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Doctoral Thesis Summary

Polymeric blends based on linear and branched polypropylene: crystallization, polymorphism and properties

Polymerní směsi na bázi lineárního a větveného polypropylenu: krystalizace, polymorfismus a vlastnosti

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ABSTRACT

The objective of the presented doctoral thesis aims to investigate the morphology of linear and long-chain branched polypropylene, with a particular focus on identifying optimal conditions for controlling the phase structure. This includes exploring the influence of process parameters and chemical composition on the phase formation and structure. Special attention is dedicated to the effect of incorporating long branches of long-chain branched polypropylene into the linear polypropylene.

Key findings of the study reveal that long-chain branched polypropylene can enhance the crystallization process, outperforming traditional nucleating agents. Long-chain branched polypropylene not only reduces haze and speeds up crystallization but also promotes the formation of finer crystalline structures in polypropylene blends, even at low concentrations. The research further identifies long-chain branched polypropylene as a potential alternative to conventional nucleating agents, especially in high-temperature processing applications.

Additionally, the thesis explores annealing as a method for improving the crystalline phases and mechanical properties of polypropylene. It also highlights the transformation of the β-phase into the α-phase as an effective method of improving material performance.

ABSTRAKT

Předkládaná disertační práce se zabývá morfologií lineárního a polypropylenu s dlouhými větvemi se zvláštním zaměřením na identifikaci optimálních podmínek pro řízení fázové struktury. Je zkoumán vliv procesních parametrů a chemického složení na tvorbu a strukturu vznikajících fází. Zvláštní pozornost je věnována vlivu inkorporace dlouhých větví na vlastnosti lineárního polypropylenu.

Klíčová zjištění ukazují, že dlouhé větve polypropylenu zlepšují proces krystalizace a předčí svou efektivitou tradiční nukleační činidla. Polypropylen s dlouhými větvemi nejenže snižuje zákal a urychluje krystalizaci, ale také podporuje tvorbu jemnějších krystalických struktur ve směsích s lineárním polypropylenem, a to i při nízkých koncentracích. Výzkum dále identifikuje polypropylen s dlouhými větvemi jako potenciální alternativu ke konvenčním nukleačním činidlům, zejména při použití vysokých krystalizačních teplot.

Mimo jiné je práce zaměřena i na temperaci jako metodu pro zlepšení krystalických fází a mechanických vlastností polypropylenu. Důsledkem žíhání je rekrystalizace β-fáze na α-fázi, která se jeví jako účinná metoda zlepšení vlastností materiálu.

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INTRODUCTION

Polymer materials undergo various stages throughout their life that can be divided into four main phases: production, processing, application, and disposal or recycling. During the production stage, the chemical structure of the polymer is determined. In the processing stage, the polymer acquires shape and develops a supermolecular structure (morphology) that significantly impacts its properties. Throughout the service life stage, the material undergoes ageing and experiences changes in its properties. Finally, when these changes exceed acceptable limits, or the article becomes unusable, the material is either disposed of or recycled. These stages exhibit feedback behaviour and mutually influence each other.

Polymer´s chemical nature primarily determines the macroscopic behaviour of polymers throughout their lifecycle. However, various innovative approaches can significantly influence plastics' processability, applicability, and durability. In the case of semicrystalline polymers, one such approach involves modifying their supermolecular structure, i.e. by adding specific nucleating agents (NA). Heterogeneous nuclei influence crystallization kinetics, spherulite size, and, consequently, the properties of the materials. Furthermore, the nucleating agent can promote crystallization in polymorphic polymers into the desired crystalline form. Isotactic polypropylene (iPP) serves as a clear example. Typically, iPP crystallizes into the monoclinic α-phase (α-PP) [1]. However, with specific β-nucleating agents (β-NAs), the β-phase can become predominant (constituting over 90 % of the crystalline portion). This material, known as β-nucleated iPP, exhibits distinct mechanical properties compared to conventional α-PP, including increased toughness and durability but decreased stiffness and strength [2,3]. Consequently, isotactic polypropylene containing the predominant β-phase (β-PP) is now considered a common polymeric material and is regarded as a suitable alternative to conventional polypropylene for specific applications. More recently, emphasis has been placed on research of long-chain branched polypropylene (LCB-PP) and the effect of incorporated long branches on the crystallization and final properties of linear polypropylene (L-PP) [4–10]. The temperature, applied shear rate (or strain rate), and total strain during flow has also non-negligible effect and strongly influence crystallization and resulting morphology [11–14]. Understanding how polymer morphology develops during processing is crucial for linking processing conditions to the final product properties and understanding the interrelationships between crystallization conditions, morphology and properties is essential for assessing the applicability of polymer materials.

1. AIMS OF THE WORK

This thesis aims to study the morphology of polymorphic polypropylene with an emphasis on finding suitable conditions that allow effective control of the phase structure of such materials, both in terms of process parameters, molecular structure and chemical composition. The interrelations are studied by the differential scanning calorimetry, wide-angle X-ray scattering, optical and electron microscopy, spectrophotometry or infrared spectroscopy. The relationship between the polymorphic structure and the final properties is investigated through a set of mechanical tests.

This thesis is mainly focused on the following points:

- The effect of crystallization temperatures on the polymorphic composition of L-PP and LCB-PP;
- The effect of long branches incorporated to the L-PP and its effect on the crystallization process;
- Comparison of commercially available NA with long-chain branched polypropylene acting as a NA to the PP;
- The effect of annealing on material performance.

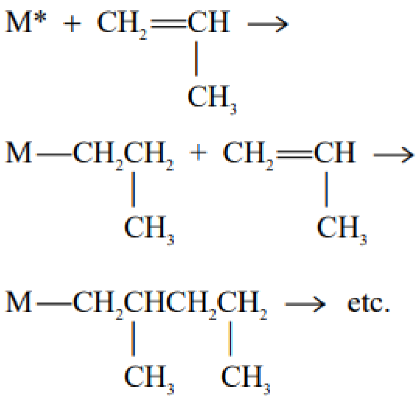
2. THEORETICAL BACKGROUND

2.1 Polypropylene

Polypropylene (PP) ranks among the most commercially used polymer materials due to its low prices and good technological processability. PP is a polymer belonging to the group of olefinic thermoplastics. It is a highly adjustable material known for its outstanding mechanical properties, good chemical resistance, and thermal stability, making it suitable for many applications. PP is widely used in automotive, packaging, electrical engineering and healthcare. PP was first synthesized in 1951 by chemists J.P. Hogan and R. Banks. Three years later, in 1954, G. Natta synthesized the isotactic and syndiotactic forms of polypropylene for the first time. PP can be easily processed using various methods, including injection moulding, extrusion, and blow moulding, allowing for a high degree of design flexibility and efficient production. [9]

2.1.1 Chemical structure

Polypropylene belongs to linear polymers; the chain contains 10,000 to 20,000 monomer units. The monomer propylene is produced during the heat treatment of crude oil. PP is obtained by catalytic polymerization of the monomer and using the Ziegler-Natta catalysts, providing a site for the reaction. Molecules of monomer are sequentially added to the chain due to the reaction between a metallic functional group (M*) on the growing main polymer chain and the unsaturated monomer´s bond (Fig. 1).



$$M^* + CH_2{=}\underset{CH_3}{CH} \longrightarrow$$

$$M{-}CH_2\underset{CH_3}{CH_2} + CH_2{=}\underset{CH_3}{CH} \longrightarrow$$

$$M{-}CH_2\underset{CH_3}{CH}CH_2\underset{CH_3}{CH_2} \longrightarrow \text{etc.}$$

Fig. 1 A reaction of the functional group and growing polymer chain [15]

The propylene molecule's double-bonded carbon atom integrates into the bond connecting the metallic group and the last carbon atom in the emerging polypropylene chain. This forms a long linear polymer chain composed of carbon atoms, where methyl (-CH_3) groups are attached to alternating carbon atoms throughout the chain. This sequential addition of propylene molecules continues until the reaction is terminated [16]. Methyl groups (-CH_3) extend from the main chain, determining the so-called tacticity of polypropylene determined by the type of catalyst and its chemical and crystal structure, solvent, and polymerization conditions. Polypropylene (PP) exists in three stereoisomers: isotactic PP (iPP), syndiotactic PP (sPP), and atactic PP (aPP) [17].

2.1.2 Morphology

PP is a semicrystalline polymer, and the degree of crystallinity ranges from 60 to 75 %. When cooled to crystallization temperatures, molecules form various supermolecular structures. The polymer chain forms a helical structure organization due to the pendant methyl groups as it tries to order atoms closely without distortion of the bonds along the chain. The helical chains start to fold and creates so-called lamellae. Thickness of created lamellar structure depends on the processing methods and crystallization temperature. Lamellae, growing in the radial directions, form spherullites. Lamellae are connected by amorphous regions resulting from the chain irregularities. These amorphous "ties" ensure flexibility to the crystalline regions. Spherulites, observable in optical microscope (Fig. 2), range in size from 1 to 50 µm [15].

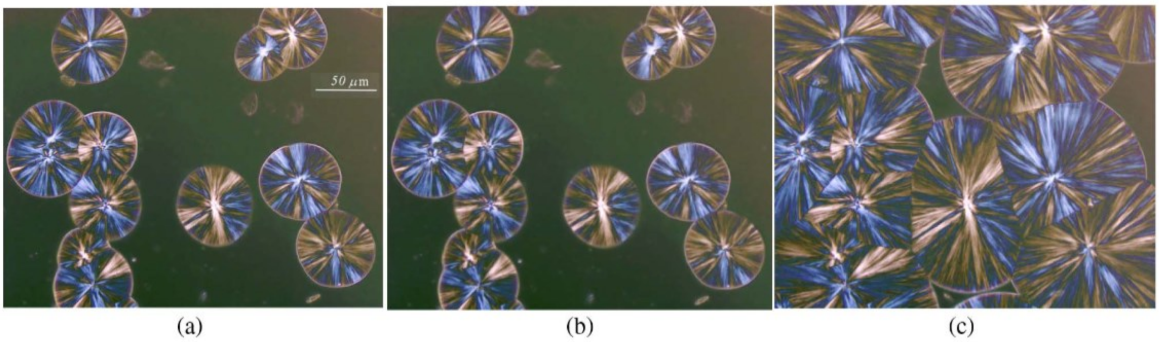


Fig. 2 Optical microscopy of polypropylene spherulites, isothermal crystallization at T_c=120 °C, a) 23 s b) 54 s c) 105 s [18]

PP exists in three crystalline structures, α structure, β structure and γ structure. These structures depend on crystallization conditions (crystallization temperature [12,13,19,20], crystallization pressure [5,21] and cooling rate [14,22]). Recrystallization can occur with changing conditions.

α-phase

The prevailing monoclinic α structure of PP (α-PP), with a crystallographic density of around 0.94 g/cm^3, is formed under normal processing conditions. Turner Jones et al. [1] determined the parameters of a unit cell containing four three-fold helical chains. The calculated values were as follows: $a = 0.666$ nm, $b = 2.078$ nm, $c = 0.6495$ nm, $\beta = 99.62°$, and $\alpha = \gamma = 90°$. The α-phase can recrystallize from a less ordered α_1-phase with a random distribution of 'up' and 'down' chain packing of methyl pendant groups to a more ordered α_2-phase with a well-defined deposition of 'up' and 'down' helices in the crystal unit cell [23].

The lamellar structure of PP exhibits different types of birefringence; positive, negative, and mixed. Negative birefringence occurs in spherulites with dominant radial lamellae, while positive birefringence is observed in spherulites with predominantly tangential lamellae. When viewed under crossed polarisers, both negatively and positively birefringent spherulites display a Maltese cross pattern (visible in Fig. 3). In spherulites with mixed birefringence, neither tangential nor radial lamellae are predominantly present, resulting in the absence of a distinct Maltese cross pattern. The birefringence changes from positive to negative as the crystallization temperature increases, which is attributed to the pre-melting of the tangential lamellae.

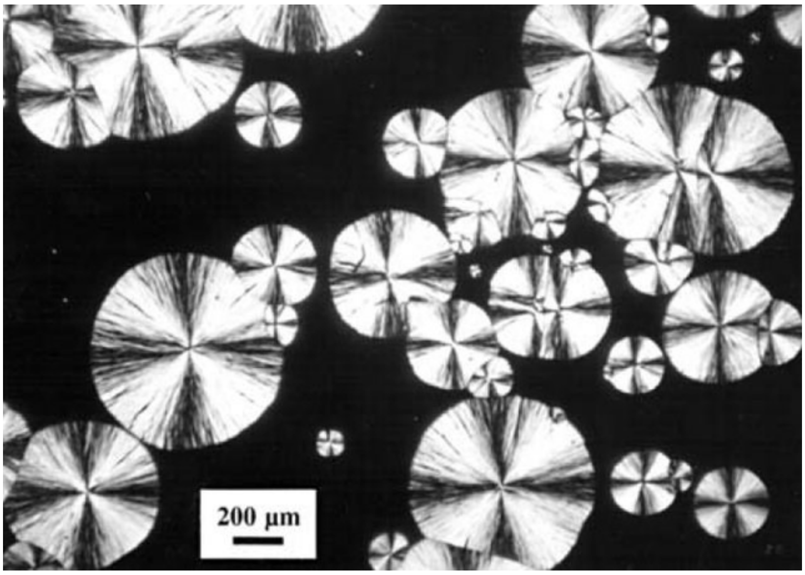


Fig. 3 Spherulites of iPP growing from the melt, visible Maltese crosses [24]

The equilibrium melting temperature T_m of the α-phase was reported between 185 °C and 209 °C [25]. Krigbaum [26], and Miller [27], determined to be T_m 186 ± 2 °C, whereas Fatou [28] and Monnasse [29] extrapolated T_m to 208 °C.

β-phase

Identifying the β-phase of isotactic polypropylene (β-PP) dates back to 1959, when Keith et al. [30] first discovered it as a hexagonal unit cell. Numerous researchers have attempted to determine the β-phase unit cell parameters. Turner Jones proposed the unit cell parameters: a = b = 1.103 nm and c = 0.649 nm, α = β = 90°, γ = 120° [1]. On the other hand, Varga et al. have described the β-phase as having a trigonal unit cell with parameters a = b = 1.101 nm and c = 0.65 nm, consisting of three isochiral helices [2]. The crystallographic density of the β-phase has been calculated to be 0.92 g/cm^3 [25].

In the conventional crystallization process of PP grades, a small amount of β-phase appears at high supercooling conditions (crystallization temperature less than 130 °C) or in rapidly cooled samples. However, a significant amount of β-phase can be produced under specific crystallization conditions, such as the temperature gradient method or the presence of selective β-nucleating agents. β-nucleating agents, like quinacridone pigment [31], calcium or zinc salts of aliphatic and aromatic dicarboxylic acids [32–34] or N,N′-dicyclohexylnaphthalenedicarboxamide (commercialy known as NJ Star NU 100) [20] , are widely recognized for their ability to generate even pure β-phase under appropriate thermal crystallization conditions [15,23]. Like the α-phase, the β-phase can transform within its crystalline structure, known as β to β recrystallization. Although the β-phase is less thermally stable than the α-phase (with a melting point T_m of ~155 °C compared to ~170 °C), its growth rate is up to 70 % faster than α-PP within most of the typical crystallization temperature range. However, due to its higher melting temperature, α-PP exhibits faster growth than β-PP at higher temperatures, above a critical temperature T(βα) ~ 140 °C. Conversely, at lower temperatures (below a second critical temperature of T(αβ) ~ 100 °C), the growth rate of α-PP surpasses that of β-PP [35].

A noteworthy characteristic of β-phase growth is the transition from β- to α-phase [35,36]. This recrystallization process can be induced by temperature changes in crystallization's upper and lower temperature (T_c), where α-growth is accelerated. The occurrence of β to α recrystallization, both above and below T_c, indicates the existence of theoretical upper and lower temperature limits for forming pure β-PP. Furthermore, this recrystallization can also occur during heating, as melted β-phase crystallizes into the α-phase. With further heating, the α-phase melts, resulting in a melting profile with mixed polymorphic content. Additionally, phase transitions can occur during the deformation of β-PP [11,37–39].

The characterization of the β-content in PP samples, the effectiveness of β-nucleating agents and the influence of thermal and mechanical conditions on the polymorphic composition, can be evaluated by different methods. These include determining the *k*-value through wide-angle X-ray scattering (WAXS), differential scanning calorimetry (DSC) on non-re-cooled samples, or polarized optical microscopy (POM) with thin sections of the samples [3]. The *k*-value (k_β), introduced by Turner Jones et al. [1], serves as a semiquantitative measure of the β-content and can be calculated from X-ray diffractograms as follows (Eq. 1):

$$k_\beta = \frac{H_{\beta(300)}}{H_{\alpha1(110)}+H_{\alpha2(040)}+H_{\alpha3(130)}+H_{\beta(300)}} \qquad (1)$$

where $H_{\alpha1(110)}$, $H_{\alpha2(040)}$, $H_{\alpha3(130)}$ are intensities of α-phase peaks at angles 2θ = 14.2°; 17° and 18.8° and $H_{\beta(300)}$ is intensity of β-phase peak (2θ = 16.2°).

γ-phase

The most distinctive polymorph of isotactic polypropylene was identified in 1961 by Addink and Beitema [40], who associated it with the presence of short chains. Subsequent research revealed that even small amounts (4–10 %) of comonomers such as ethylene, 1-butene, and 1-hexene could induce the crystallization of the γ-polymorph (γ-PP). However, the primary pathway for γ-PP crystallization is under high pressure, the γ-phase coexist with the α-phase until it dominates at a pressure of about 200 MPa [15], even high molecular weight and highly stereoregular PP can crystallize in a nearly pure γ-phase. Additionally, the amount of the γ-phase is higher at low supercoolings [41].

Initially was γ-phase indexed as triclinic, but after study by Brückner and Meille [42] led to a reassignment of the structure as an orthorhombic unit cell with parameters a = 0.85 nm, b = 0.993 nm and c = 4.241 nm featuring nonparallel polymer chains coexisting within the same crystal lattice. The crystallographic density of equals to α-phase and has an epitaxial relationship with the α phase; both can grow onto lamellae of the other phase. In general, the α phase is observed to grow first, followed by epitaxial growth of the γ-phase. The packing energy calculations showed that it is at least as stable as α-phase [25]. When crystallized under high pressures (200 MPa), the γ-phase displays three categories of spherulites determined by the type of exhibited birefringence. Spherulites with positive birefringence appear when the crystallization temperatures are below 184 °C and above 199 °C, negative birefringence emerges during crystallization between 187–198 °C, while spherulites with mixed birefringence occur within the temperature ranges 182–188 °C and 196–200 °C. The findings suggest a previously unreported lamellar feather-like arrangement. This feather-like structure is formed exclusively through the self-epitaxial growth of the γ-phase lamellae. The melting experiments involving 'mixed birefringent' spherulites show that the feather-like structures formed through epitaxial growth possess higher melting points than the radial lamellae that grow simultaneously within the same spherulite. This observation leads to the conclusion that it is possible to obtain significant quantities of two distinct lamellar types concurrently, and these cannot be differentiated using traditional wide and small-angle X-ray analyses [43].

The melting point of the γ-phase is reported in the range ~ 125–150 °C for samples with low molecular weight. In the case of samples crystallized by high pressure of high molecular weight PP, the melting occurs above 150 °C [15,44].

Due to the close alignment of characteristic peaks in both the α- and γ-phases, determining the phase structure is challenging. The difference between diffraction patterns of α- and γ-crystals lies within the 2θ range of 2θ = 18 to 21°, two distinct diffraction peaks can be identified: one originating from the (130) plane of the α-phase at 2θ = 18.8°, and the other from the (117) plane of the γ-phase at 2θ = 20.1°. By comparing the intensities of these peaks, it is possible to estimate the proportion of α- and γ-phases present within the sample. Turner Jones [45] proposed an equation to calculate the fraction of γ-phase within the crystalline component of a specimen containing both α- and γ-crystals, as follows (Eq. 2):

$$k_\gamma = \frac{H_{\gamma(117)}}{H_{\gamma(117)} + H_{\alpha 3(130)}} \qquad (2)$$

where k_γ is value of γ-phase, $H_{\alpha 3(130)}$ is intensity of α-phase peak at angle 2θ = 18.8° and $H_{\gamma(117)}$ is intensity of γ-phase peak (2θ = 20.1°).

Smectic phase

The smectic phase, the so-called mesomorphic phase, is an intermediate between crystalline and fully amorphous phases of PP. When polypropylene is rapidly cooled from its melt to 0 °C, a disordered lattice structure is formed (i.e. changes in the folding of the polymer chain, impurities in the chain lattice, dislocations disrupting the spherulitic structure, causing the spherulitic growth in the irregular location), resulting in the formation of the smectic phase. The disordered phase can be stable up to 155 °C and can also be formed when iPP is deformed in the solid state by uniaxial stretching [46,47]. The lack of lamellar arrangement, in addition to a low density and small size of ordered structures, results in a high transparency of the material [15].

2.1.3 Properties of iPP

Polypropylene is a highly utilized thermoplastic and is prominent in the industry. The popularity of polypropylene results from its versatility. It possesses a favourable combination of properties, maintains a relatively low cost, and can be processed using various techniques. With the possibility to control used catalysts, monomers or affect processing conditions, it is possible to produce a wide variety of tailored polypropylenes. The properties of polypropylene, as a viscoelastic material, depend on the crystallinity, supermolecular structure, orientation and furthermore, time, temperature and stress. Homopolymer grades of iPP are available with a degree of crystallinity ranging from 60 % to 75 %. The average molecular weights of iPP typically fall within the range of M_n = 38,000 to 60,000 g/mol and M_w = 220,000 to 700,000 g/mol, with a polydispersity index (M_w/M_n) ranging from about 5.6 to 11.9. Pure iPP has a melting point of around 170 °C, while its glass transition point occurs near -10 °C, where the polymer becomes brittle [23].

The mechanical properties of iPP strongly depend on its crystallinity and tacticity. Higher levels of tacticity in material increase crystallinity, leading to elevated softening points, stiffness, yield stress, and flexural strength. Increasing crystallinity lowers toughness and impact strength [15]. In some properties, iPP is similar to polyethylene; mainly swelling, solution behaviour, and electrical properties. Nevertheless, a methyl group attached to alternate carbon atoms on the polymer chain backbone can cause distinct changes in the material's properties. For instance, a tertiary carbon atom makes the polymer less stable to oxidation compared to polyethylene [23].

As previously mentioned, iPP exhibits polymorphism, meaning that physical properties vary depending on the crystalline form. From a commercial point of view, polypropylene with a predominant β-phase has been considered a suitable alternative to conventional polypropylene. β-PP possesses different properties than α-PP (Tab. 1), making it more favourable for specific applications, i.e. pipeline.

Tab. 1 Comparison of α-PP and β-PP mechanical properties [3]

	α-PP	β-PP
Elastic modulus [GPa]	2.0	1.8
Yield stress [MPa]	36.5	29.5
Elongation at yield [%]	~ 12	~ 7
Tensile strength [MPa]	39.5	44
Elongation at break [%]	~ 420	~ 480
Impact strength [kJ/m^2]	6.2	9.3

Recently, researchers are focused on the mechanical properties of γ-PP, but mostly in micromechanical testing. Concerning semicrystalline polymers like iPP, microindentation offers two benefits. Firstly, micromechanical properties like indentation hardness, microhardness, and indentation modulus demonstrate a high sensitivity to variations in the structure of semicrystalline polymers. These properties also strongly correlate with macroscopic mechanical properties such as elastic moduli and yield stress [48,49]. Secondly, microindentation hardness testing can be applied to quite small samples, selected regions within specific samples and/or samples available in relatively small amounts [50]. This is frequently the case of iPP specimens with high content of γ-phase, that must be crystallized under very high pressures, as mentioned before. Slouf et al. studied relationship between morphology and micromechanical properties of α-, β- and γ-phases of iPP. It was demonstrated that γ-PP does not necessarily exhibit better mechanical performance than α- and β-PP, as suggested by some previous studies [51], because the final properties are strongly influenced not only by the phase composition, but also by the overall crystallinity and average lamellae thickness.

2.2 Long-chain branched polypropylene

As mentioned before, commercial iPP is commonly prepared using iso-specific Ziegler-Natta or metallocene catalysts. This type of preparation produces highly linear chains and narrow molecular weight distribution, resulting in low melt strength and no strain hardening, which limits its processing by thermoforming, coating, foaming or film-blowing [9,52]. An effective method for improving these limiting properties is the introduction of long chains on the polypropylene backbone [5,53].

There are two primary approaches for producing long-chain branched polypropylene. The first method, the post-reactor method, involves breaking the PP´s main chain and then grafting long branches onto the main chain through chemical grafting reactions in the molten state. This can be achieved, for instance, by utilizing peroxides [53–55] or subjecting the polymer to high-energy irradiation in its solid state [6,56]. The second, rarely used method, involves achieving long-chain branching in situ during the polypropylene polymerization by introducing a suitable comonomer [10,57].

2.2.1 Morphology

The introduction of long-chain branching in PP significantly impacts the crystallization process and resulting morphology. LCB-PP contains structural defects that affect both nucleation and crystallite growth. When LCB-PP is produced through a radical-driven synthesis process using peroxides in the molten state, the formation of long branches is associated with chain scission and gel formation, which can significantly influence the nucleation rate. The self-seeding effect of LCB-PP has been observed, indicating its impact on crystallization [8,58,59]. On the other hand, the presence of branching points as defects reduces the rate of crystallite growth. However, overall crystallization is faster in the case of LCB-PP [4,8]. According to Tian [4], the activation energy of LCB-PP is higher than that of linear PP. Regarding polymorphic composition, long branches with increased irregularities on the polymer backbone enhance PP's ability to crystallize into the orthorhombic γ-phase alongside the α-phase, even at higher pressures [5]. Additionally, the crystallization temperature has a notable effect on the regularity of helical conformation, thus strongly influencing the resulting crystalline phase structure of LCB-PP [9].

2.2.2 Properties of LCB-PP

The presence of branching in polyolefins generally impacts their physical properties. Increasing the content of branched polypropylene (PP) can influence blends' strain-hardening behaviour [60]. A particular focus is the effect of adding small amounts of branched PP on foamability. Research conducted by various groups suggests that higher levels of branched PP in linear PP (L-PP) result in increased cell density, thereby improving the foaming characteristics of conventional PP [61,62]. However, excessive branches can lead to suboptimal foamability [62]. Additionally, introducing branches into the PP melt may reduce mechanical properties, such as strain at break [63]. Therefore, achieving favourable foaming conditions while maintaining satisfactory mechanical properties requires an optimal content of branches in L-PP.

The study of Auhl et al.[6] focused on the rheological behaviour of a series of LCB-PP achieved through the electron beam irradiation of a linear precursor by different irradiation doses. They noted that the degree of strain hardening decreased as the strain rate increased in the case of polypropylenes irradiated with lower doses. On the contrary, polypropylenes subjected to higher irradiation doses transitioned towards an increased strain hardening with increasing strain rates. The observed difference in strain hardening behaviour was attributed to modifications in the branching structure induced by the irradiation. For polypropylene samples treated with lower irradiation doses, a branching structure akin to the star-like structure was developed. In contrast, an arrangement resembling a tree-like branching structure was anticipated for the extensively branched polypropylene resulting from higher irradiation doses.

For the LCB-PP/L-PP blends investigated in the study of Stange et al. [7], it is assumed that even a small number of long branches with a tree-like topography significantly influences long relaxation times and the strain hardening behavior at low strain rates. Consequently, for polypropylene, even minimal amounts of long branches – whether star-shaped, H-shaped, or tree-like – exhibit a similar strain rate dependence of strain hardening. In this case, strain hardening diminishes as the strain rate increases. Furthermore, the production of LCB-PP can increase melt strength and enable blending with L-PP. Similar findings were observed by Fang et al. [64], who noted that adding LCB-PP to L-PP improved melt strength, resulting in a strain-hardening behaviour even at the 10% content of LCB-PP. Moreover, McCallum et al. [65] found that L-PP/LCB-PP blends exhibited increased melt strength and improved mechanical properties than L-PP.

According to the theory the entanglement of long branching increases molecular interaction and decreases molecular slippage [66,67]. As the result of the experiments of Zhao et al. [68], the long branches of LCB-PP entangled as soon as formed, and the molecular weight of LCB-PP was higher than that of iPP. As for the tensile test, the main reason for the fracture of iPP was the fracture of chemical bonds and failure of Van der Waals forces (the breakage of molecules and slippage between molecules). However, for LCB-PP, the chemical bonds, Van der Waals forces, and the entanglements of long branches resisted more applied stress. Moreover, spherulitic size is another essential factor affecting a material's impact strength. The higher nucleation rate and lower crystal growth rate of LCB-PP led to the formation of a larger number of small spherulites compared to iPP. iPP exhibited larger spherulites with a less dense distribution than LCB-PP. This larger but looser structure resulted in more stress-concentrating points, reducing impact strength. As a result, LCB-PP demonstrated overall higher tensile and impact strength than iPP.

2.3 Influencing morphology by crystallization conditions

The process of polymer crystallization involves the arrangement of polymer chains into a crystalline form, resulting in increased strength, stiffness and thermal stability of the material. Many factors, including temperature, pressure, cooling rate and the presence of other substances in the material, can influence crystallization. For crystallization to occur, the so-called Gibbs free energy (ΔG) must decrease; thus, the change in enthalpy (ΔH) be negative; the heat release during the crystal lattice formation is an exothermic process [69]. Crystallization is associated with an increase in the orderliness of the molecules, and from this, the change in entropy (ΔS) must be negative (Eq. 3) [69] :

$$\Delta GV = \Delta H - T\Delta S < 0 \qquad (3)$$

In the case of a material that contains an amorphous and a crystalline component, it is necessary to use a different equation (Eq. 4), where the free energy of the crystalline phase must be less than the free energy of the amorphous phase [69].

$$\Delta GV = GK - GA < 0 \qquad (4)$$

For the crystallization process to occur, a sufficiently significant decrease in enthalpy (ΔH) must be ensured that exceeds the thermodynamic change in a structure characterized by the product of the change in temperature and entropy $T\Delta S$ [69].

2.3.1 Nucleating agents

Nucleating agents (NAs) are unique materials known for enhancing nucleation and playing a crucial role in various industrial applications. They are widely utilized in the polymer industry to improve the performance of polymer materials. Two explanations have been proposed to elucidate how NAs affect heterogeneous nucleation. The first, widely accepted explanation suggests that the nucleation process is controlled by the "epitaxy" between the nucleating agents and the crystals [70]. The role of epitaxy in nucleation was only acknowledged relatively recently, despite the long-standing industrial development of these additives. Epitaxy refers to an interaction between the nucleating agent and a foreign substrate, which promotes crystallization, particularly during the initial nucleation step. A deeper understanding of this process becomes crucial in developing new and improved nucleating agents. By harnessing the principles of epitaxy, researchers can explore innovative approaches to enhance nucleation and optimize the performance of materials. According to this view, the nucleating agents serve as templates for crystal growth. The second explanation proposes that the addition of NAs hinders the mobility of molecular chains. In this scenario, the nucleating agents restrict the movement of polymer chains, facilitating the formation of nuclei [69,70].

Nucleating agents must meet several requirements, including compatibility with the (molten) polymer, dispersion of the NA, particle shape, thermal stability within the polymer's processing window, and more. In the case of clarifying agents, achieving a fine dispersion within the polymer is crucial. This is often achieved by creating a physical gel of the nucleating agent prior to the crystallization of the polymer, such as with sorbitol derivatives [71]. The specific details and quality of the interactions between the polymer and the nucleating agent may be of secondary importance for clarifying agents. In this case, the main focus is on achieving effective dispersion. Even a mild interaction that triggers nucleation of the polymer slightly above its conventional range for heterogeneous nucleation would qualify the nucleating agent as a clarifying agent. This is because nucleation would be initiated on the highly dispersed additive rather than the conventional impurities that typically trigger crystallization. Conversely, nucleating agents that trigger nucleation at higher temperatures become essential when the goal is to enhance the processing speed. These agents enable faster processing by initiating nucleation at higher temperatures, allowing for accelerated crystallization and overall production speed.

An additional challenge arises when searching for nucleating agents that are specific to one crystal phase. In the case of iPP, the α and β crystal structures are based on the same helix geometry, resulting in very similar interchain distances. Consequently, it becomes complicated, if not impossible, to predict which crystal structure will be nucleated by a particular nucleating agent. Two observations support this challenge. Firstly, a series of nucleating agents derived from a substituted trisamide have been synthesized and tested for iPP nucleation. Depending on the specific substituent, these agents induce the α- or the β-phase of iPP without any apparent logical pattern based on substituent size, packing differences, crystal structure, or symmetry [72]. Secondly, the nucleating agent γ-quinacridone, also known as "permanent red" with the code name E3B, has been patented for over 40 years and is widely regarded as a β-PP nucleating agent [73]. However, it has been inferred and recently demonstrated that E3B functions as an α-

PP nucleating agent above 140 °C while acting as a β-PP nucleating agent only below 140 °C [74]. These examples highlight the complexity of nucleating agents' behaviour and the need for detailed structural analysis to understand the specific interactions that determine their nucleation preferences for different crystal phases in iPP.

2.3.2 Processing conditions

Understanding and controlling structure development is crucial in polymer processing for achieving desired final product properties, mainly mechanical performance. Crystallization is a significant factor in this process, influenced by a range of factors such as mechanical conditions (flow, pressure), thermal conditions (cooling rates, temperature gradients), and geometric considerations (contact with processing tools).

Thermoplastics consist of flexible macromolecules that exhibit in melt a random-coil conformation. During flow, these macromolecules align along the flow direction, resulting in orientation. The stretching and orientation of macromolecules in the molten state have significant implications for the thermodynamics and kinetics of crystallization, thus, the resulting material morphology. The flow has several effects on the development of morphology, i.e., flow decreases the size of crystalline entities due to an increased number of nuclei. Flow arranges nuclei parallel to the flow direction. This arrangement also involves a change in the shape of nuclei, transitioning from point-like to thread-like shapes. Overall, the flow influences the changes in the size, shape, and arrangement of the crystalline structures within the material [75–77].

During the processing, the applied pressure can influence the formation of crystalline modifications. This problem was already widely studied. For example, higher pressure can affect crystallization of iPP and LCB-PP into γ-phase [78,79]. The injection moulding process is strongly influenced by pressure, which significantly impacts the crystallization process and affects shrinkage. The effects of pressure can be explored through pVT diagrams (pressure, specific volume, temperature). These diagrams provide insights into the specific volume of the material as a function of temperature and pressure. By pVT diagrams (Fig. 6), one can predict how pressure influences the material's behaviour during the injection moulding process and better understand its crystallization characteristics and possible shrinkage.

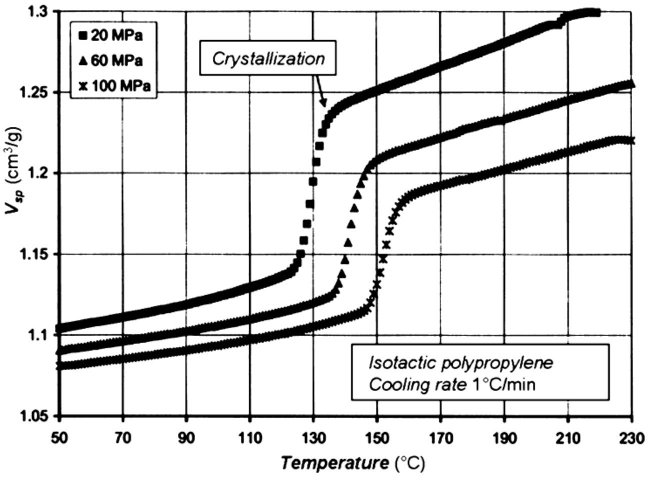


Fig. 4 pVT diagram of iPP, isobaric cooling [80]

When speaking about affecting the crystallization and thus final morphology, it is necessary to mention the effect of the cooling rate. The effect of the cooling rate is possible to study by the differential scanning calorimetry and flashDSC with very high cooling rates up to 2 400 000 °C/min. Generally, when increasing the cooling rate, the nucleation density increases and affects the spherulitic size, which is decreasing, potentially affecting the perfection of arrangements. Study of Rhoades et al.[14] proved, that the cooling rate controls the temperature of crystallization affecting the formation of specific polymorphs of iPP containing β-NA. This research even confirmed, that when the cooling rate exceed critical value, in further melting β to α recrystallization occurs. Study of Mollova et al. [22] suggest the critical cooling rate value for formation of β-phase is up to 50 °C/s. For cooling rates from 50 to 300 °C/s α-phase is predominantly formed. Higher cooling rates promote formation of smectic or vitrified material.

LIST OF PAPERS

I. Zenzingerova, S., Kudlacek, M., Navratilova, J., Gajzlerova, L., Jaska, D., Benicek, L., & Cermak, R. (2023). The competition between self-seeding and specific nucleation in crystallization of long-chain branched polypropylene. *Express Polymer Letters, 17*(11), 1110–1120. https://doi.org/10.3144/expresspolymlett.2023.84

II. Zenzingerova, S., Navratilova, J., Gajzlerova, L., Kudlacek, M., Jaska, D., Benicek, L. & Cermak, R. (2024). Polypropylene blends: Impact of long chain-branched polypropylene on crystallization of linear polypropylene. *Express Polymer Letters, 18*(9), 921–930. https://doi.org/10.3144/expresspolymlett.2024.69

III. Gajzlerova, L., Navratilova, J., Polaskova, M., Benicek, L., Jaska, D., Zenzingerova, S., & Cermak, R. (2024). Tailoring end-use properties of polypropylene through a combination of specific nucleation and long-chain branching. *Chinese Journal of POLYMER SCIENCE. Published on-line* https://doi.org/10.1007/s10118-024-3234-1

IV. Gajzlerova, L., Navratilova, J., Zenzingerova, S., Jaska, D., Benicek, L., Kudlacek, M., Cermak, R. & Obadal, M. (2022). On isotactic polypropylene annealing: Difference in final properties of neat and β-nucleated polypropylene. *Express Polymer Letters*, *16*(5), 453–464. https://doi.org/10.3144/expresspolymlett.2022.34

SUMMARIES OF PAPERS

In the following, short summaries and the major results of Papers I to IV are presented.

Paper I focuses on the investigation of competing behavior of long-chain branches, present in the LCB-PP, and the specific α-nucleating/clarifying agent Millad 3988 (α-NA). The aim of this study was to compare how long-chain branching and α-NA affect the crystallization kinetics, optical properties and supramolecular structure of polypropylene.

Addition of the α-NA significantly reduced the haze of L-PP. Interestingly, LCB-PP, due to its self-nucleation capability, displayed a lower value of the haze, even without the α-NA. When the α-NA was added to LCB-PP, the haze decreased slightly. This indicates that while the NA improves the optical clarity of L-PP, self-nucleation of LCB-PP is more effective in the haze reduction.

DSC revealed that LCB-PP exhibits faster crystallization than L-PP, even without the α-NA. The presence of long-chain branching induces self-nucleation, which accelerates crystallization. Addition of the α-NA, as expected, significantly enhanced the crystallization rate in L-PP. However, for LCB-PP, the α-NA had a minimal effect, particularly at higher crystallization temperatures (148–150 °C), where its efficacy diminished.

WAXS in connection with a temperature cell was used to investigate the morphological characteristics of isothermally crystallized samples. Two crystallization temperatures, 140 and 150 °C, were selected as representatives based on outcomes derived from thermal analysis. WAXS demonstrated that the crystallization of LCB-PP resulted predominantly in the formation of the α-phase, similar to the nucleated L-PP. It was also observed that at lower crystallization temperatures (140 °C), a small amount of the γ-phase was present in both LCB-PP and nucleated L-PP. However, at higher temperatures (150 °C), γ-phase fully disappeared.

The research concluded that while the α-NA effectively improves the crystallization kinetics and optical properties of L-PP, its impact on LCB-PP is limited due to the self-nucleation capability of the branches. The findings highlight the complexity of crystallization in LCB-PP and suggest that the material's self-nucleation properties dominate the effects of external nucleating agents, particularly at higher temperatures.

Paper II focuses on the comparison of the efficiency of commercially available sorbitol-based clarifying agent Millad 3988 (α-NA) and varying amounts of long chain-branched polypropylene, in concentrations of 1, 2, 5 and 10 wt.% in the blends with linear polypropylene. This paper builds on the findings of a previous study (Paper I); it was assumed, that LCB-PP can potentially act as a specific α-nucleating agent at high crystallization temperatures compared to the commonly used α-NA. The comparison of the effect of α-NA and long branches on the crystallization process, crystallinity and polymorphic composition was realized by DSC and WAXS.

The DSC analysis compared the nucleation efficiencies and their impact on the crystallization process under isothermal conditions (ranging from 130 to 150 °C as in previous study). Although the α-NA accelerates crystallization of more than 10% content of long branches, its efficiency diminishes with increasing crystallization temperatures (over 146 °C). LCB-PP and its long branches, acting as a heterogenous nucleation seeds, maintains nucleating ability across various crystallization temperatures even at low concentrations in the blends.

WAXS in connection with a temperature cell was used to investigate the morphological characteristics of isothermally crystallized samples. Two crystallization temperatures, 140 and 150 °C, were selected as representatives based on outcomes derived from thermal analysis and for possibility to compare this study with the previous study (Paper I). Neat PP, at $T_c = 140$ °C is a three-phase crystalline system, and after addition of α-NA, the β-phase fully disappeared, present was only α- and γ-phase. As expected, at higher T_c γ-phase disappeared and crystallization process retarded. Concerning the blends, the concentration of the long branches assists in forming α- and γ-phases, leading to faster crystallization and higher overall crystallinity even at high T_c.

The Scherrer equation analysis revealed, that addition of α-NA in the case of $T_c = 140$ °C, reduce the crystal dimensions. However, in the case of high T_c (150 °C), this effect is not visible; the non-functionality of NA at high crystallization temperatures was confirmed. That blends with LCB-PP have shorter crystal dimensions, indicating finer crystalline structures even compared to the nucleated PP at low T_c. Findings arising from this study highlight the significant impact of long branches on the crystallization behavior and supermolecular structure of PP blends, making it an effective nucleating agent.

Paper III shows a relationship between long-chain branching of polypropylene, specific nucleation, and end-use properties of polypropylene blends. Blends of linear polypropylene (L-PP) and long-chain branched polypropylene (LCB-PP) with various LCB-PP compositions (0, 1, 2, 5, 10, 20, 50 and 100 wt.%) were modified by specific β-nucleating agent NJ STAR NU 100 (β-NA) and prepared under complex flow fields by injection molding.

WAXS was employed to capture X-ray patterns of both skin and core of specimens, determining overall crystallinity and amounts of individual polymorphs. The injection-molded specimens displayed α-, β-, and γ- polymorphic crystalline structures, The presence of stereodefects, arising from LCB-PP content in the blends and confirmed by the broader reflections, led to smaller, less ordered crystals. L-PP mostly crystallized into the α-phase, with the β-phase content expectedly increasing upon adding β-NA, especially in the core (up to 95%). However, 100% β-phase was not achieved due to the duality of the used nucleating agent. LCB-PP showed self-nucleation into the α-phase, and β-NA had little effect on its crystallinity and phase composition. γ-phase was present in LCB-PP, with higher concentrations in the core. β-NA positively affected the β-phase content of L-PP and blends in the core. As the LCB-PP content increased, the amount of β-phase decreased, and γ-phase increased. At the same time, the increasing content of LCB-PP and γ-phase in the blends is reflected in increasing overall crystallinity.

The highest value of lamellae lengths can be observed in β-crystallites. β-crystallites were larger than α-crystallites, sometimes twice as large, due to a higher growth rate under given crystallization conditions. Lamellae length did not significantly increase with β-NA.

As the overall crystallization and phase composition change, mechanical properties are influenced. β-NA influenced the mechanical properties of L-PP, leading to a broader yield peak and strain hardening but lower yield stress (30 MPa) compared to LCB-PP, which showed higher yield stress due to strong physical chain entanglements. The blends' yield stress increased with LCB-PP content, while β-NA had little effect on the yield stress in the blends. The addition of β-NA led to higher elongation at break for L-PP; however, increasing LCB-PP content reduced elongation due to the high density of entanglements in branched structures. On the other hand, the composition of the blends has no significant effect on the impact strength except for the nucleated L-PP. It has been demonstrated that adding a relatively small amount of LCB-PP is sufficient to modify the mechanical properties of linear polypropylene. Even a minimal amount of LCB-PP in L-PP suppresses the effectiveness of β-NA.

Paper IV investigates the impact of isotactic polypropylene (iPP) molecular weight and annealing on crystallization, its crystalline structure and mechanical properties using WAXS, DSC, tensile testing, and Scanning Electron Microscopy (SEM). The study focuses on neat and β-nucleated iPP with two different molecular weights (Mw_{iPP} = 1 300 000 and Mw_{iPP} = 570 000). As β-nucleating agent NJ STAR NU 100 was used (β-NA). β-crystals are metastable with the possibility of transformation into the more stable α-phase under heating conditions. By annealing at temperatures above the melting temperature of the β-phase but below that of the α-phase, recrystallization of β-phase into α-phase can be achieved, due to the faster crystallization of α-crystals at high temperatures. β-nucleated and neat samples were annealed at temperatures above the melting point of the β-phase but below that of the α-phase (160 °C) with the aim to obtain β→α recrystallization.

Thermal analysis revealed that during the first heating, untreated samples showed multiple melting peaks corresponding to their phases, whereas the β-nucleated materials, which underwent annealing, revealed no peak of β-phase, marking during the annealing the recrystallization of β-phase into more stable α-phase happened. Annealing process, in the case of β-nucleated material, caused improvement of α-crystallites and β→α recrystallization. WAXS confirmed that untreated iPP with lower Mw consist predominantly of α-phase, while iPP with higher Mw crystallizes into α-phase and moreover into the β-phase (skin layer). The strong dependence of the molecular weight on the polymorphic composition is visible. Addition of β-NA forms in both Mw higher amount of β-phase, on the other hand, after annealing, the β-phase almost entirely converted to the α-phase.

Results from mechanical testing suggests, that neither the crystallinity nor the crystallite size has a major impact on the strength and stiffness, but in the iPP with lower Mw significant increase in stiffness and strength, accompanied by a decrease in drawability is achievable.

Based on the testing, annealing seems to be the effective way to perform β→α transformation. It can lead to the improvement of supermolecular structure as thickening and enhancement of lamellae. The increase in lamellar thickness further supports enhancing mechanical properties. This improvement is assigned to enhancing the crystalline phase and partially preserving the specific structure in the amorphous phase of recrystallized samples with lower molecular weight, which comprises many interconnecting chains which pass through several lamellae, providing long-range effect and thus influence end-use properties of polypropylene.

CONTRIBUTIONS TO THE SCIENCE AND PRACTICE

Polypropylene is widely used due to its low cost and good processability, but its linear structure limits its performance in applications requiring strong extensional properties and melt strength. Introducing long-chain branching into PP can enhance these properties, however at a higher cost. Combining LCB-PP with linear PP can improve processing properties while keeping costs low.

The contributions of the current study to the level of scientific knowledge are as follows:

- The limits of α-NA when used with branched polypropylene, especially under certain thermal conditions, were defined. The long branches, due to the self-nucleation capabilities, reduce haze and speed up crystallization, outperforming the effect of α-NA. At higher crystallization temperatures, α-NA's effect diminishes, emphasizing the dominance of self-nucleation in LCB-PP.
- Even at low concentrations, LCB-PP in the blends with L-PP promotes crystallization at elevated crystallization temperatures where α-NA becomes ineffective. LCB-PP facilitates the formation of finer crystalline structures, which improves crystallization kinetics and crystallinity in blends.
- LCB-PP is defined as a potential alternative to traditional nucleating agents, particularly for high-temperature applications.
- The incorporation of LCB-PP as a nucleating agent in L-PP enhances recyclability due to their shared chemical composition.
- Annealing is introduced as an effective method to fine-tune the crystalline phases and improve material performance.
- β→α transformation in β-nucleated samples enhances the crystalline structure, improving mechanical properties.

Together, the doctoral thesis contributes valuable insights into how nucleating agents, molecular branching, and processing conditions control the crystallization process in polypropylene. The doctoral thesis presents LCB-PP as a powerful tool for modifying the properties of PP, offering alternatives to conventional nucleating agents and showcasing methods such as annealing for enhancing crystallinity and mechanical performance. These findings have practical implications for industries that develop high-performance polymer materials with tailored properties for specific applications.

CONCLUSION

The presented doctoral thesis aims to investigate the morphology of linear and long-chain branched polypropylene. Specifically, attention is focused on identifying optimal conditions for controlling the phase structure. The study includes findings from the investigation of the influence of process parameters and chemical composition on the formation and structure of the resulting phases, and special attention is paid to the effect of the incorporation of long branches on the properties of linear polypropylene.

Key findings of the study revealed that long branches of polypropylene accelerate the crystallization process and outperform traditional nucleating agents in efficiency. Long-chain branched polypropylene not only reduces haze and accelerates crystallization but also promotes the formation of finer crystal structures in blends with linear polypropylene, even at low concentrations. The research further identified long-chain branched polypropylene as a potential alternative to conventional nucleating agents, primarily when high crystallization temperatures are used. Among others, the study focused on tempering as a method for improving the crystalline phases and mechanical properties of polypropylene. The consequence of annealing is the recrystallization of the β-phase to the α-phase, which appears to be an effective method of improving material properties. These findings have practical implications for industries that develop high-performance polymer materials with tailored properties for specific applications.

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LIST OF TABLES AND FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS USED

NA	Nucleating agent
iPP	Isotactic polypropylene
α-PP	α-phase of polypropylene
β-NAs	β-nucleating agents
β-PP	β-phase of polypropylene
γ-PP	γ-phase of polypropylene
LCB-PP	Long-chain branched polypropylene
L-PP	Linear polypropylene
PP	Polypropylene
sPP	Syndiotactic polypropylene
aPP	Atactic polypropylene
WAXS	Wide-angle X-ray scattering
DSC	Differential scanning calorimetry
POM	Polarized optical microscopy
T_m	Melting temperature
T_c	Crystallization temperature
M_w	Molecular weight
ΔG	Gibbs free energy
ΔS	Change in entropy
$\Delta \mathrm{H}$	Change in enthalpy

AUTHOR´S PUBLICATIONS AND OTHER ACTIVITIES

Journal articles

1. Gajzlerova, L., Navratilova, J., Polaskova, M., Benicek, L., Jaska, D., Zenzingerova, S. & Cermak, R. (2024). Tailoring end-use properties of polypropylene through a combination of specific nucleation and long-chain branching. *Chinese Journal of POLYMER SCIENCE. Published on-line* https://doi.org/10.1007/s10118-024-3234-1
2. Zenzingerova, S., Navratilova, J., Gajzlerova, L., Kudlacek, M., Jaska, D., Benicek, L. & Cermak, R. (2024). Polypropylene blends: Impact of long chain-branched polypropylene on crystallization of linear polypropylene. *Express Polymer Letters, 18*(9), 921–930. https://doi.org/10.3144/expresspolymlett.2024.69
3. Zenzingerova, S., Kudlacek, M., Benicek, L., Jaska, D., Navratilova, J., Gajzlerova, L. & Cermak, R. (2024). The degradation of poly(1-butene) extrudates subjected to artificial and natural aging. *Iranian Polymer Journal.* https://doi.org/10.1007/s13726-024-01348-z
4. Zenzingerova, S., Kudlacek, M., Navratilova, J., Gajzlerova, L., Jaska, D., Benicek, L. & Cermak, R. (2023). The competition between self-seeding and specific nucleation in crystallization of long-chain branched polypropylene. *Express Polymer Letters, 17*(11), 1110–1120. https://doi.org/10.3144/expresspolymlett.2023.84
5. Gajzlerova, L., Navratilova, J., Zenzingerova, S., Jaska, D., Benicek, L., Kudlacek, M., Cermak, R. & Obadal, M. (2022). On isotactic polypropylene annealing: Difference in final properties of neat and β-nucleated polypropylene. *Express Polymer Letters*, *16*(5), 453–464. https://doi.org/10.3144/expresspolymlett.2022.34

Conference contributions

1. Navratilova, J., Zenzingerova, S., Gajzlerova, L., Jaska, D. & Cermak, R. (2024). Blends of linear and branched polypropylene: effect of nucleating agent on crystallization. *Polymer Processing 2024, Ferrol, Spain*
2. Zenzingerova, S., Navratilova, J., Gajzlerova, L., Kudlacek, M., Jaska, D. & Cermak, R. (2023). The effect of various β-nucleating agents on the morphology of polypropylene. *3rd Journal of Thermal Analysis and Calorimetry Conference and*

9th V4 (Joint Czech-Hungarian-Polish-Slovakian) Thermoanalytical Conference, Balatonfüred, Hungary

3. Navratilova, J., Zenzingerova, S., Gajzlerova, L., Kudlacek, M., Jaska, D. & Cermak, R. (2023). Crystallization of long-chain branched polypropylene with nucleating agents. *3rd Journal of Thermal Analysis and Calorimetry Conference and 9th V4 (Joint Czech-Hungarian-Polish-Slovakian) Thermoanalytical Conference, Balatonfüred, Hungary*
4. Zenzingerova, S., Kudlacek, M., Jaska, D., Benicek, L., Navratilova, J., Gajzlerova, L. & Cermak, R. (2022). The effect of accelerated and natural ageing on the properties on Poly-1-butene extrudates. *European Polymer Congress, Prague, Czech Republic*
5. Jaska, D., Zenzingerova, S., Kudlacek, M., Cermak, R., Navratilova, J. & Gajzlerova, L. (2022). Effect of silanized silica on crystallization of polypropylene. *European Polymer Congress, Prague, Czech Republic*
6. Jaska, D., Zenzingerova, S., Chalupa, V., Cermak, R., Saha, P., Stanek, M., Martinek, T., Vojta, O. & Klabalova, E. (2022). Damping properties of 3D printed structures. *European Polymer Congress, Prague, Czech Republic*

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IGA/FT/2022/003 Natural and synthetic polymers - their preparation, properties and applications.

IGA/FT/2023/008 Study of polymer systems - preparation and evaluation of properties.

JUNG-2020-019 Zonal personalized footwear

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Váňová, Ch. (2021). In-situ crystallization of polypropylene with beta nucleating agent. Tomas Bata University in Zlín. Bachelor thesis.

Váňová, Ch. (2023). Overview of selective nucleating agents for isotactic popylpropylene. Tomas Bata University in Zlín. Master thesis.

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Polymeric blends based on linear and branched polypropylene: crystallization, polymorphism and properties

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