# **Nonisothermal Crystallization of s-PP Fractions**

JUNTING XU,<sup>1</sup> LINXIAN FENG,<sup>1</sup> ZHENGXI LIU,<sup>1</sup> LINSHEN CHEN,<sup>2</sup> YI DENG,<sup>3</sup> CHUNMING CUI,<sup>3</sup> WEI CHEN<sup>3</sup>

<sup>1</sup> Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

<sup>2</sup> Center of Measurement and Analysis, Hangzhou University, Hangzhou 310013, China

<sup>3</sup> Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China

Received 3 December 1997; accepted 7 March 1998

ABSTRACT: Syndiotactic polypropylene (s-PP) was prepared by metallocene catalyst and was fractionated with the temperature rising elution fractionation (TREF) technique. The nonisothermal behavior of the obtained fractions was investigated. Fractions was first cooled at different rates and then heated at a constant rate. The parameters such as the peak crystallization temperature  $(T_c)$ , the onset crystallization temperature  $(T_{on})$ , the difference between  $T_{on}$  and  $T_c$  ( $\Delta T_1 = T_{on} - T_c$ ), the crystallization enthalpy ( $\Delta H$ ), the peak melting temperatures  $(T_{m1}, T_{m2})$ , and the difference between the  $T_{m1}$  and  $T_{m2}$  ( $\Delta T_2 = T_{m2} - T_{m1}$ ) were obtained. The dependence of these parameters on cooling rate, syndiotacticity, and molecular weight was discussed. It is found that  $T_c$ ,  $T_{on}$ ,  $\Delta H$ ,  $T_{m1}$ , and  $T_{m2}$  systematically increase with increasing syndiotacticity and are depressed on increasing the cooling rate. Cooling rate, syndiotacticity, and molecular weight show different influences on  $\Delta T_1$ . In the melting process of s-PP, double peaks were observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 897–901, 1999

**Key words:** syndiotactic polypropylene; metallocene catalyst; temperature rising elution fractionation; nonisothermal crystallization

## INTRODUCTION

Syndiotactic polypropylene (s-PP) was first synthesized with conventional vanadium-based Ziegler–Natta catalyst, but this polymer had a syndiotactic sequences prevailing structure and the syndiotacticity was not high enough.<sup>1</sup> The discovery of metallocene catalysts made it possible to acquire highly syndiotactic PP, and the obtained s-PP may have practical applications.<sup>2</sup> Data concerning the crystalline structure of s-PP were published by many authors.<sup>3–6</sup> In the most stable crystal form (orthorhombic form) three kinds of unit cells were identified. The isothermal crystallization and the morphology of s-PP was also extensively studied.<sup>7–12</sup> However, there are few reports on the nonisothermal crystallization of s-PP. On the other hand, the crystallization behavior and crystal structure of s-PP were found to strongly depend on the stereodefects in the polymer chain and molecular weight.<sup>9,10,11,13</sup>

In this study the temperature rising elution factor (TREF) technique was applied to the fractionation of s-PP prepared by metallocene catalyst, and fractions with different syndiotacticities and molecular weights were obtained. The influences of syndiotacticity, molecular weight, and

Correspondence to: J. Xu.

Contract grant sponsor: NSFC; contract grant number: 59703002.

Journal of Applied Polymer Science, Vol. 71, 897-901 (1999)

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mrmm +										
Fraction	mmmm	mmmr	rmmr	mmrr	rmrr	mrmr	rrrr	rrrm	mrrm	( × 10 <sup>-4</sup> )
s-PP3	0.0	0.019	0.031	0.067	0.050	0.0	0.749	0.085	0.0	12.8
s-PP5	0.0	0.0	0.026	0.055	0.036	0.0	0.812	0.071	0.0	24.7
s-PP6	0.0	0.0	0.023	0.045	0.024	0.0	0.852	0.055	0.0	29.3
s-PP8	0.0	0.0	0.020	0.040	0.016	0.0	0.874	0.050	0.0	40.5
s-PP9	0.0	0.0	0.027	0.033	0.008	0.0	0.895	0.038	0.0	35.9

Table I Pentad Distributions and Molecular Weight of s-PP Fractions

cooling rate on the nonisothermal crystallization of these s-PP fractions were examined.

## **EXPERIMENTAL**

#### **Materials**

The s-PP was prepared with a  $SiO_2$ -supported metallocene catalyst in a slurry process. The obtained polymer was fractionated by using preparative temperature rising elution fractionation (TREF) technique.<sup>14</sup> Some fractions was selected for the nonisothermal crystallization experiments. The tacticity distribution and viscosity average molecular weight are listed in Table I. The pentad distributions of fractions were obtained with a Bruker AMX-400 spectrometer operating at 100.7 MHz in PFT mode at 100°C. The intrinsic viscosity of the samples was measured with a modified Ubbelohde type viscometer at 135°C employing decalin as the solvent. The concentration of the solution was 0.15% g/mL, and a small amount of antioxidant was added to the solution.

# Nonisothermal Crystallization

Nonisothermal crystallization and melting processes were carried out on a Perkin–Elmer DSC-7 calorimeter. The weight of the sample was about 1.5 mg. The s-PP fractions were first heated to 200°C and maintained for 5 min at this temperature to remove the thermal history; then they were cooled to  $-5^{\circ}$ C at 2, 10, 20, and 40°C/min. Subsequently, the cooled samples were heated to 180°C at a constant rate of 10°C/min. During the crystallization process, an interacooler was used to obtain the cooling rate as fast as 20 and 40°C/min. The temperature was calibrated with indium at a corresponding cooling rate.

# Wide-Angle X-Ray Diffraction (WAXD) Experiments

WAXD experiments were carried out using a Rigaku diffractor. The monochromatized X-ray beams were CuK $\alpha$  radiation with a wavelength of 0.15438 nm.

### **RESULTS AND DISCUSSION**

Each fraction was cooled from 200°C to -5°C at four cooling rates: 2, 10, 20, and 40°C/min; then the crystallized samples were heated to 180°C at the rate of 10°C/min. The peak crystallization temperature  $(T_c)$ , the onset crystallization temperature  $(T_{\rm on})$ , the difference between  $T_{\rm on}$  and  $T_c$  ( $\Delta T_1 = T_{\rm on} - T_c$ ), the crystallization enthalpy ( $\Delta H$ ), the peak melting temperatures  $(T_{m1}, T_{m2})$ , and the difference between  $T_{m1}$  and  $T_{m2}$  ( $\Delta T_2 = T_{m2} - T_{m1}$ ) for all runs are summarized in Table II.

### Nonisothermal Crystallization

The  $T_{\rm on}$  is the critical temperature at which the polymer chain begins to crystallize. Above this temperature the polymer is in a molten state. A higher  $T_{\rm on}$  means that the polymer crystallite is more regular, so it melts at higher temperature. It is observed that the  $T_{\rm on}$  of the s-PP fractions increased with syndiotacticity. This indicates that higher syndiotacticity leads to a more perfect crystalline structure. The variation of  $T_c$  and  $\Delta H$ with syndiotacticity showed a tendency similar to that of  $T_{\rm on}$  (Fig. 1). The  $T_c$  is a function of cooling rate and is a measure of supercooling. A decrease in  $T_c$  implies an increase in supercooling.<sup>15</sup> From Table II it can be seen that  $T_c$  decreases systematically with increasing cooling rate. Correspondingly, a decrease in crystallization enthalpy and

Fractions	Cooling Rate (°C/min)	$\begin{array}{c} T_c \\ (^{\circ}\mathrm{C}) \end{array}$	$\begin{array}{c} T_{\rm on} \\ (^{\circ}{\rm C}) \end{array}$	$\begin{array}{c} \Delta T_1{}^{\rm a} \\ (^{\circ}{\rm C}) \end{array}$	$\Delta H$ (J/g)	$\begin{array}{c}T_{m1}^{\mathbf{b}}\\(^{\circ}\mathrm{C})\end{array}$	$\begin{array}{c}T_{m2}^{\mathbf{b}}\\(^{\circ}\mathrm{C})\end{array}$	$\begin{array}{c} \Delta T_2^{\mathrm{c}}\\ (^{\circ}\mathrm{C})\end{array}$	${\Delta T_3}^{ m d}$ (°C)
s-PP3	2	78.5	86.5	8.0	23.03	106.2	114.7	8.5	27.3
	10	61.7	66.5	4.8	22.51	104.1	113.9	9.8	42.4
	20	55.6	62.1	6.5	21.88	103.0	113.8	10.8	47.4
	40	35.2	46.8	11.6	20.43	101.5	114.5	13.0	66.3
s-PP5	2	86.5	93.9	7.4	28.33	Shoulder	122.4		
	10	64.3	70.9	6.6	25.95	112.1	122.5	10.4	47.8
	20	56.8	65.8	9.0	24.95	111.2	122.3	11.1	54.4
	40	38.6	48.7	10.1	22.22	110.1	122.8	12.7	71.5
s-PP6	2	90.4	96.4	6.0	29.45	Shoulder	124.1		
	10	69.6	78.3	8.7	27.70	116.5	124.0	7.5	46.9
	20	57.9	68.8	10.9	26.07	114.3	123.5	9.2	56.4
	40	36.8	49.1	12.3	23.14	113.0	123.7	10.7	76.2
s-PP8	2	95.4	100.9	5.5	30.39	Shoulder	128.1		
	10	77.7	84.6	6.9	26.54	119.5	128.2	8.7	41.8
	20	70.0	78.9	8.9	24.46	116.6	128.3	11.7	46.6
	40	51.2	65.1	13.9	23.88	115.1	128.8	13.7	63.9
s-PP9	2	97.5	102.4	4.9	30.97	Shoulder	130.2		
	10	79.1	85.6	6.5	29.69	121.9	129.7	7.8	42.8
	20	71.7	79.8	8.1	29.28	119.8	130.2	10.4	48.1
	40	54.1	67.1	13.0	26.00	118.0	130.1	12.1	63.9

Table II Nonisothermal Crystallization and Melting Data of Different s-PP Fractions

 ${}^{\rm a} \Delta T_1 = T_{\rm on} - T_c. \\ {}^{\rm b} {\rm Heating \ rate: \ 10^{\circ} C/{\rm min.}} \\ {}^{\rm c} \Delta T_2 = T_{m2} - T_{m1}. \\ {}^{\rm d} \Delta T_3 = T_{m1} - T_c.$ 

 $T_{\rm on}$  is also observed. This is because the fast cooling rate results in large supercooling; then a less perfect crystal is formed.

Compared with  $T_c$  and  $T_{on}$ , the variation of  $\Delta T_1$  is more complicated. The following phenomena were observed:

- 1. The  $\Delta T_1$  of s-PP6, s-PP8, and s-PP9 monotonously increases with increasing cooling rate.
- 2. Fractions s-PP3 and s-PP5 have a larger  $\Delta T_1$  value at the cooling rate of 2°C/min; this value is also larger than that of s-PP6, s-PP8, and s-PP9 at the same cooling rate.
- 3. All fractions show the largest  $\Delta T_1$  value at the cooling rate of 40°C/min.

The difference between the onset crystallization temperature and the peak crystallization temperature is generally used to measure the overall crystallization rate of polymer in the nonisothermal crystallization process.<sup>16</sup> The smaller the  $T_{\rm on} - T_c$ , the larger the overall rate of crystallization. The different variation tendency of fractions with cooling rate is the cooperative



Figure 1 Crystallization curves of s-PP fractions. The cooling rate was 10°C/min.

result of multiple factors. A polymer chain with high syndiotacticity is easier to arrange regularly and is thus favorable to crystallization. Fractions s-PP3 and s-PP5 have lower syndiotacticity, and the nucleation rate is very slow at the cooling rate of 2°C/min. On the other hand, a high cooling rate has two effects on  $T_{\rm on} - T_c$ . The first leads to higher supercooling of crystallization and a faster nucleation rate. The second is the mechanical width factor from the cooling rate: the higher the cooling rate, the wider the crystallization exothermic peak. Comparing the data in Table II, we can see that the second factor mainly takes effect at a higher cooling rate. At the cooling rate of 2°C/min the s-PP3 and s-PP5 possess larger  $\Delta T_1$  due to a slower nucleation rate and lower syndiotacticity, while other fractions may crystallize faster because of higher syndiotacticity. In addition, molecular weight may also play an important role. A higher molecular weight decreases molecular mobility and a larger activation energy is needed for the polymer chain to diffuse into the crystalline lattice, which leads to a lower crystallization rate. The  $T_{\rm on}$  –  $T_c$  values of fractions at the cooling rate of 40°C/min agree with the molecular weight of the fractions very well. Fraction s-PP8 had the highest molecular weight; correspondingly, the  $T_{\rm on} - T_c$  of this fraction at the cooling rate of 40°C/min was the largest.

### Melting Behavior of s-PP Fractions

In the DSC traces of the melting process, double melting peaks were observed in most cases. Both peak melting temperatures  $(T_{m1} \text{ and } T_{m2})$  increased as the syndiotacticity of fractions increased (Fig. 2). Because the peak melting temperature is related to the crystallinity of the polymer, it can be inferred that the s-PP fractions of higher syndiotacticity have higher crystallinity. This conclusion is supported by the results of the WAXD experiment. With the increase of syndiotacticity, the peak at  $2\theta = 12.4^{\circ}$  becomes sharper and sharper and the relative intensity of it increases steadily (Fig. 3). On increasing the cooling temperature the  $T_{m1}$  was depressed, suggesting that a faster cooling rate results in a less perfect crystal. This in accordance with the conclusion drawn from the variation of  $T_c$  and  $T_{on}$  with cooling rate.

Multiple melting peak phenomena were observed by many authors.<sup>5,11,17,18</sup> There are still controversies about the origination of the double melting peak. Boor and Youngman attributed



**Figure 2** Melting curves of s-PP fractions cooled at 10°C/min. The heating rate was 10°C/min.

these two peaks to the helical form and the planar zigzag form, respectively.<sup>17</sup> Marchettis believed that the two peaks are respectively produced by the fusion of a crystal incorporated with stereodefects and a relatively perfect crystal.<sup>10</sup> Lovinger et al. suggested that the lower peak may be due to lower molecular weight materials rejected during crystallization.<sup>5</sup> Haftka and Konnecke assumed that double melting peaks came from polymorphism.<sup>18</sup> It is observed that when a fraction was cooled at different rates in our experiment, the first peak melting temperature  $(T_{m1})$  declined with increasing cooling rate, but the  $T_{m2}$  was nearly constant. Combined with the fact that only a single exothermic peak was observed in the nonisothermal crystallization of s-PP fractions and that the polymer studied in the present work was fractionated s-PP, we believe that the second endothermic peak was generated by recrystallization or reorganization of polymer chains during the process of melting, which was proposed by Rodriguez–Arnold et al.<sup>11</sup>

The value of  $T_{m1} - T_c$  indicates the supercooling needed for crystallization of the polymer. The larger the  $T_{m1} - T_c$ , the more easily crystallization takes place.<sup>19</sup> Fractions s-PP5 and s-



Figure 3 WAXD pattern of s-PP fractions.

PP6 were found to have larger  $T_{m1} - T_c$ . A possible explanation is that these two fractions had lower syndiotacticity, as well as higher molecular weight, because a decrease in syndiotacticity and an increase in molecular weight will impede crystallization. In the meantime,  $T_{m1} - T_c$  is also related to cooling rate. A faster cooling rate leads to a larger  $T_{m1} - T_c$ , indicating that larger supercooling is needed for the crystallization at larger cooling rates.

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