

NOTE

Multiple Melting Behavior of Nucleated Polypropylene

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INTRODUCTION

The multiple melting behaviors of most semicrystalline polymers have been investigated extensively. Multiple melting peaks were generally observed on differential scanning calorimetry (DSC) of polypropylene (PP),^{1–11} similar to that displayed by many other polymers such as poly(phenylene sulfide) (PPS),^{12–18} poly(ether ether ketone) (PEEK),^{19,20} poly(ethylene terephthalate) (PET),²¹ poly(butylene terephthalate) (PBT),²² poly(ethylene 2,6-naphthalate) (PEN),²³ poly(butylene 2,6-naphthalate) (PBN),²⁴ syndiotactic polystyrene (sPS) and isotactic polystyrene (iPS),^{25,26} and others.²⁷ In order to explain the phenomenon of the multiple melting peaks of PP, several models have been proposed. In the samples containing α - and β -spherulates, the two different peaks represent melting of the α - and β -forms, respectively. When the appearance of the β -phase has been excluded, recrystallization during the heating process and segregation during crystallization have been suggested as possible causes of multiple endotherms. Another explanation for the occurrence of double endotherms suggested that the double melting peaks may be related to the existence of processes of primary and secondary crystallization in the sample. The higher melting peak corresponds to the melting of crystals formed during the process of primary crystallization, while the lower melting peak corresponds to the melting of crystals grown mainly in interfibrillar regions during the secondary crystallization process. Both causes for

the multiple melting often cooperate with each other to make the melting characteristics of PP very complex, and sometimes it is very difficult to differentiate these two effects.

Addition of a nucleating agent into PP has become an important method to optimize the physical and mechanical properties of PP. Nucleating agents not only increase the physical and mechanical properties of PP, but also shorten the cycle time of production.^{28–31} In our laboratory, nonisothermal and isothermal crystallization behavior and melting characteristics, self-nucleation, and heterogeneous nucleation of PP have been studied by DSC.^{32,33} Although there are many articles on nucleated PP, the multiple melting behavior for nucleated PP has not been reported. In this work, the multiple melting characteristic for nucleated PP was studied by DSC.

MATERIALS AND EXPERIMENTAL

A commercial grade of PP (J 900GP) was supplied by the Idemitsu Petrochemical Co. Ltd. (Japan). The nucleating agent A was sodium 2,2'-methylene-bis(4,6-di-tert-butylphenyl) phosphate (trade name; NA-11) supplied by the Asahi Denko Co. Ltd. (Japan), and the nucleating agent B was bis(*p*-methylbenzylidene) sorbitol supplied by Mitsui Totsu Chemicals (Japan). The nucleating agent was dissolved in a volatile solvent and a solution was obtained. PP and the solution were mixed in a high-speed blending machine. After the solvent evaporated completely, the mixtures were extruded with a twin screw SHJN-200 extruder produced by the Xinli Plastic Mechanical Factory of Nanjing Aero-space University, China. The extruding temperatures were 205–220°C, and the screw rotation rate was 80r/min. The master batches of nucleated PP containing 2.1% of the nucleating agent were prepared. PP alone was also treated similarly, as was a blank sample. The nucleated master batches and PP (w/w 1/20) were mixed. The tensile bars were injection-molded by 150ME-NC injection molder (Zhengde Plastic Mechanical Ltd. Co., Chian) with set temperatures of 225–230°C. PP was mixed with a blank sample and the PPs nucleated with nucleating agents A and B were named PPA and PPB, respectively.

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Isothermal crystallization of PP and nucleated PP was carried out in a mode CDR-1 DSC made by the Shanghai Balance Instrument Factory, China. The DSC specimens cut out from tensile bars were heated to 210°C at a rate of 100°C/min, held at 210°C for 3 min to eliminate thermal history, then cooled to designated crystallization temperatures at a rate of 100°C/min and isothermally crystallized for a certain period of time, and finally cooled to 50°C at a rate of 100°C/min in a static air atmosphere. Melting characteristics of isothermally crystallized samples were studied by Perkin-Elmer DSC-7 in a nitrogen atmosphere in the heating rate of 20°C/min. The melting parameters were obtained from the heating scans. The transition temperature and heat of fusion were calibrated using an indium standard.

RESULTS AND DISCUSSION

Multiple melting behavior of PP

Figure 1 shows the DSC melting curves of PP. The DSC melting results are presented in Table I. Although the double melting peaks were observed for PP crystallized at 126–140°C, the shape of melting peaks depended upon the isothermal crystallization temperature, T_c , and crystallization time, t_c . For the PP crystallized at 126 and 128°C, the temperatures of the higher melting peak, T_{m2} , and the temperatures of the lower melting peak, T_{m1} , do not change with

TABLE I
DSC Melting Results of PP and Nucleated PP
Crystallized at (T_c) for (t_c)

T_c (°C)	t_c (h)	PP		PPA		PPB	
		T_{m1} (°C)	T_{m2} (°C)	T_{m1} (°C)	T_{m2} (°C)	T_{m1} (°C)	T_{m2} (°C)
126	1	S	172.5	169.1		165.7	S
	2	S	172.9	170.4		166.4	S
	4	161.5	172.4	166.1	S	162.0	172.7
128	1	164.3	172.1	168.4	S	168.2	S
	2	161.0	172.4	168.9		168.6	
	4	161.9	172.9	166.3	S	168.9	S
130	1	167.7	S	169.3	S	169.5	S
	2	165.9	S	168.4	S	166.8	174.1
	4	163.6	S	166.9	S	163.2	174.1
135	1	165.0	173.9	170.3			
	2	164.2	175.4	170.6		164.3	S
	4	166.7	176.9	170.5	S	163.8	176.6
137	1	163.2		172.2		166.8	
	2	165.2	176.4	173.1	S	166.1	S
	4	164.0	175.9	172.6	S	161.8	S
140	1	162.0					
	2	164.8					
	4	166.3	179.9				

S: shoulder peak; T_c : isothermal crystallization temperature; t_c : isothermal crystallization time; T_{m1} : peak temperature of the low temperature melting peak; T_{m2} : peak temperature of the high temperature melting peak.

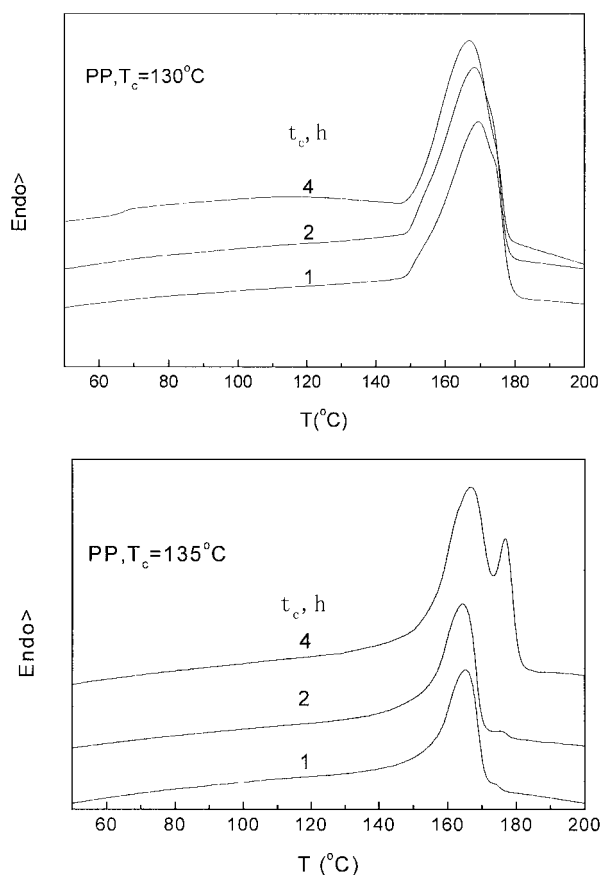


Figure 1 DSC melting curves of PP crystallized at various temperatures for different times.

increasing the T_c and t_c . The T_{m2} is about 10°C higher than the T_{m1} . However, the different shape of melting peak was observed. For the PP crystallized at 126°C for 1 h, a shoulder peak in the lower temperature region of main melting peak was observed. Although the intensity of the shoulder peak increases with an increasing the t_c , its intensity is always lower than that of the T_{m2} peak. However, for the PP crystallized at 128°C for 1 h, the double melting peaks were observed and the intensity of the T_{m1} peak is higher than that of the T_{m2} peak. Although the intensity of the T_{m2} peak also increases with an increasing the t_c at T_c of 126 and 128°C, the intensity of the T_{m1} peak increases at T_c of 126°C, while that of the T_{m1} peak decreases at T_c of 128°C. Although the intensity of the T_{m1} peak is higher than that of the T_{m2} peak of PP crystallized at 128°C for 1 h, the intensity of the T_{m2} peak is higher than that of the T_{m1} peak of PP crystallized at 128°C for 2 and 4 h. As the T_c increases, the T_{m1} peak shifts to higher temperature and the two peaks merge into a single peak. For the PP crystallized at 130°C, one main melting peak and a shoulder peak in the high temperature region of the main melting peak were observed. The temperature of the main melting peak is between the T_{m1} and T_{m2} of the PP crystallized at 128°C and is 5–6°C higher than T_{m1} , and 5–6°C lower than T_{m2} of the PP crystallized at 128°C. The shape of melting peak was also affected by the t_c . The temperature of the main melting peak shifts to lower temperature region and the shoulder peak disappears with an increasing the t_c , which is different from that of PP crystallized at 126 and 128°C. It is suggested that the crystallization perfection further increased by recrystallization at 130°C for longer times, resulted in the increase in the T_{m1} and the two peaks merge into a single peak. However, it is difficult to recrystallization for the crystals with lower per-

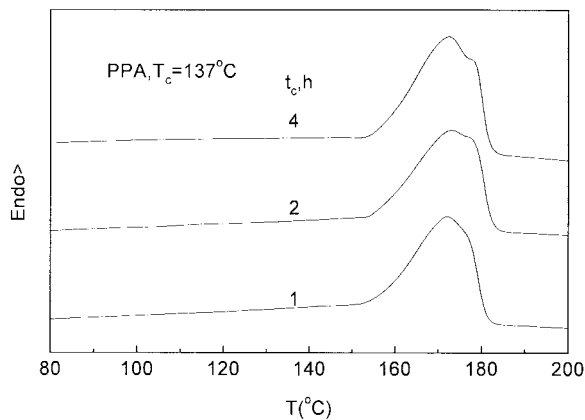


Figure 2 DSC melting curves of PPA crystallized at various temperatures for different times.

fection. After the recrystallization of the crystals with higher perfection, the melting temperatures for the crystals with much lower perfection further decreased with the increase the t_c . For the PP crystallized at 135°C for 1 h, although two melting peaks were observed, the shape of melting peak is different from that of the PP crystallized at T_c below 130°C. A main melting peak at 165°C and a small melting peak in the high temperature region of main melting peak was observed. Compared with the PP crystallized at T_c below 130°C, the temperature of the main melting peak is between the T_{m1} and T_{m2} of the PP crystallized at 126 and 128°C. The temperature of the main melting peak (T_{m1}) and the temperature of the shoulder or small melting peak (T_{m2}) in the high temperature region are 4 to 5°C higher than those of the PP crystallized at 128°C. It is suggested that the main melting peaks were attributed to merge the T_{m1} peak with the T_{m2} peak of the PP crystallized at 128°C. A small melting peak at 173.9°C in the high temperature region of the main melting peak is different from that of the higher melting peak of the PP crystallized at 126 and 128°C. With increasing the t_c , both the temperatures and the intensities of the T_{m2} peak increase, but the temperatures of T_{m1} peak are nearly unchanged. A significant melting peak with high temperature is observed for the PP crystallized at 135°C for 4 h. For the PP crystallized at 137°C for 1 h, a higher melting peak appears and the intensity of the peak increases with increasing the t_c . When the T_c is up to 140°C, a small melting peak at temperature of 179.9°C is observed for the PP crystallized for 4 h.

It can be seen from Table I that the T_c and t_c have little effect on the T_{m1} in the T_c of 126–140°C for 1–4 h. The T_{m1} is as same as the melting point (163.8°C) of PP crystallized nonisothermally from the melt state.³² This result is different from that of most semicrystalline polymers such as PPS, PEEK, and PET crystallized or annealed isothermally from the melt state or glassy state.^{17–21} For the latter, the T_{m1} generally increases with increasing the T_c or annealing temperatures, $T_{a'}$, and is about 10°C higher than the T_c or $T_{a'}$. At the low T_c or $T_{a'}$, the T_{m2} is not influenced by the T_c or $T_{a'}$. At the high T_c or $T_{a'}$, the T_{m2} generally also increases with increasing the T_c or $T_{a'}$. In our experiment, the increases in both T_c and t_c all increase the T_{m2} of PP. It is suggested that the double melting peaks of PP crystallized at 126–140°C are

the melting of both crystal morphologies with different perfections formed during the crystallization process rather than the melting of recrystallization. PP crystalline morphology with high perfection and high melting temperature has been formed during the crystallization process, and crystalline perfection increases as the T_c and t_c increased.

Multiple melting behavior of nucleated polypropylene

Figure 2 is the DSC melting curves of nucleated PP. The DSC melting results are also presented in Table I. For the PPA crystallized at $T_c = 126^\circ\text{C}$ for 1 and 2 h, one melting peak was observed. The shape of the melting peak is different from that of pure PP crystallized at $T_c = 126^\circ\text{C}$ for 1 and 2 h. A shoulder peak was observed in the higher temperature region of the main melting peak as the t_c was increased up to 4 h. The small shoulder peak in the higher temperature region of the melting peak was also observed for PPA crystallized at $T_c = 128^\circ\text{C}$ and 130°C for 1 ~ 4 h. The shape of melting peak is different from that of pure PP. For the PPA, the melting peak also shifts to lower temperature as the t_c is increased. It is suggested that two kinds of crystalline morphology with different perfection were formed for PPA crystallized at 120 ~ 130°C for 1 h. With the increasing the t_c , the crystalline perfection increases by recrystallization. The melting for crystals with increased crystalline perfection occurs at the nearly same melting temperature of crystals with the high melting point. One melting peak was observed. As the t_c is increased up to 4 h, the crystalline perfection further increases. Therefore, the shoulder peak in the high temperature region of main melting peak is more significant. Due to the further increase in the crystalline perfection of PP with higher melting point, PP crystals with lower perfection remain. Therefore, the T_{m1} further shifts to lower temperature. Two melting peaks were observed for the PPA crystallized at $T_c = 135^\circ\text{C}$ for 1 h and one melting peak was observed for 2 or 4 h. The T_{m1} is higher than that of PPA crystallized at $T_c < 135^\circ\text{C}$ due to the higher crystalline perfection. For the PPA crystallized at T_c of 137°C , a shoulder peak in the higher temperature region of main melting peak was observed and became more significant with the increasing the t_c due to the formation of two kinds

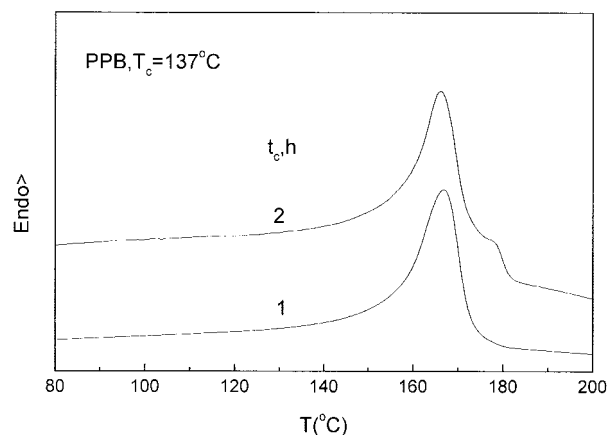


Figure 3 DSC melting curves of PPB crystallized at various temperatures for different times.

of crystallization with different perfection. In the case, the T_{m1} is also higher than that of PPA crystallized at $T_c < 137^\circ\text{C}$.

The same results were observed for the PPB (Figure 3). For the PPB crystallized at different T_c , the shoulder peak in the high temperature region of the main melting peak also became more significant with increasing the t_c . When the T_c is lower than 140°C , the T_{m1} shifts to lower temperature and the opposite results are obtained for the T_{m2} with increasing the T_c due to the change of crystalline perfection.

CONCLUSION

Although the double melting peaks were observed for PP crystallized at temperatures of $126\text{--}140^\circ\text{C}$, the shape of melting peak of PP crystallized at temperatures above 130°C is different from that of the PP crystallized at temperature below 130°C . The T_{m1} is as same as the melting point of PP crystallized nonisothermally from the melt state. The increases in both T_c and t_c all increase the T_{m2} of PP, which is different from that of most semicrystalline polymers such as PPS, PEEK, and PET. The shape of the melting peak of nucleated PP is different from that of pure PP. A small shoulder peak in the higher temperature region of the main melting peak was observed. As the t_c is increased, the shoulder peak in the high temperature region of the main melting peak is more significant. It is suggested that the double melting peaks of PP crystallized at temperatures of $126\text{--}140^\circ\text{C}$ are the melting of both crystalline morphologies with different perfections formed during the crystallization process rather than the melting of recrystallization.

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