Study on the Thermal Stability of Heterogeneous Nucleation Effect of Polypropylene Nucleated by Different Nucleating Agents

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ABSTRACT: The thermal stability of the heterogeneous nucleation effect of polypropylene (PP) nucleated with an organic phosphate (A) and two kinds of sorbitol derivatives (B and D) was investigated by DSC multiscanning. For pure PP, the peak temperature of crystallization (T_c^p) was little changed with an increasing number of DSC scans, indicating that nucleation of PP is thermally stable. For the PP nucleated with an organic phosphate (PPA), the temperatures at the onset of crystallization (T_c^{on}) and at the completion of crystallization (T_c^f); the peak temperature of crystallization (T_c^p) and melting (T_m^p); and the heat of crystallization (ΔH_c) and fusion (ΔH_m) of PP are higher than those of pure PP and were little influenced with an increasing number of DSC scans. For PP nucleated with the sorbitol derivatives (PPB and PPD), the T_c^{on}, T_c^p, T_c^f, and T_m^p decreased with an increasing the number of scans. These results indicated that the thermal stability of heterogeneous nucleation effect of the nucleating agent A is higher than that of nucleating agents B and D. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1643–1650, 2002

Key words: polypropylene; nucleated polypropylene; thermal stability of heterogeneous nucleation

INTRODUCTION

In the processing of polypropylene (PP), a nucleating agent is usually used to reduce the size of the PP spherulite, improve the optical clarity, decrease the cycle time of the process, and enhance the mechanical properties.[1–14] Protection of environment is a topic of focus all over the world today. Reuse of waste plastic is an important method to resolve the problem of plastic waste. Although nucleated PP has excellent properties, there are few articles on the thermal stability of the heterogeneous nucleation effect of PP nucleated with a nucleating agent during reuse. Chen et al.[15] studied the thermal stability of the heterogeneous nucleation effect of PP nucleated with some nucleating agents. The effect of the number of heating and cooling cycles on the crystallization temperature of nucleated PP was characterized. It was found that the crystallization temperature of PP nucleated with aliphatic diacids gradually

decreased in multiscanning while no change for the PP nucleated with calcium carbonate, terephthalic acid, and sodium benzoate was observed. It was suggested that the thermal stability of heterogeneous nucleation effect of PP nucleated with calcium carbonate, terephthalic acid, and sodium benzoate is better than that of PP nucleated with aliphatic diacids. Obviously, the thermal stability of the heterogeneous nucleation effect of nucleated PP depends on the type of nucleating agents. In recent years, sorbitol derivatives and organic phosphate have been found as new types of nucleating agents with a high nucleating effect for PP. But there is no article on the thermal stability of the heterogeneous nucleation effect of PP nucleated with sorbitol derivatives and organic phosphate. In our laboratory, we investigated the isothermal crystallization and melting characteristics of injection samples of nucleated PP and the crystallization behavior and melting characteristics of the heterogeneous nucleation and self-nucleation of injection samples of nucleated PP.[16,17] In this article, multiple melting and crystallization processes and the thermal stability of the heterogeneous nucleation effect of PP nucleated with two kinds of sorbitol derivatives and an organic phosphate were inversitaged by DSC multiscanning.

EXPERIMENTAL

Materials

A commercial grade of PP (J 900 GP) 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 (tradename: NA-11) supplied by the Asahi Denko Co. Ltd. (Japan). The nucleating agent B was millad 3988 and D was bis(*p*-ethylbenzylidene)-sorbitol (tradename: NC-4) supplied by Mitsul Tontsu Chemicals (Japan).

Sample Preparation

Preparation of Nucleated PP Masterbatches

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 Aerospace University. The extruding temperatures were 205–220°C and the

screw rotation rate was 80 r/min. The nucleated PP masterbatches containing 2.1% of the nucleating agent were prepared and PP alone was also treated similarly as was a blank sample.

Preparation of Injection Sample of Nucleated PP

The nucleated masterbatches and PP (w/w: 1/20) were mixed. The tensile bars were injection-molded by an 150ME–NC injection molder (Zhengde Plastic Mechanical Ltd. Co.) with set temperatures of 225–230°C. PP was mixed with a blank sample, and the PPs nucleated with nucleating agents A, B, and D were named PPA, PPB, and PPD, respectively.

DSC Analysis

The DSC experiment was carried out in Perkin–Elmer DSC-7 in a nitrogen atmosphere. The DSC specimens were heated to 210°C at a rate of 20°C/min, held at 210°C for 10 min, followed by cooling to 50°C at a rate of 20°C/min. Then, the heating and cooling process was carried out for multiscanning at the same scanning condition.

RESULTS AND DISCUSSION

Crystallization and Melting Behavior of Multiscanning of PP

Figure 1 shows the crystallization and melting curves of PP in the DSC multiscanning processes. The crystallization and melting results of pure PP are shown in Table I. The temperatures at the onset of crystallization (T_c^{on}) and at the completion of crystallization (T_c^f), the peak temperature of crystallization (T_c^p), and the heat of crystallization (ΔH_c) did not change as the number of DSC scans was increased. These results indicated that the crystallization behavior of pure PP had no change with an increasing number of DSC scans. It can be seen from Table I that little increase of the width in the low-temperature region of the crystallization peak ($\Delta T_c^1 = T_c^p - T_c^f$) was observed, but the width in the high-temperature region of the crystallization peak ($\Delta T_c^2 = T_c^{on} - T_c^p$) decreased with an increasing number of scans. The reason was that the T_c^{on} shifted to a low temperature. It was suggested that it became difficult for PP to nucleate after DSC multiscanning, but for PP, once nucleated, the rate of crystallization increased quickly. According to the melting results, although the temperatures at the
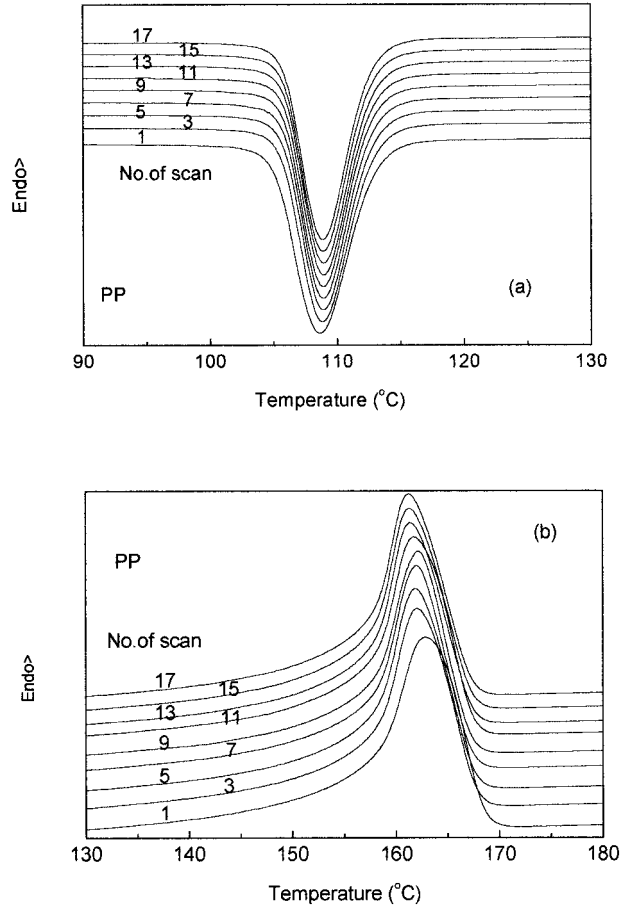
Figure 1 DSC (a) crystallization and (b) melting curves of multiscan of PP.

onset of melting (T_m^{on}) and at the completion of melting (T_m^f) did not change, the peak temperature of melting (T_m^p) decreased a little with an increasing number of the scans. Due to the T_m^p shifting to a low temperature, the width in the high-temperature region of the melting peak ($\Delta T_m^1 = T_m^f - T_m^p$) increased and the width in the low-temperature region of the melting peak ($\Delta T_m^2 = T_m^p - T_m^{on}$) decreased. The degree of nominal supercooling ($\Delta T_c = T_m^p - T_c^p$) also decreased in the DSC multiscanning. However, the heat of crystallization (ΔH_c) and fusion (ΔH_m) of PP had no significant change in the DSC multiscanning.

Crystallization and Melting Behavior of Multiscanning of Nucleated PP

Crystallization and Melting Behavior of Multiscanning of PPA

The crystallization and melting curves of PP nucleated with nucleating agent A (PPA) are shown in Figure 2. The crystallization and melting parameters of PP are seen in Table II. It can be seen from Table II and Figure 2 that the T_c^{on}, T_c^p, and T_c^f of PPA did not change and were higher than those of pure PP in the DSC multiscanning. The ΔT_c^1 and ΔT_c^2 of PPA decreased as the number of DSC scans was increased. The ΔT_c^2 of PPA was obviously smaller than that of PP, which indicated that the rate of crystallization of PPA was

Table I   DSC Results of Multiscanned PP

No. Scan	T_c^{on} (°C)	T_c^p (°C)	T_c^f (°C)	ΔT_c^1 (°C)	ΔT_c^2 (°C)	T_m^{on} (°C)	T_m^p (°C)	T_m^f (°C)	ΔT_m^1 (°C)	ΔT_m^2 (°C)	ΔH_c (J/g)	ΔH_m (J/g)	ΔT_c (°C)
1	113.1	108.6	99.6	9.0	4.5	156.8	162.7	170.3	7.6	5.9	92.4	90.3	54.1
2	113.2	108.9	99.6	9.3	4.3	156.9	162.2	170.2	8.0	5.3	92.3	91.7	53.3
3	113.1	109.0	99.6	9.4	4.1	156.9	161.9	170.0	8.1	5.0	92.2	91.5	52.9
4	113.1	109.0	99.6	9.4	4.1	156.9	161.7	170.0	8.3	4.8	92.3	91.8	52.7
5	112.9	108.9	99.5	9.4	4.0	156.9	161.8	169.9	8.1	4.9	92.2	91.9	52.9
6	113.0	109.0	99.6	9.4	4.0	156.7	161.4	170.0	8.6	4.7	92.2	91.9	52.4
7	112.8	108.9	99.5	9.4	3.9	156.9	161.9	170.0	8.1	5.0	92.1	91.9	53.0
8	112.8	108.9	99.5	9.4	3.9	156.9	161.4	170.0	8.6	4.5	92.0	91.8	52.5
9	112.9	109.0	99.6	9.4	3.9	156.8	162.0	170.0	8.0	5.2	92.2	91.8	53.0
10	112.8	108.9	99.5	9.4	3.9	156.8	161.8	170.0	8.2	5.0	91.8	91.2	52.9
11	112.9	109.1	99.3	9.8	3.8	156.8	161.6	170.0	8.4	4.8	91.7	91.3	52.5
12	112.8	108.9	99.5	9.4	3.9	156.8	161.4	170.0	8.6	4.6	91.9	91.8	52.5
13	112.9	109.1	99.8	9.3	3.8	156.8	161.3	170.0	8.7	4.5	91.8	92.1	52.2
14	112.8	108.9	99.5	9.4	3.9	156.7	161.2	169.9	8.7	4.5	91.9	91.8	52.3
15	113.0	109.2	99.7	9.5	3.8	156.7	161.2	170.0	8.8	4.5	92.2	91.9	52.0
16	112.9	109.0	99.3	9.7	3.9	156.7	161.1	170.0	8.9	4.4	92.2	91.9	52.1
17	112.7	108.9	99.5	9.4	3.8	156.7	161.1	170.0	8.9	4.4	91.8	91.9	52.2

$\Delta T_c^1 = T_c^p - T_c^f$, $\Delta T_c^2 = T_c^{on} - T_c^p$, $\Delta T_m^1 = T_m^f - T_m^p$, $\Delta T_m^2 = T_m^p - T_m^{on}$, $\Delta T_c = T_m^p - T_c^p$.
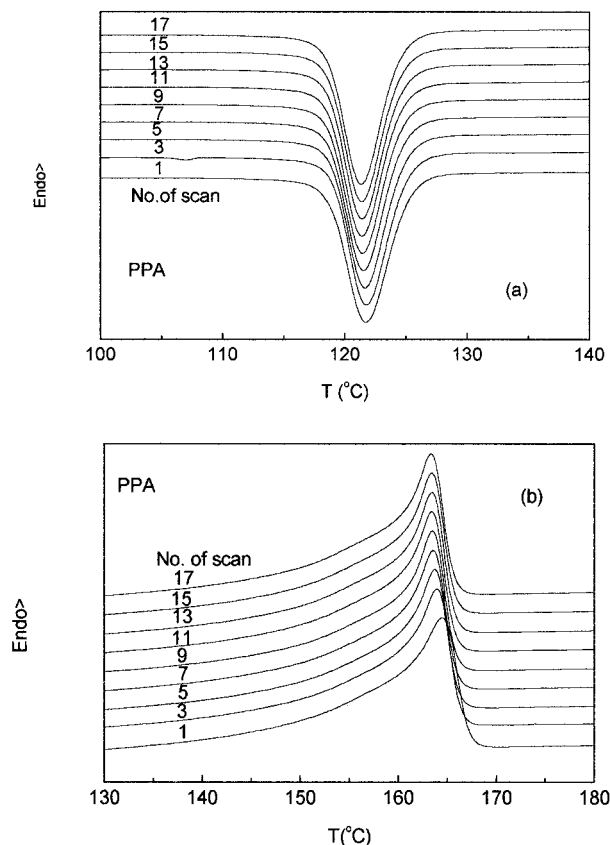
Figure 2 DSC (a) crystallization and (b) melting curves of multiscan of PPA.

faster than that of neat PP due to the heterogeneous nucleation effect of the nucleating agent A. It could be said that the thermal stability of the heterogeneous nucleation effect of the nucleating agent A was good and the heterogeneous nucleation effect of the nucleating agent A for reused PPA did not decrease.

According to the melting results, the T_m^p of PPA was higher than that of PP in the DSC multiscanning. The shape of the melting peak of the DSC curves of PPA differed from that of pure PP. The peak width (ΔT_m) of PPA and the ΔT_m^1 were narrower than those of PP, but the ΔT_m^2 was wider than that of pure PP in the DSC multiscanning. However, no change of the ΔT_m^1 was observed. Although the T_m^{on} and T_m^p of PPA were higher than those of PP, the T_m^f of PPA was lower than that of PP. Although a little decrease in the T_m^p of PPA was observed, the ΔH_c and ΔH_m of PPA did not change and were higher than those of PP with an increasing number of DSC scans. This also indicated that the heterogeneous nucleation effect of nucleation agent A was stable in the DSC multiheating and cooling processes.

Crystallization and Melting Behavior of Multiscanning of PPB and PPD

The crystallization and melting curves of PPB and PPD are shown in Figures 3 and 4, respec-

Table II   DSC Results of Multiscanned PPA

No. Scan	T_c^{on} (°C)	T_c^p (°C)	T_c^f (°C)	ΔT_c^1 (°C)	ΔT_c^2 (°C)	T_m^{on} (°C)	T_m^p (°C)	T_m^f (°C)	ΔT_m^1 (°C)	ΔT_m^2 (°C)	ΔH_c (J/g)	ΔH_m (J/g)	ΔT_c (°C)
1	125.4	121.7	110.8	10.9	3.7	157.3	164.2	168.7	4.5	6.9	95.6	98.5	42.5
2	125.2	121.8	111.5	10.3	3.4	158.0	164.0	168.5	4.5	6.0	95.0	99.5	42.2
3	125.3	121.9	111.8	10.1	3.4	158.2	163.8	168.2	4.4	5.6	94.3	99.2	41.9
4	125.1	121.7	111.5	10.2	3.4	158.3	163.7	167.9	4.2	5.4	94.5	99.2	42.0
5	125.0	121.7	111.5	10.2	3.3	158.3	163.6	167.9	4.3	5.3	94.4	98.8	41.9
6	125.1	121.7	111.6	10.1	3.4	158.3	163.5	167.9	4.4	5.2	94.3	98.7	41.8
7	125.0	121.7	111.6	10.1	3.3	158.2	163.4	167.9	4.5	5.2	94.2	99.5	41.7
8	124.9	121.6	111.6	10.0	3.3	158.5	163.4	167.9	4.5	4.9	94.1	99.2	41.8
9	124.9	121.6	111.6	10.0	3.3	158.5	163.4	167.9	4.5	4.9	94.3	99.4	41.8
10	124.7	121.4	111.5	9.9	3.3	158.3	163.3	167.9	4.6	5.0	94.0	99.5	41.9
11	124.8	121.5	111.6	9.9	3.3	158.3	163.3	167.9	4.6	5.0	94.0	99.5	41.8
12	124.7	121.4	111.5	9.9	3.3	158.2	163.2	167.9	4.7	5.0	94.4	99.7	41.8
13	124.7	121.4	111.5	9.9	3.3	158.4	163.3	167.9	4.6	4.9	94.0	99.6	41.9
14	124.8	121.5	111.6	9.9	3.3	158.4	163.3	167.9	4.6	4.9	94.1	99.2	41.8
15	124.6	121.4	111.5	9.9	3.2	158.4	163.3	167.9	4.6	4.9	94.0	99.3	41.9
16	124.6	121.4	111.5	9.9	3.2	158.3	163.2	167.8	4.6	4.9	94.0	99.2	41.8
17	124.6	121.4	111.5	9.9	3.2	158.3	163.2	167.5	4.3	4.9	94.0	98.6	41.8

$\Delta T_c^1 = T_c^p - T_c^f$, $\Delta T_c^2 = T_c^{on} - T_c^p$, $\Delta T_m^1 = T_m^f - T_m^p$, $\Delta T_m^2 = T_m^p - T_m^{on}$, $\Delta T_c = T_m^p - T_c^p$.
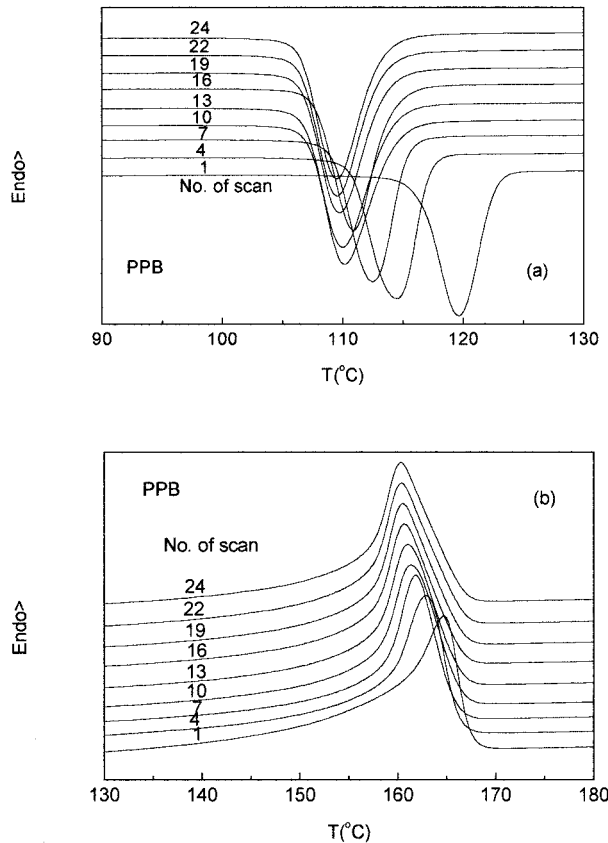
Figure 3 DSC (a) crystallization and (b) melting curves of multiscan of PBP.

tively. The crystallization and melting parameters are shown in Tables III and IV, respectively. It can been seen that the T_c^p of PPB and PPD decreased before the 20th and the 5th scanning, respectively, as the number of scans increased. The T_c^p of PPB and PPD decreased significantly in the first several scannings and finally was close to the T_c^p of pure PP. Because the heterogeneous nucleation effect of nucleating agent B was higher than that of nucleating agent D, the T_c^p of PPB was higher than that of PPD. But the T_c^p of PPB decreased more rapidly than that of PPD with an increasing number of scans. Due to the worse heterogeneous nucleation effect and the lower T_c^p of PPD, the T_c^p of PPD was close to that of pure PP after the fourth scanning. It indicated that the heterogeneous nucleation effect of nucleating agent D of PPD had been lost. The T_c^p of PPB was still higher than that of pure PP after the 24th scanning. It indicated that although the heterogeneous nucleation effect of nucleating agent B decreased quickly in the DSC multiscanning, it still existed. The ΔT_c^2 of PPB increased in the

DSC multiscanning, also indicating that the rate of crystallization decreased. Chen et al.[15] studied PP nucleated with aliphatic diacids. They observed that the crystallization peak changed to double peaks and then to a single peak again in the multiscanning. But the single peaks of PP and nucleated PP were observed in our experiment.

From the results of melting of PPB and PPD samples, it could be seen that the T_m^{on}, T_m^p, and T_m^f decreased in the DSC multiscanning. This meant that the crystals with a higher melting point decreased and the perfection of crystals became worse in the DSC multiscanning. The high-temperature region of the melting peak of PPB became wide gradually, but the opposite phenomenon was observed in the low-temperature region of the melting peak of PPB. The reason was that the T_m^p shifted to the low temperature.

The ΔH_c and ΔH_m of PPB and PPD gradually decreased in the DSC multiscanning. It indicated that the heterogeneous nucleation effect of nucleating agents B and D became worse. The ΔT_c of PPB increased with increase in the number of
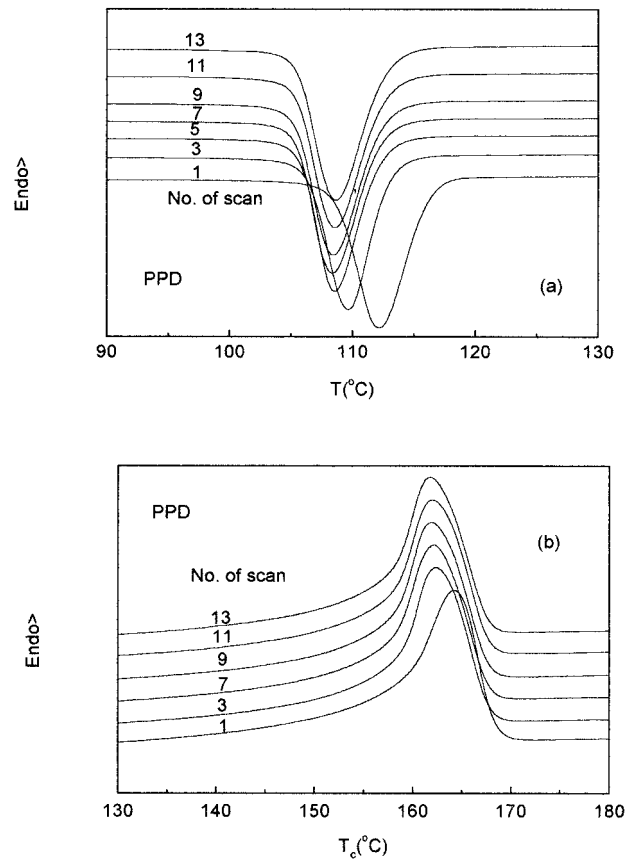

Figure 4 DSC (a) crystallization and (b) melting curves of multiscan of PPD.

Table III DSC Results of Multiscanned PPB

No. Scan	T_c^{on} (°C)	T_c^p (°C)	T_c^f (°C)	ΔT_c^1 (°C)	ΔT_c^2 (°C)	T_m^{on} (°C)	T_m^p (°C)	T_m^f (°C)	ΔT_m^1 (°C)	ΔT_m^2 (°C)	ΔH_c (J/g)	ΔH_m (J/g)	ΔT_c (°C)
1	122.7	119.6	110.3	9.3	3.1	158.4	164.6	170.0	5.4	6.2	96.1	97.4	45.0
2	120.3	117.3	107.8	9.5	3.0	158.2	163.3	168.5	5.2	5.1	94.7	95.0	46.0
3	118.8	115.7	104.9	10.8	3.1	158.4	163.2	168.5	5.3	4.8	94.2	93.5	47.5
4	117.2	114.5	104.0	10.5	2.7	157.9	162.8	168.7	5.9	4.9	93.8	94.2	48.3
5	116.6	113.8	103.4	10.4	2.8	157.8	162.8	168.3	5.5	5.0	93.3	93.1	49.0
6	116.1	113.3	102.4	10.9	2.8	157.7	162.4	168.0	5.6	4.7	92.7	92.2	49.1
7	115.4	112.5	102.2	10.3	2.9	157.7	161.7	168.5	6.8	4.0	92.6	92.4	49.2
8	114.8	111.9	101.8	10.1	2.9	157.3	161.5	168.5	7.0	4.2	92.7	92.3	49.6
9	114.3	111.4	101.4	10.0	2.9	157.1	161.2	168.3	7.1	4.1	92.5	91.0	49.8
10	114.2	111.0	101.1	9.9	3.2	157.0	161.2	168.5	7.3	4.2	92.4	91.0	50.2
11	114.1	110.6	101.0	9.6	3.5	157.0	161.0	168.5	7.5	4.0	92.2	91.0	50.4
12	114.4	110.5	101.1	9.4	3.9	156.9	161.2	168.5	7.3	4.3	92.3	90.7	50.7
13	114.4	110.2	101.0	9.2	4.2	156.8	160.9	168.5	7.6	4.1	91.9	91.1	50.7
14	114.3	110.1	101.0	9.1	4.2	156.8	160.7	168.3	7.6	3.9	92.0	90.7	50.6
15	114.2	110.1	101.0	9.1	4.1	156.7	160.6	168.5	7.9	3.9	91.7	91.3	50.5
16	114.2	110.1	101.0	9.1	4.1	156.7	160.5	168.5	8.0	3.8	91.6	91.2	50.4
17	113.9	109.9	101.0	8.9	4.0	156.6	160.5	168.5	8.0	3.9	91.6	91.2	50.6
18	113.9	110.0	101.0	8.9	3.9	156.6	160.4	168.5	8.1	3.8	92.0	91.0	50.4
19	113.7	109.9	101.0	8.8	3.8	156.5	160.4	168.5	8.1	3.9	92.1	91.1	50.5
20	113.4	109.6	101.0	8.6	3.8	156.5	160.3	168.5	8.2	3.8	91.4	91.0	50.7
21	113.3	109.6	101.0	8.6	3.7	156.4	160.3	168.5	8.2	3.9	91.6	90.9	50.7
22	113.4	109.7	101.0	8.7	3.7	156.4	160.2	168.5	8.3	3.8	91.7	90.9	50.5
23	113.3	109.5	101.0	8.5	3.8	156.4	160.2	168.5	8.3	3.8	91.2	90.8	50.7
24	113.2	109.5	101.0	8.5	3.7	156.4	160.2	168.5	8.3	3.8	91.7	90.7	50.7

$\Delta T_c^1 = T_c^p - T_c^f$, $\Delta T_c^2 = T_c^{on} - T_c^p$, $\Delta T_m^1 = T_m^f - T_m^p$, $\Delta T_m^2 = T_m^p - T_m^{on}$, $\Delta T_c = T_m^p - T_c^p$.

scans. The same phenomenon was observed for PPD before the fifth scanning, but the ΔT_c of PPD did not change in the following scanning. It is known that the bigger the ΔT_c, the worse is the heterogeneous nucleation effect. Therefore, the heterogeneous nucleation effect of nucleating

Table IV DSC Results of Multiscanned PPD

No. Scan	T_c^{on} (°C)	T_c^p (°C)	T_c^f (°C)	ΔT_c^1 (°C)	ΔT_c^2 (°C)	T_m^{on} (°C)	T_m^p (°C)	T_m^f (°C)	ΔT_m^1 (°C)	ΔT_m^2 (°C)	ΔH_c (J/g)	ΔH_m (J/g)	ΔT_c (°C)
1	116.3	112.2	100.3	11.9	4.1	157.5	164.1	172.0	7.9	6.6	95.0	93.9	51.9
2	114.3	110.8	100.1	10.7	3.5	157.4	162.9	170.5	7.6	5.5	93.2	92.1	52.1
3	113.1	109.7	100.0	9.7	3.4	157.4	162.2	170.0	7.8	4.8	92.2	91.2	52.5
4	112.6	109.1	100.1	9.0	3.5	157.0	161.9	170.5	8.6	4.9	92.9	91.8	52.8
5	112.4	108.6	99.3	9.3	3.8						91.9		
6	112.4	108.4	99.3	9.1	4.0	156.7	161.8	170.0	8.2	5.1	92.2	91.1	53.4
7	112.3	108.4	99.3	9.1	3.9	156.6	162.0	170.5	8.5	5.4	92.5	91.3	53.6
8	112.4	108.4	99.3	9.1	4.0	156.7	162.0	170.0	8.0	5.3	93.0	91.2	53.6
9	112.6	108.6	99.3	9.3	4.0	156.8	161.7	170.1	8.4	4.9	92.9	91.1	53.1
10	112.6	108.6	99.5	9.1	4.0	156.8	161.8	169.6	7.8	5.0	92.9	89.9	53.2
11	112.7	108.6	99.6	9.0	4.1	156.7	161.9	169.4	7.5	5.2	92.8	90.5	53.3
12	112.8	108.6	99.5	9.1	4.2	156.7	161.7	169.2	7.5	5.0	92.0	89.6	53.1
13	112.8	108.7	99.5	9.2	4.1	156.7	161.6	169.2	7.6	4.9	91.5	89.7	52.9
14	112.9	108.8	99.6	9.2	4.1	156.7	161.6	169.2	7.6	4.9	91.8	89.9	52.8

$\Delta T_c^1 = T_c^p - T_c^f$, $\Delta T_c^2 = T_c^{on} - T_c^p$, $\Delta T_m^1 = T_m^f - T_m^p$, $\Delta T_m^2 = T_m^p - T_m^{on}$, $\Delta T_c = T_m^p - T_c^p$.

agents B and D became worse and the rate of crystallization of PPB and PPD decreased with an increasing number of DSC scans.

Thermal Stability of Heterogeneous Nucleation Effect of PP Nucleated with Different Nucleating Agents

The above results indicate that the crystallization temperatures of PPA were higher than those of PPB, PPD, and pure PP. The crystallization temperatures of PPA and pure PP did not change with an increasing number of DSC scans. This meant that the thermal stability of the heterogeneous nucleation effect of nucleating agent A was high and the nucleation effect of pure PP was thermally stable. The crystallization temperatures of PPB and PPD gradually shifted to lower temperature as the number of DSC scans increased and the heterogeneous nucleation effect of nucleating agent B and D was low. The crystallization temperature of PPD reached that of pure PP after the fifth scanning, indicating the heterogeneous nucleation effect of nucleating agent D in the PP was easily lost in the process of DSC multiscanning. The T_c^p of PPB decreased gradually and was still higher that of pure PP after the 24th scanning, but that of PPD was close to that of pure PP after the fifth scanning. So, it could be said that the thermal stability of nucleating agent B was better than that of nucleating agent D in the process of multiscanning.

Although the ΔT_c^2 of PPA was smaller than that of PP, the ΔT_c^2 changed in the same way in the DSC multiscanning and all decreased a little for the first several number of scans and then did not change. However, the ΔT_c^2 of PPB and PPD significantly changed in the DSC multiscanning. The ΔT_c^2 of PPB and PPD first decreased, then increased, and finally decreased with an increasing the number of scans. It might be related to the thermal instability of the sorbitol derivatives. The heterogeneous nucleation effect of nucleating agents B and D gradually decreased with an increasing number of DSC scans and the crystallization temperatures of nucleated PP decreased. So the shape of the crystallization peak significantly changed.

The melting temperatures of PP, PPA, PPB, and PPD all decreased with increase of the number of scans, but that of PPB and PPD decreased more significantly than that of PP

and PPA. Because the melting points of polymers are largely determined by the thickness of the crystal lamellae, it indicated that the thickness of the crystal lamellae decreased during the multiscanning. The melting temperature of PPD decreased mostly sharply during the first 4th scanning and then did not change in the following scan. However, the T_m^p of PPD was higher than was the relevant T_m^p of pure PP, which indicated that the thickness of the crystal lamellae was higher than that of pure PP. The T_m^p of PPB was lower than that of pure PP after the eight scanning, meaning that, although the nucleating effect of nucleating agent B existed, the thickness of the crystal lamellae of PPB was lower than that of pure PP.

The nominal supercooling degree (ΔT_c) of PP and PPA did not change, but that of PPB and PPD increased with an increased number of scans. The bigger the ΔT_c, the slower the crystallization rate and the worse the nucleating effect. The crystallization rate of pure PP and PPA did not change, while the crystallization rate of PPB and PPD decreased with an increased number of DSC scans. It also meant that the heterogeneous nucleation effect of nucleating agents B and D gradually decreased in the DSC multiscanning processes.

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