

# Effect of Polycyclopentene on Crystallization of Isotactic Polypropylene

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## SYNOPSIS

The application of some polymers as nucleating agents for polypropylene has been examined. Among various polymeric nucleating agents, polycyclopentene was found to be a superior nucleating agent to typical organic nucleating agents. When polycyclopentene was added to polypropylene, the crystallization temperature and the degree of crystallinity of polypropylene increased. In addition, the crystallization rate and the number of spherulites increased whereas the size of spherulites decreased remarkably. As a result of polycyclopentene addition, the transparency of polypropylene film could be improved considerably.

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## INTRODUCTION

Early interest in nucleating agents for polypropylene (PP) arose from industrial efforts<sup>1</sup> to produce a fine-grained spherulitic structure for the improvement of optical and mechanical properties of PP film. Qualitatively the effect of nucleating agent was judged by the decrease in size and the increase in number of spherulites compared to those of pure polymer. A good nucleating agent was noted when the spherulite diameter decreased to about one-fifth to one-tenth that of pure polymer.<sup>2</sup>

As nucleating agents for PP, sodium benzoate, aluminium benzoate, and dibenzylidene sorbitol are especially effective and research has been concentrated on them.<sup>3,4</sup> These organic nucleating agents have less miscibility and dispersity for PP.<sup>5</sup>

In recent years, Kakugo et al.<sup>5</sup> announced that the addition of polyvinylcyclohexane to PP caused a marked reduction in spherulite size and an increment in crystallization temperature of PP.

In this work, we report the effect of polycyclopentene as nucleating agent on the crystallization temperature, degree of crystallinity, crystallization rate, spherulite formation, and transparency for isotactic PP.

## EXPERIMENTAL

### Materials

Isotactic polypropylene (PP) (grade 1088, Korea Petrochemical Ind. Co., Korea) had a melt index (MI) of 9.4 g/10 min. Polyamides (nylon 6, nylon 66) and polyethylene terephthalate (PET) (Tongyang Nylon Co., Ltd., Korea) were precipitated with formic acid and phenol, respectively. Poly(ether-ether-ketone) (PEEK) powder was commercial grade (Victrex 450P, ICI, England). Polyvinylcyclohexane (PVCH)<sup>6</sup> and poly(4-vinyl-1-cyclohexene) (PVChE)<sup>6</sup> were synthesized with a Solvay-type  $\text{TiCl}_3$  catalyst. Polycyclopentene (PCP)<sup>7</sup> and polynorbornene (PN)<sup>8</sup> were obtained with  $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  catalyst.

### Analysis of Thermal and Optical Properties

Various polymers (nylon 6, nylon 66, PET, PEEK, PVCH, PVChE, PCP, PN) were added to PP as polymeric nucleating agents (PNAs). PP powder was mixed with 500–5000 ppm of PNA for 10 min at 165°C with 50 rpm in a Brabender. Melting temperature and crystallization temperature were determined by using differential scanning calorimetry (DSC) (Du Pont 2000 system) under  $\text{N}_2$  atmosphere. The rates of heating and cooling temperatures were 20°C/min. For determination of transition temperatures, the specimen was heated to 200°C and kept

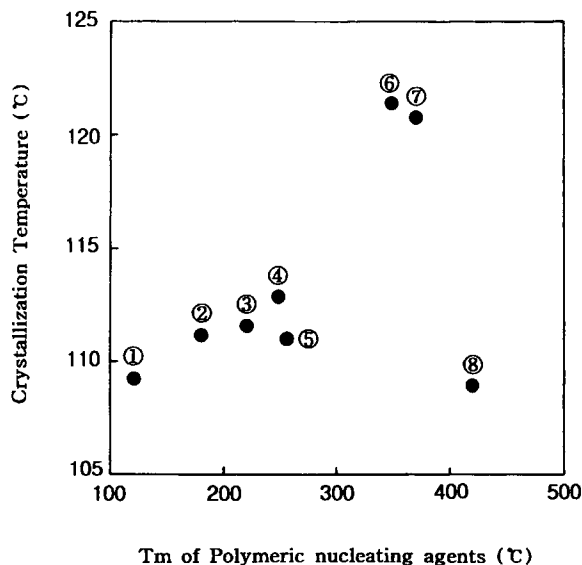
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for 5 min at this temperature and then cooled to room temperature. The isothermal crystallization rate of sample from the melt was measured by employing the following procedure: The sample was kept for 5 min at 200°C followed by rapid cooling at 50°C/min to the isothermal crystallization temperature. Sample weighing of approximately 6 mg into the aluminium pan was used throughout these experiments. X-ray diffraction patterns of sample films were recorded on a X-ray diffractometer (JEOL, JDX-8E) in the  $2\theta$  range of  $10^\circ$ – $40^\circ$  using  $\text{CuK}\alpha$  radiation with scan speed of  $4^\circ/\text{min}$  at room temperature. Optical micrographs of films were taken with a polarizing microscope (Leitz, Orthplan). The haze of the film was measured by a Hazemeter (BYK Garder Inc., XL-211) at room temperature. Sample film was prepared by a hot-press at 200°C with  $1000 \text{ kg}/\text{cm}^2$ . The obtained films were about  $90 \mu\text{m}$  thick.

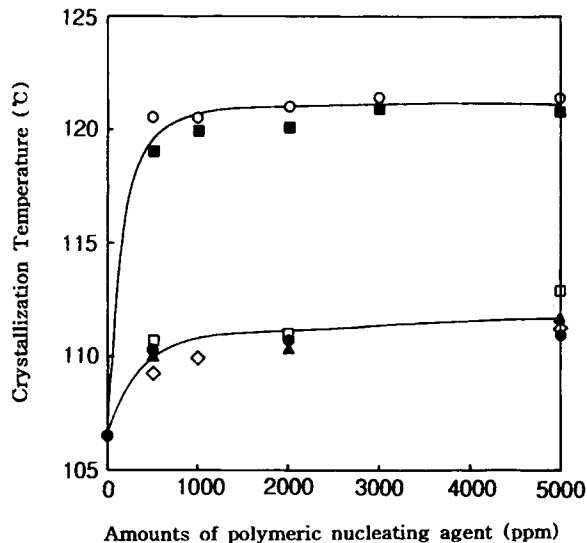
## RESULTS AND DISCUSSION

### Crystallization Behavior

As Kakugo et al.<sup>5</sup> pointed out, a PNA of higher melting temperature ( $T_m$ ) than PP ( $T_m = 160^\circ\text{C}$ ) can remain as solid particles to become crystallization nuclei in a PP melt.



**Figure 1** Effect of melting temperature of polymeric nucleating agent on crystallization temperature of polypropylene: 1, PVCHe; 2, PN; 3, nylon 6; 4, PET; 5, nylon 66; 6, PCP; 7, PVCH; 8, PEEK. Content of polymeric nucleating agent: 5000 ppm.

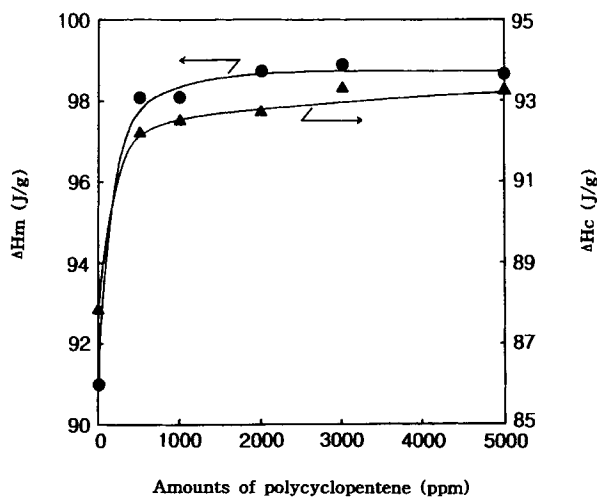


**Figure 2** Effect of amount of polymeric nucleating agent on crystallization temperature of polypropylene: (○) PCP, (▲) nylon 6, (●) nylon 66, (■) PVCH, (□) PET, (◇) PN.

The relationship of the crystallization temperature ( $T_c$ ) of PP adding various PNAs with the  $T_m$  of PNA was examined and is plotted in Figure 1.

As shown in the figure, it was confirmed that the  $T_c$  of PP increased by adding PNA of higher  $T_m$  than for PP. Among various PNAs, PCP and PVCH showed remarkable nucleating effects.

Surprisingly, PVCHe of low  $T_m$  ( $118^\circ\text{C}$ ) showed a small positive effect on  $T_c$  while PEEK gave less effect in spite of its high  $T_m$  ( $416^\circ\text{C}$ ). In addition, it



**Figure 3** Effect of amount of polycyclopentene on (●) heat of fusion ( $\Delta H_m$ ) and (▲) heat of crystallization ( $\Delta H_c$ ) of polypropylene.

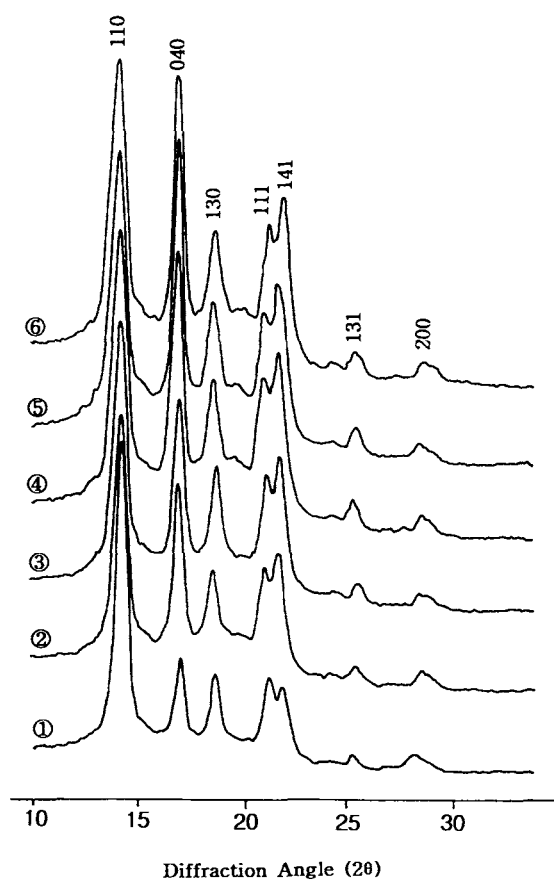
has been reported<sup>9</sup> that low molecular weight PP can improve the second crystallization of PET ( $T_m = 249^\circ\text{C}$ ).

With the above results, it could be considered that crystallization nuclei are not necessarily in the solid phase in the melted matrix and interaction of components might be one important parameter for PNA, although the exact reason is not clear at present.

Therefore, phenomenological studies of PNA, especially PCP, for PP have been examined.

The dependence of the  $T_c$  of PP on the amount of PNA is given in Figure 2.

As expected, the  $T_c$  of PP increased with amount of PNA, up to 1000–2000 ppm, and changed less for a larger amount. When 1000 ppm (0.1 wt %) PCP or PVCH was added to PP, the  $T_c$  became approximately  $15^\circ\text{C}$  higher. With 5 wt % aluminium benzoate, sodium benzoate, or zinc benzoate, the  $T_c$  of PP increased only about  $13$ – $17^\circ\text{C}$ .<sup>10,11</sup> In other words, PCP and PVCH were superior nucleating agents to typical organic nucleating agents for PP.



**Figure 4** X-ray diffractograms of polypropylene with various amounts (ppm) of polycyclopentene: 1, 0; 2, 500; 3, 1000; 4, 2000; 5, 3000; 6, 5000.

**Table I** Values of Parameters Determined from X-ray Diffraction and DSC

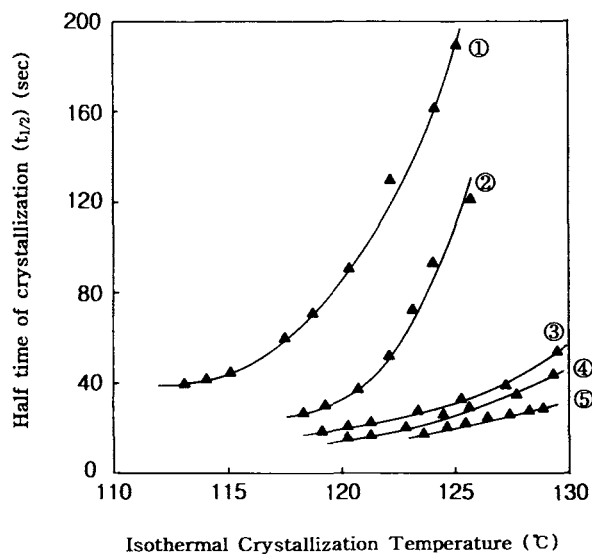
| PCP Content (ppm) | Degree of Crystallinity (%) |            | Intensity Ratio $I_{040}/I_{110}$ |
|-------------------|-----------------------------|------------|-----------------------------------|
|                   | From DSC                    | From X ray |                                   |
| 0                 | 48.1                        | 69.0       | 0.24                              |
| 500               | 52.0                        | 71.8       | 0.73                              |
| 1000              | 52.2                        | 72.0       | 0.77                              |
| 2000              | 52.2                        | 72.1       | 0.89                              |
| 3000              | 52.4                        | 73.4       | 1.06                              |
| 5000              | 52.3                        | 73.1       | 0.96                              |

On the other hand, nylon 6, nylon 66, PET, and PN showed a minute effect and the  $T_c$  of PP increased only  $4$ – $7^\circ\text{C}$  even with a larger amount of 5000 ppm.

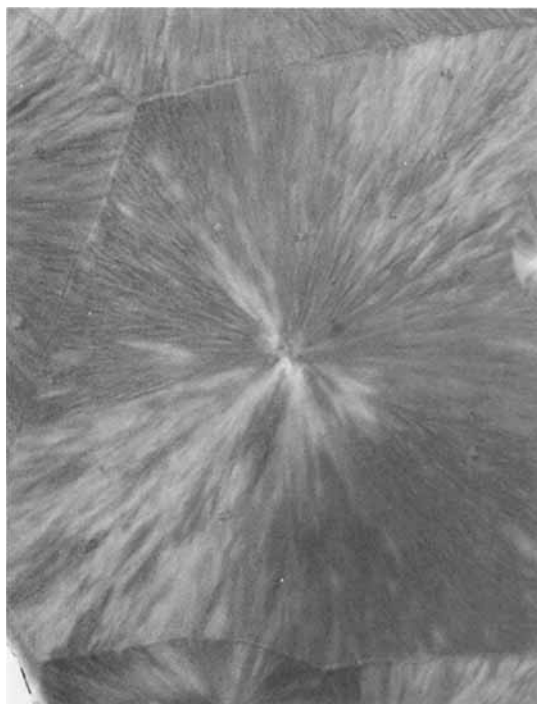
### Melting Behavior

The  $T_m$  of PP with added PCP was found to be almost constant ( $\pm 1^\circ\text{C}$ ) even with a larger amount of PCP. The heat of fusion ( $\Delta H_m$ ) and heat of crystallization ( $\Delta H_c$ ) of PP were measured with various amounts of PCP and are shown in Figure 3.

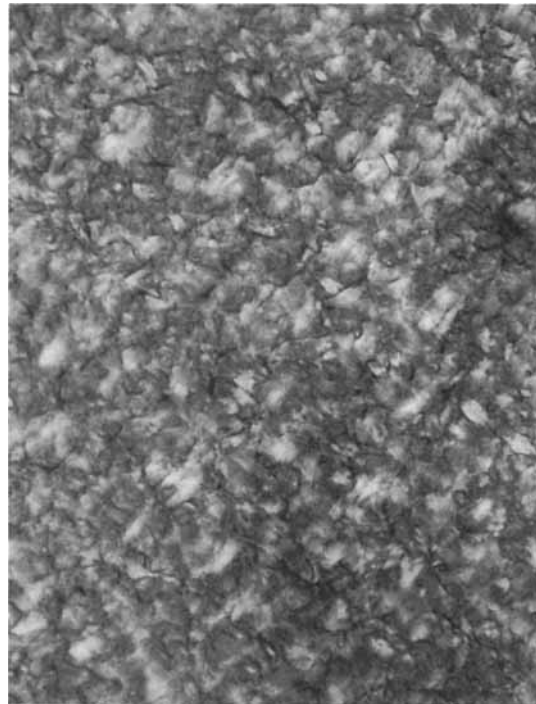
With addition of PCP,  $\Delta H_m$  and  $\Delta H_c$  of PP increase  $7$ – $8$  J/g and  $4$ – $5$  J/g, respectively. From these observations, it might be considered that the degree of crystallinity of PP increased with addition of PCP. To confirm the above consideration, X-ray dif-



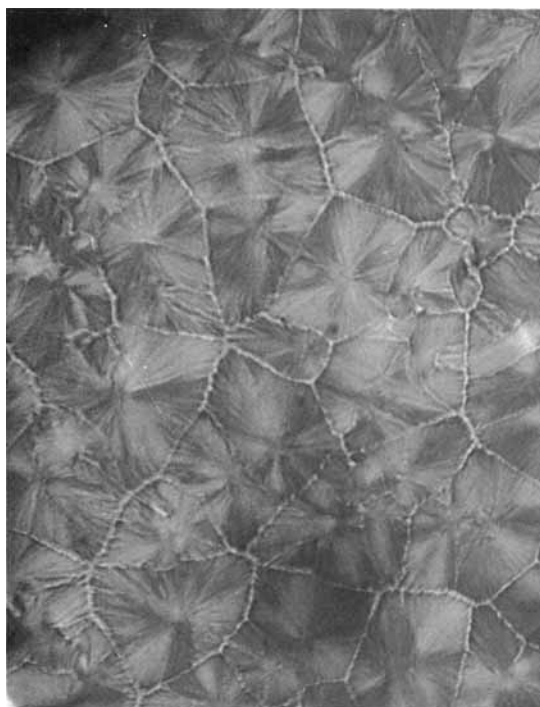
**Figure 5** Half-time of crystallization of polypropylene with various amounts (ppm) of polycyclopentene: 1, 0; 2, 500; 3, 1000; 4, 2000; 5, 5000.



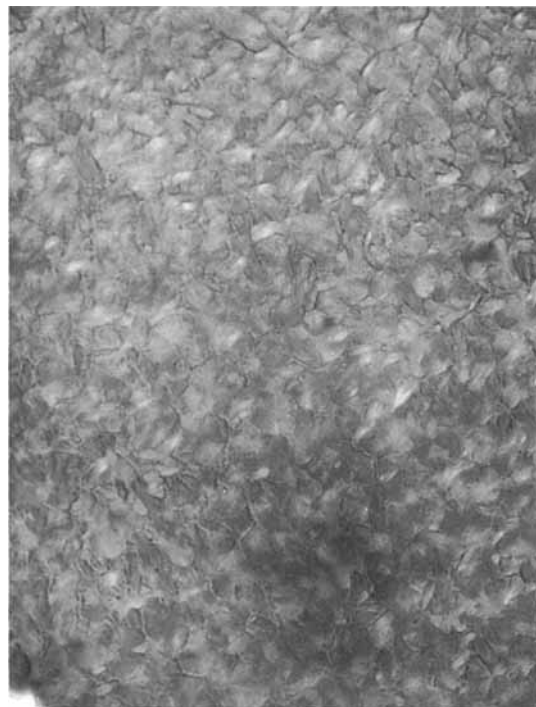
(1) PP



(2) PP/PVCH (3000ppm)



(3) PP/PCP (1000ppm)



(4) PP/PCP (3000ppm)

**Figure 6** Spherulite of polypropylene with and without polymeric nucleating agent ( $\times 250$ ).

fractograms of PP with different amounts of PCP were obtained and are given in Figure 4.

As shown in Figure 4, the characteristic diffrac-

tion maxima of the monoclinic  $\alpha$ -crystalline form<sup>12</sup> of PP appeared without any additional crystalline peak. With increasing amounts of PCP, the peak of

the  $2\theta = 17.2^\circ$  corresponding (040) crystal plane became larger. The degree of crystallinity was calculated from  $\Delta H_m$ <sup>13</sup> and the diffraction pattern,<sup>14</sup> as shown in Table I. As expected, the degree of crystallinity of PP increased with the amount of PCP.

According to the theory of WAXS,<sup>15</sup> the intensity of a diffraction plane is proportional to the number and size of crystallites along its axial direction in the crystal. The relative intensity  $I_{040}/I_{110}$  of the (040) and (110) crystal planes for each sample are shown in Table I. The increase of  $I_{040}/I_{110}$  with amount of PCP implies that PCP promotes the growth of crystallite in the direction perpendicular to the (040) plane rather than the (110) plane.

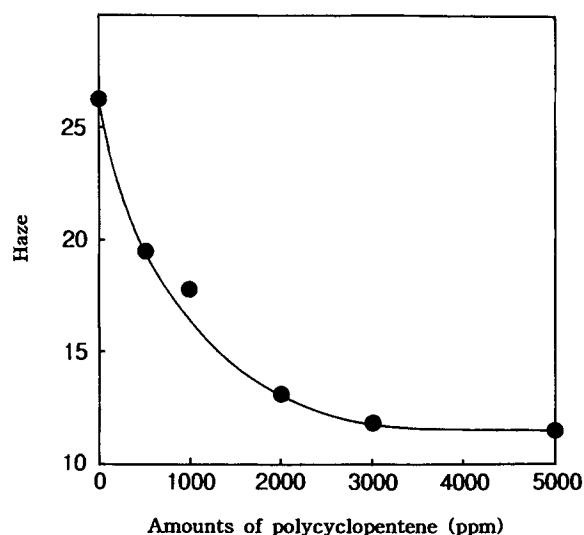
### Crystallization Rate

To examine the effect of PCP on crystallization rate of PP, the half times of crystallization ( $t_{1/2}$ ) were measured for various amounts of PCP and are shown in Figure 5.

From the trend of these curves, it is evident that the crystallization rate of PP with added PCP is faster than that of the original PP at an isothermal crystallization temperature. For PCP at more than 2000 ppm, the enhancement of crystallization rate becomes less.

### Optical Property

The spherulite shapes of PP with various amounts of PCP and PVCH were observed and are shown in Figure 6.



**Figure 7** Effect of polycyclopentene on haze of polypropylene film.

When PCP was added to PP, the spherulite size decreased to a great extent and the number of spherulites increased. The PVCH had also shown a similar behavior. From these results, it could be concluded that PCP as well as PVCH is a powerful nucleating agent for PP.

The spherulite size of PP was diminished by addition of PCP so that transparency of film could be improved. For evaluation of transparency, the haze of PP film with various amounts of PCP was measured, as shown in Figure 7.

The haze of PP decreased remarkably with addition of PCP. In other words, the transparency of PP could be improved to a great extent by the addition of only 2000–3000 ppm of PCP.

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