Thermochimica Acta, 205 (1992) 235–243
Elsevier Science Publishers B.V., Amsterdam

Effect of β-nucleator content on the crystallization and melting behaviour of β-crystalline phase polypropylene

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(Received 22 October 1991)

Abstract

The effect of β-nucleator content on the isothermal and non-isothermal crystallization of β-phase polypropylene was studied using differential scanning calorimetry (DSC). The melting curves of such samples under isothermal and non-isothermal crystallization conditions were also measured by DSC. The results obtained indicated that the samples containing 0.005% of β-nucleator have the highest β-form crystallinity as measured from the apparent enthalpy of fusion, the highest melting temperature of the β-form and the lower α-form crystallinity. Measurement by wide angle X-ray diffraction shows that the samples crystallized in the presence of a higher content of nucleator have lower relative intensities of the (301) diffraction peak, which signifies the lower order of packing of β-form crystals along the chain direction.

INTRODUCTION

Isotactic polypropylene (PP) is known to exhibit several crystalline forms. These are the monoclinic α-form, the hexagonal β-form and the triclinic γ-form. The α-form is the most stable and the most prevalent one. The β-form is occasionally found in commercial polypropylene, but usually at a low level. In order to obtain the β-form with high purity, various additives, the so-called β-nucleators, are used [1–5]. The relative amount of the β-form is usually described in terms of the K value, which is defined as

$$K = \frac{\mathrm{H}(300)}{\mathrm{H}(300) + \mathrm{H}(110) + \mathrm{H}(040) + \mathrm{H}(130)} \qquad (1)$$

where $H(110)$, $H(040)$ and $H(130)$ are the heights of the three strong equatorial α-form peaks (110), (040) and (130), respectively, and $H(300)$ is the height of the strong single β peak (300) [6].

In a previous paper we studied the effect of β-nucleator content c on the K value for isotactic polypropylene crystallized over a range of 60–140°C using the wide angle X-ray diffraction (WAXD) technique [4]. It was

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0040-6031/92/$05.00

found that K increases with increasing c, then reaches a maximum value of 0.93–0.94 around 0.005 wt%, which is similar to the results of Moos and Tilger [2]; however, less ordered β-form crystals, as evidenced by the decrease in relative intensity of the β (301) diffraction, were formed for samples containing higher contents of β-nucleator.

In the present paper, the effect of β-nucleator content on isothermal crystallization kinetics, the melting temperature T_{m_β} and the apparent enthalpy of fusion of the β-form ΔH_{m_β} are investigated for PP crystallized under both isothermal and non-isothermal conditions using differential scanning calorimetry. The origin of the unusual dependence of T_{m_β} and ΔH_{m_β} on c and the mechanism of β-phase crystallization of PP are discussed.

EXPERIMENTAL

Isotactic polypropylene SOF (viscosity average molecular weight 4.0×10^5) supplied by Xiangyang Chemical Works was used in this study. The β-nucleator is a mixture of pimelic acid and calcium stearate (1:1 by weight). In order to prepare PP samples containing different amounts of nucleator, pellets of PP were premixed with a weighed amount of nucleator and then extruded, operating at a melt temperature of 200°C. The quenched pelletized extruder blend, denoted as the β-PP sample, was used for crystallization and melting behaviour study.

A Perkin-Elmer DSC-2C differential scanning calorimeter equipped with a thermal analysis data station was used for thermal measurement in a flowing nitrogen atmosphere. The samples (about 7 mg) were heated or cooled at a scanning rate of 10°C min^{-1} for samples crystallized under isothermal conditions and at a scanning rate of 20°C min^{-1} for samples crystallized under non-iosthermal conditions. The melting temperature or the crystallization temperature T_c was obtained from the maximum of the endotherm or the minimum of the exotherm, respectively. The apparent enthalpies of the α- or β-form were calculated from the area of the respective endothermic peaks. Indium was employed to calibrate the temperature scale and the heat of transition.

WAXD experiments were conducted with a Rigaku Geigerflex Model D/max rA X-ray diffractometer with Ni-filtered Cu Kα radiation.

RESULTS

Isothermal crystallization

It has been proved by several investigations that the experimental data for the isothermal crystallization of PP can be described by the Avrami equation

$$1 - X_c = \exp(-Kt^n) \qquad (2)$$

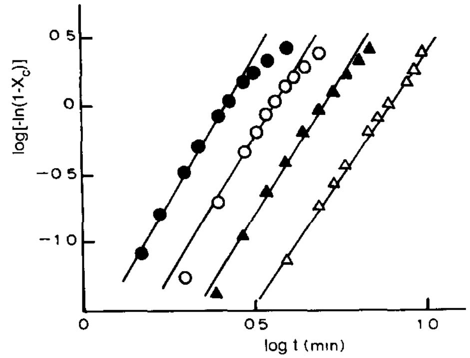

Fig. 1. Avrami plots for polypropylene samples crystallized at 130°C containing 0.0001 (△), 0.0005 (▲), 0.005 (○) and 0.1 (●) wt% of β-nucleator.

where Xc is the weight fraction of material that crystallizes at time t, K is the crystallization rate constant, and n is the Avrami exponent. Usually, eqn. (2) can be written as follows

$$\log[-\ln(1-X_c)] = n \log t + \log K \tag{3}$$

where a plot of $\log[-\ln(1-X_c)]$ vs. $\log t$ will give a straight line of slope n and intercept $\log K$.

When the calorimetric method is used to study the isothermal crystallization kinetics, the weight fraction of crystallized material at any time t can be evaluated by taking the ratio of the heat evolved up to that time to the total heat released as represented by

$$X_c = \frac{\Delta H_t}{\Delta H_\infty} = \frac{\int_0^t \mathrm{d}H/\mathrm{d}t\ \mathrm{d}t}{\int_0^\infty \mathrm{d}H/\mathrm{d}t\ \mathrm{d}t} \tag{4}$$

Typical double logarithmic plots according to eqn. (3) for PP containing 0.0001-0.1 wt% of nucleator and crystallized at 130°C are shown in Fig. 1. It can be seen from Fig. 1 that all curves except that for PP containing 0.0001 wt% of nucleator deviate from a straight line. The curvature of these curves increases with increasing c. The half-time of crystallization $t_{1/2}$, the melting temperature of the β-form T_{m_β}, the apparent enthalpy of fusion of the β-form ΔH_{m_β} and the apparent enthalpy of fusion of the α-form ΔH_{m_α}, as deduced from the DSC traces, are summarized in Table 1. The data in Table 1 indicates a non-monotonic dependence of all these values on c, and the maxima of these values appear at around 0.005 wt%.

The degree of crystallinity of the semi-crystalline polymer can be measured by means of the calorimetric method using

$$X_c = \frac{\Delta H}{\Delta H_u} \tag{5}$$

TABLE 1

Effect of β-nucleator content on thermal quantities for polypropylene crystallized at 130°C

β-Nucleator content (wt%)	$t_{1/2}$ (min)	T_{m_β} (°C)	ΔH_{m_β} ($J\ g^{-1}$)	ΔH_{m_α} ($J\ g^{-1}$)	X_β (%)	X_α (%)
0.0001	7.12	152.5	73.5	5.5	37.7	2.6
0.0005	4.58	153.4	76.3	3.2	39.1	1.5
0.005	3.28	153.7	78.4	3.6	40.2	1.7
0.1	2.38	153.0	76.0	4.9	39.0	2.3
0.5	1.87	153.4	71.9	7.5	36.9	3.6

where ΔH is the apparent enthalpy of fusion of the semi-crystalline sample as deduced from the DSC trace and ΔH_u is the total melting enthalpy for the completely crystallized material. It was reported that at a low heating rate, after initial melting of the β-form, recrystallization in the α-form occurs, giving rise to a small exotherm, which is followed by the melting of the original α-form and the newly formed α-phase. At a high heating rate, recrystallization in the α-form will be suppressed, and in this case only eqn. (5) can be used to estimate the degrees of crystallinity of the β-form and α-form in the samples.

The β–α recrystallization tendency of the rather pure β-form obtained by isothermal crystallization is very small when melting starts from T_c. For example, the exothermic peak of β–α recrystallization was not observed even at low heating rate (2.5°C min^{-1}) for PP containing 0.0005 and 0.5 wt% of nucleator (Fig. 2). However, for a sample containing 0.5 wt% of nucleator three endothermic melting peaks, attributed to melting of the β-form, the α-form originally present and the recrystallized α-form, were observed as shown in Fig. 2, curve a. The last of the peaks is rather small, therefore it can be neglected. In Fig. 2, curve b there is no peak corresponding to the melting of the α-phase formed during β–α recrystallization. Consequently, the degrees of crystallinity (in Table 1) were estimated by comparing the observed melting enthalpies with those presented in the literature ($\Delta H_{u_\alpha} = 209$ J g^{-1} [7], $\Delta H_{u_\beta} = 195$ J g^{-1} [3]) for the completely crystalline polymorphs (by eqn. (5)).

When the quantity $\log[-\ln(1-X_c)]$ is plotted against $\log t$ for the samples containing 0.0001 wt% of nucleator crystallized at 124–128°C and for the samples without nucleator also crystallized at 124–128°C, a linear trend is observed. The values of $t_{1/2}$ and the Avrami exponent n are summarized in Table 2. The values of n are practically independent of T_c and an increase in the value of n from 2.3–2.4 for α-phase crystallization to 3.5–3.6 for β-phase crystallization may be noticed.

For α-phase crystallization of PP, if sporadic nucleation and three-dimensional growth are assumed, the Avrami exponent should be 4; with the

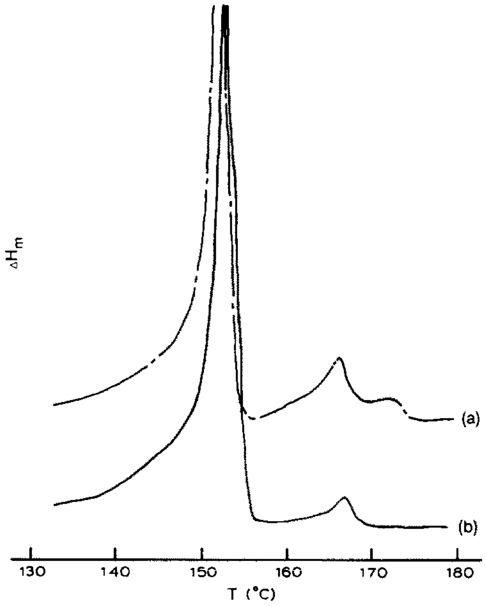

Fig. 2. Melting curves for polypropylene samples crystallized at 130°C containing (a) 0.5 and (b) 0.0005 wt% of β-nucleator; heating rate 2.5°C min^{-1}.

addition of the nucleator the nucleation mechanism may change from sporadic to predetermined nuclei, and then the value of n must decrease from 4 to 3. This is contradicted by the results summarized in Table 2, as the value of n increases from 2.4 to 3.6 instead of decreasing. Although sporadic nucleation is seldom encountered in the crystallization of real semi-crystalline polymers, it is also difficult to explain why the n value

TABLE 2

Effect of addition of 0.0001 wt% of β-nucleator on the crystallization kinetics data for isothermal crystallization of polypropylene

β-Nucleator content (wt%)	T_c (°C)	n	$t_{1/2}$ (min)
0	124	2.38	4.67
	125	2.36	6.23
	126	2.36	8.12
	127	2.34	9.90
	128	2.44	12.42
0.0001	124	3.65	1.65
	125	3.56	2.06
	126	3.60	2.64
	127	3.58	3.17
	128	3.63	4.22

TABLE 3

Effect of β-nucleator content on thermal quantities and K values for polypropylene crystallized at a cooling rate of 20°C min^{-1}

β-Nucleator content (wt%)	T_c (°C)	ΔH_c ($\mathrm{J\,g^{-1}}$)	T_{m_β} (°C)	ΔH_{m_β} ($\mathrm{J\,g^{-1}}$)	ΔH_{m_α} ($\mathrm{J\,g^{-1}}$)	K	S
0	104.4	83.1					
0.0001	111.3	83.2	146.9	60.0	27.7	0.64	0.15
0.0005	112.8	81.8	148.6	68.7	19.2	0.90	0.15
0.005	114.5	85.7	150.2	74.3	16.3	0.92	0.14
0.1	116.2	83.8	149.1	73.4	16.8	0.94	0.084
0.5	116.7	83.2	150.4	72.8	17.4	0.93	0.067

increases with the addition of nucleator, even for cases where predetermined nuclei existed in the commercial PP.

Non-isothermal crystallization

The effect of c on T_c and the heat of crystallization ΔH_c for β-phase samples crystallized at a cooling rate of 20°C min^{-1} were also studied using DSC. The results are summarized in Table 3. The rapid increase of T_c with increasing c signifies the effectiveness of the pimelic acid–calcium stearate mixture as a nucleator. The melting temperatures and apparent heats of fusion, as deduced from melting curves, are also listed in Table 3. The dependence of T_{m_β} on T_c is rather strange because an increase of T_{m_β} with increasing T_c is observed only at nucleator contents below 0.005 wt%.

As concerns the experimental results presented in Table 3, the fact that the sample containing 0.005 wt% of nucleator has a maximum value of ΔH_c and ΔH_{m_β} must also be emphasized.

The WAXD patterns of these samples are presented in Fig. 3, from which the K value and the relative intensity of the β (301) diffraction peak, as expressed by the S value, are calculated. These are also listed in Table 3. The high K values indicate the high purity of the β-form in these samples. However, the results contradict the relatively high values of ΔH_{m_α} in Table 3. Our previous studies revealed that significant amounts of α-phase are formed during β–α recrystallization for samples crystallized at a cooling rate of 20°C min^{-1}. Therefore, the value of ΔH_{m_α} in Table 3 does not coincide with the degree of crystallinity of the α-form in the samples. The relative intensity of the β (301) peak is expressed by the S value, where

$$S = \frac{\mathrm{H}(301)}{\mathrm{H}(300) + \mathrm{H}(301)} \qquad (6)$$

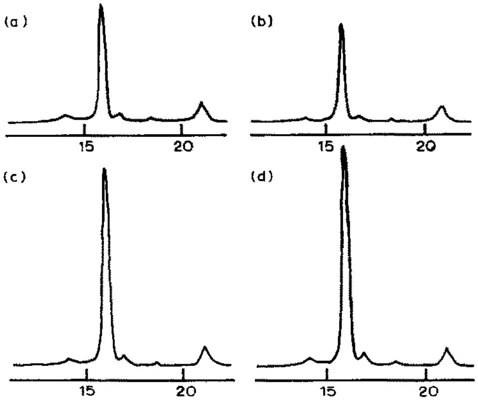

Fig. 3. WAXD patterns for polypropylene samples containing (a) 0.0005, (b) 0.005, (c) 0.1 and (d) 0.5 wt% of β-nucleator, crystallized under non-isothermal conditions.

and $H(300)$, $H(301)$ are the heights of the two strong β-form peaks (300) and (301), respectively.

The meaning of S is as follows. The molecular chains of the β-form are packed in a hexagonal lattice. In this lattice the plane (300) is parallel to the chain direction and therefore the intensity of the (300) plane is proportional to the fraction of chains which are packed in the hexagonal lattice, irrespective of their order of packing along the chain direction. The (301) plane intersects the plane of the chains and the intensity of the (301) plane relates to the order of chain packing along the chain direction.

It can be noticed from Table 3 that the decrease of S with increasing c starts from c above 0.005 wt%, which coincides with the results of Table 1. From the data listed in Tables 1 and 3, it can be concluded that the PP samples crystallized in the presence of an amount of nucleator above a critical content c' (0.005 wt%) have less ordered structure than those crystallized in the presence of a lower content of nucleator ($c \leqslant c'$). Consequently the former samples have lower T_{m_β} and lower ΔH_{m_β} values than the latter. This is also the reason why T_{m_β} ceases to increase with increasing T_c for samples containing 0.1–0.5 wt% of nucleator.

DISCUSSION

In order to explain the dependence of T_{m_β} and $\Delta H_{m\beta}$ on c, it should be assumed that a critical content c' is required for inducing the crystallization of the β-form with the maximum β-form content and more ordered structure, as evidenced by the high value of S. Although a β-nucleator content as low as 0.0001 wt% or 5.4×10^{-9} mol cm^{-3} is capable of inducing the β-phase PP, this is not the optimum condition. The raising of c from c' to (20–100)c' increases the rate of crystallization so much that the less ordered β-phase (low value of S) is formed. It is expected that the latter will have lower $T_{m\beta}$ and ΔH_{m_β} than the more ordered β-form.

Investigations of the mode of action and the molecular and crystallographic characteristics of foreign substances capable of inducing the crystallization of polymers have been discussed in several papers. In a classical work, Binsbergen, following the earlier conclusions of Beck [8], established that the best nucleators have a chemical and crystallographic structure in which both polar and non-polar parts coexist, the latter being in contact with the polymer melt [9]. However, epitaxy was rejected as a possible mechanism. The analysis of the data pointed strongly towards non-specific polymer–substrate relationships thought to be incompatible with epitaxy. In particular, (i) homologous series of substrates have similar nucleating power toward the same polymer, and (ii) a single substrate may be efficient toward polymers of different chemical nature. The studies of Wittmann and Lotz have shown that the nucleating activity may result from epitaxy of the polymer onto the apolar part of the nucleating agent and physical interaction of epitaxial character is responsible for the activity of the nucleator [10,11].

Although the mechanism of nucleation and growth for the crystallization of PP in the presence of pimelic acid–calcium stearate is not clear, it is most probable that specific physical and/or chemical interaction of epitaxial character is responsible for the activity of a specific β-nucleator. In particular, (i) calcium stearate is an inert substance and pimelic acid is a weak α-nucleator, whereas their mixture is an effective β-nucleator, (ii) the optimum content of our β-nucleator is 0.005 wt%, but no nucleation activity was observed at such low content for any α-nucleator, and (iii) homologous series of dibasic acids, when combined with calcium stearate, have completely different nucleation power. For instance, an adipic acid–calcium stearate mixture does not show any activity towards inducing the β-phase.

CONCLUSIONS

The crystallization of isotactic polypropylene in the presence of pimelic acid–calcium stearate mixture as β-nucleator shows unusual behaviour. The isothermal crystallization deviates from the Avrami equation except for PP containing 0.0001 wt% of β-nucleator. The deviation increases with increasing nucleator content. The addition of 0.0001 wt% of nucleator raises the Avrami exponent from the original value of 2.4 to 3.6, which is impossible to explain by the current theory of crystallization.

The maximum values of T_{m_β} and ΔH_{m_β} were obtained at nucleator content around 0.005 wt% for samples crystallized under both isothermal and non-isothermal conditions. This is understandable, because the less ordered β-phase is formed for samples containing a much higher amount of nucleator and crystallized at a much higher rate, as revealed by the WAXD patterns.

ACKNOWLEDGEMENTS

This work was supported by the Academia Sinica Selected Research Program and the National Natural Science Foundation of China.

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