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Articles

Synthesis of Stereoblock Polypropylene Using Bis(2-phenylindenyl)zirconium Dichloride with Water/Pentafluorophenol Modified Methylaluminoxane

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ABSTRACT: The influence of cocatalyst on the molecular weight and stereoregularity of stereoblock polypropylene (SB-PP) synthesized with bis(2-phenylindenyl)zirconium dichloride (**2**) catalyst system was investigated. The highest tacticity SB-PP was produced from the catalyst derived from **2** with water and pentafluorophenol modified isobutylmethylaluminoxane (MMAO) (W/PM-MMAO) whereas triphenylcarbenium tetrakis(pentafluorophenyl)borate, $[Ph_3C][B(C_6F_5)_4]$ (**3**), activated **2** yielded the lowest tacticity SB-PP. In particular, the [mmmm] pentad content of SB-PP polymerized by **2** at 20 °C drastically increased from 41 to 63% by changing cocatalyst from MMAO to W/PM-MMAO. When the solvent fractionation was carried out, the size of the amorphous fraction decreased, and the amount of higher crystalline material increased upon using W/PM-MMAO. Furthermore, from the ^{13}C NMR spectra of all fractions, it was revealed that there are no significant difference in the microstructure of each fractions of polymer produced by **2**/MMAO and **2**/W/PM-MMAO. These results show that only the content of isotactic segments increases, and higher tacticity SB-PP was obtained when W/PM-MMAO was employed as a cocatalyst. As a result of the structural change induced by the addition of water and pentafluorophenol to aluminoxane, we propose W/PM-MMAO prevents ligand oscillation and locks in the *rac*-like structure which is more stable than *meso*-like structure. Therefore, the stereoselectivity of SB-PP synthesized by **2**/W/PM-MMAO increases. Furthermore, the reduction of amount of free trialkylaluminum using water and pentafluorophenol causes increasing productivity and the molecular weight.

Introduction

Over the past two decades, significant research has been directed toward the development of single-site olefin polymerization catalysts. Through these studies, it was revealed that the modification of the coordination environment around the metal center by ligand design can control polymerization activity, the ability of comonomer incorporation, the molecular weight, and stereoregularity of yielding polymer.[1−4] One of the most important advances in this area is the discovery of new types of stereoregular polyolefins, such as syndiotactic polystyrene,[5] syndiotactic polypropylene,[6] and stereoblock polypropylene (SB-PP).[7−10] In 1995, Coates and Waymouth have developed an oscillating catalyst strategy for the synthesis of isotactic−atactic SB-PP.[9] In this system, it is possible to control stereoregularity by reaction conditions and ligand modification. Using this strategy, stereoregularity and block size were decided by the relative rates of propagation and ligand isomerization.

On the contrary, the study of the influence of the nature of the cocatalyst on the stereoselectivity is still in its infancy. Only a few groups have reported the correlation between electronic and/or steric structure of cocatalyst and stereoregularity of the obtained polypropylene.[11−20]

Recently, several research groups have studied the effect of the influence of cocatalyst on the stereoregularity of propylene polymerization.[17,21,22] We have also reported the enhancement of productivity, molecular weight, and stereoregularity of 1-butene polymerization with 2,2′-thiobis(phenoxy)titanium complex (**1**)[23−26] by MMAO modification using water[27] or both water and pentafluorophenol.[28]

Waymouth and co-workers have reported the influence of cocatalyst on the stereoselectivity of unbridged bis(2-phenylindenyl)zirconium catalysts (**2**).[17,29] In this paper, the catalyst derived from MMAO (isobutylmethylaluminoxane) was more active and produced polypropylene of higher tacticity ([mmmm] = 42%) than those derived from MAO (methylaluminoxane) ([mmmm] = 23−29%) and trityl tetrakis(pentafluorophenyl)borate ([mmmm] = 26%). In addition, when triisobutylaluminum (TIBA) was added to the **2**/MAO system, polypropylenes of similar tacticity to that of MMAO ([mmmm] = 43−46%) were synthesized. In this paper, we report the enhancement of productivity, stereoregularity, and molecular weight of SB-PP synthesized with **2** and

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Table 1. Propylene Polymerization Using 2 with Several Kinds of Cocatalysts

entry	cocatalyst	T_p (°C)	productivity [kg/(mol Zr h)]	M_w[a] (g/mol × 10^{-3})	M_w/M_n[a]	mmmm[b] (%)	T_m[c] (°C)
1[d]	**3**	40	3720	66	5.4	20.6	136.0
2[e]	PMAO	40	2970	102	2.9	29.5	145.9
3[e]	MMAO	40	5676	207	3.1	29.8	142.3
4[f]	W/PM-MMAO	40	7820	241	3.2	32.9	148.3

[a] Determined by GPC in *o*-dichlorobenzene at 145 °C vs polystyrene standards. [b] Determined by ^{13}C NMR. [c] Determined by DSC. [d] Conditions: 2.5 mmol of TIBA solution, 10 μmol of (2-Ph-Ind)$_2$ZrCl$_2$ in toluene (5 mL), and 30 μmol of [Ph$_3$C][B(C$_6$F$_5$)$_4$] added to a propylene (280 g). [e] Conditions: 10 mmol of MAO solution and 10 μmol of (2-Ph-Ind)$_2$ZrCl$_2$ in toluene (5 mL) added to a propylene (280 g). [f] Conditions: 280 g of propylene was charged and 10 mmol of MMAO-3A was added, then water (2 mmol) added and stirred 10 min, and 2 mmol of pentafluorophenol in toluene (1 mL) was added and stirred 10 min, then 10 μmol of (2-Ph-Ind)$_2$ZrCl$_2$ in toluene (5 mL) added.

Table 2. Propylene Polymerization Using 2 with MMAO or W/PM-MMAO

entry	cocatalyst	T_p (°C)	Al/Zr	H_2O/Al	C_6F_5OH/Al	mmmm[a] (%)	T_m[b] (°C)
5[c]	MMAO	20	2000	0	0	40.9	142.7
6[d]	W/PM-MMAO	20	2000	0.3	0.1	63.1	151.6

[a] Determined by ^{13}C NMR. [b] Determined by DSC. [c] Conditions: 100 mL of hexane and 200 g of propylene was charged, then 20 mmol of MAO solution and 10 μmol of (2-Ph-Ind)$_2$ZrCl$_2$ in toluene (5 mL) added. [d] Conditions: 100 mL of hexane and 200 g of propylene was charged and 20 mmol of MMAO-3A was added, then water (6 mmol) added and stirred 10 min, and 2 mmol of pentafluorophenol in toluene (1 mL) was added and stirred 10 min, then 10 μmol of (2-Ph-Ind)$_2$ZrCl$_2$ in toluene (5 mL) added.

Table 3. Solvent Fractionation of SB-PPs

entry	cocatalyst	T_p (°C)	Al/Zr	M_w[a] (g/mol × 10^{-3})	mmmm[b] (%)	T_m[c] (°C)	CXS[d] (%)	HS[e] (%)	HIS[f] (%)
7[g]	MMAO	30	1500	380	39.9	146.1	66.5	28.1	5.4
8[h]	W/PM-MMAO	30	2000	389	45.3	148.1	55.9	23.5	20.6

[a] Determined by GPC in *o*-dichlorobenzene at 145 °C vs polystyrene standards. [b] Determined by ^{13}C NMR. [c] Determined by DSC. [d] % fraction soluble in xylene at 20 °C. [e] % fraction soluble in boiling *n*-heptane. [f] % fraction insoluble in boiling *n*-heptane. [g] Conditions: 15 mmol of MAO solution and 10 μmol of (2-Ph-Ind)$_2$ZrCl$_2$ in toluene (5 mL) added to a propylene (280 g). [h] Conditions: 280 g of propylene was charged and 15 mmol of MMAO-3A was added, then water (3 mmol) added and stirred 10 min, and 3 mmol of pentafluorophenol in toluene (1 mL) was added and stirred 10 min, then 7.5 μmol of (2-Ph-Ind)$_2$ZrCl$_2$ in toluene (5 mL) added.

water and pentafluorophenol modified MMAO (W/PM-MMAO).

Results and Discussion

Polymerization of propylene was carried out using **2** with triphenylcarbenium tetrakis(pentafluorophenyl)borate, [Ph$_3$C][B(C$_6$F$_5$)$_4$] (**3**), methylaluminoxane (PMAO), isobutylmethylaluminoxane (MMAO), and water/pentafluorophenol-modified MMAO (W/PM-MMAO) as a cocatalyst at 40 °C (Table 1). It was revealed that the different cocatalysts yield polymers with different [mmmm] pentad contents. When W/PM-MMAO was used as a cocatalyst, the productivity was the highest and the molecular weight of obtained polymer was also highest. It was revealed that the different cocatalysts yield polymers with different [mmmm] pentad contents. Expectedly, the catalyst formed using W/PM-MMAO produced the highest tacticity SB-PP while **3** yielded the lowest tacticity SB-PP (W/PM-MMAO > MMAO, PMAO > **3**).

All the polymers have the melting temperature (T_m) value between 136.0 and 148.3 °C (Table 1). The polymer synthesized by **2**/W/PM-MMAO showed the highest T_m. From these results, we realized that MMAO modification enhanced of the productivity, molecular weight, and stereoregularity of the yielding polymer when **2** was employed as an olefin polymerization catalyst, in similar fashion when **1** was employed.

We were also interested in producing SB-PP of higher isotacticity using W/PM-MMAO; therefore, further investigations were carried out. Table 2 shows the polymerization results at 20 °C. When W/PM-MMAO was used, the [mmmm] pentad content of the produced SB-PP increased significantly from 40.9 to 63.1%. The T_m of obtained SB-PP also increased from 142.7 to 151.6 °C.

How does the cocatalyst affect the stereoregularity of the SB-PP? One hypothesis is that the W/PM-MMAO enhances the stereospecificity of isotactic propagations by suppressing the misinsertion of propylene or epimerization of the growing polymer chain. Another theory is that W/PM-MMAO prevents ligand rotation and locks to *rac*-like structure therefore the isotactic content increases. If the former is correct, the microstructure, such as pentad distribution or specific stereoerror signals derived from monomer misinsertion or chain epimerization, of the isotactic segments in SB-PP synthesized by **2**/MMAO and that synthesized by **2**/W/PM-MMAO should be different. If latter is correct, the microstructure of the isotactic segments in both SB-PPs should be same, and the only detectable difference should be the contents of the isotactic segment in the polymers. To understand the mechanism of the influence of cocatalyst on the stereoregularity, the solvent fractionation of SB-PPs was carried out (Table 3).

As already reported, SB-PP synthesized by **2**/MAOs can be separated into amorphous part (cold xylene soluble part: CXS), lower crystalline part (boiling *n*-heptane soluble part: HS), and higher crystalline part (boiling *n*-heptane insoluble part: HIS).[30] The fractionation results of the polymers (sample **7**, synthesized by **2**/MMAO, and sample **8**, synthesized by **2**/W/PM-MMAO) are shown in Table 3. It was revealed that the ratio of amorphous part decreased and the ratio of higher crystalline part increased in sample **8**. For characterizing more details of each fractions, GPC and ^{13}C NMR were measured (Table 4). Although the molecular weights of each fractions of both samples **7** and **8** were slightly different, the stereosequence distributions of each CXS, HS, and HIS of sample **7** and **8** were very similar.

Table 4. Characterization of Each Fraction of SB−PPs

	CXS[a]			HS[b]			HIS[c]		
entry	wt (%)	M_w[d] (10^{-3})	mmmm[e] (%)	wt (%)	M_w[d] (10^{-3})	mmmm[e] (%)	wt (%)	M_w[d] (10^{-3})	mmmm[e] (%)
7	66.5	269	25.0	28.1	335	62.4	5.4	827	79.8
8	55.9	299	24.1	23.5	275	63.6	20.6	673	82.0

[a] % fraction soluble in xylene at 20 °C. [b] % fraction soluble in boiling *n*-heptane. [c] % fraction insoluble in boiling *n*-heptane. [d] Determined by GPC in *o*-dichlorobenzene at 145 °C vs polystyrene standards. [e] Determined by ^{13}C NMR.

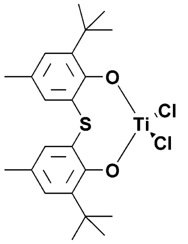

Figure 1. 2,2′-Thiobis(4-methyl-6-*tert*-butyl-phenoxy)titanium dichloride (**1**).

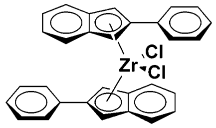

Figure 2. Bis(2-phenylindenyl)zirconium dichloride (**2**).

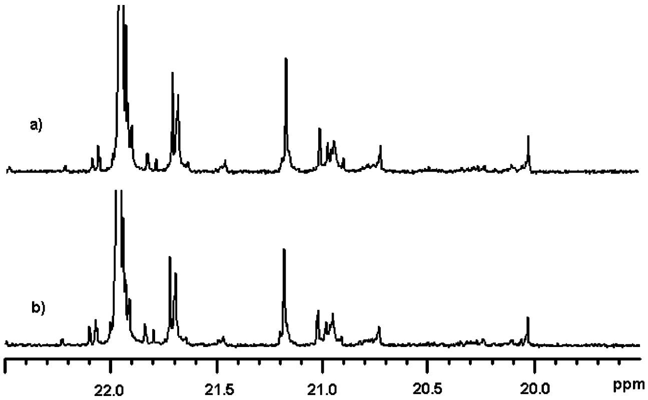

Figure 3. ^{13}C NMR spectra of HIS fractions of SB-PP: (a) sample **7**; (b) sample **8**.

Figure 3 shows the methyl region of the ^{13}C NMR spectra of HIS fractions of sample **7** and sample **8**. From the ^{13}C NMR spectra of the other fractions, no differences were also observed. Comparing these spectra, it was concluded that there are no difference in the microstructure of each fractions of sample **7** and sample **8**. The only difference between sample **7** and **8** was the percentage of composition of CXS, HS, and HIS fractions. These results strongly suggest that the latter hypothesis is favorable; W/PM-MMAO prevents the ligand oscillation and locks to *rac*-like structure which is more stable than *meso*-like structure, and therefore it causes the production of longer and/or larger amount of isotactic polymer segment.

Waymouth reported that the reduction of free TMA from MAOs has very little influence on the stereospecificity ([mmmm] = 23%−29%).[17] On the contrary, when triisobutylaluminum (TIBA) was added to MAO, the tacticity of yielding SB-PP was strongly enhanced ([mmmm] = 23%−43%). However, even if TIBA was added to MMAO, the highest [mmmm] pentad was 49%. In our results, when W/PM-MMAO was used as a cocatalyst, the highest [mmmm] of obtained SB-PP reached 63.1%. This is a significant difference. Recently, we revealed that only 4- and 6-coordinate aluminum species existed in the MMAO; on the other hand, a new peak derived from 5-coordinate Al species appeared when the water or water/phenol modification was carried out, and 4-, 5-, and 6-coordinated species are observed from W/PM-MMAO.[28] Therefore, we believe that the MMAO modification by water and pentafluorophenol induces the structural change of aluminoxane, and this structural change effects on stereoselectivity of SB-PP obtained.

Marks and co-workers have proposed that strong coordination of the borate counteranion to the cationic zirconium metal center.[15] The increase in stereoselectivity when a stronger anionic cocatalyst was employed was attributed to a stronger ionic interaction of cocatalyst which prevents isomerization of the growing polymer chain. In our case, the steric and electronic properties of W/PM-MMAO are very different from the original MMAO, and we propose that W/PM-MMAO interacts more strongly to the cationic metal center of **2** than MMAO. It is still unclear which steric or electronic effects provide the most significant influence; however, we believe the W/PM-MMAO suppresses ligand oscillation, resulting in improved isotacticity during propylene polymerization.

The next question is why the productivity of **2**/W/PM-MMAO and molecular weight of SB-PP produced by it were higher. Does the added water and pentafluorophenol also work for a reduction of free TMA which works as a chain transfer agent and also generates inactive species by reacting with the metallocene to produce M-(μ-Me)-Al species? Busico et al. utilized the 2,6-^{t}Bu$_2$-Ph-OH for trapping free TMA, so there may be a possibility that pentafluorophenol works as a trapping reagent as same as 2,6-^{t}Bu$_2$Ph-OH.[18] Water can also react with alkylaluminum easily. Therefore, the reduction of free trialkylaluminum might occur by adding water and pentafluorphenol with structural change of MMAO. As the result, the productivity of **2**/W/PM-MMAO was higher than that of **2**/MMAO due to the suppression of inactive dinuclear Zr-(μ-Me)-Al species derived from free TMA. The molecular weight of produced SB-PP with **2**/W/PM-MMAO was also higher than that of **2**/MMAO by decreasing in chain transfer to free TMA. The addition of water and pentafluorophenol causes not only the reduction of free TMA, which causes increasing the productivity and the molecular weight of polymer obtained, but also the structural change of aluminoxane, which affects the microstructure of SB-PP obtained.[31]

Conclusions

When W/PM-MMAO was employed, the productivity, molecular weight, [mmmm] pentad content, and melting temperature of SB-PP were enhanced. In particular, the [mmmm] pentad of the SB-PP polymerized by **2**/W/PM-MMAO at 20 °C was drastically increased from 41 to

63%. From solvent fractionation, it was revealed that the amorphous fraction decreased, and the crystalline fraction increased following MMAO modification. From the microstructural analysis of each fraction, there were no difference in the microstructure of each fractions of SB-PPs produced by **2**/MMAO and **2**/W/PM-MMAO. The only difference between them was the percentage of composition of CXS, HS, and HIS. From these results, it can be suggested that W/PM-MMAO prevents the ligand oscillation and locks the *rac*-like structure which is more stable than *meso*-like structure, which cause the production of longer and/or larger amount of isotactic segment of polymer. Furthermore, the reduction of free TMA, which works as a chain transfer agent and also generates inactive species by reacting with the metallocene to produce M-(μ-Me)-Al species, occurred by the addition of water and pentafluorophenol. As a result, the enhancement of productivity and molecular weight of SB-PP were observed. Not only the addition of water and pentafluorophenol reduces free trialkylaluminum, which causes increasing the productivity and the molecular weight of the polymer obtained, but also it induces the structural change of aluminoxane, which affects the isotacticity of the polymer obtained.

Experimental Section

Materials. Bis(2-phenylindenyl)zirconium dichloride (**2**) was prepared according to the literature.[9] Triisobutylaluminum (TIBA 1 mol/L in toluene), methylaluminoxane (PMAO 8.0 wt % Al in toluene), and isobutylmethylaluminoxane (MMAO; MMAO-3A 5.7 wt % Al in toluene) were purchased from Tosoh-Akzo. Pentafluorophenol was purchased from Tokyo Kasei Kogyo (TCI). Triphenylcarbenium tetrakis(pentafluorophenyl)borate (**3**) was purchased from Asahi Glass Co., Ltd.

Bulk Propylene Polymerization Using 2 with 3. Polymerization was conducted in a 1 L stainless steel reactor equipped with a mechanical stirrer. The reactor was charged with 280 g of liquid propylene and heated at 40 °C. 2.5 mmol of TIBA was injected by pressured nitrogen. 10 μmol of **2** was dissolved in toluene (5 mL) under nitrogen. The solution was then injected. Finally, 30 μmol of **3** (5 mmol/L toluene solution) was charged into the reactor. After 1 h, the reactor was vented. The polymer was precipitated from methanol/HCl, filtered, and then dried in vacuo to constant weight.

Bulk Propylene Polymerization Using 2 with MAOs. Polymerization was conducted in a 1 L stainless steel reactor equipped with a mechanical stirrer. The reactor was charged with 280 g of liquid propylene and heated at 40 or 30 °C. 10 mmol of MAO under nitrogen was injected by nitrogen pressure. 10 μmol of **2** was dissolved in toluene (5 mL) under nitrogen. The solution was then injected to the reactor. After 1 h, the reactor was vented. The polymer was precipitated from methanol/HCl, filtered, and then dried in vacuo to constant weight.

Bulk Propylene Polymerization Using 2 with W/PM-MMAO. Polymerization was conducted in a 1 L stainless steel reactor equipped with a mechanical stirrer. The reactor was charged with 280 g of liquid propylene and heated at 40 or 30 °C. 10 mmol of MAO under nitrogen was injected by nitrogen pressure. Then 2 mmol of water was injected into the reactor and reacted for 10 min. Subsequently, 2 mmol of pentafluorophenol (dissolved in 5 mL of toluene) was injected into the reactor and reacted for 10 min. 10 μmol of catalyst was dissolved in toluene (5 mL) under nitrogen. Finally, the solution was injected to the reactor. After 1 h, the reactor was vented. The polymer was precipitated from methanol/HCl, filtered, and then dried in vacuo to constant weight.

Propylene Polymerization Using 2 with MAOs in *n*-Hexane. Polymerization was conducted in a 1 L stainless steel reactor equipped with a mechanical stirrer. 100 mL of *n*-hexane and 200 g of liquid propylene were charged into the reactor and kept at 20 °C. 20 mmol of MAO under nitrogen was injected by nitrogen pressure. 10 μmol of catalyst was dissolved in toluene (5 mL) under nitrogen. The solution was then injected to the reactor. After 1 h, the reactor was vented. The polymer was precipitated from methanol/HCl, filtered, and then dried in vacuo to constant weight.

Propylene Polymerization Using 2 with W/PM-MMAO in *n*-Hexane. Polymerization was conducted in a 1 L stainless steel reactor equipped with a mechanical stirrer. 100 mL of *n*-hexane and 200 g of liquid propylene were charged into the reactor and kept at 20 °C. 20 mmol of MAO under nitrogen was injected by nitrogen pressure. Then 6 mmol of water was injected into the reactor and reacted for 10 min. Subsequently, 2 mmol of pentafluorophenol (dissolved in 5 mL of toluene) was injected into the reactor and reacted for 10 min. 10 μmol of catalyst was dissolved in toluene (5 mL) under nitrogen. Finally, the solution was injected to the reactor. After 1 h, the reactor was vented. The polymer was precipitated from methanol/HCl, filtered, and then dried in vacuo to constant weight.

Polymer Characterization. Molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) were determined by high-temperature GPC. All analyses were performed with a Waters 150 CV at 145 °C in *o*-dichlorobenzene using a Shodex M/S 80 column and were calibrated using polystyrene standards. ^{13}C NMR spectra of the polymers (dissolved in *o*-dichlorobenzene-d_4) were obtained at 135 °C on a Bruker AVANCE600 spectrometer at 150 MHz. DSC analyses were performed on a Seiko DSC SSC-5200. The measurements were made in aluminum crimped pans under nitrogen with first heating rate 20 °C/min from 25 to 200 and cooling rate 20 °C/min from 200 to −50 °C and then second heating rate 20 °C/min from −50 to 300 °C. The reported DSC profiles originated from the second heating scan.

Solvent Extraction. The sample was completely dissolved in boiling xylene, and the solution was cooled gradually to 20 °C. The precipitated polymer was separated from the solution by filtration. The polymer soluble in xylene at 20 °C was recovered by evaporation (cold xylene soluble part; CXS). Further, the precipitated polymer was extracted with boiling *n*-heptane in a Soxhlet extractor (*n*-heptane soluble part; HS, *n*-heptane insoluble part; HIS).

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(31) We polymerized 1-butene using **1** with dried MMAO which was completely dried in vacuo for removing free trialkylaluminum. In this case, the productivity and the molecular weight slightly increased; however, the stereoselectivity of produced poly(1-butene) was not changed from the result of original MMAO at all. This result strongly suggests that the most important influence on the stereoselectivity of polymer obtained is the structural change of MMAO by the addition of water and phenol (unpublished data).

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