Propylene homo- and copolymerization with ethylene using an ethylenebis(1-indenyl)zirconium dichloride and methylaluminoxane catalyst system

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Isotactic polypropylene obtained with a *rac*-ethylenebis(1-indenyl)zirconium dichloride and methylaluminoxane catalyst system in the range −30 to 50°C was successively fractionated by boiling pentane, hexane, heptane and trichloroethylene, with the result that the hexane-insoluble/heptane-soluble portion was the major fraction for all samples. The whole and fractionated polymers were characterized in comparison with those of an $MgCl_2/TiCl_4$–Et_3Al catalyst system by ^{13}C nuclear magnetic resonance, gel permeation chromatography and differential scanning calorimetry. In copolymers with ethylene, three types of regio-irregular structures depending on ethylene content were observed by ^{13}C nuclear magnetic resonance.

(Keywords: zirconium catalyst; aluminoxane; microstructure; isotactic polypropylene; propylene copolymer)

INTRODUCTION

Polypropylene (PP) produced with a soluble catalyst system comprising a bis(cyclopentadienyl)zirconium or -titanium compound and methylaluminoxane is known to be of atactic structure[1–6]. On the other hand, Ewen[7] has reported that the PP obtained with a soluble mixture of 56% chiral-racemic and 44% achiral ethylenebis(1-indenyl)titanium dichloride ($Et(Ind)_2TiCl_2$) in conjunction with methylaluminoxane was composed of 63% isotactic and 37% atactic polymers (71% and 38% of the *meso–meso* triad sequence contents by ^{13}C n.m.r., respectively). He concluded that the isotactic PP was formed from the *rac*-$Et(Ind)_2TiCl_2$ site by the enantiomorphous site control mechanism. Kaminsky[5,8–10] has obtained more highly isotactic PP with a soluble *rac*-$Et(Ind)_2ZrCl_2$ or *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (*rac*-$Et(TH\text{-}Ind)_2ZrCl_2$) and methylaluminoxane catalyst system. Furthermore, Kaminsky has synthesized optically active PP or poly(1-butene) by using (*S*)-$Et(TH\text{-}Ind)_2ZrCl_2$.

In this paper, the influences of polymerization temperature and ethylene comonomer on the microstructure of the polymers produced have been investigated in propylene polymerization with a catalyst system comprising *rac*-$Et(Ind)_2ZrCl_2$ and methylaluminoxane. Moreover, the results obtained were compared with those of PP with an $MgCl_2/TiCl_4$–Et_3Al catalyst system.

EXPERIMENTAL

Preparation of rac-*$Et(Ind)_2ZrCl_2$*

Into a 200 ml glass flask equipped with a stirrer were placed 50 ml of tetrahydrofuran (THF) and 5.43 g of 1,2-bis(1-indenyl)ethane ($Et(Ind)_2$), prepared according to a previous paper[11], and the system was cooled to −20°C. Then, 26.3 ml of n-butyllithium (1.6 M solution in hexane) was added dropwise over 30 min, keeping the temperature fixed at −20°C, and further stirred for 1 h at −20°C. By the above treatment, the dilithium salt of $Et(Ind)_2$ was obtained. Next, 60 ml of THF was placed in another 200 ml glass flask and cooled to −20°C. Subsequently, 4.9 g of $ZrCl_4$ was slowly added to the THF. After the addition, the system was heated to 60°C and stirred for 1 h at that temperature to dissolve $ZrCl_4$. The dilithium salt prepared above was dropped into the $ZrCl_4$ solution over 30 min and reacted at 60°C for 1 h. Then the system was cooled to room temperature and further stirred for 24 h. Finally, *rac*-$Et(Ind)_2ZrCl_2$ was obtained by evaporating off the THF and washing with methanol.

Preparation of an $MgCl_2$-supported $TiCl_4$ catalyst and methylaluminoxane

The Ti catalyst[12] and methylaluminoxane[13] were prepared according to previous papers.

Polymerization of propylene with Zr catalyst system

Toluene (500 ml), 250 ml of propylene and 10 mmol, as Al atom, of methylaluminoxane were placed at room temperature in a 2 litre stainless-steel reactor equipped with a stirrer. The system was cooled or raised to the polymerization temperature and then 1×10^{-3} mmol of *rac*-$Et(Ind)_2ZrCl_2$ was added. Polymerizations were carried out for 1 or 6 h at the prescribed temperature, and were terminated by introducing a small amount of methanol. The whole product was poured into a large

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excess of methanol. The resulting powdery polymer was collected by filtration and vacuum dried at 80°C for 12 h.

Polymerization of propylene with Ti catalyst system

Into a 1 litre glass reactor equipped with a stirrer was placed 500 ml of n-decane, and a gas mixture of propylene and hydrogen was introduced into the system, at rates of 200 and 10 l h^{-1}, respectively. Subsequently, 2.5 mmol of Et_3Al and 0.1 mmol, as Ti atom, of Ti catalyst were added at 50°C in that order. Polymerization was performed under atmospheric pressure at 50°C for 30 min and stopped by the addition of a small amount of methanol. The polymer obtained was collected by the same method as for the Zr catalyst system.

Copolymerization of propylene and ethylene with Zr catalyst system

Copolymerizations were carried out in the same manner as for the propylene polymerization with Ti catalyst system, except for introducing a gas mixture of propylene and ethylene in the prescribed amount and the following conditions: 2.5 mmol, as Al atom, of methylaluminoxane, 5×10^{-3} mmol of $Et(Ind)_2ZrCl_2$, 250 ml of toluene, 30°C polymerization temperature and 0.5 or 1 h polymerization time under atmospheric pressure.

Fractionation of polymer

Five grams of polymer were dissolved at 130°C in 1 litre of n-decane and the resulting polymer solution was poured into a large amount of methanol. The precipitated polymer was collected by filtration and vacuum dried at 80°C for 12 h. The dried polymer was pulverized to a fine powder less than 42 mesh in particle size in a mortar and pestle. Next, 3 g of the pulverized polymer was extracted for 5 h by 180 ml of boiling n-pentane (C_5), n-hexane (C_6), n-heptane (C_7) and trichloroethylene (T) using a Soxhlet extractor as in *Scheme 1*. The insoluble polymer fraction was vacuum dried and used for the next extraction, while the soluble fraction was recovered by evaporating off the solvent from the extract.

^{13}C n.m.r. analysis

The polymer solution was prepared by dissolving ~150 mg of the polymer sample at 120°C in a mixture of 0.5 ml hexachlorobutadiene and 0.1 ml deuteriobenzene. ^{13}C n.m.r spectra were recorded on a Jeol GX-500 spectrometer operating at 125.8 MHz under proton noise decoupling in Fourier-transform mode. Instrument conditions were as follows: pulse angle 45°, pulse repetition 4.2 s, spectral width 7500 Hz, number of pulses 5000–10 000, temperature 110°C, data points 64 000.

G.p.c. analysis

The molecular weight of the polymer sample was determined by g.p.c. (Waters Associates, model ALC/GPC/150C) using a mixed polystyrene gel column (10^6–10^3 Å pore size) and *o*-dichlorobenzene as solvent at 140°C.

D.s.c. analysis

D.s.c. analyses were carried out with a differential scanning calorimeter (Perkin–Elmer 7). The calibration of the instrument was performed by measurement of the melting points of indium and lead. The weight of the sample was ~2.5 mg. A heating rate of 10°C min^{-1} was used in the runs.

RESULTS AND DISCUSSION

Characterization of homo-PP with the Zr and Ti systems

Propylene polymerizations were performed with *rac*-$Et(Ind)_2ZrCl_2$ in conjunction with methylaluminoxane ($Al/Zr = 2 \times 10^3$ or 1×10^4) in the range −30 to 50°C. As shown in *Table 1*, the catalyst activity per unit Zr atom depended strongly upon the polymerization temperature, i.e. very high (82 600 g PP/mmol Zr h) at 50°C, but low (60 g PP/mmol Zr h) at −30°C. The

Scheme 1

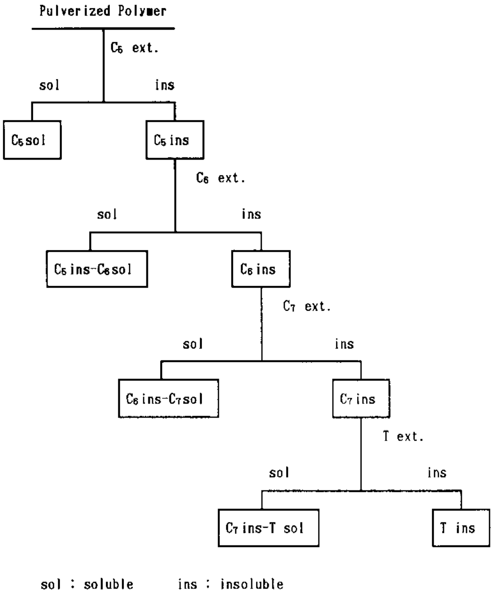


Table 1 Results of propylene polymerization[a]

Run no.	Temperature (°C)	Yield (g)	Activity (g PP/mmol Zr h)	C_5-sol (wt%)	C_5-ins/C_6-sol (wt%)	C_6-ins/C_7-sol (wt%)	C_7-ins/T-sol (wt%)
1	50	82.6	82 600	1.5	13.5	85.0	0
2	30	67.5	67 500	1.5	2.2	96.3	0
3	10	21.2	21 200	0.8	0.7	94.3	4.2
4	−10	12.6	2 100	0.9	0.6	84.0	14.5
5	−20	3.9	130	3.3	1.9	65.8	29.0
6	−30	1.8	60	9.3	3.7	46.3	41.0

[a] Polymerization conditions: 0.001 mmol of Zr (0.005 mmol for runs 5 and 6) and 10 mmol of Al in a mixture of propylene (3 mol) and toluene (500 ml) for 1 h (6 h for runs 4, 5 and 6)

powdery polymer samples were successively fractionated by boiling n-pentane (C_5), n-hexane (C_6), n-heptane (C_7) and trichloroethylene (T) into four portions: pentane-soluble (C_5-sol); pentane-insoluble/hexane-soluble (C_5-ins/C_6-sol); hexane-insoluble/heptane-soluble (C_6-ins/C_7-sol); and heptane-insoluble/trichloroethylene-soluble (C_7-ins/T-sol). No trichloroethylene-insoluble (T-ins) fraction was present for all samples; and the C_5-sol fraction was present in very small amounts, 1–3 wt%, except for 9.3 wt% in the -30°C polymerization. On the other hand, 84–96 wt% (-10 to 50°C) and 87–95 wt% (-20 and -30°C) of the whole polymer was C_6-ins/C_7-sol fraction or C_6-ins/C_7-sol and C_7-ins/T-sol fractions, respectively. These results indicate that the samples examined are of considerably homogeneous composition.

The whole and fractionated polymers were characterized by g.p.c., ^{13}C n.m.r and d.s.c. analyses. The results are listed in *Table 2*.

The values of the polydispersity ($\bar{M}_w/\bar{M}_n$) of the whole polymers were 1.77–2.90 (*Table 2a*), and thus there is a relatively narrow molecular-weight distribution. The observed homogeneity of the polymer composition would be attributable to the homogeneous nature of the active centres in the soluble catalyst system.

The molecular weight of the whole polymers was increased significantly on lowering the polymerization temperature in the range -10 to 50°C ($\bar{M}_n = 1.98 \times 10^4$ at 50°C, $\bar{M}_n = 5.53 \times 10^4$ at -10°C), but $\bar{M}_n$ was limited to $(4\text{–}5) \times 10^4$ at -20 and -30°C polymerization, suggesting that the maximum molecular weight obtainable with this Zr catalyst system would be rather low.

The molecular weight ($\bar{M}_n$) of the fractionated polymers tended to be higher in the following order: C_7-ins/T-sol > C_6-ins/C_7-sol > C_5-ins/C_6-sol. However, the $\bar{M}_n$ value of the C_7-ins/T-sol fraction in run no. 3 (5.46×10^4) was comparable to that of the C_6-ins/C_7-sol fraction in run no. 4 (5.16×10^4). Thus, the fractionation was due not merely to a difference in molecular weight.

From *Table 2b*, the following conclusions can be obtained:

(1) The *mm* (*meso–meso*) triad sequence contents (*mm* = *mmmm* + *mmmr* + *rmmr*) of all the samples examined including C_5-ins/C_6-sol and C_6-ins/C_7-sol fractions were ~92–97%, high enough to define these fractions as 'isotactic polypropylene', although most of them were soluble in boiling n-heptane.

(2) A trend of increase in *mmmm* values could be noticed among C_6-ins/C_7-sol fractions lowering the polymerization temperature.

(3) In *rr* (*rac–rac*) triad sequences, almost exclusively *mrrm* was observed; while, in *mr* triad sequences, *mmrr* was predominant over *mmrm* or *mrmr*. These findings strongly suggest that the steric structures of the active centres, but not polymer chain ends, would be responsible for isotactic chain formation.

Next, in order to compare the observed features of the Zr system with those of a typical heterogeneous Ti catalyst system, a polypropylene (PP) was prepared with an $MgCl_2$-supported $TiCl_4$ catalyst in conjunction with Et_3Al and was fractionated by the same method as in the Zr catalyst system. The data are shown in *Table 3*.

The molecular weight ($\bar{M}_n$) of the whole PP obtained was 8.3×10^3 with the use of H_2 as a chain transfer agent.

Table 2 Characterization of PP with Zr system

(a) Data by g.p.c. and d.s.c. analysis

Run no.		Whole	C_5-ins/C_6-sol	C_6-ins/C_7-sol	C_7-ins/T-sol
1	$\bar{M}_n$ ($\times 10^{-4}$)	1.98	1.43	2.13	
	$\bar{M}_w/\bar{M}_n$	1.77	1.82	1.77	
	T_m (°C)	130.6	127.0	131.0	
2	$\bar{M}_n$ ($\times 10^{-4}$)	3.20	0.97	3.10	
	$\bar{M}_w/\bar{M}_n$	1.73	1.74	1.68	
	T_m (°C)	137.7	133.9	138.2	
3	$\bar{M}_n$ ($\times 10^{-4}$)	4.28		3.99	5.46
	$\bar{M}_w/\bar{M}_n$	1.77		1.89	1.68
	T_m (°C)	143.5		142.4	144.0
4	$\bar{M}_n$ ($\times 10^{-4}$)	5.53		5.16	7.02
	$\bar{M}_w/\bar{M}_n$	1.80		1.87	1.75
	T_m (°C)	147.5		146.6	147.8
5	$\bar{M}_n$ ($\times 10^{-4}$)	4.64		4.60	7.44
	$\bar{M}_w/\bar{M}_n$	2.27		2.10	1.69
	T_m (°C)	149.2		148.5	149.4
6	$\bar{M}_n$ ($\times 10^{-4}$)	3.76		3.81	7.18
	$\bar{M}_w/\bar{M}_n$	2.90		2.39	1.83
	T_m (°C)	151.2		148.7	151.2

(b) Data by ^{13}C n.m.r.[a]

Run no.	Fraction	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm* + *rmrr*	*mrmr*	*rrrr*	*rrrm*	*mrrm*
1	C_5-ins/C_6-sol	86.3	5.2	0.1	5.2	0.8	0	0	0.1	2.2
1	C_6-ins/C_7-sol	88.6	4.4	0	4.4	0.7	0	0	0	1.9
3	C_6-ins/C_7-sol	93.4	2.5	0	2.7	0.2	0	0	0	1.3
4	C_6-ins/C_7-sol	95.2	1.8	0	2.1	0	0	0	0	1.0
4	C_7-ins/T-sol	94.6	2.3	0	2.1	0.2	0	0	0	0.8
6	C_7-ins/T-sol	95.4	1.8	0	1.8	0.2	0	0	0	0.8

[a] Methyl groups of regio-irregular sequence were excluded in the estimation of tacticity

Table 3 Characterization of PP with Ti system

	Fraction (wt%)	M_n ($\times 10^{-4}$)	M_w/M_n	T_m [a] (°C)	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*mmrm*+*rmrr*	*mrmr*	*rrrr*	*rrrm*	*mrrm*
Whole		0.83	5.53	144.1, $\underline{156.4}$									
C_5-sol	43.9	0.46	4.95	n.d.	23.4	12.5	2.9	15.1	12.4	3.6	12.1	11.1	6.7
C_5-ins/C_6-sol	16.5	0.99	3.05	$\underline{117.9}$, 129.0	59.4	10.0	0.6	10.0	3.2	0.7	3.1	2.3	4.7
C_6-ins/C_7-sol	10.9	1.21	2.57	$\underline{135.8}$, 143.9	77.5	7.3	0.5	6.9	3.1	0.1	0.9	0.8	2.9
C_7-ins/T-sol	7.2	1.82	2.70	$\underline{147.8}$, 157.2	85.5	4.9	0.3	4.7	1.1	0.2	0.7	0.6	2.0
T-ins	21.5	3.50	2.50	$\underline{156.5}$, 163	93.5	2.7	0	2.3	0.3	0.1	0	0.1	1.0

[a] n.d., not detected; main peak underlined

Unlike the Zr system, the value of the polydispersity was rather large ($\bar{M}_w/\bar{M}_n = 5.53$) and there was a considerable amount of residue (21.9 wt%) after boiling trichloroethylene extraction and a large amount of C_5-sol fraction (43.9 wt%).

Further, by comparing the results in *Table 3* with those of the Zr system, the following can be pointed out for the polymers of the Ti system:

(1) The *mm* values of the fractions varied over a broad range (96.2% (T-ins), 70.0% (C_5-ins/C_6-sol) and 38.8% (C_5-sol)), indicating that this Ti-catalysed polymer was a mixture of polymers having much different stereospecificities and that fractionation was due at least to a difference in stereo-specificity of the polymer.

(2) The *mm* values were always considerably smaller than those of the corresponding Zr-catalysed fractions (in particular for the C_5-ins/C_6-sol fraction, i.e. 70.0% (Ti) compared to 91.6% (Zr)).

(3) The pentad sequences such as *rmmr*, *mrmr*, *rrrr* and *rrrm*, unlike the Zr-catalysed polymers, were present significantly and the amount increased in the fraction soluble in the poorer solvent.

(4) The C_5-sol fraction, which was hardly present in the Zr-catalysed polymers, was present in the highest quantity. The ^{13}C n.m.r data showed that this fraction was most likely atactic PP.

(5) The *mm* value of the T-ins fraction was comparable to those of C_7-ins/T-sol fractions or even C_6-ins/C_7-sol fractions, with the Zr system having almost the same or even higher molecular weight.

The observed higher solubility of the highly stereospecific polymers with the Zr system cannot be clearly explained, but would be due to the distinctive microstructure of the polymer chain, as discussed next.

The ^{13}C n.m.r spectra of C_6-ins/C_7-sol fractions of the Zr and Ti catalyst systems are shown in *Figures 1* and *2*, respectively.

The spectrum of the Zr system exhibited a number of small irregular peaks, which were not observed in the Ti system, showing a significant difference in microstructure between the two catalyst systems. They were assigned to peaks arising from 2,1-insertion of propylene monomer (the formation of head-to-head or tail-to-tail enchainment) and 1,3-insertion of propylene monomer (that of $-(CH_2)_4-$ unit), based on the additive rules for chemical-shift calculation[14], d.e.p.t. (distortionless enhancement by polarization transfer) measurement for the determination of carbon species and two-dimensional n.m.r. in ^{13}C–H correlation. These peak assignments are shown in *Table 4* and *Figure 1*. Soga[15] and Zambelli[16] have also reported that 2,1- and 1,3-insertions take place in propylene polymerization with a similar Zr catalyst system.

The frequency of 2,1- and 1,3-insertions can be calculated by:

$$2,1\text{-insertion } (\%) = \frac{0.5 I_{\alpha\beta}}{I_{\alpha\alpha} + I_{\alpha\beta} + I_{\alpha\delta}} \times 100 \qquad (1)$$

$$1,3\text{-insertion } (\%) = \frac{0.5 I_{\alpha\delta}}{I_{\alpha\alpha} + I_{\alpha\beta} + I_{\alpha\delta}} \times 100 \qquad (2)$$

where I denotes the sum of the intensity of each peak resonated at 41.84, 42.92 and 46.22 ppm for α,α-methylene carbon, 30.13, 32.12, 35.11 and 35.57 ppm for α,β-methylene carbon, and 37.08 ppm for α,δ-methylene carbon. The results of the calculation for C_6-ins/C_7-sol or C_7-ins/T-sol fractions are shown in *Table 5*. As shown, the higher the polymerization temperature, the more frequently 2,1- and 1,3-insertions occurred.

Furthermore, the relations between T_m and *mm* values were apparently different between the Zr and Ti systems, as seen in *Figure 3* (for PP of the Ti system, two T_m values were plotted owing to the presence of two peaks in the d.s.c. curves, unlike PP of the Zr system, which has a single peak). T_m values of the Zr system were always more than 10°C or even 20°C lower than those of the Ti system having the same *mm* values. In other words, for example, the *mm* value to give $T_m = 150°C$ was 97% for the Zr system but only 90% for the Ti system.

These results and the higher solubility of the Zr-catalysed polymers would be attributable to the characteristic microstructure of the subject polymers, i.e. the presence of head-to-head or tail-to-tail enchainments and the $-(CH_2)_4-$ units in a polymer chain.

The above consideration may be supported by the fact that in two fractions with almost the same *mm* value (C_6-ins/C_7-sol of run no. 4 and C_7-ins/T-sol of run no. 6), the sample having larger amount of 2,1-inserted propylene units showed 4.6°C lower T_m.

Characterization of copolymer with the Zr system

Copolymerizations of propylene with various amounts of ethylene were performed at 30°C. The whole polymers obtained were characterized by ^{13}C n.m.r analysis. The results are listed in *Table 6*. With the introduction of ethylene, the activity was enhanced a maximum of eight times by incorporating 22 mol% ethylene units into the copolymer, while the *mm* values of propylene unit sequences were hardly affected.

Next, the change of the frequency of 2,1-insertion by the introduction of ethylene was investigated. Here, when 2,1-insertion takes place in copolymerization, β,γ-methylene carbon based on ethylene monomer might be formed in addition to α,β-methylene carbon as shown in *Scheme 2*.

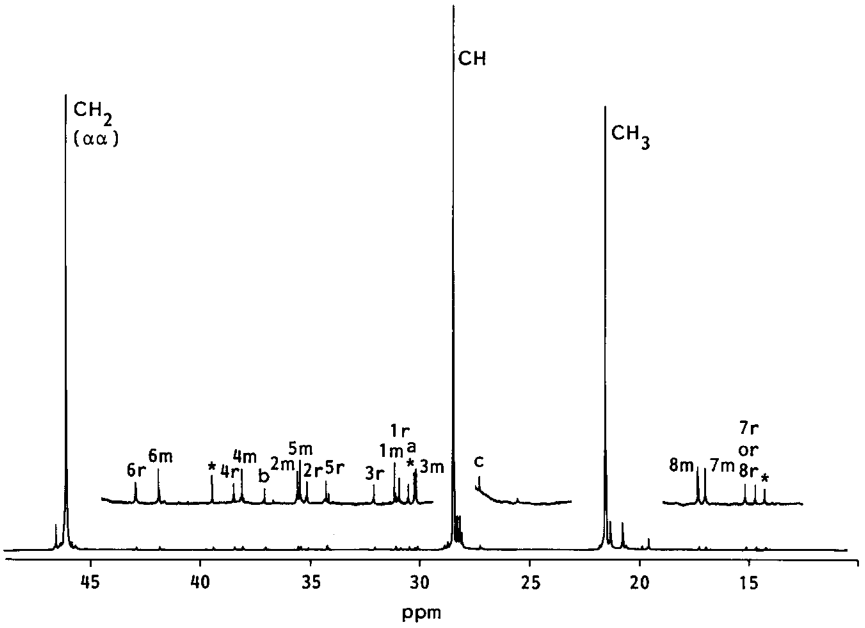
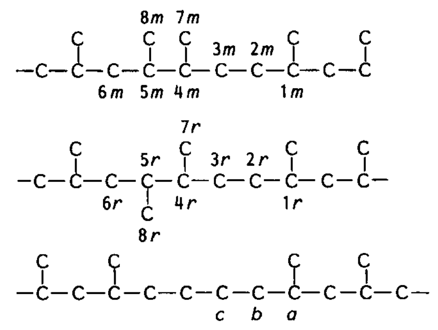


Figure 1 ^{13}C n.m.r. spectrum of C_6-ins/C_7-sol fraction with Zr catalyst system. Asterisks (*) indicate peaks based on polymer chain end

Table 4 Chemical shift of irregular peaks in C_6-ins/C_7-sol fraction with Zr system

Peak no.	Chemical shift (ppm) Obs.	Calc.	Carbon species
1*m*	31.12	31.36	CH
2*m*	35.57	35.55	CH_2 (α,β)
3*m*	30.13	30.25	CH_2 (α,β)
4*m*	38.06	38.38	CH
5*m*	35.44	35.89	CH
6*m*	41.84	41.87	CH_2
7*m*	17.00	17.14	CH_3
8*m*	17.26	17.83	CH_3
1*r*	30.92	31.32	CH
2*r*	35.11	35.09	CH_2 (α,β)
3*r*	32.12	32.12	CH_2 (α,β)
4*r*	38.52	38.08	CH
5*r*	34.25	34.92	CH
6*r*	42.92	43.02	CH_2
7*r* or 8*r*	14.63	15.34	CH_3
8*r* or 7*r*	15.15	15.12	CH_3
a	30.50	30.96	CH
b	37.08	37.31	CH_2 (α,δ)
c	27.35	27.61	CH_2



However, in the observed charts (particularly runs no. 7–10), the number of β,γ-methylene carbons was negligibly small, less than one-tenth the number of α,β-methylene carbons, indicating that 2,1-insertion to Zr–EP~ active centre or ethylene insertion to Zr–EP′~ hardly occurs, where E, P and P′ are ethylene,

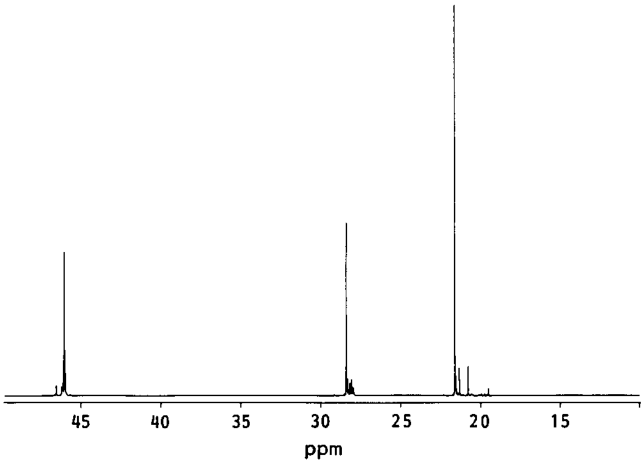


Figure 2 ^{13}C n.m.r. spectrum of C_6-ins/C_7-sol fraction with Ti catalyst system

Table 5 Frequency of 2,1- and 1,3-insertions of propylene monomer

Run no.	Polymerization temperature (°C)	Fraction	Insertion 2,1- (%)	1,3- (%)
1	50	C_6-ins/C_7-sol	0.60	0.10
3	10	C_6-ins/C_7-sol	0.47	0.05
4	−10	C_6-ins/C_7-sol	0.32	<0.02
6	−30	C_7-ins/T-sol	0.09	<0.02

Scheme 2

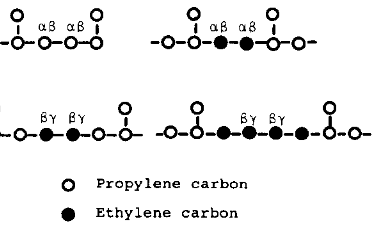


Table 6 Results of copolymerization of propylene with a small amount of ethylene[a]

Run no.	Propylene ($l\,h^{-1}$)	Ethylene ($l\,h^{-1}$)	Yield (g)	Activity (g polymer/mmol Zr h)	Ethylene content (mol%)	*mm*[b] (%)
7	100	0	11.1	2200	0	92
8	160	3	22.9	4580	1.3	93
9	95	5	18.2	3640	4.7	92
10	90	10	21.2	8480	7.4	91
11	80	20	43.9	17600	22	89

[a] Polymerization conditions: 30°C for 1 h (0.5 h for runs 10 and 11) under atmospheric pressure, 0.005 mmol of Zr and 2.5 mmol of Al in 250 ml of toluene

[b] *mm* value in propylene sequences

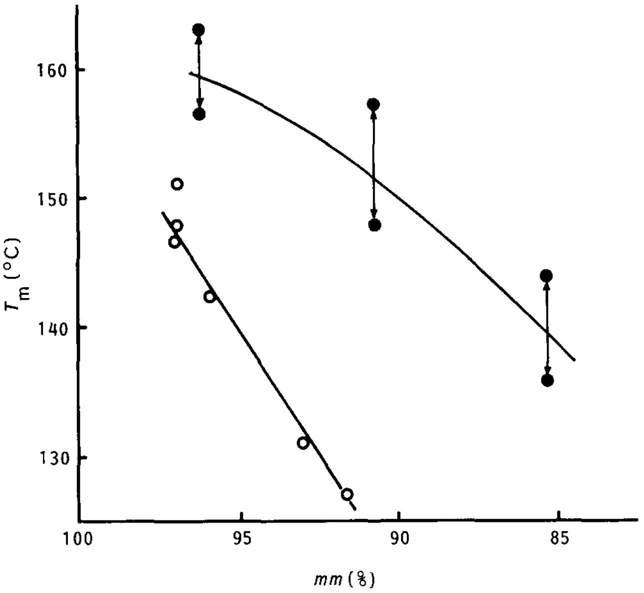


Figure 3 Relation between T_m and *mm* value in Zr- and Ti-catalysed PP: (○) Zr; (●) Ti

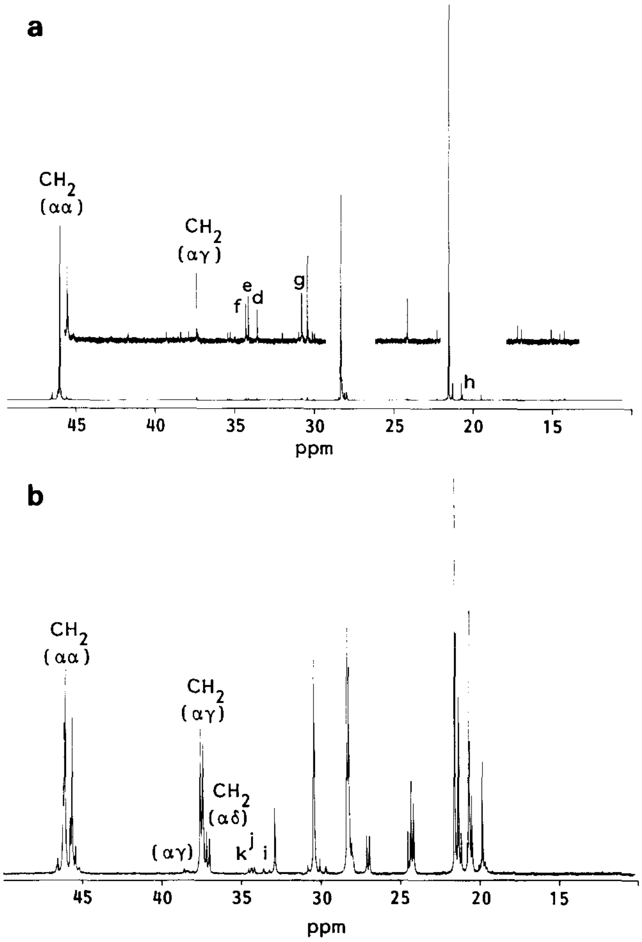
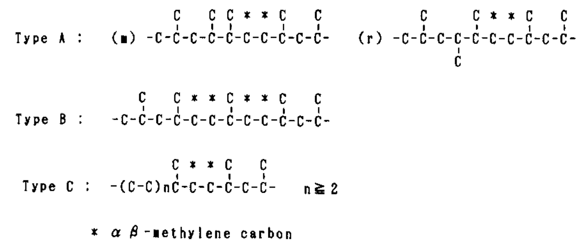


Figure 4 ^{13}C n.m.r. spectra of copolymers having ethylene content of (a) 1.3 mol% and (b) 22 mol%

Scheme 3



1,2-inserted propylene and 2,1-inserted propylene, respectively.

The ^{13}C n.m.r spectra of runs no. 8 and 11 are shown in *Figure 4* with the assignments for the irregular peaks (see also *Table 7*). From these, it was clear that three types of α,β-methylene carbons, types A (divided further into (*m*) and (*r*)), B and C, were present in the examined polymers (*Scheme 3*).

A reaction scheme that generates α,β-methylene carbons of types A, B and C can be drawn as shown in *Scheme 4*.

From the spectra, the numbers ($N_{\alpha\beta}$) of α,β-methylene carbons per incorporated propylene unit for each type were determined by:

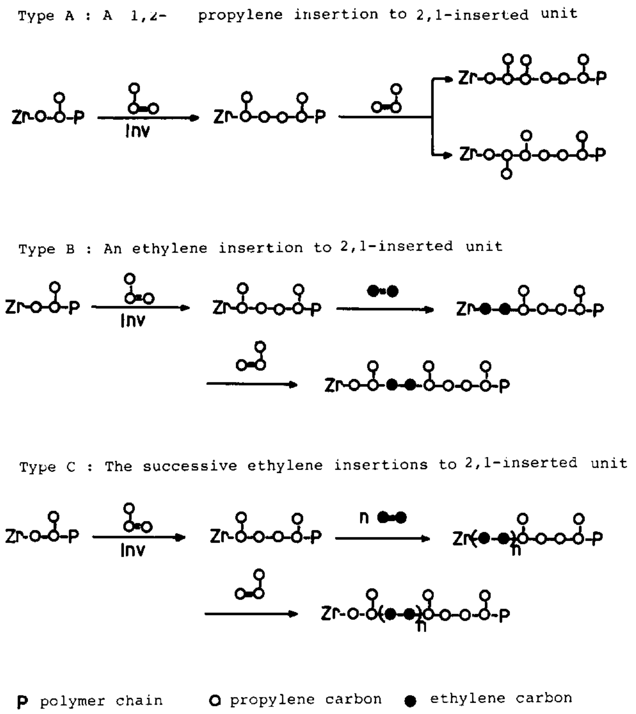
$$N_{\alpha\beta}=\frac{I_{\alpha\beta}\,(\text{in each type})}{I_{\alpha\alpha}+I_{\alpha\beta}+0.5(I_{\alpha\gamma}+I_{\alpha\delta})} \tag{3}$$

These values are given in *Table 8*; as seen in the table, in the homopolymer, of course, only type A was present. With the introduction of a small amount of ethylene unit, type A decreased rapidly and type B appeared as the major type. On further increase of ethylene units, type A disappeared completely, while only type B was observed. These facts reveal that monomer insertion at 2,1-inserted propylene unit chain ends was preferentially made by ethylene.

As is expected, type C was found in the copolymer having a high ethylene content (22 mol%). Further, it is to be noted that the ratios of (*r*)/(*m*) placement (0.61 (run 7), 0.60 (run 8)) were considerably high, showing the lowering of stereo-specificity after 2,1-insertion of propylene monomer.

According to the above reaction scheme, the number of α,β-methylene carbons formed by one 2,1-insertion is

Scheme 4



two for types A and C and four for type B. Therefore, the frequency (*F*) of 2,1-insertion in all propylene insertions can be calculated by:

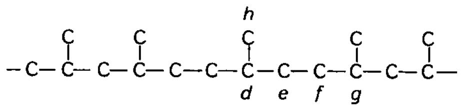
$$F\,(\%) = \frac{0.5 I_{\alpha\beta}\ (\text{in types A and C}) + 0.25 I_{\alpha\beta}\ (\text{in type B})}{I_{\alpha\alpha} + I_{\alpha\beta} + 0.5(I_{\alpha\gamma} + I_{\alpha\delta})} \times 100 \tag{4}$$

As shown in *Table 8*, the frequencies were slightly increased from 0.58% to 0.88% with increase of ethylene content in the polymer, suggesting that 2,1-insertion would take place more frequently when the ethylene unit is present at or near a growing polymer chain.

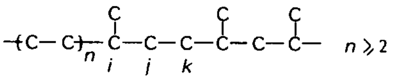
Similar phenomena were also observed in the amorphous copolymer fractions with an $MgCl_2$-supported $TiCl_4$ catalyst system in a previous paper by the authors[17].

Table 7 Chemical shift of irregular peaks in copolymer

	Chemical shift (ppm)		
Peak no.	Obs.	Calc.	Carbon species
d	33.62	33.98	CH
e	34.17	34.49	CH_2 (α,β)
f	34.33	34.79	CH_2 (α,β)
g	30.82	31.32	CH
h	20.05	20.31	CH_3
i	33.24	33.62	CH
j	34.41	34.69	CH_2 (α,β)
k	34.57	34.79	CH_2 (α,β)



$$-\mathrm{C}-\overset{\mathrm{C}}{\mathrm{C}}-\mathrm{C}-\overset{\mathrm{C}}{\mathrm{C}}-\mathrm{C}-\mathrm{C}-\underset{d}{\overset{\overset{h}{\mathrm{C}}}{\mathrm{C}}}-\underset{e}{\mathrm{C}}-\underset{f}{\mathrm{C}}-\underset{g}{\overset{\mathrm{C}}{\mathrm{C}}}-\mathrm{C}-\overset{\mathrm{C}}{\mathrm{C}}-$$



$$-(\mathrm{C}-\mathrm{C})_n-\underset{i}{\overset{\mathrm{C}}{\mathrm{C}}}-\underset{j}{\mathrm{C}}-\underset{k}{\mathrm{C}}-\overset{\mathrm{C}}{\mathrm{C}}-\mathrm{C}-\overset{\mathrm{C}}{\mathrm{C}}- \quad n \geqslant 2$$

Table 8 Frequency of 2,1-insertion in copolymerization[a]

		$N_{\alpha\beta} \times 100$				
	Ethylene content	Type A				
Run no.	(mol%)	(*m*)	(*r*)	Type B	Type C	*F* (%)
7	0	0.72	0.44	–	–	0.58
8	1.3	0.20	0.12	1.72	–	0.59
9	4.7	–	–	2.40	–	0.60
10	7.4	–	–	2.56	–	0.64
11	22	–	–	1.40	1.06	0.88

[a] Dash (–) indicates not detected

REFERENCES

1 Sinn, H. and Kaminsky, W. *Adv. Organomet. Chem.* 1980, **18**, 99
2 Kaminsky, W., Miri, M., Sinn, H. and Woldt, R. *Makromol. Chem., Rapid Commun.* 1983, **4**, 417
3 Herwig, J. and Kaminsky, W. *Polym. Bull.* 1983, **9**, 464
4 Kaminsky, W. 'Transition Metal Catalyzed Polymerization', Vol. 4, 'Alkenes and Dienes' (Ed. R. P. Quirk), Harwood, New York, 1983, p. 225
5 Kaminsky, W., Külper, K. and Niedoba, S. *Makromol. Chem., Macromol. Symp.* 1986, **3**, 377
6 Kaminsky, W. and Schlobohm, M. *Makromol. Chem., Macromol. Symp.* 1986, **4**, 103
7 Ewen, J. A. *J. Am. Chem. Soc.* 1984, **106**, 6355
8 Kaminsky, W., Külper, K., Brintzinger, H. H. and Wild, F. R. W. P. *Angew. Chem., Int. Edn. Engl.* 1985, **24**, 507
9 Kaminsky, W. *Angew. Makromol. Chem.* 1986, **145/146**, 149
10 Kaminsky, W. 'Catalytic Polymerization of Olefins' (Eds. T. Keii and K. Soga), Kodansha and Elsevier, Tokyo, 1986, p. 293
11 Marechal, E. and Lepert, A. *Bull. Soc. Chim.* 1967, 2954
12 Kashiwa, N., Yoshitake, J. and Tsutsui, T. *Polymer* 1987, **28**, 1227
13 Tsutsui, T. and Kashiwa, N. *Polym. Commun.* 1988, **29**, 180
14 Cheng, H. N. and Benett, M. A. *Makromol. Chem.* 1987, **188**, 135
15 Soga, K., Shiono, T., Takemura, S. and Kaminsky, W. *Makromol. Chem., Rapid Commun.* 1987, **8**, 305
16 Grassi, A., Zambelli, A., Resconi, L., Albizzati, E. and Mazzocchi, R. *Macromolecules* 1988, **21**, 617
17 Kashiwa, N., Yoshitake, J. and Tsutsui, T. *Polym. Bull.* 1988, **19**, 339