Journal of Thermal Analysis and Calorimetry, Vol. 86 (2006) 3, 687–691

CRYSTALLIZATION OF POLYPROPYLENE WITH A MINUTE AMOUNT OF β-NUCLEATOR

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The work deals with crystallization of isotactic polypropylene (iPP) containing a low amount of β-nucleating agent. Commercially available iPP was modified by 0.01 and 0.03 mass% of β-specific nucleating agent and crystallized isothermally and non-isothermally under precisely controlled conditions in a differential scanning calorimeter. A strong effect of crystallization temperature (T_c) and content of β-nucleating agent on β-phase formation was observed. In the sample with the high amount of nucleating agent, the β-phase formation ceased with T_c increase. In case of low-nucleated sample the opposite effect was observed. A non-isothermal crystallization showed that iPP with 0.01 mass% of the nucleating agent crystallized in the lowest temperature range, lower than that of non-nucleated iPP.

Keywords: *βα-growth transition, isotactic polypropylene, α-phase, β-phase, polymorphism, specific nucleation*

Introduction

Polymer crystallization forms an interesting field of research because in many cases the findings explain service behaviour of the semicrystalline materials. Particularly, crystallization strongly influences final supermolecular structure and properties of polymorphic polymers.

One of the most important polymorphic materials is isotactic polypropylene (iPP). It is widely used and easy-to-obtain polymer. Nevertheless, its mechanical and thermal properties are rather deficient in more sophisticated applications. In order to obtain significantly enhanced properties, iPP modification in various ways is required. Beside the common treatments, such as filling or direct adjustment of crystallizability during polymerization, iPP offers the possibility of controlled crystallization into a specific morphological lattice. Three basic crystal phases of iPP have been described: monoclinic α-phase, trigonal β-phase and orthorhombic γ-phase [1–3]. As for the melt and solution crystallization under the atmospheric pressure, the material crystallizes into α-phase, which is rated as the most stable [1–3]. It can occur either in less organized form α_1, or in α_2, which possesses regularly ordered methyl-groups in neighbouring chains of helixes with opposite orientation [4]. On the other hand, β-phase grows during melt-crystallization in only a small amount as a supplement of α-phase. A higher content of β-phase can be obtained via intensive-melt cooling, shear-field crystallization, and particularly with the aid of specific nucleation [3, 5, 6]. A number of nucleating agents, which differ in both nature and activity, is described.

As for physical characteristics, β-phase compared to α-phase has a lower melting temperature and density. β-phase also shows strong differences in mechanical properties, namely higher toughness and drawability, but lower stiffness and strength [7–10]. Consequently, isotactic polypropylene containing the prevailing β-phase (β-iPP) is currently classified among common polymeric materials, and for specific applications it is rated as a suitable alternative to the conventional polypropylene (α-iPP).

Several studies deal with the supermolecular structure of β-nucleated iPP [3, 5, 11]. It is revealed that the formation of pure β-polypropylene has an upper and lower limit temperature $T(\beta\alpha)$~140°C and $T(\alpha\beta)$~100°C, respectively [5, 12]. Between these temperatures, β-phase grows faster than α-phase and different types of β-phase structure can be formed. The formed types and structural features are significantly influenced by thermal conditions of crystallization, melt history, mechanical stresses and presence of extraneous materials [5]. An interesting feature of the β-phase growth is a β to α phase transition (βα-growth transition). Compared with the formation of pure β-polypropylene, the transition has the same upper and lower critical temperatures. The high critical temperature of growth transition, which takes place above 140°C is observed by Varga [13] during the stepwise crystallization of non-nucleated iPP and later during the isothermal crystallization of β-nucleated iPP in the presence of high-selective nucleating

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1388–6150/$20.00

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agent [5]. Lotz [11, 14] observes that the βα-growth transition occurs if the samples are cooled below the low critical temperature at approx. 100°C during the crystal growth. According to Varga [5], it can be generally stated that the βα-growth transition always takes place if the growth rate of the α-phase is higher than that of β-phase, i.e. below 100°C ($T(\alpha\beta)$) and over 140°C ($T(\beta\alpha)$).

Within previous works [7, 8], structure and properties of isotactic polypropylene modified by high-active β-nucleating agent based on *N*,*N*'-dicyclohexylnaphthalene-2,6-dicarboxamide are studied. It is found that the 'boundary' concentration of this nucleating agent in iPP is 0.03 mass%: the content of β-phase reaches saturation level and mechanical properties show sharp extremes [8]. Thus, the aim of the present paper is to give an analysis of crystallization of the iPP containing minute amounts of β-nucleating agent.

Experimental

Materials

Commercially available isotactic polypropylene homopolymer, Mosten 58412, produced by Chemopetrol Litvínov a.s., Czech Republic, was used as an experimental material. The relevant properties were following: melt flow index (at 230°C and 2.16 kg) 3 g/10 min (ISO 1133), isotacticity index 98% (ISO 9113) and a mass-average molecular mass approx. 170000. As a specific β-nucleating agent, NJ STAR NU 100 based on *N*,*N*'-dicyclohexylnaphthalene-2,6-dicarboxamide (NU 100) produced by Rika Int., Great Britain, was applied.

Sample preparation

Blends of iPP were prepared in two steps. First, paraffin oil (0.30 mass%) for homogeneous dispergation of the nucleating agent and subsequently NU 100 in different amounts (0, 0.01, 0.03 mass%) were properly dispersed within iPP pellets at ambient temperature. Then the blends were processed using a Brabender DSK 42/6D twin-screw extruder and pelletized [15]. From the blends, plates with dimensions 125.0×60.0×0.5 mm were processed using a manual press. Processing parameters of extrusion and compression moulding were summarized in Table 1. Cylindrical specimens for differential scanning calorimetry (DSC) with a diameter of 5 mm and mass of 9 mg were cut out from the prepared plates using a hole-puncher.

Table 1 Processing parameters of blend extrusion and plate compression moulding

Twin-screw extrusion	
Screw speed	75 min^{-1}
Temperature of headed zones	
1. zone	190°C
2. zone	200°C
3. zone	210°C
Compression moulding	
Temperature	210°C
Preheating time	2 min
Compression time	5 min
Cooling time at 20°C	5 min

Methods

DSC analysis

Crystallization measurements were carried out using a Perkin-Elmer Pyris 1 power-compensated differential scanning calorimeter with a nitrogen purge (20 mL s^{-1}). The temperature calibration was performed using indium. As for isothermal measurements, samples were heated from 50 to 220°C at a heating rate of 50°C min^{-1}, then melted at 220°C for 5 min, and subsequently cooled at 200°C min^{-1} to the given crystallization temperature (T_c=130, 135 and 140°C). Regarding dynamic DSC scans, samples were heated from 50 to 220°C, annealed for 5 min and then cooled to 50°C at the given rate (5 and 20°C min^{-1}).

Wide-angle X-ray scattering

Final structure of the samples crystallized under controlled conditions in DSC was examined by wide-angle X-ray scattering. A HZG 3 diffractometer equipped with CuK_α was employed in a transmission mode. Radial scans of intensity *vs.* diffraction angle 2θ were recorded in the range of 10–30°. The k value representing the β-phase portion in the crystalline part of the sample was calculated from X-ray diffractograms according to Turner-Jones *et al.* [2]:

$$k = H_\beta/(H_{\alpha1} + H_{\alpha2} + H_{\alpha3} + H_\beta) \qquad (1)$$

where $H_{\alpha1}$, $H_{\alpha2}$, $H_{\alpha3}$ are the intensities of α-diffraction peaks corresponding to angles 2Θ=14.2; 17.0 and 18.8°, respectively, and H_β is the intensity of β-peak at 2Θ=16.2°.

Polarized-light microscopy

In order to study morphology of the crystallized samples, a Zeiss NU microscope was used. Thin slices with thickness of 40 μm were cut from samples already examined by WAXS using microtome. Micrographs of the observed structure were taken using a SONY F-717 digital camera.

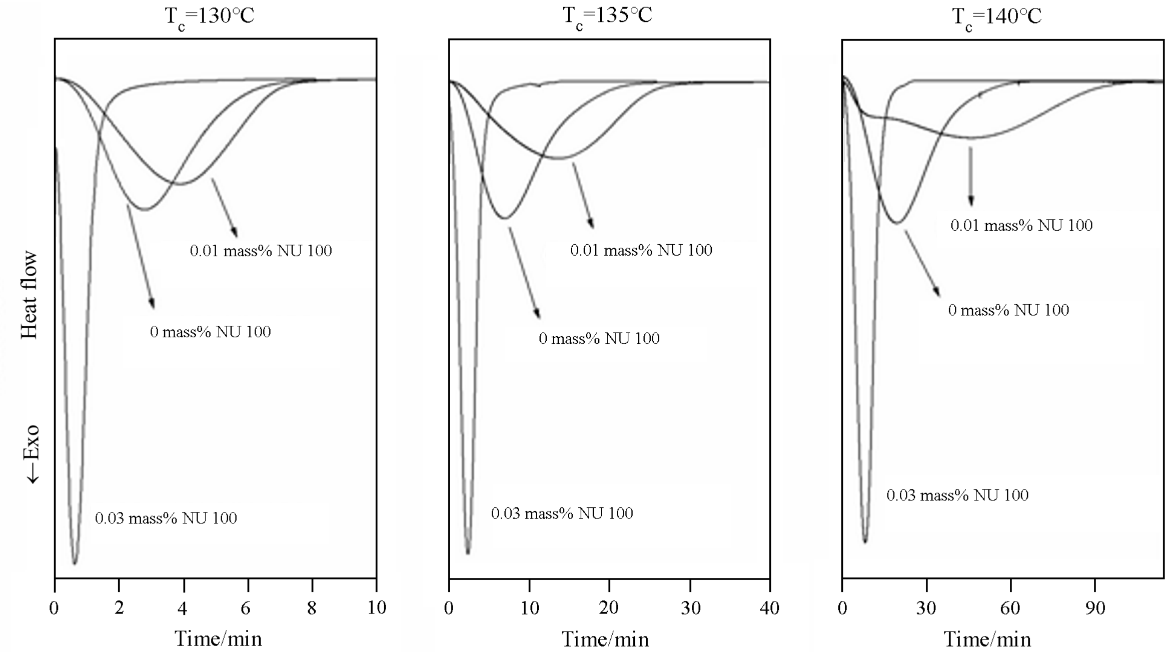

Fig. 1 Crystallization exotherms of iPP containing different amounts of NU 100 crystallized at given T_c

Results and discussion

The isothermal crystallization of neat and β-nucleated iPP was carried out at three temperatures (130, 135, 140°C) using DSC. Figure 1 shows the corresponding crystallization exotherms. According to the crystallization theory [3], the temperature decrease causes a sharping and narrowing of the exothermic peak and a shortening of the crystallization time (Fig. 1). Correspondingly, the addition of a nucleating agent should lead to similar effect. Indeed, the crystallization exotherms of high-nucleated samples (i.e. containing 0.03 mass% NU 100) validate the theory; these samples crystallize the fastest (Fig. 1). However, low nucleated samples (i.e. containing 0.01 mass% NU 100) possess an opposite behaviour; unexpectedly they crystallize at even slower rate than the neat iPP. This effect is particularly pronounced at higher T_c as can be seen in Fig. 2, which illustrates the dependence of crystallization halftime on crystallization temperature. A comparison of crystallization halftime values evidences that the sample with 0.01 mass% of the nucleating agent crystallizes for 5 min longer at T_c=135°C and even for 20 min longer at T_c=140°C than the neat sample. What can be also observed in Fig. 1 is a peculiar peak-doubling for the sample containing 0.01 mass% NU 100, particularly at T_c=140°C. The doubling is detected neither in neat iPP nor in iPP containing 0.03 mass% NU 100. This phenomenon may indicate separate growth of α- and β-phase. In order to confirm this hypothesis, the melting measurement of partly crystallized sample was carried out. The sample containing 0.01 mass% NU 100 was annealed at T_c=140°C until the first exothermic peak was virtually completed (approx. 20 min) and subsequently melted at heating rate of 5°C min^{-1}. As can be seen in Fig. 3, dominant peak (approx. at 155°C) assigned to β-phase is manifested (see solid line). This confirms preferred β-phase growth in the initial crystallization period. For comparison, the melting curve of totally crystallized sample is also shown in the same figure (dashed line). In this case, contrary to partial-crystallized sample, significant and dominant α-phase endothermic peak (approx. at 170°C) can be observed. It points to the considerable formation of α-phase during the second stage of isothermal crystallization.

It is interesting to observe final structure of sample crystallized at T_c=140°C via polarized-light mi-

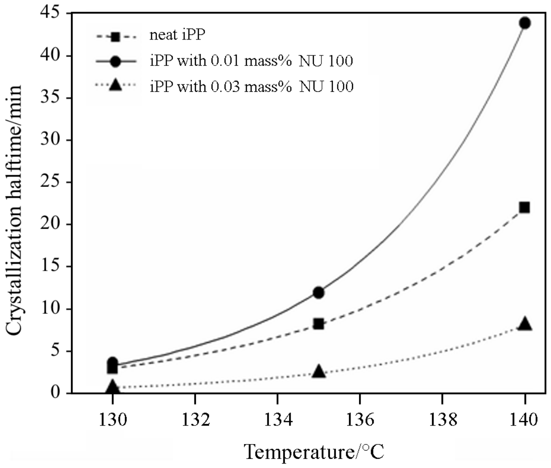

Fig. 2 Dependence of crystallization halftime on T_c

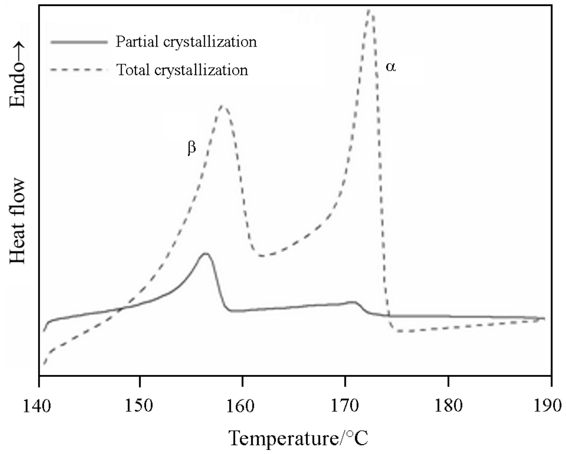

Fig. 3 Melting curves of the sample containing 0.01 mass% NU 100 crystallized at 140°C and heated at 5°C min^{-1}

croscopy. As can be seen in Fig. 4, the peculiar βα-twin structure is formed. It consists of the extensive β-spherulites in the core with α-spherulitic overgrowths on them. Varga [5] assigns the formation of such βα-twin structures to the βα-growth transition proceeding at high crystallization temperatures in iPP samples containing high-active β-nucleating agent. During this transition α-nuclei are formed on the growing β-crystal front, which results in the growth of α-spherulitic segments. The kinetic precondition of the βα-growth transition is a growth rate of the new phase higher than that of the basic crystal. The growth rate of β-phase exceeds that of α-phase between low and high critical temperature of growth transition (T(αβ)~100°C and T(βα)~140°C). Accordingly, discussed crystallization temperature (T_c=140°C) is a border temperature and the βα-growth transition can proceed. However, as mentioned above, the exotherm doubling is observed only in the sample with 0.01 mass% NU 100, and therefore particularly intensive βα-growth transition can be expected in this case. At the same time, the crystallization halftime of the low nucleated samples is significantly prolonged as compared to the neat samples. In this context, it can be suggested that the competitive and partly separated growth of both phases prolongs the overall crystallization time.

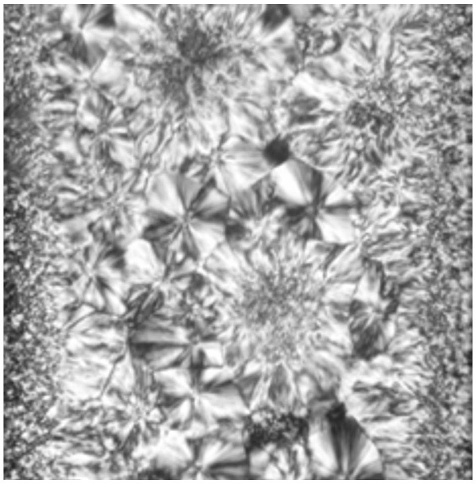

Fig. 4 Cross-sectional cut of isothermally crystallized sample containing 0.01 mass% NU 100; T_c=140°C, sample thickness approx. 500 µm

For the quantification of β-phase content in isothermally crystallized samples, wide-angle X-ray scattering was used. Figure 5 illustrates the dependence of k value on both the crystallization temperature and the amount of nucleating agent. As can be seen, in the sample containing 0.03 mass% NU 100, k value decreases with the rising T_c. It corresponds to the well-known fact that the growth rate of β-phase is reduced at high crystallization temperatures [5]. Accordingly, it can be predicted that at high crystallization temperatures the specificity of β-nucleating agent decreases and originally heterogeneous β-nuclei can act as α-nuclei, which manifests itself in the increase of α-phase content with the T_c increase. However, the sample containing 0.01 mass% NU 100 shows the opposite tendency; the content of β-phase unexpectedly increases with an increasing crystallization temperature. This peculiar crystallization behaviour of low nucleated sample is most probably caused by a different origin of α-phase, compared to the samples with a higher NU 100 content. Indeed, in low-nucleated samples, the α-phase originates from homogeneous nucleation or βα-growth transition. It is worth noting that the homogeneous α-nucleation is inhibited with the crystallization temperature rise. In addition, as mentioned above, β-phase starts growing in these samples earlier (Fig. 3). Then, the heat released during initial β-phase crystallization can even more complicate the formation of homogeneous α-nuclei. Consequently, the homogeneous α-nucleation is virtually excluded in the case of the highest T_c

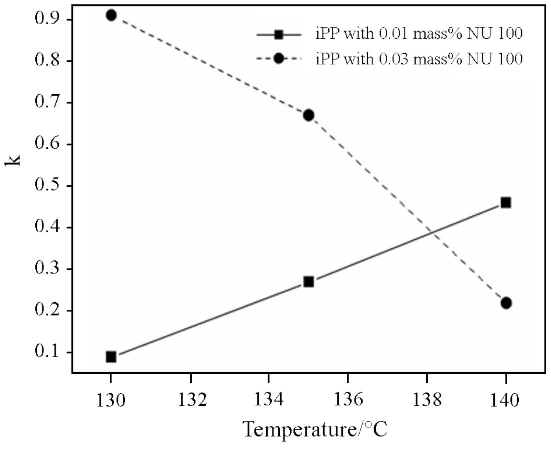

Fig. 5 Dependence of k value on T_c of the sample containing 0.01 and 0.03 mass% NU 100

and most of the α-phase is originated only from βα-growth transition, as illustrated in Fig. 4. It can be thus predicted that the β-structures could grow to larger dimensions. Actually, β-spherulites crystallized at 140°C were visible as intensive white domains in microtome cuts even by naked eye.

The non-isothermal crystallization of neat and nucleated iPP was also studied by DSC using cooling rates of 5 and 20°C min^{-1}. As can be seen in Figs 6 and 7, the integration of the exothermic peaks during the non-isothermal scans gives typical sigmoid crystallization curves. It is evident that the temperature range of crystallization is affected by the cooling rate. The higher is the cooling rate the lower is the onset crystallization temperature (compare Figs 6 and 7). Furthermore, it can be recognized that, at both cooling rates, the crystallization of sample containing 0.01 mass% NU 100 starts at the lowest temperature, even when compared to that of neat iPP. This effect corresponds distinctly to the longest crystallization times during isothermal crystallization of iPP with 0.01 mass% NU 100. Such behaviour can be related again to the separate and competitive growth of both α- and β-phases.

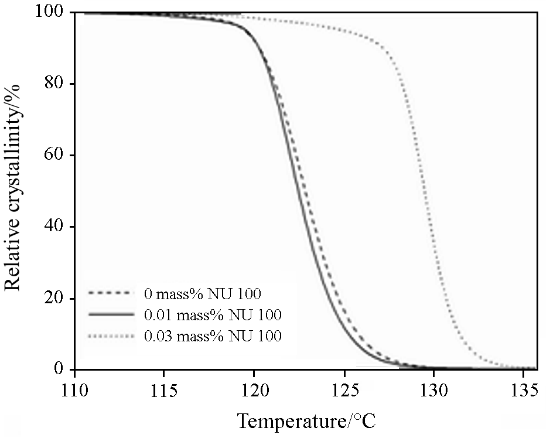

Fig. 6 Crystallization curves of the samples crystallized at 5°C min^{-1}

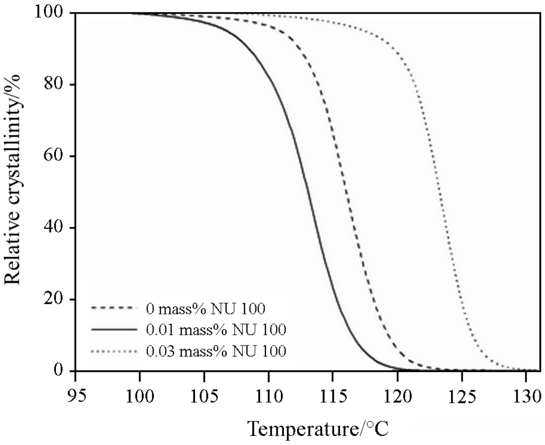

Fig. 7 Crystallization curves of the samples crystallized at 20°C min^{-1}

Conclusions

The research focused on crystallization behaviour of β-nucleated isotactic polypropylene shows that the crystallization process depends strongly on both the nucleating agent concentration and crystallization temperature. Polypropylene nucleated by the lower amount of nucleating agent (0.01 mass%) possesses unique crystallization behaviour; the crystallization exotherms are doubled, particularly in the case of high T_c. This doubling is ascribed to an earlier growth of β-phase. In addition, the crystallization halftime of this sample is longer as compared to high-nucleated and even neat iPP. Moreover, the sample containing 0.01 mass% NU 100 crystallizes in the lowest temperature range during non-isothermal crystallization. The contents of β-phase (*k*-values) possess an opposite tendency in low- and high-nucleated samples reflecting different nucleation mechanisms.

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DOI: 10.1007/s10973-006-7894-6