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COMPARISON OF DIFFERENT β-NUCLEATORS FOR ISOTACTIC POLYPROPYLENE, CHARACTERISATION BY DSC AND TEMPERATURE-MODULATED DSC (TMDSC) MEASUREMENTS

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The nucleating efficiency and selectivity of different β-nucleating agents was characterised and compared by differential scanning calorimetry, (DSC) and temperature-modulated DSC (TMDSC). The nucleating agents were the calcium salts of pimelic and suberic acid (Ca-pim and Ca-sub), linear *trans*-γ-quinacridone (LTQ), a commercial nucleator NJ Star (NJS) and an experimental product (CGX-220). The efficiency and the selectivity of Ca-sub and Ca-pim are extremely high. NJS is efficient above a critical concentration, which is connected with its partial dissolution in polypropylene melt. LTQ and CGX-220 possess strong overall nucleating ability and moderate selectivity. Using TMDSC, we found that three consecutive processes take place during the heating of β-nucleated samples cooled down to room temperature: reversible partial melting of the β-form, irreversible βα-recrystallisation, and the melting of the α-modification formed during βα-recrystallisation or being present in samples prepared with non-selective β-nucleators. Melting of the α-phase contains both reversible and irreversible components.

Keywords: *calorimetry, crystallisation, efficiency, isotactic polypropylene, melting,* α*-modification,* β*-modification,* β*-nucleators, recrystallisation, selectivity, temperature-modulated DSC*

Introduction

Isotactic polypropylene (iPP) is one of the most commonly used polymers. Semicrystalline iPP is a polymorphic material, with several crystalline modifications including the monoclinic (α), trigonal (β), and orthorhombic (γ) [1] forms. Commercial grades of polypropylene crystallise essentially in the α-form. In practice, selective β-nucleators have to be introduced into the polymer for the preparation of the β-modification of iPP (β-iPP) [2]. β-iPP has several advantageous properties, e.g. high impact and tear strength, in comparison with the traditional α-form. Hence, the preparation and properties of this new type of iPP have been studied extensively in the last two decades [2]. The first effective β-nucleating agent proposed by Leugering [3] was the γ-modification of linear *trans* quinacridone (LTQ), which was later used by several research groups [2 and references therein]. We found that the Ca-salt of suberic (Ca-sub) and pimelic acid (Ca-pim) possess very high β-nucleating selectivity and efficiency [4]. Ca-pim is very similar to the two-component β-nucleating agent consisting of pimelic acid and Ca-stearate, which was first applied by Shi *et al.* [5] for the preparation of β-iPP. A new commercially available β-nucleator is N,N'-dicyclohexyl-2,6-naphthalene dicarboxamide. It is marked under the trade name NJStar NU-100 (NJS). Its β-nucleating ability was characterised by calorimetry [6–12]. The proper evaluation of calorimetric melting curves permits the exact determination of the polymorphic composition of β-nucleated iPP as a function of the type and amount of β-nucleators and the thermal condition of crystallisation. However, during calorimetric measurements one should take into account the melting memory effect of β-iPP. The melting behaviour of β-iPP depends strongly on the thermal posthistory of the samples [13, 14]. β-iPP cooled below the critical temperature (T_R^*=100°C) recrystallises into the α-modification during the partial melting of the β-phase (βα-recrystallisation), which leads to an enhanced apparent α-content determined from the melting curves. On the contrary, no βα-recrystallisation occurs during heating, and a separate β-melting peak appears on the DSC trace, if β-iPP is not cooled down below T_R^* after crystallisation. In this case, the polymorphic composition of β-nucleated samples having mixed polymorphic content can be determined from the calorimetric melting curves [13, 14].

The main goals of the present study are the determination and comparison of the efficiency as well as the selectivity of different nucleating agents by the evaluation of the melting curves of non-cooled samples crystallised under adequate circumstances using one and the

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same iPP type and methodology. We also study the influence of the nature of different β-nucleators on the βα-recrystallisation process taking place during the heating of β-iPP cooled down to room temperature. The βα-recrystallisation process can be observed directly with the aid of synchrotron radiation [15–19]. In this approach, the decrease of β-content during the heating can be followed by the determination of the *k* value introduced by Turner Jones *et al.* [20]. The drawback of this method is that the *k* value is only a semiquantitative measure of β-content. Moreover, the synchrotron radiation is a very expensive method for the routine measurements. For the studying of βα-recrystallisation, the temperature-modulated DSC (TMDSC) seems to be a useful method, because according to former observations it permits the separation of the melting and recrystallisation processes [2, 21–23]. Moreover, samples with different thermal history can be prepared directly in the calorimeter [13]. However, the phenomenon has not been studied systematically by TMDSC up to now.

Experimental

Materials

The Tipplen H-890 grade iPP homopolymer (MFR= 0.35 g/10 min at 230°C/2.16 kg) used in the study was supplied by Tisza Chemical Works (TVK, Hungary). The β-nucleators studied are listed in Table 1. We also studied a new experimental β-nucleator (CGX-220) for comparison. This product has been provided by Ciba Specialty Chemicals Inc. for the present investigations.

Table 1 List of the studied β-nucleating agents

Nucleating agent	Mark
Ca salt of suberic acid, (Ca-suberate)	Ca-sub
Ca salt of pimelic acid, (Ca-pimelate)	Ca-pim
Linear *trans* γ-quinacridone	LTQ
N'N'-dicyclohexyl-2,6-naphthalene-dicarboxamide (NJ Star NU-100)	NJS
Experimental product (CGX-220)	CG

Methods

The samples were homogenised at 220°C, and 50 rpm using a Brabender W 50 EH internal mixer. Their melting and crystallisation behaviour was studied in a Perkin-Elmer DSC-7 calorimeter at heating (V_h) and cooling rate (V_c) of 10°C min^{-1}. The samples were heated up to 220°C and held there for 5 min in order to erase their thermal and mechanical history. During non-isothermal crystallisation, the end temperature of cooling (T_R) was set to T^*_R =100°C in order to eliminate the effect of βα-recrystallisation disturbing the determination of polymorphic content. The βα-recrystallisation process was studied on samples cooled down to 25°C in a non-isothermal crystallisation step. The temperature-modulated DSC (TMDSC) melting curves of the samples crystallised at a cooling rate of V_c=10°C min^{-1} were recorded with a Universal V4.0B TA Instrument at V_h=2°C min^{-1}, ±0.3°C with 50 s modulation.

Results and discussion

The melting curves of β-nucleated iPP samples recorded after cooling to T^*_R are plotted in Fig. 1. Ca-sub and Ca-pim are extremely selective and efficient, practically only the β-modification of iPP forms in their presence in accordance with the former observations [4]. NJS is also very efficient, but it is not completely selective, since always some α-phase can be also detected in the samples. A considerable amount of α-modification was formed always as concomitant phase in the presence of LTQ and CG indicating the moderate selectivity of these nucleators. The exact determination of the β-content is difficult for the latter nucleators because the melting peaks of the α- and β-modifications overlap each other.

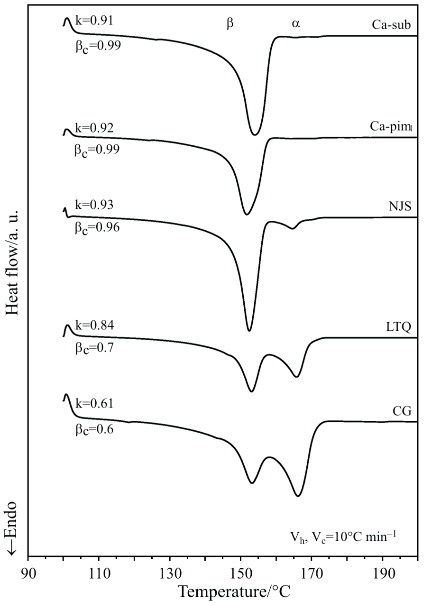

Fig. 1 Melting curves of samples containing 1000 ppm of β-nucleating agents (T_R=T^*_R=100°C)

The polymorphic composition can be estimated approximately by evaluating the peak area below the minimum values and the total peak area of the double melting peaks. The quotient of the peak areas is a semiquantitative value and is designated as relative β-content ($β_c$). The polymorphic composition of the samples was also characterized by *k* values deter-

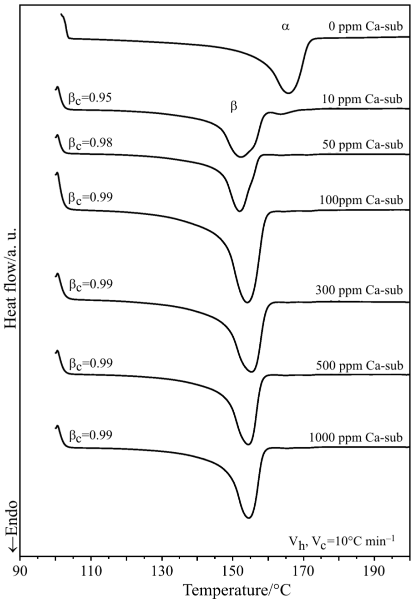

Fig. 2 Melting curves of samples containing Ca-sub in the concentration range of 10–1000 ppm; ($T_\mathrm{R}=T_\mathrm{R}^{*}=100°\mathrm{C}$)

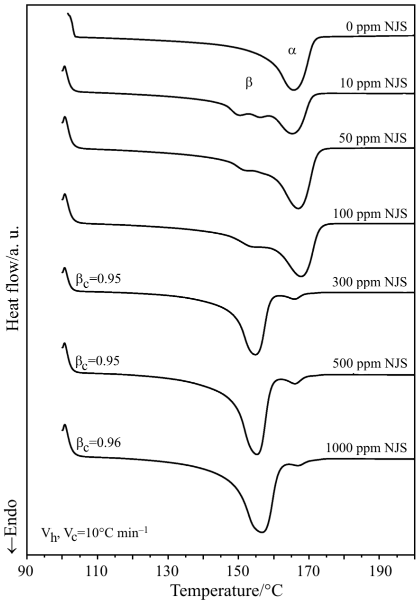

Fig. 4 Melting curves of samples containing NJS in the concentration range of 10–1000 ppm ($T_\mathrm{R}=T_\mathrm{R}^{*}=100°\mathrm{C}$)

mined from X-ray measurements by the method of Turner Jones *et al.* [20]. The β_c and k values are indicated on the melting curves in Fig. 1.

The effect of the nucleating agents on the crystallisation of iPP was studied in a wide concentration range (10–1000 ppm) in order to compare their efficiency and selectivity. Melting curves recorded in the presence of different nucleators after cooling to T_R^{*} are plotted in Figs 2–6. The highly active and selective Ca-sub and Ca-pim are efficient already in very small amounts. iPP crystallises practically exclusively in the β-form if their concentration is larger than 10 ppm (Figs 2 and 3). NJS is not efficient in small amounts. Samples rich in the β-phase form if the concentration of NJS reaches 300 ppm (Fig. 4). Kotek *et al.* [9] have found a similar critical nucleator concentration for the formation of β-iPP, but they did not give an unambiguous explanation for the phenomenon. We have found that the existence of a critical nucleator concentration is connected with the partial dissolution of NJS in the polypropylene melt. This dissolution leads to some anomalies in the crystallisation and melting behaviour of this β-nucleator. A detailed study on this phenomenon will be published in the near future. The melting

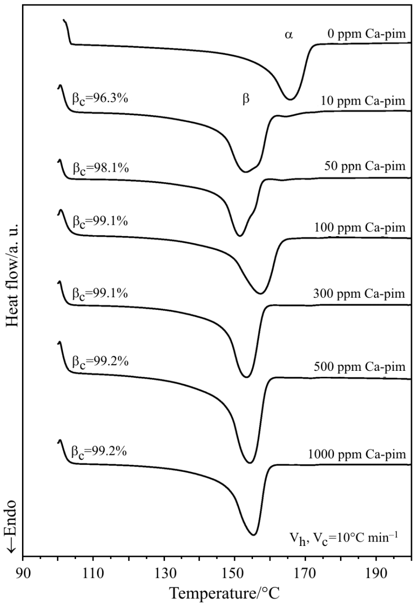

Fig. 3 Melting curves of samples containing Ca-pim in the concentration range of 10–1000 ppm ($T_\mathrm{R}=T_\mathrm{R}^{*}=100°\mathrm{C}$)

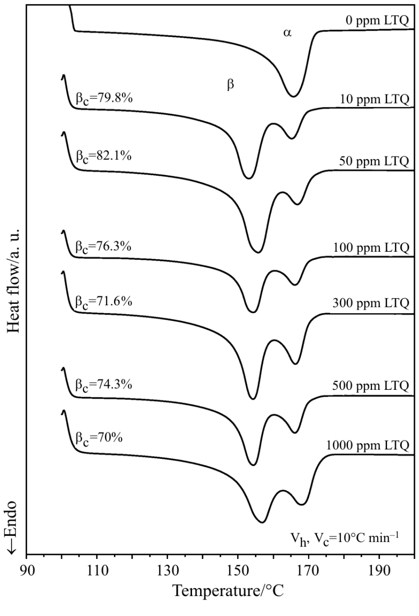

Fig. 5 Melting curves of samples containing LTQ in concentration range of 10–1000 ppm; ($T_\mathrm{R}=T_\mathrm{R}^{*}=100°\mathrm{C}$)

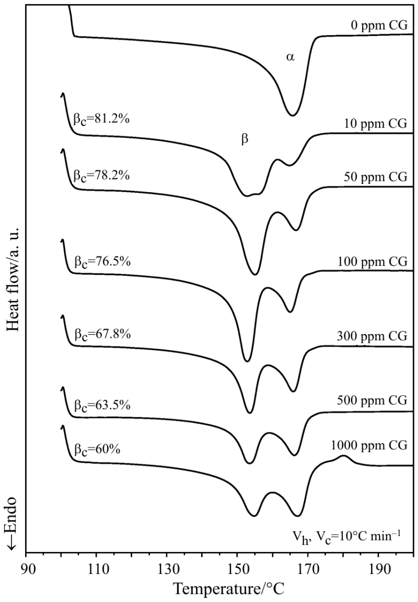

Fig. 6 Melting curves of samples containing CG in concentration range of 10–1000 ppm; (T_R=T_R^*=100°C)

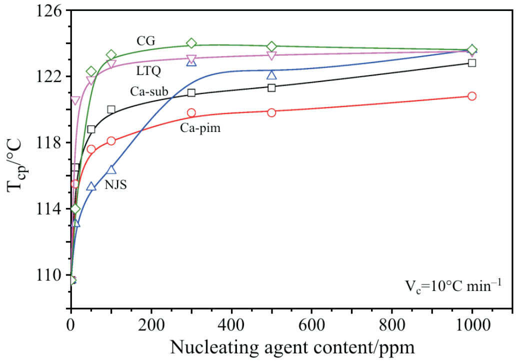

Fig. 7 Dependence of the peak temperature of crystallisation on the concentration of different β-nucleators

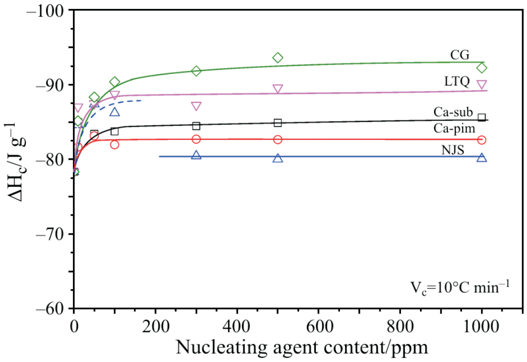

Fig. 8 Dependence of the enthalpy of crystallisation on the concentration of different β-nucleators (The subcritical concentration range of NJS indicated by dashed line)

curves reveal that NJS, LTQ and CG are not selective β-nucleators, since the presence of the α-phase can be observed in the entire concentration range used (Figs 4–6). The β-nucleators – LTQ and CG – are efficient already in very small concentrations in spite of their insufficient selectivity, which is reflected in the formation a considerable amount of the α-phase in their presence. In the case of LTQ (Fig. 5), the relative β-content has maximum of 82.1% in the low concentration range, around 50 ppm, of the nucleator. The existence of the maximum in β-content as a function of nucleator concentration agrees well with earlier observations [2, 24–26]. The maximum value of β-content in samples nucleated with CG (Fig. 6) is reached already at the lowest concentration (10 ppm). The melting curves of samples nucleated with LTQ and CG reveal that these β-nucleators possess pronounced α-nucleating effect as well.

In spite of the formation of two different polymorphic forms, the crystallisation curves show only single peak in the presence of all β-nucleators studied. This indicates that the two polymorphic modifications forming two separate phases crystallise simultaneously. The crystallisation peak temperatures (T_{cp}) and the overall enthalpy of crystallisation (ΔH_c), respectively, are plotted in Figs 7 and 8 as a function of the concentration of the nucleators. It seems that T_{cp} characterises the overall nucleating (simultaneous α- and β-nucleation) ability of the additives. It is surprising that β-nucleators with moderate selectivity (LTQ and CG) have stronger overall nucleating effect, i.e. higher T_{cp} values compared to selective nucleators. The enthalpy of crystallisation is also an average value including the crystallisation of both polymorphic forms. Figure 8 shows clearly that ΔH_c values are larger for nucleators with moderate selectivity (LTQ and CG). The ΔH_c values determined correlate well with the peak temperature of crystallisation (T_{cp}). The higher the peak temperature (or the temperature interval) of crystallisation is, the larger is the enthalpy of crystallisation (compare Figs 7 and 8). Since the α-phase possesses larger enthalpy of phase transformation (fusion or crystallisation) [14], larger α-content results in increased ΔH_c for the nucleators with moderate selectivity.

The melting curves of β-nucleated samples cooled down to room temperature are shown in Fig. 9. The samples nucleated by Ca-sub, Ca-pim and NJS have rather complicated melting curves, as a result of the superimposed traces of endothermic partial melting of the β-phase, exothermic βα-recrystallisation and endothermic melting of the α-phase formed during recrystallisation or being presented originally in samples with mixed polymorphic composition [2, 13, 14]. βα-recrystallisation is induced by a finely dispersed α-phase formed during secondary crystallisation below T_R^* within the β-phase [13, 14]. Surprisingly at this heating rate, the melting curves of iPP nucleated with LTQ and CG do not reflect the difference in the thermal history. The relative intensity of the α- and β-melting peaks of samples, which were or were not recooled,

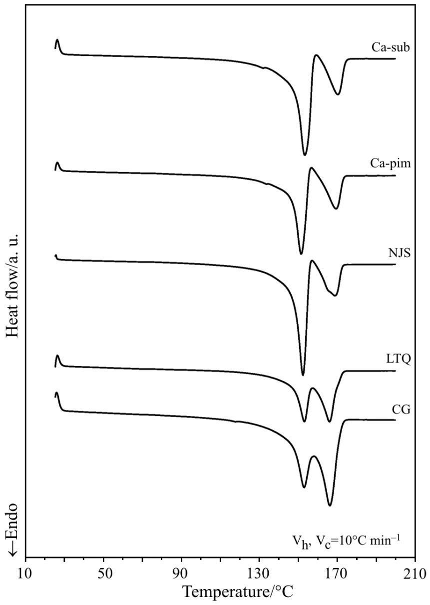

Fig. 9 Melting curves of recooled samples containing β-nucleating agents in 1000 ppm (T_R=RT)

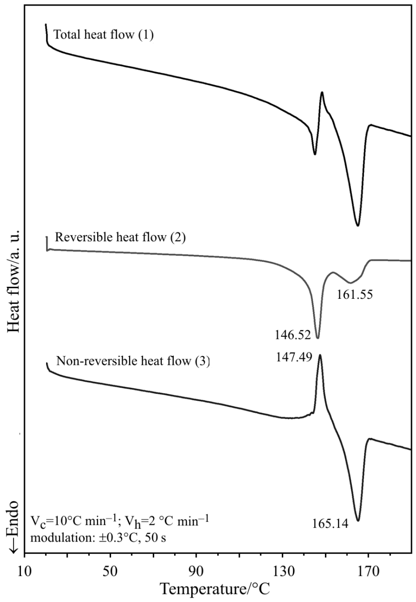

Fig. 10 TMDSC curves of β-nucleated samples containing 10 ppm Ca-Sub. The samples were cooled to room temperature

respectively, are practically identical (compare Figs 1 and 9). However, the βα-recrystallisation process in the presence of these β-nucleators can be detected at low heating rate V_h=2°C min^{-1}. The explanation of this unexpected behaviour of the β-phase induced by β-nucleators with moderate selectivity needs further, more detailed study.

The above mentioned three processes reflected in the total heat flow recorded during heating (Fig. 10, curve 1) can be partly separated by using the TMDSC technique [21–23]. The total heat flow has a reversible and an irreversible component. The partial melting of the β-phase is a reversible process with peak temperature of 146.5°C (Fig. 10 curve 2). On the contrary, the exothermic βα-recrystallisation is an irreversible process with a peak temperature of 147.5°C (Fig. 10, curve 3). It is well discernible in Fig. 10 that the temperature lag between the reversible melting of β-phase and the irreversible βα-recrystallisation is very small (about 1°C), i.e. the melted β-phase immediately recrystallises into the α-phase. Melting of the α-phase contains both reversible and irreversible components. Similar results were obtained with Ca-pim, NJS, LTQ and CG.

The peak temperatures of irreversible βα-recrystallisation, T_c(βα), as a function of the concentration of the different β-nucleators are shown in Fig. 11. The peak temperature of the reversible melting of the β-phase is plotted *vs*. nucleator concentration in Fig. 12. It was proved earlier that the tendency to βα-recrystallisation depends on the structural stability of the β-phase [2, 13, 14]. Hence, the samples crystallised at lower temperature (at larger super-

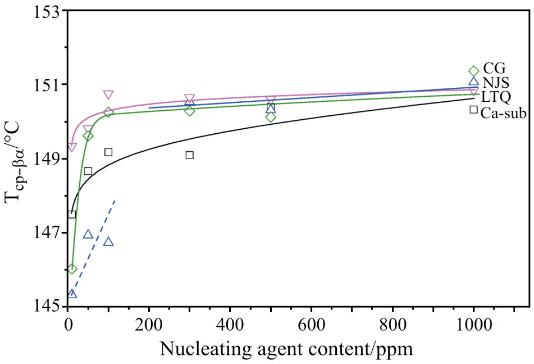

Fig. 11 Dependence of the peak temperature of irreversible βα-crystallisation on the concentration of different β-nucleators (The subcritical concentration range of NJS indicated by dashed line)

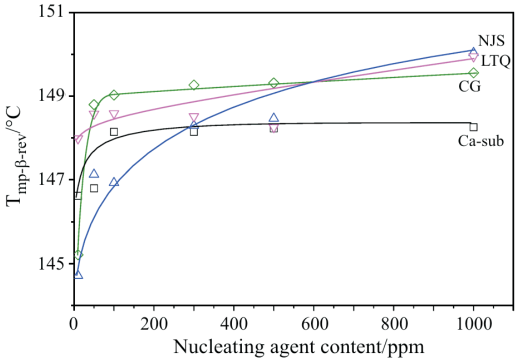

Fig. 12 Dependence of the peak temperature of reversible melting of the β-phase on the concentration of different β-nucleators

cooling) have less structural stability and enhanced tendency to recrystallisation. The surprising fact that the samples crystallise in the presence of β-nucleators with moderate selectivity have higher melting temperature ($T_{\text{mp-}\beta\text{-rev}}$) and recrystallise at higher temperature ($T_{\text{cp-}\beta\alpha}$) is in good correlation with the higher crystallisation temperatures presented in Fig. 7.

Conclusions

The β-nucleating efficiency and selectivity of Ca-suberate and Ca-pimelate are extremely high in a wide concentration range. NJS is an efficient β-nucleating agent above a critical concentration, but it is not completely selective. The existence of a critical nucleator concentration is connected with the partial dissolution of NJS in the polypropylene melt. LTQ and CG possess moderate selectivity and strong overall nucleating efficiency. Pronounced melting memory effect can be observed in the presence of Ca-sub, Ca-pim and NJS. Using temperature-modulated DSC, we found that three consecutive processes take place during the heating of β-nucleated samples cooled down below 100°C: reversible partial melting of the β-form, irreversible βα-recrystallisation, and the melting of the α-modification formed during βα-recrystallisation or being present in samples prepared with non-selective β-nucleators. Melting of the α-phase contains both reversible and irreversible components.

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