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Crystallization of isotactic polypropylene containing beta-phase nucleating agent at rapid cooling

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ABSTRACT

The crystallization behavior of isotactic polypropylene containing a β-phase nucleating agent has been investigated, focusing on evaluation of the effects of cooling rate and/or supercooling of the melt on the generation of different polymorphs. It has been found that β-crystals only form on cooling the melt at rates lower than about 50 K s^{-1} while cooling at rates between 50 and 300 K s^{-1} leads to formation of α-crystals; even faster cooling is connected with mesophase formation or vitrification of the entire melt. Fast scanning chip calorimetry revealed different mechanisms of nucleation at low and high supercooling. In comparison to non-nucleated iPP the presence of the β-phase nucleating agent only affects the crystallization kinetics at low supercooling, supporting the idea that ordering at high supercooling is governed by homogeneous nucleation. β-crystals, formed initially on slow cooling, melt below about 420 K on slow heating, followed by formation of few α-crystals on continuation of heating. The mesophase initially formed on fast cooling and aging at ambient temperature, in contrast, re-crystallizes directly into α-structure. The results of the present work provide comprehensive information about the condition of formation and the stability of different polymorphs in isotactic polypropylene containing a β-phase nucleating agent.

1. Introduction

The crystalline phase in semicrystalline isotactic polypropylene (iPP) may adopt different structures and morphologies depending on the condition of crystallization [1–3]. Slow cooling of the melt at rates lower than about 10^2 K s^{-1}, or isothermal crystallization at temperatures higher than about 330 K typically leads to formation of the thermodynamically stable monoclinic α-form [4,5]. The formation of α-crystals from the supercooled quiescent melt proceeds via spherulitic growth of lamellae. Due to lamellar branching, radially and tangentially oriented lamellae are observed, with their ratio depending on the crystallization temperature [4–9]. Cooling the melt at rates faster than 10^2 K s^{-1} to temperatures between the glass transition temperature of 270 K and 330 K, results in formation of a mesophase [4,5] which has been described as a conformationally disordered glass [10,11]. The mesophase is of non-lamellar morphology [12–14], and converts on heating to α-crystals with the initial non-spherulitic superstructure and particle-like habit of the mesophase preserved [15–20].

The β-structure of pseudo-hexagonal symmetry may be observed at special conditions of crystallization including crystallization in a temperature gradient, or crystallization of oriented melt [1,7,21–25]. The growth rate of β-crystals is higher than that of α-crystals in a wide temperature range between 378 and 414 K [8], which has been attributed to a lower surface free energy penalty on addition of molecular stems at the 110 growth face of the β-crystals,

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that is, to presence of favorable secondary nucleation sites [26,27]. However, since the rate of primary nucleation of the β-phase is lower than that of α-crystals, semicrystalline iPP containing β-crystals typically cannot be obtained without addition of special heterogeneous β-phase nucleators [28–30]. The β-phase exhibits a trigonal unit cell [31], and forms negatively birefringent radial or banded spherulites on crystallization from the quiescent melt [7]; the structure development and lamellar arrangement has been demonstrated in detail elsewhere [21]. The β-phase exhibits a unique melting behavior such if cooled below a critical temperature of about 375 K it re-crystallizes into the α-form during heating. The re-crystallization to α-crystals does not occur in samples which were not cooled below this critical temperature and the β-crystals melt separately; this phenomenon has been named "melting memory effect" [32].

From application point-of-view, iPP containing β-crystals exhibits a lower modulus of elasticity, a lower yield stress, and a higher ductility than iPP containing α-crystals; furthermore, the impact strength and toughness are higher [33–38]. It has been shown that a variation of the processing conditions affects both the formation of the β-modification and the related mechanical performance of iPP [39], however without a detailed investigation of the involved thermal history.

Finally, the γ-structure develops in low molar mass fractions of polydisperse iPP, in random copolymers with shortened isotactic sequences, or in presence of high pressure. The γ-phase is of orthorhombic symmetry, and typically forms in conjunction with the α-phase, being mixed within spherulites. Since α- and γ-crystallization leads to simultaneous occurrence of radially and tangentially aligned lamellae within spherulites, the net birefringence of spherulites is lower than that of β-spherulites, permitting straightforward identification of the latter by polarizing optical microscopy [2,3,40–42].

With the present work we attempt to shed further light onto the crystallization behavior of iPP containing a β-nucleator. As far as we are aware, systematic studies of the effect of cooling rate and supercooling of the melt on the crystallization process including generation of different polymorphs and the kinetics of crystallization have not been performed yet. For non-nucleated iPP it is known that α-crystals form via heterogeneous nucleation at temperatures higher than about 330 K while at lower temperatures a mesophase develops via homogeneous nucleation, or via heterogeneous nucleation but at different sites than are active at higher temperatures. The research object of identification of different nucleation mechanisms in crystallizable materials and in particular polymers has been discussed in detail at the 12th Lähnwitzseminar entitled "Interplay between Nucleation, Crystallization, and the Glass Transition", however, without having achieved a unanimous opinion whether homogeneous nucleation in crystallizable polymer is detectable, or not [43]. The minimum half-times of crystallization and mesophase formation of about 0.2 and 0.05 s [44,45] are observed at temperatures of about 340 and 300 K, respectively, leading to a bimodal dependence of the crystallization rate versus temperature [44–47]. It is emphasized that mesophase formation at temperatures close to the glass transition temperature is faster than crystallization due to increased primary nucleation rate but not due to increased growth rate. With the assumption that mesophase formation of iPP at temperatures lower than 330 K occurs via homogenous nucleation, the addition of a heterogeneous nucleator is expected to affect only the slower crystallization kinetics at higher temperature.

Analysis of the crystallization behavior of nucleated iPP in a wide range of different crystallization conditions including different supercooling and rates of cooling is assumed to provide valuable information about generation of different polymorphs. The efficiency of heterogeneous nucleators, which in the context of the present study is considered as the capability of a nucleating agent to promote crystallization of a specific crystal form, depends on the temperature dependencies of both the crystal form intended to generate by the addition of the nucleating agent, and the crystal form to be replaced. In the particular case of intended formation of β-crystals in iPP, solidification of the supercooled melt must occur at temperatures at which α-crystal nucleation and crystal growth is slower than in case of the β-form. It will be shown that β-crystals, α-crystals and mesophase may form as a function of the conditions of solidification in β-nucleated iPP, which implies that the efficiency of the used nucleating agent to produce measurable amount of β-phase is limited to certain conditions.

Finally, in this work we investigated the stability and the reorganization behavior of the different polymorphs of β-nucleator containing iPP, with the different polymorphs developed by variation of the condition of melt solidification. It is expected, based on earlier reports, that β-crystals reorganize to α-structure [22,32,48] and that α-crystals evident at ambient temperature increase their stability without changing the crystal structure on slow heating. The reorganization behavior of the mesophase of iPP containing a β-nucleator, in contrast, has not been studied yet. In non-nucleated iPP, the mesophase transforms to α-crystals on slow heating, starting at about 350 K [11,15–17]. It has been suggested that the mesophase–α-crystal transition proceeds by removal of conformational defects/helix reversals at local scale within existing domains, and without prior complete disordering/isotropization of the mesophase [20]. The enthalpy of the mesophase–α-crystal transition is rather low [49,50], which implies that the mesophase seemingly can be considered as a precursor for α-crystal formation. We assume that the presence of β-nucleator in semimesomorphic iPP, that is, in iPP containing mesophase besides amorphous phase, does not affect the mesophase–α-crystal transition on slow heating, which however, we intended to prove within the present work. Fast heating, in contrast, would lead to complete disordering of the mesophase at around 350 K [51], and then β-crystals may form on annealing the supercooled melt.

Summarizing the scope of this work, we intend to provide new information about the nucleation efficiency of γ-quinacridone as a widely used nucleator to obtain β-crystals in iPP [28–30,52,53]. In an extension of earlier work, we focus on analysis of the crystallization behavior