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Study on chain end structures of polypropylenes prepared with different symmetrical metallocene catalysts

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Abstract

Propylene homopolymerizations were conducted by using three kinds of metallocenes: Cp_2ZrCl_2, $En(Ind)_2ZrCl_2$ and iPr(Cp)(Flu)$ZrCl_2$, all of which were activated with methylaluminoxane. Detailed NMR analyses of the chain ends in the resulting polymers were carried out to discuss the chain end structures of the polypropylenes and the mechanism of polymerization. The characteristic of each metallocene for the mechanism of polymerization was also described.

Keywords: Metallocene catalyst; Polypropylene; Analytical characterization

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1. Introduction

The analysis of microstructures of polyolefins is of particular interest to scientists and engineers gaining a deeper understanding of the polymerization mechanism [1–20]. The study on the effect of magnesium supported titanium catalysts for the chain end structures of polypropylene have been reported with NMR analysis [21,22]. In the case of metallocene-catalyzed propylene polymerization, the termination reactions of the polymer chain are believed to be a derivative of the transfer of a β-hydrogen or a methyl group of the growing polymer chain owing to the detection of vinylidene, vinyl and vinylene groups as unsaturated chain end structures. The initiation reaction of propylene polymerization has been regarded as 1,2-insertion of a monomer by the detection of *n*-propyl group as the usual initial chain end structure of the polymer [11–17].

In previous papers, it was indicated that chain end structures depend on the species of the catalysts. However, the effect of symmetry of the catalyst on chain propagation and a termination reaction has never been clarified. This has led to interest in investigating detailed saturated and unsaturated structures of polypropylenes produced with different symmetrical metallocenes.

In this study, three kinds of metallocenes, *rac*-ethylenebis(indenyl)zirconiumdichloride ($En(Ind)_2ZrCl_2$, as C_2 symmetrical), isopropyl(cyclopentadienyl)(fluorenyl)zirconiumdichloride (iPr(Cp)(Flu)$ZrCl_2$, as C_s symmetrical), and bis(cyclopentadienyl)zirconiumdichloride (Cp_2ZrCl_2, as asymmetrical) were selected to discuss the chain end structures of the resulting polypropylenes. We will report on unsaturated groups in the polymer chain and discuss the mechanism to explain the formation of unsaturated structures.

2. Experimental section

2.1. Materials

iPr(Cp)(Flu)$ZrCl_2$ was prepared according to the literature [23]. $En(Ind)_2ZrCl_2$ was purchased from Sigma-Aldrich Co. Cp_2ZrCl_2 was purchased from Wako Pure Chemical Industries, Ltd. Those organometallic compounds were used as received. MAO was purchased as toluene solution (10 wt%) from Albemarle Co. and used without purification. Toluene purchased from Wako Pure Chemical Industries, Ltd was dried over sodium metal and distilled. Propylene monomer (Mitsui Chemicals) was used without

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any further purification. Organometallic compounds were treated under a nitrogen atmosphere.

2.2. Polymerization

All polymerization experiments were carried out in 500 ml glass flasks equipped with mechanical stirrer, thermocouple and monomer inlet tube. Dry toluene of 250 ml was added to the reactor, and monomer gas was introduced into the reactor through the inlet tube. After heating the solvent to polymerization temperature, MAO in toluene (5 mmol [Al]) was added to the reactor, and then, the polymerization was started by the addition of 5 ml of toluene solution dissolved metallocene (0.005 mmol) to the reactor. That temperature was maintained during the polymerization under the constant feed of 100 Nl/h of propylene monomer gas. After that, 5 ml of isobutanol was added to the reactor in order to terminate the polymerization. The reaction mixture was poured into 1 l of methanol. Polymers (PP2–5) were corrected by filtration and washed with 500 ml of methanol, then dried under reduced pressure at 80 °C for 10 h. Polymer (PP1) was separated from methanol by decantation and washed with methanol several times, then dried under reduced pressure at 80 °C for 10 h.

2.3. Analysis of polymer

Molecular weights and molecular weight distributions were determined by gel-permeation chromatography (GPC) using *o*-dichlorobenzene as solvent. ^{13}C NMR spectra were recorded on a JEOL JNM GSX-400 series spectrometer operated at 100 MHz in pulse Fourier transform mode. Instrument conditions were as follows: pulse angle, 45°; pulse repetition, 5.0 s; spectral width, 18,050 Hz; temperature, 118 °C; data points, 32,768. ^{1}H NMR spectra were recorded on a JEOL JNM GSX-400 series in pulse Fourier transform mode. Instrument conditions were as follows: pulse angle, 45°; pulse repetition, 5.0 s; spectral width, 8000 Hz; temperature, 118 °C; data points, 32,768. Polymer solutions used for NMR were prepared by dissolving 50 mg of polymer sample in 0.5 ml of 1,2-dichlorobenzene-d_4 (ODCB) or of decahydronaphthalene-d_{18} (Decalin) as solvents.

3. Results and discussion

Polymerizations were conducted using three kinds of metallocenes activated with excess amount of MAO in toluene under atmospheric propylene gas feeding at a constant rate. Chain end structures of the resulting polymers were identified by ^{1}H and ^{13}C NMR with ODCB or Decalin as a solvent to restrain the isomerization of vinylidene group to isobutenyl group during the measurement [24]. The results of polymerization and the data of identified groups are summarized in Table 1. Expanded ^{1}H NMR and ^{13}C

Table 1
Results of propylene polymerization

Run #	Metallocene	Polymerization temperature (°C)	Activity[a]	M_n[b]	Unsaturated and saturated groups in polymer (unit mol%)[c]. In brackets, percentages of units (A–J) in each polymer									
					Unsaturated						Saturated			
					(A) Vinylidene	(B) *i*-Butenyl	(C) 2-Butenyl	(D) 4-Butenyl	(E) (Internal vinylidene)	(F) (Internal vinylidene)	(G) *n*-Propyl	(H) *i*-Propyl	(I) *n*-Butyl	(J) Ethyl
PP1	Cp_2ZrCl_2	25	1762	2371	1.28 (48.5)	–	0.04 (1.5)	–	–	–	1.32 (50.0)	–	–	–
PP2	$En(Ind)_2ZrCl_2$	50	8984	9907	0.14 (17.3)	0.04 (4.9)	0.07 (8.6)	0.06 (7.4)	0.02 (2.5)	0.01 (1.2)	0.26 (32.1)	0.11 (13.6)	0.10 (12.4)	–
PP3	$En(Ind)_2ZrCl_2$	70	5144	3962	0.72 (33.2)	0.10 (4.6)	0.06 (2.8)	0.07 (3.2)	0.04 (1.8)	0.03 (1.4)	0.78 (35.9)	0.14 (6.5)	0.23 (10.6)	–
PP4	iPr(Cp)(Flu)$ZrCl_2$	50	672	26,423	0.09 (12.2)	0.31 (41.8)	0.04 (5.3)	0.03 (4.1)	0.03 (4.1)	0.03 (4.1)	0.05 (6.7)	0.13 (17.6)	0.03 (4.1)	Trace[d]
PP5	iPr(Cp)(Flu)$ZrCl_2$	70	466	8048	0.33 (14.7)	0.88 (39.1)	0.06 (2.7)	0.09 (4.0)	0.05 (2.2)	0.17 (7.6)	0.28 (12.4)	0.34 (15.1)	0.05 (2.2)	–

Polymerization condition: [Zr]; 0.005 mmol, MAO; 5 mmol in 250 ml of toluene at 0.1 MPa. Propylene feed; 100 Nl/h. Polymerization time; 15 min (PP1–3), 30 min (PP4, PP5).

[a] kg/mol[Zr]/h.

[b] GPC data (PP standard).

[c] Estimated by ^{1}H and ^{13}C NMR.

[d] Under 0.01 mol%.

NMR spectra of resulting polymers (PP3 and PP5) in ODCB are shown in Figs. 1 and 2 with assigned structures according to previous reports [23–26], respectively. And possible pathways to form each structure are shown in schemes 1–12 in Fig. 3.

On the basis of the previous papers described the assignment of NMR spectra [21,22,25,26], 1,2-inserted chain end could lead to vinylidene group (A), *n*-propyl group (G) and *i*-propyl group (H) as described in schemes 1–3 in Fig. 3. 2,1-Inserted active chain end could give 2-butenyl group (C), *n*-propyl group (G), *i*-propyl group (H) and *n*-butyl group (I) as shown in schemes 5–7. *i*-Butenyl group (B) and 4-butenyl group (D) are mentioned as being derived from the isomerization as shown in schemes 4 and 8 [14]. By allylic activation of the polymer chain, internal vinylidenes (E, F) would be generated as shown in schemes 9 and 10 [16]. *i*-Propyl group (H) is also derived from the 1,2-insertion of a monomer into the Zr–CH_3 bond as shown in scheme 11. Ethyl group (J) by 2,1-insertion of a monomer into the Zr–CH_3 bond is negligible for a small amount in this study.

In PP1, *n*-propyl group (G) was only identified as the saturated chain end structure, and the main unsaturated group at the chain end was vinylidene (A). Based on these results, the following is indicated: in using Cp_2ZrCl_2, the termination reaction of polymerization was the transfer of a β-hydrogen of the growing polymer chain to a monomer or to the metal center of the catalyst, and that a propylene insertion was a 1,2-insertion predominantly as shown in scheme 1. It corresponds to the result in a previous paper [11].

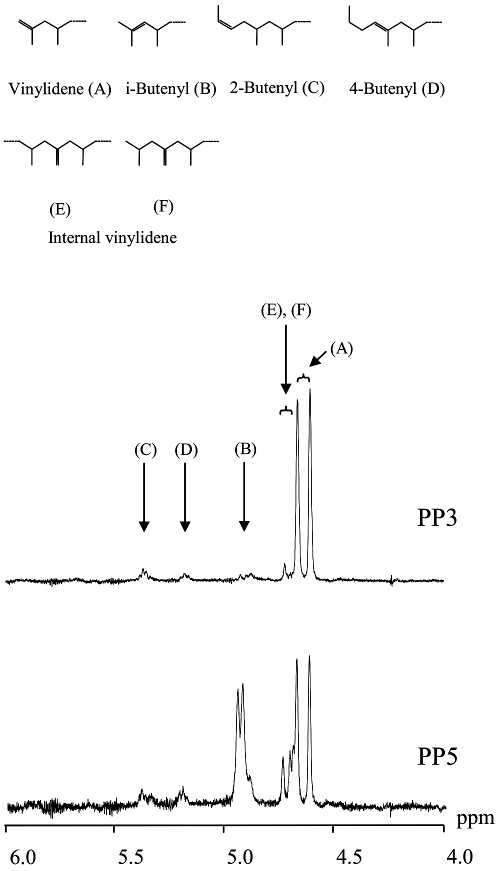

Fig. 1. Expanded ^{1}H NMR spectra (recorded in ODCB at 118 °C) of the olefinic region of the PP2 and PP5.

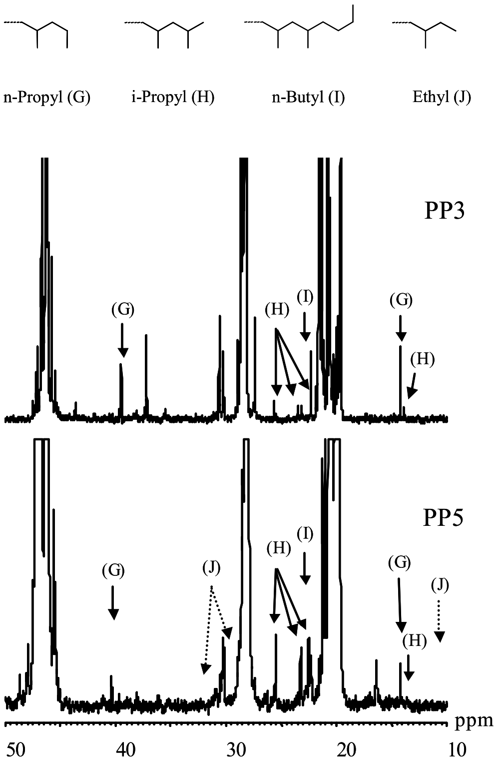

Fig. 2. Expanded ^{13}C NMR spectra (recorded in Decalin at 118 °C) between 10 and 50 ppm of the PP2 and PP5.

In PP2 and PP3 that were produced with $En(Ind)_2ZrCl_2$, all of the structures of (A)–(I) were detected. Among them, vinylidene group (A) and *n*-propyl group (G) were mainly formed as unsaturated and saturated groups, respectively. Moreover, *i*-propyl groups (H) and *n*-butyl groups (I) were identified as having almost the same amounts. Those results would indicate that the reactions as shown in schemes 7 and 11 occurred besides that shown in scheme 1. The presence of 2-butenyl group (C) could be the evidence of the chain transfer reaction as shown in scheme 5. Therefore, this would be suggested that the termination reaction at 2,1-inserted active chain end occurred. The presence of *i*-butenyl group (B) and 4-butenyl group (D) could indicate that the isomerization reactions as shown in schemes 4 and 8 occurred. Internal vinylidenes (E, F) would be formed by allylic activations occurring between the metal center of the catalyst and the growing polymer chain.

In PP4 and PP5 that were produced with *i*Pr(Cp)(Flu)$ZrCl_2$, the formation of vinylidene group (A), *i*-butenyl group (B) as the unsaturated group and *n*-propyl group (G), *i*-propyl group (H) as the saturated group would

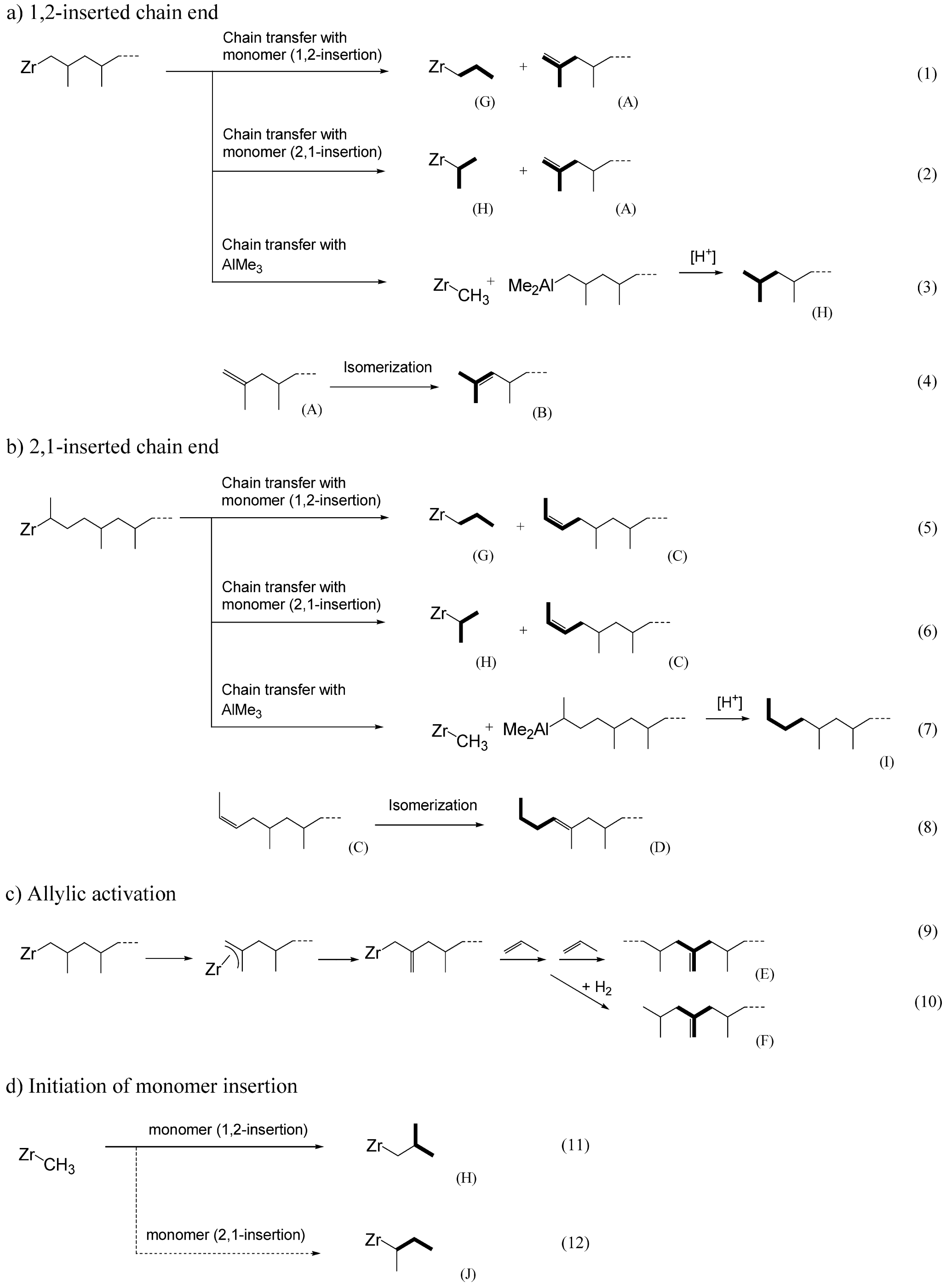

Fig. 3. Schemes of the possible formation reactions of chain ends.

indicate that the termination reactions occurred at 2,1-inserted active chain end. The presence of 2-butenyl group (C) and 4-butenyl group (D) could show that the chain end reactions as shown in schemes 5, 6 and 8 occurred at 2,1-inserted chain end. Internal vinylidenes (E, F) would be formed as in PP2 and PP3.

The important point to note here was that total amounts of unsaturated groups were too much compared with the ones of saturated chain end groups. That result could suggest the liberation of hydrogen occurred in polymerization.

In expanded ^{13}C NMR spectra shown in Fig. 4, the signals of *i*-butenyl group, which appeared between 129 and 133 ppm in PP3 [27], could be hardly observed in PP5. However, different signals that have never been known to the best of our knowledge were observed around 131.7 and 133.9 ppm. As the chemical shifts of those signals would induce a downfield shift from those of *i*-butenyl group, it

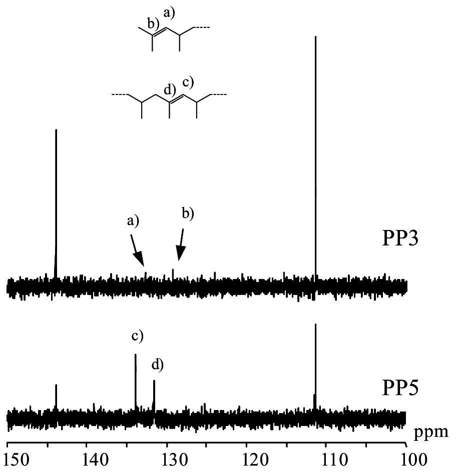

Fig. 4. Expanded ^{13}C NMR spectra (recorded in Decalin at 118 °C) between 100 and 150 ppm of the PP2 and PP5.

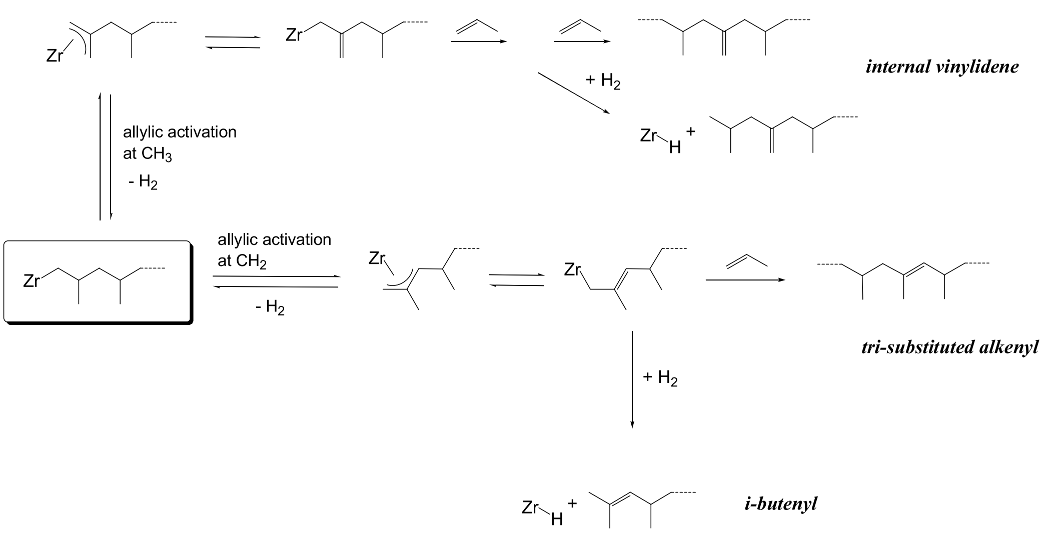

Fig. 5. Scheme of the proposed mechanism for internal unsaturated groups formation.

would suggest that those signals were assigned as the internal tri-substituted alkenyl group in the polymer chain. In PP4 and PP5, therefore, there would be much internal tri-substituted alkenyl group compared with *i*-butenyl group.

That structure would be formed via the pathways as shown in Fig. 5. Before the β-hydrogen transfer produces terminal vinylidene group, an allylic activation occurs to form a kind of π-allyl complex between the metal center of the catalyst and the end of growing polymer chain. When it occurs at methyl site near the chain end with liberation of hydrogen, internal vinylidene is generated followed by propylene monomer insertion. When the allylic activation occurs at methylene site, a tri-substituted alkenyl group is generated. Followed by the chain transfer with liberated H_2, *i*-butenyl group is formed [26]. On the other hand, followed by propylene monomer insertion, internal tri-substituted alkenyl group appears in the polymer chain. In PP4 and PP5, the latter pathway would occur more easily than the others.

4. Conclusion

Propylene homopolymerizations were conducted with three kinds of metallocenes to discuss the chain end structures of the polymer and the mechanism of polymerization. In the polymerization with Cp_2ZrCl_2, the termination reaction exclusively occurred at 1,2-inserted chain end. In cases of $En(Ind)_2ZrCl_2$ and *i*Pr(Cp)(Flu)$ZrCl_2$, besides at 1,2-inserted site, a considerable number of termination reactions occurred at 2,1-inserted chain end. Internal vinylidenes were detected in both metallocenes. Moreover, *i*-butenyl group and internal tri-substituted alkenyl group were identified in $En(Ind)_2ZrCl_2$ and *i*Pr(Cp)(Flu)$ZrCl_2$, respectively. Those structures would be formed via π-allyl complex between the metal center of the catalyst and the growing polymer chain with liberation of hydrogen.

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