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### Non-Isothermal Crystallization Behaviors of Isotactic Polypropylene with and without 1,3:2,4-Bis(3,4-Dimethylbenzylidene) Sorbitol as a Nucleating Agent

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## NON-ISOTHERMAL CRYSTALLIZATION BEHAVIORS OF ISOTACTIC POLYPROPYLENE WITH AND WITHOUT 1,3:2,4-BIS(3,4-DIMETHYLBENZYLIDENE) SORBITOL AS A NUCLEATING AGENT

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*1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (DMDBS) is the third-generation sorbitol-based nucleating agent for isotactic polypropylene (iPP). In this study, the non-isothermal crystallization behaviors of iPP with and without DMDBS as a nucleating agent were investigated by means of a differential scanning calorimeter (DSC), and the Caze method was used to analyze the non-isothermal crystallization kinetics. The results show that the addition of DMDBS can increase the crystallization peak temperature ( $T_p$ ) of iPP greatly under the same cooling rate. When concentration of DMDBS is 0.2 wt.% and the cooling rate is 10° C/min,  $T_p$  of iPP nucleated with DMDBS can be increased from 118.7° C of virgin iPP to 130.1° C. Under non-isothermal conditions, the addition of DMDBS changes the spherulite growth pattern of iPP. In addition, nucleation activity of DMDBS was calculated by using the method proposed by Dobreva and Gutzow, and the results showed that DMDBS had high nucleation activity.*

**Keywords:** 1,3:2,4-Bis(3,4-dimethylbenzylidene) sorbitol (DMDBS); Isotactic polypropylene; Non-isothermal crystallization; Nucleating agent; Nucleation activity

### INTRODUCTION

One of the widely used commodity plastics, isotactic polypropylene (iPP) has been used in many areas such as packaging, household goods, and automobiles because of its relatively low manufacturing costs and rather versatile properties.<sup>[1–3]</sup> The application of iPP, however, has been limited because its transparency and mechanical properties are not very good. Addition of nucleating agents to iPP is an effective method to improve mechanical and optical properties that are related to crystallization and morphology.<sup>[4–12]</sup> Sorbitol-based nucleating agents are a type of

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highly efficient nucleating agent for  $\alpha$ -iPP, and addition of only small amounts (i.e., 0.2 wt.%) of this type of nucleating agent may also greatly improve the transparency and reduce the haze value of iPP. In contrast to most classical nucleating agents, which are dispersion-type nucleating agents, such as organic carboxylic acid salts, as discussed in the literature,<sup>[13]</sup> sorbitol-based nucleating agents are dissolution-type nucleating agents. The sorbitol-based nucleating agents can dissolve in iPP at the melting temperature of iPP, whereas dispersion-type nucleating agents are dispersed in iPP and remain in solid state at the melting temperature of iPP,<sup>[14]</sup> so that dispersion of sorbitol-based nucleating agents in iPP melt could be improved. Therefore, sorbitol-based nucleating agents have been widely used during the past decade as nucleating agents to improve the transparency of iPP.

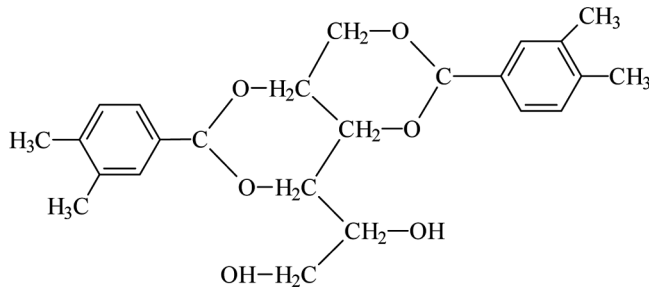
The most representative example of sorbitol-based nucleating agents is 1,3:2,4-dibenzylidene sorbitol (DBS), which is called the first generation of sorbitol-based nucleating agents. However, DBS has certain disadvantages such as evaporation during processing and bleeding out from the iPP film, which will cause unfavorable smells in iPP products. Some attempts have been made to overcome these problems by modifying the structure of DBS to produce second- and third-generation sorbitol-based nucleating agents. The second generation of sorbitol-based nucleating agents comprises its alkyl- and halo-derivatives, such as 1,3:2,4-bis(*p*-methylbenzylidene) sorbitol (MBDS). Most recently, 1,3:2,4-bis(*para*;3,4-dimethylbenzylidene) sorbitol (DMDBS) was developed as a representative of the third-generation sorbitol-based nucleating agents by Milliken Chemical Co.

Many groups have studied the effects of sorbitol-based nucleating agents on the mechanical properties and crystallization behaviors of iPP.<sup>[15–21]</sup> However, there are few systematic studies on crystallization kinetics of iPP nucleated with the third-generation sorbitol-based nucleating agent DMDBS, and the crystallization kinetics of iPP nucleated with DMDBS in these researches was mostly studied under the isothermal conditions. In addition, from a technological point of view, non-isothermal crystallization conditions approach more closely the industrial conditions of polymer processing, so that the study of crystallization of polymers under non-isothermal conditions is of great practical importance. Meanwhile, isothermal crystallization analysis is often limited to a narrow temperature range because of more errors of the crystallization rates of the samples at too high or too low crystallization temperatures.<sup>[22]</sup> In this work, non-isothermal crystallization behaviors of iPP with and without DMDBS as a nucleating agent were studied by using the Caze method, and the objective was to explain the nucleation mechanism of sorbitol-based nucleating agent in iPP, so as to provide some theoretical foundations for developing novel and highly active nucleating agents.

## EXPERIMENTAL SECTION

### Materials

iPP powders T30S with a MFR of 2.5 g/10 min, supplied by Sinopec Jiujiang Co. (China), were used in this work. Nucleating agent DMDBS (provided by Milliken Chemical Co., USA), whose structure is shown in Scheme I, was used.



Scheme 1. Molecular structure of nucleating agent DMDBS.

### Sample Preparation and DSC Analysis

The iPP powders and nucleating agents DMDBS (0.2 wt.%) were mixed in a high-speed mixer for 5 min. Then the mixture was extruded by a twin-screw extruder through a strand die and was cut into pellets, which were used for subsequent differential scanning calorimetry (DSC) analysis. A comparative sample of virgin iPP was also prepared according to the same procedures.

Non-isothermal crystallization behaviors of virgin iPP and iPP nucleated with DMDBS were studied by using a PerkinElmer Pyris 1 DSC (PerkinElmer Co., USA). All DSC operations were carried out under nitrogen environment. Sample weights were between 2 and 3 mg and all samples were heated to 200°C and held in the molten state for 5 min to erase their thermal history. Non-isothermal crystallization experiments were carried out by cooling the samples from 200° to 50°C by using constant cooling rates  $\Phi$  (selected from 2.5 to 40°C/min), and the exothermal curves of heat flow as a function of temperature were recorded.

### Theory of Crystallization

The Avrami equation is commonly used to analyze the isothermal crystallization of polymers.<sup>[23,24]</sup>

$$1 - X_t = \exp(-Z_t t^n) \quad (1)$$

where  $n$  is the Avrami exponent,  $Z_t$  is the rate constant, and  $X_t$  is the relative crystallinity at temperature  $T$ .

The Avrami equation has been extended by Ozawa<sup>[25]</sup> from the theory of Evans for isothermal crystallization to develop a simple method for studying non-isothermal crystallization kinetics. The general form of the Ozawa theory is written as follows:

$$X_v(T) = 1 - \exp(-K_T/\phi^m) \quad (2)$$

where  $K_T$  is the cooling crystallization function,  $\Phi$  is the cooling rate during non-isothermal crystallization, and  $m$  is the Ozawa exponent, which depends on the dimension of the crystal growth. However, there is a main hypothesis in the Ozawa

method that  $n$  is independent of temperature and only a limited number of  $X_v$  data are available for the foregoing analysis, as the onset of crystallization varies considerably with the cooling rate. In addition, the equation is valid exclusively for primary crystallization before crystal growth impingement takes place at high transformation.<sup>[26]</sup>

Caze and coworkers<sup>[27]</sup> raised a new method to modify the Ozawa equation. They assumed an exponential increase of  $K_T$  with  $T$  upon cooling. On this basis, the temperatures at the peak and the two inflection points of the exotherm with skew Gaussian shape are linearly related to  $\ln\Phi$  in order to estimate the exponent  $n$ .

On the basis of the findings on the crystallization behaviors of poly (ethylene terephthalate) and PP, Kim et al.<sup>[26]</sup> proposed:

$$\ln K_T = a(T - b) \quad (3)$$

where both  $a$  and  $b$  are empirical constants. If the extreme point of the pertinent  $\partial X_v(T)/\partial T$  curve occurs at  $T = T_p$  (crystallization peak temperature), i.e.,  $(\partial^2 X_v(T)/\partial T^2)_{T_p} = 0$ , we have:

$$K_T(T_p) = \phi^n \quad (4)$$

Combining Equations (2), (3), and (4) yields:

$$\ln[-\ln(1 - X_v(T))] = a(T - T_p) \quad (5)$$

Hence, a straight line will be obtained by plotting  $\ln[-\ln(1 - X_v(T))]$  versus  $T$ , and the constant  $a$  and the product  $-aT_p$  can be obtained from the slope and intercept, respectively. At  $T = T_p$  obtained from the foregoing algorithm, Equations (3) and (4) lead to:

$$T_p = n \ln \phi / a + b \quad (6)$$

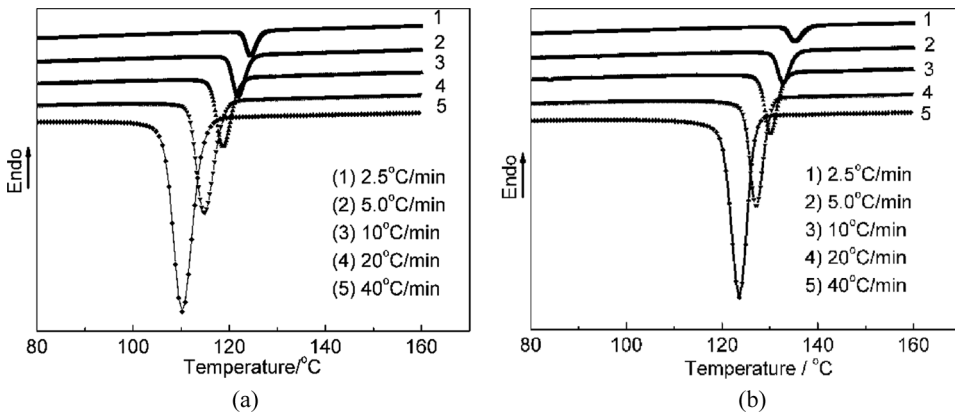
Then parameter  $n$  can be obtained from the linear plot of  $T_p$  against  $\ln\phi/a$  in accordance with Equation (6).

## RESULTS AND DISCUSSION

### Non-isothermal Crystallization Kinetics of iPP Nucleated with DMDBS

The non-isothermal crystallization of virgin iPP and iPP nucleated with DMDBS was carried out by DSC with cooling rates from 2.5 to 40°C/min. The DSC curves of virgin iPP and iPP nucleated with DMDBS are shown in Figure 1. With increasing cooling rate, crystallization peak temperature ( $T_p$ ) of iPP shifts to lower temperature. With the addition of nucleating agent DMDBS,  $T_p$  of iPP is increased greatly. When the cooling rate is 10°C/min,  $T_p$  of iPP nucleated with DMDBS is increased from 118.7°C of virgin iPP to 130.1°C.

It can be seen from Figure 1 that with the increase of cooling rate, the crystallization peak of iPP becomes wider and the position and temperature of

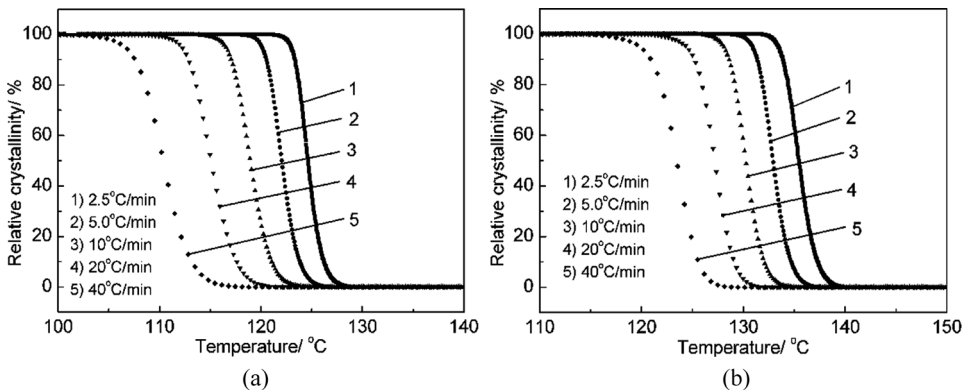


**Figure 1.** DSC cooling curves of virgin iPP (a) and iPP nucleated with DMDBS (b) during non-isothermal crystallization.

crystallization peak ( $T_p$ ) move to lower temperature, which shows that the extent of supercooling increases with the increase of cooling rate. The activity of the molecular chain becomes worse, and the difference of crystallization extent is large under low temperature so that the crystallization peak becomes wider. Comparing Figures 1(a) and 1(b) it can be seen that the crystallization temperature of iPP nucleated with DMDBS is higher than that of virgin iPP because the nucleating agent becomes the heterogeneous nuclei of crystallization, which makes crystallization easy to occur.

By means of integrating the partial areas under the DSC curves, the values of the crystalline weight fraction  $X_w(T)$  can be obtained (Figure 2).

Crystallization half-time  $t_{1/2}$  can be obtained from Figure 2 by using equation  $t = (T_0 - T)/\phi$  (where  $t$  is the crystallization time,  $T_0$  is the onset crystallization temperature,  $T$  is the crystallization temperature, and  $\phi$  is the cooling rate). The results are listed in Table I.



**Figure 2.** Relative crystallinity of virgin iPP (a) and iPP nucleated with DMDBS (b) at different cooling rates.

**Table I.** Non-isothermal crystallization kinetics parameters for virgin iPP and iPP nucleated with DMDBS

Sample	Cooling rate $\Phi$ , °C/min	$T_p$ , <sup>a</sup> °C	a	$T_p$ , <sup>b</sup> °C	$t_{1/2}$ , s	n
iPP	2.5	124.5	-1.26	124.1	118	3.71
	5	121.9	-1.16	122.0	64	
	10	118.7	-1.01	118.6	43	
	20	115.0	-0.91	115.1	25	
	40	110.2	-0.85	110.7	14	
iPP/DMDBS	2.5	135.3	-1.58	134.8	118	3.35
	5	132.8	-1.45	132.5	59	
	10	130.1	-1.30	130.3	34	
	20	127.0	-1.12	127.3	17	
	40	123.6	-0.98	124.0	9	

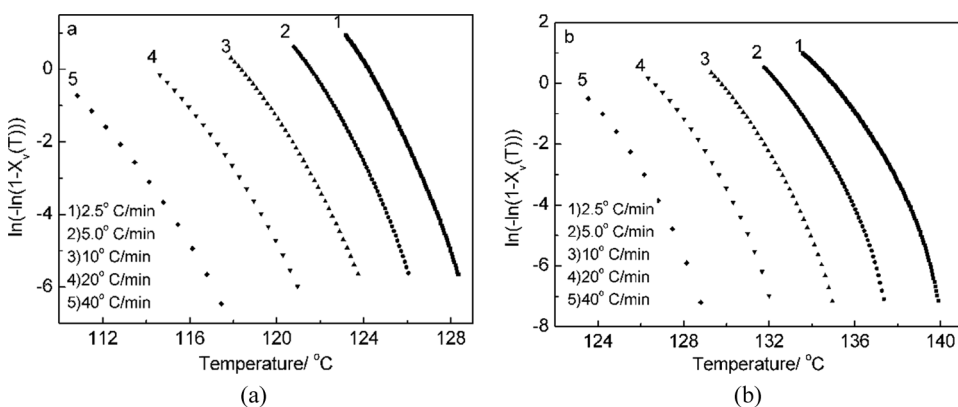
<sup>a</sup>Determined from Figure 1.<sup>b</sup>Calculated from Caze method.

$X_w(T)$  can be converted into  $X_v(T)$  by the following equation:<sup>[26]</sup>

$$X_v(T) = \frac{X_w(T) \frac{\rho_a}{\rho_c}}{1 - \left(1 - \frac{\rho_a}{\rho_c}\right) X_w(T)} \quad (7)$$

where  $\rho_a$  and  $\rho_c$  are the bulk densities of the amorphous phase and the crystallized phase, respectively. For iPP, the density of the amorphous phase is  $\rho_a = 0.852$  and that of the crystallized phase is  $\rho_c = 0.935$ . So plots of  $\ln[-\ln(1 - X_v(T))]$  versus  $T$  can be obtained (Figure 3) and there is good linear relationship between them. The values of  $a$  and  $-aT_p$  can be determined from the slope and intercept of each straight line, respectively. The results are also listed in Table I.

Straight lines can be obtained from plotting the obtained  $T_p$  and  $\ln\phi/a$  under different cooling rates (Figure 4), and the Avrami exponents of virgin iPP and iPP nucleated with DMDBS can be determined from the slope of each straight line. The results are also listed in Table I.

**Figure 3.** Plots of  $\ln[-\ln(1 - X_v(T))]$  vs.  $T$  for virgin iPP (a) and iPP nucleated with DMDBS (b).

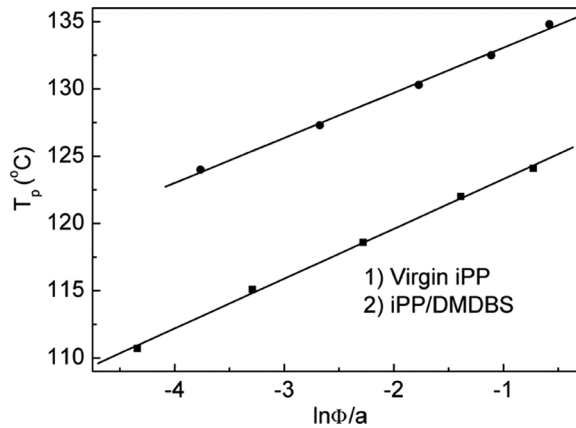


Figure 4. Plots of  $T_p$  vs.  $\ln\Phi/a$  for virgin iPP and iPP nucleated with DMDBS.

For iPP, the Avrami exponent  $n$  is 3.71 approaching 4, which indicates that in virgin iPP the crystal growth pattern is homogeneous nucleation followed by three-dimensional spherulite growth. On the other hand, the Avrami exponent  $n$  of iPP nucleated with DMDBS is 3.35 approaching 3, which indicates the crystal growth pattern of iPP nucleated with DMDBS is heterogeneous nucleation followed by three-dimensional spherulite growth. Particles of nucleating agent DMDBS in iPP will become heterogeneous nuclei of iPP, so that it will change the crystal growth pattern of iPP.

### Nucleation Activity of Nucleating Agent DMDBS in iPP

Dobrova and Gutzow<sup>[28,29]</sup> proposed a simple method for calculating the nucleation activity of nucleating agents in polymer melt. Nucleation activity ( $\varphi$ ) is a factor by which the work of three-dimensional nucleation decreases with the addition of a nucleating agent. If the foreign substrate is extremely active,  $\varphi$  approaches 0, while for inert particles,  $\varphi$  approaches 1. The nucleation activity ( $\varphi$ ) is calculated from the following equation:

$$\varphi = B^*/B \quad (8)$$

where  $B$  is a parameter that can be calculated from the following equation:

$$B = \frac{\omega\sigma^3 V_m^2}{3nk_B T_m^0 \Delta S_m^2} \quad (9)$$

where  $\omega$  is a geometric factor,  $\sigma$  is a specific energy,  $V_m$  is the molar volume of the crystallizing substance,  $n$  is the Avrami exponent,  $k_B$  is the Boltzmann constant,  $\Delta S_m$  is the entropy of melting, and  $T_m^0$  is the infinite crystal melting temperature.

Furthermore,  $B$  can be experimentally determined from the slope of the straight line obtained by plotting  $\ln\Phi$  versus  $1/\Delta T_p^2$  ( $\Delta T_p$  is supercooling degree



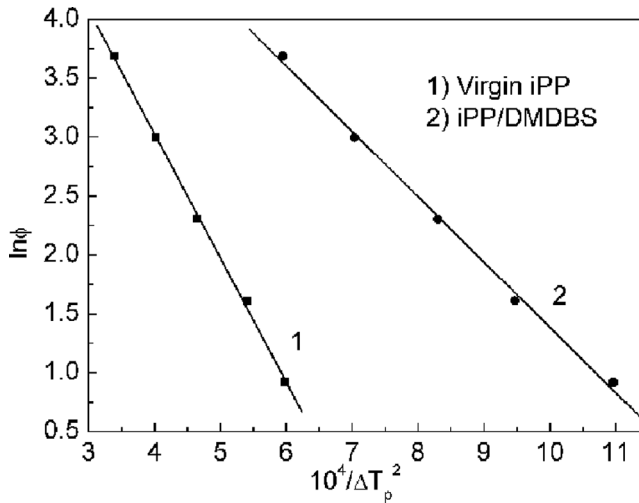


Figure 5. Plots of  $\ln \Phi$  vs.  $1/\Delta T_p^2$  for virgin iPP and iPP nucleated with DMDBS.

and  $\Delta T_p = T_m - T_p$ ) according to:

$$\ln \Phi = \text{Const} \tan t - \frac{B}{\Delta T_p^2} \quad (10)$$

The above equation holds for homogeneous nucleation from a melt, near the melting temperature. By using a nucleating agent, Equation (10) is transformed to the following form for heterogeneous nucleation:

$$\ln \Phi = \text{Const} \tan t - \frac{B^*}{\Delta T_p^2} \quad (11)$$

Plots of  $\ln \Phi$  versus  $1/\Delta T_p^2$  for virgin iPP and iPP/DMDBS are shown in Figure 5.

It can be seen from Figure 5 that straight lines are obtained for both virgin iPP and iPP nucleated with DMDBS. The values of  $B$  and  $B^*$  of virgin iPP and iPP nucleated with DMDBS can be calculated from the slopes of these two straight lines, respectively. Then the corresponding nucleation activity ( $\varphi$ ) of DMDBS is calculated from Equation (8) and the value is 0.524 (Table II). The results showed that DMDBS had strong nucleation activity in iPP.

Table II. Nucleation activity of DMDBS in iPP under non-isothermal crystallization

Sample	B (or $B^*$ )	$\varphi$
Virgin iPP	1.05	1
iPP/DMDBS	0.55	0.524

## CONCLUSIONS

Non-isothermal crystallization behaviors of iPP with and without DMDBS as a nucleating agent were investigated by adopting the Caze method. Under the same cooling rate, addition of DMDBS can increase the crystallization peak temperature ( $T_p$ ) of iPP greatly. The Caze method is successfully employed to deal with the non-isothermal crystallization behaviors of iPP. Under non-isothermal conditions, the addition of DMDBS changes the spherulite growth pattern of iPP. For virgin iPP, growth pattern is homogeneous nucleation followed by three-dimensional spherulite growth, while for iPP nucleated with DMDBS, the growth pattern is heterogeneous nucleation followed by three-dimensional spherulite growth. In addition, nucleation activity of DMDBS calculated by using the method proposed by Dobрева and Gutzow showed that DMDBS had high nucleation activity.

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