

Crystal Structure of Polypropylene Filled with Rare Earth Oxides

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SYNOPSIS

The effect of a fine powder of Y_2O_3 , Nd_2O_3 , and Ho_2O_3 on the crystal structure of isotactic polypropylene (iPP) was studied with WAXD and DSC techniques. The results showed that the addition of the three rare earth oxides (REOs) can increase the crystallite size of the α -form crystal and the degree of crystallinity of iPP at an annealing temperature of $120^\circ C$ and that both Y_2O_3 and Nd_2O_3 are the β -nucleator of iPP. REOs enhance the overall growth rate of the spherulites of iPP. All the iPP samples filled with REOs which were crystallized isothermally at $132^\circ C$ from the melt exhibited their melting peaks of the β -form on the DSC heating traces, indicating that the REOs are the nucleating agents for both the α - and β -forms of iPP under isothermal conditions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Three crystal forms— α , β , and γ —of isotactic polypropylene (iPP) have been observed. The α -form is the most stable and easy to obtain,¹ while the β - and γ -forms of polypropylene (PP) are usually achieved using special techniques, such as nucleators for β -form crystallization.² In previous publications,^{3,4} the effect of a large number of rare earth oxides (REOs) on isothermal crystallization and melting behavior was investigated with differential scanning calorimetry (DSC) in our laboratory. A series of rare earth oxides in a fine powder form may act as a nucleator and influence the growth rate of the spherulite and the mechanical and thermal properties of PP.³ In the present article, we focus on the characteristics of crystallization nucleation of REOs and crystal structure of iPP using measurements of wide-angle X-ray diffraction (WAXD) and DSC.

EXPERIMENTAL

The iPP used, PP-1300, was manufactured by the Beijing Yanshan Petrochemical Co. of China. Its

melt flow rate was 1.2 g/10 min, and density, 0.91 g/cm^3 . The fine powders of yttrium oxide (Y_2O_3), neodymium oxide (Nd_2O_3), and holmium oxide (Ho_2O_3) were precipitated from the solution of rare earth salts and then baked in our laboratory. The weight ratio of iPP and REOs in the samples was fixed as 100/1. The diameters of REO particles range from 250 to 800 nm, and the morphology can be seen clearly in Figure 1. The pure PP-1300 and filled PPs with Y_2O_3 , Nd_2O_3 , and Ho_2O_3 were coded as Samples 1, 2, 3, and 4, respectively.

A Plasti-Corder Brabender was employed to process the pure iPP and its mixtures with REOs and to determine their dynamic flow properties. Both shear rate and mixing temperature were controlled. Typically, an approximately 45 g sample was processed at 50 rpm for about 10 min at $190^\circ C$ before the equilibrium torque was achieved. Samples were removed from the mixing bowl when hot, rapidly cooled to room temperature, and stored in a desiccator prior to use. All the samples for WAXD were annealed at $120^\circ C$ for 6 h. WAXD profiles were recorded on a D/max-IIB diffractometer in a reflection mode, using graphite-filtered $CuK\alpha_1$ radiation.

In the experiments performed to study the kinetics of isothermal crystallization as a function of mixture composition, a Perkin-Elmer instrument (DSC-2C), calibrated for temperature and heat flow

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size and amount in the three directions of the crystal. In the monoclinic crystal system of the α -form, the crystallite size of (040) L_{040} is in the b -axis direction. Therefore, due to the existence of REOs, the crystallites of α -PP in the b -axis direction have an advantage.

The relative proportions of the α - and β -forms present in iPP samples were measured by an empirical parameter k as⁷

$$k = \frac{H_{\beta 1}}{H_{\beta 1} + (H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3})} \quad (4)$$

where $H_{\alpha 1}$, $H_{\alpha 2}$, and $H_{\alpha 3}$ are the heights of the three strong equatorial α -form peaks (110), (040), and (130), and $H_{\beta 1}$ is that of the strongest characteristic β -form peak (300). The k values thus obtained for Samples 2 and 3 are 18.8 and 16.8%, respectively.

The degree of crystallinity of the α -form of PP can be obtained according to eq. (5)⁵:

$$Wc, x = \frac{I_0}{I_c + 1.25I_a} \quad (5)$$

where Wc, x is the degree of crystallinity of α -PP, I_a is the integral intensity of the amorphous peak, $I_c = I_{110} + 1.63I_{040} + 2.14I_{130} + 3.51I_{04\bar{1}}$, and I_{110} , I_{040} , I_{130} , and $I_{04\bar{1}}$ are the integral intensities of corresponding crystalline peak. The degrees of crystallinity of α -PP in Samples 1, 2, 3, and 4 are 73.3, 83.0, 76.0, and 81.1%, respectively. Taking into account the existence and relatively high content of the β -form of PP, it can be concluded that three REOs can increase the crystallinity of the α -form of PP, and Y_2O_3 is the most effective.

The crystallite size of α -PP may be calculated with the Scherrer equation⁵:

$$L_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (6)$$

where $L_{hkl} (nm)$ is the crystallite size to the perpendicular direction of the (hkl) crystal plane; λ (nm), the wavelength of the incident X-ray, θ (degree), half of the Bragg angle; β (radian), the broadening of the pure diffraction ray; and k , the constant of the crystal shape factor. When $\beta_{1/2}$ was defined as the half-width of diffraction peak, $k = 0.9$; Gaussian correction was used with $\beta = (B^2 - b_0^2)^{1/2}$, where B is the half-width of peak from the X-ray measurement, and b_0 , the broadening factor of the apparatus (0.15°). The crystallite sizes of the main crystal planes of α -PP are listed in Table I.

Table I Crystallite Sizes of α - PP (nm)

Sample	L_{110}	L_{040}	L_{130}	$L_{04\bar{1}}$
1	7.08	7.73	6.94	7.79
2	7.70	9.37	7.98	9.11
3	7.93	8.47	7.32	8.52
4	7.48	7.96	7.32	8.26

Table I manifests that the crystallite sizes of in Samples 2-4 are greater than those in Sample 1. Consequently, the degree of crystal perfection of α -PP was enhanced with the addition of the fine powder of REOs.

From eq. (7) we can get unit cell parameters and its volumes of α -PP⁵:

$$(d_{hkl})^{-2} = [(h/a)^2 + (k \cdot \sin \beta/b)^2 + (l/c)^2 - (2h \cdot l \cdot \cos \beta)/(a \cdot c)]/\sin \beta \quad (7)$$

where $\beta = 99.3^\circ$; the results are summarized in Table II.

The unit cell volume of α -PP, $V = abc \sin \beta$, was enlarged and the increase in unit cell parameters seems to be beyond experimental error. The reason for this phenomenon should be studied further.

In summary, the fine powder of Y_2O_3 , Nd_2O_3 , and Ho_2O_3 can be the nucleators of the α -form of iPP; and Y_2O_3 and Nd_2O_3 are those of both the α - and β -forms at the annealing temperature of $120^\circ C$; their addition results in an increase in both crystallinity and crystallite size.

Figure 3(a) shows the isothermal crystallization curves of Samples 1 and 3 at $132^\circ C$, and Figure 3(b) shows their melting behaviors when heated after the crystallization. The melting behavior of Samples 2 and 4 are typically similar to that of Sample 3. From Figure 3(a), we can see that the induction period of the crystallization of iPP was reduced obviously by the REOs and that the crystallization period decreased while the heat effect was much enhanced, as indicated by the area of the exothermal peak. Figure 4 is a plot of $\log[-\ln(1 - \alpha)]$ against $\log t$

Table II Unit Cell Parameters (nm) and Volume (nm^3) of α - PP

Sample	a	b	c	V
1	0.662	2.080	0.654	0.894
2	0.672	2.137	0.671	0.951
3	0.671	2.102	0.651	0.906
4	0.684	2.134	0.638	0.919

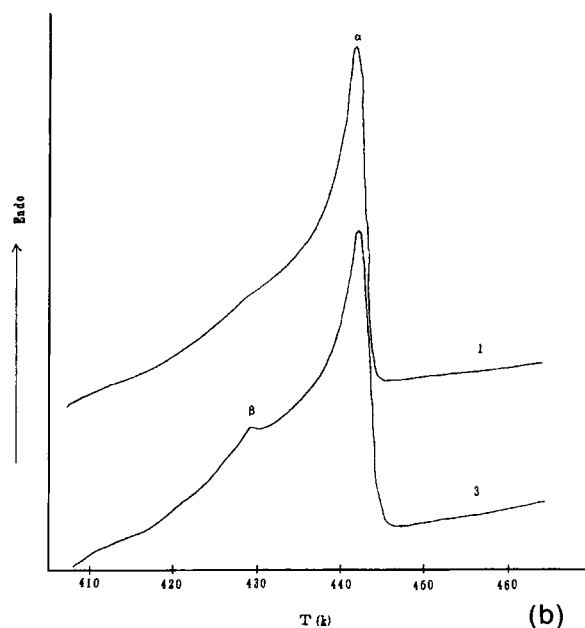
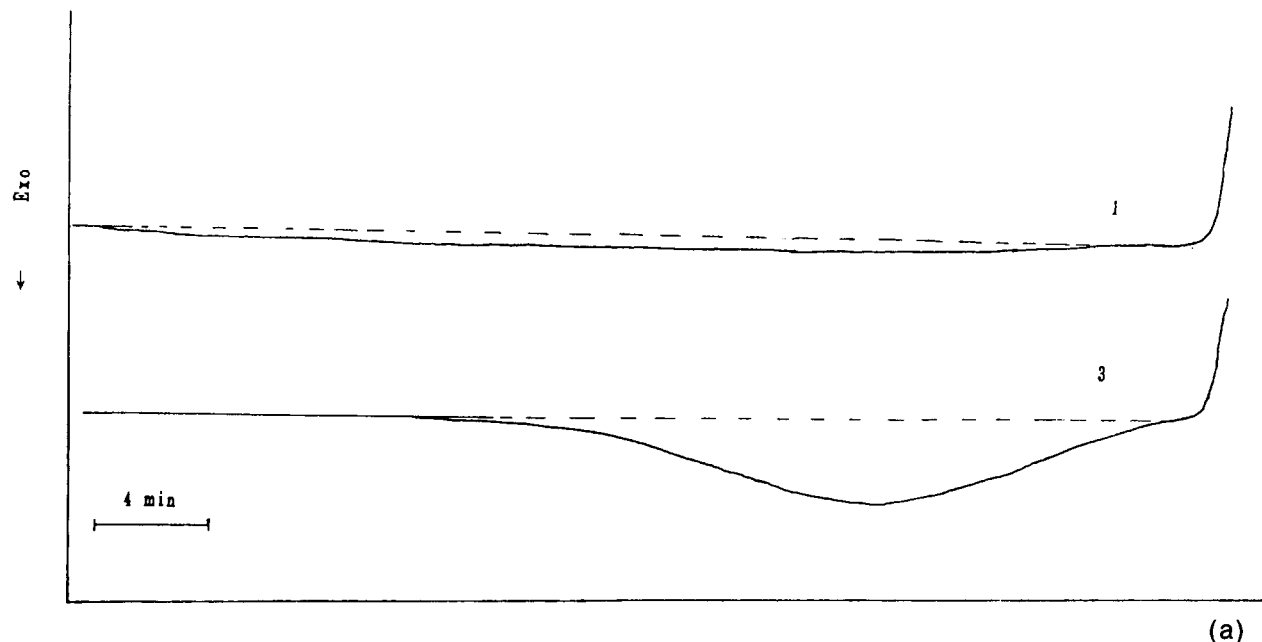


Figure 3 (a) Isothermal crystallization curves of Samples 1 and 3 in DSC; (b) melting curves of Samples 1 and 3.

for the four samples. The enthalpy of crystallization ΔH , crystallization period t_c , Avrami exponent n , and rate constant of crystallization K calculated from the Avrami equation are listed in Table III.

The n values of the four samples were in the error range, implying that REOs did not influence notably the nucleation mechanism and growth mode of the crystallization of iPP. However, the REOs enhanced the rate constant of crystallization. The K value increased by about an order of magnitude due to Y_2O_3 .

Both of the α and β melting peaks are observed on the heating scan for the samples filled with REO as shown in Figure 3(b). The double melting peaks indicate that the three REOs can act as the nucleator of β -PP at the isothermal crystallization of 132°C from the melt. As well known, the crystallization of iPP at 132°C should be controlled by the nucleation process, so the results of DSC mentioned above are in agreement with those of WAXD. The three REOs can be both α - and β -nucleators of iPP under this

condition. Similar to eq. (4)⁶ from WAXD data, a DSC parameter k_β may be defined here:

$$k_\beta = \frac{H_\beta}{H_\alpha + H_\beta} \quad (8)$$

where H_β and H_α are the heights of β and α melting peaks in the DSC trace, respectively. The k_β can be regarded as a measure of β -PP content in the sample. The results in Samples 2, 3, and 4 are 42.4, 25.8, and 27.7%, respectively. Obviously, the fine powder of yttrium oxide is the most efficient α and β nucleators of iPP under the isothermal condition. Neodymium oxide and holmium oxide may act as an α -nucleator; sometimes, they are both α and β nucleators depending on the crystallization conditions.

In conclusion, three rare earth oxides, Y_2O_3 , Nd_2O_3 , and Ho_2O_3 , are effective nucleators of the α

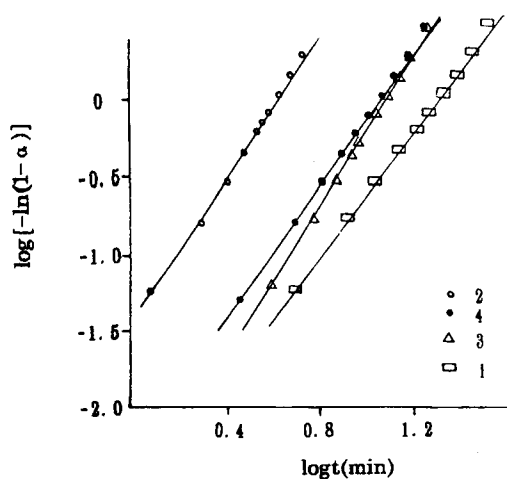


Figure 4 The plots of $\log[-\ln(1-\alpha)]$ vs. $\log t$ for Samples 1, 2, 3, and 4.

Table III n , K , ΔH , and t_c of the Samples

Sample	n	K (min^{-n})	ΔH (J/g)	t_c (min)
1	2.0	2.11×10^{-3}	35.7	37.4
2	2.3	3.55×10^{-2}	91.2	10.2
3	2.4	2.32×10^{-3}	89.5	25.8
4	2.2	5.01×10^{-3}	77.4	22.6

and β forms of iPP under the isothermal condition (132°C) and Y_2O_3 and Nd_2O_3 are effective nucleators for both under the annealing temperature (120°C). They can initiate and speed up the crystallization, resulting in short induction and crystallization periods. They help the crystallite growth, leading to larger crystallite sizes and much higher crystallinity for both α - and β -forms of iPP.

This project supported by the National Natural Science Foundation of China.

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Received August 2, 1995

Accepted November 30, 1995