

The effect of a β -nucleator on the crystallization and melting behavior of ethylene/propylene random and block copolymers

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Abstract

The effect of a bicomponent β -nucleator on the non-isothermal and isothermal crystallization of ethylene/propylene random and block copolymers, containing small amounts of ethylene and having nearly the same molecular weights, was studied using differential scanning calorimetry (DSC). The results obtained indicated that the β -nucleator is effective in inducing the β -form and in reducing undercooling in both copolymers. However, it is more effective in the E/P block copolymer than in the E/P random copolymer. The dependence of the relative content of the β -form, as expressed by the K value, on crystallization temperature for the block copolymer is similar to that for polypropylene, i.e. the K value starts to decrease significantly only above 135°C. However, for the random copolymer it starts to decrease at a much lower crystallization temperature.

INTRODUCTION

In 1980, we found accidentally that in the presence of pimelic acid, special grade isotactic polypropylene, containing substantial amounts of calcium stearate, crystallized predominantly as the β -crystalline form [1]. Systematic research was then carried out in this laboratory leading to the first discovery of a bicomponent β -nucleator, consisting of an organic dibasic acid, such as pimelic acid, azelaic acid, etc., and an oxide, a hydroxide or a salt of a Group IIa metal, such as magnesium, calcium, strontium or barium [2, 3]. A bicomponent β -nucleator for polypropylene has various advantages over β -nucleators reported previously in the literature, such as the quinacridone dye permanent red E3B (E3B) [4–7]. Firstly, the bicomponent β -nucleator is colorless, while E3B is red. Secondly, the β -form of isotactic polypropylene (β -PP) obtained by the crystallization of commercial polypropylene in the presence of a bicomponent β -nucleator has a much higher impact resistance than that obtained using other β -nucleators [2]. Thirdly, the β -PP

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TABLE 1

Physical characteristics of ethylene/propylene random and block copolymers used in this study

Sample code	Type	Ethylene content/wt. %	MFI ^a /dg min ⁻¹	Mn × 10 ⁴	Mw × 10 ⁴	Mz × 10 ⁴	T _g ^b /°C
R21	Random	2.1	9.6	4.29	24.3	88.7	8.0
B56	Block	5.6	9.7	4.78	25.2	91.6	13.0

^a Melt flow index, measured with a melt indexer according to ASTM-D1238. ^b Measured by Rheovibron DVV-II EA at 110 Hz.

obtained using the bicomponent β -nucleator tends to form numerous microvoids during tensile deformation [8]; therefore a new type of microporous polypropylene membrane can be prepared simply by uniaxial or biaxial drawing of β -PP. However, the impact strength of conventional PP at low temperature cannot be improved by α - β transformation, because the glass transition temperatures of the α - and β -forms, which determine the low-temperature brittleness, are identical [9–11].

The mechanical properties of PP can be modified by making random or block copolymers with ethylene. If only a small amount of the ethylene unit is incorporated, the copolymer retains the stiffness and the tensile strength of PP, but has improved mechanical properties at low temperature. We have reported that the β -form of E/P random or block copolymer also has improved mechanical properties over the α -form.

In the present paper, the effect of a bicomponent β -nucleator, pimelic acid-calcium stearate, on the isothermal and non-isothermal crystallization of E/P random and block copolymers, with small ethylene contents and nearly equal molecular weights, is measured using differential scanning calorimetry. The effect of crystallization temperature on the relative content of the β -form and the melting behavior of the β -form samples has also been investigated.

EXPERIMENTAL

Materials and samples

Two ethylene/propylene random and block copolymers, having nearly the same melt-flow indices and molecular weights, supplied by Tokuyama Soda Co., Ltd., were used in this study. Their characteristics are summarized in Table 1. The bicomponent β -nucleator used in the sample preparation was a mixture of equal amounts of pimelic acid and calcium stearate. In order to prepare samples which preferentially crystallize in the β -form, pellets of the copolymer were premixed with 0.1 wt.% of β -nucleator and then ex-

truded, operating at a melt temperature of 200°C. The resulting pelletized extruded blend was designated the β -form sample.

Films for a wide-angle X-ray diffraction study were prepared by compression molding. Pellets of the copolymer sample placed between two aluminum foils were premelted at 200°C, then pressed in a laboratory press equipped with heating plates. The films were then crystallized by cooling in air.

Instrumentation and experiments

The thermal measurements were carried out in a Perkin-Elmer DSC-2C differential scanning calorimeter, equipped with a thermal analysis data station. The instrument was calibrated with high-purity metal specimens according to standard procedures.

Wide-angle X-ray diffraction experiments were conducted with a Rigaku Geigerflex Model D/max-rB X-ray diffractometer with Ni-filtered Cu K α radiation. The relative content of the β -form in the specimen was measured in terms of the K value, which is defined as [12]

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

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

RESULTS

Non-isothermal crystallization

The wide-angle X-ray diffraction (WAXD) patterns of the α - and β -forms of E/P random copolymer R21 and block copolymer B56, melt-crystallized at a cooling rate of 20°C min⁻¹, are shown in Fig. 1. The formation of the rather pure β -form in sample β -B56, similar to that in propylene homopolymer, is clearly demonstrated. However, the sample β -R21 contains substantial amount of α -form, as shown by the respective α -form (110), (040) and (130) peaks. The relative amounts of the β -form as expressed by the K value for β -R21 and β -B56 are 0.73 and 0.89, respectively. It is clear that the β -nucleator is more effective in inducing the β -form in E/P block copolymer than in E/P random copolymer.

The melting curves of the four samples melt-crystallized at a cooling rate of 20°C min⁻¹ are given in Fig. 2. The absence of the melting peak of polyethylene, located in the vicinity of 130°C and the main peak temperature of 160°C, comparable to that of polypropylene for the α -B56 sample, reveals that the copolymer B56 consists of propylene block and E/P

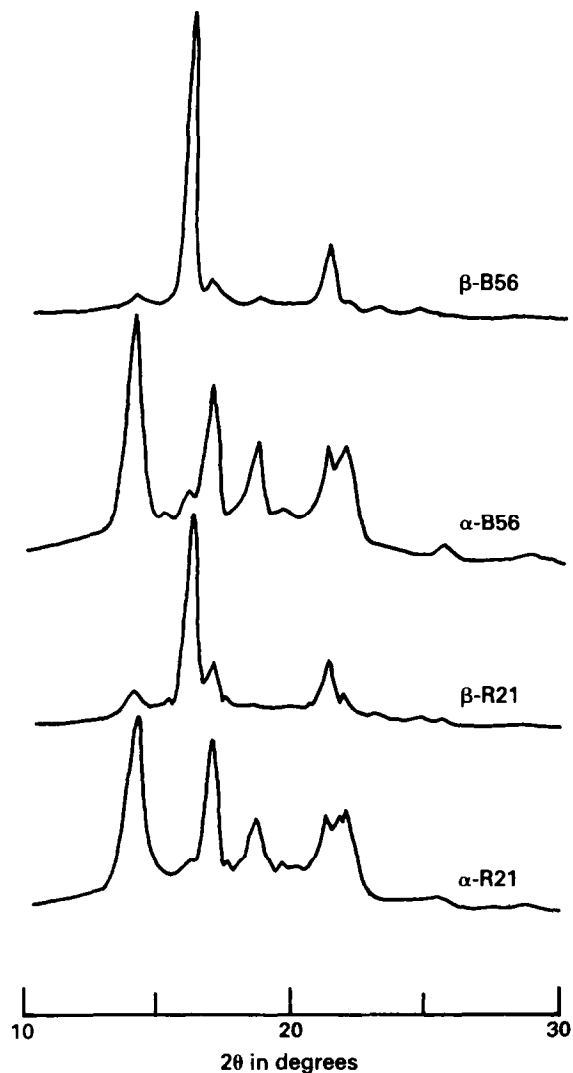


Fig. 1. WAXD patterns for the ethylene/propylene copolymers melt-crystallized at a cooling rate of $20^{\circ}\text{C min}^{-1}$.

elastomer block. For β -B56, the large endotherm peak at 150°C is due to the melting of the β -form of the propylene block, and the endotherms at 163 and 168°C are due to the melting of the original and recrystallized α -forms of the propylene block, respectively. The lower melting temperature and lower T_g , as seen from Tables 1 and 2, signify that α -R21 is a random copolymer. Correspondingly, the melting temperature of the β -form of R21 is also lower. Evidence from WAXD indicates the existence of more α -form crystals in β -R21. As expected, the ratio of the area under the α -form melting peaks to the area under all the melting peaks for β -R21 is also larger than that for β -B56, which agrees with the WAXD results.

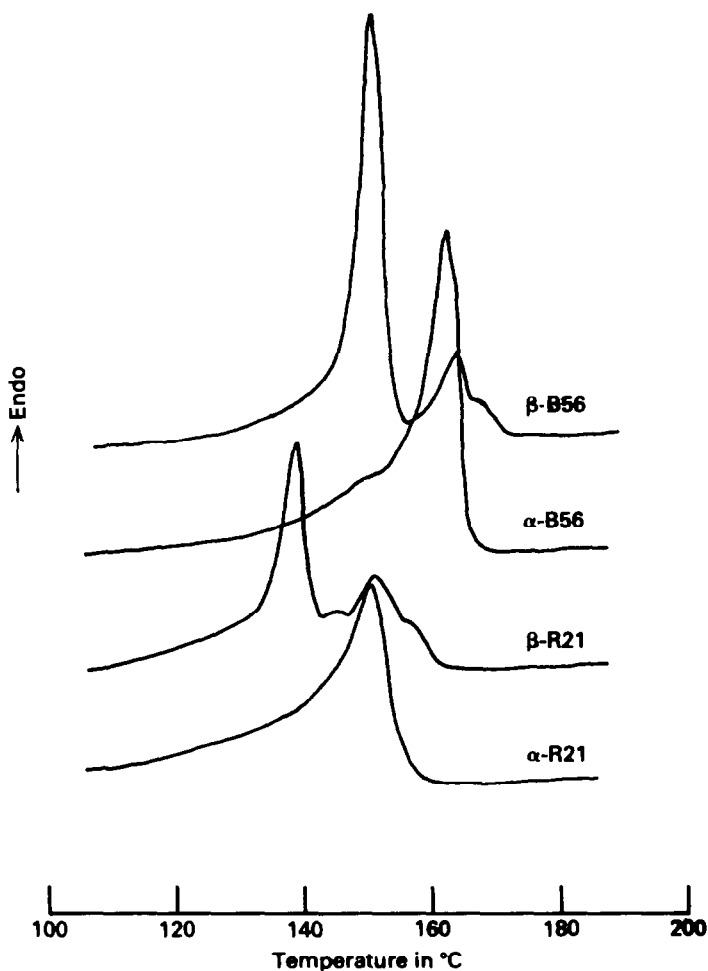


Fig. 2. DSC melting curves of the ethylene/propylene copolymers melt-crystallized at a cooling rate of $20^{\circ}\text{C min}^{-1}$.

The effectiveness of a bicomponent β -nucleator for crystallization of E/P random and block copolymers was tested by measuring their crystallization temperature T_c in DSC. The T_c of each sample, measured at a fixed cooling rate of $20^{\circ}\text{C min}^{-1}$, is shown in Table 2. The nucleation ability towards a particular polymer may be expressed by $\Delta T = T_c - T_{co}$, where T_c and T_{co} are the crystallization temperatures for the sample crystallized with and without nucleator, respectively. The ΔT_c values measured for R21 and B56 are 4.7 and 6.6°C , respectively, which means that the bicomponent β -nucleator is more effective for the block copolymer B56 rather than that for the random copolymer R21.

TABLE 2

Effect of β -nucleator on thermal parameters for E/P random copolymer R21 and block copolymer B56, crystallized at a cooling rate of $20^\circ\text{C min}^{-1}$

Sample	Nucleator content/ wt.%	Crystalline form	$T_c/^\circ\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$T_m/^\circ\text{C}$	
					β -form	α -form
R21	0	α	103.7	77.0		150.1
	0.1	β	108.4	70.6	139.3	151.4
B56	0	α	113.0	84.8		161.8
	0.1	β	119.6	77.7	150.4	162.7

Isothermal crystallization

Figure 3 shows the variation of half-time of crystallization $t_{1/2}$, measured by DSC, with T_c for R21 and B56, with and without β -nucleator. It is clear from Fig. 3 that the β -nucleator decreases the undercooling markedly for both R21 and B56, as the addition of the β -nucleator reduces $t_{1/2}$ significantly. In all cases the $t_{1/2}$ value of B56 is much lower than that of R21. Thus, the incorporation of a small amount of ethylene sequence randomly in the copolymer reduces the rate of crystallization.

In order to study the influence of T_c on the relative proportion of the β -form for R21 and B56 over a wider T_c range, the sample sandwiched between two copper foils was dipped into a silicone oil bath, thermostated to $200 \pm 1^\circ\text{C}$ for melting and then transferred to another silicone oil bath, maintained at a selected temperature between 60 and 140°C for crystallization.

Figure 4 shows the effect of crystallization temperature on the relative proportion of the β -form, as expressed by the K value, for the E/P random and block copolymers R21 and B56, respectively. It can be seen from Fig. 4 that for B56 the K value lies between 0.89 and 0.94 for a T_c range of 60 – 130°C , and it starts to decrease significantly only above 135°C , similar to the behavior of the propylene homopolymer. For R21, however, the K value starts to decrease at a much lower temperature.

Figure 5 shows the effect of T_c on the melting behavior of sample β -B56. For T_c values between 60 and 100°C , three endothermic melting peaks, similar to the DSC melting endotherms for the β -form of propylene homopolymer, were observed. By investigating the influence of the crystallization temperature and the heating rate during DSC measurements, and by partial scanning of the multiple melting endotherms, we have demonstrated in a previous paper[13] that the first two peaks are caused by melting of the original β_1 -phase and subsequent recrystallization to a more stable structure (β_2) during scanning. The last peak can be ascribed to the melting

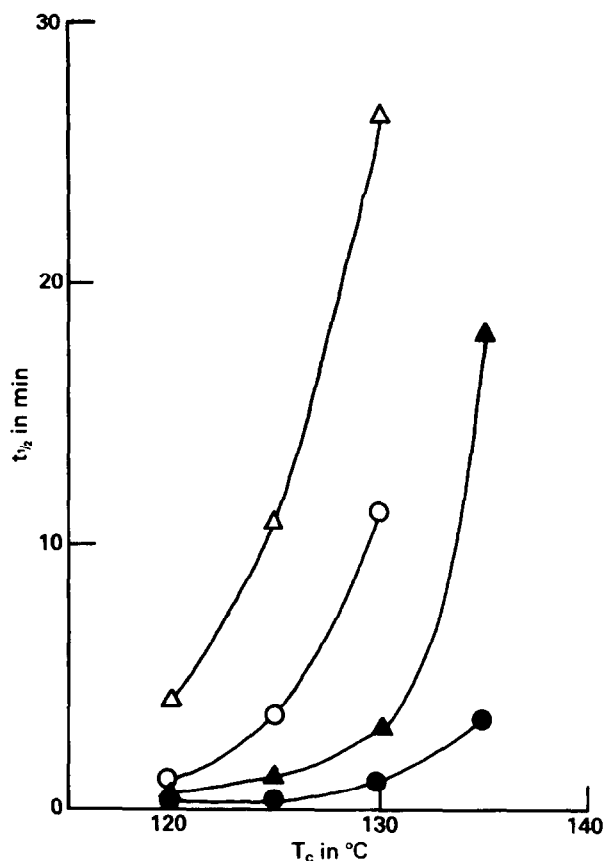


Fig. 3. The variation of the half-time of crystallization $t_{1/2}$ with the crystallization temperature T_c for samples α -R21 (Δ), β -R21 (\circ), α -B56 (\blacktriangle), and β -B56 (\bullet).

of the original and recrystallized α -phase crystals. The relative proportions of these three forms depend on the melting temperature T_m of the original β_1 -form, if the heating rate is fixed at $20^\circ\text{C min}^{-1}$. The lower the T_m of the original β_1 -form, the higher the rate of crystallization, and the larger the melting peaks of the β_2 -form and the α -form. For a T_c between 120 and 140°C , only two endothermic peaks, referring to the melting of the β - and α -forms respectively, were observed. The β -phase formed at a T_c of between 120 and 140°C has a melting temperature comparable to that of the recrystallized β_2 -form and should, thus, be ascribed to the β_2 -phase.

Figure 6 shows the effect of T_c on the melting behavior of sample β -R21. For T_c between 60 and 80°C , three endothermic melting peaks, similar to the DSC melting endotherms for β -B56, were observed. These three peaks can also be referred to the melting of the original β_1 -phase, the recrystallized β_2 -phase and the α -phase. For a T_c of 100°C , the relatively small melting peak of recrystallized β_2 -phase is superimposed on the large melting peak of

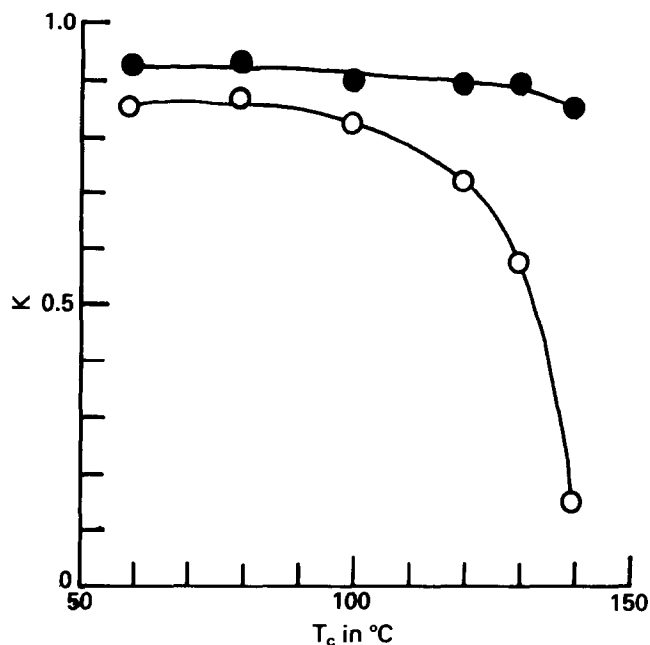


Fig. 4. The effect of crystallization temperature on the K value for β -R21 (○) and β -B56 (●) on quenching in silicone oil.

the original β_1 -phase and appears as a shoulder. For a T_c above 100°C , the β -form peak decreases rapidly and the α -form peak increases rapidly with increasing T_c , which coincides with the rapid decrease of the K value with increasing T_c for $T_c > 100^\circ\text{C}$.

DISCUSSION

In order to obtain the β -form with high purity, the nucleation and growth rates of the α - and β -forms must be controlled in such a way that the nucleation and growth rates of the α -forms are minimized. The growth rates of the α - and β -forms as a function of temperature have been measured by Padden and Keith [14], by Lovinger et al. [15] and by our group [3]. Our recent results show that the rates of growth of the α - and β -forms are equal at 140°C . Above 140°C , the rate of growth of the α -form is higher than that of the β -form. Therefore, predominantly β -form cannot be obtained by melt-crystallization of polypropylene at temperatures above 140°C . This explains why the K value decreases significantly at T_c values above 135 – 140°C . Below 140°C , the growth rate of the β -form is higher, which means that the β -form will predominate, if nucleation of the β -form is much higher than that of the α -form. Nucleation of the β -form is much more rare in a bulk sample than that of the predominant α -form. The nucleation of a bicomponent β -nucleator increases the nucleation of β -form such that preferential nucleation of the β -form results.

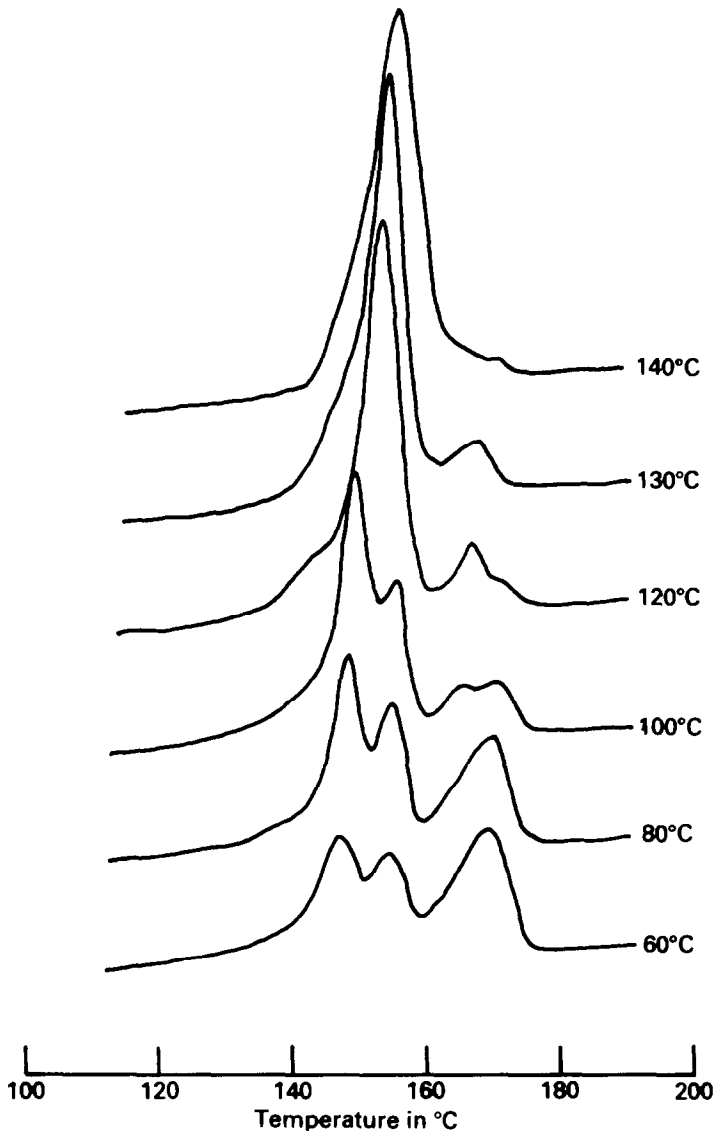


Fig. 5. The effect of crystallization temperature T_c (indicated on the curves) on the DSC traces for β -B56 samples quenched in silicone oil.

In order to clarify the mechanism of the nucleation of the β -form by pimelic acid–calcium stearate, it must be noted that pimelic acid is a weak α -nucleator with a melting point of 103–105°C; and that calcium stearate and other compounds of Group IIa metals are solid over the whole crystallization temperature range of polypropylene. It is most probable that the primary nuclei for the β -form is the liquid pimelic acid, absorbed in or complexed with the active surface of calcium stearate.

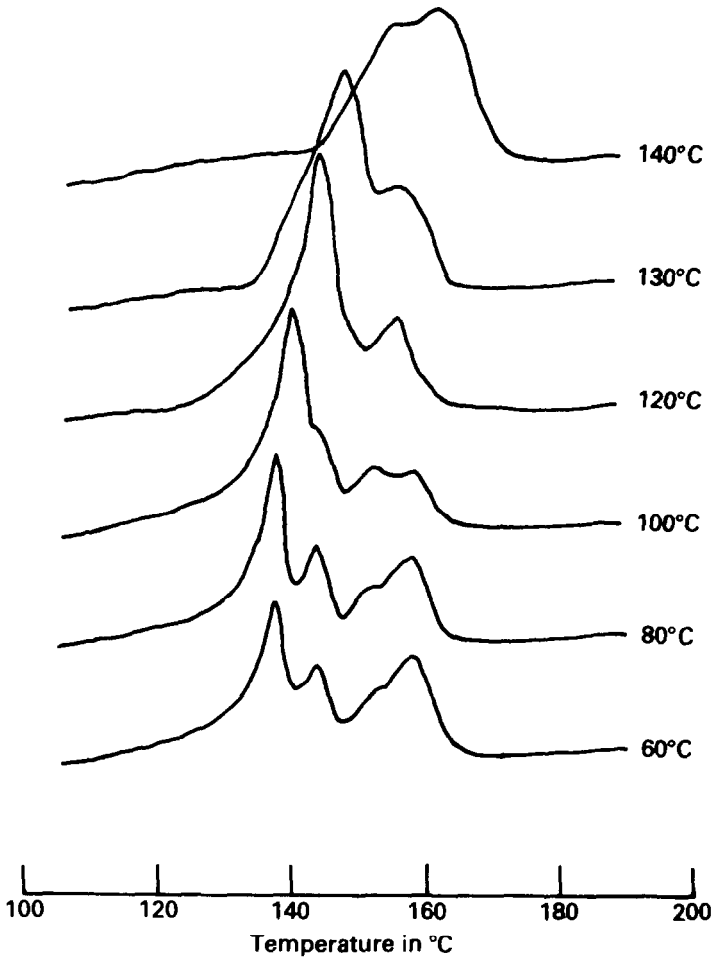


Fig. 6. The effect of crystallization temperature T_c (indicated on the curves) on the DSC traces for β -R21 samples quenched in silicone oil.

The rapid increase in the density of the α -nuclei with T_c may happen at $T_c \leq 105^\circ\text{C}$ because pimelic acid freezes at $103\text{--}105^\circ\text{C}$. As we have indicated previously, the K value for polypropylene, crystallized by quenching in silicone oil at T_c below $100\text{--}110^\circ\text{C}$, may be overestimated, because our condition for PP crystallization in silicone oil cannot ensure the fast cooling of the sample to the pre-determined temperature [16]. The argument and result detailed above coincide with the fact that only nuclei formed between 100 and 130°C will form β -form spherulites, as first indicated by Turner-Jones et al. [12].

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