Synthesis of High-Melting, Isotactic Polypropene with C_2- and C_1-Symmetrical Zirconocenes

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ABSTRACT: When polymerization of propene was conducted using the C_2-symmetrical zirconocenes *rac*-Et(2,4,7-Me$_3$Ind)$_2$ZrCl$_2$ (**I**) and *rac*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$ (**II**) combined with Ph$_3$CB(C$_6$F$_5$)$_4$, the isotacticity ([mmmm]) and the melting point (T_m) of the produced polymer markedly increased, along with a decrease of the polymerization temperature from 30 to −78 °C. Thus, isotactic polypropene (iPP) with T_m = 168.9 °C was obtained from the polymerization with catalyst **I** at −78 °C, whereas the [mmmm] and T_m of iPP were almost unchanged in the same temperature range when the C_1-symmetrical zirconocene iPr(3-tBuCp)(3-tBuInd)ZrCl$_2$ (**III** or **III′**) was employed.

Introduction

Compared with typical heterogeneous Ziegler−Natta catalysts, metallocene catalysts give a clear picture of the relation between the structures of catalysts and the produced polymer.[2] In addition, the single-site metallocene catalysts also have an advantage with respect to control of the molecular mass distribution.[2d] Due to the lower molecular weight as well as the lower regio- and stereospecificity, however, isotactic polypropene (iPP) obtained with metallocene catalysts usually shows a lower melting point (T_m), which limits the application to high-performance materials.

From such a viewpoint, much effort has been focused on the molecular design of metallocene ligands. Kaminsky's group has recently reported a new C_2-symmetrical zirconocene which can produce iPP with a very high T_m.[3] Spaleck et al. also synthesized a series of highly isospecific C_2-symmetrical catalysts.[4] On the other hand, a C_1-symmetrical catalyst has been developed by Showadenko Ltd. which produces iPP with a high T_m.[5] They proposed the Cossee's coordination mechanism for a monomer insertion into the metal−carbon bond, which has only one space available for coordination.[6] This viewpoint differs from the one proposed for a typical C_2-symmetrical metallocene, of which two equal value spaces are necessary for coordination of incoming monomer and the growing chain end, respectively.[7]

Besides the ligands of metallocene catalysts, some other factors are found to affect the stereoregularity of iPP. Polymerization temperature is believed to influence the rigidity of the metallocene frame, which directly controls the stereospecificity.[8] The concentration of propene also affects the stereoregularity caused by the epimerization or isomerization of the active metallocene species.[9] Furthermore, an α-H-agostic or β-H-agostic interaction affects the incoming monomer.[9] According to some theoretical and experimental works,[6,9−11] both the direct influence of the metallocene frame and the indirect steric control originating from the α-H-agostic or β-H-agostic interaction seem to be of great importance for the stereo- and regioregularity of an incoming monomer. It may then be asked whether iPP with a very high T_m[12] can also be obtained by controlling all these factors.

In this study, we have made an attempt to synthesize an iPP with the highest T_m reported so far using the following representative C_2- and C_1-symmetrical zirconocene catalysts (**I−III**). The catalytic behaviors along with polymerization temperature were investigated.

I   II   III
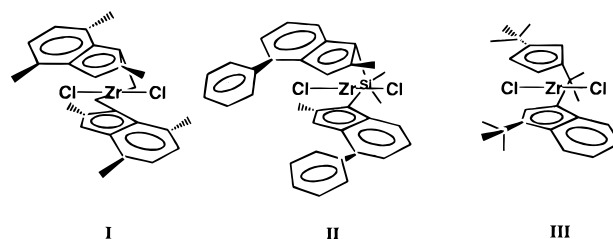
Results and Discussion

1. Polymerization with C_2-Symmetrical Zirconocenes. The catalyst *rac*-Et(2,4,7-Me$_3$Ind)$_2$ZrCl$_2$ (**I**) is reported to produce iPP with a high T_m (e.g., 163 °C at T_p = 30 °C) even at a high polymerization temperature when methylaluminoxane (MAO) is used as cocatalyst.[3] Polymerization of propene was conducted with **I** in the temperature range from −78 to 30 °C using a boron compound (Ph$_3$CB(C$_6$F$_5$)$_4$) as well, the results of which are shown in Table 1. When MAO was used as cocatalyst, the molecular weight increased moderately with a decrease in the polymerization temperature (T_p). Figure 1B displays the ^{13}C NMR spectrum of iPP obtained at −30 °C, where regiodefects are hardly detected. However, some amount of atactic PP was detected (20.2−20.9 ppm). When Ph$_3$CB(C$_6$F$_5$)$_4$ was used in place of MAO, the molecular weight increased drastically from 1.90 × 10^4 (at 30 °C) to 1.36 × 10^6 (at −78 °C). The ^{13}C NMR spectrum of iPP produced with Ph$_3$CB(C$_6$F$_5$)$_4$ at −30 °C is given in Figure 1A, which also shows very few stereo- and regiodefects. It may be said that iPP with a higher molecular weight and higher isotacticity is obtained in much higher yield when Ph$_3$CB(C$_6$F$_5$)$_4$ is used as cocatalyst. The iPP with

Table 1. Results of Polymerization of Propylene with *rac*-Et(2,4,7-Me$_3$Ind)$_2$ZrCl$_2$ (I)^a

no.	cocatalyst	[Zr] (×10^{-3} mmoL)	T_p (°C)	polym time (h)	yield (g)	T_m (°C)	$M_n{}^b$ (×10^4)	$M_w/M_n{}^b$	[mmmm]^c (%)
1^d	Ph$_3$CB(C$_6$F$_5$)$_4$	10	30	0.50	10.60	158.1	1.9		90.6
2	Ph$_3$CB(C$_6$F$_5$)$_4$	10	0	0.50	1.74	164.7	58.4	2.03	94.2
3	Ph$_3$CB(C$_6$F$_5$)$_4$	10	−30	2.0	8.44	168.0	101.0	1.86	98.2
4	Ph$_3$CB(C$_6$F$_5$)$_4$	25	−78	48	0.02	168.9	136.2	1.85	nd^f
5^e	MAO	10	−15	12	0.30	164.9	24.9	2.05	94.1
6	MAO	10	−30	24	0.15	166.2	57.7	2.39	96.7
7	MAO	25	−45	120	0.07	166.8	73.9	2.28	98.0

^{a} Polymerizations were carried out in 30 mL of toluene, [propene]$_0$ = 10.4 M. ^{b} By GPC, calibrated with standard polystyrene. ^{c} Measured by ^{13}C NMR. ^{d} Runs no. 1−4: polymerized in the presence of tributylaluminum, [Ph$_3$CB(C$_6$F$_5$)$_4$] = [Zr], [TIBA] = 33 mM. ^{e} Runs no. 5−7: [Al]/[Zr] = 2000; the calculation of the [mmmm] does not include the the atactic portion at 20.5−20.8 ppm (see Figure 1B). ^{f} The yield is too low to be measured.
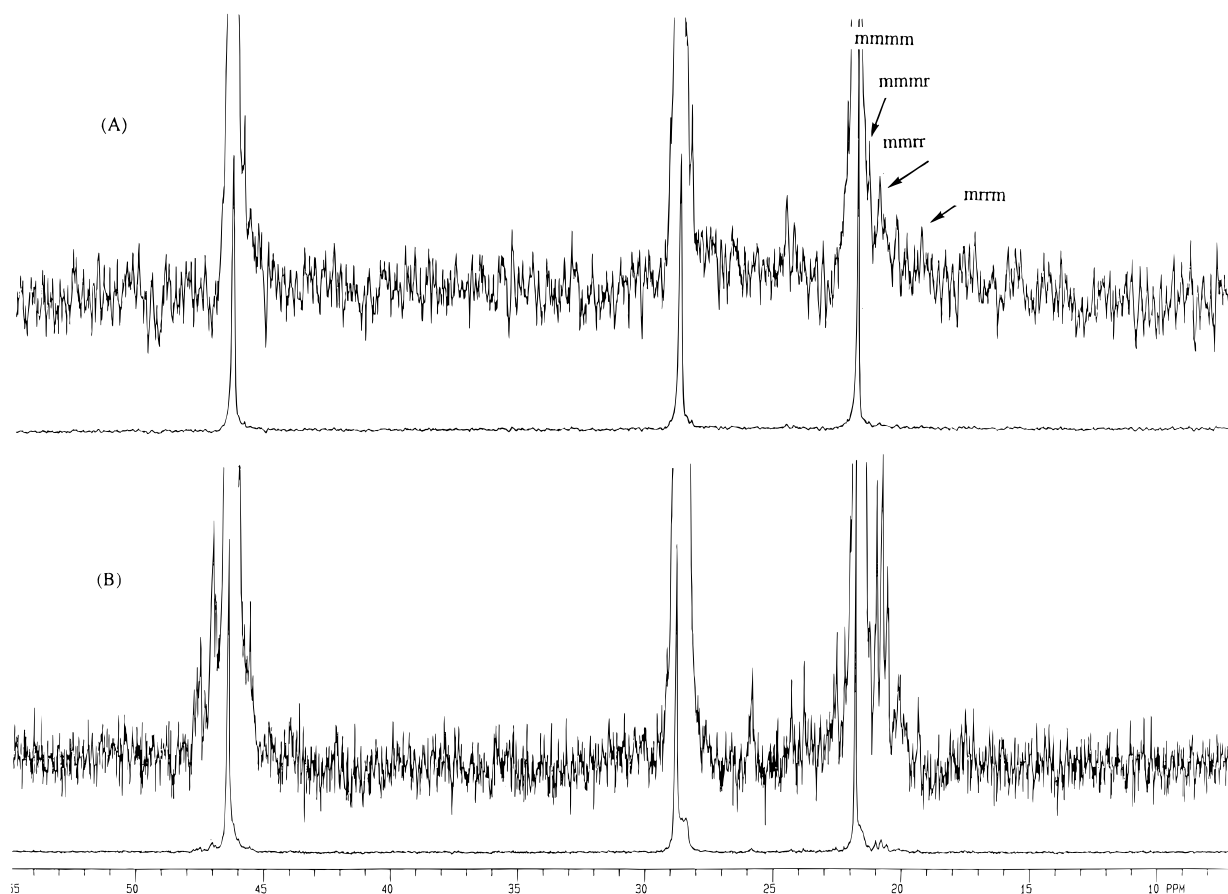
Figure 1. 75 MHz ^{13}C NMR spectra of polymers obtained at −30 °C using *rac*-Et(2,4,7-Me$_3$Ind)$_2$ZrCl$_2$ (I) combined with Ph$_3$CB(C$_6$F$_5$)$_4$ (A) (run 3) and MAO (B) (run 6), respectively. The resonances at 20.2−20.8 ppm in spectrum B may originate from an atactic site.

T_m as high as 168.9 °C could be obtained at −78 °C (run 4). This melting point is the highest reported so far using both homogeneous metallocene and heterogeneous Ziegler−Natta catalysts.[13]

Another C_2-symmetrical metallocene, *rac*-Me$_2$Si(2-Me-4-Ph-Ind)$_2$ZrCl$_2$ (II), developed by Spaleck et al.,[3] was then used in place of **I** combined with Ph$_3$CB(C$_6$F$_5$)$_4$. This silicon-bridged zirconocene has an Ind−Zr−Ind ring canting angle of 128.5°, which is bigger than that of **I** (127.6°). The results obtained are shown in Table 2. Similar to the results from **I**, the molecular weight increased upon lowering the polymerization temperature. Figure 2 displays the ^{13}C NMR spectrum of iPP obtained at −30 °C, indicating that the stereo- and regioregularity are very high. However, the molecular weight, melting point, and isotacticity of the polymer are lower than those of iPP produced with **I**.

2. Polymerization with a C_1-Symmetrical Zirconocene. Ewen et al. reported a C_1-symmetrical metallocene which produces a hemiisotactic PP.[14] In sharp contrast to that, another C_1-symmetrical metallocene (e.g., (3-tBuCp)iPr(3-tBuInd)ZrCl$_2$ (III)) developed by Miyake et al. promotes a highly isotactic polymerization.[5] The *threo*-isomer has a ring canting angle of 117.5°, which is much smaller than those of **I** and **II**. **III** and **III′** (the methylated mixture of the *threo*-**III** and the *erythro*-isomer) were employed for propene polymerization. The polymer yields, molecular weights, and some other analytical results are listed in Table 3. The use of MAO as cocatalyst gave iPP with a relatively lower T_m and lower molecular weight (run 23). Ph$_3$CB(C$_6$F$_5$)$_4$ was thus used in place of MAO. Although the methylated zirconocene **III′** contains the two isomers, iPP was selectively produced (the obtained polymer was completely insoluble in boiling heptane). It seems, therefore, that the polymer resulted from the *threo*-isomer. With both **III** and **III′**, the molecular weight increased with a decrease of T_p. The ^{13}C NMR

Table 2. Results of Polymerization of Propene with *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrMCl₂ (II)[a]

no.	[Zr] (×10⁻⁴ mmoL)	T_p (°C)	[propene]₀ (M)	polym time (h)	yield (g)	T_m (°C)	$M_n{}^b$ (×10⁴)	$M_w/M_n{}^b$	[mmmm][c] (%)
8	0.20	30	10.4	0.25	0.21	159.9	97.2	1.65	90.8
9	1.0	0	10.4	0.25	0.67	163.3	121	1.74	94.1
10	0.20	0	10.4	2.0	0.05	163.7	d	d	nd[e]
11	1.0	−30	1.5	3.0	0.03	164.2	67.6	2.03	nd
12	1.0	−30	10.4	3.0	0.10	165.1			97.3
13	1.0	−30	17.9	2.5	0.21	165.6			
14	40	−60	10.4	120	1.41	165.9	57.4	2.11	98.0
15	50	−78	10.4	48	0.01	164.7	18.1	3.16	

[a] Polymerization conditions: [TIBA] = 33 mM, [Ph₃CB(C₆F₅)₄] = [Zr], toluene = 30 mL. [b] By GPC, calibrated with standard polystyrene. [c] Measured by ¹³C NMR. [d] The M_n is too large to be measured by GPC. [e] The amount of polymer is too small to be measured by ¹³C NMR.
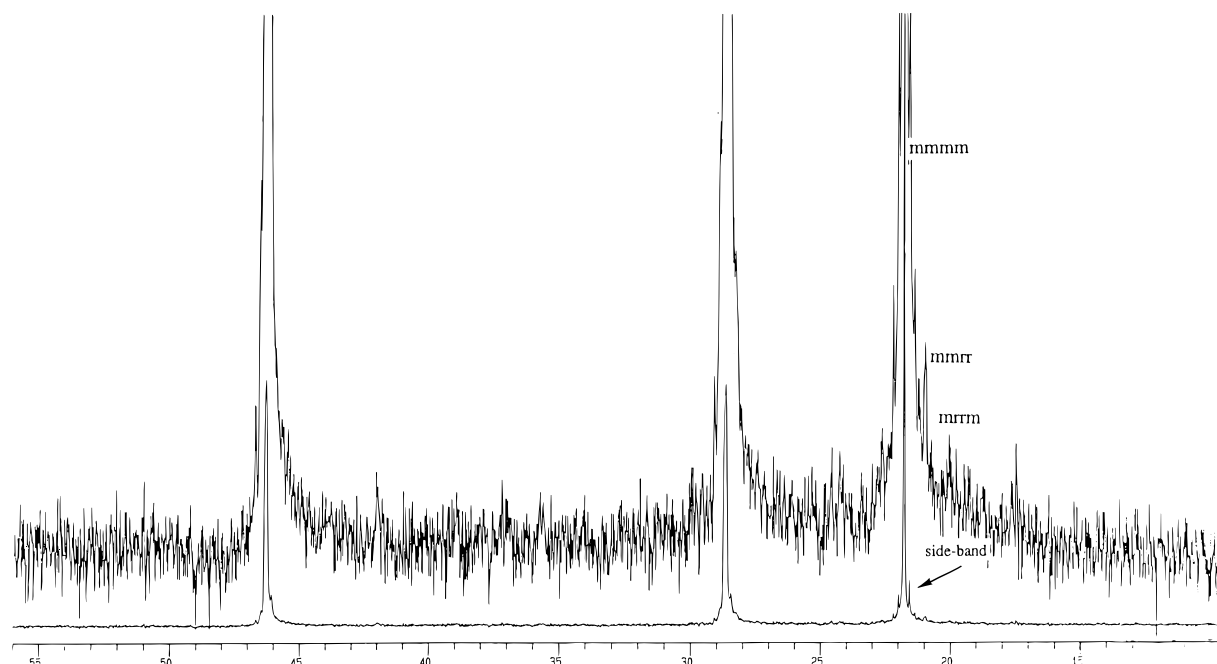
Figure 2. 75 MHz ¹³C NMR spectrum of iPP obtained at −30 °C using *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ (**II**)/Ph₃CB(C₆F₅)₄ (run 12).

Table 3. Results of Propene Polymerization with Cp(3-tBu)iPr(Ind(3-tBu))ZrMe₂ (III′)[a] and *threo*-Cp(3-tBu)iPr(Ind(3-tBu))ZrCl₂ (III)[b]

| no.	catalyst	[Zr] (×10⁻³ mmoL)	T_p (°C)	polym time (h)	yield (g)	T_m (°C)	$M_n{}^c$ (×10³)	$M_w/M_n{}^c$	[mmmm][d] (%)
16	III′	10	30	0.50	0.11	163.9	34.6	2.02	98.3
17	III′	10	0	2.0	4.20	163.7	58.1	1.98	98.2
18	III′	10	−30	3.0	1.00	166.1	61.9	3.41	98.6
19	III′	25	−60	3.0	0.05	165.2	76.8	2.42	
20	III	5.0	0	2.0	0.15	163.4	14.0	2.29	98.1
21	III	10	−30	4.0	0.27	166.1	15.6	2.51	98.5
22	III	10	−60	20	0.04	165.4	20.2	3.09	
23[e]	III	10	−60	20	0.04	158.4	7.3	2.21	

[a] [*threo*]/[*erythro*] = 1:1, [TIBA] = 33 mM, [Ph₃CB(C₆F₅)₄] = [Zr], [propene] = 10.4 M. [b] Pure threo isomer was used; the other conditions are similar to a. [c] By GPC, calibrated by standard polystyrene. [d] Measured by ¹³C NMR. [e] MAO was used as cocatalyst, [Al]/[Zr] = 1000.

spectrum of the polymer obtained at −30 °C (run 18) is shown in Figure 3, which indicates that the iPP is highly stereo- and regioregular.

3. Comparison of C_1- and C_2-Symmetrical Zirconocene Catalysts. The analytical results obtained with the above three zirconocenes are compared in some detail. It is reasonable to assume that the stereo- and regiospecificity of a catalyst for an incoming monomer are reflected in the structure of the resulting polymer. Figure 4 shows the correlation between the [mmmm] and T_p. When the C_2-symmetrical zirconocenes were employed (**I** and **II**), the [mmmm] pentad sharply decreased along with an increase of T_p. In contrast to

I and **II**, the [mmmm] pentad was roughly unchanged when the C_1-symmetrical zirconocene **III** or **III′** was used. From the data shown in Tables 1−3, the [mmmm] of iPP obtained under similar conditions appears to increase in the following order: **II** < **I** < **III**.

The melting points of iPP obtained with the three catalysts are plotted against the polymerization temperature in Figure 5. In the case of the C_2-symmetrical zirconocenes (**I** and **II**), the melting point decreased with an increase of T_p, similar to the behaviors of other C_2-symmetrical zirconocenes,[8] whereas it did not change so much in the case of the C_1-symmetrical zirconocene (**III′**).
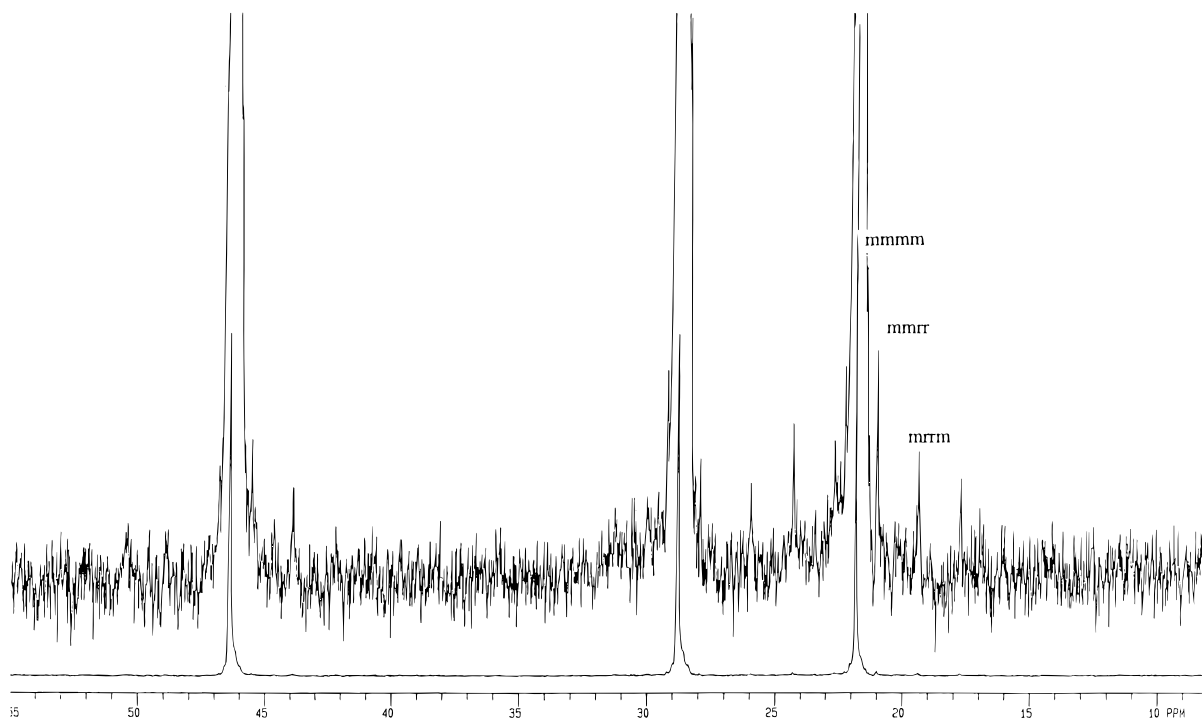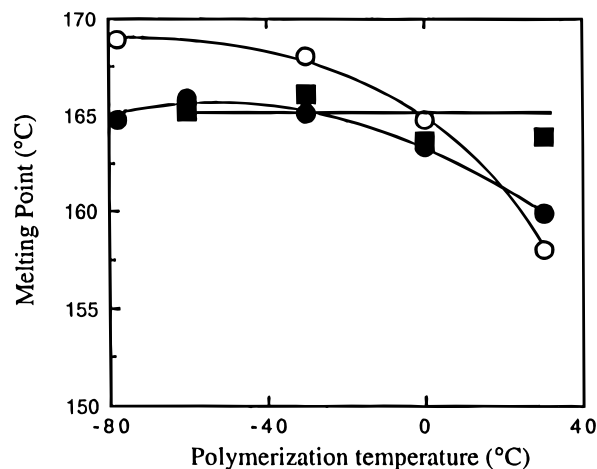
Figure 3. 75 MHz ^{13}C NMR spectrum of iPP obtained at -30 °C using *threo*-(3-tBuCp)iPr(3-tBuInd)ZrCl$_2$ (**III**)/Ph$_3$CB(C$_6$F$_5$)$_4$ (run 21).
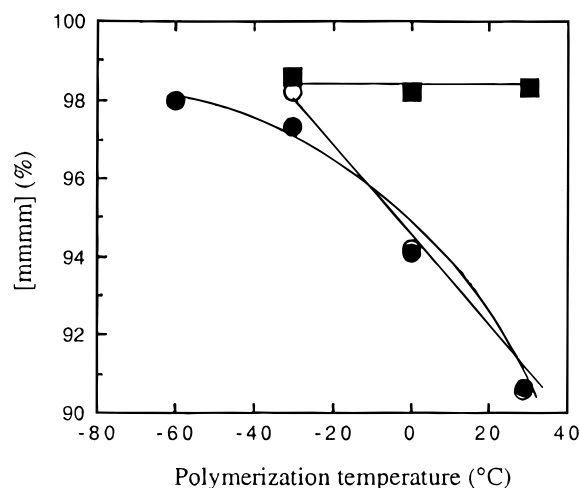
Figure 4. Plot of [mmmm] against polymerization temperature: ○, **I**; ●, **II**; and ■, **III'**.
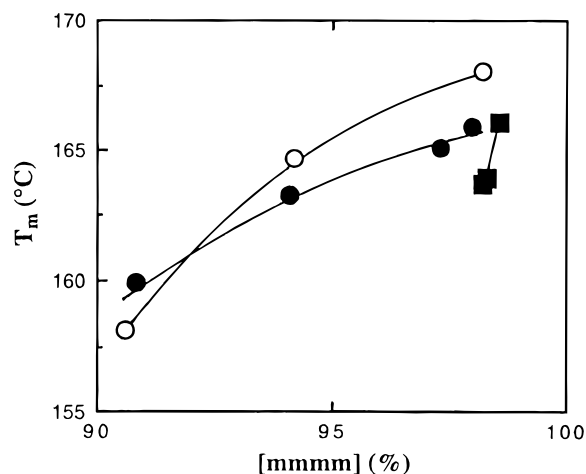

Figure 5. Plot of melting point (T_m) against polymerization temperature: ○, **I**; ●, **II**; and ■, **III'**.

In Figure 6 are plotted the melting points against the corresponding [mmmm] pentad value. It is instantly obvious from the figure that the melting point of the polymer produced by each catalyst is closely related to the [mmmm] pentad value, i.e., stereoregularity of iPP. For each catalyst, T_m increases with [mmmm]. However, the melting point at the same [mmmm] level seems to depend on the catalyst, i.e., T_m apparently decreases in the following order: T_m (**I**) > T_m (**II**) > T_m (**III**).

Besides the stereodefects, the regiodefects in the polymer chain were investigated. Figure 7 shows the ^{13}C NMR spectra of the polymers produced with the C_2-symmetrical catalysts at 0 °C. A small amount of regiodefects resulting from the 1,3-insertion (37.5 ppm) and 2,1-insertion (35.6 ppm) were found, the contents of which increase in the following order: **I** < **II**. It may be considered, therefore, that such a difference in the polymer structure has caused a change in the melting point. For the polymer prepared by C_1 catalyst **III**, however, the melting point remains lower than the
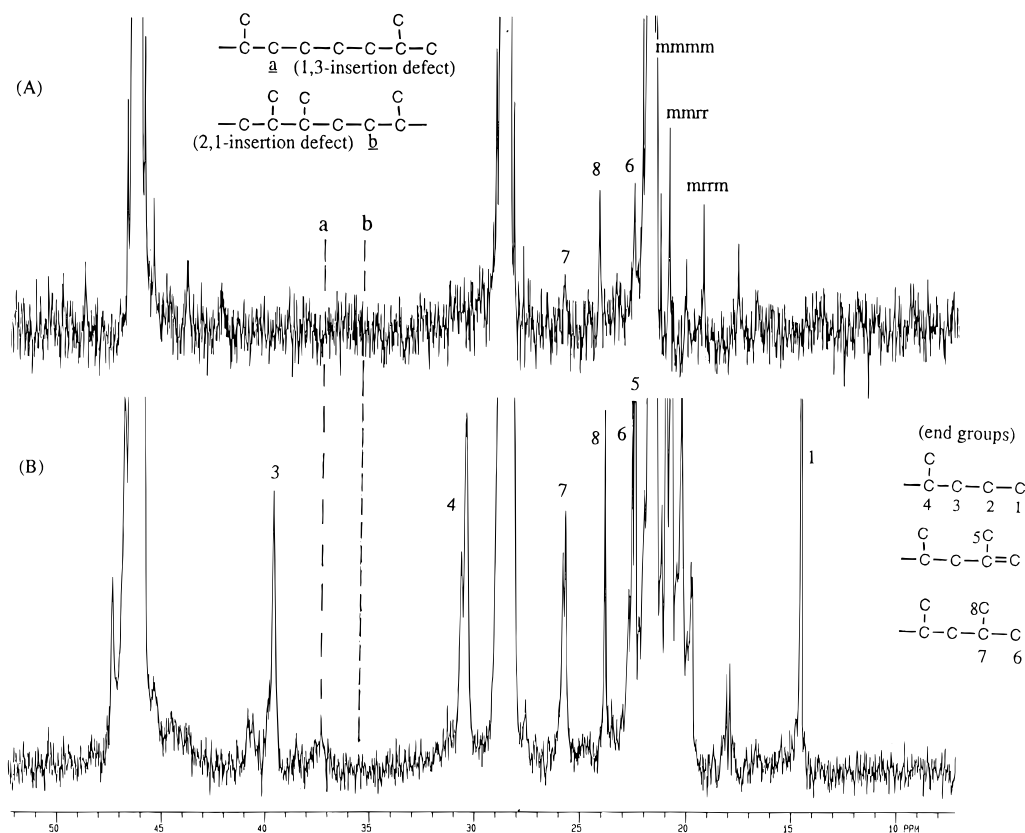

Figure 6. Plot of melting point (T_m) against [mmmm]: ○, **I**; ●, **II**; and ■, **III'**.
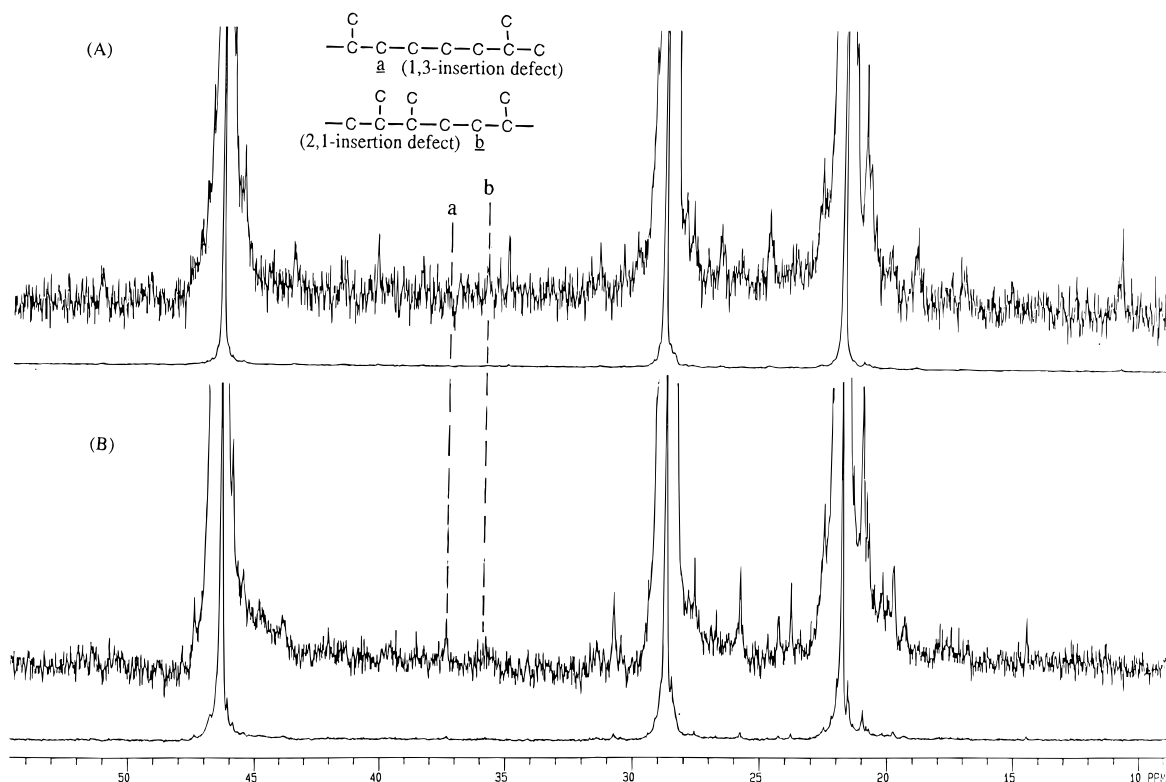
Figure 7. 75 MHz ^{13}C NMR spectra of iPP obtained with **I** at 0 °C (A) (run 2) with **II** at 0 °C (B) (run 9).

Figure 8. 75 MHz ^{13}C NMR spectra of iPP obtained at 0 °C (A) with catalyst **III′** (run 17) and 80 °C (B) (see ref 15) with catalyst **III**.

one from **I** or **II**, even though [1,3] and [2,1] are lower. Figure 8 shows that few regiodefects of 2,1-insertion were observed, even at a high polymerization temperature. It seems that the correlation between the melting point and the structural defects is different for the polymer resulting from the C_1-symmetrical catalyst. It

might be assumed that the molecular weight and the distribution of the stereo- and regiodefects in the polymer chain play a role for T_m.

As mentioned above, the dependence of stereoregularity ([mmmm]) on the polymerization temperature was found to be very different between the C_1- and C_2-

symmetrical catalysts. The [mmmm] pentad value of iPP produced with the conventional Ziegler−Natta catalysts does not change as much in a wide polymerization temperature range[6] as observed with the C_1-symmetrical catalyst, whereas the [mmmm] pentad value markedly decreases when polymerization is carried out at high temperatures using the ordinary C_2-symmetrical metallocenes.

These observations might suggest different monomer insertion behaviors for the C_1- and C_2-symmetrical catalysts. To prove this, however, much more information may be needed.

In conclusion, iPP with T_m as high as 168.9 °C could be obtained with the *rac*-Et(2,4,7-Me₃Ind)₂ZrCl₂−Ph₃-CB(C₆F₅)₄−Al(iBu)₃ catalyst at −78 °C. From the different tendencies of the temperature dependence of stereoregularity between the C_1- and C_2-symmetrical metallocenes, the possibility of different monomer insertion mechanisms was proposed for the two catalysts.

Experimental Part

Toluene was dried over calcium hydride and distilled before use. *rac*-Et(2,4,7-Me₃Ind)₂ZrCl₂ (**I**),[3] *threo*-iPr(3-tBuCp)(3-tBuInd)ZrCl₂ (**III**),[5] and iPr(3-tBuCp)(3-tBuInd)ZrMe₂ (**III'**)[16] were synthesized according to the literature. *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ (**II**) and the (3-tBuCp)iPr(3-tBuInd) ligand were donated by Sanseki Co. Ltd. and Showadenko Co. Ltd., respectively. Tri(isobutyl)aluminum (TIBA) and Ph₃CB(C₆F₅)₄ were donated by Tosoh Akzo Co. Ltd. The other chemicals (research grade) were purchased from commercial sources and used without further purification.

Polymerizations were carried out under dry nitrogen atmosphere in a 100 mL autoclave equipped with a magnetic stirrer. Typical polymerization process is as follows: toluene (26.0 mL), 1.0 M toluene solution of TIBA (1.0 mL), 10 mM toluene solution of **I** (1.0 mL), and 5.0 mM toluene solution of Ph₃CB-(C₆F₅)₄ (2.0 mL) were injected into the autoclave. After the introduction of propene (7.0 L), the autoclave was placed into a temperature-controlled bath for polymerization. The polymerization was quenched with methanol mixed with hydrochloric acid. The polymer produced was precipitated into methanol, followed by drying in vacuo at 60 °C for 8 h.

The molecular weight and molecular mass distribution were measured by GPC (Senshu Scientific, SSC7100) at 145 °C using *o*-dichlorobenzene as the solvent and calibrated with polystyrene standards. The melting point (T_m) was measured with a Seiko DSC-220C calorimeter at a heating rate of 10 °C/min. The ¹³C NMR spectra were measured in 1,2,4-trichlorobenzene/benzene-d_6 (9/1 v/v) at 140 °C with a Varian Gemini-300 spectrometer over 20 000 transients using a delay time of 7.0 s. Broadband decoupling was used to remove the

¹³C−¹H coupling. The main peak of methyl of iPP was used as the internal reference (21.78 ppm).

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(12) For a perfect isotactic **PP**, [mmmm] = 100% (p = 1.0), $T_m = T_m° = 184$ °C (estimated according to $1/T_m − 1/T_m° = −(R/\Delta H)\ln p$), from: Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 568.

(13) For an example, see the following. (a) Using heterogeneous catalyst, $T_m = 165$ °C: Soga, K.; Yanagihara, D.; Lee, H. *Makromol. Chem.* **1988**, 2839. (b) $T_m = 165$ °C at 0 °C, refs 2.

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(15) The polymer obtained with **III**/Ph₃CB(C₆F₅)₄: $M_n = 5.0 × 10^2$, $M_w/M_n = 1.8$, $T_m = 140$ °C. The functionality of the vinylene end is almost equal to 1.

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