Joint effects of long-chain branching and specific nucleation on morphology and thermal properties of polypropylene blends

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Abstract. The influence of long-chain branching and specific β-nucleation on polymorphic composition, melting and crystallization, and morphology of polypropylene blends were investigated by wide-angle X-ray scattering, differential scanning calorimetry, and scanning electron microscopy. Linear polypropylene and long-chain branched polypropylene were used for the preparation of blends in various proportions. *N,N'*-dicyclohexylnaphthalene-2,6-dicarboxamide was introduced (0 or 0.03 wt%) as a β-specific nucleating agent into prepared blends. It was found that LCB-PP strongly induces γ-phase formation in the blends and suppresses the nucleation activity of a β-specific nucleating agent. Blends containing a predominant amount of α- and γ-phases showed higher thermodynamic stability within melting, as compared to the samples rich in β-phase. During crystallization, LCB-PP in the blends increases nucleation density by self-seeding effect, manifesting itself in the shift of crystallization temperature. β-phase in the blends is distinctly separated in spherulites, while α- and γ-phases coexist on the lamellae level.

Keywords: polymer blends and alloys, polypropylene, long-chain branching, specific nucleation, thermal properties

1. Introduction

Isotactic polypropylene (PP) possesses a prominent position among semi-crystalline polymers, which is mainly a result of its structural behavior. It implies a good mechanical performance in engineering applications. However, commercial production of polypropylene with Ziegler-Natta or metallocene catalysts results in highly linear chains, relatively low melt strength, and extensional viscosity. These characteristics bring drawbacks for processes that require high melt strength, such as foaming, blown film processing, blow molding, and thermoforming [1–4]. The use of long-chain branched polypropylene (LCB-PP), recently developed and commercially available, prevents these problems and has opened up a wider field of applications. Long-chain branches are commonly introduced to linear polypropylene via direct synthesis using metallocene catalysis [5, 6], electron beam, or gamma irradiation [7, 8], and post reactor chemical modification [9, 10]. However, a higher price of LCB-PP has complicated their widespread use in industry. Thus, production of blends of linear isotactic polypropylene and LCB-PP can provide satisfactory properties at a reasonable price [11, 12].

Several crystallographic modifications have been recognized in PP – α-, β-, γ-phases, [13, 14], and the mesomorphic 'smectic' phase, which is formed during high undercooling instead of a crystalline phase [14, 15]. From a practical point of view, monoclinic α- and trigonal β-phases have relevance [16, 17]. The β-phase is thermodynamically metastable and difficult to obtain under normal processing conditions. Specific nucleation caused by an addition of heterogeneous β-nucleating agent is an efficient way of

introducing the β-phase into the PP [17–21]. This crystallographic modification shows superior toughness and drawability but slightly lower stiffness as compared to the more common α-phase [18, 22–26]. Obadal and coworkers [27–29] intensively studied lower sensitivity of β-nucleated polypropylene to photodegradation. Orthorhombic γ-phase is the most peculiar crystallographic modification of PP. It can be generated either by crystallization of a homopolymer at high pressure or by crystallization of low molecular weight fractions of PP and polypropylene-derived copolymers at atmospheric pressure. The γ-modification is especially favored in PP synthesized by metallocene catalysts, because of the presence of errors homogeneously distributed among the polymer chains [30–33]. Over the past two decades, many papers have focused on the role of long-chain branching in the crystallization of PP into the γ-phase [34–39]. Su *et al.* [34] found that LCB-PP crystallizes from the melt as a mixture of the α- and γ-phases. The content of the γ-phase increases in LCB-PP with increasing crystallization temperature until it reaches a maximum value. Agarwal *et al.* [35] studied the shear-induced crystallization of LCB-PP. They found that γ-phase content is independent of long-chain branching level and induced by regional defects of the chain and shear flow. According to Zeng *et al.* [36], long-chain branching in PP increases the number of nuclei and decreases the activation energy of nucleation as a result of enhanced chain entanglement.

Controlling the molecular and supermolecular structure of polymorphic semi-crystalline polymers is a smart way of tailoring their properties. A combination of long-chain branched and β-nucleated polypropylene can bring interesting results – enhanced toughness and, at the same time, higher melt strength. Current papers focus on the rheological properties and chemical structure of PP/LCB-PP blends [4, 37, 38], while the crystallization behavior, morphology, and mechanical properties, which are important in applications, have been reported by few authors. Wang *et al.* [39] investigated the crystallization behavior and crystalline morphology of PP/LCB-PP blends. They

found that the nucleation and overall crystallization rate are enhanced after the incorporation of LCB-PP into PP. Cao *et al.* [40] observed synergistic toughening effect of β-nucleating agent and long-chain branching on polypropylene random copolymer. Yu *et al.* [41] focused on evolution of β-crystals and better foamability of various L-PP/LCB-PP blends.

The goal of the present study is to examine the effect of long-chain branching and β-specific nucleation on the supermolecular structure and thermal properties of polypropylene blends. For these purposes, polypropylene blends with various amounts of LCB-PP, and the nucleating agent have been chosen. This approach should open new insight into the mechanism of blending and specific nucleation process and, at the same time, bring about practical instructions important for optimizing processing technology.

2. Experimental section

As starting materials, two types of commercially available polypropylenes supplied by Borealis Company Vienna, Austria, were used throughout this study. The first was linear polypropylene homopolymer Borclean HC310BF (L-PP). The second material used in this study was long-chain branched polypropylene Daploy WB130HMS (LCB-PP). It is a propylene-based polymer produced by monomer grafting during the radical-driven reactions of isotactic polypropylene with peroxides to create long-chain branches. The materials have the value of melt flow rate (230 °C, 2.16 kg, ISO 1133) of 2.2, and 2.8 g/10 min, respectively. Specific nucleating agent *N,N′*-dicyclohexylnapthalene-2,6-dicarboxamide, NJ Star NU 100 (NU 100), was supplied by Rika Int., Manchester, Great Britain.

Blends containing different amount of LCB-PP (0, 1, 2, 5, 10, 20, 50 and 100 wt%) and NU 100 (0 or 0.03 wt%) were prepared using a co-rotating twin-screw extruder (Brabender GmbH & Co, Germany) followed by cooling and pelletizing. The processing conditions were as follows: screw speed 65 min⁻¹, temperatures of barrel zones 190, 200, and 210 °C. To ensure the same processing history for all samples,

Table 1. Compositions of prepared blends.

Sample [wt%]	L-PP	BL 1	BL 2	BL 5	BL 10	BL 20	BL 50	LCB-PP
L-PP	100	99	98	95	90	80	50	0
LCB-PP	0	1	2	5	10	20	50	100
NU 100	0/0.03	0/0.03	0/0.03	0/0.03	0/0.03	0/0.03	0/0.03	0/0.03

unblended components were extruded under the same conditions. The compositions of prepared blends are listed in Table 1. From the prepared blends plates of a thickness of approx. 1 mm were compression-molded: pressing temperature 210 °C for 5 min and cooling temperature 60 °C for 5 min. Subsequently, the specimens were examined by wide-angle X-ray scattering (WAXS), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

The amount and polymorphic composition of the crystalline portion was determined by wide-angle X-ray scattering. An X'Pert PRO diffractometer (Malvern PANanalytical, United Kingdom) with Bragg-Brentano geometry in reflection mode was equipped with CuK_α radiation with Ni filter ($\lambda = 0.154$ nm) and employed in the diffraction angle interval of $2\theta = 5$–$30°$.

Overall crystallinity of all samples was estimated from the diffractograms after subtraction of the amorphous halo. The ratio of the integral intensities diffracted by a crystalline part (I_C) and amorphous part (I_A) was used to determine crystallinity (X), see Equation (1):

$$X = \frac{I_C}{I_C + I_A} \cdot 100 \quad [\%] \tag{1}$$

For a quantitative evaluation of the phase composition in β/α and γ/α crystalline systems of polypropylene, two basic relations can be used. In the β/α crystalline system, the relative content of the β-phase (B) within the crystalline portion of the material is calculated according to Turner Jones *et al.* [19] by Equation (2):

$$B = \frac{H_\beta}{H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3} + H_\beta} \cdot 100 \quad [\%] \tag{2}$$

where $H_{\alpha 1}$, $H_{\alpha 2}$, $H_{\alpha 3}$ are the intensities of α-diffraction peaks corresponding to angles $2\theta = 14.20$, 17.00, and $18.80°$, respectively, and H_β is the intensity of the β-peak at $2\theta = 16.20°$.

In the γ/α crystalline system, the reflections at $2\theta = 14.2$, $17.0°$ ($H_{\alpha 1}$ and $H_{\alpha 2}$), are common for both the α- and the γ-phases. Therefore, the γ-phase fraction (G) within the crystalline part is calculated according to Sauner and Pae [42] only from the intensities of the (130) $\alpha 3$ reflection at $18.80°$ ($H_{\alpha 3}$) and the (117) γ reflection at $20.05°$ (H_γ), which are unique reflections for each phase, as shown by Equation (3):

$$G = \frac{H_\gamma}{H_{\alpha 3} + H_\gamma} \cdot 100 \quad [\%] \tag{3}$$

The evaluation of an $\alpha/\beta/\gamma$ crystalline system can be calculated according to Obadal *et al.* [43], as follows:

1) The spectra of the $\alpha/\beta/\gamma$ crystalline system consist of all the reflections mentioned above: at diffraction angle $2\theta = 14.20°$ (α- and γ-phases), $16.20°$ (β-phase), $17.00°$ (α- and γ-phases), $18.80°$ (α-phase), and $20.05°$ (γ-phase). Since the spectra of the pure β-phase manifests only the reflection at $2\theta = 16.20°$, and, on the other hand, the spectra of the γ/α crystalline system display solely the individual and shared reflections of the α- and γ-phases, Equation (2) has to be modified by the addition of H_γ as shown by Equation (4):

$$K_\beta = \frac{H_\beta}{H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3} + H_\beta + H_\gamma} \cdot 100 \quad [\%] \tag{4}$$

where K_β provides relative the β-phase content in the three-phase crystalline system of polypropylene.

2) Shared content of both α- and γ-phases ($K_{\alpha+\gamma}$) in the three-phase crystalline system can be defined by Equation (5):

$$K_{\alpha + \gamma} = 1 - K_\beta \tag{5}$$

3) The mutual relation between the α- and γ-phases (G) is calculated from the already mentioned Equation (3). Consequently, the content of the α-phase (K_α) and the γ-phase (K_γ) in the three-phase crystalline polypropylene can be calculated by Equations (6) and (7):

$$K_\gamma = G \cdot K_{\alpha + \gamma} \tag{6}$$

$$K_\alpha = 1 - K_\beta - K_\gamma \tag{7}$$

In an above-mentioned way, the polymorphic composition in three-phase crystalline systems of polypropylene is calculated only relatively; however, the results can be used for simple quantification of multiphase crystalline systems. More accurate results can be reached using an improved method by Krache *et al.* [31].

The melting behavior of the specimens was measured by a DSC1, differential scanning calorimeter (Mettler Toledo, USA). The specimens with a mass of approx. 7 mg were inserted into standard aluminum pans and heated from 50 up to 190 °C with a heating rate of 10 °C/min. The measurements were performed under a nitrogen atmosphere (20 ml/s).

Morphology of the specimens was directly documented by a Vega-II LMU scanning electron microscope (Tescan Company, USA). Compression-moulded plates were cryo-fractured under liquid nitrogen; fracture surfaces were then exposed to a permanganic etching (1% $KMnO_4$ in concentrated H_3PO_4) and finally sputtered with gold-palladium alloy.

3. Results and discussion

3.1. Polymorphic composition of the blends

X-ray diffractograms of L-PP/LCB-PP blends with/without NU 100 are presented in Figure 1. What can be seen are typical diffraction spectra of three-phase crystalline systems manifested by the occurrence of the peaks of the main planes of the α-phase – $α_1$ (110), $α_2$ (040) and $α_3$ (130), β-phase (300) and γ-phase (117).

The overall crystallinity (Figure 2) of all samples was slightly higher than 50%, independently on blend composition. The addition of β-specific nucleator NU 100 distinctly changes the crystallinity only in the pure LCB-PP: it increases from 48 to 53%. The lower
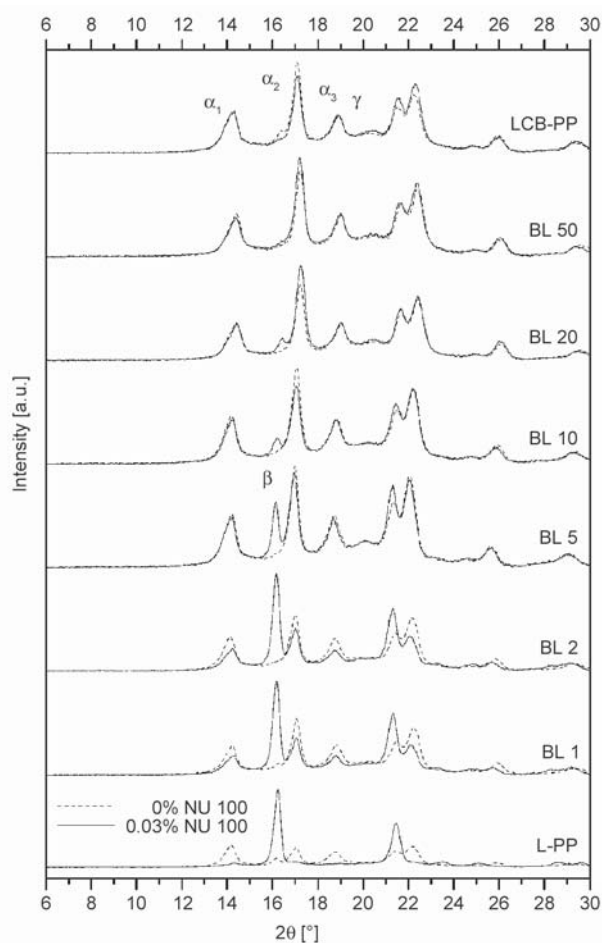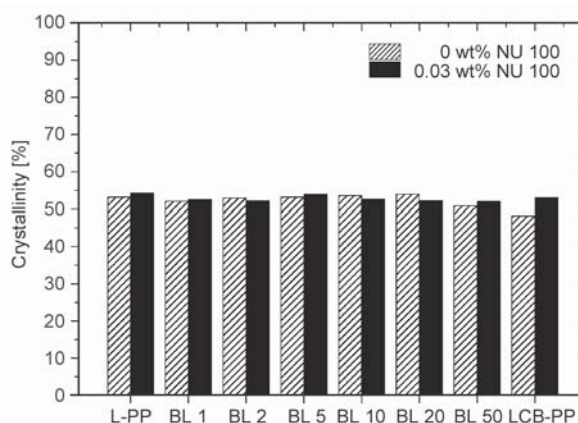

Figure 2. Dependence of crystallinity on the blend composition.

value of crystallinity in the case of pure LCB-PP can be ascribed to the fact that the long chains act as defects restricting crystalline packing. For the quantitative description of individual phase content, the *K* values defined by Equation (2)–(7) were calculated.

A strong dependence of polymorphism of the samples on the composition of the blend is evident from Figure 3. Neat L-PP consists predominantly of monoclinic α-phase, whereas the addition of 0.03 wt% of NU 100 leads to the crystallization of L-PP into almost solely trigonal β-phase ($K_β$ = 94%). This effect has already been published (*e.g.* [17, 23, 24]). On the other hand, neat LCB-PP consists largely of monoclinic α- and orthorhombic γ-phases ($K_γ$ = 26%), β-phase content $K_β$ is only 7%. In the nucleated LCB-PP β-phase vanished absolutely. Thus, it is evident that β-specific nucleator NU 100 does not induce the crystallization into the trigonal β-phase in LCB-PP under given conditions. In the case of nucleated L-PP/LCB-PP blends, the significant decrease of β-phase content with increasing LCB-PP amount can be observed, from nucleated BL 1 $K_β$ = 59% to BL 50 where the β-phase is suppressed

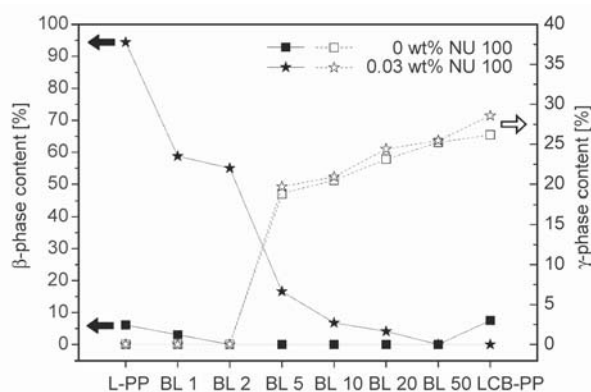**Figure 1.** X-ray diffraction patterns of the blends.

Figure 3. Dependence of β- and γ-phases content on the blend composition.

completely and the crystalline system consists only of α- and γ-phases. It is worth mentioning that even a small addition of LCB-PP to L-PP results in significant suppression of β-phase. An opposite trend is evident in the case of γ-phase of L-PP/LCB-PP blends independently on the β-nucleator concentration. The γ-phase content rises from 0% of L-PP and blends with low content of LCB-PP (BL 1 and BL 2) to almost 30% at LCB-PP. The sharpest increase of K_γ can be clearly seen between blend BL 2 and BL 5, respectively. It is evident that the β-nucleating agent does not influence the formation of orthorhombic γ-phase. These results are in agreement with the work by Jeon *et al.* [44] who studied the effect of comonomer type on the crystalline structure of random isotactic propylene 1-alkene copolymers and observed that the development of γ-phase is enhanced in copolymers with increasing comonomer content, following the general concept that the increase in short crystallisable sequences favours the formation of the γ-phase [34, 45, 46].
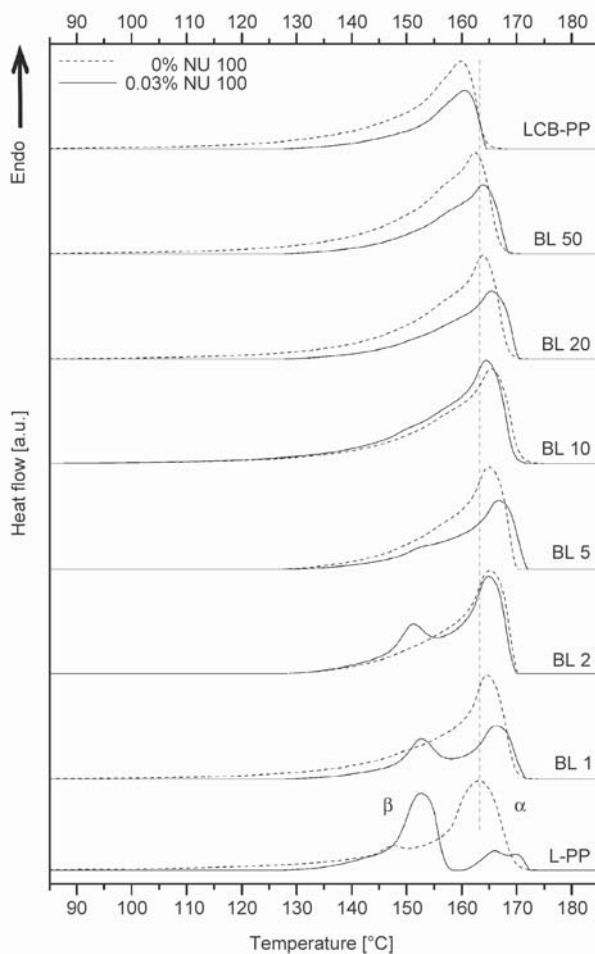
3.2. Melting and crystallization behavior of the blends

The effect of blends composition on the phase structure is also manifested by the DSC thermograms (Figures 4 and 5). Melting thermograms of the L-PP/LCB-PP blends are illustrated in Figure 4. It is evident that melting curves of blends without a nucleating agent have only one melting peak, which should be ascribed to the melting of the α-crystallites. Only the neat material L-PP shows a small peak corresponding to the β-crystallites (melting temperature T_m at 149 °C). With an increasing amount of LCB-PP in the blends, the melting temperature first slightly increases up to BL 10, while further addition reduces it. A similar trend for the melting point of L-PP/LCB-PP blends has been reported by Tabatabaei *et al.* [37]. However, McCallum *et al.* [4] reported drops of T_m of all blends compared with L-PP.

In the case of β-nucleated samples, the effect of blend composition is expressed in the different shape of the melting curves. Melting curve of the β-nucleated
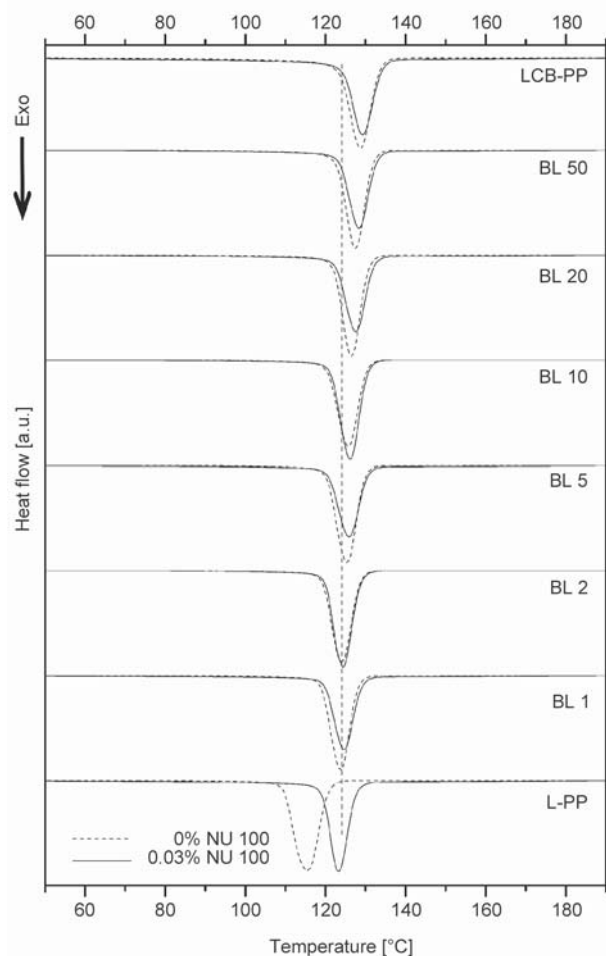

Figure 4. Melting thermograms of the blends.

Figure 5. Cooling thermograms of the blends.

L-PP shows a predominant β-melting peak at 152 °C and less visible double α-melting peak at 170 and 166 °C, respectively, which were formed during re-crystallization process [20, 28]. However, even a small addition of LCB-PP to the L-PP/LCB-PP blend leads to a significant drop of the β-melting peak. This β-melting peak disappears with the addition of only 10 wt% of LCB-PP. A slight decrease of T_m of α-phase with increasing LCB-PP content in L-PP/LCB-PP blends can be observed, similarly as in the case of blends without a β-nucleating agent. Slightly higher melting temperatures of nucleated blends in comparison with blends without nucleating agents can be ascribed to the recrystallization process, which is more pronounced in the case of nucleated materials. These results correlate well with the WAXS data.

Figure 5 shows the cooling DSC curves of L-PP and LCB-PP blends with/without a nucleating agent. The crystallization temperature (T_c) of neat L-PP (116 °C) is much lower than that of neat LCB-PP (130 °C). It is evident that with a rising amount of LCB-PP in L-PP/LCB-PP blends, the crystallization temperature increases. The addition of only 1 wt% of LCB-PP to the L-PP leads to an increase of T_c to 125 °C. These results suggest that the crystallization ability of the blends is controlled by LCB-PP content. An obvious increase of the crystallization temperature of L-PP can be seen after the addition of a nucleating agent (T_c come up to 125 °C). Much less noticeable change of crystallization temperature with the addition of a nucleating agent can be observed in the case of LCB-PP and L-PP/LCB-PP blends, respectively. The increase is approximately 1 °C. A similar phenomenon was observed by Yu *et al*. [41] with the β-nucleating agent (trade name V8) in L-PP/LCB-PP blends.

Higher crystallization temperature of LCB-PP can be assigned to long branches, which can have a self-seeding effect and thus speed the overall crystalliza-tion [46, 47]. The high rate of nucleation in LCB-PP could also be ascribed to gel formation, which arises from the radical-driven synthesis process using per-oxides. During these reactions, besides long branch-es, also chain scission and crosslinking can occur. Even local crosslinking (gel) could lower melt en-tropy and serve as nuclei during crystallization. On the other hand, branching points, defects in the poly-meric chain, decrease the ability to crystallize, and growth rate is slowed, and a formation of γ-phase is pronounced.

3.3. The morphology of the blends

To show and describe the higher structural level of the morphology, namely the detailed lamellar struc-ture and spherulite shape, scanning electron mi-croscopy was employed. The fracture surfaces pre-sented in Figure 6 show a distinct difference between α-, β-, and γ-lamellar structure. The smooth crack surface of material containing predominantly α-phase reflects fine lamellar structure – sample L-PP (Fig-ure 6a₁). However, in this micrograph, the β-phase can also be detected, spatially separated from α-phase at the spherulitic level. On the other hand, the distinctly rough surface structure of the L-PP rich in β-phase is a manifestation of thick lamellae – sample L-PP nucleated (Figure 6a₂). In the case of LCB-PP and the blends with a higher content of LCB-PP (Figure 6c, 6d), typical spherulites cannot be distin-guished. The crystallites of α- and γ-phases coexist microscopically and cannot be differentiated one from the other in contrast with coexistence α- and β-phases in L-PP. According to Zeng *et al*. [36], the LCB-PP can form branched edge-on lamellae during fast cooling and flat-on lamellar structure upon slow crystallization. According to Ni *et al*. [48], the LCB structure acts as a heterogeneous nucleating agent and influences the growth pattern of the crystal. As a result, the morphology of LCB-PP may have been a mixture that contains rodlike, disklike, and spherulite crystallites.

4. Conclusions

The experimental study shows a combined effect of specific nucleation and long-chain branching on re-sulting polymorphic composition, melting and crys-tallization behavior, and morphology of polypropy-lene blends. It is demonstrated that the efficiency of the nucleating agent NU 100 in β-phase formation decreases sharply with the addition of LCB-PP into blends, the addition of only 5 wt% of LCB-PP into L-PP leads to a substantial reduction in the trigonal β-phase content. At the same time, a significant in-crease in the γ-phase content can be seen. A positive effect of long-chain branching on γ-phase formation in prepared blends is observed, independently of presence NU 100. Melting experiments show higher thermodynamic stability of the blends containing a predominant amount of α- and γ-phases, as com-pared to the samples rich in β-phase. Strong nucle-ation efficiency of LCB-PP is manifested by the shift in the crystallization temperature of the blends. The
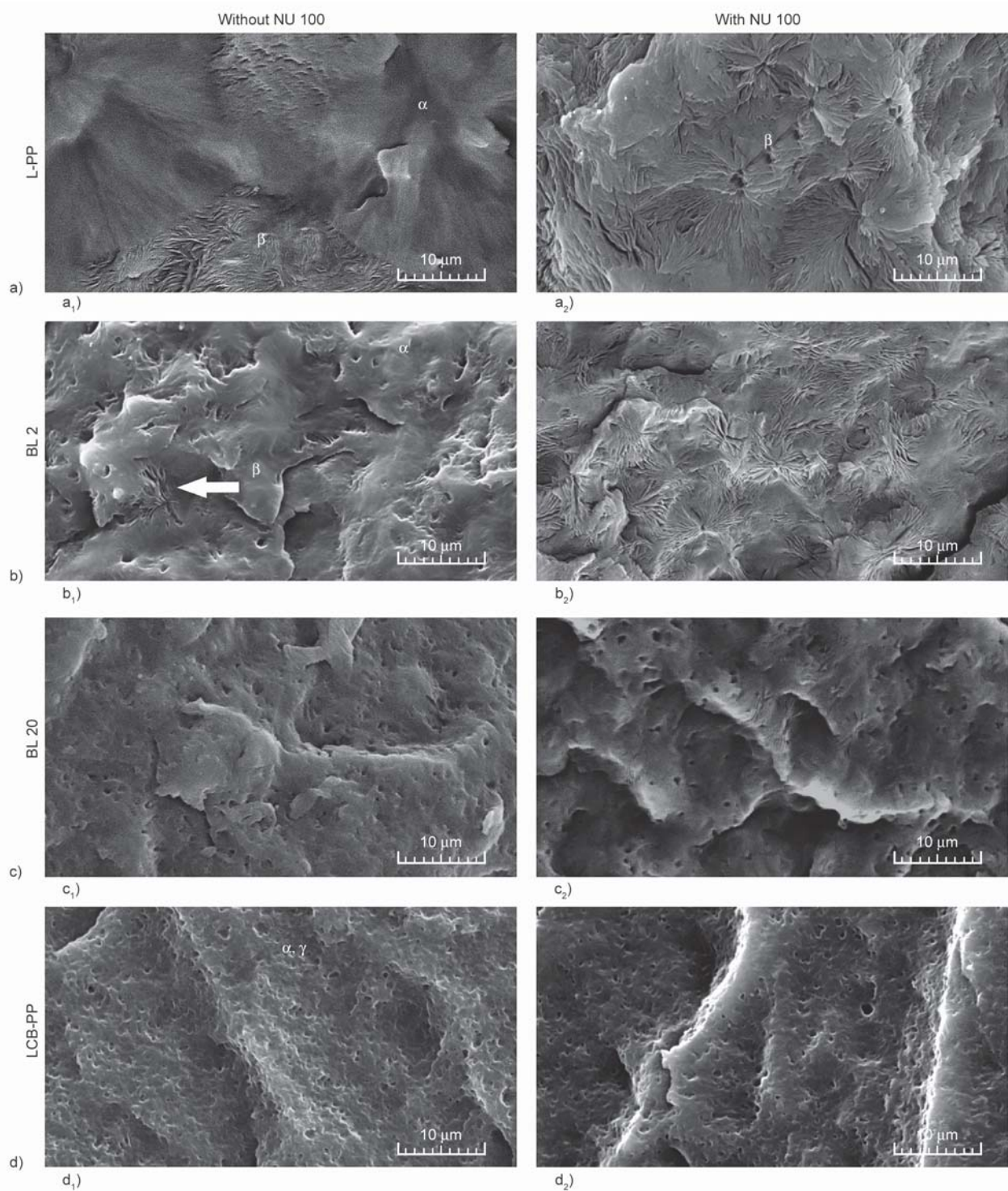
Figure 6. SEM images of L-PP (a), BL 2 (b), BL 20 (c) and LCB-PP (d) with (a_2–d_2) and without (a_1–d_1) NU 100.

nucleation efficiency of LCB-PP is ascribed to the self-seeding effect of local crosslinking. On the microscopic level, β-phase is distinctly separated in spherulites, while α- and γ- phases coexist on the lamellae level.

The next part of our study will update the knowledge by offering an assessment of the interrelations between the long-chain branching, specific nucleation, and end-use properties of polypropylene blends.

Acknowledgements

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