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Chain transfer reaction by trialkylaluminum (AlR_3) in the stereospecific polymerization of propylene with metallocene – $AlR_3/Ph_3CB(C_6F_5)_4$

Naofumi Naga* and Kooji Mizunuma
Petrochemicals Research Laboratory, Sumitomo Chemical Co. Ltd,
2-1 Kitasode Sodegaura, Chiba 299-02, Japan

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Stereospecific polymerization of propylene was carried out with *rac*-ethylenebis(indenyl)zirconium dichloride (*rac*-$Et(Ind)_2ZrCl_2$) (**1**), *rac*-dimethylsilylenebis(indenyl)zirconium dichloride (*rac*-$Me_2Si(Ind)_2ZrCl_2$) (**2**) and isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (*i*-Pr(Cp)(Flu)$ZrCl_2$) (**3**) combined with trialkylaluminum (AlR_3: R = C_2H_5, *i*-C_4H_9)/triphenylcarbenium tetrakis(pentafluorophenyl)borate ($Ph_3CB(C_6F_5)_4$) (**4**). In isospecific polymerization with **1** and **2**, the molecular weight of polypropylenes decreased with increase in the molar ratio of $AlEt_3$ (Et = C_2H_5)/Zr, whereas, an effect of Al*i*Bu_3 (*i*Bu = *i*-C_4H_9) concentration on molecular weight was not observed. The microstructures of resulting polypropylenes were studied by ^{13}C n.m.r. and an increase in the molar ratio of ethyl end groups (derived from chain transfer to $AlEt_3$) to *n*-propyl end groups (derived from β-hydrogen transfer) was observed with increase in the molar ratio of $AlEt_3$/Zr (**1** and **2**). The chain transfer reactions by both $AlEt_3$ and Al*i*Bu_3 were also detected in syndiospecific polymerization with **3**. The molar ratio of alkyl (R) end groups (derived from chain transfer to AlR_3) to *n*-propyl end groups was higher in the polypropylene obtained with $AlEt_3$ than that obtained with Al*i*Bu_3. The relative constants k_{trA}/k_p (k_{trA} = rate constant of chain transfer to AlR_3, k_p = rate constant of propagation) were determined by kinetic study. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: propylene; polymerizatrion; zirconocene)

INTRODUCTION

Since the discovery of the zirconium complex $[Cp_2ZrCH_3(THF)]^+[BPh_4]^-$ (Cp = cyclopentadienyl) that polymerizes ethylene in polar solvent by Jordan *et al.*[1], much effort has been expended in the development of cationic metallocene catalysts for olefin polymerization[2–4]. Shortly afterwards, Chien *et al.* reported the higher activity in isospecific polymerization of propylene catalyzed by *rac*-$Et(Ind)_2Zr(CH_3)_2$ combined with $Ph_3CB(C_6F_5)_4$ than combined with MAO[5]. Furthermore, the ethyl analogue produced by the reaction between *rac*-$Et(Ind)_2ZrCl_2$ and $AlEt_3$, followed by the addition of $Ph_3CB(C_6F_5)_4$ proceeded isospecific polymerization of propylene[6,7]. Stereospecific polymerization of propylene with cationic metallocene catalysts has been investigated from both industrial and theoretical points of view.

The comparison of microstructures of polymers obtained with cationic metallocene catalysts and MAO-activated catalysts in the stereospecific polymerization of propylene has been reported. Ewen performed the stereospecific polymerization of propylene with *i*-Pr(Cp)(Flu)$ZrCl_2$ and *rac*-$Et(Ind)_2ZrCl_2$ combined with MAO, $AlEt_3/Ph_3CB(C_6F_5)_4$ and $AlEt_3/Ph_3CAl(C_6F_5)_4$[8]. Judging from these results, the isotacticies of resulting polypropylenes were almost the same with any kinds of cocatalysts, in contrast, the syndiotacticities of polypropylenes obtained with $AlEt_3$/counterions were lower than that obtained with MAO. Fink *et al.* carried out propylene polymerization with *rac*-$Me_2Si(Ind)_2ZrMe_2/(C_4H_9)_3NHB(C_6F_5)_4$ and *rac*-$Me_2Si(Ind)_2ZrCl_2$/MAO, and concluded that no difference of stereospecificity was observed in polypropylenes obtained with each catalyst[9,10]. They showed in full detail the effect of the molar ratio of (ammonium borate) B/Zr to the polymerization activity, molecular weight and microstructures of polypropylenes. Much attention has been directed to the determination of the active sites of cationic metallocene catalysts in equilibrium with counterions. Chien *et al.* discussed the differences between coordinating and non-coordinating counterions on the rate constant of propagation, isospecificity and molecular weight of obtained polypropylenes[11].

End group analysis of polymer provides important insight into the chain transfer reaction in Ziegler–Natta polymerization. Four kinds of chain transfer reactions have been observed in propylene polymerization with metallocene catalysts (*Scheme 1*). The first chain transfer reaction is β-hydrogen transfer to the metal[12–20]. This reaction produces vinylidene groups at the terminated chain end and *n*-propyl groups at the initiated chain end. The second chain transfer reaction is β-hydrogen transfer to the monomer[15,17,19,21]. The same chain end groups derived from β-hydrogen transfer to the metal are formed through this reaction. The chain end structure of the 2-butenyl group,

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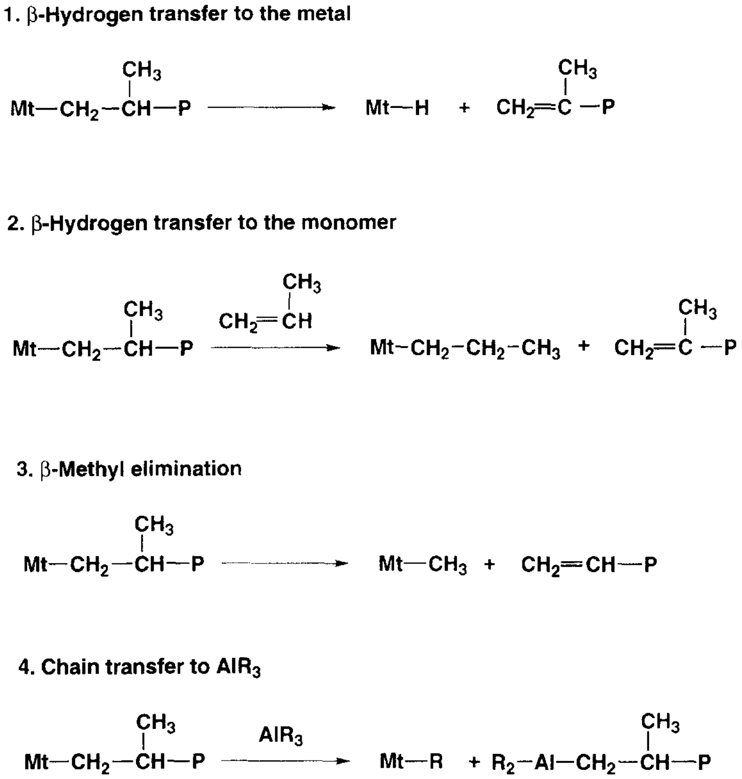
*Corresponding author. Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-Ku, Yokohama 226, Japan. Tel: 0081 45 924 5241; Fax: 0081 45 924 5276; e-mail: PX112535@niftyserve.or.jp



Scheme 1 Chain transfer reaction in propylene polymerization: Mt = metal, and P = polymer chain.

derived from the β-hydrogen transfer after secondary insertion, was also observed[22,23]. The third chain transfer reaction is β-methyl elimination[24–34]. The chain end structure of a vinyl group is formed through β-methyl elimination. The fourth chain transfer reaction is chain transfer to aluminum[18,35–38]. In the case of using MAO, this chain transfer reaction occurred at lower polymerization temperature or lower propylene concentration. In the case of using AlR$_3$ (without MAO), chain transfer to aluminum was determined by chain end analysis of resulting polypropylenes. Zambelli *et al.* carried out the polymerization of propylene with *rac*-Et(Ind)$_2$ZrCl$_2$/Al(CH$_3$)$_2$F-Al(CH$_3$)$_3$ and observed a chain transfer process to Al(CH$_3$)$_3$ by analysis of the resulting polypropylene[35]. Soga *et al.* investigated the polymerization of propylene with supported metallocenes (for example *rac*-Et(Ind)$_2$ZrCl$_2$/Al$_2$O$_3$) activated by common AlR$_3$ and reported the chain transfer to AlR$_3$[38]. Only a few investigations have been reported about the effect of AlR$_3$ concentration on the stereospecific polymerization of propylene. Bochmann *et al.* studied the effect of Al(CH$_3$)$_3$ concentration on propylene polymerization with *rac*-[Me$_2$Si(Ind)$_2$Zr(μ-Me$_2$)]-B(C$_6$F$_5$)$_4$/Al(CH$_3$)$_3$, *rac*-Me$_2$Si(Ind)$_2$ZrMe$_2$-Ph$_3$CB(C$_6$F$_5$)$_4$/AlEt$_3$, and observed decrease of molecular weight with increase in the AlR$_3$ concentration[39,40]. Uchida *et al.* also reported the stereospecific polymerization of propylene with metallocene combined with AlR$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ and a great deal of effort was made to determine the effect of AlR$_3$ concentration on the activity of polymerization[41].

In this work, we have studied the effect of AlR$_3$ concentration on the molecular weight and the chain end structures of obtained polypropylene to characterize the process of chain transfer to AlR$_3$ (AlEt$_3$ and Al*i*Bu$_3$) in stereospecific (isospecific and syndiospecific) polymerizations of propylene with metallocene — AlR$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst systems.

EXPERIMENTAL

Materials

rac-Et(Ind)$_2$ZrCl$_2$ (**1**) and *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ (**2**) were commercially obtained from Witco Co. and used without further purification. *i*-Pr(Cp)(Flu)ZrCl$_2$ (**3**) was prepared according to the literature[42]. AlEt$_3$, Al*i*Bu$_3$ and MAO were commercially obtained from Tosoh Akzo Co., Ltd. and used without further purification. Ph$_3$CB(C$_6$F$_5$)$_4$ (**4**) was commercially obtained from Tosoh Akzo Co., Ltd. and used without further purification. Toluene was commercially obtained and dried over 4 A molecular sieves.

Polymerization of propylene

Polymerizations were conducted in an agitated 1 l autoclave. The autoclave was back-flushed with argon several times, then 300 ml of toluene was injected and the system was warmed to 40°C. The argon was replaced with 4 kg cm^{-2} G of propylene, and the toluene was stirred until the monomer saturation was achieved. A 100 ml glass flask was charged with 10 ml of toluene, AlR$_3$ and catalyst, and the mixture was stirred for 5 min at room temperature in advance. The catalyst solution and toluene solution of **4** were added to start the polymerization. In the polymerization using MAO, MAO was used instead of AlR$_3$ and polymerization was started without **4**. Termination was carried out by the addition of isobutyl alcohol. After the polymerization, the unreacted monomer was vented and the mixture was quenched with plenty of methanol. The polymer was filtered, washed with methanol and dried *in vacuo* at 60°C for 6 h.

Analytical procedures

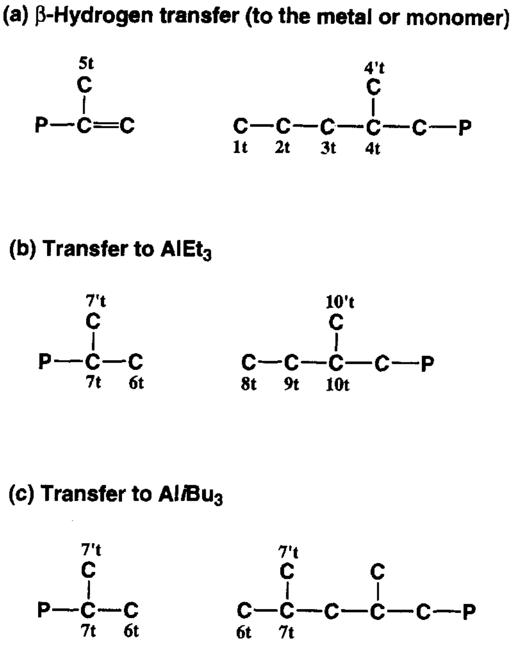
The molecular weights and molecular weight distributions of polymers were measured at 145°C by gel-permeation chromatography (GPC) (Waters 150CV) using *o*-dichlorobenzene as solvent. Weight-average molecular weight (M_w) was determined by the equation: $M_w = A_w \bullet Q$ (A_w and Q are, respectively, weight-average molecular size (Å) and Q-factor (26.4 for polypropylene)[43]. The ^{13}C n.m.r. spectrum was recorded at 135°C on a JEOL EX-270 n.m.r. spectrometer operating at 67.8 MHz. Polymers were dissolved in *o*-dichlorobenzene–benzene-d_6 (vol. ratio = 9:1) up to 5 wt%. The melting points (T_m) of polymers were determined by DSC (Perkin–Elmer DSC-VII) from the melting endotherm at a heating rate of 5°C min^{-1} after previous heating to 180°C and cooling to 50°C by 5°C min^{-1}.

The propylene–toluene vapor–liquid equilibrium at 40°C, 4 kg cm^{-2} G of propylene was estimated from the Soave–Redich–Kwong equation[44] using the ASPEN-PLUS® program.

RESULTS AND DISCUSSION

Propylene polymerization with rac-Et(Ind)$_2$ZrCl$_2$ (1) and rac-Me$_2$Si(Ind)$_2$ZrCl$_2$ (2)

Isospecific polymerization of propylene was conducted with **1** and **2** combined with $AlEt_3$ or Al*i*Bu_3/**4**. The metallocene combined with methylaluminoxane (MAO) catalyst system was also used for reference. The results of the propylene polymerization, together with the molecular weight of polypropylenes, are summarized in *Table 1 Table 2*. Increase in the molar ratio of $AlEt_3$/Zr resulted in the marked decrease of molecular weight. On the other hand, the molecular weight of polypropylenes was independent of the molar ratio of Al*i*Bu_3/Zr. These results indicate that chain transfer to $AlEt_3$ occurs frequently, wherease, Al*i*Bu_3 does not participate in the chain transfer reaction.


(a) β-Hydrogen transfer (to the metal or monomer)

(b) Transfer to $AlEt_3$

(c) Transfer to Al*i*Bu_3

Scheme 2 Chain end structures of polypropylene: P = polymer chain.

The chain end groups of polypropylenes were detected by ^{13}C n.m.r. to study the chain transfer reaction more detail. The typical polymer end groups, found in low molecular polypropylene produced by ordinary metallocene catalysts, are the vinylidene group resulting from *β*-hydrogen transfer and *n*-propyl group formed by insertion of propylene into the resulting metal-hydride [*Scheme 2(a)*]. When the chain transfer to $AlEt_3$ occurs, the polymer end groups are the isopropyl group resulting from Al-polymer connection and the ethyl group formed by insertion of propylene in to the

Table 1 Results of propylene polymerization with **1**-AlR_3/**4** and MAO[a]

Run	Cat. (μmol)	AlR_3	Molar ratio Al/Zr	Polymn. time (min)	Yield (g)	Activity (kg PP mol^{-1} Zr·h^{-1})	M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]
1	3.6	$AlEt_3$	150	60	26.4	7300	6.0	1.9
2	3.1	$AlEt_3$	250	60	44.7	14400	5.4	2.0
3	2.9	$AlEt_3$	500	60	25.6	9000	5.1	1.9
4	3.6	$AlEt_3$	1000	60	11.5	3200	3.6	2.0
5	1.6	Al*i*Bu_3	150	30	44.3	56100	7.2	1.9
6	1.2	Al*i*Bu_3	250	30	63.5	102000	6.8	1.9
7	1.3	Al*i*Bu_3	500	30	61.0	94400	6.8	2.0
8	1.1	Al*i*Bu_3	1000	30	50.0	92900	7.0	1.9
9	7.4	(MAO)	1000	10	29.2	23600	4.8	2.2

[a] Polymerization conditions: polymn. temp., 40°C; toluene, 300 ml; propylene, 4 kg cm^{-2} G; molar ratio of **4**/Zr = 1.0.
[b] Detemined by GPC: [$M_w = 26.4 \times A_w$ (Å)].

Table 2 Results of propylene polymemization with **2**-AlR_3/**4** and MAO[a]

Run	Cat. (μmol)	AlR_3	Molar ratio Al/Zr	Polymn. time (min)	Yield (g)	Activity (kg PP mol^{-1} Zr·h^{-1})	M_w[b] ($\times 10^{-4}$)	M_w/M_n[b]
10	4.7	$AlEt_3$	150	60	20.2	4300	6.4	1.9
11	4.6	$AlEt_3$	250	60	22.9	4900	5.6	1.9
12	4.2	$AlEt_3$	500	60	9.3	2200	4.8	2.0
13	5.1	$AlEt_3$	1000	60	36.0	7000	3.5	2.0
14	1.7	Al*i*Bu_3	250	10	59.3	213000	5.6	1.9
15	0.71	Al*i*Bu_3	500	10	46.3	389000	6.4	2.0
16	0.67	Al*i*Bu_3	1000	10	40.2	361000	6.1	1.9
17	0.60	(MAO)	1000	60	4.0	6600	7.4	1.9

[a] Polymerization conditions: polymn. temp., 40°C; toluene, 300 ml; propylene, 4 kg cm^{-2} G; molar ratio of **4**/Zr = 1.0.
[b] Determined by GPC [$M_w = 26.4 \times A_w$ (Å)].

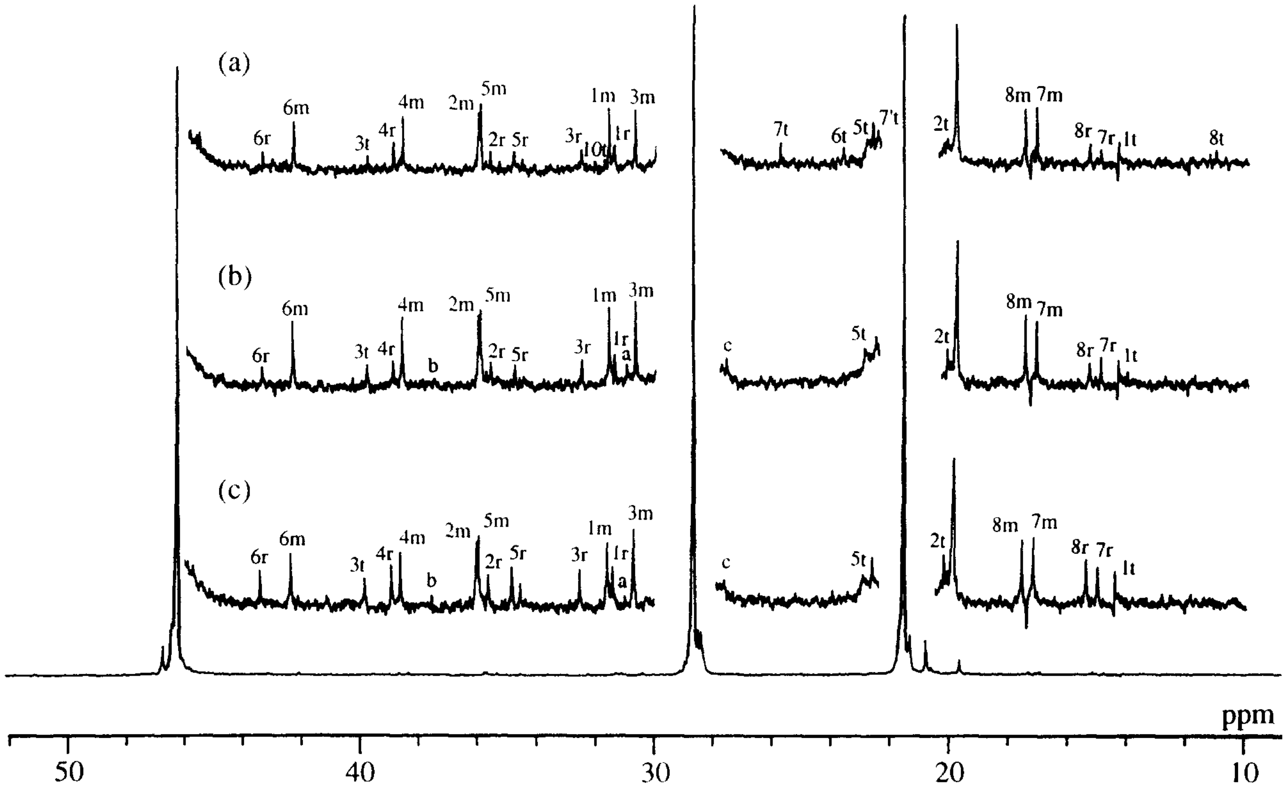


Figure 1 ^{13}C n.m.r. spectra of isotactic polypropylenes obtained with **1**: (a) $AlEt_3$/**4**; (b) $Al\textit{i}Bu_3$/**4**; and (c) MAO.

Table 3 Microstructiures of isotactic polypropylenes obtained with **1**,**2**-AlR_3/**4** and MAO

Run	Cat.	AlR_3	Molar ratio Al/Zr	[mmmm] (%)	[mmrr] (%)	[mrrm] (%)	2,1-(m) (%)	2,1-(r) (%)	1,3-(%)	End group[a] -R/-*n*Pr	T_m[b] (°C)
1	**1**	$AlEt_3$	150	88.9	4.9	1.9	0.60	0.19	0.19	0.56	141.0
4	**1**	$AlEt_3$	1000	88.2	5.2	2.0	0.65	0.21	0.14	1.76	141.0
8	**1**	$Al\textit{i}Bu_3$	1000	89.6	4.3	2.0	0.58	0.22	0.17	0.00	138.7
9	**1**	(MAO)	1000	87.4	5.6	2.1	0.53	0.26	0.08		136.9
10	**2**	$AlEt_3$	150	92.4	3.3	1.3	0.53	0.16	0.04	0.62	145.6
13	**2**	$AlEt_3$	1000	92.8	3.0	1.3	0.58	0.30	0.07	1.25	146.0
16	**2**	$Al\textit{i}Bu_3$	1000	91.8	3.4	1.5	0.64	0.23	0.17	0.00	142.3
17	**2**	(MAO)	1000	93.3	3.0	1.1	0.40	0.20			145.1

[a] Molar ratio of (R end groups)–(*n*-propyl end groups) determined by ^{13}C n.m.r., R = alkyl group in AlR_3, *n*Pr = *n*-propyl.
[b] Melting temperature.

resulting metal-ethyl group [*Scheme 2(b)*]. The chain transfer to the $AlEt_3$ was detected by Soga *et al.* in the propylene polymerization with *rac*-ethylenebis(tetrahydroindenyl)zirconium dichloride (*rac*-$Et(H_4Ind)_2ZrCl_2$)/Al_2O_3-$AlEt_3$ without MAO, and the assignment of the chemical shifts in ^{13}C n.m.r. could be made according to the report[38]. The chain transfer to $Al\textit{i}Bu_3$ in the propylene polymerization produces only an isopropyl end group resulting from Al-polymer connection and insertion of propylene into the metal-isobutyl group [*Scheme 2*(c)]. The same isopropyl end group could be formed by the chain transfer to $Al(CH_3)_3$. Busico *et al.* reported the chain transfer to $Al(CH_3)_3$ (in equilibrium with MAO) in the isospecific polymerization of propylene with **1**/MAO, and the assignment of chemical shifts in ^{13}C n.m.r. spectrum could be made according to the report[19]. *Figure 1(a–c)* illustrate the ^{13}C n.m.r. spectra of isotactic polypropylenes obtained with **1** combined with different cocatalysts, and the assignments of chain end structures are shown in *Scheme 2*. The ^{13}C n.m.r. spectrum of isotactic polypropylene obtained with $AlEt_3$/**4** displays not only the peaks attributable to *n*-propyl end groups at *ca.* 14.3 (1t), 20.2 (2t), 39.8 (3t), 22.8 (5t) ppm, but also strong peaks at *ca.* 23.6 (6t), 25.7 (7t) ppm attributable to isopropyl end groups and at *ca.* 11.1 (8t), 32.8 (10t) ppm attributable to ethyl end groups derived from chain transfer to $AlEt_3$. The molar ratio of the (ethyl end groups)/(*n*-propyl end groups) was determined by analyzing the intensity of corresponding peaks in the ^{13}C n.m.r. spectra, and the results are summarized in *Table 3*. The content of ethyl end groups was higher than that of *n*-propyl end groups in the polypropylenes obtained with both **1** and **2** at the molar ratio of $AlEt_3/Zr = 150$. Higher concentration of ethyl end groups in comparison with *n*-propyl end groups was detected in the polymers obtained at the molar ratio of $AlEt_3/Zr = 1000$. On the other hand, only the peaks attributable to *n*-propyl end groups

Table 4 Results of propylene polymerization with **3**-AlR$_3$/**4** and MAO[a]

Run	Cat. (μmol)	AlR$_3$	Molar ratio Al/Zr	Polymn. time (min)	Yield (g)	Activity (kg PP mol^{-1} Zr·h^{-1})	M_w[b] ($\times 10^4$)	M_w/M_n[b]	[rrrr] (%)	[rmrr] (%)	[rmmr] (%)	End group[c] -R/-*n*Pr
18	7.9	AlEt$_3$	250	120	3.5	220	6.3	1.9				
19	7.2	AlEt$_3$	500	120	2.5	170	5.7	2.1				
20	6.9	AlEt$_3$	1000	120	2.5	180	3.8	2.2	86.6	2.7	1.6	2.80
21	7.2	Al*i*Bu$_3$	250	120	12.5	870	13.6	2.2				
22	7.2	Al*i*Bu$_3$	500	120	11.7	810	12.9	2.5				
23	5.3	Al*i*Bu$_3$	1000	120	8.8	630	10.6	2.3	84.4	3.3	1.6	0.87
24	6.9	(MAO)	1000	30	35.8	10400	15.8	1.9	88.4	2.0	1.5	

[a] Polymerization conditions: polymn. temp., 40°C; toluene, 300 ml; propylene, 4.0 kg cm^{-2} G molar ratio of **4**/Zr = 1.0.
[b] Determined by GPC: [$M_w = 26.4 \times A_w$ (Å)].
[c] Molar ratio of (R end groups)–(*n*-propyl end groups) determined by ^{13}C n.m.r. R alkyl group in AlR$_3$, *n*Pr = *n*-propyl.

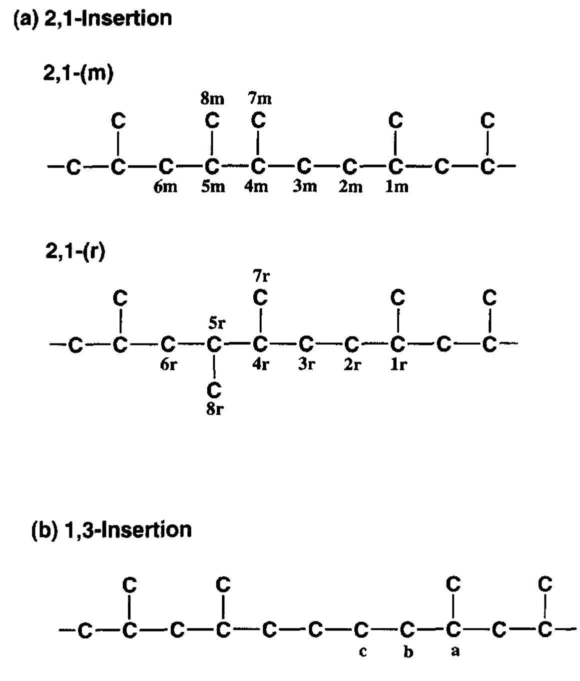
derived from β-hydrogen transfer were detected in ^{13}C n.m.r. spectrum of polypropylene obtained with Al*i*Bu$_3$/**4** (*Figure 1b*).

The microstructures of isotactic polypropylenes are also studied by ^{13}C n.m.r. The assignment of the chemical shifts of 2,1-insertion and 1,3-insertion (*Scheme 3*) was made according to the literature[12–46], and the results are summarized in *Table 3*. Clear difference of isotacticity and regio specificity was not observed between the polypropylenes obtained with different cocatalysts and at the different molar ratio of AlEt$_3$/Zr.

Propylene polymerization with i-Pr(Cp)(Flu)ZrCl$_2$ (3)

Syndiospecific polymerization of propylene was carried out with **3** combined with AlR$_3$/**4**, and the results are listed in *Table 4*. Decrease of the molecular weight of polypropylenes were observed with increase in the molar ratio of AlEt$_3$/Zr and Al*i*Bu$_3$/Zr. The polypropylenes of higher molecular weight were obtained with Al*i*Bu$_3$ in stead of AlEt$_3$.

Figure 2a–c illustrate the ^{13}C n.m.r. spectra of syndiotactic polypropylenes obtained with different cocatalysts.



Scheme 3 Stereo-irregular of isotactic polypropylene obtained with metallocene catalyst.

The ^{13}C n.m.r. spectrum of the syndiotactic polypropylene obtained with AlEt$_3$/**4** (*Figure 2a*) displays not only the peaks attributable to *n*-propyl end groups (1t, 2t, 3t, 5t) but also strong peaks attributable to ethyl end groups (8t, 10t) and isopropyl end groups (6t, 7t) derived from chain transfer reaction by AlEt$_3$. Furthermore, the ^{13}Cn.m.r. spectrum of the syndiotactic polypropylene obtained with Al*i*Bu$_3$/**4** (*Figure 2b*) displays not only the peaks attributable to *n*-propyl end groups (1t, 2t, 3t, 5t), but also weak peaks attributable to isopropyl (isobutyl) end groups derived from chain transfer reaction by Al*i*Bu$_3$. These results indicate that chain transfers not only to AlEt$_3$ but also to Al*i*Bu$_3$ occurred in syndiospecific polymerization of propylene with **3**. The molar ratio of (ethyl or isopropyl end groups)–(*n*-propyl end groups) was determined. It is very difficult to determine the end groups of syndiotactic polypropylenes obtained at the low molar ratio of AlR$_3$/Zr because the molecular weight of polymers was too high. At the molar ratio of AlR$_3$/Zr = 1000, the end groups of syndiotactic polypropylenes were barely observed in ^{13}C n.m.r. spectra. The isopropyl end groups are formed at the initiated and terminated polymer chain ends through the chain transfer reaction by Al*i*Bu$_3$, and the half intensity of the peaks in ^{13}C n.m.r. of isopropyl end groups was applied to the intensity of initiated isopropyl end groups. At the molar ratio of AlEt$_3$/Zr = 1000, high concentration of ethyl end groups were detected. On the other hand, the content of isopropyl end groups derived from the chain transfer reaction by Al*i*Bu$_3$ was less than that of *n*-propyl end groups at the molar ratio of Al*i*Bu$_3$/Zr = 1000. These results suggest that chain transfer reaction occurred more frequently by AlEt$_3$ than Al*i*Bu$_3$.

The microstructures of syndiotactic polypropylenes obtained with **3** are summarized in *Table 4*. The [rrrr] pentad fraction of syndiotactic polypropylene with **3** combined with MAO is higher than that with AlR$_3$/**4**, as reported by Ewen previously[8]. Two types of stereo-irregular sequence are found in syndiospecific polymerization of propylene with **3** as shown in *Scheme 4*[42]. One is [rmmr] that originated from reversed diastereoface selectivity (miss-insertion of propylene), the other is [rmrr] sequence originated from the migration of the propagating polymer chain to the vacant site. The stereo-irregular fraction of [rmmr] was almost the same in any syndiotactic polypropylenes, but higher [rmrr] was found in the polypropylenes obtained with AlR$_3$/**4**. These results suggest that the migration of propagating polymer chain to the vacant site occurred more frequently in syndiospecific polymerization with **3** combined with AlR$_3$/**4** than combined with MAO.

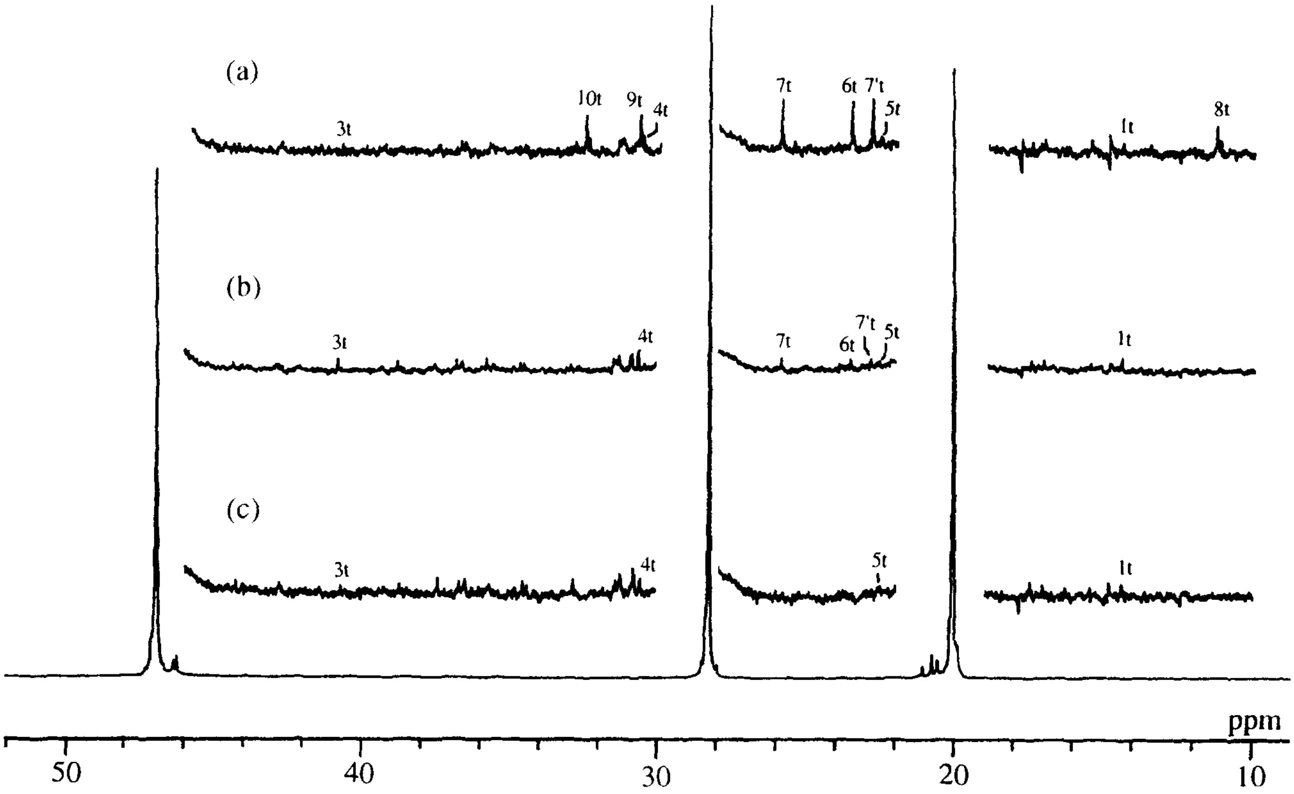


Figure 2 ^{13}Cn.m.r. spectra of isotactic polypropylenes obtained with **3**: (a) AlEt$_3$/**4**; (b) Al*i*Bu$_3$/**4**; and (c) MAO.

Kinetic study of chain transfer to trialkylaluminum

The effect of AlR$_3$ concentration ([Al]) on the molecular weight of polypropylene was investigated to characterize the chain transfer reactions by AlEt$_3$ and Al*i*Bu$_3$. The degree of polymerization (P_n) can be described by the following equation[47]

$$P_n = \int k_p[C^*][M_p]^a dt / \left\{ [C^*] + \int (k_{tr} + k_{trA}[Al]^b + k_{trM}[M_p]^c)[C^*] dt \right\}$$

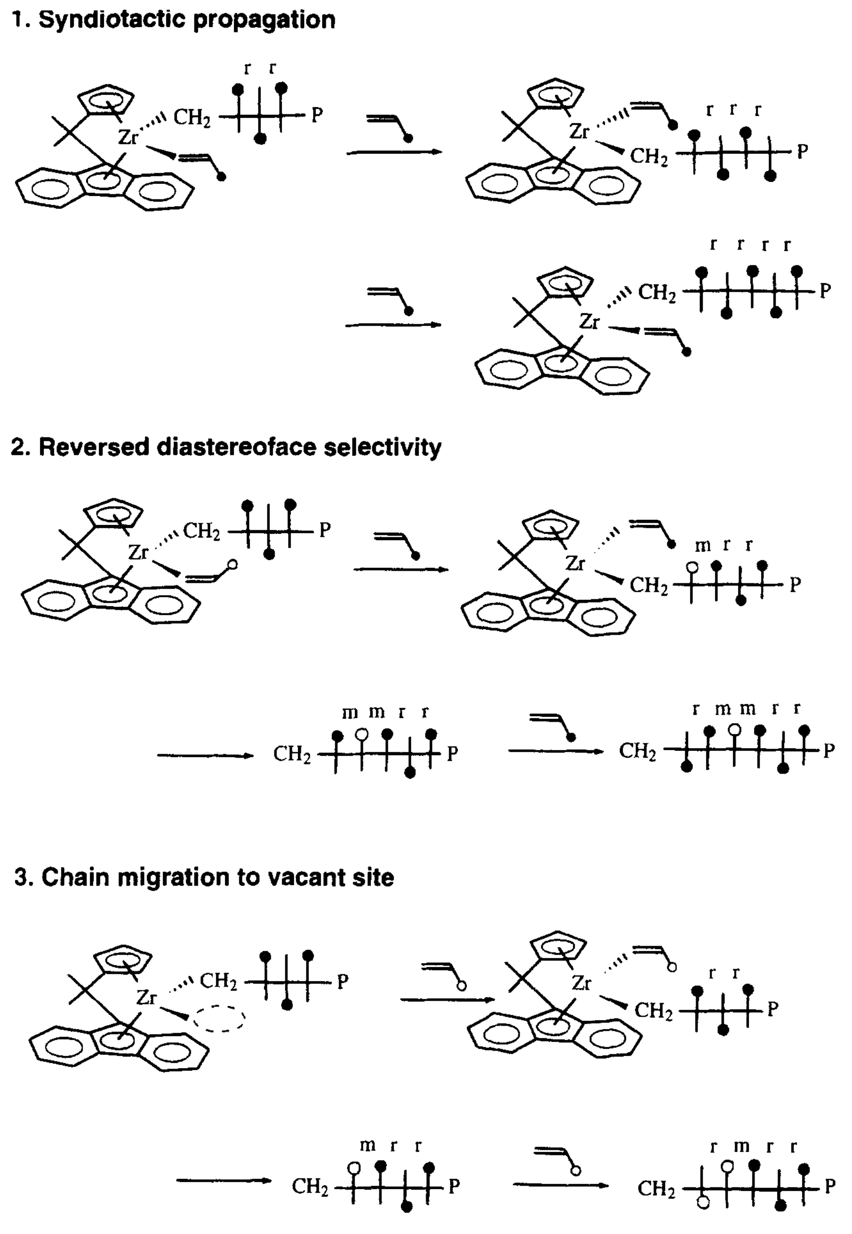
$$1/P_n = (k_{tr} + k_{trM}[M_p]^c)/k_p[M_p]^a + k_{trA}[Al]^b/k_p[M_p]^a$$

where k_p, $[C^*]$, $[M_p]$, [Al], k_{tr}, k_{trA} and k_{trM} are, respectively, rate constant of propagation, number of active centre, monomer concentration, AlR$_3$ concentration, rate constant of β-hydrogen transfer to the metal, transfer to AlR$_3$ and β-hydrogen transfer to the propylene monomer. The $[M_p]$ at the polymerization condition, propylene–toluene equilibrium at 40°C of 4 kg cm^{-2} G, was calculated by the Soave–Redich–Kwong equation[44] and total volume = 389 ml, $[M_p]$ = 2.9 mol l^{-1} was applied to the condition. a, b and c are the reaction order. According to some previous reports, polymerization activity of propylene increased in proportion to the concentration of propylene monomer. The relationship between polymerization rate and monomer concentration has been studied by Fink *et al.* for metallocene–MAO catalysts, and a reaction order in propylene of 1.2 to 1.4 for **2**/MAO and **3**/MAO[48]. On the other hand, the higher value (1.7) of reaction order of the polymerization rate with respect to propylene concentration was reported

Table 5 Kinetic study of chain transfer reaction by AlR$_3$ in stereospecific polymerization of propylene with metallocene catalysts[a]

Run	Cat.	AlR$_3$	[Al] (mol l^{-1})	$1/P_n$ (× 10^4)	k_{trA}/k_p (× 10^4)
1	**1**	AlEt$_3$	1.39	13.3	
2	**1**	AlEt$_3$	1.99	15.5	3.54
3	**1**	AlEt$_3$	3.72	15.7	
4	**1**	AlEt$_3$	9.25	23.3	
10	**2**	AlRt$_3$	1.81	12.5	
11	**2**	AlEt$_3$	2.95	14.2	2.88
12	**2**	AlEt$_3$	5.40	17.5	
13	**2**	AlEt$_3$	13.1	24.0	
18	**3**	AlEt$_3$	2.76	12.7	
19	**3**	AlEt$_3$	9.25	15.5	2.29
20	**3**	AlEt$_3$	17.7	24.3	
21	**3**	Al*i*Bu$_3$	4.63	6.80	
22	**3**	Al*i*Bu$_3$	9.25	8.15	0.49
23	**3**	Al*i*Bu$_3$	17.7	9.11	

[a]Propylene monomer concentration [M] = 2.9 (mol l^{-1})



Scheme 4 Syndiospecific polymerization mechanism of propylene: P = polymer chain, ●, ○ = CH_3.

for *rac*-$Me_2Si(benz[e]indenyl)_2ZrCl_2$ and *rac*-$Me_2Si(2\text{-}Me\ benz[e]\ indenyl)_2ZrCl_2/MAO$ by Mülhaupt *et al.*[23]. In this study, we assume that only one propylene molecule is involved in the propagation step, and apply $a = 1$ for the reaction order. The $1/P_n$ increases in proportion to the concentration of AlR_3 ([Al]) as shown in *Figure 3*, and we apply the reaction order of the chain transfer rate with respect to AlR_3 concentration $b = 1$. The relative constants k_{trA}/k_p were calculated from the plots in *Figure 3*, and the results are summarized in *Table 5*. The values of relative constants k_{trA}/k_p with **1**, **2**, **3** combined with $AlEt_3$/**4** at this polymerization condition range from 2.3×10^{-4} to 3.5×10^{-4}. The list is in order of relative constants k_{trA}/k_p combined with $AlEt_3$/**4**: **1** > **2** > **3**. The value of relative constants k_{trA}/k_p with **3** combined with $Al\textit{i}Bu_3$/**4** is 0.49×10^{-4} about one fifth of that combined with $AlEt_3$/**4**.

CONCLUSION

In the stereospecific polymerization of propylene with metallocene combined with AlR_3/**4**, chain transfer to AlR_3 plays an important role in determining the molecular weight of polypropylene. The chain transfer reactions by $AlEt_3$ and $Al\textit{i}Bu_3$ were studied by the analysis of molecular weight, chain end structures of obtained polymers and kinetic study.

In isospecific polymerization with **1** and **2** combined with AlR_3/**4**, the molecular weight of resulting polymers decreased with increase in the molar ratio of $AlEt_3/Zr$, and the chain end groups resulting from chain transfer to $AlEt_3$ were detected. On the other hand, the molecular weight of polymers was independent of the molar ratio of $Al\textit{i}Bu_3/Zr$ and the chain end groups resulting from chain transfer to $Al\textit{i}Bu_3$ could not be observed by ^{13}C n.m.r. Syndiospecific polymerization of propylene was conducted with **3** combined with AlR_3/**4** and the chain transfer reactions by $AlEt_3$ and $Al\textit{i}Bu_3$ were observed. The chain transfer to $AlEt_3$ occurs more frequently than to $Al\textit{i}Bu_3$.

The relative constants k_{trA}/k_p with **1**, **2**, **3** combined with $AlEt_3$/**4** were calculated from the plots of $1/P_n$ against [Al]. The k_{trA}/k_p with **3** combined with $Al\textit{i}Bu_3$/**4** is about one fifth of that combined with $AlEt_3$/**4**.

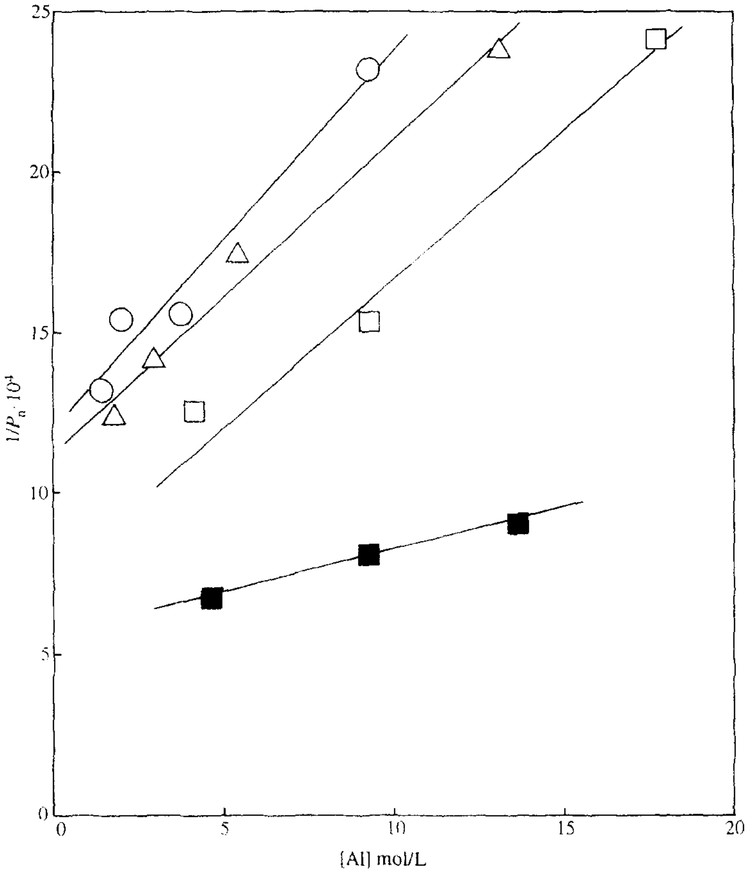


Figure 3 Plots of $1/P_n$ against trialkylaluminium concentration ([Al]): (○) **1**-$AlEt_3$/4; (△) **2**-$AlEt_3$/4; (□) **3**-$AlEt_3$/4 and (■) **3**-Al*i*Bu_3/4.

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