Asian Journal of Chemistry Vol. 19, No. 7 (2007), 5385-5390

Comparison Between Crystalline Morphology of Isotactic Polypropylene with Di-*p*-methylbenzylidene Sorbitol and Sodium Benzoate

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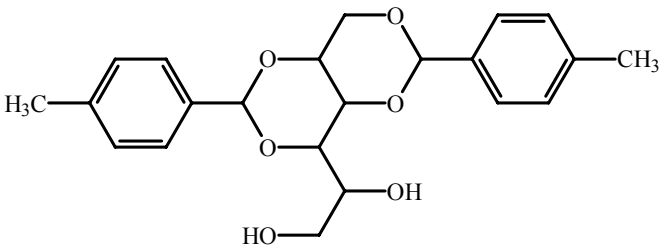
Isothermal crystalline morphology of isotactic polypropylene (iPP) with di-*p*-methylbenzylidene sorbitol (Me-DBS), a clarifying nucleating agent, under different crystallization conditions was observed and compared with that of iPP containing sodium benzoate (SB). The results showed that the crystalline morphology of iPP/Me-DBS and iPP/SB were much different. It was concluded that the crystallization mechanism of Me-DBS was not simply the heterogeneous nucleation, but to provide small amount of growth points, on which iPP segments could attach and grow effectively.

Key Words: Morphology, Isotactic polypropylene, Di-*p*-methylbenzylidene Sorbitol, Sodium benzoate.

INTRODUCTION

In 1975, Hamada *et al.*[1] reported that dibenzylidene sorbitol (DBS) could improve the transparency of polypropylene (PP). Di-*p*-methylbenzylidene sorbitol (Me-DBS), a derivate from DBS, is also highly suitable for improving transparency of PP products[2,3]. The molecular formula of Me-DBS is shown as.



Reports of influence of clarifying nucleator on iPP were mainly about how it influenced the mechanical properties and transparency of polypropylene materials[4,5]. For the crystalline morphology of PP with clarifying nucleator under different crystallization conditions, few reports could be

found. Comparison between the crystalline morphology of clarifying nucleator and ordinary nucleator like sodium benzoate was not performed too. Here in this study, the crystalline morphology of isotactic polypropylene (iPP) containing different content of Me-DBS crystallized at different temperature for different time was investigated carefully. Comparison between morphology of iPP/Me-DBS and iPP/SB were also done.

EXPERIMENTAL

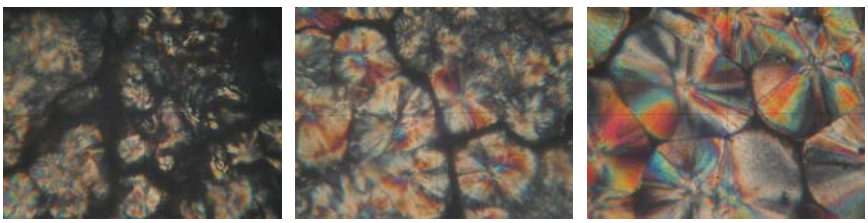
Isotactic polypropylene (iPP), F401, provided by Yangzi Petrochemical Co. Ltd. (China); Me-DBS, provided by Shanxi Institute of Chemistry (China); sodium benzoate, provided by Shanghai reagents group (China); Constant Temperature Hot-plate, self-made; Polarized Light Microscope (PLM), Jiangnan Optical Instruments Co. Ltd.

Experimental conditions: (a) Nucleators were added into iPP by physical mixing, the content of nucleator was 0.1, 0.3 and 0.5 wt %, respectively; (b) Isothermal crystallization temperature was 110, 125, 140 and 155°C, crystallization time was 1, 5, 10 and 24 h under a certain temperature; (c) PLM was equipped with 10 × eye lens and 25 × objective lens, photographed by Canon digital camera.

RESULTS AND DISCUSSION

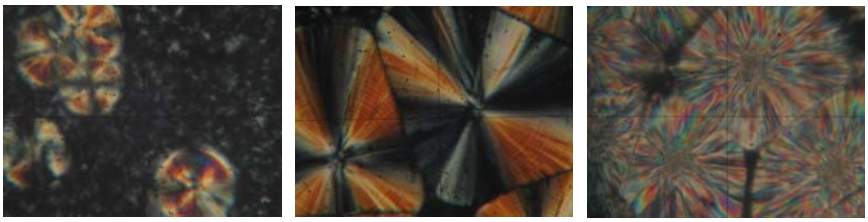
Crystallization time is an important factor that will influence the crystalline morphology of iPP. Observation to the crystalline morphology of iPP containing different nucleator showed that there were many differences in crystalline morphology.

As the crystallization time became longer, the crystalline morphology of iPP/SB was more and more perfect and the crystal size was also bigger and bigger (Figs.1 and 2). While for iPP/Me-DBS, it was much different. Morphology of iPP/Me-DBS was not better and better as crystallization time became longer. The most perfect morphology of iPP containing Me-DBS was presented after 10 h of crystallization and the crystal size was also the biggest (Fig. 2).



(a) (b) (c)

Fig. 1. Crystalline morphology of iPP/SB crystallized for different time (0.1 wt %, 155°C) (a) after 5 h, (b) after 10 h, (c) after 24 h



(a) (b) (c)

Fig. 2. Crystalline morphology of iPP/Me-DBS crystallized for different time (0.1wt %, 155°C) (a) after 5 h, (b) after 10 h, (c) after 24 h

Crystalline morphology of iPP/SB at 5 h was so imperfect that they could not be called spherulites, but for iPP/Me-DBS under the same condition, apparent spherulites with clear black cross could be observed. It was very interesting that the spherulites of iPP/Me-DBS were isolated from each other.

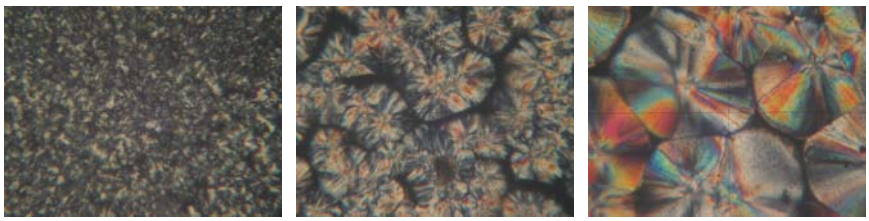
As the crystallization time was longer, morphology of iPP/SB was better and spherulites with black-cross were observed, but it was still less perfect than that of iPP/Me-DBS under the same conditions. Large and beautiful spherulites were presented for iPP/Me-DBS crystallized for 10 h. It was so perfect that the morphology was even better than that of iPP/SB crystallized for 24 h. However, the crystalline morphology of iPP/Me-DBS crystallized for 24 h was less perfect than that of iPP/SB for 24 h. The spherulites for iPP/Me-DBS were bigger than iPP/SB, but there was no obvious black-cross. Instead, morphology of balls full of radius was found.

Although Me-DBS is also a type nucleator as sodium benzoate, the mechanism of Me-DBS was much different from that of sodium benzoate. It was very interesting that perfect spherulites with clear black-cross could be formed in a relatively short time [(a) in Fig. 1] for iPP/Me-DBS, while no clear spherulites could found for iPP/SB under the same conditions. Such a phenomenon indicated that Me-DBS could accelerate the formation of spherulites. It could provide a few, but effective growth points, on which the iPP segments attached and grew rapidly and efficiently. As the crystallization time was longer, more and more segments would join in and spherulites would become bigger and bigger [(b) in Fig. 2]. At last, spherulites became overgrowth and overcrowded, resulting in congestion and deformation. Lamellas inside the spherulites were deformed and the spherulites were not as homogeneous as before, so that the black-crosses disappeared. The size of the spherulites became smaller should be contributed to congestion and disappear of black-cross should be contributed to deformation of spherulites [(c) in Fig. 2].

Crystallization temperature

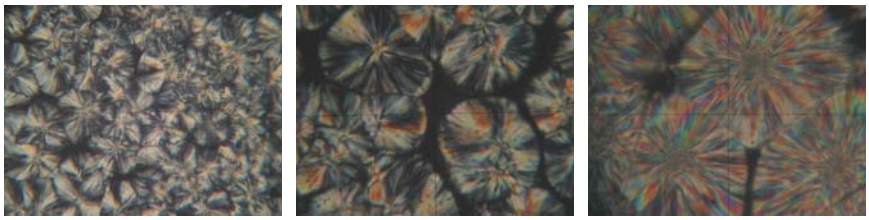
It could be clear from Figs. 3 and 4 that at higher crystallization temperature, the crystalline morphology of iPP/Me-DBS and iPP/SB were all better than lower temperature. Crystal sizes were also bigger.

With increasing of crystallization temperature, the mobility of iPP segments increased correspondingly. Higher temperature will be helpful for segments to fill in the lattices to form more perfect crystal.



(a) (b) (c)

Fig. 3. Crystalline morphology of iPP with SB at different temperature (0.1 wt %, 24 h) (a) at 125ºC, (b) at 140ºC, (c) at 155ºC



(a) (b) (c)

Fig. 4. Crystalline morphology of iPP with Me-DBS at different temperature (0.1wt %, 24 h) (a) at 125ºC, (b) at 140ºC, (c) at 155ºC

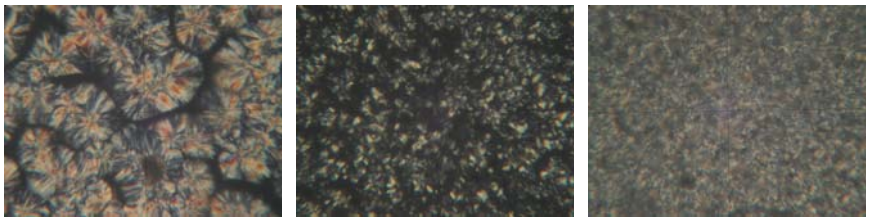
By comparing the crystal size of iPP/SB and iPP/Me-DBS, interesting phenomenon were observed the crystal size of iPP/Me-DBS was bigger than that of iPP/SB under the same conditions. Beside that, the black-crosses were much clearer for iPP/Me-DBS than iPP/SB at 140°C. However, when crystallization temperature increased to 155°C, it was iPP/SB that showed the most perfect morphology. The radius morphology was observed.

The bigger crystal size and more perfect crystalline morphology of iPP/Me-DBS also proved that Me-DBS would provide a few effective growth points for iPP segments. It could help iPP to form relatively larger and more perfect spherulites than sodium benzoate when temperature was not too high (≤ 140°C). At 155°C, mobility of iPP segments was so strong that the morphology of iPP/Me-DBS was like overcrowded owing to over-growth.

Effects of nucleator content

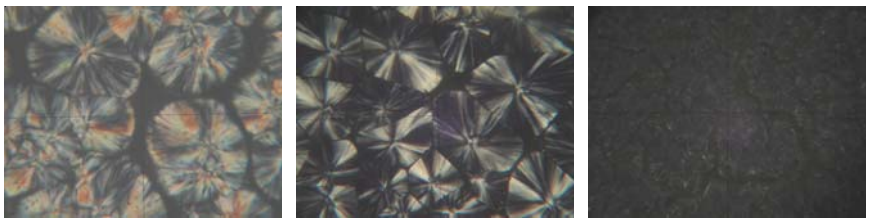
It can be concluded from Fig. 5 that the crystal size of iPP was smaller and smaller as sodium benzoate content increased. When the nucleator content was 0.1 wt %, though the crystals were not much clear, they still could be recognized as spherulites. As the content increased a little to 0.3 wt %, the crystal size dropped rapidly and no spherulites could be found. As the content reached 0.5 wt %, only numerous tiny crystals were observed.

The crystalline morphology of iPP/Me-DBS was much different from that of iPP/SB (Fig. 6). The crystal size and perfection of iPP/Me-DBS were pretty good when Me-DBS content was less than 0.5 wt %. The most favorable Me-DBS content was 0.3 wt % according to present experiments-spherulites were the most perfect. Not like the morphology of iPP containing 0.1 wt % Me-DBS, there was no void and spherulites piled up more closely. As the content of Me-DBS reached 0.5 wt %, no clear crystals could be found, just like the morphology of an amorphous material.



(a) (b) (c)

Fig. 5. Crystalline morphology of iPP with sodium benzoate of different content (140°C, 24 h) (a) 0.1 wt% SB (b) 0.3 wt% SB, (c) 0.5 wt% SB



(a) (b) (c)

Fig. 6. Crystalline morphology of iPP with Me-DBS of different content (140°C, 24 h) (a) 0.1 wt% Me-DBS (b) 0.3 wt% Me-DBS, (c) 0.5 wt% Me-DBS

Function of nucleator was to provide heterogeneous nuclei. After the sodium benzoate was added in, nuclei number increased. It was hard for iPP to form beautiful spherulites and the crystal sizes would be smaller. By

comparing Figs. 5 and 6, it was found that Me-DBS did not function that way. Under certain isothermal crystallization conditions, small amount of Me-DBS will be helpful for iPP to form fairly large and perfect spherulites. The nucleation mechanism of Me-DBS was not simply heterogeneous nucleation. It provided effective growth points and accelerated the formation of spherulites efficiently.

Conclusion

After comparison of effects of nucleator content, crystallization temperature and crystallization time on crystalline morphology of iPP, it was concluded that:

(a) The crystalline morphology of iPP/ Me-DBS at 10 h was the most perfect. It was not like iPP/SB, for which the most perfect morphology corresponding to 24 h, (b) The most favourable temperature corresponding to the most perfect crystalline morphology of iPP/Me-DBS was 140°C, not a higher 155°C as iPP/SB, (c) With SB content increasing, the crystalline morphology was worse and worse; but as the content of Me-DBS equaled to 0.3 wt %, crystalline morphology was the most perfect and (d) As a new type of nucleator, the crystallization mechanism of Me-DBS was not just simple heterogeneous nucleation. It should be to provide not so many, but effective growth points, on which the iPP segments could attach and grow. It should be pointed out that, Me-DBS could accelerate the formation of spherulites efficiently.

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(*Received*: 13 October 2006; *Accepted*: 18 June 2007) AJC-5714