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ORIGINAL CONTRIBUTION

# Crystallization behaviors and optical properties of isotactic polypropylene: comparative study of a trisamide and a rosin-type nucleating agent

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**Abstract** The effects of concentrations of N, N', N"-tris-*tert*. butyl- 1,3,5- benzene- tricarboxamide (NA) and a hemiacid of dehydroabietic acid (1:1 K) on the optical properties of iPP were compared with each other. It revealed that the NA was an effective transparent nucleating agent for iPP. The NA had advantage at very concentration (0.02 wt%), while the 1:1 K had some advantage at high concentrations (0.3 wt%~0.5 wt%), The optimal concentration range of the NA was 0.1 wt% to 0.4 wt%, while the value for 1:1 K was 0.3 wt% to 0.5 wt%. The absence of detectable spherulites in nucleated iPP was confirmed by SEM and POM. This was an important reason why the nucleated iPPP showed improved optical properties. The results of WAXD showed that preferential growth along the b-axis during crystallization and more disordered structures were formed in the nucleated samples. The results of DSC disclosed increased crystallization peak temperature and melting temperature in the nucleated samples.

**Keywords** Polypropylene · Trisamide· Nucleating Agent · Crystallization · Transparency

## Introduction

In industry, nucleating agent is widely used as additive for improving the performance of semi-crystalline polymers, such as isotactic polypropylene (iPP) [1]. The nucleating agent can accelerate the nucleation rate, therefore much fine crystals would form during crystallization, so the ultimate optical properties and mechanical properties are improved [2–4]. At the present time the mostly used nucleating agents are sorbitol acetals and organic phosphate salts [5–6], in addition, the rosin-based nucleating agents are also used [7–9]. In recent years, a new type nucleating agent, the trisamide based nucleating agents were developed [10–11]. It was found that this family of nucleating agents had excellent thermal stability, rendered iPP highly transparency at exceedingly low concentrations (as low as a weight fraction of 0.0002), thus provided marked benefits of these nucleating agents over the presently employed ones [10]. In addition, this type nucleating agents also influenced the electrical properties of iPP, it was found that by adding of 0.02 wt% of N, N', N"-tris- cyclohexyl - 1,3,5- benzene-tricarboxamide, the charge storage properties of iPP films were improved [12]. The nucleating agent added to the iPP can act as heterogeneous nuclei, and the density of nuclei is increased significantly, therefore, the induction time for iPP crystallization is reduced, the crystallization is accelerated, which modifies the size and density of spherulites formed, consequently alter the optical properties and mechanical properties of the ultimate products[13]. So it was important to investigate the effect of nucleating agent on the crystallization behavior and its connection to the ultimate properties of iPP.

Because of the trisamide based nucleating agents were developed in recent years [10–11], and compared to the traditional nucleating agent, their effects on the crystal structure and the ultimate properties of iPP were not known thoroughly [13], it was important to investigate the effects of them on the crystallization process and the ultimate properties of iPP, so that more information can be provided to tailor the ultimate properties of iPP. In this paper, the

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effects of different concentration of a trisamide based nucleating agent, N, N', N"-tris- *tert*. butyl- 1,3,5- benzene-tricarboxamide (Chart 1, identified as NA), on the crystal structure and morphology of iPP, and its connection to the ultimate optical properties were discussed with the help of WAXD, DSC, SEM, POM, a glossmeter and a hazemeter. In addition, a hemiacid of dehydroabietic acid, which was always called 1:1 cocrystal of potassium dehydroabietate and dehydroabietic acid (identified as 1:1 K), which was a well-known efficient transparent nucleating agent for iPP [8], was used as an contrast.

## Experimental part

*Materials* Commercial isotactic polypropylene homopolymer powder without any additives H-XD-140 (injection molding grade, MFI=11.6 g/10 min at 230°C and 2.16 kg according to ISO1133:1997) was supplied by Jinlin Plastic and Rubber Co. Ltd, and was used directly. Antioxidant Chimassorb 944, Irgafos 168 and calcium stearate were commercially available. Trimesic acid chloride, tert-Butylamine and DMF were analytical reagent and were bought from China Pharmaceutical Group Corporation Shanghai Chemical Reagent Co. Ltd. and used as received. The NA and 1:1 K [8] were prepared in our laboratory.

*Preparation of NA* The chemical structure of NA was shown in Chart 1. 0.01 mol trimesic acid chloride, 0.03 mol amine and 10 ml dry triethylamine were dissolved in 80 ml dry DMF. The mixture was stirred under 80 °C for 2 h, then the mixture was precipitated in 500 ml ice water and filtered to retrieve the solid, washed with water and dried. The resulting product was purified by recrystallization from DMF. FTIR spectra were recorded on a Bruker VECTOR22. $^1$H NMR spectra was recorded in DMSO-*d6* at room temperature using a Bruker AV400D instrument. Elemental analysis was performed with an Elementar Vario EL III (Germany). The resulting NA had m.p.: sublimation at 358 °C (no melting); $^1$H NMR (DMSO-*d6*, 400 MH$_z$): δ=1.56 ppm (s, 27H, CH$_3$), δ=8.03 ppm (s, 3H, CONH), δ=8.19 ppm (s, 3H, Ar-H); FTIR (KBr, cm$^{-1}$): 3231 *v*(NH), 3067 *v*(CH$_{arom.}$), 2963 and 2874 *v* (CH$_{aliph.}$), 1641 *v* (CO), 1561 *v* (NHdeform.); Anal. Calc. for $C_{21}H_{33}N_3O_3$ (375): C, 67.20%; H, 8.80%; N, 11.20%, Found: C, 66.99%; H, 8.93%; N, 10.95%.

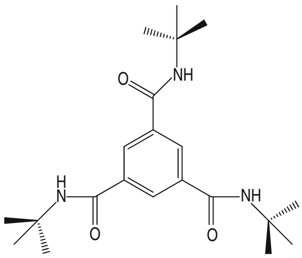

**Chart 1** Chemical structure of the N, N', N"-tris- tert. butyl- 1,3,5- benzene-tricarboxamide

*Sample preparation* Dry blends of iPP and different concentrations of nucleating agent, 0.1 wt% Irganox 944, 0.1 wt% Irgafos 168, and 0.05 wt% calcium stearate were compounded in a laboratory co-rotating twin screw extruder (TE-20, Coperion Keya (Nanjing) Machinery Co, Ltd, China) under 210 °C. The melt was cooled and pelletized. A blank control sample of iPP without nucleating agent was prepared in a similar way. iPP nucleated with NA and 1:1K were marked as PP-NA and PP-1:1 K, respectively. Samples for optical characterization (Φ50× 1 mm) were injection-molded with a reciprocating-screw injection molding machine (CJ80M3V, Chen De Plastics Machinery Co. Ltd. China), the temperature were 200°C, 205°C, 200°C, from the hopper to the die, and the mould temperature was room temperature.

*Differential scanning calorimetry (DSC) measurement* Crystallization of iPP with and without nucleating agent was performed with a Perkin-Elmer Pyris 1 DSC instrument in a dry nitrogen atmosphere. For sample measurement, about 5 mg of each sample was sealed into an aluminum pan, heated from 50 to 220 °C at the rate of 30 °C/min, and held at that temperature for 5 min to erase all the thermal memory, then cooled to 50 °C at a constant cooling rate of 10 °C/min, held at that temperature for 2 min, then heated to 220°C at the rate of 10 °C/min. The heat flow vs. temperature was recorded, the crystallization behavior of the samples was characterized. The crystallinity was calculated from the melting enthalpies according to eq. (1):

$$Xc1 = \frac{\Delta Hm}{\Delta H0} \times 100\% \qquad (1)$$

where $\Delta H_0$=207 J/g[14], the accepted value for the melting enthalpy for 100% crystalline iPP. The degree of crystallinity was determined with an experimental accuracy of 1%.

*Polarized optical microscope (POM)* Morphology of the iPP with and without nucleating agents was observed with a polarized optical microscope (POM) equipped with cross polars and a CCD camera (LW-200–4JS, Shanghai LW Scientific Co. Ltd.) A small piece of sample was clamped between two microscope glass slides, heated to 220 °C and kept for 10 min, then squeezed on the slides and moved away from the hot stage, cooled in air to room temperature and crystallized for 48 h.

*Scanning electron microscopy (SEM)* For SEM measurement, samples for optical characterization were used and fractured under liquid nitrogen. The fractured surfaces were

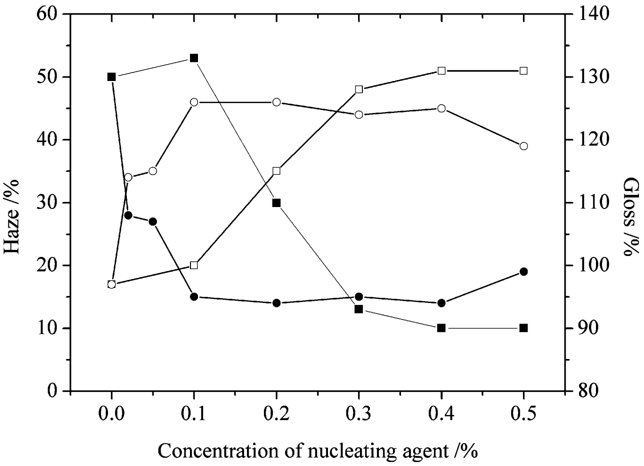

**Fig. 1** Optical properties of iPP with different concentration of nucleating agents: -■- haze of iPP containing 1:1 K; -□- gloss of iPP containing 1:1 K; -●- haze of iPP containing NA; -○- gloss of iPP containing NA

etched for 2 h at room temperature in a 1% w/v solution of potassium permanganate in a 10:4:1 mixture (by volume) of sulphuric acid, 85% orthophosphoric acid and distilled water [15], then the surfaces were carefully washed with distilled water several times. All the surfaces to be studied were coated with gold under vacuum and SEM images were observed with a JEOL JSM-5900.

*Wide angle X-ray diffraction (WAXD)* Samples prepared similarly to those used in POM and SEM were used to determine the crystal structure of iPP with and without nucleating agents. WAXD measurements were made with a ARL X'TRA X-ray diffractometer (Thermo Electron Corporation, USA) with a Cu $K_\alpha$ source. The equipment was operated at 45 kV and 35 mA under ambient temperature, and the scan range was between 5° and 40°, with a scan rate of 2°/min. WAXD analyses were obtained based on the two phase concept. The crystallinity for each sample was obtained from the ratio between the area under the crystalline peaks and the total area under the diffraction curve. The separation of crystalline peaks from the amorphous halo was made by fitting the WAXD curve to a pseudo-Voigt function [8]. The overall crystallinity $X_{c2}$ was calculated by

$$Xc2 = \frac{\sum Acryst}{\sum Acryst + \sum Aamorp} \times 100\% \qquad (2)$$

where $A_{cryst}$ and $A_{amorp}$ are the fitted crystalline and amorphous areas, respectively. The degree of crystallinity was determined with an experimental accuracy of 1%.

*Optical characterization* The iPP samples were injection-molded into discs of 1 mm thickness and 50 mm diameter. The haze of the samples was measured by a photoelectric hazemeter (WGW, Shanghai Precision & Scientific Instrument Co. Ltd., China) according to ISO 14782:1999. The gloss was tested using a glossmeter (WGG60-Y4, Keshijia Institute of Photoelectrical Instrument, Quanzhou, China) according to ISO 2813:1994. Three samples were measured and the averages were reported.

## Results and discussion

### Optical properties

Figure 1 shows the optical properties of iPP with different concentration of nucleating agents. As can be seen, the haze and gloss critically depended on the concentrations of the nucleating agents. The NA had nucleation ability even at very low concentration (0.02 wt%). By adding 0.02 wt% of NA, the haze was decreased by 44%, and the gloss was increased by 18%. And a small increased concentration of NA (from 0.02 wt% to 0.05 wt%) changed the optical properties little. After that, a linear decreased in haze and increased in gloss was observed. Between the range of 0.1 wt% and 0.4 wt%, the values of the haze and gloss of the iPP almost kept constantly with the increasing concentration of NA. Then followed by a slight increased haze and

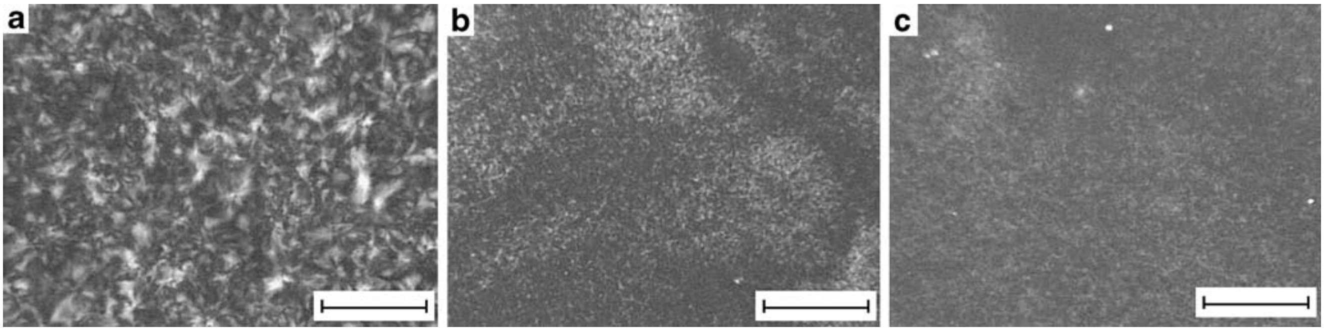

**Fig. 2** Crossed-polarized light micrographs of iPP with and without nucleating agents. **a** blank iPP; **b** PP-NA, **c** PP-1:1 K, the scale bar is 50 μm

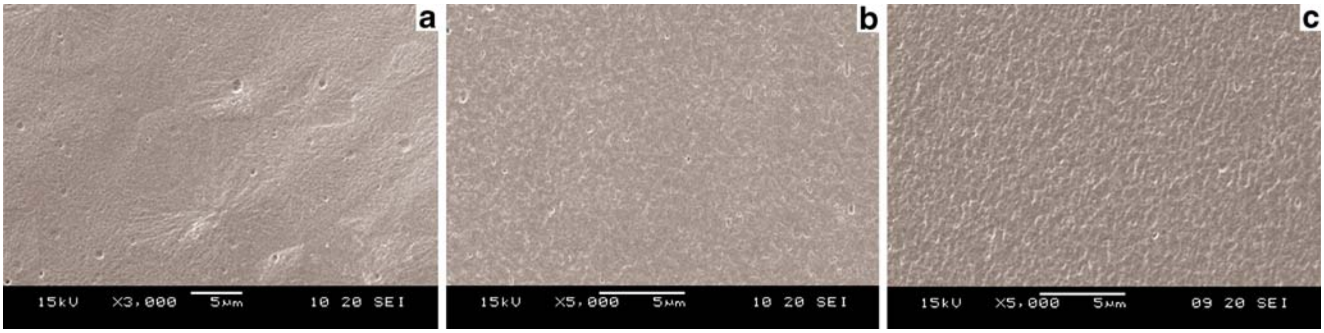

**Fig. 3** SEM micrographs of the core layer for injected iPP samples with and without nucleating agents. **a** Blank PP, **b** PP-NA, **c** PP-1:1 K

decreased gloss when the concentration of the NA exceeded 0.4 wt%. This was conflicted with the results of literature [10], in which the haze was increased when the concentration of nucleating agent exceeding 0.02 wt%. The divergence between our results and that of the literature[10] can be ascribed to different processing conditions and the different iPPs used. It was well known that the optical properties of iPP containing this family nucleating agent was determined by the phase structure of iPP/trisamide [12] which, in turn was determined by the solubility of such compound in iPP. In literature [12], the author reported that the dissolution temperature of 0.02 wt% of NA in iPP was about 290°C, therefore under our processing condition, the NA was insoluble or partial soluble in the iPP, thus may have significant impact on the optical properties of iPP. In addition, the characteristic of the iPP, such as melting flow rate, was different from the literature [12], and it also influenced the optical properties of the product. Therefore, by combination of the two effects, the dependence of optical properties on the concentration of NA was quite different from the literature[10]. By contrast, the 0.1 wt% of 1:1 K increased the haze and gloss somewhat, then, a linear dropping of the haze and increasing of the gloss were observed in the concentration range of 0.1 wt% and 0.3 wt%. When the concentration of 1:1 K exceeding 0.3 wt%, the changes of the optical properties of were slight. And plateaus of haze and gloss also presented in the concentration between 0.4 wt% and 0.5 wt%. In sum, the NA had its advantage compared to the 1:1 K, because it improved the optical properties of iPP at very concentration (0.02 wt%), sharply compared to the effects of the 1:1 K, which the effective concentration was 0.2 wt% or more, this was about 10 times more than that of the NA. However, the 1:1 K had some advantage at high concentrations, which indicated somewhat lower haze and higher gloss, compared to these of the counterpart of iPP containing NA. The optimal concentration range of the NA was 0.1 wt% to 0.4 wt%, while the value for 1:1 K was 0.3 wt% to 0.5 wt%. So we chose the iPP containing 0.3 wt% of nucleating agents as model to investigate the effect of these nucleating agents on the morphology, crystal structure, crystallization and melting of iPP.

## Morphology

Figure 2 shows the POM pictures of iPP with and without nucleating agents. It was obviously seen that the blank PP shown the typical spherulites structures of the α form with the diameter of about 40~60 μm (Fig. 2a), and it had the biggest spherulites in the three samples. After adding of 0.3 wt% of NA or 1:1 K, the sizes of the spherulites were decreased drastically, a very fine and uniform morphology was observed (Fig. 2b and c). It was difficult to precisely determine the sizes of crystals under this magnification. It may be assumed that aggregated lamellar created the structure of nucleated iPP, instead of fully developed spherulites, this was the reason why the PP contained NA or 1:1 K presented excellent transparency and gloss, which had been discussed in the previous part of this paper. The same structure was reported in the literatures [8,16].

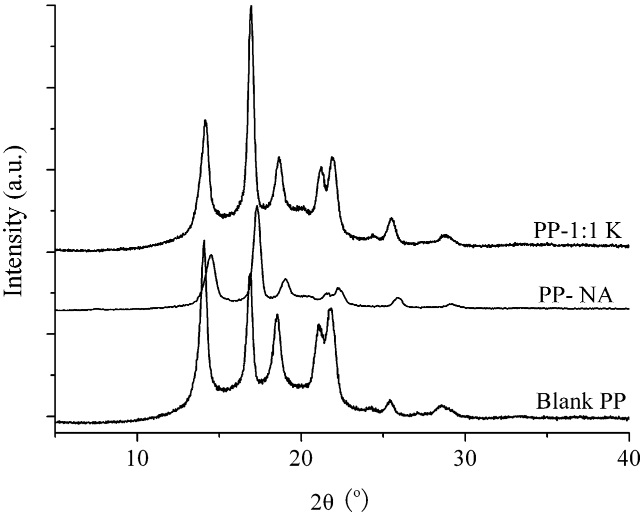

**Fig. 4** WAXD patterns of iPP with and without nucleating agents

**Table 1** Crystallization data of iPP with or without 0.3 wt% nucleating agents

| Samples | Melting peak temperature ($T_m$)/°C | Crystallization peak temperature ($T_c$)/°C | Degree of crystallinity /% | | Intensity ratio $I_{(110)}/I_{(040)}$ | FWHM/° |
|---|---|---|---|---|---|---|
| | | | $X_{c1}$ | $X_{c2}$ | | |
| Blank PP | 161.5 | 114.0 | 42 | 54 | 1.44 | 0.56 |
| PP-NA | 166.3 | 128.2 | 40 | 61 | 0.50 | 0.72 |
| PP-1:1 K | 165.8 | 128.2 | 44 | 57 | 0.53 | 0.60 |

SEM provided a powerful tool to investigate the morphology of the samples at high magnification. Figure 3 presents the SEM micrographs of the core layer for injected iPP samples with and without nucleating agents. As can be seen, for the blank iPP, in the core region the typical spherulites with a diameter between 5~20 μm and a crosshatch-type lamellar branching structure, which was the typical characteristic of the α iPP [17], were clearly shown in Fig. 3a. By adding of 0.3 wt% of NA or 1:1 K, no spherulites can be seen and only the small uniform aggregated crystals were observed. The formation of such structure in the nucleated sample was reasonable, because of more nuclei formed after the addition of nucleating agent, and the crystallization rate increased significantly, therefore a shorter growth time and limited space was provided in the nucleated samples than that of the blank one, and the structure can't develop fully to form the spherulites before solidification of the sample. It was known that the big spherulites in the bulk of semi-crystalline polymer can scatter the light, therefore the optical properties of the samples deteriorated [18]. The addition of NA and 1:1 K prohibited the formation of spherulites and led to the formation of fine uniform crystals with a diameter smaller than the wavelength of visible light, therefore the light scattering in the core layer was reduced, and the optical properties of the samples improved.

## Crystal structure

Figure 4 shows the WAXD patterns of iPP with and without nucleating agents, and the crystallization data derived from the patterns are listed in Table 1. It was clearly shown that only the monoclinic α-phase was presented in all the samples, because of the characteristic reflections at the following angles, $2\theta = 14.2°$, 17°, 18.8°, 21.2° and 22.0°, corresponding to the following respective crystalline planes (110), (040), (130), (111) and (041) of the α iPP [14]. No evidence of the β form was observed. Furthermore, the NA and 1:1 K increased the degree of crystallinity a little, and compared to the 1:1 K, the NA had more pronounced effect.

The WAXD patterns of these samples shows some phenomena related to the unite cell of nucleated iPP. It was obviously seen that the intensity of (040) was increased accompanied by a reduction in the intensity of the (110) in the nucleated samples. It is known that the ratio between the (110) and (040) provided information on the relationship between the orientation of a axes and b axes of the α-phase [19]. The values of the intensity ratio of the (110) and (040) reflections were summarized in Table 1. As can be

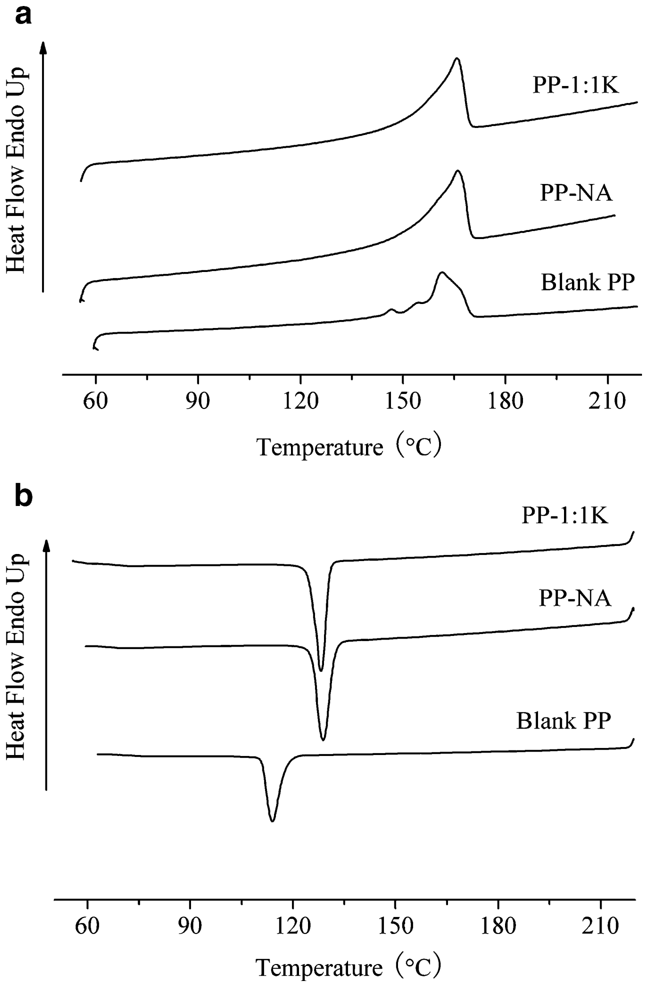

**Fig. 5** DSC thermograms of PP containing 0.3 wt% of nucleating agents. **a** Heating under 10 °C/min, **b** cooling under 10 °C/min

seen, the ratio of $I_{(110)}/ I_{(040)}$ was diminished clearly with the addition of NA or 1:1 K, which may be associated with the increasing in the orientation of b-axis due to the presence of nucleating agents, indicating that during crystallization growth along the b-axis was favored. This was more distinctive for PP nucleated with NA. The same trends were observed by Marco et al in iPP nucleated with sorbitol-based nucleating agents [13].

The degree of perfection of the α-phase can be evaluated from the full width at half maximum (FWHM) of the (110) face [20]. Table 1 presents the FWHM values of the (110) face of iPPs with or without 0.3 wt% of nucleating agents. As can be seen, compared to the corresponding blank iPP, the nucleated one had a bigger FWHM value, indicating that the packing order of the α-phase decreased in the nucleated sample. This was accord with the results of the POM, which showed that only small uniform crystals presented in the nucleated samples. In addition, the PP-NA had the biggest FWHM value, which means that it decreased the degree of perfection more pronounced.

### Crystallization and melting behavior

The melting and non-isothermal crystallization behaviors of iPP with and without nucleating agent were determined by using of DSC, and the thermal curves are shown in Fig. 5. The thermal properties analyzed from the DSC curves are also summarized in Table 1. From Fig. 5a, it was clearly shown that the blank iPP presented multiple melting peaks, which may be due to the melting-recrystallization -melting of α-phase of iPP with different order or the β-α transition during heating [19]. The result of the WAXD clearly showed that there was no evidence of β phase in the blank iPP, so the peak duplication may be due to the recrystallization of α-phase superimposed on melting process [21]. By adding 0.3 wt% of NA or 1:1 K, only one melting peak and increased $T_m$ was observed, the same trend was published elsewhere [21]. Moreover, the crystallization peak temperature was increased significantly by adding of NA or 1:1 K. Compared to the PP-1:1 K, the PP-NA had the same $T_c$, which means that the NA had the same nucleating efficiency to 1:1 K. This quite agreed with the results reported in the previous part of the paper. However, the divergent values of the crystallinity of iPP samples were obtained between DSC and WAXD. As can be seen, the NA decreased the crystallinity a little, but the 1:1 K increased it a little, this was conflicted with the values deduced from the WAXD patterns. This can be ascribed to the normalization factor used for crystallinity determination by DSC [22].

## Conclusion

The effects of concentrations of a trisamide based nucleating agent, N, N', N"-tris- *tert*. butyl- 1,3,5- benzenetricarboxamide (NA) and a hemiacid of dehydroabietic acid (1:1 K) at the optical properties of iPP were compared using of a glossmeter and a hazemeter, it revealed that the NA had advantage compared to the 1:1 K, because it improved the optical properties of iPP at very concentration (0.02 wt%), sharply compared to that of the 1:1 K, which the effective concentration was 0.2 wt% or more, which was about 10 times more than that of the NA. However, the 1:1 K had some advantage at high concentrations (0.3 wt%~0.5 wt%), indicating somewhat lower haze and higher gloss, compared to these of the counterpart of iPP containing NA. The optimal concentration range of the NA was 0.1 wt% to 0.4 wt%, while the value for 1:1 K was 0.3 wt% to 0.5 wt%. The effects of 0.3 wt% of nucleating agents on the crystal structure and morphology of iPP, and its connection to the ultimate optical properties were discussed with the help of WAXD, DSC, SEM, and POM. The absence of detectable spherulites in nucleated iPP was confirmed by SEM and POM. Therefore, the haze and gloss of ultimate samples were improved significantly. WAXD showed that preferential growth along the b-axis during crystallization and more disordered structures were formed in the nucleated samples. This was according with the result of the POM. The results of DSC showed that increased crystallization peak temperature and melting temperature presented in the nucleated samples.

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