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Effect of an external donor upon chain-transfer reactions in propylene polymerization with a MgCl$_2$-supported titanium catalyst system

Shin-ichi Kojoh[a],*, Toshiyuki Tsutsui[a], Norio Kashiwa[a], Masaaki Itoh[b] and Akira Mizuno[b]

[a]*Polymers Laboratories, Mitsui Petrochemical Industries Ltd., 6-1-2 Waki, Waki-cho, Kuga-gun, Yamaguchi-ken, 740, Japan*
[b]*Analysis Laboratories, San Analysis and Consulting Service, Ltd., 6-1-2 Waki, Waki-cho, Kuga-gun, Yamaguchi-ken, 740, Japan*

The chain-end groups of the polypropylene (PP) polymerized without addition of molecular hydrogen over a MgCl$_2$·TiCl$_4$·dioctylphthalate/Et$_3$Al catalyst system consisted of *n*-butyl, *n*-propyl, vinylidene and vinyl groups in addition to ethyl and *i*-butyl groups which were detected in the PP prepared under the same polymerization conditions except for the addition of diphenyldimethoxysilane (DPDMS) as an external donor. The newly detected chain-end groups indicate that the additional chain-transfer reactions were brought about by Et$_3$Al at 2,1-inserted sites and by β-hydrogen elimination at both 1,2- and 2,1-inserted sites. These chain-transfer reactions could account for the observed drops of the activity and the molecular weight in the absence of DPDMS. In addition, the detected chain ends in the PP polymerized with addition of molecular hydrogen over this catalyst system having no DPDMS suggest that the molecular hydrogen addition leads not only to the conversion of the dormant 2,1-inserted sites into the active sites, but also to a decrease in the frequency of 2,1-insertion. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

It is generally accepted that the mechanisms of chain-transfer reactions in propylene polymerization can be classified into the following four types, which are caused by (i) alkylaluminium as a 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.

However, such an investigation for polypropylene (PP) polymerized with an MgCl$_2$·TiCl$_4$·phthalate/Et$_3$Al/alkoxysilane catalyst system, which is the most commonly used in the current industrial processes and gives high activity and high stereospecificity[1–3], has been reported only in polymerizations with the addition of molecular hydrogen[4–6]. This is because analysis of chain ends produced without addition of molecular hydrogen over the above-mentioned catalyst system is usually difficult owing to the high molecular weight of the PP produced, in which the concentration of the chain ends becomes too low to detect. Recently, although a new MgCl$_2$-supported titanium catalyst system[7] which contains a diether as its component has promoted the study of chain-end structures for the PPs owing to its high sensitivity to the added molecular hydrogen[8,9], the chain-end groups of the PP prepared in the absence of molecular hydrogen could not be determined for the above-mentioned reason. In our previous paper[10], we reported that the molecular weight of the PP polymerized at 100°C using the MgCl$_2$·TiCl$_4$·phthalate/Et$_3$Al/alkoxysilane catalyst system even without the addition of molecular hydrogen is appropriate for the analysis of the chain-end structures by ^{13}C n.m.r.

On the other hand, it has been reported that the addition of an external donor (ED) causes the molecular weight of the PP obtained to increase[11,12]. It has also been reported that the effect of hydrogen on the molecular weight of PP depends upon the nature of the ED[6,12–14]. However, the function of an ED is still unclear, because the chain-transfer reactions using this catalyst system have not been studied in detail.

In this paper, we report the significant differences in the chain-end structures between PP prepared with and without diphenyldimethoxysilane (DPDMS) as an ED using the catalyst system MgCl$_2$·TiCl$_4$·dioctylphthalate (DOP)/Et$_3$Al. Furthermore, we discuss the effect of an ED upon the chain-transfer reactions on the basis of the analysis of the chain-end structures.

EXPERIMENTAL

Preparation of catalyst

An MgCl$_2$·TiCl$_4$·DOP catalyst was prepared as follows.

In an 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 *n*-hexane.

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* To whom correspondence should be addressed

Propylene polymerization

In a 1 L glass autoclave equipped with a stirrer, 500 ml of *n*-decane were added and the system was charged with propylene. Then 6 mM of Et$_3$Al, 0.1 mM of the catalyst (in terms of Ti) and 0 or 0.6 mM of DPDMS were added at polymerization temperature (100°C). Polymerization was carried out under atmospheric pressure at this temperature for 1 h. During the polymerization, 50 L h^{-1} of propylene and 0 or 2.5 L h^{-1} of hydrogen were supplied continuously. After the polymerization time, a small amount of *i*-butanol was added to the autoclave to terminate the 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 50 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 using a Millipore Waters 150 C gel permeation chromatograph 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 (M_n) and weight-average molecular weight (M_w) were calculated on the basis of a polystyrene standard calibration. The melting temperature was measured on a Perkin-Elmer DSC-7 differential scanning calorimeter 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

Propylene polymerization without molecular hydrogen addition

Propylene polymerization over an MgCl$_2$·TiCl$_4$·DOP/ Et$_3$Al catalyst system was performed at 100°C without addition of molecular hydrogen. The results concerning polymer yield, catalyst activity, molecular weight and its distribution are shown as run No. 1 in *Table 1*, compared with the results[10] under the same polymerization condition except for the addition of DPDMS as run No. 2.

Figure 1 shows the saturated hydrocarbon region of ^{13}C n.m.r. spectra of the PPs of runs No. 1 and 2 in *Table 1*. The carbon peaks associated with chain-end
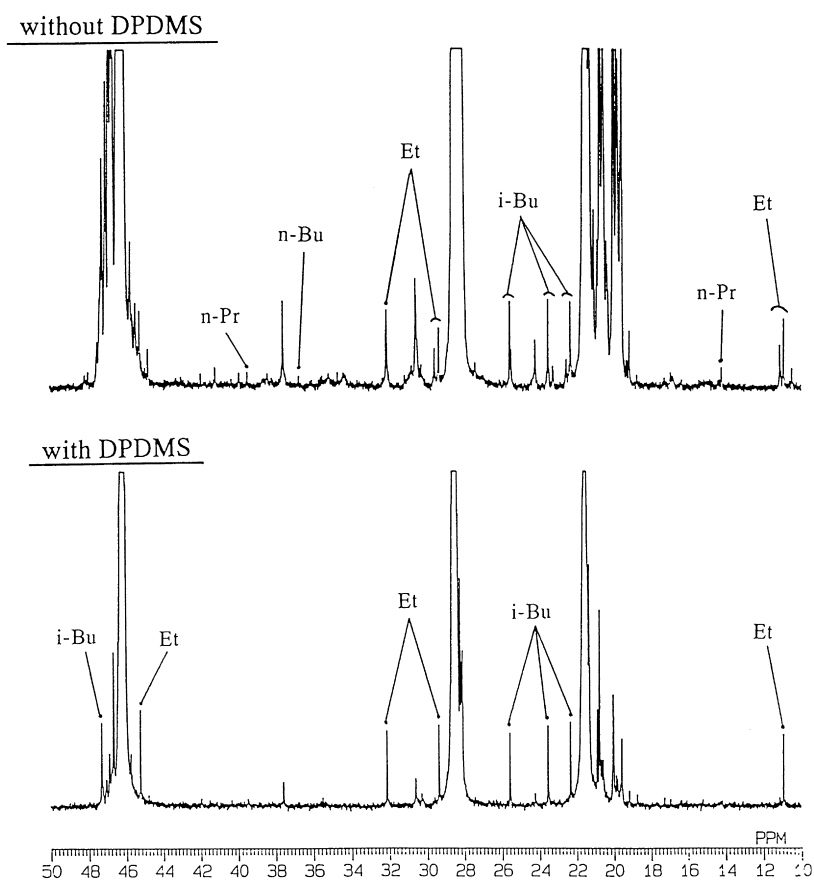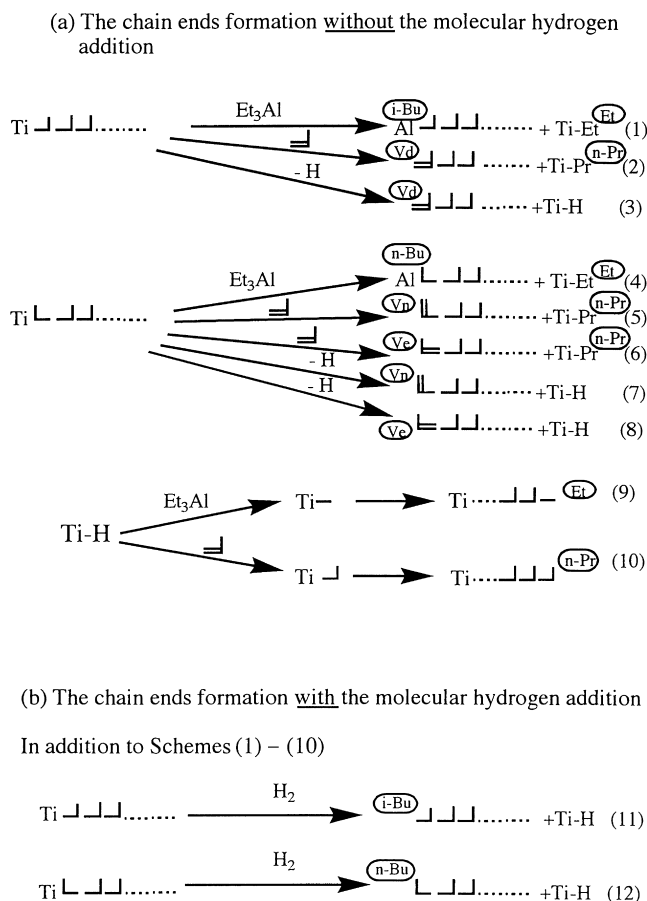

Figure 1 Saturated terminal groups region of ^{13}C n.m.r. spectra of PP polymerized at 100°C with and without DPDMS in the polymerization without molecular hydrogen addition

Table 1 The influence of DPDMS and molecular hydrogen addition on propylene polymerization[a]

Run no.	DPDMS (mmol L^{-1})	Hydrogen (L h^{-1})	Yield (g)	Activity (g-PP per mmol-Ti)	M_n	$M_n M_w$
1	0	0	0.84	17	6000	10.6
2	0.6	0	1.79	36	9900	10.0
3	0	2.5	2.68	54	4900	5.3
4	0.6	2.5	2.90	58	7300	5.3

[a]Polymerization conditions; 50 L h^{-1} of propylene and 0 or 2.5 L h^{-1} of hydrogen under atmospheric pressure, 0.1 mmol L^{-1} of Ti, 0 or 0.6 mmol L^{-1} of DPDMS and 6.0 mmol L^{-1} of Et$_3$Al in 0.5 L of n-decane, 1 h at 100°C

(a) The chain ends formation <u>without</u> the molecular hydrogen addition

(b) The chain ends formation <u>with</u> the molecular hydrogen addition

In addition to Schemes (1) – (10)

Figure 2 Schemes of all the possible formation reactions of chain end groups

groups were assigned using Lindeman–Adams empirical parameters[15].

From the spectra, head-to-head regioirregularities are found to be negligible in both runs. All the possible chain-end groups formed by chain-transfer reactions without molecular hydrogen addition are shown in Schemes (1)–(10) in *Figure 2*.

The chain-end groups of the PP polymerized with DPDMS consist of ethyl group (Et) and i-butyl group (i-Bu), indicating that the chain-transfer reaction by Et$_3$Al at 1,2-inserted sites as shown in equation (1) occurs predominantly among all the possible chain-transfer reactions under this polymerization condition[10]. In addition to the peaks assigned to Et and i-Bu, some other peaks appear in the PP without DPDMS, which are assigned to n-butyl group (n-Bu) and n-propyl group (n-Pr).

The presence of n-Bu indicates the occurrence of the chain-transfer reaction by Et$_3$Al at the 2,1-inserted sites as shown in equation (4). It suggests that the absence of the steric hindrance of DPDMS occasionally allows Et$_3$Al to act as a chain-transfer reagent at the 2,1-inserted sites.

n-Pr is formed through the chain-transfer reactions of equations (2), (5) or (6) and the monomer insertion reaction shown in equation (10) which occurs immediately after the reactions shown in equations (3), (7) or (8). The existence of n-Pr shows that some of these reactions are permitted by the absence of DPDMS. To obtain detailed information on this matter, the unsaturated hydrocarbon region of ^{13}C n.m.r. spectra was investigated (see *Figure 3*).

The peaks detected in the PP without DPDMS, but not in the PP with DPDMS, are assigned to vinylidene group (Vd) and vinyl group (Vn). The presence of Vd shows that the chain-transfer reaction by monomer shown in equation (2) or by elimination of β-hydrogen shown in equation (3) occurs at 1,2-inserted sites. The existence of Vn suggests that the chain-transfer reaction by monomer shown in equation (5) or by elimination of β-hydrogen shown in equation (7) occurs at 2,1-inserted sites. Furthermore, the absence of vinylene group (Ve) indicates that the occurrence of the chain-transfer reaction by monomer shown in equation (6) or by elimination of β-hydrogen shown in equation (8) can be negligible.

On the other hand, Chadwick *et al.*[9] have reported that the unsaturated chain ends of PP prepared at a low molecular hydrogen concentration with a similar catalyst system except for using diether as an ED instead of DPDMS were mainly assigned to Vd. It shows that the chain-transfer reactions which form Vd were allowed even in the presence of diether, although they did not occur in the use of DPDMS. It indicates that the chain-transfer reactions by monomer or by the elimination of β-hydrogen would depend on the nature of EDs.

The proportions of chain-end groups are summarized in *Table 2*.

As shown in *Figure 2*, i-Bu is formed only through the reaction of equation (1). Therefore, the existence of 31 mol.% of i-Bu means that 62% of chain-transfer reactions are caused by Et$_3$Al at 1,2-inserted sites. Moreover, the chain-transfer reactions of equations (3) and (7) form Ti–H bonds followed by the formation of Et or n-Pr through the reactions of equation (9) or (10), while the reactions of equations (2) and (5) form Ti–Pr leading to the formation of n-Pr in the further chain-propagation reactions. Therefore, the presence of only 4 mol.% of n-Pr compared with 9 mol.% of Vn and 8 mol.% of Vd implies that the reactions of equations (3) and (7) predominate over equations (2) and (5). In addition, this fact shows the dominance of the reaction shown in equation (9) over that of equation (10). After all, the frequency of the chain-transfer reactions is as follows, by alkylaluminium > by elimination of β-hydrogen > by propylene monomer.

Table 1 shows that the absence of DPDMS leads to a drop in the molecular weight (M_n). We believe that the above-mentioned additional chain-transfer reactions due to the absence of DPDMS would cause an increase in the
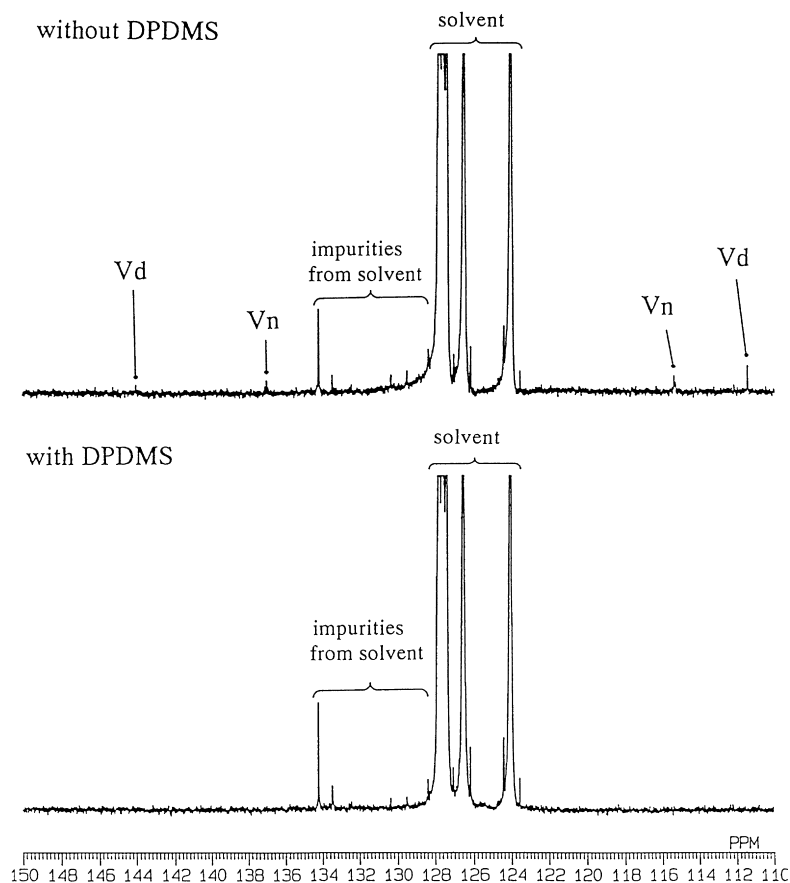
Figure 3 Unsaturated terminal groups region of ^{13}C n.m.r. spectra of PP polymerized at 100°C with and without DPDMS in the polymerization without molecular hydrogen addition

Table 2 The proportion of chain end groups

Run no. in *Table 1*	DPDMS addition	H$_2$ addition	Chain end groups (mol.%)						
			α-end groups		ω-end groups				
			Et	*n*-Pr	*i*-Bu	*n*-Bu	Vn	Vd	Ve
1	no	no	45	4	31	3	9	8	n.d.[a]
2	yes	no	50	n.d.	50	n.d.	n.d.	n.d.	n.d.
3	no	yes	37	12	44	7	n.d.	n.d.	n.d.
4	yes	yes	40	10	44	6	n.d.	n.d.	n.d.

[a]Not detected

frequency of chain-transfer reactions as a whole, resulting in the decrease of M_n. Moreover, *Table 1* shows the drop in the activity due to the absence of DPDMS. A plausible explanation is that the 2,1-insertion would be related to the dormant sites[10]. Both *n*-Bu and Vn detected only in the PP without DPDMS show the chain-transfer reactions at the 2,1-inserted sites. Therefore, it is safe to say that the absence of DPDMS causes the increase of 2,1-insertion.

Furthermore, the absence of DPDMS gives the additional low melting temperature peak in differential scanning calorimetry (d.s.c.) analysis (see *Figure 4*). This fact suggests the presence of low stereospecific sites interacting with no ED, owing to the release of DOP from the catalyst by the interaction with Et$_3$Al[16]. The addition of DPDMS leads not only to the disappearance of the low melting temperature peak, but also to the appearance of high melting temperature shoulder peak. It would be clear that the low stereospecific sites were converted into high stereospecific

sites by the addition of DPDMS. Consequently, the changes in the chain-end structures due to the addition of DPDMS indicate that the low stereospecific sites interacting with no ED are the sites where the chain-transfer reactions forming *n*-Pr, *n*-Bu, Vd and Vn occur.

Propylene polymerization with molecular hydrogen addition

The polymerization with addition of molecular hydrogen was performed without DPDMS. The results were shown as run No. 3 in *Table 1*, compared with those[10] in the presence of DPDMS as run No. 4. The drop in M_n in the absence of DPDMS is observed as well as the polymerization without addition of molecular hydrogen. As shown in *Table 2*, with regard to the proportion of chain-end groups, no significant differences were observed between runs No. 3 and 4. All the possible chain-end groups formed by chain-transfer reactions with molecular hydrogen addition are shown in equations (1)–(12) in *Figure 2*. The disappearance of
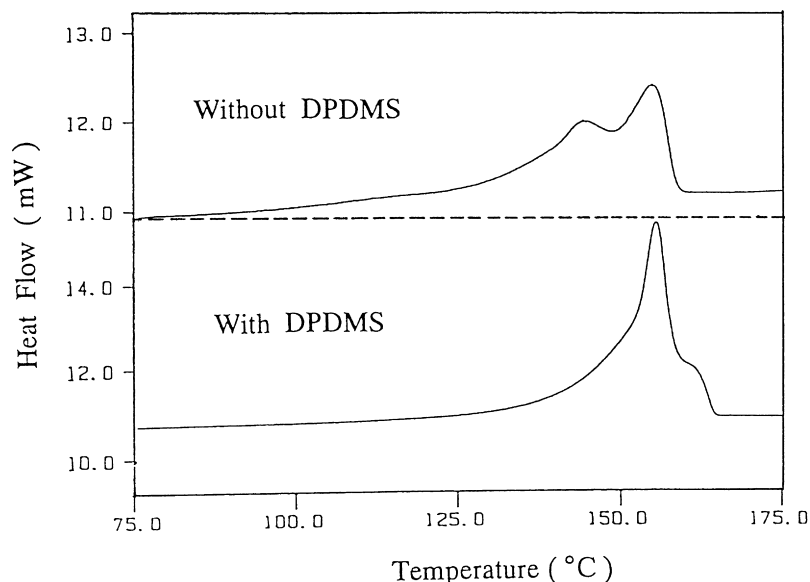
Figure 4 D.s.c. curves of PP polymerized at 100°C with and without DPDMS in the polymerization without molecular hydrogen addition

Vn and Vd due to the addition of molecular hydrogen indicates the predominance of the chain-transfer reactions by molecular hydrogen over those by elimination of β-hydrogen or by propylene monomer. In the polymerization without addition of molecular hydrogen, the chain-transfer reactions in the absence of DPDMS occur more frequently than that in the presence of DPDMS owing to the above-mentioned additional chain-transfer reactions. On addition of molecular hydrogen, chain-transfer reactions by molecular hydrogen replace those additional chain-transfer reactions. Therefore, even in the polymerization with addition of molecular hydrogen, the frequency of the chain-transfer reactions in the absence of DPDMS is considered to be higher than that in the presence of DPDMS, leading to the lower M_n.

On the other hand, the activity without DPDMS is similar to that with DPDMS, unlike the polymerizations without addition of molecular hydrogen. Since ^{13}C n.m.r. analysis shows no occurrence of the head-to-head regioirregularity, the total proportion of n-Bu and Vn in itself corresponds to the frequency of 2,1-insertion (see *Figure 2*). Namely, the similar proportion of n-Bu and the absence of Vn in the polymerizations with and without DPDMS show that the frequency of 2,1-insertion is not significantly changed by the absence of DPDMS, explaining almost the same activity in runs No. 3 and 4 shown in *Table 1*, although the frequency of 2,1-insertion without DPDMS would be higher than that with DPDMS in the polymerization without addition of molecular hydrogen. This suggests that some of the chain-transfer reactions by molecular hydrogen replace 2,1-insertion and hence diminish the frequency of 2,1-insertion into the same level with DPDMS. That is to say, in the polymerizations without DPDMS, addition of molecular hydrogen leads not merely to the chain-transfer reaction at dormant 2,1-inserted sites, but also to a decrease in the frequency of 2,1-insertion. This may be the reason why the catalyst activity was enhanced up to 3.2 times by the addition of molecular hydrogen only in the polymerization without DPDMS as shown in *Table 1*.

In conclusion, the proportions of chain-end groups in the PP polymerized without DPDMS and molecular hydrogen addition show that the frequency of the chain-transfer reactions is as follows under this polymerization condition, by alkylaluminium > by elimination of β-hydrogen > by propylene monomer. The absence of DPDMS causes the chain-transfer reactions which form n-Bu and Vn at the 2,1-inserted sites and Vd at 1,2-inserted sites in the propylene polymerization without addition of molecular hydrogen, resulting in the drops of M_n and the activity. Moreover, the changes of the terminal structures of the PP polymerized without DPDMS by the addition of molecular hydrogen indicate that the chain-transfer reactions by molecular hydrogen leads to the decrease of the 2,1-insertion in addition to the conversion of the dormant 2,1-inserted sites into the active sites, so that it would contribute to the increase of the activity more effectively than the polymerization with DPDMS.

REFERENCES

1. Parodi, S., Nocci, R., Giannini, U., Barke, P. K. and Sacata, U., *Japanese Patent* No. kokai 57-63311. 1982.
2. Kioka, M. and Kashiwa, N., *Japanese Patent* No. kokai 58-83006. 1983.
3. Soga, K. and Shiono, T., in *Transition Metal Catalyzed Polymerizations*, ed. R. P. Quirk. Cambridge University Press. New York, 1988, p. 266.
4. Busico, V., Cipullo, R. and Corradini, P., *Makromol. Chem.*, 1993, **194**, 1079.
5. Chadwick, J. C., Miedema, A. and Sudmeijer, O., *Macromol. Chem. Phys.*, 1994, **195**, 167.
6. Chadwick, J. C., Kessel, G. M. and Sudmeijer, O., *Macromol. Chem. Phys.*, 1995, **196**, 1431.
7. Albizzati, E., Giannini, U., Morini, G., Galimberti, M., Barino, L. and Scodamaglia, R., *Macromol. Symp.*, 1995, **89**, 73.
8. Chadwick, J. C., Morini, G., Albizzati, E., Balbontin, G., Mingozzi, I., Cristofori, A., Sudmeijer, O. and Kessel, M. M., *Macromol. Chem. Phys.*, 1996, **197**, 2501.
9. Chadwick, J. C., Morini, G., Balbontin, G., Mingozzi, I., Albizzati, E. and Sudmeijer, O., *Macromol. Chem. Phys.*, 1997, **198**, 1181.
10. Kojoh, S., Kioka, M., Kashiwa, N., Itoh, M. and Mizuno, A., *Polymer*, 1995, **26**, 5015.
11. Soga, K., Shiono, T. and Doi, Y., *Makromol. Chem.*, 1988, **189**, 1531.
12. Seppala, J. V., Harkonen, M. and Luciani, L., *Makromol. Chem.*, 1989, **190**, 2535.
13. Proto, A., Oliva, L., Pellecchia, C., Sivak, A. J. and Cullo, L. A., *Macromolecules*, 1990, **23**, 2904.
14. Guyot, A., Spitz, R., Journaud, C. and Eisenstein, O., *Macromol. Symp.*, 1995, **89**, 39.
15. Lindeman, L. P. and Adams, J. Q., *Anal. Chem.*, 1971, **43**, 1245.
16. Kioka, M. and Kashiwa, N., *J. Mol. Catal.*, 1993, **82**, 11.