

MELTING BEHAVIOR OF LOW ETHYLENE CONTENT POLYPROPYLENE COPOLYMERS WITH AND WITHOUT NUCLEATING AGENTS*

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ABSTRACT

The melting behavior of polypropylene (PP) and low ethylene content polypropylene copolymer with and without nucleating agent samples crystallized under both isothermal and non-isothermal conditions were studied by Differential Scanning Calorimeter (DSC) and X-ray diffraction. Multiple melting behavior were observed depending on the existence of nucleating agent and crystallization conditions. The observed phenomena have been discussed by the effect of nucleating agent on perfection of crystal and the melting and recrystallization of imperfect crystal to a more perfect crystal during the heating process of samples.

INTRODUCTION

The phenomenon of multiple melting endotherms exists for most crystalline polymers^[1]. Such multiple melting peaks have also been observed in polypropylene (PP) crystallized from melt. The appearance of this phenomenon has been studied by several workers^[2-12] and attributed to such factors as different crystal structure^[3,13,14], different crystal size^[5], and reorganization and perfection during heating process.

There are at least three types of crystal form of PP crystalline structure. The α form is the primary and the most stable crystalline phase, it can easily be obtained by crystallization from melt or solution. Recently, two limiting modification of α form, α_1 and α_2 , which can be obtained by different thermal treatment, have been reported^[8-12,22]. The α_1 form, obtainable by rapid crystallization from the melt, is characterized by a random distribution

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of up and down chain packing like that described for the space group $C_{2/c}$. The α_2 form, obtainable by annealing at relatively higher temperature, is characterized by a well defined deposition of up and down helices, as in the space group $P_{2/c}$. It was reported that the multiple melting behavior may be attributed to the recrystallization of less ordered α_1 form to the more ordered α_2 form^[9 10].

With some special nucleating agents or thermal treatment, the β form of PP crystal can be formed^[15 16]. This crystal form has the melting temperature around 415–425K^[17 18]. With a certain heating rate, the transformation of β form to the α form may occur. This transformation must occur through a melt recrystallization process at temperature above the β form melting point since two unit cells are so different. Once this transformation takes place, the multiple melting peaks will be observed. Under some crystallization conditions, the presence of γ form in PP and especially in PP random copolymers have been observed^[19 20]. The thermal behavior of this form has also been studied by some workers^[19 21].

The low ethylene content polypropylene copolymers are commercially important for their high impact resistance. For these materials, the addition of nucleating agent is a useful method to tailor the stiffness and toughness of the materials and to shorten the molding cycle time. In spite of the practical significance of these copolymers, there are only a few reports concerning their structure and properties. In this paper, the observation of multiple melting behavior of the low ethylene content polypropylene copolymers with and without nucleating agents have been reported and the effect of nucleating agent and thermal conditions on the melting behavior of these systems have been studied.

EXPERIMENTAL

The pure polymer materials used in this work were supplied by Jingshan Chemical Company in powder form without antioxidant additives. Their ethylene contents which were determined by IR and ^{13}C -NMR spectra as described in previous paper^[23], and the results were shown in Table 1. The nucleating agent is talc (300 mesh) which was supplied from Shandong Jiexian Talc Factory.

A Perkin-Elmer Differential Scanning Calorimetry (DSC-2C) was used for thermal analysis. Each sample was heated up to 500K at a heating rate of 40K/min and kept at this temperature for 10 minute to erase any previous

thermal history. Non-isothermally crystallized sample was cooled from 500K to 300K at various cooling rates and then heated at various rates to obtain the melting endotherms (In order to obtain the cooling rate as high as 80K/min, the intracooler II was used). The isothermal crystallization samples were prepared by rapidly cooled from 500K to 405K on a hot stage to crystallize for 2.5 hours. The melting endotherms were obtained by heating at 10 K/min. Sample weight is about 10mg. The measurement was carried out under nitrogen atmosphere. The temperature was calibrated against the melting temperature of standard reference materials.

Table 1 Samples and their characteristics

Samples	Description	Ethylene Content	<i>M. I.</i>
		(mol %)	(g/10min.)
PP	PP Homopolymer		2.9
EPR1	PP Random Copolymer	3.34	1.8
EPB1	PP Block Copolymer	5.61	3.4

Wide angle X-ray diffraction (WAXD) measurements were conducted on a D/Max X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation at 30kV and 30 mA.

RESULTS AND DISCUSSION

The melting behavior of isothermally crystallized PP copolymer samples with and without nucleating agent at heating rate of 10 K/min are represented by the DSC curves shown in Fig. 1. The observed peaks are labelled as m_1 , m_2 and m_3 corresponding to their ascending order of appearance with temperature for different samples. These peaks appeared at different temperatures. From the curves of isothermal crystallized samples of random copolymer with and without nucleating agent, three melting endotherm peaks can be observed. The peak m_1 , which appears at a lower temperature, is very broad and not notable. The phenomenon similar to the observation of Mabilon et al.^[21] is concerned to the melting of the γ form of PP crystal. It has been reported that there is γ form of PP crystal in this kind of copolymers^[19, 21]. According to Turner-Jones^[19], the development of γ form is favored by very low supercooling. In our thermal treatment, the isothermal crystallization temperature (405K) is very close to the melting point of random copolymer ($T_m = 415\text{K}$), so that the formation of γ form of PP

crystal is possible. In order to prove the existence of the γ form in these copolymers, X-ray diffraction patterns were taken (shown in Fig. 2). The X-ray diffraction pattern of random copolymer sample EPB1 shows a small peak at $19.9^\circ(2\theta)$, which has been confirmed in literature, is related with the γ form of PP crystal. That means the γ form exactly exists in these random

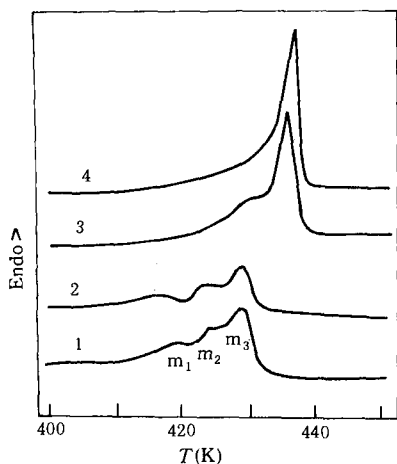


Fig. 1 DSC thermograms of samples after isothermally crystallized at 405K for 3 hours and then heated at a rate of 10K/min.

- | | |
|----------|------------|
| 1. EPB1; | 2. EPB1+N; |
| 3. EPB1; | 4. EPB1+N. |

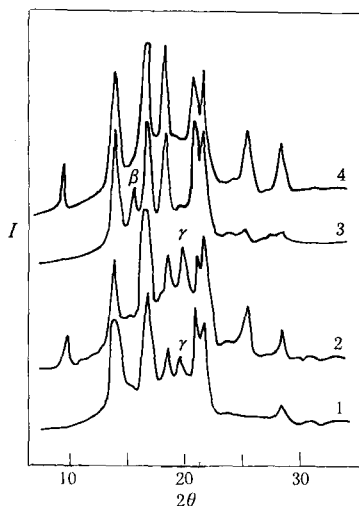


Fig. 2 X-Ray diffraction patterns of samples isothermally crystallized at 405K for 3 hours.

- | | |
|----------|------------|
| 1. EPB1; | 2. EPB1+N; |
| 3. EPB1; | 4. EPB1+N. |

copolymer samples. The relatively smaller intensity of the peak at $19.9^\circ(2\theta)$ implied that only a small portion of γ form exists in these samples. The contents of γ form increased with the addition of nucleating agent.

X-ray diffraction patterns of these samples, also show that the α form of PP crystal is a main existing crystal form. The double melting peaks of m_2 and m_3 must be concerned to the α form.

The DSC curve of isothermally crystallized PP block copolymer without nucleating agent shows a weak melting peak at 420K, which is corresponding to the melting point of β form of PP crystal^[17,18]. From the X-ray diffraction pattern of this sample (Fig. 2), we can find a small peak at $16.1^\circ(2\theta)$. This reflection peak is related to the β form of PP crystal^[13]. Thus, the X-ray result confirmed the existence of β form in isothermally crystallized PP block copolymer without nucleating agent. From the X-ray diffraction results, we

can also find that the reflection peak corresponding to β form is more evident than the melting peak of β form showing in the DSC curve in this sample. This phenomenon may account for the recrystallization of the β form to the α form of PP crystal during the melting of β form, the exotherm of the recrystallization may reduce the endothermic peak of the β form. For the

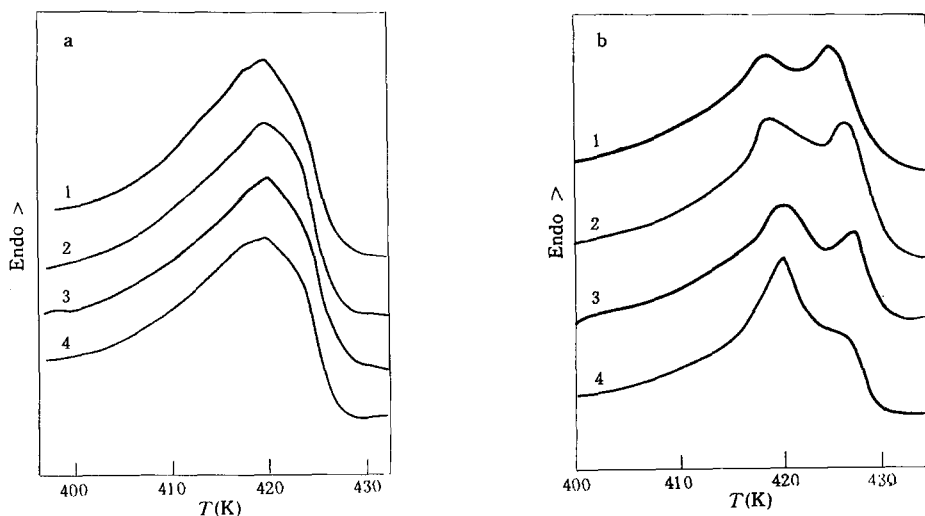


Fig. 3 DSC thermograms of non-isothermally crystallized samples at heating rate of 5K/min. Curves 1,2,3 and 4 correspond to cooling rate 80, 40, 20 and 5 respectively.

a. EPR1;

b. EPR1+N

sample of PP block copolymer with nucleating agent, the β form endotherm trace was not observed, and the reflection peak at $16.1^\circ(2\theta)$ in X-ray diffraction pattern did not appear. This indicates that the nucleating agent used is not favorable to the formation of β form in the PP block copolymer. In the studied sample, the ethylene content was small and we did not observe the melting endothermic peak of PE crystal at about 400K.

The DSC results of non-isothermally crystallized samples are shown in Fig. 3, Fig. 4 and Table 2. In Fig. 3a, we can find the sample of PP random copolymer without nucleating agent shows a broad endotherm peak with a shoulder at about 415K. The location of the peak and shoulder did not change with the variation of cooling rate. However, for this copolymer with nucleating agent, the DSC heating traces show a different thermal behavior, two distinct endotherm peak can be observed and their location and relative area change with the cooling rate (Fig. 3b).

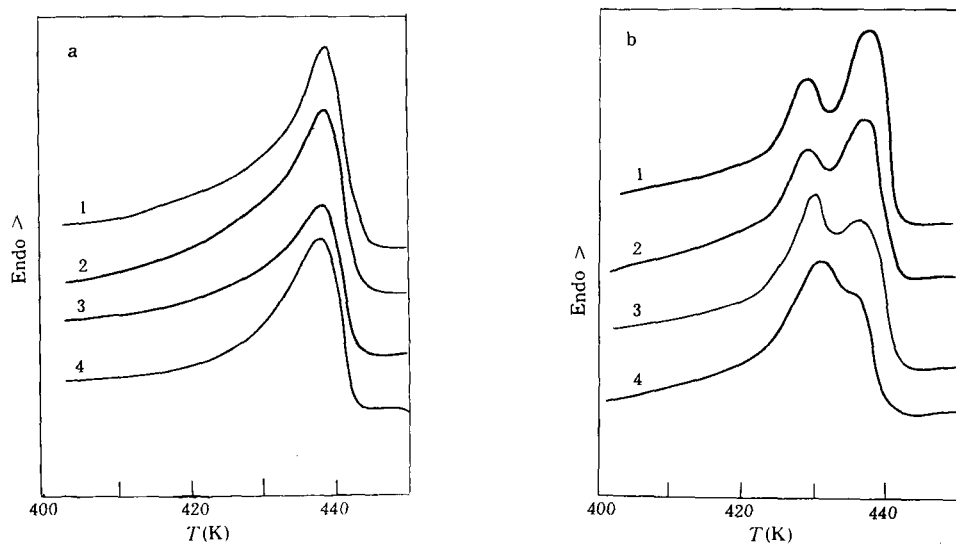


Fig. 4 DSC thermograms of non-isothermally crystallized samples at heating rate of 5K/min. Curves 1,2,3 and 4 correspond to cooling rate 80,40,20 and 5 respectively.
a. EPB1; b. EPB+N

In Fig. 4, similar melting behavior of the PP block copolymer with and without nucleating agent are also observed. The DSC curves show one main melting peak with a weak shoulder trace in PP block copolymer without nucleating agent, and two distinct melting peaks in this copolymer with nucleating agent. Their variation trends of the location and relative area are similar to the random copolymer.

Table 2 Effect of cooling rate on the melting temperature of non-isothermally crystallized PP copolymer with and without nucleating agent

Cooling rate K/min	EPR1	EPR1+N		EPB1	EPB1+N	
80	418.7	414.0	423.9	438.9	427.5	435.7
40	418.7	414.3	423.5	438.4	427.8	435.9
20	418.6	414.8	423.7	437.8	428.8	434.9
5	418.3	418.4	424.0	437.8	431.1	435.8

The effect of cooling rate on the location and relative area of the melting

peaks of PP copolymers with nucleating agent is apparent as shown in Fig. 3b and Fig. 4b. With the increasing cooling rate, the low melting peak shifted to lower temperature and the fractional area of higher melting peak increased. When the cooling rate was small enough, we could only observe a low melting peak with a shoulder of the high melting peak. For the PP copolymer without nucleating agent (Fig. 3a, Fig. 4a), the location and shape of the melting endotherm peak almost did not vary with the change of the cooling rate. From these results, it appears that the melting behavior of PP copolymer samples with nucleating agent crystallized at non-isothermal condition is more complicated than these copolymers without nucleating agent crystallized at the same condition.

As described above, two melting peaks can be observed during heating of PP copolymer after non-isothermal crystallization. Comparing these DSC curves with the thermograms of the isothermal crystallization sample, the trace of the melting peak of β form and γ form of PP crystal has not been observed. The X-ray analysis also confirmed that the α form is a dominant crystal form from nonisothermal crystallization of PP copolymer samples. For the multiple melting peaks of PP crystal, it has been explained as a contribution from the different crystal form, different size of the crystal or recrystallization and perfection during heating. In this case, the contribution of the β and γ crystal form can be ruled out, thus these double melting peaks may only contribute from the imperfect α form of the PP crystal affected by nucleating agent and thermal history which may recrystallize and perfect during the heating process.

In PP copolymer with nucleating agents, the rapid heterogeneous nucleation rate of PP crystallization may give a large amount of imperfect α crystal form (smaller and more irregular spherulites have been observed in these samples)^[24]. When these samples were heated at a slow heating rate, the imperfect crystal could easily melt at relative low temperature and recrystallize to transform to a relative perfect crystal having a higher melting temperature, thus an apparent double melting peak as shown in DSC curves. For PP copolymer samples without nucleating agents, the slow nucleation rate may form more perfect α crystal with a small amount of imperfect crystal and the melting and recrystallization during the heating process is not so evident to show double melting peaks. In nonisothermal crystallization process, the cooling rate also affect the perfection of the crystal. With the increasing of the cooling rate, the content of the imperfect crystal may

increase and its melting and recrystallization at lower temperature become easy and the content of perfect crystal having higher melting temperature obtained from recrystallization during the heating process may also increase. Thus, we can observe that the low melting peak shifts to lower temperature and the fraction area of the high melting peak increases.

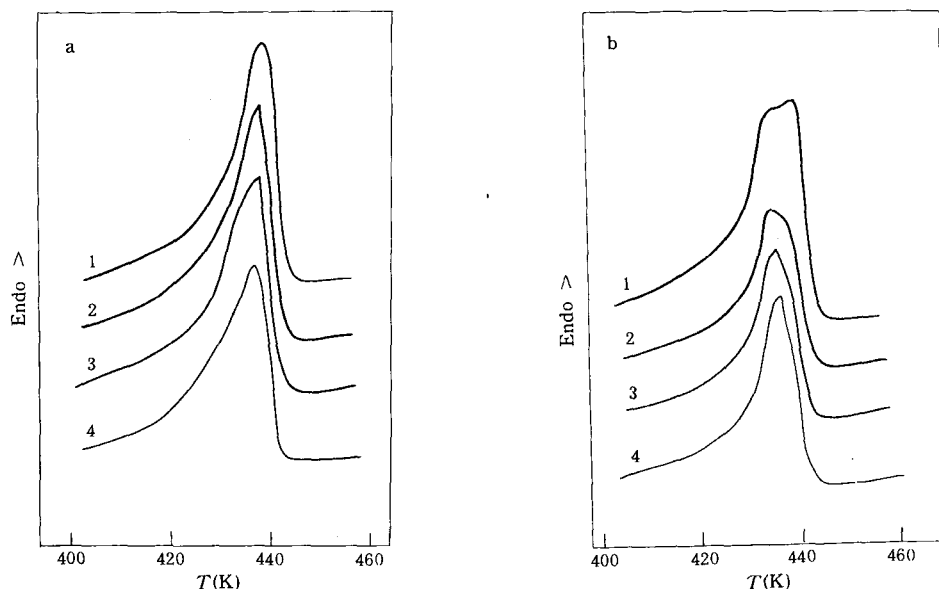


Fig. 5 DSC thermograms of non-isothermally crystallized samples at heating rate of 5K/min. Curves 1, 2, 3 and 4 correspond to cooling rate 80, 40, 20 and 5 respectively.
a. PP; b. PP+N

In the PP homopolymer with the nucleating agent, the very weak double melting peak traces have been observed when the cooling rate is 80K/min. Below this cooling rate, a single high melting peak could be observed as the PP homopolymer without nucleating agent (Fig. 5). From these results, we can conclude that the effect of the nucleating agent on the melting behavior of PP homopolymer is not so obvious as its effect on the PP copolymer. As we know, the molecular chain structure of the PP homopolymer is more regular than the molecular chain structure of PP copolymer. For this reason, the crystallization of PP homopolymer is easier than PP copolymer and its crystal structure may be more perfect than the crystal structure of PP copolymer. During the same crystallization condition, the addition of heterogeneous nucleating agent may not greatly change the perfection of the

crystal of PP homopolymer. When the cooling rate is high enough, the small amount of the imperfect crystal exist and its transformation to a more perfect crystal form can be detected (Fig. 5b).

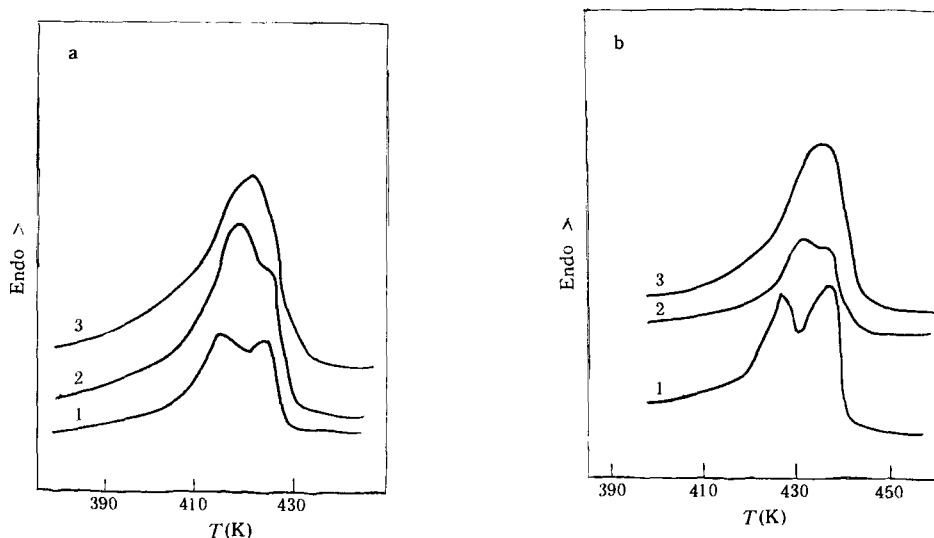


Fig. 6 DSC thermograms of non-isothermally crystallized samples at cooling rate of 40K/min and then heated at various rate. Curves 1, 2 and 3 correspond heating rate 5, 10 and 20 respectively.

a. EPR1+N b. EPB1+N

Fig. 6 shows the effect of heating rate on the melting behavior of non-isothermally crystallized samples of PP copolymer with nucleating agent. From the endotherms of these samples, we can find that the double peaks become apparent with the decreasing of heating rate. This is also consistent with the transition of imperfect crystal to more stable perfect crystal. In the opinion of Guerra et al.^[9], the melting process is fast and recrystallization is slow. When the heating rate is slow, the time is long enough to let the recrystallization take place and lead to the formation of perfect crystal with a higher melting temperature. Thus, the double peak shape of melting endotherm can be observed.

Key words:

Melting behavior; Crystal form; DSC; PP copolymer; Nucleating agent

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