

Polyolefins Containing 1,3-Disubstituted Cyclopentane Units as Nucleating Agents for Isotactic Polypropylene

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ABSTRACT: Polyolefins containing 1,3-disubstituted cyclopentane units in the main chain have been synthesized by 1,3-polymerization of cyclopentene (PCP), cyclization polymerization of 1,5-hexadiene (PHD), and ring-opening metathesis polymerization of norbornene following hydrogenation of the unsaturated main chain (H-PNB) with various transition metal catalysts. These polyolefins were applied to nucleating agents for isotactic polypropylene, and relationship between the structure of the polyolefins and nucleating effect was studied by DSC, polarized optical

microscope, and WAXD. All the polyolefins had an effect of nucleation for isotactic polypropylene (PP). Of the polymeric nucleating agents, H-PNB showed the most effective nucleation. Addition of PCP, which was obtained with a nickel catalyst with diimine ligand, to PP induced β -modification. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2953–2958, 2006

Key words: polyolefin; 1,3-cyclopentane; nucleating agent; isotactic polypropylene

INTRODUCTION

Isotactic polypropylene (PP) is one of the most widely used resins due to their excellent characteristics. Commercial PP normally contains some additives such as light stabilizer, antioxidation agent, flame retardant, antistatic agent, and nucleating agent. Of the additives, the nucleating agent plays an important role to improve optical and mechanical properties, such as transparency and stiffness, of PP. Some low molecular organic materials, sodium benzoate, aluminum benzoate, dibenzylidene sorbitol, and so on, are known as effective nucleating agents for PP.^{1,2} Polymeric nucleating agents for PP also have been investigated. In general, the polymeric nucleating agents are superior to the organic nucleating agents in miscibility and dispersity for PP. Polyvinylcyclohexane and polycyclopentene (PCP) induce efficient nucleation of PP.^{3–5} We focused on crystalline polyolefins containing 1,3-cyclopentane units in the main chain. PCP synthesized via polymerization of cyclopentene with some transition metal catalysts forms poly(1,3-cyclopentane).^{6–11} Cyclization polymerization of 1,5-hexadiene with transition metal

catalysts yields poly(methylene-1,3-cyclopentane) (PMCP).¹² Poly(ethylene-1,3-cyclopentane) is obtained by hydrogenation of ring-opened polynorbornene (H-PNB).^{13,14} In this study, we investigated the effect of structure of polyolefins containing 1,3-cyclopentane units on the nucleation of PP.

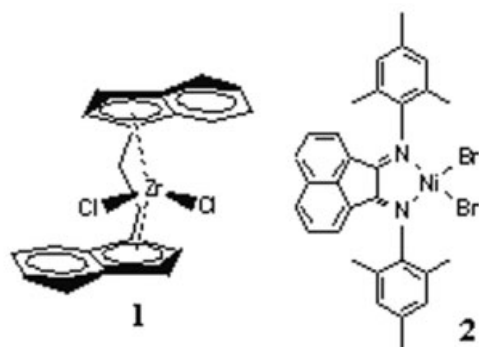
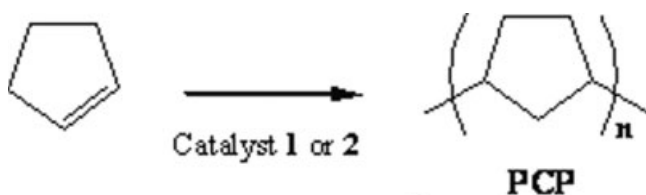
EXPERIMENTAL

Materials

Isotactic polypropylene (PP) was prepared by a highly isospecific metallocene catalyst, *rac*-dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dichloride combined with triisobutylaluminum-triphenylcarbenium tetrakis(pentafluorophenyl)borate as a cocatalyst system in toluene at 0°C. The structure and thermal properties of the resulting isotactic polypropylene were described below; $T_m = 157.2^\circ\text{C}$, $\Delta H_m = 91.0 \text{ J/g}$, $T_c = 112.4^\circ\text{C}$, $\Delta H_c = 91.3 \text{ J/g}$, $[\eta] = 2.92 \text{ dL/g}$. Polycyclopentene was synthesized by *rac*-ethylenebis(indenyl)zirconium dichloride (**1**) using methylaluminoxane (MAO) as a cocatalyst (Scheme 1).^{3,4} The resulting PCP was separated into boiling toluene soluble fraction (PCP1), boiling toluene insoluble-boiling xylene soluble fraction (PCP2), and boiling xylene insoluble-*o*-dichlorobenzene (ODCB) soluble fraction (PCP3). Polymerization of cyclopentene was also investigated with [(2,3,6-Me3Ph)2DABAn]NiBr₂ (**2**) (Scheme 1).⁵ The obtained PCP was extracted with boiling ODCB, and the solu-

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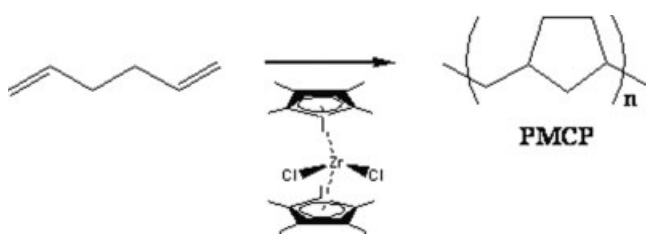


Scheme 1 Synthesis of PCP.

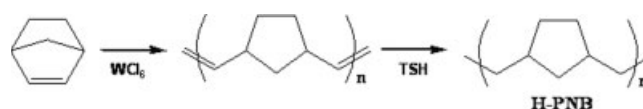
ble fraction was collected as PCP4. Poly(methylene-1,3-cyclopentane) (PMCP) was synthesized by cyclization polymerization of 1,5-hexadiene by bis(pentamethylcyclopentadienyl)zirconium dichloride using MAO as a cocatalyst (Scheme 2). The obtained PMCP was extracted with boiling ODCB, and the soluble fraction was collected. Hydrogenated ring-opened polynorbornene (H-PNB) was synthesized by ring-opening polymerization of norbornene with WCl_6 combined with $Sn(CH_3)_4$ catalyst system at room temperature following hydrogenation by *p*-toluenesulfonylhydrazide (TSH) in xylene at 135°C for 4 h (Scheme 3). Completion of the reactions was confirmed by 1H -NMR spectroscopy. A conventional low molecular weight nucleating agent, sodium 2,2'-methylenebis(4,6-di-*tert*-butylphenyl) phosphate (trade name; NA-11 supplied by Asahi Denko) was kindly donated from Sumitomo Chemical.

Preparation of samples

Isotactic polypropylene (1.0 g) and a polymeric nucleating agent (1 mg) were dissolved in 20 mL of *o*-dichlorobenzene at 180°C for 2 h. The polymer solution was slowly poured into large excess of methanol. The precipitated polymer was recovered by filtration, washed with methanol and dried



Scheme 2 Synthesis of PMCP.



Scheme 3 Synthesis of H-PNB.

in vacuo at 60°C for 6 h. The sample containing NA-11 was prepared by mixing with melting PP on a hot-stage at 200°C, and cooled to room temperature.

Analytical procedures

Limiting viscosity number ($[\eta]$) of polymers was determined by Ubbelohde viscometer at 135°C using decahydronaphthalene as a solvent. Number average molecular weight of polymers were measured at 140°C by means of gel-permeation chromatography (GPC) (Waters 150°C) using ODCB as a solvent and calibrated with standard polystyrene samples. Thermal properties of polymers were investigated by a Rigaku DSC-8230 (Rigaku). Melting temperature (T_m) of polymeric nucleating agents was recorded in the heating process from 25 to 300°C at a heating rate of 20°C/min. Crystallization temperature (T_c) and T_m of the PP samples were recorded in the cooling process at a rate of 10°C/min from 200 to 25°C and in the 2nd heating process from 25 to 200°C at a rate of 10°C/min, respectively, after previous heating to 200°C at a heating rate of 20°C/min. WAXD patterns of the polymers were recorded on a Rigaku RAD-IIC using Cu K α radiation. Samples for WAXD measurements were melted at 200°C and were pressed under 10 MPa pressure followed by annealing in 120°C oil. The optical microscope photographs of the PMCPs were observed using an optical microscope (Olympus BX50). The samples for optical microscope were prepared after previous heating to 200°C at a rate of 20°C/min, held for 5 min, and cooling to room temperature at a rate of 10°C/min on a glass sample holder.

RESULTS AND DISCUSSION

Structure and property of polymeric nucleating agents

Structure and property of the polymeric nucleating agents are summarized in Table I. All the polymeric nucleating agents used in the present work had crystalline structure and showed melting peak in the DSC scan. PCP prepared by the catalyst **1** was fractionated by boiling organic solvents, toluene, xylene, and ODCB, and separated into PCP1, PCP2, and PCP3, as described in the experimental parts. T_m of the PCP samples increased with increasing the boiling point of the extraction solvents from 150 to 263°C. The difference in the T_m of PCP1-3 should be

TABLE I
Structure and Property of Polymeric Nucleating Agents

| Sample | Catalyst | M_n^a | T_m^b (°C) | ΔH_m^b (J/g) |
|--------|----------|-------------------|--------------|----------------------|
| PCP1 | 1 | 2240 | 96.7 | |
| PCP2 | 1 | 2420 | 232.1 | 61.3 |
| PCP3 | 1 | 2650 | 263.3 | 94.3 |
| PCP4 | 2 | — ^c | 231.8 | 11.6 |
| PMCP | | n.d. ^d | 110.7 | 44.6 |
| H-PNB | | 63,000 | 148.7 | 73.4 |

^a Determined by GPC.

^b Melting temperature and heat of fusion determined by DSC.

^c $\eta = 0.80$ dL/g.

^d Not determined.

derived from the difference in stereo-regularity of the each fraction. (Note: It is impossible to determine the stereo-regularity of PCP by means of ¹³C NMR spectroscopy). The T_m of PCP4, which was obtained with catalyst 2, was 230°C. The crystalline structure of PCPs obtained with catalysts 1 and 2 was different from each other due to their difference in the stereo-regularity; catalysts 1 and 2 yielded isotactic and atactic polymers, respectively.¹¹ In the WAXD patterns¹ of PCPs 1-3, diffraction peaks were observed at $2\theta = 16.0, 19.5,$ and 24.0° .⁶⁻¹⁰ Whereas, PCP4 obtained with catalyst 2 showed the diffraction peaks at $2\theta = 17.3, 19.1,$ and 21.0° with a wide-based reflection peak.¹¹ The T_m of PMCP used in this experiment was 111°C. A sharp diffraction peak was observed at 18.4° in the WAXD pattern derived from hexagonal crystalline structure.¹² H-PNB showed the T_m at 149°C. The WAXD pattern of melt-quenched H-PNB sample showed the diffraction peaks at $2\theta = 18.6^\circ$. Whereas, the sample annealed at 120°C for 6 h showed multiple diffraction at $2\theta = 13.8, 16.6, 18.1, 18.9,$ and 25.1° , as previously reported.¹⁴ These polymers containing 1,3-disubstituted cyclopentane were applied to the nucleating agents for PP.

DSC measurement

The results of DSC analysis of PP samples containing the polymeric nucleating agents are summarized in Table II. Addition of these polymeric nucleating agents did not affect or slightly increased the T_c of the PP samples. On the other hand, obvious increase of T_c was observed in Sample 7 containing NA-11. A higher melting peak was detected at around 160°C as a shoulder peak (T_{m2}) with a main melting peak (T_{m1}) in the DSC traces of all the PP samples containing the polymeric nucleating agents. Increase of the ΔH_c and ΔH_m of PP were observed in all the PP

TABLE II
Results of DSC Analysis of PP Samples Containing Polymeric Nucleating Agents

| Sample | NA ^a | T_c^b (°C) | ΔH_c^b (J/g) | T_{m1}^c (°C) | T_{m2}^c (°C) | ΔH_m^c (J/g) |
|--------|-----------------|--------------|----------------------|-----------------|-------------------|----------------------|
| PP | — | 112.4 | 91.3 | 157.2 | n.d. ^d | 91.0 |
| PP1 | PCP1 | 114.5 | 108.1 | 154.1 | 161.5 | 104.5 |
| PP2 | PCP2 | 112.8 | 112.9 | 153.5 | 160.5 | 105.6 |
| PP3 | PCP3 | 114.0 | 118.8 | 152.6 | 159.5 | 107.7 |
| PP4 | PCP4 | 111.8 | 126.3 | 153.8 | 160.3 | 111.5 |
| PP5 | PMCP | 115.4 | 117.5 | 153.7 | 159.6 | 106.3 |
| PP6 | H-PNB | 112.8 | 132.3 | 153.3 | 160.1 | 116.5 |
| PP7 | NA-11 | 118.8 | 104.9 | 153.6 | n.d. ^d | 101.3 |

^a Nucleating agent.

^b Crystallization temperature and heat of crystallization determined by DSC on the cooling process.

^c Melting temperature and heat of fusion determined by DSC on the second heating process.

^d Not detected.

samples. The ΔH_m and nature of PP samples containing the nucleating agents are summarized in Figure 1. The PP sample containing H-PNB (Sample PP6) showed the highest ΔH_m . PCP4, which was obtained by catalyst 2, induced the most effective increase of the ΔH_c and ΔH_m of PP among the PCPs used in the experiment. PCP4 has different stereo-regularity and crystalline structure from those of PCPs1-3 obtained with catalyst 1,¹¹ and the difference should induce the effective nucleation. In comparison of the PP samples with PCP prepared by catalyst 1, the ΔH_m increased with increasing the T_m and M_n of PCPs. The ΔH_m s of all the PP samples containing the polymeric nucleating agents were larger than that of PP containing NA-11.

Optical microscope observation

The spherulites of PP samples were observed using an optical microscope. Figures 2(a-f) show the optical microscope photographs of PP, PP3, PP4, PP5,

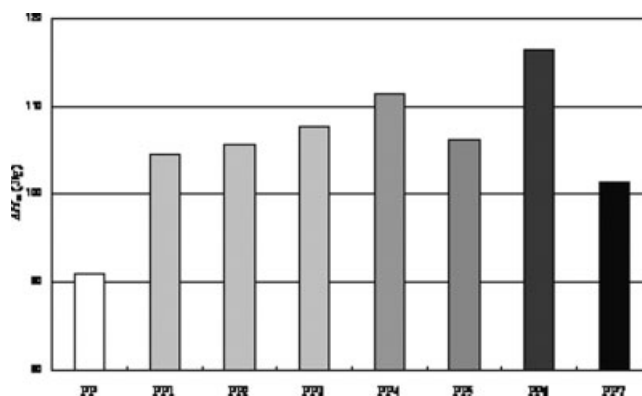


Figure 1 ΔH_m of PP samples.

¹ WAXD patterns of the polymeric nucleating agents are available in Supporting Information.

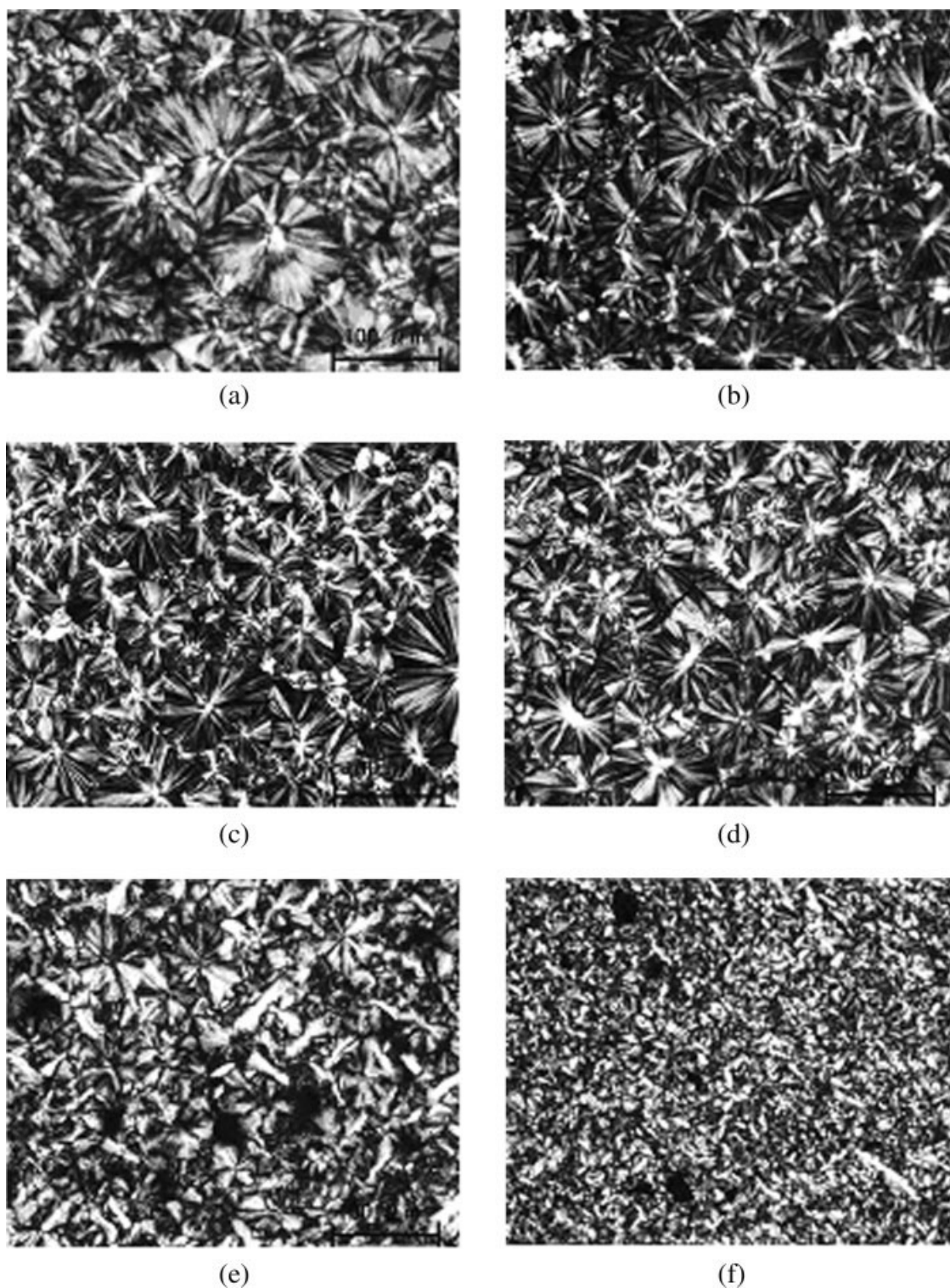


Figure 2 Optical microscope photographs of (a) PP, (b) PP3, (c) PP4, (d) PP5, (e) PP6, and (f) PP7.

PP6, and PP7, respectively. NA-11 (for a reference) reduced the spherulites size of PP most effectively among the nucleating agents. The same observation applied to the spherulites of PP containing the polymeric nucleating agents. Of the PP samples with polymeric nucleating agents, PP6 that contained H-

PNB, showed the smallest spherulite size. Two types of nucleating agents are used to improve the properties of PP. One improves the optical property (clarity) and the other dose the mechanical property of PP. The polymeric nucleating agents applied in the experiment were not so effective for improvement

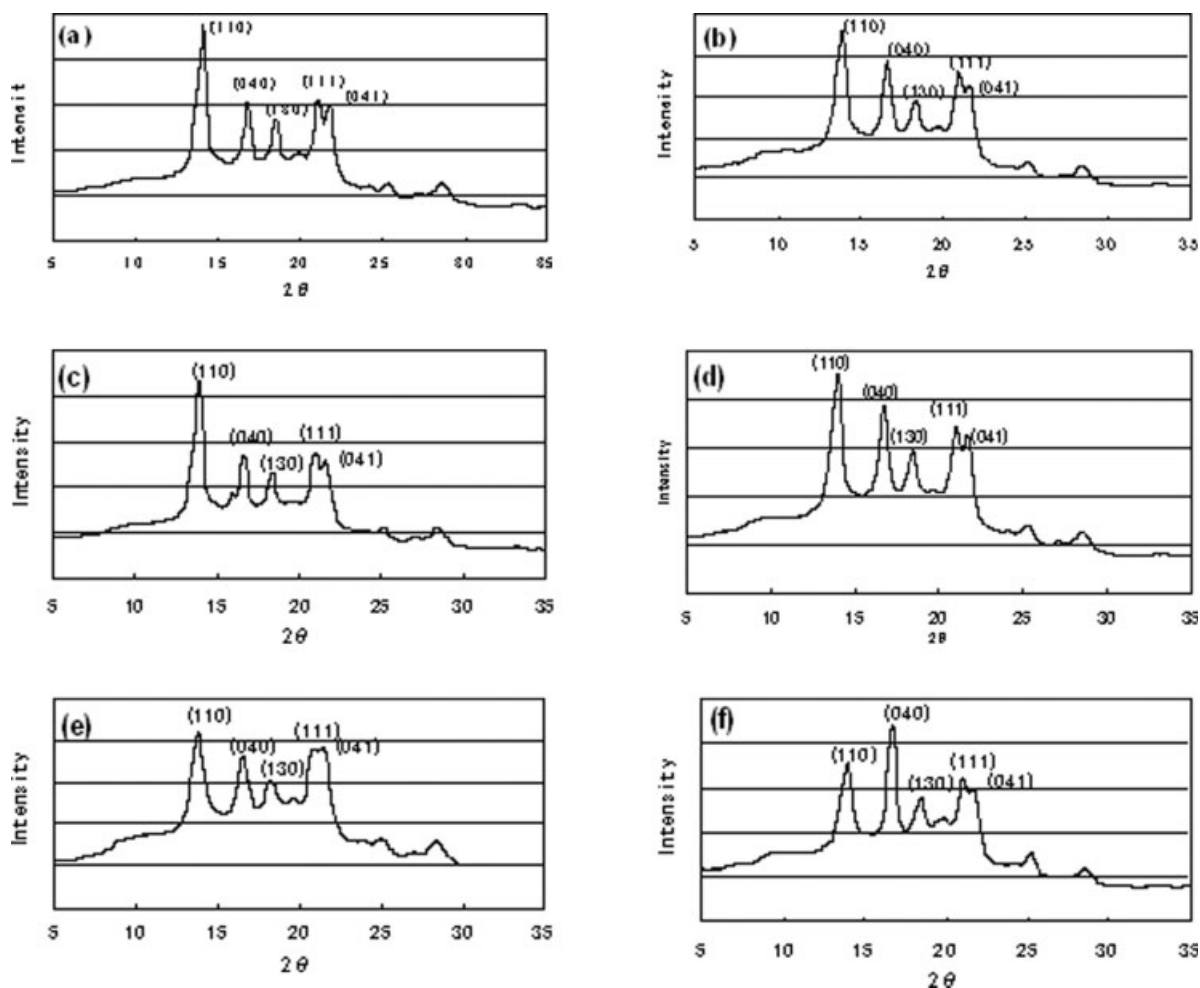


Figure 3 WAXD patterns of (a) PP, (b) PP3, (c) PP4, (d) PP5, (e) PP6, and (f) PP7.

of the optical property of PP. Mechanical properties of the PP samples containing these nucleating agents will make clear the features of the polymeric nucleating agents.

WAXD analysis

WAXD patterns of PP samples, PP, PP3, PP4, PP5, PP6, and PP7, are shown in Figures 3(a–f), respectively. Increase of diffraction intensity derived from (040) plane, at around $2\theta = 14^\circ$, was observed in almost all the PP samples. This phenomenon was previously reported in the PP including nucleating agents.⁵ The diffraction intensity ratios of (040) plane to (110) plane, at around $2\theta = 16.5^\circ$, of PP samples are summarized in Table III. The intensity ratio of the (040) plane to the (110) plane shows the growth direction of crystallite. It would be better to say that the increase of (040)/(110) intensity ratio indicates the growth of crystallite proceeds in the direction perpendicular to the (040) plane rather than the (110) plane. PP7 containing NA-11 (for a reference) showed

the highest values of (040)/(110) intensity ratio of 1.15. The same observation was applied to the WAXD patterns of PP samples containing the polymeric nucleating agents, except PP4. Of the PP samples with polymeric nucleating agents, the PP6 sample, which contained H-PNB, showed the highest values of (040)/(110) intensity ratio of 0.60. We can recognize from optical microscope observation and WAXD patterns of PP samples that the sample with small spherulites size had high value of (040)/(110) inten-

TABLE III
Diffraction Intensity Ratios of (040) Phase to (110) Phase in the WAXD Patterns of PP Samples

| Sample | NA ^a | Intensity ratio of (040)/(110) |
|--------|-----------------|--------------------------------|
| PP | — | 0.348 |
| PP3 | PCP3 | 0.566 |
| PP4 | PCP4 | 0.346 |
| PP5 | PMCP | 0.559 |
| PP6 | H-PNB | 0.602 |
| PP7 | NA-11 | 1.149 |

^a Nucleating agent.

sity ratio. It seems reasonable to suppose that the direction of crystallite growth is relevant to the spherulites size of PP, though there should be room for further investigation. On the other hand, the intensity ratio of PP4 containing PCP4 was same that of PP. Meanwhile, a reflection at $2\theta = 15.9^\circ$ derived from β -modification in the WAXD pattern of PP4 [Fig. 3(c)]. The results indicate that PCP4 induces the different crystalline structure of PP from PCPs1-3. The difference in crystalline structure between PCPs1-3 and PCP4, described above, should cause those results.

CONCLUSIONS

Polyolefins containing 1,3-disubstituted cyclopentane units were prepared by 1,3-polymerization of cyclopentene, cyclization polymerization of 1,5-hexadiene (PHD), and metathesis polymerization of norbornene following hydrogenation of the unsaturated main chain (H-PNB). All the polyolefins used in the present study play a role of nucleation agent for PP. Nucleating effect of these polymers for PP was studied by DSC measurement, optical micrograph, and WAXD. Of the polymeric nucleating agents, H-PNB induced the most effective increase of ΔH_m and decrease of the spherulites' size of PP. PCP obtained with catalyst **2** induced the β -modification of PP, as observed in PP4. Although the improvement of the optical property is inferior to the conventional nucleating agent, crystalline polyolefins containing 1,3-disubstituted cyclopentane units should be effective nucleating agents for PP with potentialities. Mechan-

ical properties of the PP samples containing these nucleating agents are now being carried out, and the results will be reported elsewhere.

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