Polymer 49 (2008) 5137–5145

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Crystallization behavior and melting characteristics of PP nucleated by a novel supported β-nucleating agent

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ARTICLE INFO

Article history:
Received 4 May 2008
Received in revised form 29 August 2008
Accepted 2 September 2008
Available online 20 September 2008

Keywords:
β-Nucleating agent
β-Polypropylene
Nano-$CaCO_3$

ABSTRACT

The β-nucleated PP with high β-PP content was prepared by a novel supported β-nucleating agent, which was prepared with pimelic acid supported on nano-$CaCO_3$ as support. The influences of the content of the support and supported β-nucleating agent, pre-melting temperature (T_{melt}) and scan rates on crystallization behavior and melting characteristics, and the β-PP content of β-nucleated PP were determined by Differential Scanning Calorimeter (DSC) and Wide-Angle X-ray Diffraction (WAXD). The results indicated that the addition of supported β-nucleating agent markedly increased the crystallization temperature (T_c) of PP. Increasing the content of supported β-nucleating agent slightly increased the T_c, but had no influence on the melting temperatures (T_m) of β-nucleated PP. The T_c and T_m of β-nucleated PP decreased slightly with increasing the content of the support nano-$CaCO_3$. The effects of scan rates and multiple scans with different T_{melt} on the crystallization and melting behavior of PP nucleated by supported β-nucleating agent are similar to that of PP nucleated by calcium pimelate (CaHA). The β-PP content above 90 percent was obtained in PP nucleated by supported β-nucleating agent and was not influenced by the content of nano-$CaCO_3$. The supported β-nucleating agent prepared by supporting pimelic acid on nano-$CaCO_3$ is a β-nucleating agent with high efficiency and selectivity, and low cost.

1. Introduction

Since Padden and Keith classified the crystal forms of isotactic polypropylene (PP) [1], the study on the formation, microstructure and morphology of β-PP has attracted a great deal of interest [2–36]. The metastable β-PP might be formed under some special conditions such as quenching the melt to a certain temperature range [2], directional crystallization in a temperature gradient field [3], shearing or elongation of the melt during crystallization [4,5], vibration-induced crystallization [6,7], or addition of β-nucleating agents into the PP [8–36]. The introduction of β-nucleating agent into PP is the most reliable method for preparation of β-PP. Until now, only four classes of compounds have been mainly used as β-nucleating agents for preparation of β-PP. The first class is a minority of aromatic ring compounds, for example γ-quinacridone (Dye Permanent Red E3B) [8]. The second class is certain group IIA metal salts or their mixtures with some specific dicarboxylic acids [9,10], for example, calcium pimelate or suberate. The third class is a minority of aromatic amide compounds, for example *N*,*N*′-dicyclohexylterephthalamide [11,12]. And the last one is rare earth β-nucleating agent [13] and other [14]. Up to now, a supported β-nucleating agent had not been reported. The β-nucleated efficiency and selectivity of nucleating agent could be mainly determined by the content of β-PP, which is dependent on the kinds and the content of β-nucleating agents. The β-PP content of β-nucleated PP sample can be characterized by the *K* value determined from wide-angle X-ray scattering [2] and by differential scanning calorimetry [15,16]. However, The β-PP content in the latter depends on the thermal history [17–19] and the melting memory effect of the samples [3,17,20–22].

It is widely reported on the crystallization behavior and melting characteristics, and the β-PP content of PP nucleated by β-nucleating agents [7–36]. Shi et al. [9] found that two component systems containing dicarboxylic acid and different calcium compounds exhibited a very high β-nucleating activity for preparation of β-PP. Li et al. reported the crystallization of PP nucleated by pimelic acid, sodium pimelate, calcium pimelate or pimelic acid/calcium stearate under different conditions [23], the effect of mould temperature on the β-PP content [24], the heat of fusion of the β-PP [25], and growth as well as recrystallization of β-PP [26]. Tjong et al.

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doi:10.1016/j.polymer.2008.09.009

prepared nucleated PP with high β-PP content with bi-component nucleator, pimelic acid/calcium stearate, and investigated the β-PP content, the mechanical properties [27], the morphology and the thermal behavior of nucleated PP [28].

Tomasz et al. [29] investigated the effect of the isotacticity and molecular weight distribution of PP on the crystallization temperatures of PP nucleated by different β-nucleating agents. The effect of various heterogeneous β-nucleating agents on the mechanical properties of heterophasic copolymer of PP and ethylene–propylene rubber blends was reported by Trongtorsak et al. [30]. Dou [31] investigated the influence of the composition ratio of pimelic acid/calcium stearate bi-component nucleator and crystallization temperatures on the β-PP content in nucleated PP. Subsequently, Varga et al. found a single component nucleator, calcium suberate or calcium pimelate, prepared by calcium dicarboxylates of different dicarboxylic acids in aqueous solution [10], and investigated the efficiency and the selectivity of calcium suberate or calcium pimelate [32], thermal stability [33] and equilibrium melting point of β-PP [34]. The results indicated that calcium suberate or calcium pimelate is a thermally stable β-nucleating agent with high efficiency and selectivity. Li et al. also supported the conclusion [35]. It is valuable to point out that Menyhárd et al. [16] characterized and compared the nucleating efficiency and selectivity of different β-nucleating agents by differential scanning calorimetry and temperature-modulated differential scanning calorimetry. The results indicated that the calcium suberate or calcium pimelate exhibited the highest efficiency and selectivity in the known β-nucleating agent. Although the commercial product of NJ Star NU-100 (*N*,*N*′-dicyclohexylterephthalamide) is efficient above a critical concentration, its partial dissolution with the melt of PP decreased the selectivity and efficiency of NJ Star NU-100 [36].

Although β-PP possesses superior impact performance and high heat distortion temperature [37,38], which has attracted a great deal of interest [39,40], the lower yield stress and stiffness of β-PP compared with non-nucleated or α-PP would restrict its applications. To improve the yield stress and stiffness of β-nucleated PP is an interesting subject of industry, science and technology. In order to increase the nucleation efficiency and decrease the price of β-nucleating agent, and improve the mechanical properties of β-nucleated PP, a new supported β-nucleating agent was prepared in our laboratory [41,42]. Based on the preparation principles of high efficiency supported catalyst of ethylene polymerization and the nucleation mechanism of calcium pimelate, the β-nucleating agent supported on nano-$CaCO_3$ for PP was prepared by supporting pimelic acid on nano-$CaCO_3$ with high surface area. The support nano-$CaCO_3$ with high surface area may not only disperse β-nucleating agent active component effectively and increase the efficiency, and reduce the cost of β-nucleating agent, but also increase the yield stress and stiffness of β-nucleated PP due to the reinforce and toughen of nano-$CaCO_3$ [43–45]. Therefore, it is significant for the nano-$CaCO_3$ supported β-nucleating agent to increase the nucleation efficiency and reduce the cost of β-nucleating agent, and spreading application of β-nucleating agents and β-nucleated PP.

Because the β-PP content is dependent on the content of the support nano-$CaCO_3$ in supported β-nucleating agent, the content of supported β-nucleating agent, the thermal history and so on. The purpose of this paper is to investigate the influences of the thermal history, the content of support nano-$CaCO_3$ and the content of nucleating agents on the crystallization behavior, and melting characteristics as well as the β-PP content in PP nucleated by nano-$CaCO_3$ supported β-nucleating agent. The melting characteristics and the β-PP content of PP nucleated by calcium pimelate (CaHA) were compared.

2. Experiment

2.1. Materials

A commercial grade isotactic polypropylene (H030SG, MFR = 3 g/10 min at 200 °C) used in the study was supplied by Reliance Industries Limited. A commercial grade active nano-$CaCO_3$ with the particle diameter between 40 nm and 60 nm was obtained from Guangping Chemical Industry Limited Company, China, which had been pretreated with fatty acid in its production process. Calcium pimelate (CaHA) and a novel nano-$CaCO_3$ supported β-nucleating agent (NA*x*, the *x* means the mass ratio of support/pimelic acid (HA), $m_{\mathrm{Support}}/m_{\mathrm{HA}}$) were prepared in our laboratory [41,42].

2.2. Sample preparation

Before sample preparation, all the materials were adequately dried in a vacuum oven at appropriate temperatures. The PP nucleated by supported β-nucleating agents with the content of 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt% with different $m_{\mathrm{Support}}/m_{\mathrm{HA}}$ was homogenized at 190 °C, and 50 rpm for 8 min using an HL-200 internal mixer (Jinlin University Science and Education Instrument

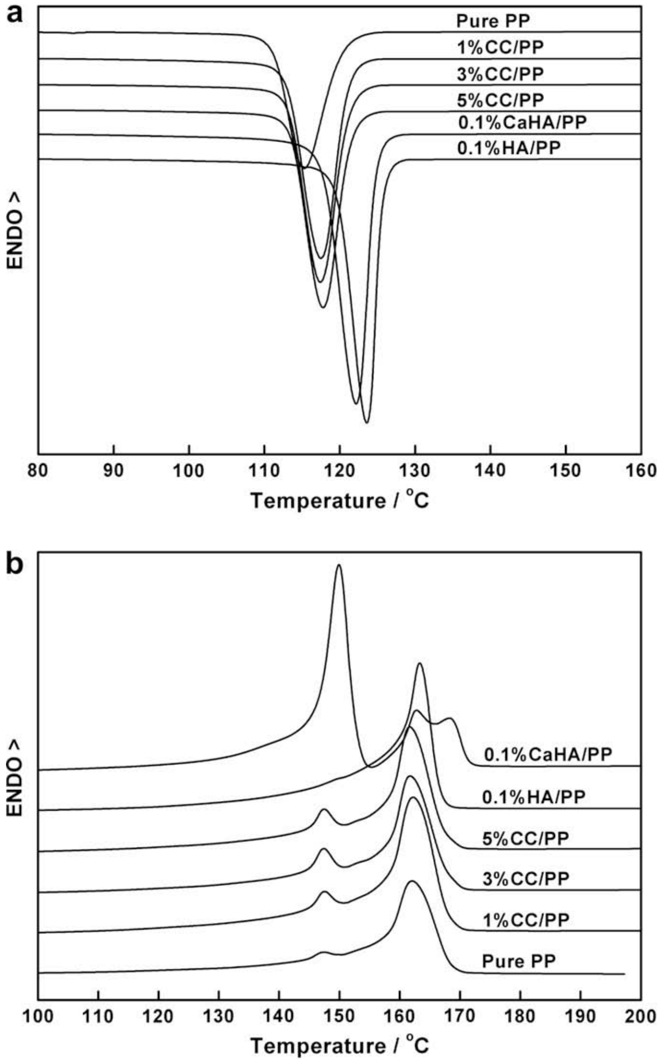

Fig. 1. Crystallization (a) and melting (b) curves of pure PP, PP nucleated by HA and CaHA, and PP filled by nano-$CaCO_3$.

Table 1
DSC data of PP and nucleated PP

Sample	T_c(°C)	ΔH_c (J/g)	T_β^m (°C)	ΔH_β^m (J/g)	$T_{\alpha1}^m$ (°C)	$\Delta H_{\alpha1}^m$ (J/g)	$T_{\alpha2}^m$ (°C)	$\Delta H_{\alpha2}^m$ (J/g)	K_β
Pure PP	115.3	91.9	146.8	1.2	162.1	88.8	–	–	0.30
0.1 wt% HA/PP	124.0	102.9	–	–	163.3	104.5	–	–	0
1 wt% $CaCO_3$/PP	117.5	99.4	147.3	2.7	162.3	95.7	–	–	0.21
3 wt% $CaCO_3$/PP	117.8	95.4	147.2	5.0	161.8	89.3	–	–	0.19
5 wt% $CaCO_3$/PP	117.8	97.5	147.3	4.2	161.7	95.3	–	–	0.10
0.1 wt% CaHA/PP	122.2	92.2	149.9	73.2	163.1	18.7	168.3	9.9	0.90
1%NA100/PP	120.0	92.9	148.9	79.8	163.1	18.2	168.1	14.8	0.93
2%NA100/PP	120.8	93.4	148.7	81.4	163.1	17.7	167.9	15.4	0.99
3%NA100/PP	121.4	94.2	148.7	82.9	163.0	19.4	167.9	14.5	0.94
4%NA100/PP	121.5	92.8	148.7	83.1	162.8	19.4	167.9	14.2	0.95
5%NA100/PP	121.7	93.2	149.0	83.4	162.9	16.6	168.0	16.8	0.93

NA100: notes that the mass ratio of HA and nano-$CaCO_3$ in supported β-nucleating agent is 1/100; T_β^m: the melting peak temperature of β-PP; $T_{\alpha1}^m$: the melting peak temperature of α_1-PP; $T_{\alpha2}^m$: the melting peak temperature of α_2-PP; ΔH_β^m: the heat of fusion of β-PP; $\Delta H_{\alpha1}^m$: the heat of fusion of α_1-PP; $\Delta H_{\alpha2}^m$: the heat of fusion of α_2-PP.

Factory, China). The PP nucleated by 0.1 wt% CaHA and HA, and PP filled by 1–5 wt% nano-$CaCO_3$ was also prepared as same conditions, respectively.

2.3. Characterizations

2.3.1. Differential scanning calorimeter

The crystallization behavior and melting characteristics of the samples were carried on a TA DSC Q10 Differential Scanning Calorimeter (DSC), the temperature and the enthalpy have been calibrated with indium at different rates in our experiments. All DSC curves in this paper have been normalized. About 5 mg of sample was weighted very accurately. The sample was heated up to melting temperature (T_{melt}) and held there for 5 min in order to erase their thermal and mechanical history. The sample after premelting was cooled to 50 °C at certain cooling rate (V_c) for crystallization behavior investigation, and then subsequently reheated to T_{melt} at certain heating rate (V_h) for melting behavior and polymorphism investigation. Besides especially noting, the T_{melt} is 220 °C, V_c and V_h are 10 °C/min.

2.3.2. Wide-angle X-ray diffraction

Wide-angle X-ray diffraction experiment was conducted with a Rigaku Geigerflex Model D/Max-IIIA rotating anode X-ray diffractometer. Graphite monochromatic Cu-Kα radiation was employed as a radiation source. The scanning range was 5°–40° with the rate of 4°/min and a step length of 0.02. In order to remain the thermal history as same as the DSC measures, the samples used in WAXD measures had been prepared in DSC by heating up to 220 °C and held there for 5 min, then cooled to 50 °C with the cooling rate 10 °C/min. The *K* value representing the β-PP content in

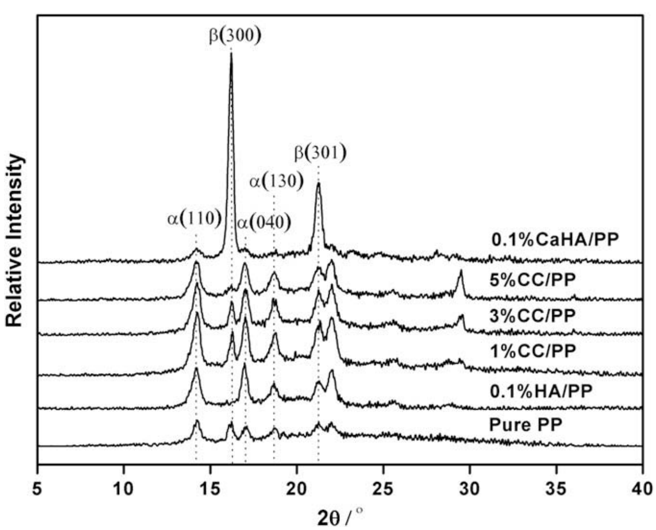

Fig. 2. X-ray diffraction diagrams of pure PP, PP nucleated by HA and CaHA, and PP filled by nano-$CaCO_3$.

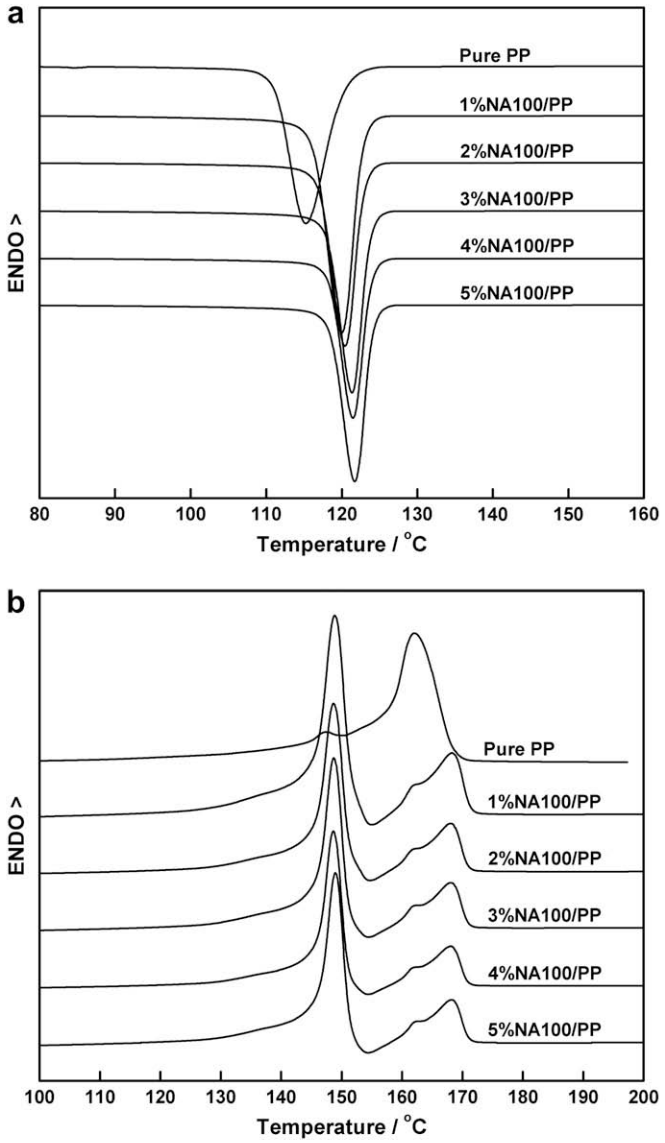

Fig. 3. DSC crystallization (a) and melting (b) curves of PP nucleated by nano-$CaCO_3$ supported β-nucleating agent.

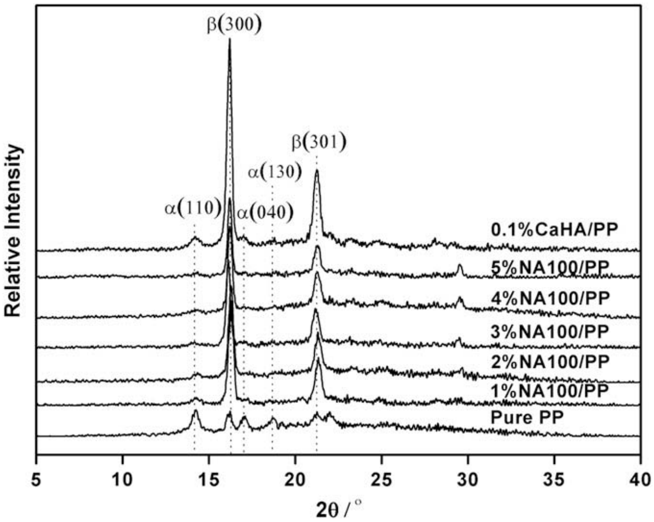

Fig. 4. X-ray diffraction diagrams of PP nucleated by nano-$CaCO_3$ supported β-nucleating agent.

the β-nucleated PP was calculated from X-ray diffractograms according to Turner-Jones et al. [2]:

$$K_\beta = H_\beta / \left(H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3} + H_\beta\right) \quad (1)$$

where $H_{\alpha 1}$, $H_{\alpha 2}$ and $H_{\alpha 3}$ are the intensities of α-diffraction peaks corresponding to angles $2\Theta = 14.2°$, 17.0° and 18.8°, respectively, and H_β is the intensity of β-diffraction peak at $2\Theta = 16.2°$.

3. Results and discussion

3.1. Effect of nano-$CaCO_3$, HA and CaHA on crystallization behavior and melting characteristics of PP

The supported β-nucleating agent containing nano-$CaCO_3$ and nucleated active component CaHA was prepared by HA supported on the support nano-$CaCO_3$ with high specific surface area. In the preparation process, the chemical reaction took place between HA and nano-$CaCO_3$ to form the CaHA β-nucleating agent on nano-$CaCO_3$ surface. Thus the influence of nano-$CaCO_3$, CaHA and HA on crystallization behavior and melting characteristics of PP was studied firstly. Fig. 1 shows the DSC crystallization and melting curves of PP nucleated by CaHA and HA, and filled by nano-$CaCO_3$, and the corresponding data is listed in Table 1. The results indicated

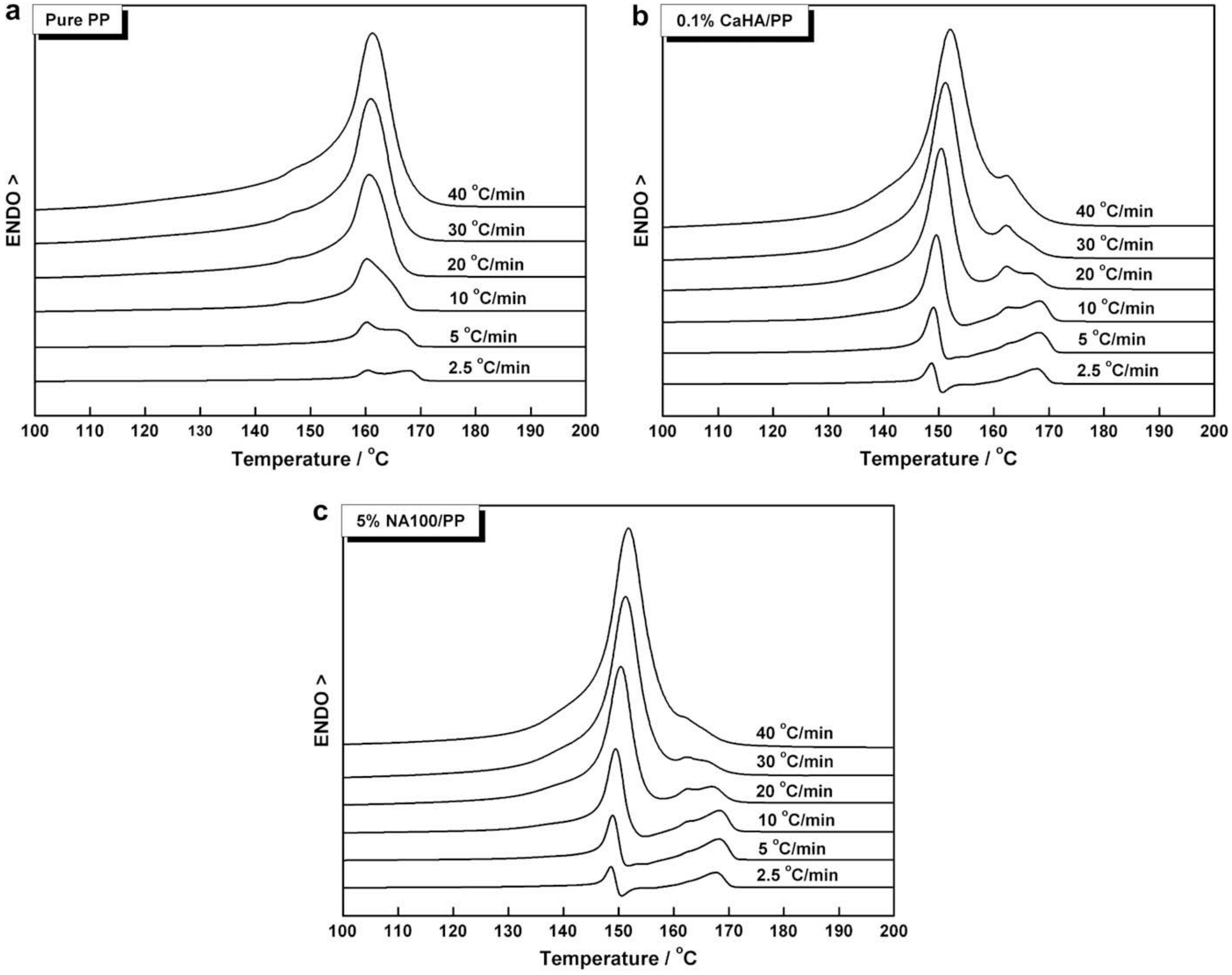

Fig. 5. DSC melting curves of PP (a), PP nucleated by 0.1 wt% CaHA (b) and 5 wt% NA100 (c) with different heating rates.

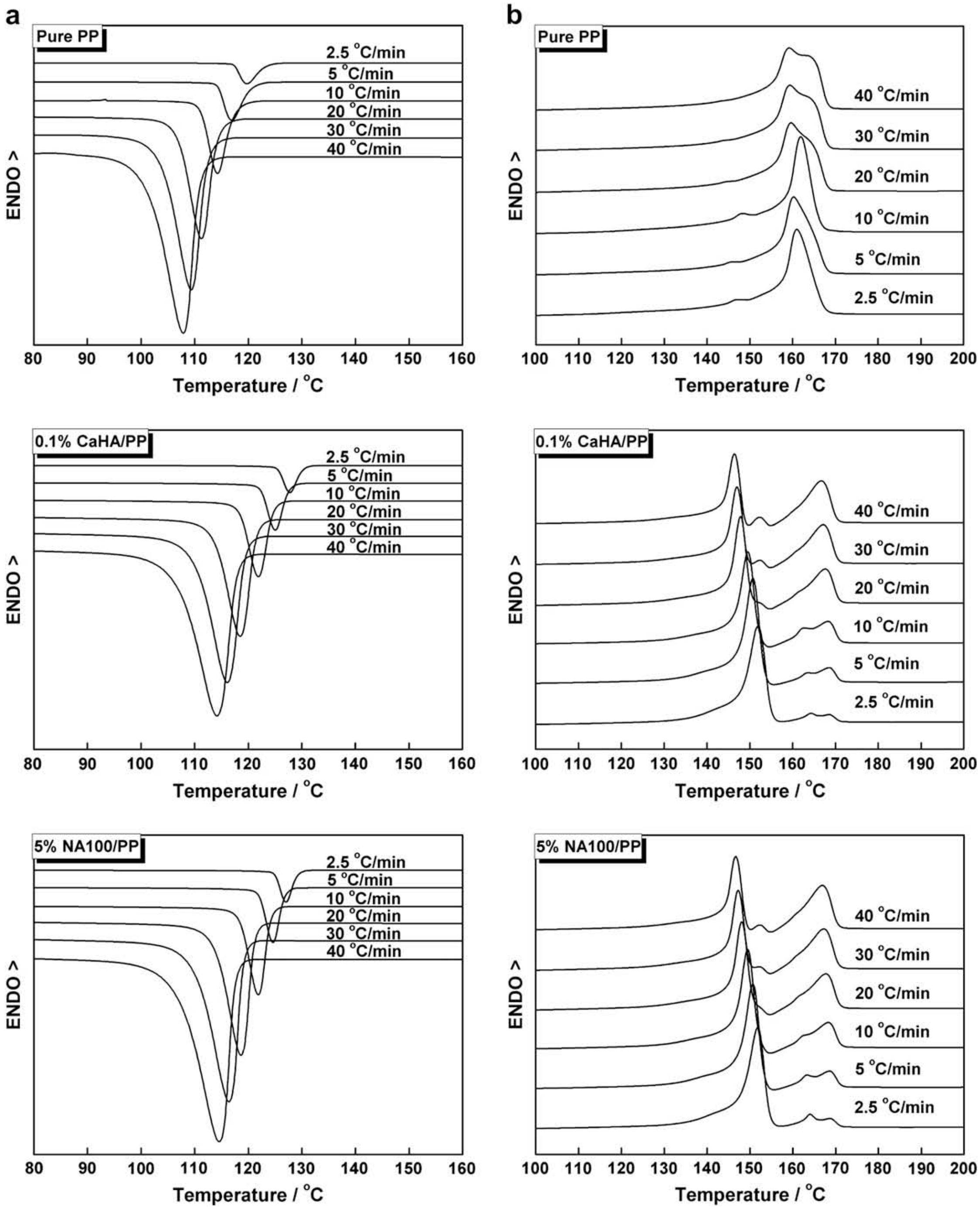

Fig. 6. DSC crystallization (a) and melting (b) curves of PP (1), PP nucleated by 0.1 wt% CaHA (2) and 5 wt% NA100 (3) with different cooling rates and the same heating rate of 10 °C/min.

that CaHA and HA increased T_c of PP remarkably, especially HA. However, nano-$CaCO_3$ slightly influenced the T_c of PP. The melting characteristics of PP nucleated by CaHA and HA, and filled by nano-$CaCO_3$ are much more different from each other. It can be seen from Fig. 1b that three melting peaks of PP nucleated by CaHA are observed and the intensity of β-PP is higher than that of the other samples. Therefore, the CaHA is a β-nucleating agent with high efficiency and selectivity.

Fig. 2 presents X-ray diffraction diagrams of PP, PP filled by nano-$CaCO_3$, PP nucleated by 0.1 wt% HA and CaHA. Table 1 shows the K values of the samples calculated by Eq. (1). The K value of pure PP is 0.30. The addition of nano-$CaCO_3$ and increase in the nano-$CaCO_3$ content decrease the K values of PP. Addition of 0.1 wt% HA into PP results in the formation of only α-PP. On the contrary, the K value of 0.93 is obtained for PP nucleated by CaHA. The above results approve that the HA and nano-$CaCO_3$ are α-nucleating agents for PP crystallization, but the CaHA is a β-nucleating agent with high β-nucleating ability.

3.2. Effect of nano-$CaCO_3$ supported β-nucleating agent on crystallization behavior and melting characteristics of PP

Fig. 3 shows the DSC crystallization and melting curves of PP nucleated by supported β-nucleating agent NA100, the related

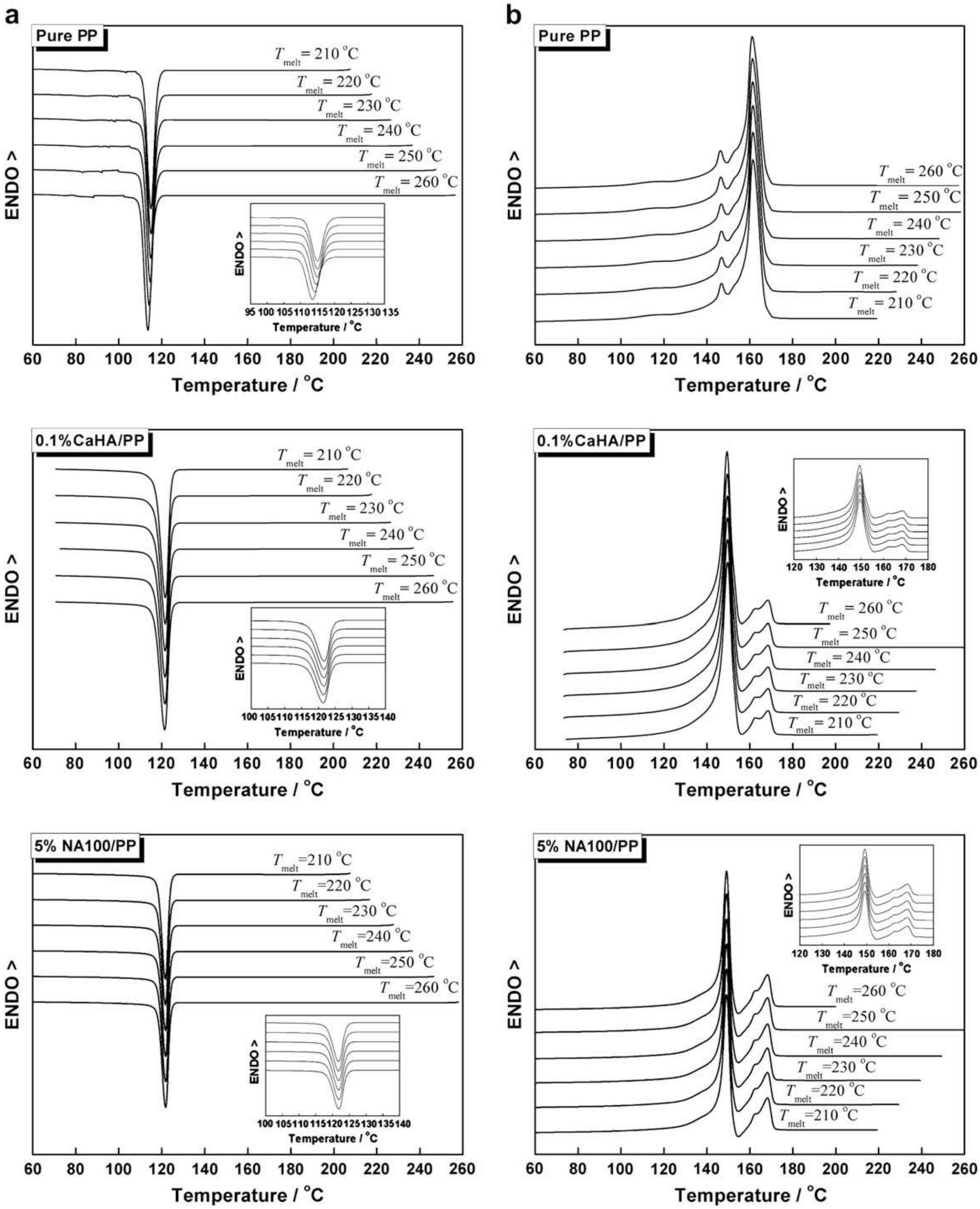

Fig. 7. Crystallization (a) and melting (b) curves of PP (1), PP nucleated by 0.1 wt% CaHA (2) and 5 wt% NA100 (3) with different melting temperatures.

data can be seen in Table 1. It is apparent that the supported β-nucleating agent significantly increases the T_c of PP. The addition of 1 wt% supported β-nucleating agent NA100 into PP increased the T_c from 115.3 °C of pure PP to 120.0 °C and the T_c of PP slightly increases with increasing the content of supported β-nucleating agent. The melting curves exhibit three endothermic melting peaks, which are similar to that of PP nucleated by CaHA. Fig. 4 shows X-ray diffraction diagrams of PP nucleated by β-nucleating agent NA100. The K values are listed in Table 1. It can be observed that the K value of PP nucleated by supported β-nucleating agent is higher than that of PP nucleated by 0.1 wt% CaHA. Although the crystallization behavior and melting characteristics of PP nucleated by supported β-nucleating agent are similar to that of PP nucleated by CaHA, the content of β-nucleating agent active component CaHA in supported β-nucleating agent nucleated PP is less than 0.1 wt% CaHA and the K value is higher than that of PP nucleated by 0.1 wt% CaHA. Therefore, the nano-$CaCO_3$ supported β-nucleating agent prepared in our lab possesses high β-nucleating ability and lower price.

3.3. Effect of scan rates on crystallization behavior and melting characteristics of PP nucleated by nano-$CaCO_3$ supported β-nucleating agent

Fig. 5 shows the DSC melting curves of pure PP, PP nucleated by supported β-nucleating agent NA100 and CaHA with different heating rates. In order to erase the effect of the thermal history, the samples were heated up to 220 °C and held there for 5 min, then cooled to 50 °C with the same cooling rate of 10 °C/min before recorded the melting curves with different heating rates. For pure PP, double melting peaks can be observed when the heating rate is lower than 10 °C/min. The intensity of low-temperature melting peak increased and that of high-temperature melting peak decreased with increasing the heating rates. This effect is typically associated with melting followed by recrystallization into more stable crystals and remelting of the recrystallized material at higher temperature. At higher heating rates, the process of recrystallization (and thus also remelting) is hindered, resulting in only one low-temperature melting peak. It is suggested that the original α crystals melt and recrystallize into more perfect α crystals.

For PP nucleated by supported β-nucleating agent NA100 and CaHA, the intensity of the first melting peak of α crystals is growing and that of the high-temperature peak is decreasing with the heating rates increasing, which is the same as the melting of pure PP attributed to the original α crystals melt and recrystallize into more perfect α crystals. It can also be seen clearly that at low heating rate the originally formed β crystals are able to recrystallize into α crystals during heating. At low heating rate, it even shows an exothermic effect (due to crystallization) right after the β melting peak. This effect also disappears at higher heating rates where it only shows a big β melting peak together with some α melting peaks that seems to have been present from the start. In one word, the melting curves of PP nucleated by supported β-nucleating agent NA100 are similar to that of PP nucleated by CaHA.

Fig. 6 shows the DSC crystallization and melting curves of pure PP and PP nucleated by supported β-nucleating agent NA100 and CaHA with different cooling rates and the same heating rate of 10 °C/min. The samples were heated up to 220 °C and held there for 5 min, then cooled to 50 °C with different cooling rates before recording the melting curves with the heating rates of 10 °C/min. It can be seen from the DSC crystallization curves that the crystallization peaks of the samples shift to high temperature with decreasing the cooling rates. For pure PP, it can be seen from Fig. 6a1 and b1 that the material only crystallized at low temperature (during fast cooling) is able to recrystallize and remelt leading to two peaks, which basically is a superposition of two endotherms and one exotherm in-between. This makes sense because when such unstable crystals formed at low temperature are melting at low temperature, this happens at a sufficiently high supercooling to allow for recrystallization. The crystals that were grown at high temperature during slow cooling are more stable and therefore melt at higher temperature where recrystallization is too slow because of the reduced supercooling. For PP nucleated by CaHA and supported β-nucleating agent, the supercooling also effects the crystallization and melting behavior of the samples. The melting peaks of β-modification shift to high temperature with decreasing the cooling rates. When the cooling rate was higher than 10 °C/min, the β-nucleated PP exhibited a shoulder peak or a melting peak at the high-temperature region of β-PP melting peak, but the shoulder peak at the region of α-PP melting disappeared. In addition the β crystals seem to be able to recrystallize into higher melting β crystals and then maybe again recrystallize into higher melting α crystals when the preceding cooling rate was sufficiently high. In one word, the crystallization behavior and melting characteristics affected by scan rates of PP nucleated by supported β-nucleating agent NA100 are similar to that of PP nucleated by CaHA.

3.4. *Effect of multiple scans on crystallization behavior and melting characteristics of nano-$CaCO_3$ supported β-nucleating agent PP*

Fig. 7 shows the DSC crystallization and melting curves of pure PP, PP nucleated by supported β-nucleating agent NA100 and CaHA under multiple scans with different T_{melt}. It can be observed that the T_{melt} between 210 °C and 260 °C had no influence on the shape of melting peak and enthalpy of crystallization and melting of β-nucleated PP with supported β-nucleating agent. Although the crystallization and melting peaks of the samples shifted to low temperature with the increasing T_{melt}, the decrease was lower than that of pure PP. For the T_{melt} between 210 °C and 260 °C, pure PP formed mainly α-PP, but nucleated PP rich in β-PP. It indicates that the T_{melt} between 210 °C and 260 °C has no influence on the nucleating efficiency of supported β-nucleating agent and possesses high β-nucleated efficiency in a wide range of temperatures. It can be used to prepare the β-PP alloy with engineering plastic and β-PP composites.

3.5. *Effect of the content of support in nano-$CaCO_3$ supported β-nucleating agent on β-PP content*

Fig. 8 shows the DSC crystallization and melting curves of PP nucleated by supported β-nucleating agent with different mass ratios of nano-$CaCO_3$/HA, and the relationship of the T_c and the content of supported β-nucleating agent is shown in Fig. 9. It can be seen that addition of supported β-nucleating agents into PP results in increasing the T_c remarkably. For the same content of supported

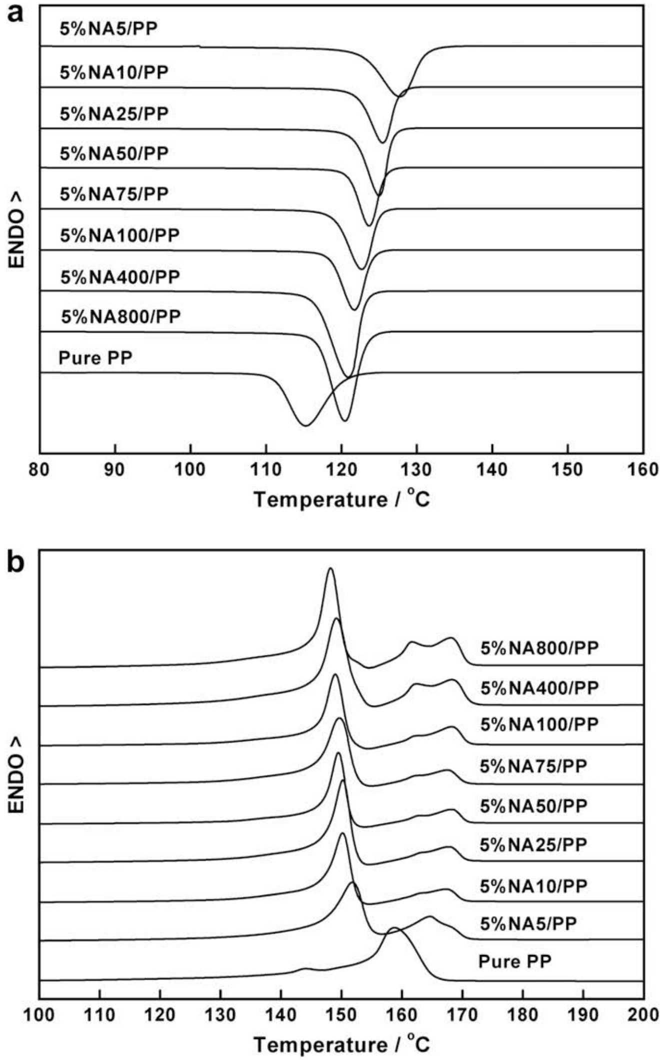

Fig. 8. Crystallization (a) and melting (b) curves of PP nucleated by supported β-nucleating agent with different contents of nano-$CaCO_3$.

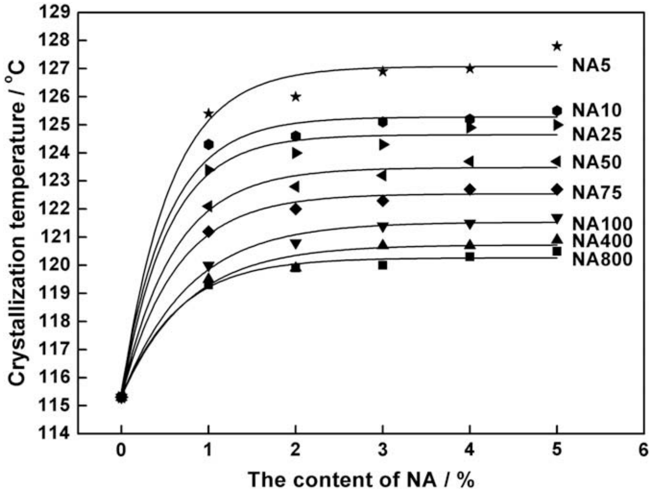

Fig. 9. Relationship of the contents of supported β-nucleating agent and crystallization temperatures.

Table 2
Crystallization temperatures and *K* values of PP nucleated by supported β-nucleating agent with different contents of nano-$CaCO_3$

HA/Ca	T_c (°C)	K_β
1/5	127.8	0.92
1/10	125.5	0.98
1/25	125.0	0.99
1/50	123.7	0.96
1/75	122.7	0.92
1/100	121.7	0.93
1/400	120.9	0.90
1/800	120.5	0.89

β-nucleating agent, the T_c of nucleated PP decreases with increasing the content of support nano-$CaCO_3$. For the same mass ratios of Nano-$CaCO_3$/HA, addition of 1 wt% supported β-nucleating agents causes the T_c of PP to increase significantly, but the increase in the content of nucleating agents has little influence on the T_c of PP. Above results indicated that the nucleating ability of nano-$CaCO_3$ supported β-nucleating agents depended on the content of HA. The increase in the content of support nano-$CaCO_3$ with weakly heterogeneous nucleating effect and decrease in the content of HA in the supported β-nucleating agents increased slightly the T_c of nucleated PP.

Fig. 10 shows X-ray diffraction diagrams of PP nucleated by supported β-nucleating agent with different mass ratios of Nano-$CaCO_3$/HA. The *K* values of β-PP content are listed in Table 2. It can be seen that the *K* values are above 90% for PP nucleated by supported β-nucleating agent with the mass ratios of Nano-$CaCO_3$/HA between 5/1 and 800/1. It is indicated that the nano-$CaCO_3$ supported β-nucleating agent prepared in our lab possesses high nucleating ability for preparation of β-PP. For the β-nucleating agent, the cost is an important factor for its application. For the CaHA and nano-$CaCO_3$ supported β-nucleating agent, the price of β-nucleating agents depends on the content of HA. Comparing with CaHA or bi-component nucleating agents containing HA, the content of expensive HA in supported β-nucleating agent reduces markedly. Moreover, the increase in the content of the support nano-$CaCO_3$ further decreases the cost of supported β-nucleating agent. Therefore, the nano-$CaCO_3$ supported β-nucleating agent prepared by supporting pimelic acid on nano-$CaCO_3$ is very important for reducing the cost of β-nucleating agent and spreading application of β-nucleating agent and β-nucleated PP.

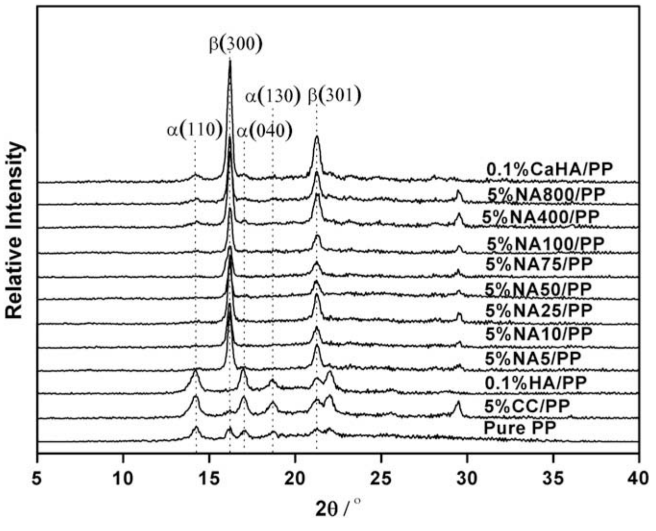

Fig. 10. X-ray diffraction diagrams of PP nucleated by supported β-nucleating agent with different contents of nano-$CaCO_3$.

4. Conclusion

The β-nucleated PP with high β-PP content was prepared by a novel supported β-nucleating agent prepared with pimelic acid supported on nano-$CaCO_3$. The crystallization behavior and melting characteristics and the β-PP content of β-nucleated PP were investigated and compared with PP nucleated by calcium pimelate. The results indicated that the crystallization temperature of PP is markedly increased by addition of supported β-nucleating agent. The increase in the content of supported β-nucleating agent slightly increased the crystallization temperature of PP and had no influence on the melting temperature of β-PP in nucleated PP. The crystallization temperature and melting temperature of β-nucleated PP decreased with increasing the content of the support nano-$CaCO_3$. The effects of scan rates on the crystallization and melting behavior of PP nucleated by supported β-nucleating agent are similar to that of PP nucleated by CaHA. The T_{melt} between 210 °C and 260 °C had no influence on the shape of melting peak of PP nucleated by supported β-nucleating agent. The β-PP content above 90 percent was obtained in PP nucleated by supported β-nucleating agent and was not influenced by the content of nano-$CaCO_3$. The supported β-nucleating agent prepared by supporting pimelic acid on nano-$CaCO_3$ is a β-nucleating agent with high efficiency and selectivity, and low cost.

Acknowledgements

The project was supported by Natural Science Foundation of Chin (Grant NO. 50873115), Natural Science Foundation of China (Grant No. 50573094) and Project of Science Technology of Guangdong Province, China (Grant No. 0711020600002).

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