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Kinetic studies on the syndiotactic propylene polymerization catalyzed over *i*Pr(Cp)(Flu)ZrCl$_2$

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Abstract

Kinetic studies on the syndiospecific polymerizations of propylene with *i*Pr(Cp)(Flu)ZrCl$_2$/methylaluminoxane (MAO) were performed at 20, 40 and 70 °C and at 5 atm with various Al/Zr molar ratios. The average polymerization activity for 60 min decreased, and the time to reach a maximum activity (t_{max}) decreased as Al/Zr molar ratio increased. However, at Al/Zr molar ratio of 10,000, catalytic activity decreased rapidly and became the smallest among any other Al/Zr molar ratios after 20 min of polymerization. At higher Al/Zr molar ratio, methylation and cationization progress rapidly, but its polymerization rate decayed quickly due to strong interaction between MAO and metallocene, resulting in less active species. Regardless of change in polymerization temperature, t_{max} was maintained around 15 min. Stereoregularity was strongly dependent on the polymerization temperature, and active site isomerization was dominant source for stereoirregularity, and it was strongly influenced by polymerization temperature.

Keywords: Syndiotactic polypropylene; Polymerizations; *i*Pr(Cp)(Flu)ZrCl$_2$; Methylaluminoxane; Metallocene

1. Introduction

Ewen et al. reported for the first time that syndiotactic polypropylene (sPP) was produced with *i*Pr(Cp)(Flu)-ZrCl$_2$ catalyst (1) with high activity that could be suitable for production of sPP in commercial scale [1]. There have been other studies on the synthesis of catalyst for the sPP [2], and on the polymerization with *i*Pr-(Cp)(Flu)ZrCl$_2$ catalyst [3–7]. It was proposed that syndiotactic polymerization was proceeded with enantiomorphic site control that would be coming from Cs symmetry of (1). Herfert and Fink reported that polymerization rate decreased as Al/Zr molar ratio increased, but there have been no precise reasons for explaining it [5]. The kinetic behavior of syndiotactic polymerization of PP as a function of temperature, and Al/Zr molar ratio has not been studied yet even though there were several studies on the synthesis of catalyst and its brief polymerization.

In this study, the kinetic behavior during the polymerization of sPP with (1) was observed with respect to Al/Zr molar ratio and polymerization temperature, and this study could give more information on catalytic characteristics of (1). The effect of polymerization condition on the stereoregularity and defects of sPP was also studied.

2. Experimental section

(1) was kindly donated from Atofina Co. in Belgium. MAO was purchased from Akzo Co. and used without any further purification. Propylene (donated from Korea Petrochem. Ind. Co., Korea) and nitrogen of extra pure grade were further purified with columns of Fisher

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RIDOX and molecular sieve 5A/13X. Toluene (Duksan Ltd., Korea) of extra pure grade was further purified with refluxing over sodium metal in a nitrogen atmosphere. Propylene polymerization was carried out in a 1-L autoclave filled with 350 cm^3 toluene under a constant pressure of propylene, 5 atm. Propylene consumption rate (polymerization rate) was measured by a hot wire flowmeter with a personal computer directly connected to it through an A/D converter. The precipitated polymer was recovered by filtration, washed with fresh ethanol and dried in vacuo. ^{13}C-NMR (75 MHz) spectra of the syndiotactic polypropylenes were recorded at 120 °C on a Bruker AMX-300 FT-NMR spectrometer. Polypropylene samples were dissolved in 1,2,4-trichlorobenzene/benzene-d$_6$ (4/1 by vol.) up to a concentration of 15 wt.% at 120 °C in NMR tubes (10 mm o.d.). Number and weight average molecular weight (M_n and M_w), and molecular weight distribution (MWD) were measured at 145 °C by means of gel-permeation chromatography (Waters Associates; model ALC-GPC-150C) using *o*-dichlorobenzene as a solvent. Molecular weight was calculated on the basis of a polystyrene standard calibration, meaning that its numerical value is an apparent one. The melting temperature and heat of fusion of polymers was measured by DSC (Dupont Analyst 2000).

3. Results and discussion

3.1. Polymerization of syndiotactic polypropylene

Table 1 summarized the results of polymerization and properties of syndiotactic polypropylene. The weight average molecular weight (M_w) and MWD were insignificantly changed and maintained at about 110,000 and 1.8, respectively regardless of Al/Zr molar ratio at 40 °C. The dependence of M_w and MWD on polymerization temperature, however, revealed to be strong. M_w decreased, and MWD increased as polymerization temperature increased. This should result from an enhancement of β-hydride elimination. A fraction of rrrr pentad was also quite sensitive to polymerization temperature. The fraction of rrrr decreased drastically from 84.4% to 67.6% as polymerization temperature increased from 20 to 70 °C. However, Al/Zr molar ratio did not give significant effect on M_w, MWD, and rrrr. Only at Al/Zr molar ratio of 1000, rrrr value was decreased slightly, and M_w was slightly increased compared to higher Al/Zr molar ratio.

Fig. 1 reveals the dependence of polymerization activity of propylene with (1) on Al/Zr molar ratio between 1000 and 10,000. The average polymerization activity for 1 h decreased as Al/Zr molar ratio increased in agreement with other results [5,8]. In the case of Cp$_2$ZrCl$_2$ and Et(ind)$_2$ZrCl$_2$ catalyst, the average polymerization rates increased, and/or maintained as Al/Zr molar ratio increased. However, there has not yet been a precise reason for the reduction of activity as Al/Zr molar ratio increased for (1) catalyst. With polymerization rate profiles, the reason for a decrease in the polymerization rate could be explained. Fig. 2 shows the polymerization rate profiles as a function of Al/Zr molar ratio. The maximum activity (R_{max}) increased, and t_{max} was getting shorter as Al/Zr molar ratio increased. At Al/Zr molar ratio of 10,000, the polymerization rate decreased rapidly at polymerization time of 8–20 min, and the polymerization rate after 20 min of polymerization was the smallest among all Al/Zr molar ratios. At Al/Zr molar ratio of 1000, t_{max} about 17 min. However, R_{max} was decreased as Al/Zr molar ratio decreased to 2000, then it increased again at Al/Zr of 5000, and showed about 2000 kg sPP/(mol Zr atm h). It was shown that the half-life time ($t_{1/2}$) of the polymerization was

Table 1
Results of polymerization and physical properties of syndiotactic polypropylene[a]

Run no.	Al/Zr	Temperature (°C)	Activity[b]	$t_{1/2}$[c] (min)	M_w	MWD	rrrr (%)	T_m (°C)		Heat of fusion (J/g)
								Lower	Higher	
1	10,000	40	1010	17	110,000	1.8	82.1	129.9	141.9	40.4
2	5000	40	1040	42	110,000	1.6	80.9	129.2	141.2	39.4
3	2000	40	1138	75[d]	100,000	1.8	81.6	127.9	140.8	41.2
4	1000	40	1378	65[d]	120,000	1.7	78.2	127.8	140.8	39.3
5	2000	70	210	28	63,000	2.3	67.6	108.5	135.2	25.0
6	2000	20	75	20	140,000	1.9	84.4	137.7	147.4	46.2
7	2000	22 → 27[e]			170,000	1.9				

[a] Polymerization condition: $P = 5$ atm, toluene of 350 cc.

[b] Activity = kg sPP/(mol Zr atm hr).

[c] The half-life time.

[d] Calculated value based on extrapolated kinetic curve.

[e] Change in polymerization temperature during polymerization.

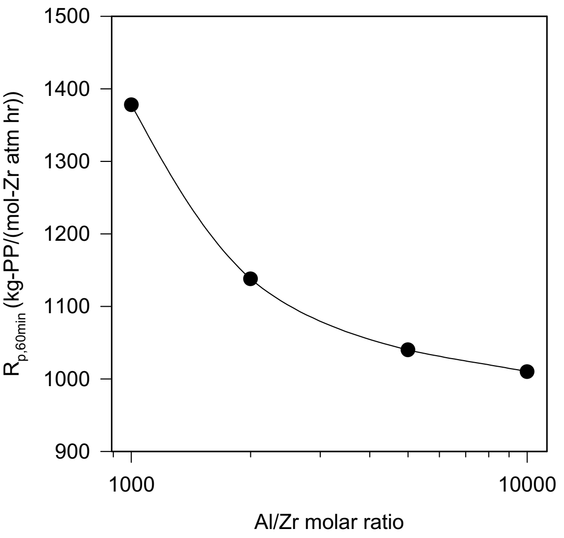


Fig. 1. Dependence of average polymerization activity on Al/Zr molar ratio in the syndiotactic polypropylene polymerization with *i*Pr(Cp)(Flu)$ZrCl_2$.

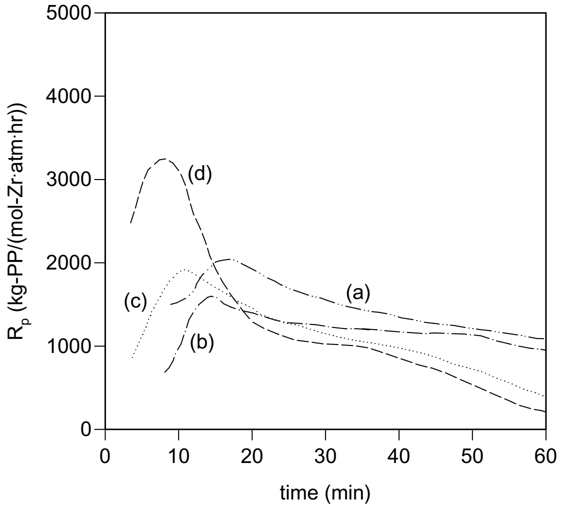
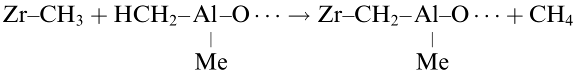


Fig. 2. Kinetic behavior of propylene polymerization with *i*Pr(Cp)(Flu)$ZrCl_2$ catalyst with respect to Al/Zr molar ratio. Al/Zr = 1000 (a), 2000 (b), 5000 (c), and 10,000 (d). Polymerization condition: $T = 40$ °C, $P_t = 5$ atm, solvent = 350 cc of toluene, $t = 1$ h.

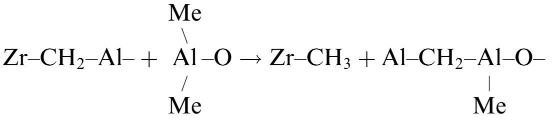
changed with respect to Al/Zr molar ratio, and they were 17, 42, 75 and 65 min at Al/Zr molar ratio of 10,000, 5000, 2000 and 1000, respectively. Polymerization rates at Al/Zr molar ratio of 1000 and 2000 did not show drastic deactivation, and were stable compared to those of Al/Zr molar ratio of 5000 and 10,000.

This could be explained by characteristics of molecular structure of (1) and interaction with MAO during polymerization. It is well known that MAO plays a role in making the metallocene catalyst alkylated, ionized and stabilized [9,10]. If there was α-hydrogen transfer in the complex between MAO and metallocene molecule, condensation reaction could be occurred, and this reaction must be related to the Al/Zr molar ratio [11].



$$\mathrm{Zr{-}CH_3 + HCH_2{-}\underset{\underset{Me}{|}}{Al}{-}O\cdots \rightarrow Zr{-}CH_2{-}\underset{\underset{Me}{|}}{Al}{-}O\cdots + CH_4}$$

This Zr–CH_2–Al complex could not show any activity in polymerization, but can be changed to Zr–CH_3 by additional MAO as described below.



$$\mathrm{Zr{-}CH_2{-}Al{-} + \overset{\overset{Me}{\backslash}}{\underset{\underset{Me}{/}}{Al}}{-}O \rightarrow Zr{-}CH_3 + Al{-}CH_2{-}\underset{\underset{Me}{|}}{Al}{-}O{-}}$$

It was assumed that zirconocene activated with MAO during polymerization was a cationic alkyl(olefin)-zirconocene complex of the type $[Cp_2ZrR(olefin)]^+H_3C$–MAO^-, and it was generated by displacement of an anion H_3C–MAO^- from its $[Cp_2ZrR]^+$ counterion by an olefin molecule. The interaction between MAO anion and metallocene cation was known to be have an ionic nature and polar character [12]. The interaction between them can affect the polymerization rate because the stability of a complex and the insertion rate of olefin monomer must be influenced by it. Molecular structure of (1) studied by Ewen et al. was different from that of other metallocenes like $Et(ind)_2ZrCl_2$ [13], and showed a larger aperture around metal center. The angle of ∠ Flu–Zr–Cp measured by X-ray is 117.9° smaller than that of ∠ ind–Zr–ind of $Et(ind)_2ZrCl_2$, 126°. The metal center of (1) was more pulled out from the inside of metallocene ligands compared to that of $Et(ind)_2ZrCl_2$. Therefore, the interaction between MAO and cationic metal center could be stronger than $Et(ind)_2ZrCl_2$. Furthermore, the bonding between MAO and (1) is known to be in dynamic equilibria between ionic and covalent state, and might be stronger due to more open-up structure of (1). Putting these into consideration, at higher Al/Zr molar ratio, methylation and cationization progressed quickly, but its polymerization rate decayed quickly due to the strong coordination between MAO and (1) that can result in the formation of inactive species.

Fig. 3 shows the dependence of polymerization rate on temperature. Polymerization rate was strongly dependent on the temperature, and it showed very low activity at low and high polymerization temperature (20 and 70 °C). The activation energy between 20 and 40 °C was about 100 kJ/mol, which relatively higher than the activation energy of other metallocenes. $t_{1/2}$ were 20 and 28 min for 20 and 70 °C, respectively, whereas that of 40 °C was around 75 min as shown in Table 1.

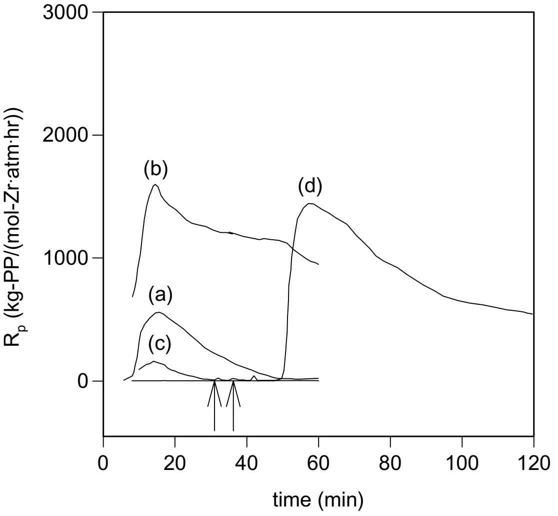


Fig. 3. Kinetic behavior of propylene polymerization with *i*Pr(Cp)(Flu)ZrCl$_2$ catalyst with respect to temperature. Polymerization condition: Al/Zr ratio = 2000, $P_t = 5$ atm, solvent = 350 cc of toluene, $t = 1$ h, $T =$ 70 °C (a), 40 °C (b), 20 °C (c), 22 °C from 0 to 30 min and 27 °C from 36 to 120 min (d).

Interestingly, $t_{\max}$ was not significantly changed with polymerization temperature, but it was maintained at around 15 min. This can be explained as follows: The dynamic equilibrium reaction between Zr$^+$–MAO$^-$ and Zr$^+$ + MAO$^-$ is strongly dependent on polymerization temperature. To form isolated cationic species, it is necessary to have enough energy to dissociate strong interaction between two species in ionic complex. It was reported that the interaction between (1) and MAO is stronger than that between Me$_2$Si(ind)$_2$ZrCl$_2$ and MAO [5]. To observe a change in polymerization rate with respect to polymerization temperature, it was changed from 22 to 27 °C during the polymerization as shown in Fig. 3. The time to reach at temperature of 27 °C took around 5 min after temperature was set again by control unit. Eventually, the polymerization rate was increased significantly at the polymerization temperature of 27 °C. This indicates that the activation energy in the narrow range of low polymerization temperatures is relatively high.

3.2. Effect of polymerization condition on stereochemical and regiochemical error of sPP

Table 2 summarized the results and value of each pentad fraction that was measured by ^{13}C-NMR spectrum. It is known that enantiomorphic site control is dominant mechanism in propylene polymerization using *i*Pr(Cp)(Flu)ZrCl$_2$ [3,6,7]. The Al/Zr molar ratio in the range between 2000 and 10,000 appeared to have little influence on rrrr pentad (around 81%). The value of rrrr pentad at 1000 of Al/Zr molar ratio was decreased slightly. There are two characteristic stereoerrors, rrmr and rmmr, of enantiomorphic site control during polymerization of syndiotactic polypropylene. The former was known to result from isomerization of active site, and the latter from stereochemical misinsertion of olefin monomer. Herfect and Fink reported that rmmr from stereochemical error was larger than that of rrmr from site isomerization [5]. As shown in Fig. 4, under the condition of polymerization of 5 atm and 40 °C, rrmr

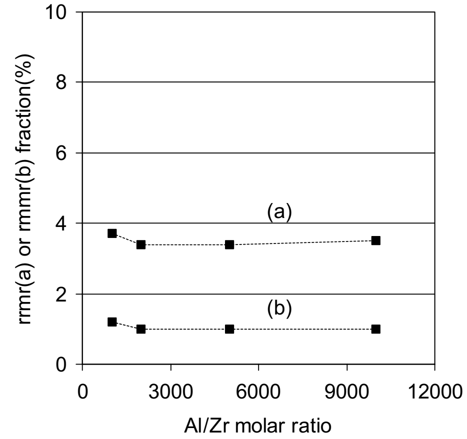


Fig. 4. Change in fraction of defects, (a) rrmr and (b) rmmr with respect to Al/Zr molar ratio.

Table 2
Results of analysis of ^{13}C-NMR spectrum

Al/Zr	Temperature (°C)	rmmr	rrmm	rrmr	rmrm	rrrr	rrrm	mrrm
10,000	40	1.0	2.5	3.5	2.1	82.1	6.5	2.4
5000	40	1.0	3.1	3.4	2.5	80.9	6.9	2.5
2000	40	1.0	2.2	3.4	2.2	81.6	7.1	2.5
1000	40	1.2	3.0	3.7	2.2	78.2	5.7	4.0
2000	70	1.0	2.7	9.2	0.0	67.6	12.4	2.4
2000	20	0.6	1.7	3.0	1.8	84.4	6.3	2.2

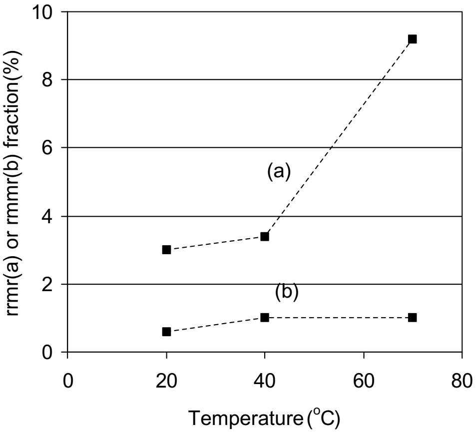


Fig. 5. Change in fraction of defects, (a) rrmr and (b) rmmr with respect to polymerization temperature.

fraction always was 3 times larger than rmmr fraction. rrmr was decreased slightly as Al/Zr molar ratio decreased from 1000 to 2000, and maintained at about 3.5% above Al/Zr molar ratio of 2000. However, rrmr pentad was strongly influenced by the polymerization temperature, and increased to 9.2% drastically at polymerization temperature of 70 °C as depicted in Fig. 5. In the case of rmmr pentad, it was not influenced by Al/Zr molar ratio as rrmr value showed, and polymerization temperature also did not change its value significantly. The activation energy for rrmr and rmmr were 19.1 and 8.1 kJ/mol, respectively. rrmr value was two times higher than that of rmmr, meaning that the active site isomerization was quite dependent on the polymerization temperature. The activation energy was calculated from the slope of regression line, which was calculated again from the plotting of data, ln(stereoerror's percentage) vs. reciprocal of absolute temperature.

These results imply that the active site isomerization results in dominant stereoregular error in enantiomorphic site control with (1), and it had low probability compared to active site isomerization for propylene monomer to interact to metal center incorrectly even at higher polymerization temperature. The active site isomerization without any further insertion of monomer during the polymerization would be fastened at higher temperature, and can be easier when the concentration of MAO around active site is relatively lower. Furthermore, it can be stated that opposite insertion of prochiral face of monomer is not strongly influenced by polymerization condition like temperature and Al/Zr molar ratio.

In addition, resulting syndiotactic polypropylene showed two melting endotherms as shown in Table 1. The dependence on polymerization temperature was significant due to change in stereoregularity of resulting polymers. Thermal studies on the effect of polymerization conditions on the two melting endotherms will be reported at other manuscript.

4. Conclusion

(1) showed the opposite effect of Al/Zr molar ratio on the activity and kinetic behavior to other metallocene catalysts for isotactic polypropylene or polyethylene. It was shown a decrease in activity as Al/Zr ratio increased in the range of 1000–10,000. This would be explained by the characteristic molecular structure of (1), having larger aperture, and more exposure of central metal. This could result in strong interaction between MAO and catalyst. (1) also revealed a strong dependence on the polymerization temperature. Especially, it started showing activity in a narrow range of polymerization temperature, 20–30 °C.

Stereoregularity of syndiotactic polypropylene was influenced by Al/Zr molar ratio insignificantly, but mostly by temperature. It was also observed that the isomerization of active site was dominant source for stereoirregularity compared to stereochemical misinsertion of propylene monomer. Stereochemical misinsertion of monomer was not dependent on the polymerization temperature significantly, but site isomerization was influenced by polymerization temperature. The apparent activation energy for rrmr and rmmr were 19.1 and 8.1 kJ/mol, respectively.

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