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Kinetics of competitive crystallization of *β*- and *α*-modifications in *β*-nucleated iPP studied by isothermal stepwise crystallization technique

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Abstract Crystallization kinetics of β-nucleated isotactic polypropylene (β-iPP) under isothermal conditions were investigated by differential scanning calorimetry. iPP was nucleated by a trisamide derivative, namely tris-2,3-dimethyl-hexylamide of trimesic acid (TATA). In the presence of TATA possessing dual nucleating ability, the formation of the α- and β-form occurs simultaneously. An isothermal stepwise crystallization method is suggested in this study, which can separate the crystallization process of β- and α-iPP and consequently their crystallization kinetics can be evaluated separately. The results indicated that the mechanism of crystallization changes in temperature especially in the vicinity of the upper critical temperature of the formation of the β-phase. In addition, it was found that the ratio of the growth rates of β- and α-modification determines the characteristics of crystallization and influences the apparent rate constant of crystallization of both polymorphs.

Keywords Crystallization kinetics · Avrami method · Mixed polymorphic composition · α- and β-iPP · Isothermal stepwise crystallization (ISC) technique

Introduction

Isotactic polypropylene (iPP) is a commodity polymer, which has three polymorphic modifications [1–4]. The α-form is the thermodynamically stable modification, which is developed during traditional processing technologies [2]. The β-modification is processed industrially, because its advantageous impact properties compared to the traditional α-iPP. γ-Modification can be observed in propylene copolymers and in iPP homopolymers with moderate chain regularity mainly [5, 6] and it has limited industrial importance. The application of β-nucleating agents is the most reliable way to produce β-iPP. The first highly active β-nucleating agent was introduced by Leugering [7]. The β-nucleating effect of two component systems based on Ca-stearate and some dicarboxylic acids was reported by Shi et al. [8]. Varga [9, 10] has found that Ca-salt of suberic and pimelic acids are highly efficient β-nucleating agents with outstanding thermal stability. A commercial β-nucleating agent is *N*,*N*′-dicyclohexyl-2,6-naphthalenedicarboxamide, which is sold under the trade name NJS NU100 [11, 12]. The derivatives of terephthalamide [13, 14] can be used for triggering β-modification. Recently, it was demonstrated that a tris-amide of trimesic acid is an efficient β-nucleating agent [15]. Dou et al. [16–19] have found that the metal salts of various organic acids possess beta nucleating ability. Zhang et al. [20, 21] prepared two component systems based on nano-sized $CaCO_3$ and pimelic acid. These systems induce the formation of β-form significantly. A few complexes based on rare earth metals may act as β-nucleating agent as well [22]. It should be noticed that Ca-suberate and Ca-pimelate are exclusively selective to the β-form [2, 10]. In their presence pure β-iPP can be prepared under appropriate thermal conditions [9]. It is worth mentioning that other known

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β-nucleating agents induce the crystallization of iPP, however, mixed (α and β) polymorphic composition form in their presence, thus they possess dual nucleating ability.

The crystallization kinetics of β-nucleated iPP has also been studied extensively in the literature. The most common method for the evaluation kinetic parameters of crystallization at isothermal conditions in iPP was developed by Avrami, Kolmogoroff, and Evans (AKE method) [23–27]. Based on this theory, the so called "Avrami equation":

$$x = 1 - e^{-kt^n} \tag{1}$$

is the most common technique to evaluate kinetic parameters of isothermal crystallization of iPP. In Eq. 1, x is the relative fraction of crystalline phase, k is the overall rate constant of crystallization, t is the time, and n is the Avrami exponent. The linearized form of Eq. 1 is used during evaluation:

$$\ln(-\ln(1-x)) = n \ln t + \ln k. \tag{2}$$

The crystallization curves (crystallization isotherms) of iPP can be linearized by plotting $\ln(-\ln(1-x))$ as a function of $\ln(t)$. n and $\ln k$ can be obtained from the slope and the intercept of the plotted straight line, respectively. The determined n refers to the mechanism of crystallization. If the number of nuclei increases in time (thermal nucleation) during crystallization, n is equal to the dimension of growth + 1. In the case of athermal nucleation (the number of nuclei is constant in time), n gives the dimension of crystal growth directly [23]. In the presence of a heterogeneous nucleating agent the crystallization is supposed to be athermal and consequently n refers directly to the dimension of growth.

Avrami equation is capable of description the development of a single crystalline phase. However, in the presence of β-nucleating agents with dual nucleating ability, β- and α-phases crystallize simultaneously with different nucleation and growth rates. Therefore, the relative amounts of α- and β-modifications are not constant [15] during the crystallization. In spite of the formation of two separate phases, only a single crystallization peak can be observed during cooling or isothermal crystallization experiments [2, 10, 28]. In these cases, the linearization according to Avrami equation does not work, although these kinds of formal kinetic evaluation have appeared often in the recent literature [29, 30]. The crystallization of simultaneously developing α- and β-modifications in iPP can be monitored with wide angle X-ray (WAXS) experiments. Such a study was performed by Chen et al. [31].

The aim of this study is the introduction of a simple experimental calorimetric procedure [Isothermal stepwise crystallization (ISC) technique], which is able to separate the simultaneous crystallization processes of β- and α-modifications in iPP samples. An evaluation method is also suggested in this study for the description of the crystallization kinetics of the two simultaneously growing polymorphs separately. Thus, Avrami constant and the rate constant of the overall crystallization can be obtained for the α- and β-modifications accordingly.

Experimental

Materials

Tipplen H-890 polypropylene homopolymer (MFR = 0.35 dgmin^{-1} at 230 °C, 2.16 kg) was used as received from TVK Hungary. The β-nucleating agent applied in this study was a trisamide of trimesic acid (TATA). The detailed synthesis of this nucleating agent was described in our earlier study [15]. 100 ppm nucleating agent was added to the polymer and the sample was homogenized in a Brabender W EH50 at 220 °C and 50 rpm. The homogenization time was approximately 5 min.

Techniques

The calorimetric measurements were carried out using a Perkin Elmer DSC 7 power compensated apparatus. Temperature and heat flow values of the apparatus were calibrated using high purity Indium and Zinc reference materials. Samples about 1–3 mg were measured in hermetically sealed aluminum pans under nitrogen atmosphere. The samples were heated to 220 °C and held there for 5 min to erase any thermal and mechanical prehistory (referred as step 1). Subsequently, the samples were cooled to room temperature and reheated again to 220 °C during the standard DSC measurement (referred as step 2). After completing step 2 the samples were cooled to 100 °C (T_R^* [32]) and reheated to 200 °C again (step 3). One minute long isothermal steps were inserted between heating and cooling runs to establish the stable starting condition of each run. The heating and cooling rate was 10 °C min^{-1}.

During standard isothermal measurements, the samples were cooled to the temperature of crystallization after completing step 1 (T_c = 130, 132, and 135 °C) at 40 °C min^{-1} and held there isothermally for 15 min. After complete crystallization the samples were heated up to 220 °C at 5 °C min^{-1} and polymorphic composition was determined from the melting curve. We have to remark here that polymorphic composition can be evaluated from melting curves only if the samples were not cooled below T_R^* (step 3), because $\beta\alpha$-recrystallization occurs below T_R^*. This process disturbs the melting profile and prevents the reliable estimation of polymorphic composition from the melting curve as it was pointed out earlier [2, 10, 28, 32].

The melting peak around 150 °C and the peak in the vicinity of 163 °C are relating to β- and α-modification, respectively. The α and β-melting peaks were separated by a "vertical line" as it was proposed in our previous studies [10, 15]. The partial area of these two peaks refers of the polymorphic composition, which can be easily calculated according to Eq. 4 [15]:

$$\beta_c = \frac{q}{q + \frac{\Delta H_\alpha}{\Delta H_\beta}} \tag{4}$$

where β_c is the β-content. ΔH_α and ΔH_β are the partial enthalpy of fusion of α- and β-modifications obtained from the partial area of the corresponding melting peaks. The constant of "q" is the ratio between the equilibrium enthalpy of fusion of α- and β-iPP ($q = \Delta H^0_\alpha / \Delta H^0_\beta$). The numerical values of equilibrium enthalpies for α- and β-forms reported in the literature [2] differ considerably. On the contrary q factor is altered unnoticeably, if equilibrium enthalpies of fusion were determined by the same way for both modifications [15]. We have used 148 J g^{-1} [33] and 113 J g^{-1} [34, 35] for equilibrium enthalpy of fusion of the α- and β-modifications, respectively. In this case, q equals to 1.31.

Table 1 The time increments used during isothermal crystallization measurements

Crystallization temperatures, T_c/°C		
130 °C	132 °C	135 °C
Time, t_c/min		
0.6	1.0	2.3
0.7	1.2	2.7
0.8	1.4	3.0
0.9	1.6	3.3
1.0	1.7	3.6
1.1	1.8	3.9
1.3	2.0	4.2
1.5	2.2	4.6
1.9	2.4	6.0

ISC technique

First, the time required for complete crystallization (t_∞) for a given T_c was determined. Subsequently, t_∞ was divided into ten stages at each T_c. The isothermal crystallization experiment was carried out again ten times using the previously defined time lengths (t_c) at each T_c. The time increments for all crystallization temperatures are presented in Table 1. Accordingly, the crystallization was stopped at different conversions, then the samples were heated up to 220 °C for registration of the melting curves. On the basis of the melting curves, the polymorphic compositions were determined for each time increments (t_c). The only difficulty of this method is that the crystallization does not stop immediately after the equipment switch from isothermal step to the heating run, because crystallization process at the chosen T_c is relatively fast. As a consequence, the amount of crystalline phase was significantly larger according to the melting curve than that determined from the crystallization isotherms. In order to solve this problem, we have modified the standard isothermal crystallization measurement procedure. We have determined the time at the peak of crystallization curve, which time (t_{cp}) corresponds to the maximum rate to crystallization. The overall rate of crystallization increases before t_{cp} and decreases afterward. Accordingly, we inserted a fast heating step from T_c to 140 °C with a rate of 20 °C min^{-1} to avoid additional crystallization if the t_c was shorter than t_{cp}. After this fast heating step the sample was heated to 220 °C at 5°C min^{-1} as it was described earlier. If t_c was longer than t_{cp} the samples were heated up to 220 °C at 5 °C min^{-1}, because in these cases the change in crystallinity was negligible after the isothermal crystallization step. The temperature program in the two cases is demonstrated in Fig. 1.

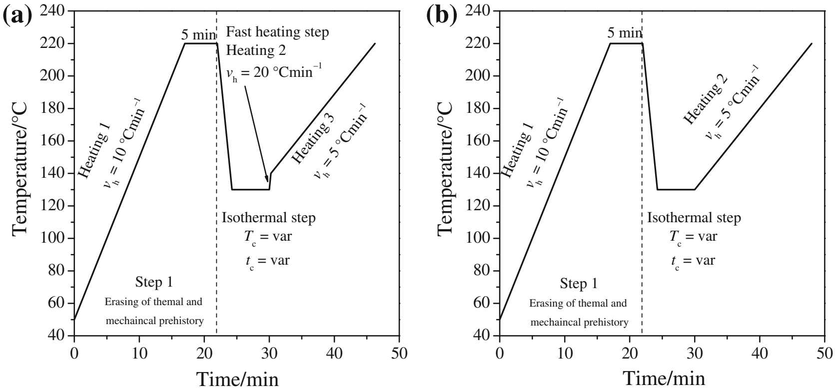

Fig. 1 The experimental procedure applied during isothermal measurements **a** if $t_c < t_{cp}$ and **b** if $t_c > t_{cp}$

Results and discussion

Standard melting and crystallization of iPP nucleated by TATA

The melting and crystallization characteristics of iPP nucleated by 100 ppm of TATA are demonstrated in Fig. 2. Curve a represents melting during step 3 (limited recooling step). It is well discernable that the two modifications melt separately, and the polymorphic composition can be obtained from the partial enthalpies of the melting peaks. The calculated β_c indicates that the sample crystallizes predominantly in β-form ($\beta_c = 0.81 = 81\%$), but considerable amount of α-modification develops during crystallization as well. The crystallization curve proves clearly that the crystallization of the two modifications takes place simultaneously and only one peak can be recorded by DSC technique. The peak temperature of crystallization is around 120 °C, indicating the efficient nucleating ability of the β-nucleating agent. The melting characteristics of sample heated from room temperature are demonstrated in curve c in Fig. 2. The effect of $\beta\alpha$-recrystallization can be observed unambiguously. β-Modification melts at lower temperature and the $\beta\alpha$-recrystallization starts meanwhile the melting of β-phase. The apparent peak at lower temperature refers to that point, where the $\beta\alpha$-recrystallization becomes faster than the melting of the β-phase and definitely not to the melting peak temperature of β-phase. After the recrystallization α-modification melts, which was present originally in the sample, and subsequently those α-phase melts, which formed during recrystallization. The shoulder indicating the melting of recrystallized α-phase indicated by an arrow on curve c in Fig. 2. The evaluation of partial areas of the melting peaks in curve c lead to significantly smaller and erroneous β_c. As we described, curve c represents four separate processes and the separation of those is difficult. We have to note here that temperature modulated DSC (TMDSC) is an excellent technique for separating the abovementioned processes qualitatively [10], but the quantitative results of TMDSC measurement should be treated with caution. The standard DSC results also revealed that mixed polymorphic structure develops in the presence of TATA.

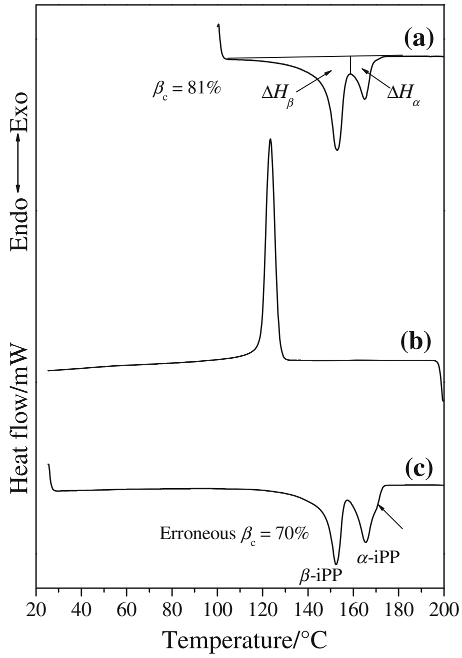

Fig. 2 Melting and crystallization characteristics of iPP containing 100 ppm TATA *a* melting after limited recooling, *b* crystallization, and *c* melting after cooling to room temperature

Avrami's evaluation of crystallization kinetics of simultaneously growing polymorphs in iPP

The crystallization isotherms recorded at $T_c = 135$ °C by ISC technique and subsequent melting curves are included in Fig. 3. The enthalpy of crystallization of the α- and β-modifications was evaluated using a horizontal baseline in the case of incomplete peaks. The position of the peaks is very close to each other indicating the good reproducibility of the isothermal crystallization experiments. The melting curves recorded after the isothermal steps are presented in Fig. 3b. The overall enthalpy of melting (ΔH_m) and crystallization (ΔH_c) can be calculated by dividing the area under the crystallization or melting curve with the sample mass. The actual values of the crystallization and melting enthalpies should be compared to check the reliability. Enthalpy of crystallization values as a function of melting enthalpy is given in Fig. 4. The data plots fit to a straight line with the slope equals to one indicating that $\Delta H_m = \Delta H_c$. The scattering of data is originated from the baseline fitting of incomplete peaks, but despite of the scattering the equality can be clearly observed and the measurements at 132 and 135 °C also provide reliable results. Unfortunately, the crystallization at 130 °C is too fast and the melting enthalpies are larger than the crystallization enthalpy values, consequently additionally crystallization occurs at 130 °C between the isothermal step and the melting of the sample. The deviation is significant especially in the case of the early stage of crystallization. Consequently, the results in obtained from $T_c = 130$ °C should be treated with caution. Especially, Avrami exponent is sensitive to the beginning of the conversion curve. These results indicate clearly that the lower temperature limit of this technique is 132 °C in the case of the iPP nucleated with TATA and using the given equipment (Perkin Elmer DSC-7). It should be noticed here that the upper temperature limit of the crystallization of β-iPP

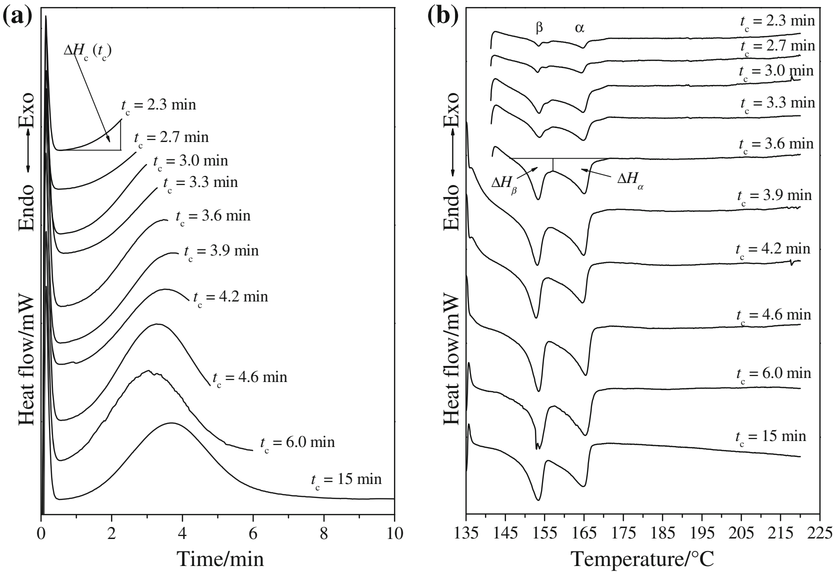

Fig. 3 Crystallization isotherms (**a**) and melting curves (**b**) of iPP containing 100 ppm TATA ($T_c = 135$ °C)

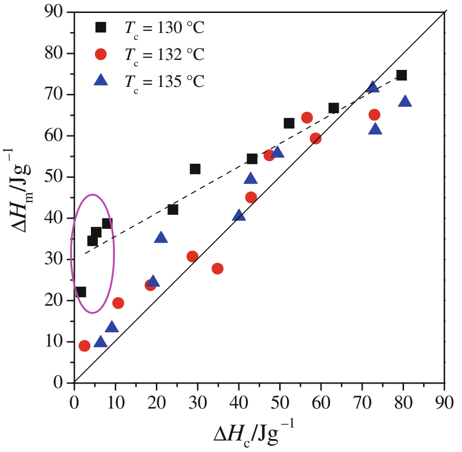

Fig. 4 The enthalpies of melting after the isotherm crystallization as a function of crystallization enthalpies determined from the crystallization isotherms

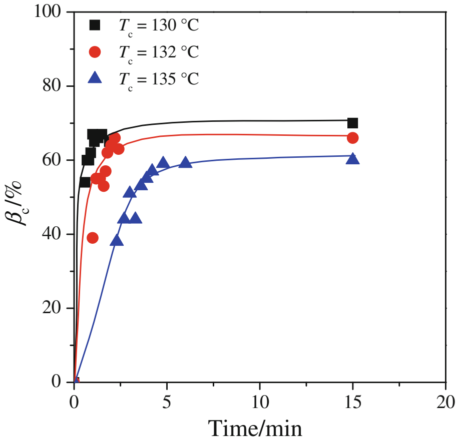

Fig. 5 The β-content during isotherm crystallization at different crystallization temperatures

($T(\beta\alpha)$) is around 140 °C [2, 28, 35]. As a consequence, the temperature range of this experimental technique is limited, but could be possibly widened by using a chip calorimeter developed by Schick and his co-workers [36, 37] in the past decades.

The melting peak of β-and α-modification separate clearly (see Fig. 3b), so the polymorphic composition can be easily calculated from their partial areas according to Eq. 5:

$$X_\alpha = \frac{U_\alpha}{M\Delta H_\alpha^0} \quad \text{and} \quad X_\beta = \frac{U_\beta}{M\Delta H_\beta^0} \tag{5}$$

X_α and X_β are the crystallinity of α- and β-phase, respectively. U_α and U_β (given in mJ) are the area under the partial melting peaks corresponding to the two modifications. M is the sample mass given in mg. We have to remark here that U_α/M and U_β/M are the ΔH_α and ΔH_β appearing in Eq. 4, therefore the β_c can be calculated as a function of conversion. The β_c values presented in Fig. 5 indicate clearly that the relative β-content changes in relatively wide range during crystallization. Moreover, we have to recall that the relative amount of β-phase decreases with increasing temperature, since the overall crystallization rate of β-iPP decreases steeply in the vicinity of $T(\beta\alpha)$. The conversion of both modifications can be calculated if $X_\alpha(t)$ and $X_\beta(t)$ is divided by the crystallinity of the corresponding modification after complete crystallization, respectively, ($X_\alpha(\infty)$ and $X_\beta(\infty)$). The obtained conversion curves of both modifications at $T_c = 135$ °C are given in

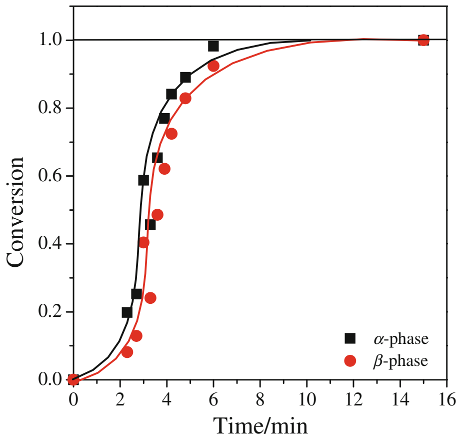

Fig. 6 Conversion curves of α- and β-modifications determined from the melting curves after isothermal crystallization steps at $T_c = 135$ °C

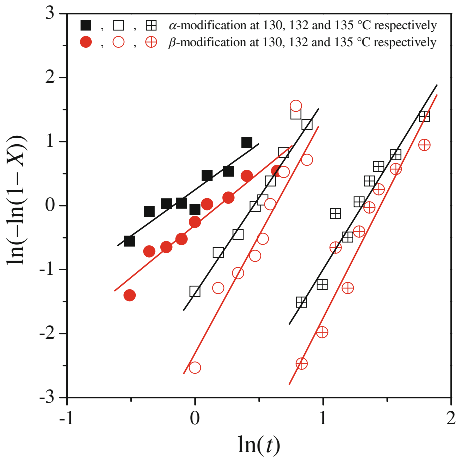

Fig. 7 Avrami plots of samples with mixed polymorphic composition crystallized at 130, 132, and 135 °C

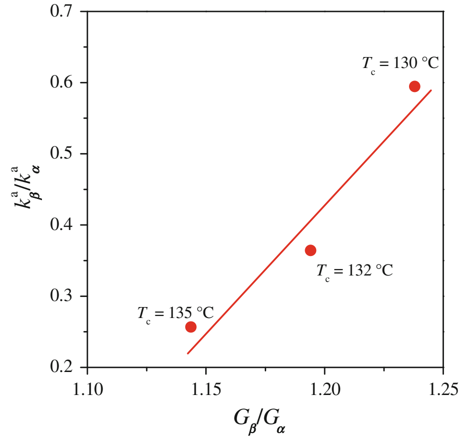

Fig. 8 The correlation between growth rate ratio of β- and α-iPP and the ratio of k^{a}_{β} and k^{a}_{α} at different temperatures

Fig. 6. Although, the curves are similar they are definitely not the same. Similar conversion curves were obtained at 132 and 130 °C as well. In addition, the difference between the conversion curves of the α- and β-modifications is larger at lower temperatures. The conversion data presented in Fig. 6 can be plotted according to Avrami equation (Eq. 2), which is represented in Fig. 7. Despite the scattering data points, they fit to straight lines. The slope and intercept of each line results in the kinetic constants of crystallization for the two modifications separately (Table 2). The results reveal that kinetic constants of crystallization are different for α- and β-iPP at all temperatures. This is the reason why a single Avrami's evaluation is not correct in the case of β-nucleating agents with dual nucleating ability resulting in the samples with mixed polymorphic composition.

The Avrami exponents and overall rate constants deduced by the above described technique are reported in Table 2. The results obtained indicate that the nucleation is athermal and spherulitic ($n \approx 3$) in the case of α-modification. The Avrami exponent of β-phase is significantly larger than that of the α-modification, indicating that the mechanism of nucleation is different. The nucleation is rather thermal and spherulitic ($n = 4$) in the case of β-form, because the chosen T_c is close to $T(\beta\alpha)$. Unfortunately, the results at 130 °C are questionable, especially the Avrami exponent, because crystallization proceeds between the isothermal and heating. This might cause the large decrease of n at 130 °C, indicating that 132 °C is the lower temperature limit in this series of experiments.

The overall rate constants of crystallization (k) can be determined from the intercept of Avrami line. The obtained ln$k$ values are presented in Table 2 as well. The two modifications develop simultaneously, β-phase grows faster compared to α-form [35]. Therefore, β-phase encapsulate

Table 2 Avrami constants and overall rate of crystallization values determined for both α- and β-modifications

	Temperature					
	130 °C		132 °C		135 °C	
	n	lnk^a	n	lnk^a	n	lnk^a
α-iPP	1.4	0.25	3.2	−1.40	3.1	−4.00
β-iPP	1.9	−0.27	4.1	−2.41	3.7	−5.36

the slowly growing α-phase and the development of α-modification stops earlier as it was shown in our previous study [38]. Consequently, the conversion curve of α-phase indicates apparently faster crystallization since the development of the α-form ends earlier in time. In other words, $X_\alpha(t)$ reach $X_\alpha(\infty)$ faster. Accordingly, the obtained k values are apparent values for both modifications (k_α^a and k_β^a). The ratio of the growth rate for two modifications (G_α and G_β) as a function of the temperature was determined earlier [35]. The G_β/G_α ratio is plotted against to k_β^a/k_α^a in Fig. 8 to check the value of the estimated k_α^a and k_β^a. The clear linear correlation proves that k_β^a and k_α^a are in connection with the growth rate, which proves that these apparent values are characteristic to the crystallization process.

The crystallization kinetics of samples with mixed polymorphic composition can be studied by WAXS technique as well, which requires fast equipment and unique experimental technique. Chen et al. [31] conducted a thorough experimental study on sheared iPP melt at 134 °C isothermally. They induced the formation of β-form by shearing or by β-nucleating agent (TMB-5) and all of their samples crystallized in mixed polymorphic structure. They recorded WAXS patterns at different times during crystallization and X_α and X_β values were obtained directly from the diffractograms. They found that Avrami exponent is around 3 in the case of sheared and nucleated samples. The results are in good agreement with the Avrami exponents determined in this study for α-iPP. However, we have to point out that the Avrami exponent for β-iPP is close to four according to our results, indicating that the β-phase is close to the upper temperature limit of its formation. The lower Avrami exponents obtained by Chen et al. [31] for the β-nucleated samples can be explained by the effect of shearing, which also promotes the formation of β-form and the shearing acts like a nucleating agent in the samples. Based on the correlation between the two techniques it can be established that the calorimetric technique presented in this study is also a reliable procedure for determination of crystallization kinetic parameters in iPP with mixed polymorphic composition.

Conclusions

Crystallization kinetics of β-nucleated iPP with mixed polymorphic composition was studied in this study. Since, the crystallization process of α- and β-iPP takes place simultaneously, the evaluation of the crystallization isotherms according to a single Avrami model is fundamentally erroneous. A novel calorimetric method (ISC technique) is reported in this study, which is able to separate the crystallization process of α- and β-modifications and allows the evaluation of the crystallization kinetics of α- and β-phases separately according to Avrami method. The results indicate clearly that the relative β-content of the sample change during crystallization. The conversion curves of α- and β-modifications can be determined and evaluated according to Avrami method and the results reveal that the crystallization is spherulitic in the case of both modifications, which is in good agreement with the previous literature. In addition, we found that the nucleation mechanism of the two phases is different according to the obtained Avrami exponents. The nucleation of the β-phase is thermal and spherulitic since the experiments introduced here were close to the upper temperature limit of formation of β-iPP. However, the nucleation of α-phase is athermal and spherulitic in the presence of active nucleating agent possessing dual nucleating ability. The obtained overall rate constants of crystallization are apparent values for both modifications and they correlate strongly with the growth rate of the modification at each T_c, thus k_α^a and k_β^a are reliable parameters.

The ISC technique reported here is capable to separate any simultaneous crystallization processes of samples with mixed polymorphic composition, if the polymorphic composition can be obtained from the melting curve after isothermal step.

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