distinct boundaries. According to WAXS measurements, PP

1 crystallized at these pressures contains predominantly α -form. On the other hand, relatively
2 rough fracture surface and indistinguishable spherulite boundaries of PP crystallized at 160
3 MPa indicate dominating γ -form in crystalline portion. Entirely different scenario is
4 manifested by LCB-PP – distinctly rough fracture surface does not show spherulitic structure.
5 Such structure results from a high nucleating density, enhanced formation of γ -form and
6 reduced grow rate of crystallites in LCB-PP [18]. It has been reported that LCB-PP consists of
7 aggregates with incorporated nuclei from which the arrays grow up. The arrays contains
8 probably radial (mother) lamellae which seem to be overgrown epitaxially [19].
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16 **Conclusion**

17 The effect of both the long chain branching and a high pressure on crystallization behaviour
18 and structure of PP is studied in this work. Pressure-volume-temperature technique was used
19 for a high pressure crystallization (20, 40, 80, 120 and 160 MPa) at constant cooling rate of 5
20 $^{\circ}\text{C min}^{-1}$ of linear and long chain branched polypropylene. The results show that under low
21 pressure LCB-PP crystallizes easily than PP due to higher nucleating density arising from
22 molecular structure. The opposite situation is observed at high pressures (120 and 160 MPa):
23 negative effect of long chain branches on regularity of backbone manifests itself in lower
24 crystal growth rate of LCB-PP and overall faster crystallization of PP.
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33 As for polymorphic composition the results show that prepared samples consist of α - and γ -
34 forms, while β -form is not present. γ -form content increases with rising pressure in both PP
35 and LCB-PP. LCB-PP can easily crystallize into γ -form and reaches 100 % at pressure 120
36 and 160 MPa.
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40 Differential scanning calorimetry shows that the melting peak broadens and even splits in
41 LCB-PP with increasing crystallization pressure, which reflects the presence of γ -form. PP
42 possesses systematically higher values of melting temperature as compared to LCB-PP.
43 Scanning electron microscopy shows that the structure of PP consists of spherulites, however,
44 their boundaries can be clearly distinguished only at low crystallization pressure. On the
45 contrary, morphology of LCB-PP does not show typical spherulitic structure and the
46 crystallites are significantly smaller.
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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

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

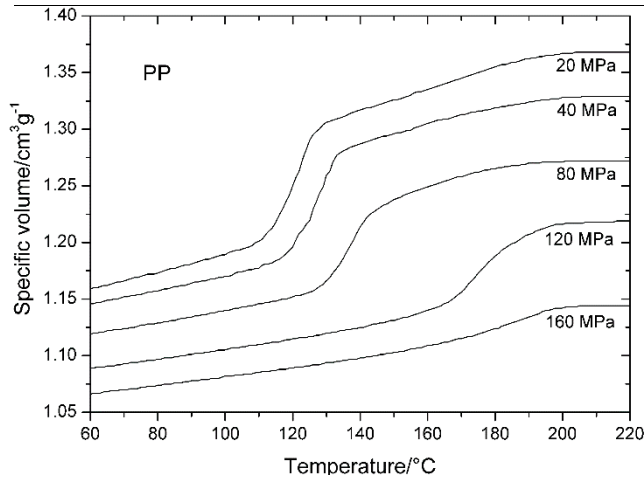


Fig. 1 The dependence of specific volume on temperature of PP crystallized at various pressures

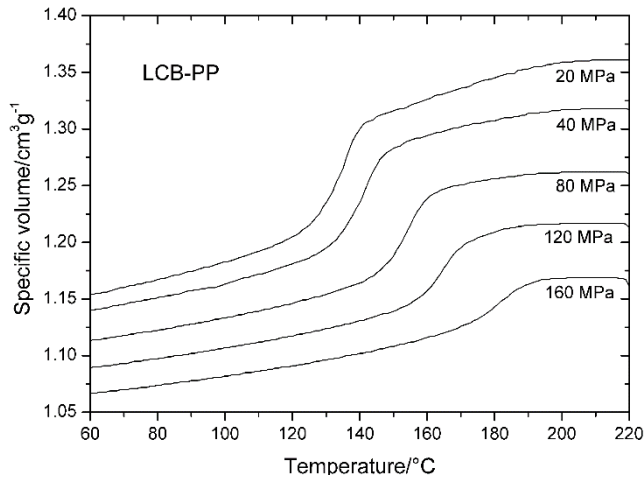


Fig. 2 The dependence of specific volume on temperature of LCB-PP crystallized at various pressures

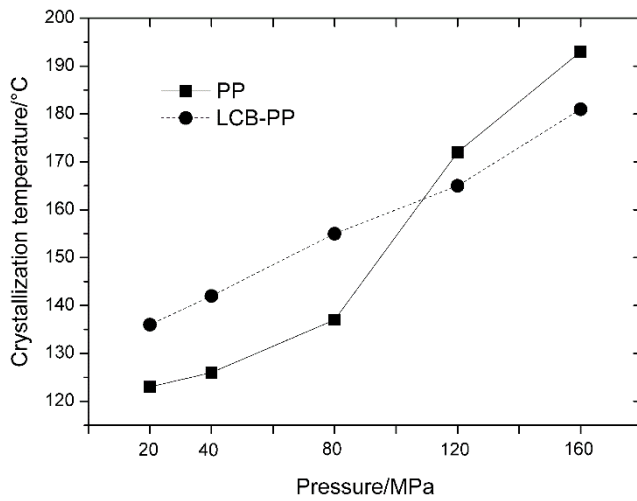


Fig. 3 Crystallization temperatures of PP and LCB-PP crystallized at various pressures

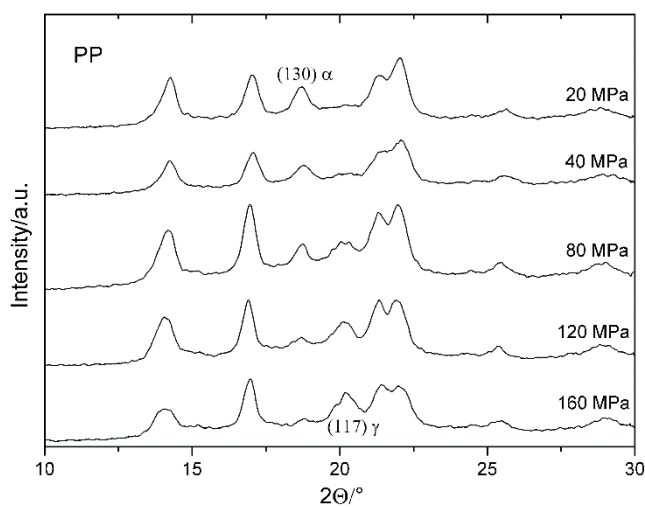


Fig. 4 Diffractograms of PP samples crystallized at various pressures

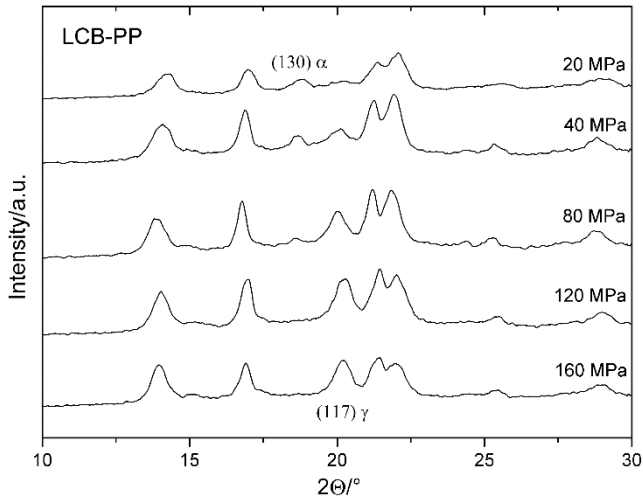


Fig. 5 Diffractograms of LCB-PP samples crystallized at various pressures

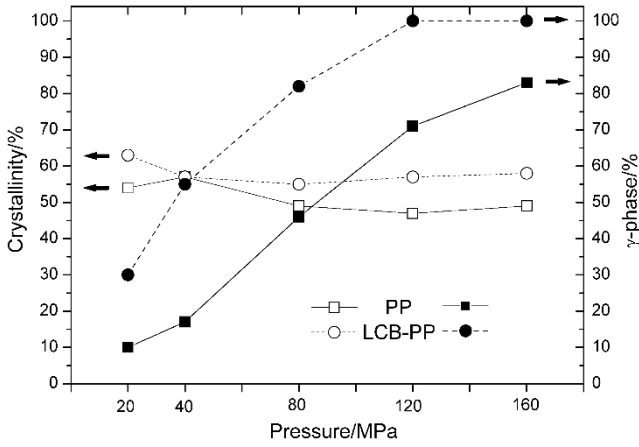


Fig. 6 Crystallinity and relative content of γ -form of PP and LCB-PP crystallized at various pressures

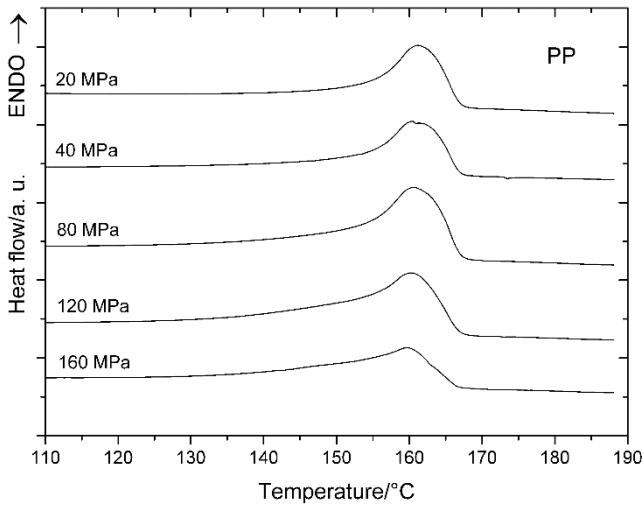
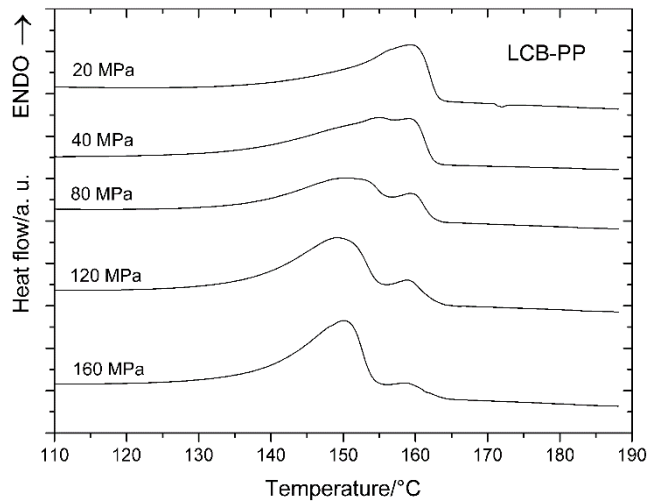
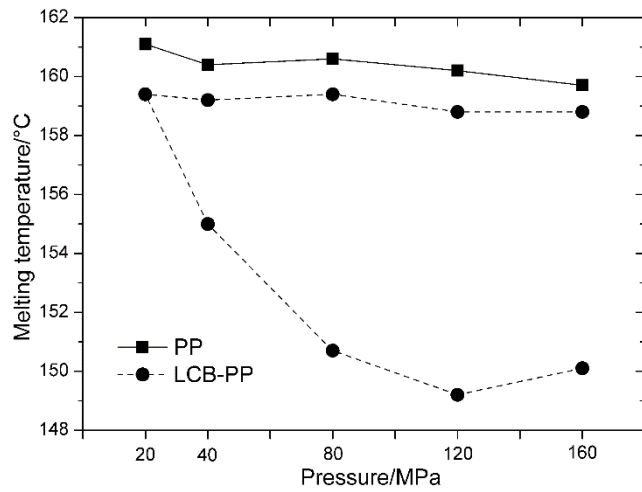


Fig. 7 DSC heating curves of PP crystallized at various pressures



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



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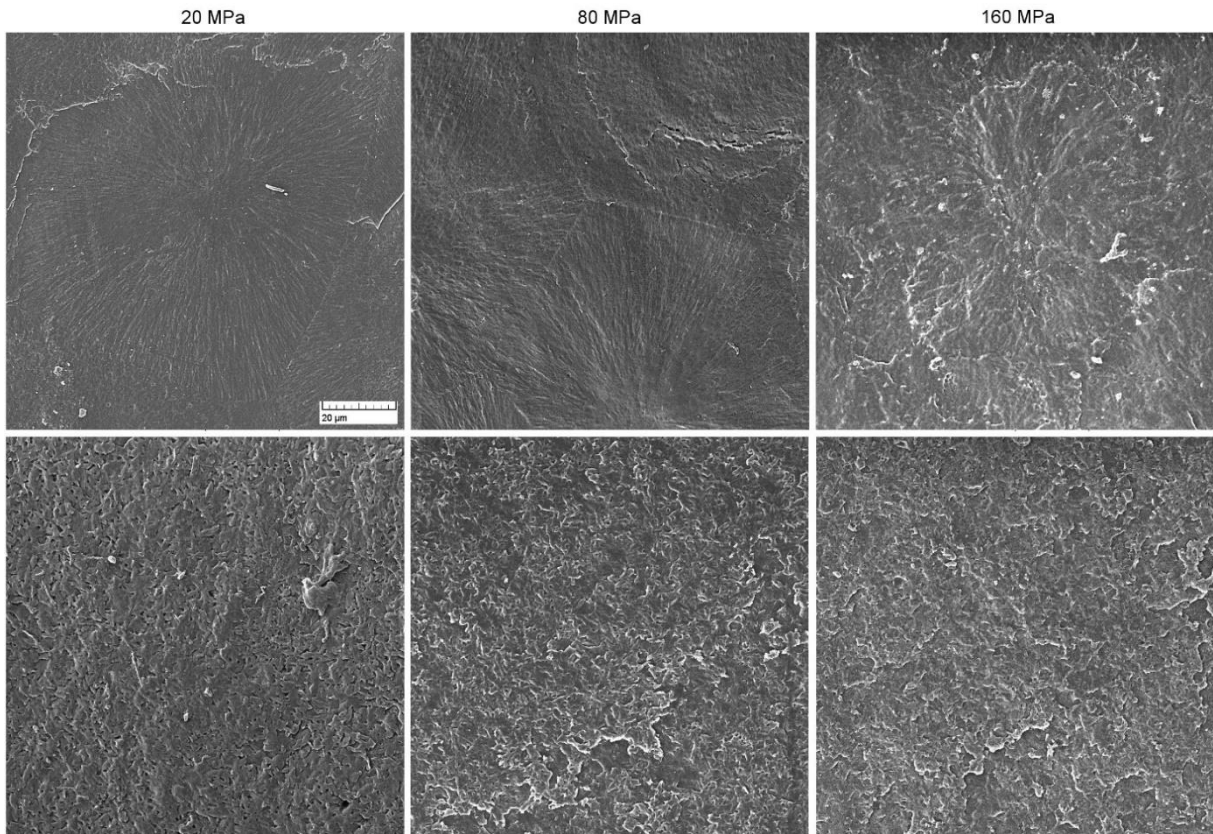


Fig. 10 SEM morphology of PP (up) and LCB-PP (down) samples crystallized at 20, 80 and 160 MPa

