

# Crystalline Memory Effects in Isothermal Crystallization of Syndiotactic Polypropylene

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**ABSTRACT:** Isothermal crystallization behavior after partial or complete melting of syndiotactic polypropylene was investigated by differential scanning calorimetry (DSC). On partial melting, the total concentration of predetermined nuclei was found to decrease with increasing fusion temperature and increasing time period that the sample spent at a specific fusion temperature. A significant effect of the rate of heating to the fusion temperature was also observed. On complete melting, the total concentration of predetermined nuclei was found to approach a constant value, which is the concentration of infusible heterogeneous nuclei (e.g., impurities, catalyst residues) present originally in the sample. At a specific fusion temperature, the concentration of predetermined athermal nuclei was found to decrease exponentially with the time period spent in the melt. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 337–346, 2000

**Key words:** syndiotactic polypropylene; crystalline memory effect; self-nucleation effect; isothermal crystallization

It is known that crystallization of polymers is mainly controlled by nucleation and growth mechanisms. Since it is well established that the rate of crystal growth is primarily a function of crystallization temperature  $T_c$ , it can then be considered a constant when considering crystallization under isothermal conditions. The nucleation mechanism and rate are quite variable and much less well understood. It is known, however, that the nucleation rate depends on the number of infusible heterogeneous nuclei present in the polymer (e.g., impurities, catalyst residues) and the thermal history of the sample, as well as the crystallization temperature  $T_c$ . Because of its importance in determining overall crystallization kinetics and morphology, it is necessary that we

understand better the nucleation mechanism and rate. It is therefore very important that the influences of impurities, additives, nucleating agents, and especially “crystalline memory” be evaluated. The latter refers to clusters of molecules that retain their crystal structure because of insufficient temperature or holding time at the fusion temperature. If these are retained at the crystallization temperature, they can act as nuclei, provided they exceed the critical nucleus size. In practice, the crystalline memory can be erased by melting the polymer at a sufficiently high fusion temperature  $T_f$  for a certain period of time. Such temperature is usually greater than the polymer’s equilibrium melting temperature ( $T_f > T_m^o$ ). If the melting temperature or the holding time in the melt is insufficient (i.e., partial melting), upon subsequent cooling the crystalline residues can act as predetermined athermal nucleation sites, which greatly enhance the overall crystallization rate. This phenomenon is also referred to as “self-nucleation.”

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In actual polymer processing, the polymer sample is not only subjected to thermal treatment, but also to mechanical treatment. Such mechanical deformation can lead to molecular orientation, which also increases nucleation rate. This effect is referred to as "orientation memory." Both types of memory can greatly affect the crystallization behavior upon subsequent cooling of the sample. To eliminate both kinds of memory effects, it is necessary to keep the sample at a sufficiently high fusion temperature for a sufficiently long time period (depending on the fusion temperature  $T_f$  used) in order to eradicate as many traces of crystalline and oriented structures as possible. In some cases, we wish to use these memory effects to control the overall crystallization rate or morphology of the crystallized polymer. Thus, we need to understand the character of these effects in detail.

Because of their important influence on the crystallization behavior of polymers, memory effects (crystalline and orientation memories) have been of considerable interest and have been studied by several investigators.<sup>1-12</sup> However, no studies have appeared on memory effects in syndiotactic polypropylene. In this article, we investigate the effect of crystalline memory on isothermal crystallization characteristics of syndiotactic polypropylene (s-PP).

## EXPERIMENTAL

### Materials

The s-PP sample used in this study was synthesized using a metallocene catalyst and was produced commercially in the pellet form by Fina Oil and Chemical Company (La Porte, Texas). Molecular characterization data, which were kindly performed by Dr. Roger A. Phillips and his group at Montell USA, Inc. (Elkton, Maryland) show the following molecular weight information:  $M_n = 76,200$ ,  $M_w = 165,000$ ,  $M_z = 290,000$ , and  $M_w/M_n = 2.2$ . In addition, the syndiotacticity measured by <sup>13</sup>C-NMR shows the racemic dyad content [%*r*] to be 91.4%, the racemic triad content [%*rr*] to be 87.3%, and the racemic pentad content [%*rrrr*] to be 77.1%.

### Sample Preparation and Experimental Methods

Sliced pellets were melt-pressed between a pair of Kapton films, which in turn were sandwiched be-

tween a pair of thick metal plates, in a Wabash compression molding machine preset at 190°C under a pressure of 67 kpsi. After 10 min holding time, a film of 275 μm thickness was taken out and allowed to cool at ambient condition down to room temperature between the two metal plates. This treatment assumes that previous thermo-mechanical history was essentially erased and provides a standard crystalline memory condition for our experiments.

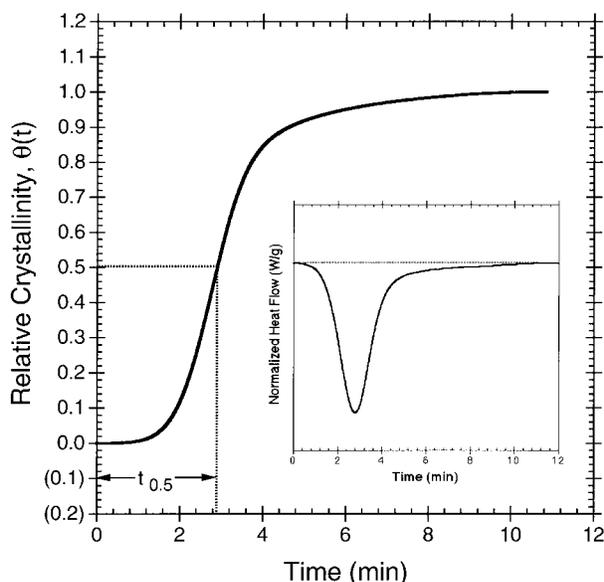
In this study, a Perkin-Elmer Series 7 differential scanning calorimeter (DSC-7) was used to follow isothermal crystallization behavior of s-PP. The DSC-7 equipped with an internal liquid nitrogen cooling unit reliably provided a cooling rate up to 200°C min<sup>-1</sup>. Temperature calibration was performed using an indium standard ( $T_m^o = 156.6^\circ\text{C}$  and  $\Delta H_f^o = 28.5 \text{ J g}^{-1}$ ). The consistency of the temperature calibration was checked every other run to ensure reliability of the data obtained. To make certain that thermal lag between the polymer sample and the DSC sensors was kept to a minimum, each sample holder was loaded with a single disc, weighing  $4.5 \pm 0.3 \text{ mg}$ , which was cut from the standard film already prepared. It is noteworthy that each sample was used only once, and all the runs were carried out under nitrogen purge.

The experiments started with heating the sample from  $-40^\circ\text{C}$  at a certain heating rate  $\phi$ , ranging from  $5^\circ\text{C min}^{-1}$  to  $80^\circ\text{C min}^{-1}$ , to a specified fusion temperature  $T_f$ . It should be noted that  $T_f$  is taken such that it is always greater than the highest melting point observed. For the purposes of this article, the highest observed melting point was taken to be approximately  $125^\circ\text{C}$ , which is the peak temperature observed from the melting endotherm of a sample isothermally crystallized at  $95^\circ\text{C}$ , using a scanning rate of  $20^\circ\text{C min}^{-1}$ . The sample was then held at  $T_f$  for a certain holding time period  $t_h$ , ranging from 3 to 300 min. After that, it was rapidly cooled at  $200^\circ\text{C min}^{-1}$  from  $T_f$  to a fixed crystallization temperature  $T_c$  (cf.  $T_c = 85^\circ\text{C}$ ), where it was left until the crystallization process was completed (approximately 15 min). The purpose of this article is to investigate the effect of changes in  $\phi$ ,  $T_f$ , and  $t_h$  on the crystalline memory behavior in isothermal crystallization of s-PP.

## ANALYSIS, RESULTS, AND DISCUSSION

### Analysis of DSC Measurements

DSC is an excellent device for following thermal transitions of polymers. When used to follow crys-



**Figure 1** Relative crystallinity  $\theta(t)$  as a function of time for syndiotactic polypropylene. Inset: the original DSC crystallization exotherm as a function of time. Conditions:  $\phi = 80^\circ\text{C min}^{-1}$ ,  $T_f = 135^\circ\text{C}$ ,  $t_h = 10$  min, and  $T_c = 85^\circ\text{C}$ .

tallization of polymers, what DSC measures is the heat flow  $\dot{Q}$  released due to the exothermic nature of the crystallization process. Intuitively, heat flow is directly proportional to the weight of the sample  $w$ , the heat of crystallization  $\Delta H_c^\circ$ , and the overall crystallization rate  $\dot{\theta}(t)$ . The crystallization enthalpy is a product of the absolute crystallinity  $\chi_c$  and the enthalpy of crystallization of an infinitely thick crystal  $\Delta H_c^\circ$  (i.e., 100% crystalline sample). Consequently, we may write an equation for the heat flow as

$$\dot{Q} = c_1 \cdot w \cdot \chi_c \cdot \Delta H_c^\circ \cdot \dot{\theta}(t), \quad (1)$$

where  $c_1$  is a combined physical constant specific for each DSC used.

By setting  $\dot{q} = \dot{Q}/(c_1 \cdot w \cdot \chi_c \cdot \Delta H_c^\circ)$ , the relative crystallinity  $\theta(t)$  can be obtained by integration of the transient normalized heat flow  $\dot{q}(t)$  over the course of the crystallization. One finally gets

$$\theta(t) = \int_0^t \dot{\theta}(t) dt = \int_0^t \dot{q}(t) dt. \quad (2)$$

Figure 1 illustrates the plot of relative crystallinity as a function of time for s-PP, which was melted at a fusion temperature  $T_f$  of  $135^\circ\text{C}$  for a

holding time  $t_h$  of 10 min before being isothermally crystallized at  $T_c = 85^\circ\text{C}$ . The raw DSC exotherm is shown as the inset to Figure 1. An important parameter, which can easily be obtained from the plot similar to Figure 1, is the crystallization half-time  $t_{0.5}$ . The crystallization half-time is defined as the time spent from the onset of the crystallization to the point where the crystallization is 50% complete. It should be noted that the reciprocal of the half-time value (i.e.,  $t_{0.5}^{-1}$ ) is usually used to describe the overall rate of the crystallization process.

Analysis of isothermal bulk crystallization kinetics is often performed using the Avrami theory of phase transformation,<sup>13</sup> which is normally written in the form:

$$1 - \theta(t) = \exp(-kt^n), \quad (3)$$

where  $k$  denotes the bulk crystallization rate constant, and  $n$  the Avrami exponent. Both  $k$  and  $n$  are constants typical of a given morphology and nucleation type. It should be noted that  $t$  is the time elapsed during the course of crystallization since the onset of crystallization (incubation time is excluded).

The bulk crystallization rate constant  $k$  can be deduced directly from the crystallization half-time  $t_{0.5}$  through the following equation (by substitution of 0.5 for  $\theta(t)$  in eq. (3)):

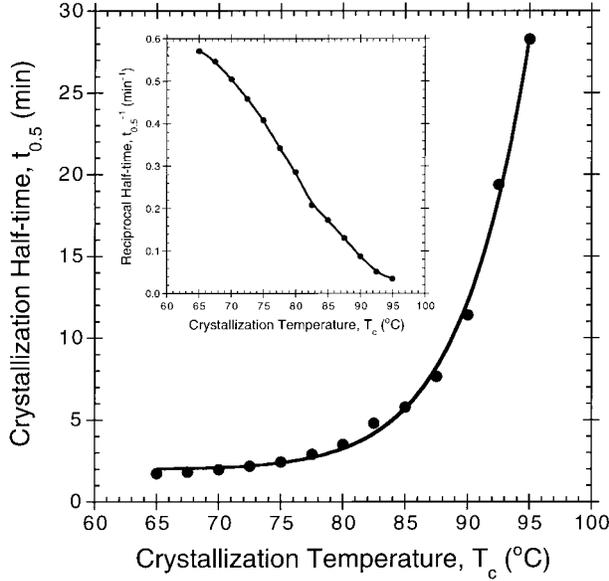
$$k = \frac{\ln 2}{t_{0.5}^n}. \quad (4)$$

In the case of predetermined nucleation and three dimensional growth (cf. later), the crystallization rate constant  $k$  is directly proportional to the total concentration of predetermined nuclei  $N_{\text{tot}}$  through the following equation:

$$k = \frac{4\pi}{3} N_{\text{tot}} G^3. \quad (5)$$

Based on eqs. (4) and (5), the total concentration of predetermined nuclei  $N_{\text{tot}}$  can be calculated directly from the crystallization half-time  $t_{0.5}$ , according to the following equation:

$$N_{\text{tot}} = \frac{3}{4\pi G^3} \frac{\ln 2}{t_{0.5}^3}. \quad (6)$$



**Figure 2** Effect of crystallization temperature  $T_c$  on the observed crystallization half-time  $t_{0.5}$ . Inset: Effect of crystallization temperature on the rate of overall crystallization (reciprocal half-time  $t_{0.5}^{-1}$ ). Conditions:  $\phi = 80^\circ\text{C min}^{-1}$ ,  $T_f = 190^\circ\text{C}$ , and  $t_h = 5$  min.

Once the value of  $N_{\text{tot}}$  is determined, the average spherulite size  $D$  can also be calculated based on the following relationship:

$$D = \left( \frac{6}{\pi N_{\text{tot}}} \right)^{1/3}. \quad (7)$$

### Effect of Crystallization Temperature

We recently performed an investigation on the bulk crystallization kinetics of this particular s-PP sample and have reported our results in refs. 14 and 15. Only the data taken for the crystallization temperature  $T_c$  range of  $60^\circ\text{C}$  to  $95^\circ\text{C}$  will be presented and discussed in this article. Each sample was cut in the form of a disc from a film prepared, based on the same procedure as mentioned previously in the experimental section, and was put in a DSC sample holder. The sample was heated in a well calibrated DSC-7 from  $-40^\circ\text{C}$  to  $T_f = 190^\circ\text{C}$  at a heating rate  $\phi$  of  $80^\circ\text{C min}^{-1}$  and was held at  $T_f = 190^\circ\text{C}$  for a holding period  $t_h$  of 5 min before being quenched at a rate of  $200^\circ\text{C min}^{-1}$  to a desired crystallization temperature  $T_c$ .

Figure 2 shows the plot of crystallization half-time  $t_{0.5}$  as a function of crystallization temperature  $T_c$ . The plot clearly shows an increase of  $t_{0.5}$  value with increasing  $T_c$  within the  $T_c$  range of

interest. This means that the rate of isothermal crystallization (i.e., the reciprocal value of the crystallization half-time ( $t_{0.5}^{-1}$ )) decreases as  $T_c$  increases (as shown in the inset figure of Fig. 2). Earlier results<sup>14,15</sup> suggested that s-PP crystallizes primarily in three dimensional growth and instantaneous nucleation at predetermined sites (within  $T_c$  range of interest); therefore, it is legitimate to calculate the total concentration of predetermined nuclei  $N_{\text{tot}}$  and the average spherulite diameter  $D$  by applying eqs. (6) and (7) to the  $t_{0.5}$  data obtained directly from the crystallization exotherms. The linear growth rate  $G$  as a function of crystallization temperature  $T_c$  can be approximated based on the following equation<sup>16</sup>:

$$G (\mu\text{m}\cdot\text{min}^{-1}) = 9.1 \times 10^8 \times \exp\left(-\frac{754.8}{T_c - 237.0} - \frac{3.6 \times 10^5}{T_c(441.8 - T_c)}f\right), \quad (8)$$

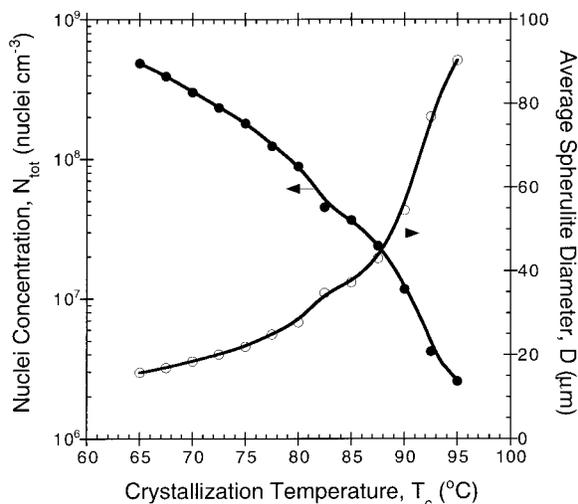
where  $f = 2T_c/(T_c + 441.8)$ . It should be noted that eq. (8) is valid only in the temperature range where  $T_c \leq 110^\circ\text{C}$ .

Table I summarizes the effect of crystallization temperature  $T_c$  on crystallization half-time  $t_{0.5}$ , heat of crystallization  $\Delta H_c$ , total concentration of predetermined nuclei  $N_{\text{tot}}$ , and average spherulite diameter  $D$ . Evidently, as the  $T_c$  value increases, the total concentration of predetermined nuclei

**Table I** Effect of Crystallization Temperature  $T_c$  on Crystallization Half-time  $t_{0.5}$ , Heat of Crystallization  $\Delta H_c$ , Total Concentration of Predetermined Nuclei  $N_{\text{tot}}$ , and Average Spherulite Diameter  $D$

$T_c$ (°C)	$t_{0.5}$ (min)	$\Delta H_c$ (J g <sup>-1</sup> )	$N_{\text{tot}}$ (nuclei cm <sup>-3</sup> )	$D$ (μm)
65.0	1.75	28.0	$4.9 \times 10^8$	16
67.5	1.83	28.7	$3.9 \times 10^8$	17
70.0	1.98	29.3	$3.0 \times 10^8$	18
72.5	2.18	30.1	$2.3 \times 10^8$	20
75.0	2.45	30.7	$1.8 \times 10^8$	22
77.5	2.92	31.5	$1.2 \times 10^8$	25
80.0	3.50	31.9	$8.9 \times 10^7$	28
82.5	4.81	32.1	$4.5 \times 10^7$	35
85.0	5.78	33.4	$3.7 \times 10^7$	37
87.5	7.65	34.5	$2.4 \times 10^7$	43
90.0	11.40	35.2	$1.2 \times 10^7$	55
92.5	19.40	35.5	$4.2 \times 10^6$	77
95.0	28.30	36.1	$2.6 \times 10^6$	90

Conditions:  $\phi = 80^\circ\text{C min}^{-1}$ ,  $T_f = 190^\circ\text{C}$ , and  $t_h = 5$  min.



**Figure 3** Effect of crystallization temperature  $T_c$  on the total concentration of predetermined nuclei  $N_{\text{tot}}$  and the average spherulite diameter  $D$ . Conditions:  $\phi = 80^\circ\text{C min}^{-1}$ ,  $T_f = 190^\circ\text{C}$ , and  $t_h = 5$  min.

$N_{\text{tot}}$  decreases monotonically, whereas, the average spherulite diameter  $D$  is found to be an increasing function of  $T_c$  (see Fig. 3). In addition, the heat of crystallization  $\Delta H_c$  also is found to increase with increasing  $T_c$ , suggesting that the absolute crystallinity is an increasing function of the crystallization temperature  $T_c$ .

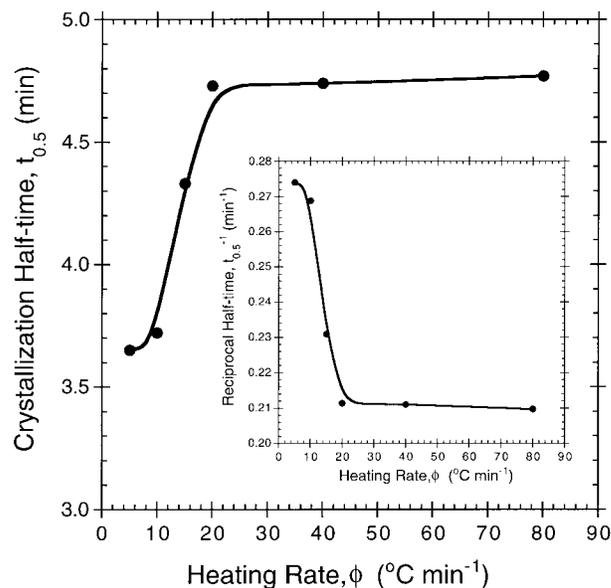
As mentioned previously in the experimental section, we need to find a crystallization temperature that gives a reliable crystallization exotherm, and the completion of crystallization does not take too long. By looking at all of the crystallization exotherms taken for this experiment, we chose  $85^\circ\text{C}$  as the standard crystallization temperature, since crystallization is completed within 15 min and it gives a low noise-to-signal ratio crystallization exotherm, which provides an optimal balance between the accuracy of the measurements and total time needed to complete the experiments.

### Effect of Heating Rate

In this experiment, the samples were heated from  $-40^\circ\text{C}$  to  $T_f = 150^\circ\text{C}$  at six different heating rates  $\phi$  ranging from  $5^\circ\text{C min}^{-1}$  to  $80^\circ\text{C min}^{-1}$ . The samples were held at  $T_f = 150^\circ\text{C}$  for a holding time  $t_h$  of 5 min before being brought down to isothermally crystallize at  $T_c = 85^\circ\text{C}$ . Figure 4 illustrates the effect of heating rate  $\phi$  on the crystallization half-time  $t_{0.5}$ , obtained directly from the resulting DSC exotherms. Evidently, the

observed  $t_{0.5}$  value or the rate of isothermal crystallization (shown in Fig. 4 as the inset) seems to have a strong correlation with the heating rate used when  $\phi \leq 20^\circ\text{C min}^{-1}$  and is seemingly independent of the heating rate used when  $\phi \geq 20^\circ\text{C min}^{-1}$ . The result is very interesting in the sense that it clearly demonstrates that low heating rates (i.e.,  $\phi \leq 20^\circ\text{C min}^{-1}$ ) affect, to some extent, the original crystallinity of the sample during a DSC heating scan.

By assuming that the linear growth rate  $G$  is independent of the nucleation mechanism and is therefore constant (i.e., based on eq. (8),  $G = 2.86 \mu\text{m min}^{-1}$  at  $T_c = 85^\circ\text{C}$ ), the total concentration of predetermined nuclei  $N_{\text{tot}}$  and the average spherulite diameter  $D$  can directly be estimated based on eqs. (6) and (7). Table II summarizes the effect of heating rate  $\phi$  on crystallization half-time  $t_{0.5}$ , heat of crystallization  $\Delta H_c$ , total concentration of predetermined nuclei  $N_{\text{tot}}$ , and average spherulite diameter  $D$ . Apparently, for the case of  $\phi \leq 20^\circ\text{C min}^{-1}$ , as the  $\phi$  value increases, the total concentration of predetermined nuclei  $N_{\text{tot}}$  decreases monotonically, whereas, the average spherulitic diameter  $D$  is found to be an increasing function of  $\phi$  (see Fig. 5). On the other hand, in the range where  $\phi \geq 20^\circ\text{C min}^{-1}$ , both  $N_{\text{tot}}$  and  $D$  values do not seem to change with the heat rate  $\phi$  used.



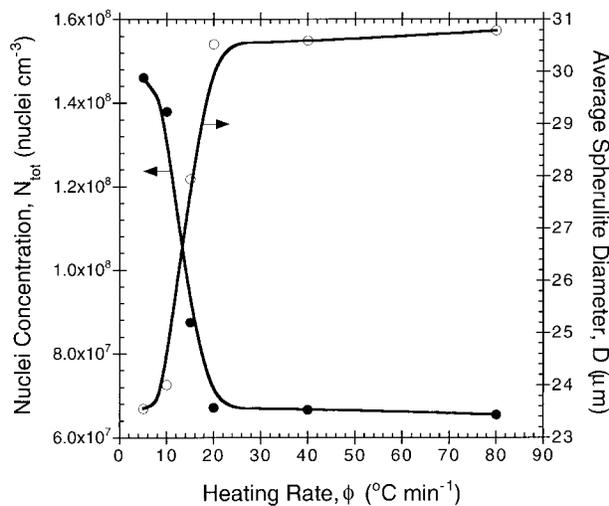
**Figure 4** Effect of heating rate  $\phi$  on the observed crystallization half-time  $t_{0.5}$ . Inset: Effect of heating rate on the rate of overall crystallization (reciprocal half-time  $t_{0.5}^{-1}$ ). Conditions:  $T_f = 150^\circ\text{C}$ ,  $t_h = 5$  min, and  $T_c = 85^\circ\text{C}$ .

**Table II** Effect of Heating Rate  $\phi$  on Crystallization Half-time  $t_{0.5}$ , Heat of Crystallization  $\Delta H_c$ , Total Concentration of Predetermined Nuclei  $N_{tot}$ , and Average Spherulite Diameter  $D$

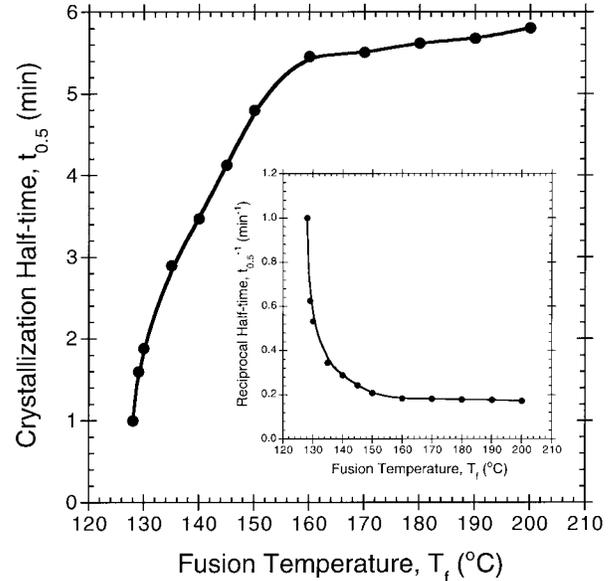
$\phi$ ( $^{\circ}\text{C min}^{-1}$ )	$t_{0.5}$ (min)	$\Delta H_c$ ( $\text{J g}^{-1}$ )	$N_{tot}$ (nuclei $\text{cm}^{-3}$ )	$D$ ( $\mu\text{m}$ )
5	3.65	31.1	$1.5 \times 10^8$	24
10	3.72	32.3	$1.4 \times 10^8$	24
15	4.33	31.6	$8.7 \times 10^7$	28
20	4.73	31.9	$6.7 \times 10^7$	31
40	4.74	32.4	$6.7 \times 10^7$	31
80	4.77	32.3	$6.5 \times 10^7$	31

Conditions:  $T_f = 150^{\circ}\text{C}$ ,  $t_h = 5$  min, and  $T_c = 85^{\circ}\text{C}$ .

The result suggests that when low heating rates (i.e.,  $\phi \leq 20^{\circ}\text{C min}^{-1}$ ) are used in a DSC heating scan, the original crystalline structure is affected such that the sample may need to be kept in the melt for a longer holding time period in order to eliminate the previous crystalline memory. The reason why the original crystalline structure is affected by low heating rates is not entirely clear, but it may be a result of crystal thickening or recrystallization of some imperfect crystals originally present in the sample. Importantly, it has to be kept in mind that low heating rates used in an observation of melting behavior of a polymer may lead to anomalous results, as demonstrated



**Figure 5** Effect of heating rate  $\phi$  on the total concentration of predetermined nuclei  $N_{tot}$  and the average spherulite diameter  $D$ . Conditions:  $T_f = 150^{\circ}\text{C}$ ,  $t_h = 5$  min, and  $T_c = 85^{\circ}\text{C}$ .



**Figure 6** Effect of fusion temperature  $T_f$  on the observed crystallization half-time  $t_{0.5}$ . Inset: Effect of fusion temperature on the rate of overall crystallization (reciprocal half-time  $t_{0.5}^{-1}$ ). Conditions:  $\phi = 80^{\circ}\text{C min}^{-1}$ ,  $t_h = 5$  min, and  $T_c = 85^{\circ}\text{C}$ .

by this experiment (as reflected by the increase in total concentration of predetermined nuclei  $N_{tot}$ ) when the heating rate used was lower than  $20^{\circ}\text{C min}^{-1}$ .

### Effect of Fusion Temperature

In this experiment, the samples were heated from  $-40^{\circ}\text{C}$  to a specified fusion temperature  $T_f$ , ranging from  $128^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ , at a heating rate  $\phi$  of  $80^{\circ}\text{C min}^{-1}$ . The samples were kept at the fusion temperature  $T_f$  for a holding time  $t_h$  of 5 min before being brought down to isothermally crystallize at  $T_c = 85^{\circ}\text{C}$ . Figure 6 shows the plot of the crystallization half-time  $t_{0.5}$ , obtained directly from the resulting DSC exotherms, as a function of fusion temperature  $T_f$ . Apparently, the observed  $t_{0.5}$  value or the rate of isothermal crystallization (shown as the inset in Fig. 6) seems to have a strong correlation with the fusion temperature used, especially in the range where  $T_f \leq 160^{\circ}\text{C}$ , and it becomes independent of the fusion temperature used when  $T_f \geq 160^{\circ}\text{C}$ .

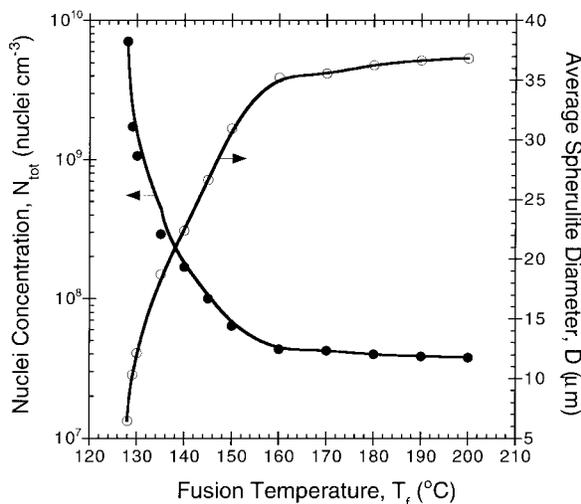
Based on eqs. (6) and (7), the total concentration of predetermined nuclei  $N_{tot}$  and the average spherulite diameter  $D$  can be directly calculated. Table III summarizes the effect of fusion temperature  $T_f$  on crystallization half-time  $t_{0.5}$ , heat of

**Table III** Effect of Fusion Temperature  $T_f$  on Crystallization Half-time  $t_{0.5}$ , Heat of Crystallization  $\Delta H_c$ , Total Concentration of Predetermined Nuclei  $N_{tot}$  and Average Spherulite Diameter  $D$

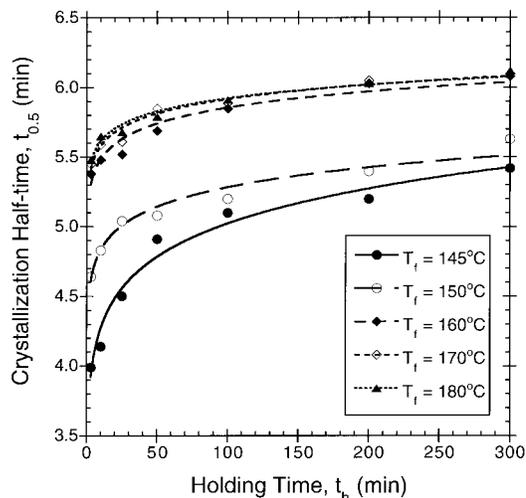
$T_f$ (°C)	$t_{0.5}$ (min)	$\Delta H_c$ (J g <sup>-1</sup> )	$N_{tot}$ (nuclei cm <sup>-3</sup> )	$D$ (μm)
128	1.00	26.3	$7.1 \times 10^9$	6
129	1.60	31.4	$1.7 \times 10^9$	10
130	1.88	31.3	$1.1 \times 10^9$	12
135	2.90	32.3	$2.9 \times 10^8$	19
140	3.47	33.7	$1.7 \times 10^8$	22
145	4.13	33.2	$1.0 \times 10^8$	27
150	4.80	33.2	$6.4 \times 10^7$	31
160	5.46	34.0	$4.4 \times 10^7$	35
170	5.51	34.6	$4.2 \times 10^7$	36
180	5.62	34.5	$4.0 \times 10^7$	36
190	5.68	34.5	$3.9 \times 10^7$	37
200	5.71	34.4	$3.8 \times 10^7$	37

Conditions:  $\phi = 80^\circ\text{C min}^{-1}$ ,  $t_h = 5$  min, and  $T_c = 85^\circ\text{C}$ .

crystallization  $\Delta H_c$ , total concentration of predetermined nuclei  $N_{tot}$ , and average spherulite diameter  $D$ . Apparently, for the case of  $T_f \leq 160^\circ\text{C}$ , as the  $T_f$  value increases the average number of predetermined nuclei  $N_{tot}$  decreases monotonically; whereas, the average spherulitic diameter  $D$  is found to be an increasing function of  $T_f$  (see Fig. 7). On the other hand, when  $T_f \geq 160^\circ\text{C}$ , both  $N_{tot}$



**Figure 7** Effect of fusion temperature  $T_f$  on the observed crystallization half-time  $t_{0.5}$ . Inset: Effect of fusion temperature on the rate of overall crystallization (reciprocal half-time  $t_{0.5}^{-1}$ ). Conditions:  $\phi = 80^\circ\text{C min}^{-1}$ ,  $t_h = 5$  min, and  $T_c = 85^\circ\text{C}$ .



**Figure 8** Effect of holding time  $t_h$  on the observed crystallization half-time  $t_{0.5}$  for five different fusion temperatures  $T_f$ , ranging from  $145^\circ\text{C}$  to  $180^\circ\text{C}$ . Conditions:  $\phi = 80^\circ\text{C min}^{-1}$  and  $T_c = 85^\circ\text{C}$ .

and  $D$  values do not seem to vary much with  $T_f$ . This suggests that prolonged melting of s-PP at  $T_f > 160^\circ\text{C}$  is mandatory in order for any measurement on crystallization behavior to be free from the influence of the predetermined athermal nuclei (i.e., the nuclei that were present as a result of an earlier crystallization process).

### Effect of Holding Time

In this experiment, the samples were heated from  $-40^\circ\text{C}$  to a specified fusion temperature  $T_f$ , ranging from  $145^\circ\text{C}$  to  $180^\circ\text{C}$ , at a heating rate  $\phi$  of  $80^\circ\text{C min}^{-1}$ . The samples were held at a specific fusion temperature  $T_f$  for a series of holding times  $t_h$ , ranging from 3 to 300 min, before being quenched to the isothermal crystallization temperature  $T_c$  of  $85^\circ\text{C}$ . Figure 8 shows the plot of the crystallization half-time  $t_{0.5}$ , obtained directly from the resulting DSC exotherms, as a function of holding time  $t_h$  for five different fusion temperatures  $T_f$ . Apparently, for each fusion temperature  $T_f$ , the  $t_{0.5}$  value is found to increase with increasing holding time  $t_h$ .

Based on eqs. (6) and (7), the total concentration of predetermined nuclei  $N_{tot}$  and the average spherulite diameter  $D$  can be directly calculated. Table IV summarizes the effect of holding time  $t_h$  on crystallization half-time  $t_{0.5}$ , heat of crystallization  $\Delta H_c$ , total concentration of predetermined nuclei  $N_{tot}$ , and average spherulite diameter  $D$  for five different fusion temperatures  $T_f$ . Evidently,

**Table IV** Effect of Holding Time  $t_h$  in the Melt at Five Different Fusion Temperatures  $T_f$ , Ranging from 145°C to 180°C, on Crystallization Half-time  $t_{0.5}$ , Heat of Crystallization  $\Delta H_c$ , Total Concentration of Predetermined Nuclei  $N_{\text{tot}}$ , and Average Spherulite Diameter  $D$

$T_f$ (°C)	$t_h$ (min)	$t_{0.5}$ (min)	$\Delta H_c$ (J g <sup>-1</sup> )	$N_{\text{tot}}$ (nuclei cm <sup>-3</sup> )	$D$ (μm)
145	3	3.99	32.3	$1.1 \times 10^8$	26
	10	4.14	32.1	$1.0 \times 10^8$	27
	25	4.50	33.6	$7.8 \times 10^7$	29
	50	4.91	35.1	$6.0 \times 10^7$	32
	100	5.10	35.5	$5.4 \times 10^7$	33
	200	5.20	34.9	$5.1 \times 10^7$	34
	300	5.42	33.4	$4.5 \times 10^7$	35
150	3	4.64	33.1	$7.1 \times 10^7$	30
	10	4.83	32.9	$6.3 \times 10^7$	31
	25	5.04	33.7	$5.5 \times 10^7$	33
	50	5.08	34.6	$5.4 \times 10^7$	33
	100	5.20	34.6	$5.1 \times 10^7$	34
	200	5.40	33.2	$4.5 \times 10^7$	35
	300	5.63	35.4	$4.0 \times 10^7$	36
160	3	5.38	33.8	$4.6 \times 10^7$	35
	10	5.48	35.6	$4.3 \times 10^7$	35
	25	5.52	35.3	$4.2 \times 10^7$	36
	50	5.69	34.8	$3.9 \times 10^7$	37
	100	5.85	36.0	$3.5 \times 10^7$	38
	200	6.03	34.5	$3.2 \times 10^7$	39
	300	6.08	36.0	$3.2 \times 10^7$	39
170	3	5.45	33.4	$4.6 \times 10^7$	35
	10	5.59	30.9	$4.5 \times 10^7$	35
	25	5.61	33.2	$4.5 \times 10^7$	35
	50	5.85	34.6	$4.2 \times 10^7$	36
	100	5.89	35.4	$4.2 \times 10^7$	36
	200	6.05	34.6	$3.2 \times 10^7$	39
	300	6.10	34.5	$3.1 \times 10^7$	39
180	3	5.48	34.6	$4.3 \times 10^7$	35
	10	5.65	35.9	$3.9 \times 10^7$	36
	25	5.68	33.8	$3.9 \times 10^7$	37
	50	5.79	34.6	$3.7 \times 10^7$	37
	100	5.91	35.9	$3.4 \times 10^7$	38
	200	6.03	33.9	$3.2 \times 10^7$	39
	300	6.12	34.9	$3.1 \times 10^7$	40

Conditions:  $\phi = 80^\circ\text{C min}^{-1}$ , and  $T_c = 85^\circ\text{C}$ .

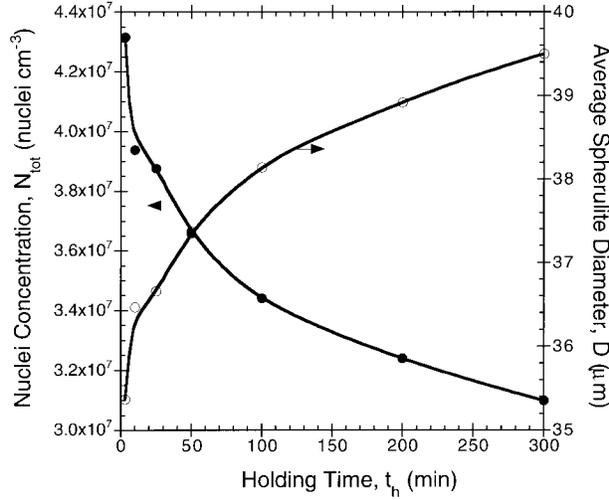
for a particular value of  $T_f$ , the total concentration of predetermined nuclei  $N_{\text{tot}}$  is found to decrease with increasing holding time  $t_h$ , whereas, the average spherulite diameter  $D$  is an increasing function of  $t_h$  (shown, as an example, in Fig. 9 for the case of  $T_f = 180^\circ\text{C}$ ).

Based on the plot of  $N_{\text{tot}}$  versus  $t_h$  shown in Figure 9, it is intuitive to interpret that the total average number of predetermined nuclei per unit volume  $N_{\text{tot}}$  is a certain decreasing function with the holding time  $t_h$  for a particular fusion temper-

ature  $T_f$ . Recently, Ziabicki and Alfonso<sup>17,18</sup> proposed that the total concentration of predetermined nuclei is an exponential decay function with the residence time in the melt, which reads

$$N_{\text{tot}}(T_f, t_h) = N_0 \exp\left[-\frac{t_h}{\tau(T_f)}\right] + N_{\text{het}}, \quad (9)$$

where  $N_{\text{tot}}$  is the total concentration of predetermined nuclei and is a function of both  $T_f$  and  $t_h$ ,



**Figure 9** Effect of holding time  $t_h$  on the total concentration of predetermined nuclei  $N_{\text{tot}}$  and the average spherulite diameter  $D$ . Conditions:  $\phi = 80^\circ\text{C}$   $\text{min}^{-1}$ ,  $T_f = 180^\circ\text{C}$ , and  $T_c = 85^\circ\text{C}$ .

$N_0$  the initial concentration of predetermined athermal nuclei (as a result of residual crystalline structure), and  $\tau$  the relaxation time for the dissociation of nucleation cluster. Furthermore,  $N_{\text{het}}$  denotes the concentration of infusible heterogeneous nuclei (e.g., impurities, catalyst residues) and can be obtained by extrapolation of the plot of  $N_{\text{tot}}$  versus  $t_h$  to infinite holding time. Thus,

$$N_{\text{het}} = N_{\text{tot}}(T_f, \infty). \quad (10)$$

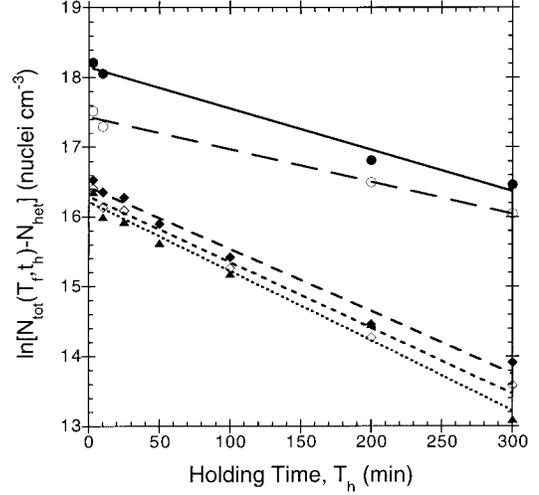
Mathematical rearrangement of eqs. (9) and (10) results in the following equation:

$$N_{\text{tot}}(T_f, t_h) - N_{\text{tot}}(T_f, \infty) = N_0 \exp\left[-\frac{t_h}{\tau(T_f)}\right]. \quad (11)$$

Equation (11) can also be written in its logarithmic form:

$$\ln[N_{\text{tot}}(T_f, t_h) - N_{\text{tot}}(T_f, \infty)] = \ln N_0 - \frac{1}{\tau(T_f)} t_h. \quad (12)$$

Based on Equation (12), it is clear that the relaxation time  $\tau$  can be extracted directly from the plot of  $\ln[N_{\text{tot}}(T_f, t_h) - N_{\text{tot}}(T_f, \infty)]$  against  $t_h$ , where  $\tau$  is taken as the reciprocal value of the slope (i.e.,  $\tau(T_f) = \text{slope}^{-1}$ ). In addition, the initial concentration of predetermined athermal nuclei  $N_0$  also can



**Figure 10** Plot of  $\ln[N_{\text{tot}}(T_f, t_h) - N_{\text{tot}}(T_f, \infty)]$  versus holding time  $t_h$  for five different fusion temperatures  $T_f$ : (●),  $145^\circ\text{C}$ ; (○),  $150^\circ\text{C}$ ; (◆),  $160^\circ\text{C}$ ; (◇),  $170^\circ\text{C}$ ; and (▲),  $180^\circ\text{C}$ .

be estimated directly from the plot (i.e.,  $N_0 = e^{(y\text{-intercept})}$ ).

Based on the plot of  $N_{\text{tot}}$  versus  $t_h$  shown in Figure 9, the concentration of infusible heterogeneous nuclei  $N_{\text{het}}$  was approximately estimated to be  $3.0 \times 10^7$  nuclei  $\text{cm}^{-3}$ . Combined with the calculated values of  $N_{\text{tot}}$  listed in Table IV, the plots of  $\ln[N_{\text{tot}}(T_f, t_h) - N_{\text{tot}}(T_f, \infty)]$  versus  $t_h$  for five different fusion temperatures  $T_f$  can be drawn as shown in Figure 10. The values of  $N_0$  and  $\tau(T_f)$ , which were obtained from Figure 10 are summarized in Table V. As expected, the relaxation time  $\tau$  is a certain decreasing function of  $T_f$  (with the exception of the data at  $T_f = 150^\circ\text{C}$ ).

**Table V** Summary of the Relaxation Time for the Segregation of Nucleation Cluster  $\tau$ , the Initial Concentration of Predetermined Athermal Nuclei  $N_0$ , and the Initial Total Concentration of Predetermined Nuclei  $N_{\text{tot}}(T_f, 0)$  for Five Different Fusion Temperatures  $T_f$

$T_f$ ( $^\circ\text{C}$ )	$\tau(T_f)$ (min)	$N_0$ (nuclei $\text{cm}^{-3}$ )	$N_{\text{tot}}(T_f, 0)^a$ (nuclei $\text{cm}^{-3}$ )
145	167.9	$7.6 \times 10^7$	$1.1 \times 10^8$
150	214.2	$3.7 \times 10^7$	$6.7 \times 10^7$
160	111.8	$1.4 \times 10^7$	$4.4 \times 10^7$
170	106.0	$1.2 \times 10^7$	$4.2 \times 10^7$
180	100.3	$1.1 \times 10^7$	$4.1 \times 10^7$

<sup>a</sup>  $N_{\text{tot}}(T_f, 0) = N_0 + 3.0 \times 10^7$ .

## CONCLUSIONS

Isothermal crystallization behavior of s-PP after partial or complete melting has been investigated by DSC. On partial melting, the total concentration of predetermined nuclei  $N_{\text{tot}}$  was found to decrease with increasing fusion temperature  $T_f$  up to a critical value (i.e.,  $T_f \approx 160^\circ\text{C}$ ), where the  $N_{\text{tot}}$  value approaches a constant (i.e., complete melting). At a specific fusion temperature  $T_f$ , the total concentration of predetermined nuclei  $N_{\text{tot}}$  was found to be a certain decay function with the holding time  $t_h$ , characterized by a relaxation time  $\tau$ , and it also was found to approach a constant value as the holding time  $t_h$  becomes long (i.e., complete melting). This constant value of total concentration of predetermined nuclei  $N_{\text{tot}}$  observed after prolonged melting of the sample at sufficiently high fusion temperature (i.e.,  $T_f > 160^\circ\text{C}$ ) is the concentration of infusible heterogeneous nuclei  $N_0$  (e.g., impurities, catalyst residues), and was approximated to be  $3.0 \times 10^7$  nuclei  $\text{cm}^{-3}$  for this particular s-PP sample. The relaxation time  $\tau$  also was found to be a certain decreasing function of fusion temperature  $T_f$  which ranges from 168 min at  $T_f = 145^\circ\text{C}$  to 100 min at  $T_f = 180^\circ\text{C}$ .

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