

# Interaction of Self-Nucleation and the Addition of a Nucleating Agent on the Crystallization Behavior of Isotactic Polypropylene

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**ABSTRACT:** The relationship between heterogeneous or homogeneous nucleation and self-nucleation of polypropylene (PP) and PP nucleated by an organic phosphate salt (PPA) was studied by DSC. For pure PP, it homogeneously nucleated during cooling after melting at the selected temperature ( $T_s$ ) of 170–200°C for 3 min, but at the  $T_s$  of 160–168°C self-nucleation occurred; PPA only nucleated heterogeneously at the  $T_s$  of 168–200°C, and there existed self nucleation at the  $T_s$  of 160–168°C. The double melting peaks of PP and PPA at the  $T_s$  of 162°C were observed. Once the self-nucleation occurred, the change of the crystallization temperature and heat of fusion of PP is more significant than that of PPA with the change of the  $T_s$ , depending upon the crystallization conditions. Results were explained by homogeneous nucleation, heterogeneous nucleation, self-nucleation, and annealing crystallization. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 78–84, 2001

**Key words:** PP; nucleated PP; heterogeneous nucleation; homogeneous nucleation; self-nucleation; crystallization behavior; melting characteristics

## INTRODUCTION

As a widely used plastic, polypropylene (PP) has good mechanical and physical properties and low price. PP is a crystallizable polymer, and can crystallize through heterogeneous nucleation, homogeneous nucleation, and self-nucleation. There are many articles reported about heterogeneous

nucleation and homogeneous nucleation of PP and nucleated PP.<sup>1–10</sup> In recent year, Fillon et al.<sup>11–13</sup> studied self-nucleation of PP. They observed that the crystallization temperature of PP in a certain cooling rate did not change after PP was melted at selected melting temperatures ( $T_s$ ) of 170°C or higher. They believed that PP was melted completely in this temperature region and crystallized by homogeneous nucleation during the cooling process at this time. However, at the  $T_s$  of 166–170°C the crystallization temperature of PP increased with decreasing the  $T_s$ . They thought that PP was melted incompletely in this temperature region, and self-nucleation occurred during the cooling process. The memory effect of morphology of PP was observed at the  $T_s$  of 166–168°C. When the  $T_s$  was lower than 166°C, a

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shoulder peak of PP was observed in the high temperature region of the crystallization peak. They suggested that the efficiency of nucleation induced by homogeneous nucleation and self-nucleation were the two extreme points during the crystallization of PP. Efficiency of heterogeneous nucleation induced by adding the nucleating agent would be between that of the homogeneous nucleation and self-nucleation, and can be characterized through comparing crystallization peak temperature of the nucleated PP with that of the homogeneous nucleation and self-nucleation of pure PP.

Although the homogeneous and self-nucleation of pure PP and heterogeneous nucleation of nucleated PP have been investigated, the relationship between heterogeneous nucleation and self-nucleation of nucleated PP has not been reported. In our laboratory, isothermal crystallization behavior and melting characteristics of nucleated PP has been investigated.<sup>14</sup> In the present work, self-nucleation and heterogeneous nucleation of PP nucleated by the nucleating agent, an organic phosphate salt, were studied. The homogeneous, heterogeneous, and self-nucleation of PP and nucleated PP were compared, and the effect of nucleating agent on self-nucleation was discussed.

## EXPERIMENTAL

### Materials

A commercial grade of PP (J 900 GP) was supplied by Idemitsu Petrochemical Corp., Japan. The nucleating agent A is an organic phosphate salt.

### Sample Preparation

#### *Preparation of Masterbatch of Nucleated Polypropylene*

The nucleating agent was dissolved in easily volatile solvent and was mixed with the PP in a high-speed mixing machine. After the solvent had evaporated completely, the mixtures were extruded in a twin-screw SHJN-25 extruder (Xinli Plastic Mechanical Factory of Nanjing Aero-space University, China) at the temperatures of 205–220°C with a screw speed of 80 rpm. The extruded products, master batches of nucleated PP containing 2.1 wt % concentration of the nucleating agent, were frozen in-line in a water bath and

granulated to less than 3 mm. PP alone was also treated similarly as a blank sample.

#### *Preparation of the Injection Sample of Nucleated Polypropylene*

The mixture of nucleated masterbatches/PP (w/w : 1 : 20) was dried at a temperature of 90°C for 3 h before injection molding. The tensile, flexural bars, and notched impact specimens were injected using a CJ150ME-NC injection mold machine (Zhengde Plastic Mechanical Limited Co.) set with the temperatures of 225–230°C. PP mixed with a blank sample and masterbatch of PP were shown as PP and PPA, respectively.

### Thermal Analysis Process

Crystallization behavior and melting characteristics of samples were studied by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 in a nitrogen atmosphere in the heating and cooling rate of 20°C/min. In the first heating and cooling scans, the samples were heated from 30 to 210°C, held at that temperature for 3 min to eliminate thermal history, then the nonisothermal crystallization process was recorded from 210 to 50°C, and a standard status of crystallization was created. In the second heating and cooling scans, the sample in standard status of crystallization was heated to selected melting temperature ( $T_s$ ), held at that temperature for 3 min, followed by cooling from the  $T_s$  to 50°C, then from 50 to 210°C in the third heating run. The crystallization and melting parameters were obtained from the first, the second cooling, and third heating scans. The transition temperature and heat of crystallization and fusion were calibrated using an indium standard.

## RESULTS AND DISCUSSION

### Self-Nucleation and Homogeneous Nucleation of Pure Polypropylene

#### *Crystallization Behavior of Self-Nucleation of Pure Polypropylene*

The crystallization and melting data of pure PP melted at the different selected melting temperatures ( $T_s$ ) were presented in Table I. The DSC curves for the second cooling and the third heating scans were shown in Figures 1 and 2. It can be seen from Table I that the same temperature of

**Table I** DSC Crystallization and Melting Results of PP Melted at Different Temperature ( $T_s$ ) for 3 min

$T_s$ (°C)	160	162	164	166	168	170	175	180	200
$T_{c1}^o$ (°C)	118.4	118.8	119.3	118.8	119.1	120.4	119.6	118.5	119.4
$T_{c1}^p$ (°C)	108.4	108.5	109.1	109.1	109.1	109.0	108.8	109.0	108.8
$T_{c1}^f$ (°C)	97.1	98.2	96.2	97.2	96.1	96.7	97.6	97.7	95.7
$T_{c1}^{on}$ (°C)	114.0	113.6	113.7	113.8	113.8	113.7	113.5	113.8	113.6
$T_{c2}^o$ (°C)	154.1	152.1	150.2	136.0	124.2	122.7	121.7	119.3	118.8
$T_{c2}^p$ (°C)	145.0	142.8	133.9	124.5	111.9	109.2	108.9	109.3	109.0
$T_{c2}^f$ (°C)	109.0	113.8	109.9	103.4	97.7	95.3	96.3	96.2	96.2
$T_{c2}^{on}$ (°C)	154.1	151.2	139.2	129.6	117.6	114.2	113.6	113.9	113.7
$\Delta T_{c2}^a$ (°C)	45.1	38.3	40.3	32.6	26.5	27.4	25.4	23.1	22.6
$\Delta T_{c2}^b$ (°C)	9.1	8.4	5.3	5.1	5.7	5.0	4.7	4.6	4.7
$\Delta T_{c2}^{1/2}$ (°C)			6.0	5.5	6.0	5.0	5.0	5.0	5.5
$T_{m3}^o$ (°C)	139.1	130.4	129.0	125.0	120.3	120.5	121.0	119.6	121.0
$T_{m3}^p$ (°C)	175.2	177.1	166.5	165.5	163.1	162.5	163.0	163.0	163.5
$T_{m3}^f$ (°C)	182.6	184.4	179.2	171.9	170.1	170.5	170.5	171.0	171.9
$T_{m3}^{on}$ (°C)	166.7	170.8	149.2	149.2	157.3	156.4	156.8	156.0	156.7
$\Delta T_{m3}^a$ (°C)	43.5	54.0	50.2	46.9	49.8	50.0	49.5	51.4	50.9
$\Delta T_{m3}^{1/2}$ (°C)	8.0	15.3	14.0	11.3	6.7	7.3	7.3	7.3	8.0
$\Delta H_{c1}$ (J/g)	93.2	92.1	93.8	93.2	93.8	92.2	93.2	92.0	94.1
$\Delta H_{c2}$ (J/g)	31.5	42.1	95.8	95.0	94.1	92.7	93.5	93.3	94.1
$\Delta H_{m3}$ (J/g)	106.3	107.9	98.8	97.7	92.0	91.2	90.1	91.2	91.0

1: data of the first cooling crystallization; 2: data of the second cooling crystallization; 3: data of melting for the sample crystallized from the second cooling crystallization.

$T_c^o$ : the temperature at the onset point of the cooling exotherm.

$T_c^f$ : the temperature at the completion of crystallization.

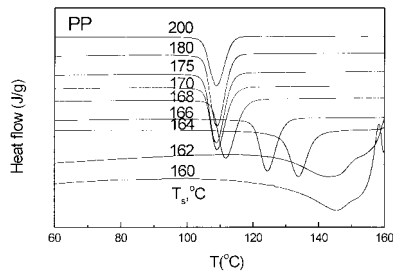
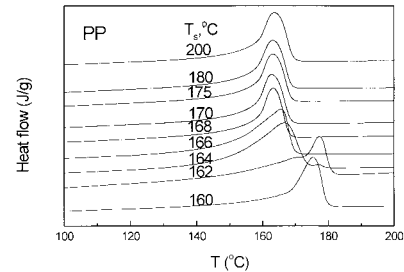
$T_c^{on}$ : the temperature at the intercept to the tangents at the baseline on the high temperature side of the exotherm.

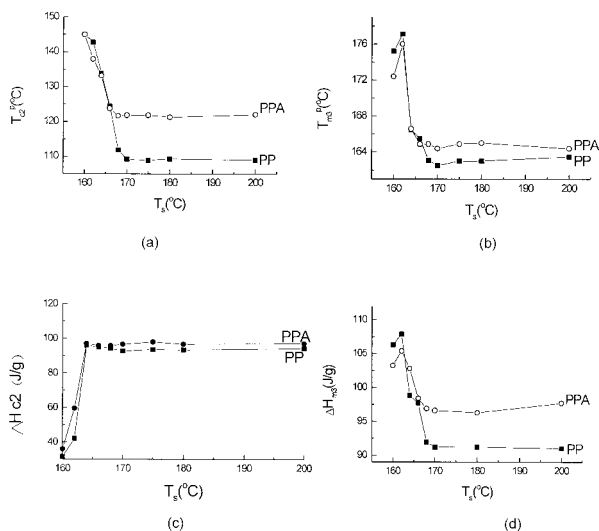
$T_m^o$ : the temperature at the onset point of the heating endotherm.

$T_m^{on}$ : the temperature at the intercept to the tangents at the baseline on the low temperature side of the endotherm.

crystallization peak ( $T_{c1}^p$ ) and the same heat of crystallization ( $\Delta H_{c1}$ ) in the first cooling run of nine samples of pure PP were obtained. The values of  $T_{c1}^p$  and  $\Delta H_{c1}$  were about 109°C and 92–94 J/g, respectively, indicating that error was small in the DSC experiment. Therefore, samples with the same thermal history were obtained after the first cooling scan, which acted as standard status of crystallization to investigated the nucleation of PP.

As the samples in standard status of crystallization were heated to the  $T_s$ , followed by cooling from the  $T_s$  to 50°C, the crystallization parameters were obviously changed. The effects of  $T_s$  on the temperature of crystallization peak ( $T_{c2}^p$ ) and the heat of crystallization ( $\Delta H_{c2}$ ) in the second cooling run were shown in Figure 3. It was found that the  $T_{c2}^p$  and  $\Delta H_{c2}$  were not affected by changing the  $T_s$  at 170–200°C. This suggests that homogeneous nucleation of PP occurs due to the

**Figure 1** DSC crystallization curves of PP after melting at  $T_s$  for 3 min.**Figure 2** Melting curves of PP crystallized by cooling from the  $T_s$ .



**Figure 3** Effect of  $T_s$  on  $T_{c2}^p$  (a),  $T_{m3}^p$  (b),  $\Delta H_{c2}$  (c),  $\Delta H_{m3}$  (d).

complete melting at higher melting temperature. Because the  $T_{c2}^p$  and  $\Delta H_{c2}$  were equal to the  $T_{c1}^p$  and  $\Delta H_{c1}$ , respectively, it is believed that no self-nucleation happened. At the  $T_s$  of 160–168°C, the  $T_{c2}^p$  and  $\Delta H_{c2}$  significantly increased with decreasing the  $T_s$ . At this temperature region of 160–168°C, the temperatures were not enough high to melt PP completely. The remained crystals of PP acted as nuclei and self-nucleation happened. The lower the  $T_s$ , the more the remained crystals, the more obvious the self-nucleation, the higher the  $T_{c2}^p$ . Once self-nucleation happened, the  $T_{c2}^p$  and  $\Delta H_{c2}$  significantly increased.

The effect of the  $T_s$  on the shape of crystallization peak was also observed. The width of crystallization peak  $\Delta T_{c2}^a (T_{c2}^o - T_{c2}^f)$  and the width of the high temperature region of the crystallization peak  $\Delta T_{c2}^b (T_{c2}^{on} - T_{c2}^p)$  of pure PP with self-nucleation ( $T_s < 170$ °C) were larger than that of pure PP without self-nucleation ( $T_s \geq 170$ °C) in the second cooling scan. And the decrease in the  $T_s$  led to increase  $\Delta T_{c2}^a$  and  $\Delta T_{c2}^b$ . However, half-height width of crystallization peak  $\Delta T_{c2}^{1/2}$  in the second cooling scan little changed at the  $T_s$  of 164–200°C; these results were opposite to that of heterogeneous nucleation of PP nucleated by nucleating agent.<sup>14,15</sup> The results of heterogeneous nucleation demonstrated that the  $\Delta T_{c2}^b$  and  $\Delta T_{c2}^{1/2}$  decreased by addition of nucleating agent. Although the single crystallization peak at the  $T_s$  of 164–200°C was observed, double crystallization peaks or one wider crystallization peak at the  $T_s$  of 160 and 162°C appeared.

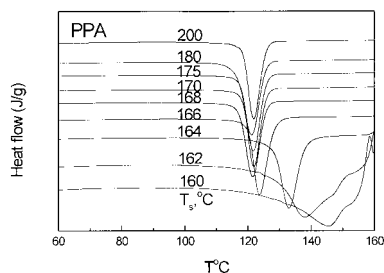
The heat of crystallization of PP ( $\Delta H_{c2}$ ) in the second cooling scan depended on the  $T_s$ . The  $\Delta H_{c2}$  was equal to  $\Delta H_{c1}$  at the  $T_s$  of 170–200°C, suggesting that only homogeneous nucleation occurred. When the  $T_s$  was lower than 170°C, the  $\Delta H_{c2}$  increased and reached a maximum at the  $T_s$  of 164°C due to the effect of self-nucleation. This result indicated that the effect of self-nucleation not only increased crystallization temperature, but also caused the noncrystallizing PP chain to crystallize, which was the same as that of nucleated PP. However, the  $\Delta H_{c2}$  slightly decreased below the  $T_s$  of 164°C. The reason was that  $T_s$  was too low to completely melt the crystals of PP. A large amount of crystals of PP remained, and were annealed to show different melting behaviors.

### Melting Characteristics of Self-Nucleation of Pure Polypropylene

It can be seen from Table I and Figure 3(b) and 3(d) that the temperature of melting peak ( $T_{m3}^p$ ) and heat of fusion ( $\Delta H_{m3}$ ) in the third heating scan was not affected with changing the  $T_s$  at 170–200°C. It was attributed to melting of PP formed by the homogeneous nucleation. It is found that the  $T_{m3}^p$  and  $\Delta H_{m3}$  at the  $T_s$  of 160–168°C were higher than that at the  $T_s$  of 170–200°C and increased with decrease of  $T_s$ . It believed that there existed self-nucleation at the  $T_s$  of 160–168°C. At the  $T_s$  of 160–168°C, an amount of unmelted crystals of PP increased with decreased  $T_s$ , where the crystal perfection of unmelted PP was improved by annealing during the melting process. The annealed crystals of PP acted as nucleating agent for the crystallization of melted PP and caused the normally noncrystallizing PP chain to crystallize. Therefore, the PP melted at 160–168°C showed higher melting points and heat of fusion.

Although the  $T_{m3}^p$  increased a little at the  $T_s$  of 164–170°C, the significant increased of  $T_{m3}^p$  was observed at the  $T_s$  below 164°C. It was suggested that large amounts of PP crystals was unmelted and annealed, resulting in a larger crystallite size and better crystal perfection. The  $T_{m3}^p$  and  $\Delta H_{m3}$  reached the maximum at the  $T_s$  of 162°C. However, the  $T_{m3}^p$  of PP at the  $T_s$  of 160°C was lower than that at the  $T_s$  of 162°C. It is well known that the crystallite perfection increase with increasing the annealing temperature. So the increase in the annealing (or premelting) temperature resulted in an increased of crystal perfection of PP below





**Figure 4** DSC crystallization curves of PPA after melting at  $T_s$  for 3 min.

the annealing (or premelting) temperature of 162°C. Therefore, the  $T_s$  of 162°C was best melting (or annealing) temperature to increase the  $T_{m3}^p$  and  $\Delta H_{m3}$  of PP.

The half-height width of melting peak ( $\Delta T_{m3}^{1/2}$ ) did not change when the  $T_s$  changed from 170 to 200°C. However, the  $\Delta T_{m3}^{1/2}$  increased with decreasing the  $T_s$  at the  $T_s$  of 164–168°C, and the  $\Delta T_{m3}^{1/2}$  was larger than that at the  $T_s$  of 170–200°C. Because the  $T_{m3}^p$  and  $\Delta H_{m3}$  increased with decreasing the  $T_s$  at the  $T_s$  of 160–168°C, it indicated that the effect of self-nucleation not only improved the degree of crystallinity but also improved the crystal perfection of the parts in the low temperature region of melting peak. At the  $T_s$  of 164°C a small peak above the high temperature of melting peak was observed. The main melting peak and the small higher temperature peak corresponded to the melting peak of self-nucleation crystallization and annealed crystallization, respectively. At this  $T_s$ , the effect of self-nucleation was dominant, and the effect of annealing was weak. At the  $T_s$  of 162°C the small, higher temperature peak became main melting peak. It demonstrated that the effect of annealing was more significant. At the  $T_s$  of 160°C, the melting peak became a single peak, attributed to the melting of PP crystals formed during annealing because the melting temperature was too low to melt the PP crystals, and unmelted PP was annealed during the premelting process at the  $T_s$ .

### The Relationship of Self-Nucleation and Heterogeneous Nucleation of Nucleated Polypropylene

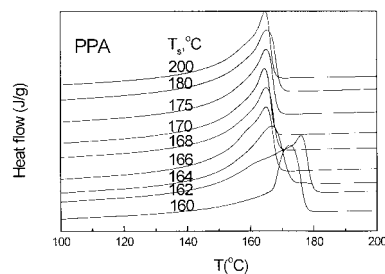
#### The Crystallization Behaviors of Nucleated Polypropylene

Figures 4 and 5 were the cooling and heating DSC curves of nucleated Polypropylene melted at the

different  $T_s$ . The crystallization and melting data were shown in Table II. The  $T_{c1}^p$  of nine samples of PPA were almost equal and between 121 and 122°C in the first cooling process. The  $T_{c1}^p$  of PPA was higher than that of PP due to the heterogeneous nucleation by the addition of a nucleating agent.

Samples in standard status of crystallization melted at different  $T_s$  showed different crystallization behaviors. The  $T_{c2}^p$  were equal with  $T_{c1}^p$  of PPA and higher than that of pure PP at the  $T_s$  of 168–200°C. This result indicated that there was no self-nucleation. It was attributed to the heterogeneous nucleation. Comparing the  $T_{c2}^p$  of PP with that of PPA at the  $T_s$  of 168°C, although the  $T_{c2}^p$  of PPA is higher than that of PP, the increase in the  $T_{c2}^p$  of PP was observed relative to the  $T_{c2}^p$  of PP at the  $T_s$  above 170°C. This suggests that the self-nucleation began to occur. However, the same  $T_{c2}^p$  of PPA at the  $T_s$  of 168°C and above 170°C was observed. It is believed that the self-nucleation of PP was suppressed by the heterogeneous nucleation at the  $T_s$  of 168°C. When the  $T_s$  was lower than 166°C, crystallization by self-nucleation occurred. The  $T_{c2}^p$  of PPA began to increase with decreasing the  $T_s$ . However, once the self-nucleation of PP occurred, the increase in the  $T_{c2}^p$  of neat PP is more significant than that of PPA. At the  $T_s$  of 166°C, the  $T_{c2}^p$  of neat PP was equal with that of PPA. At the  $T_s$  of 160°C and 162°C,  $T_{c2}^p$  increased further, and there was a small crystallization peak in the high-temperature region of the crystallization peak. The crystallization behavior of PPA was the same as that of pure PP in this temperature range. It was suggested that the effect of the self-nucleation become more dominant as the  $T_s$  decreased, while the heterogeneous nucleation by nucleation agent was suppressed, even disappeared at the low  $T_s$ .

The width of crystallization peak of PPA ( $\Delta T_{c2}^a$ ) was also influenced by the  $T_s$ . The width of crys-



**Figure 5** DSC melting curves of PPA crystallized by cooling from the  $T_s$ .

**Table II DSC Crystallization and Melting Results of PP Nucleated by the Nucleating Agent A Melted at Different Temperature ( $T_s$ ) for 3 min**

$T_s$ (°C)	160	162	164	166	168	170	175	180	200
$T_{c1}^o$ (°C)	134.0	133.2	130.5	131.9	129.3	130.2	130.2	130.2	131.5
$T_{c1}^p$ (°C)	121.6	121.1	121.4	122.0	121.6	121.9	121.7	121.2	121.9
$T_{c1}^f$ (°C)	105.1	105.7	105.7	108.3	105.1	104.9	107.5	105.1	106.6
$T_{c1}^{on}$ (°C)	126.0	125.6	125.8	126.1	125.8	125.9	126.0	125.9	125.8
$T_{c2}^o$ (°C)	151.2	154.6	150.2	136.1	130.1	132.2	130.0	129.8	129.8
$T_{c2}^p$ (°C)	145.0	137.9	133.1	123.8	121.7	121.9	121.9	121.3	122.0
$T_{c2}^f$ (°C)	113.4	111.4	110.9	109.0	103.5	106.0	103.2	105.6	105.1
$T_{c2}^{on}$ (°C)	150.6	151.7	138.2	128.5	125.9	125.8	126.0	125.8	125.9
$\Delta T_{c2}^a$ (°C)	37.8	43.2	39.3	27.1	26.6	26.2	26.8	24.2	24.7
$\Delta T_{c2}^b$ (°C)	5.6	13.8	5.1	4.7	4.2	3.9	4.1	4.5	3.9
$\Delta T_{c2}^{1/2}$ (°C)			6.0	5.0	5.0	6.0	5.0	5.5	4.0
$T_{m3}^o$ (°C)	135.7	132.1	122.3	122.3	122.3	120.1	122.3	122.3	120.3
$T_{m3}^p$ (°C)	172.4	176.0	166.6	164.9	164.9	164.4	164.9	165.0	164.4
$T_{m3}^f$ (°C)	179.9	183.9	178.6	171.2	171.0	169.2	171.0	171.9	169.4
$T_{m3}^{on}$ (°C)	165.8	164.0	151.1	153.2	155.8	156.7	155.9	156.0	157.5
$\Delta T_{m3}^a$ (°C)	44.2	51.8	56.3	48.9	48.7	49.1	48.7	49.6	49.1
$\Delta T_{m3}^{1/2}$ (°C)	8.7	18.0	12.7	10.7	10.0	8.7	9.3	8.9	9.0
$\Delta H_{c1}$ (J/g)	97.2	96.7	96.4	95.7	96.5	97.0	96.3	96.4	96.8
$\Delta H_{c2}$ (J/g)	35.9	59.6	97.0	95.8	95.8	96.6	97.9	96.6	97.0
$\Delta H_{m3}$ (J/g)	103.2	105.4	102.8	98.4	96.9	96.6	96.8	96.3	97.7

tallization peak, the width in the high temperature region ( $\Delta T_{c2}^b$ ) and the half-height width of crystallization peak ( $\Delta T_{c2}^{1/2}$ ) increased a little with decreasing the  $T_s$  between 164 and 200°C. These results were the same as that of pure PP. However, PPA showed a lower  $\Delta T_{c2}^b$  value than that of pure PP due to the heterogeneous nucleation.

It could be seen from Table II and Figure 3(c) that the  $\Delta H_{c2}$  did not change at the  $T_s$  of 166–200°C and equal with the  $\Delta H_{c1}$ , but was slightly higher than that of PP due to the heterogeneous nucleation. At the  $T_s$  of 160 and 162°C, the  $\Delta H_{c2}$  decreased with decreasing the  $T_s$ . It is attributed to the unmelted crystals increased and melted crystals decreased. The  $\Delta H_{c2}$  of PPA was significantly higher than that of pure PP, but the opposite trend was observed for the  $T_{c2}^p$  at the  $T_s$  of 162°C. It is attributed to be affected by the heterogeneous nucleation. The heterogeneous nucleation caused the normally noncrystallizing PP chain crystallized to form the crystal with the low crystal perfection, which increased the degree of crystallization. That parts with the low crystal perfection would melt completely at the  $T_s$  of 162°C. When cooled from 162°C, they could crystallize and gave out the crystallization heat, so the  $\Delta H_{c2}$  of PPA was higher than that of pure PP.

### Melting Characteristics of Nucleated PP

From Table II and Figure 3, it can be seen that the  $T_{m3}^p$  and  $\Delta H_{m3}$  was not effected by the  $T_s$  at the  $T_s$  of 168–200°C due to the presence of the heterogeneous nucleation. The  $T_{m3}^p$  increased a little with decreasing the  $T_s$  at the  $T_s$  of 164–166°C. It is suggested when the  $T_s$  was in the high temperature region of melting peak ( $T_{m1}^p = 164^\circ\text{C}$ ) of PPA in the standard status, for example,  $T_s = 166^\circ\text{C}$ , most crystals were melted and only little unmelted crystals remained, acting as a nucleation agent for self-nucleation of PP. However, the  $T_{m3}^p$  increased significantly at the  $T_s$  of 160–162°C. It was believed that at the  $T_s$  lower than the temperature of melting peak of PPA in the standard status, most crystals were not melted and were annealed at the  $T_s$ . Crystal-lite perfection was improved, leading to the increase of the  $T_{m3}^p$ . It was also found that the  $T_{m3}^p$  and  $\Delta H_{m3}$  reached a maximum at the  $T_s$  of 162°C. The  $T_{m3}^p$  and  $\Delta H_{m3}$  decreased with decreasing the  $T_s$  at the  $T_s$  below 162°C. It is attributed to the lower crystal perfection formed by annealing at the lower  $T_s$ . The above results indicated that whether adding a nucleating agent or not, the highest melting point and largest crystallinity of PP were observed at the  $T_s$  of 162°C.

The  $T_s$  had no influence on the half-height width  $\Delta T_{m3}^{1/2}$  of the melting peak of PPA at the  $T_s$  of 168–200°C, but the  $\Delta T_{m3}^{1/2}$  was larger than that of pure PP. It was attributed to the effect of heterogeneous nucleation. The heterogeneous nucleation caused the normally noncrystallizing PP chain crystallized to form the lower crystallite perfection, and led to the wider crystallite size distribution. At the  $T_s$  of 162–166°C the  $\Delta T_{m3}^{1/2}$  increased with decreasing the  $T_s$ . However, the increase in the  $\Delta T_{m3}^{1/2}$  of pure PP was more significant than that of PPA, and the  $\Delta T_{m3}^{1/2}$  of pure PP became to be higher than that of PPA due to the self-nucleation of PP at the  $T_s$  of 164 and 166°C. A small peak in the higher temperature region of melting peak at the  $T_s$  of 164°C was observed, and the melting peak began to shift to the high temperature. As the  $T_s$  decreased further, the effect of annealing was dominant, at the  $T_s$  of 162°C the small peak in the higher temperature became the main peak, which was attributed to the melting of crystals formed during the annealing. Therefore, at the  $T_s$  of 160°C only a single melting peak was observed due to the melting of the annealed PP. This result was the same as that of pure PP.

## CONCLUSION

Crystallization of pure PP occurred by homogeneous nucleation at the premelting temperature ( $T_s$ ) of 170–200°C and self-nucleation was observed at the  $T_s$  of 160–168°C. Heterogeneous nucleation of PP nucleated by nucleating agent A (PPA) occurred at the  $T_s$  of 168–200°C. At the  $T_s$  below 166°C, the heterogeneous nucleation was suppressed by the self-nucleation of PP.

Pure PP and PPA melted at different  $T_s$  exhibited different melting behavior. Double melting peak appeared in the DSC curves at the  $T_s$  of 162 and 164°C. Only one melting single peak at the  $T_s$  of 160 and 166–200°C for PP and PPA was observed.

In this experiment, the crystallization temperature ( $T_{c2}^p$ ), heat of crystallization ( $\Delta H_{c2}$ ), melting temperature ( $T_{m3}^p$ ), and heat of fusion ( $\Delta H_{m3}$ )

of pure PP changed significantly when the  $T_s$  changed, but that of PPA changed little. Once the self-nucleation of nucleated PP occurred, the heterogeneous nucleation by addition of the nucleating agent should be suppressed.

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