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A study of chain-end structures of polypropylene prepared with $MgCl_2$-supported titanium catalyst

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The chain ends of polypropylene (PP) polymerized at 100°C without molecular hydrogen addition over an $MgCl_2 \cdot TiCl_4 \cdot$ dioctylphthalate/Et_3Al/diphenyldimethoxysilane catalyst system consisted of ethyl and isobutyl groups. This indicates that the chain-transfer reaction in the production of this PP occurred mainly by Et_3Al at 1,2-inserted sites. On the other hand, the terminal groups of PP obtained at 100°C with molecular hydrogen addition over this catalyst system were ethyl, isobutyl, n-propyl and n-butyl groups. The newly detected terminal groups were formed by chain-transfer reactions by hydrogen at 2,1-inserted sites. The observed activity enhancement in this catalyst system would be due to the conversion of dormant 2,1-inserted sites into the active sites by hydrogen addition.

(Keywords: chain transfer; regioregularity; $MgCl_2$-supported Ti catalyst)

INTRODUCTION

It is generally accepted that the mechanism of chain-transfer reactions in propylene polymerization are classified into the following four types, which are caused by (i) alkylaluminium as the cocatalyst, (ii) elimination of β-hydrogen in the chain ends, (iii) propylene monomer and (iv) molecular hydrogen. The analysis of chain-end structures provides an effective method to investigate what types of chain-transfer reactions occur.

A ^{13}C n.m.r. investigation of the chain-end structures of polypropylene (PP) produced with ethylenebis-(1-indenyl)zirconium dichloride has already been reported in polymerizations with and without the addition of molecular hydrogen[1].

However, such an investigation for PP polymerized over the $MgCl_2 \cdot TiCl_4 \cdot$ phthalate/Et_3Al/alkoxysilane catalyst system, which gives a high activity and a high stereospecificity[2–4], has been reported only in the polymerization with the addition of molecular hydrogen at high content[5,6]. This is because the analysis of the chain ends produced without the addition of molecular hydrogen over the above-mentioned catalyst is usually difficult owing to the high molecular weight of the produced PP, in which the concentration of the chain ends becomes too low to detect.

In this paper, propylene polymerization is performed at relatively high temperature over the $MgCl_2 \cdot TiCl_4 \cdot$ dioctylphthalate (DOP)/Et_3Al/diphenyldimethoxysilane (DPDMS) catalyst system. In this polymerization condition, the molecular weight of the obtained PP is low enough even without the addition of molecular hydrogen to analyse the chain-end structures by ^{13}C n.m.r. From the identification of the terminal structures, the chain-transfer reactions associated with this catalyst system will be discussed.

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EXPERIMENTAL

Preparation of catalyst

$MgCl_2/TiCl_4$/DOP catalyst was prepared as follows. In a 800 ml stainless-steel pot containing 2.8 kg of stainless-steel balls (15 mm diameter), 20 g (0.21 mol) of $MgCl_2$ were milled with 0.03 mol of DOP for 8 h under a nitrogen atmosphere. The milled $MgCl_2$ was treated with 200 ml of $TiCl_4$ at 80°C for 2 h. Subsequently, the solid product was separated by filtration and washed twice with hexane.

Propylene polymerization

In a 1 litre glass autoclave equipped with a stirrer, 500 ml of decane was added and the system was charged with propylene. Then 6 mM of Et_3Al, 0.6 mM of DPDMS and 0.1 mM of the catalyst (in terms of Ti) were added at the polymerization temperature. Polymerization was carried out under atmospheric pressure at that temperature for 15 min or 1 h. During polymerization, 50 litre h^{-1} of propylene and from 0 to 5.0 litre h^{-1}

of hydrogen were supplied continuously. After the polymerization time, a small amount of isobutanol was added to the autoclave to arrest polymerization, and then the whole product was poured into a large amount of methanol containing a small amount of hydrochloric acid. The resulting polymer was filtered and vacuum dried at 80°C for 12 h.

Polymer analyses

^{13}C n.m.r. analyses were performed in the following manner. The polymer solution was prepared by dissolving 150 mg of the polymer sample at 120°C in a mixture of 0.5 ml of hexachlorobutadiene and 0.1 ml of perdeuteriobenzene. The ^{13}C n.m.r. spectrum was recorded on a JEOL GX-500 spectrometer operating at 125.8 MHz under proton noise decoupling in Fourier-transform mode. Instrumental conditions were as follows: pulse angle 45°, pulse repetition 4.2 s, spectral width 7500 Hz, number of scans 20 000, temperature 110°C, data points 64 K. The molecular weight of PP was measured by a Millipore Waters 150C gel permeation chromatograph (g.p.c.) equipped with a refractive index detector, using a TSK mixed polystyrene gel column (G3000–G7000, exclusion limits 400 000 000 for polystyrene molecular weight) and *o*-dichlorobenzene as solvent at 140°C. The number-average and weight-average molecular weights (M_n and M_w, respectively) were calculated on the basis of a polystyrene standard calibration. The melting temperature was measured on a Perkin-Elmer DSC-7 differential scanning calorimeter (d.s.c.) in the following manner. First, the sample was heated to 200°C at 20°C min^{-1}, which is well above the melting temperature, and maintained at this temperature for 10 min. Then it was cooled to 30°C at 10°C min^{-1} to crystallize, followed by reheating at 10°C min^{-1}. The thermogram of each sample was recorded in the second heating run in order to remove the thermal history. The instrument was calibrated by the melting points of indium and lead.

RESULTS AND DISCUSSION

First of all, the molecular weights of PP obtained in the range of 50–100°C over $MgCl_2 \cdot TiCl_4 \cdot DOP/Et_3Al/$ DPDMS catalyst system without molecular hydrogen addition were measured to estimate whether any sample could be analysed by ^{13}C n.m.r. in order to identify the terminal groups. The results of the polymerizations at 50–100°C are summarized in *Table 1*, which shows that the molecular weight of the obtained PP drops as the polymerization temperature is raised.

Since the molecular weight of the PP obtained at 100°C was low enough, the terminal groups of this PP were studied by ^{13}C n.m.r. The upper part of *Figure 1* shows the ^{13}C n.m.r. spectrum of PP polymerized at 100°C without molecular hydrogen addition. The carbon peaks associated with the terminal groups of the PP sample were assigned by using Lindeman–Adams empirical parameters[7].

The terminal groups of this PP were ethyl group (Et) and isobutyl group (i-Bu) with 1 : 1 ratio. All the possible terminal groups formed by chain-transfer reactions without molecular hydrogen addition are shown in equations (1)–(10) in *Figure 2a*. The PP having the same ratio of Et to i-Bu as the terminal groups is formed only though the reaction by Et_3Al in accordance with equation (1) in *Figure 2a* followed by solvolysis by methanol. This indicates that the chain-transfer reaction by Et_3Al at 1,2-inserted sites was much faster than any other chain-transfer reactions in this polymerization condition.

In fact, by increasing the concentration of Et_3Al, the molecular weight of the obtained PP was clearly decreased (see *Table 2*). Besides, the molecular-weight distribution widened and the melting temperature dropped with the decrease of the molecular weight. These changes on increasing the concentration of Et_3Al correspond to those obtained by raising the polymerization temperature, as summarized in *Table 1*, suggesting that the decrease of the molecular weight with rising polymerization temperature would be due to the promotion of the chain-transfer reaction by alkylaluminium.

Next, propylene polymerization at 100°C over this catalyst system was performed with the addition of molecular hydrogen (see *Table 3*).

With a view to investigating the chain-end structures, the PP of run No. 3 in *Table 3* was analysed by ^{13}C n.m.r. The spectrum is shown in the lower part of *Figure 1* in comparison with that of the PP produced without the molecular hydrogen addition. Et, i-Bu, n-propyl group (n-Pr) and n-butyl group (n-Bu) were detected as terminal groups in the proportions of 40, 44, 10 and 6%, respectively, where n-Pr and n-Bu were newly detected terminal groups by the addition of molecular hydrogen. All the schemes that form the terminal groups in the polymerization with the molecular hydrogen addition are shown in *Figure 2b*.

n-Pr as the terminal group can be formed through 1,2-insertion of propylene monomer into the Ti–H bond in equation (10) in *Figure 2*. n-Bu as the terminal group can be formed through the chain-transfer reaction by Et_3Al at 2,1-inserted sites in equation (4) followed by solvolysis by methanol or chain-transfer reaction by molecular hydrogen at 2,1-inserted sites in equation (12).

Table 1 Results of propylene polymerization without hydrogen addition at various polymerization temperatures[a]

Run no.	Temp. (°C)	Yield (g)	Activity (g PP/mmol Ti)	M_n	M_w/M_n	M.p. (°C) Main	M.p. (°C) Shoulder
1	50	5.80	116	78 200	5.83	157.6	162.7
2	70	8.29	166	24 800	7.97	158.4	
3	100	1.79	36	9 900	10.0	155.0	160.9

[a] Polymerization conditions: 50 litre h^{-1} of propylene under atmospheric pressure, 0.1 mmol^{-1} of Ti, 0.6 mmol l^{-1} of DPDMS, 6.0 mmol l^{-1} of Et_3Al in 0.5 litre of n-decane, 15 min (run nos 1, 2) or 1 h (run no. 3) of polymerization time

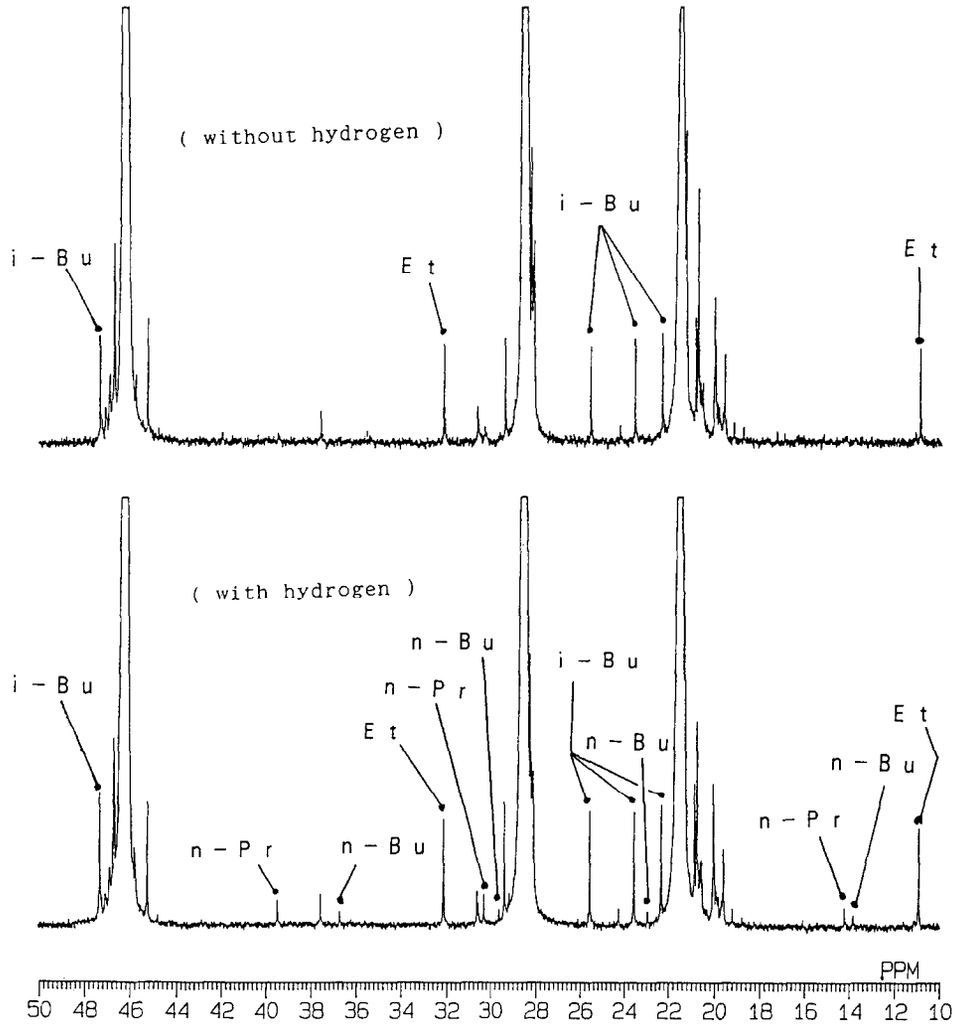

Figure 1 ^{13}C n.m.r. spectra of PP polymerization at 100°C with or without hydrogen, with assignment of chain ends

Though the chain-transfer reaction of equation (4) can occur even without the molecular hydrogen addition, equation (12) cannot take place without molecular hydrogen addition. Since n-Bu was not detected in the polymerization without the molecular hydrogen addition as mentioned above, the frequency of equation (4) would be very low. Therefore, we believe n-Bu is formed mainly though 2,1-insertion of propylene monomer accompanied by the chain-transfer reaction by molecular hydrogen in equation (12).

Furthermore, no head-to-head regioirregularity in the polymer chain was detected by ^{13}C n.m.r., indicating that the chain propagation reaction after 2,1-insertion is extremely slow in this catalyst system, while the chain-transfer reaction by molecular hydrogen at this site would occur easily, forming n-Bu as a terminal group.

In addition, *Table 3* shows that the activity is enhanced by the molecular hydrogen addition, which is in accord with other reports[8–11].

Eventually, in the polymerization at 100°C, both the chain-transfer reactions and the chain-propagation reactions would seldom occur after 2,1-insertion in the absence of molecular hydrogen (dormant sites). The activity enhancement in this catalyst system by the addition of molecular hydrogen suggests that only the chain-transfer reaction by molecular hydrogen would immediately convert the dormant 2,1-inserted sites into active sites.

Furthermore, in the range of 50–100°C, the rates of activity enhancements by the addition of 0.1 molar

Table 2 Influence of the concentration of Et_3Al on the molecular weight of PP[a]

Run no.	Et_3Al (mmol l^{-1})	Yield (g)	Activity (g PP/mmol Ti)	M_n	M_w/M_n	M.p. (°C) Main	M.p. (°C) Shoulder
1	6	1.79	36	9900	10.0	155.0	160.9
2	18	1.84	37	6700	14.1	151.9	158.9

[a] Polymerization conditions: 50 litre h^{-1} of propylene under atmospheric pressure, 0.1 mmol l^{-1} of Ti, 0.6 mmol l^{-1} of DPDMS in 0.5 litre of n-decane, 1 h at 100°C, without hydrogen addition

Table 3 Influence of hydrogen addition on the results of propylene polymerization[a]

Run no.	H_2 flow ($l\,h^{-1}$)	Yield (g)	Activity (g PP/mmol Ti)	M_n	M_w/M_n	M.p. (°C) Main	M.p. (°C) Shoulder
1	0	1.79	36	9900	10.0	155.0	160.9
2	1.25	3.11	62	8500	6.4	154.6	160.9
3	2.5	2.90	58	7300	5.3	153.7	160.5
4	5.0	2.30	46	6800	4.7	153.3	160.3

[a] Polymerization conditions: 50 litre h^{-1} of propylene under atmospheric pressure, 0.1 mmol l^{-1} of Ti, 0.6 mmol l^{-1} of DPDMS, 6.0 mmol l^{-1} of Et_3Al in 0.5 litre of n-decane, 1 h at 100°C

Table 4 Effect of activity enhancement by hydrogen addition at various polymerization temperatures[a]

Run no.	Temp. (°C)	H_2 flow ($l\,h^{-1}$)	H_2/C_3 mol. ratio in C_{10}	Yield (g)	Activity (g PP/mmol Ti)	Activity ratio (with/without H_2)
1	50	2.5	0.0009	11.23	225	1.94
2	70	2.5	0.0013	14.88	298	1.80
3	100	1.25	0.0009	3.11	62	1.72

[a] Polymerization conditions: 50 litre h^{-1} of propylene under atmospheric pressure, 0.1 mmol l^{-1} of Ti, 0.6 mmol l^{-1} of DPDMS, 6.0 mmol l^{-1} of Et_3Al in 0.5 litre of n-decane, 15 min (run nos 1, 2) or 1 h (run no. 3) of polymerization time

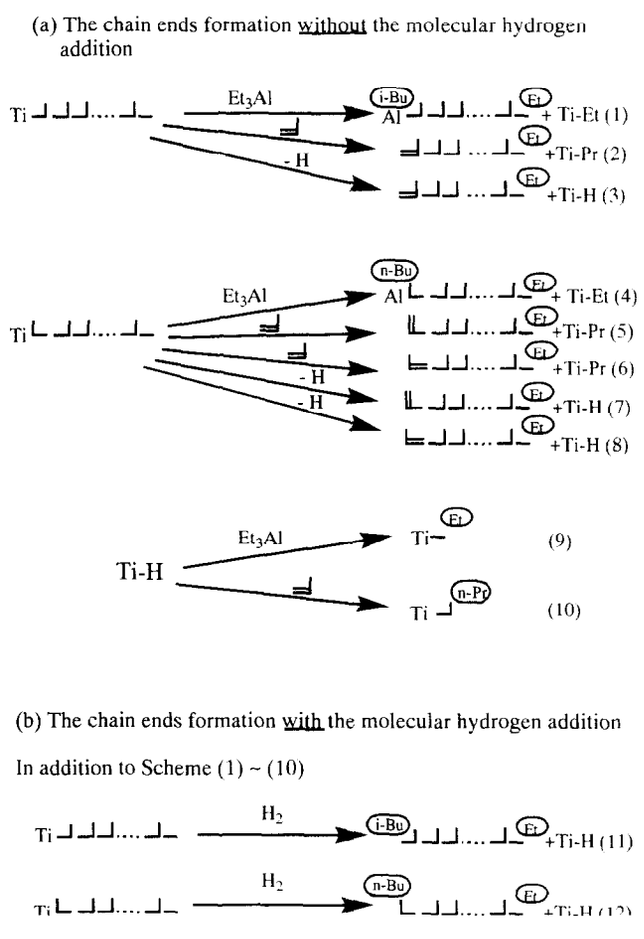

Figure 2 Schemes of all the possible formation reactions of chain ends

hydrogen per 100 molar propylene were investigated (see *Table 4*). The rate of activity enhancements by hydrogen addition tends to increase with the decrease of polymerization temperature in this range. This tendency might imply that the polymerization temperature has a slight influence on the extent of the revival of the dormant sites.

In conclusion, the analysis of the terminal groups in this paper has made clear which chain-transfer reaction occurs dominantly in each polymerization condition, how the 2,1-insertion of the propylene monomer affects the active sites and why the activity is enhanced by molecular hydrogen addition.

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