



## Additive effects of alkylaluminium compounds on propylene-1,3-butadiene copolymerization using isospecific zirconocene catalysts

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### ABSTRACT

Additive effects of diisobutylaluminum hydride (DiBAL-H) was studied in copolymerization of propylene and 1,3-butadiene with a series of C<sub>2</sub>-symmetric ansa-bis(indenyl)zirconocene derivatives, i.e., rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride (**4Ph**), dichloride, rac-dimethylsilylbis(2-methyl-benzoindenyl)zirconium dichloride (**Bz**), rac-dimethylsilylbis(2-methyl-indenyl) zirconium dichloride (**2Me**), rac-dimethylsilylbis(1-indenyl)zirconium dichloride (**1-Ind**), rac-ethylenebis(1-indenyl)zirconium dichloride (**Et-Ind**), activated by modified methylaluminoxane (MMAO). Without DiBAL-H, the activity of the copolymerization decreased in the following order, **2Me** > **1-Ind** > **Et-Ind** > **4Ph** ≈ **Bz**, whereas butadiene content decreased in the following order, **4Ph** > **Bz** ≥ **Et-Ind** > **1-Ind** > **2Me** ≈ 0.1 mol%. The addition of DiBAL-H affected the activity but hardly changed the butadiene content. The copolymer obtained without DiBAL-H contained the butadiene units of 1,2-insertion (1,2-BD) and 1,4-insertion (1,4-BD). The addition of DiBAL-H decreased the amount of 1,4-BD and produced hydrogenated 1,4-BD in the **4Ph** and **Bz** systems accompanied by the increase of the copolymerization activity. The additive effect of other alkylaluminums was investigated in the **Bz** system, and DEAL-H was found to show the similar effects with DiBAL-H. The <sup>13</sup>C NMR analysis of the polymer terminated with deuterated methanol indicated the hydroalumination of 1,4-BD in the **Bz** system. Hydroxyl groups can be also introduced by oxidative cleavages of the Al–C bonds.

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### 1. Introduction

Polypropylene (PP) has been expanding its usage due to its mechanical balance and economical advantage. PP is, however, so hydrophobic that many attempts have been made to improve affinity of PP with other polar materials [1,2]. There is a great demand for PP to be compatibilized with other materials, such as metals, fillers and other polymers that contain functional groups.

Chemical modification of PP has been attempted by many researchers to introduce functional groups to PP [3–8]. These reactions, however, needed highly reactive reagents or severe reaction conditions. Among them, radical modification has been commonly adopted in industry, but is not able to control the amount and position of functional groups precisely.

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We have been developing copolymerization techniques to control the amount and the location of polar groups in PP chain and succeeded in the selective introduction of carbon–carbon double bond as a precursor of polar group by the copolymerization of propylene and 1,3-butadiene using isospecific zirconocene catalysts [9,10]. The addition of hydrogen was found to hydrogenise the 1,4-inserted butadiene units (1,4-BD) in the copolymer, and selectively produced PP with pendant vinyl groups.

We have also found that the addition of dialkylaluminium hydrides on the copolymerization with an isospecific zirconocene, rac-dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium dichloride (**4Ph**), activated by MMAO produced PP having dialkylaluminium group on the main chain of the copolymer with pendant vinyl group [11]. In this paper, therefore, we investigated the effects of di-isobutylaluminium hydride (DiBAL-H) and other alkylaluminums on the copolymerization using a series of isospecific zirconocene catalysts and an attempt was made to introduce hydroxyl group to the PP copolymer by oxidative cleavage of aluminium–carbons after the copolymerization.

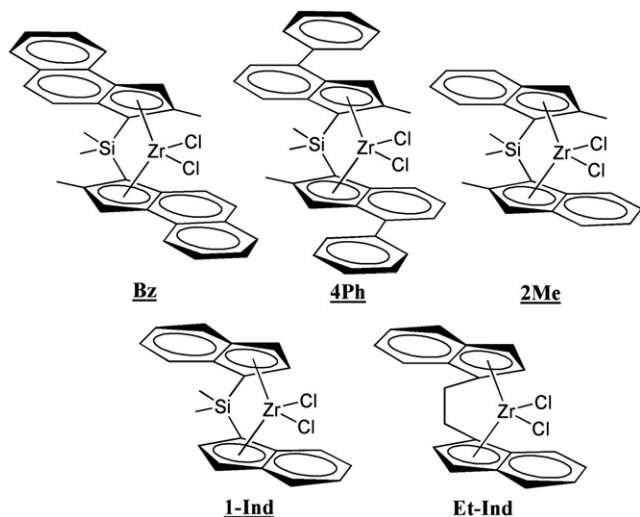


Fig. 1. Chemical structures of  $C_2$ -symmetric *ansa*-bis(indenyl)zirconocene derivatives.

## 2. Results and discussion

### 2.1. Results

The additive effect of DiBAL-H on propylene-1,3-butadiene copolymerization was examined with a series of  $C_2$ -symmetric *ansa*-bis(indenyl)zirconocene derivatives, **4Ph**, *rac*-dimethylsilylbis(2-methyl-benzoindenyl)zirconium dichloride (**Bz**), *rac*-dimethylsilylbis(2-methyl-indenyl)zirconium dichloride (**2Me**), *rac*-dimethylsilylbis(1-indenyl)zirconium dichloride (**1-Ind**) and *rac*-ethylenebis(1-indenyl)zirconium dichloride (**Et-Ind**) (Fig. 1).

Copolymerizations of propylene with 1,3-butadiene using **4Ph** were conducted in a 100-mL stainless steel autoclave by batch-wise operation at 0 °C as follows. Toluene solutions of MMAO and the catalyst, toluene as the solvent, toluene solutions of DiBAL-H and 1,3-butadiene were added to the reactor in this order at room temperature (entry 2) or the addition order of DiBAL-H and 1,3-butadiene were reversed (entry 3). Gaseous propylene was then introduced after cooling the autoclave with liquid nitrogen and copolymerization was started by setting the reactor at the polymerization temperature.

The results of copolymerization are shown in Table 1. The addition of DiBAL-H increased the polymer yields regardless of the addition order of DiBAL-H and 1,3-butadiene. Whereas the number-average molecular weight ( $M_n$ ) and molecular weight distribution (MWD) were strongly affected by the addition order. When DiBAL-H was added first, the  $M_n$  value was decreased and

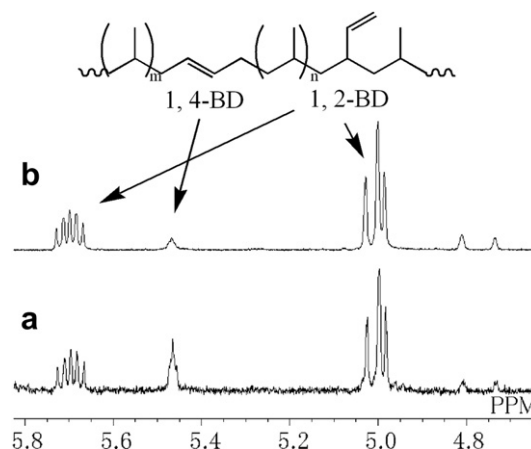


Fig. 2.  $^1\text{H}$  NMR spectra of poly(propylene-*ran*-1,3-butadiene) obtained with **4Ph**/MMAO system (Table 1). a) Without DiBAL-H (entry 1), b) with DiBAL-H 0.01 mol (entry 2).

MWD was broadened. On the other hand, the  $M_n$  value increased and MWD became narrow when DiBAL-H was introduced after the addition of 1,3-butadiene. This should be due to unfavorable reaction between DiBAL-H and MMAO-activated **4Ph** in the absence of 1,3-butadiene, which should have caused the heterogeneity of the active centers. In the following experiments, DiBAL-H was injected into the autoclave after the introduction of butadiene.

The structure of the copolymers obtained was investigated by NMR. The  $^1\text{H}$  NMR spectra of the poly(propylene-*ran*-1,3-butadiene) (PPBD) obtained without and with DiBAL-H are illustrated in Fig. 2a and b, respectively. The copolymer without DiBAL-H showed several signals between 5 ppm and 6 ppm assignable to two types of olefin units, i.e., 1,2-inserted butadiene unit (1,2-BD) and 1,4-inserted one (1,4-BD). The addition of DiBAL-H selectively decreased the intensity of 1,4-BD.

In the  $^{13}\text{C}$  NMR spectrum of PPBD with DiBAL-H, several new resonances appear accompanied by diminishing the intensity of 1,4-BD. These new resonances can be assigned to hydrogenated 1,4-BD (Fig. 3b). The mole fraction of each butadiene unit and the total butadiene content were determined from the NMR spectra and are summarized in Table 1. The addition of DiBAL-H decreased the mole fraction of 1,4-BD but did not affect the total content of butadiene-derived units. The selectivity of pendant vinyl to all the butadiene units incorporated were 60–70% irrespective of the addition of DiBAL-H.

The results of the copolymerizations with a series of  $C_2$ -symmetric *ansa*-bis(indenyl)zirconocene derivatives are summarized in Table 2.

Table 1  
Additive effect of DiBAL-H on propylene-1,3-butadiene copolymerization.<sup>a</sup>

Entry	Additive	Yield (g)	Rsp <sup>b</sup>	$M_n^c$ ( $\times 10^3$ )	MWD <sup>c</sup>	Mole fraction <sup>d</sup>				S 1 <sup>e</sup> (%)	S 2 <sup>f</sup> (%)	$T_m^g$ (°C)
						All BD <sup>h</sup>	1,2-BD	1,4-BD	H-1,4-BD			
1	Non	0.08	13	35.7	2.4	2.2	1.43	0.76	0	65	0	138
2	DiBAL → Bd	0.21	36	13.0	3.9	2.3	1.59	0.26	0.48	68	65	134
3	Bd → DiBAL	0.20	33	62.6	1.7	2.0	1.22	0.16	0.65	60	80	139

<sup>a</sup> Polymerization conditions: solvent (toluene) = 40 mL, **4Ph** = 2  $\mu\text{mol}$ , MMAO = 4.0 mmol, 0 °C, 3 h, propylene concentration 1.8 mol L<sup>-1</sup>, butadiene concentration 90 mmol L<sup>-1</sup>.

<sup>b</sup> kg-polymer mol-Zr<sup>-1</sup> h<sup>-1</sup>.

<sup>c</sup> Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration.

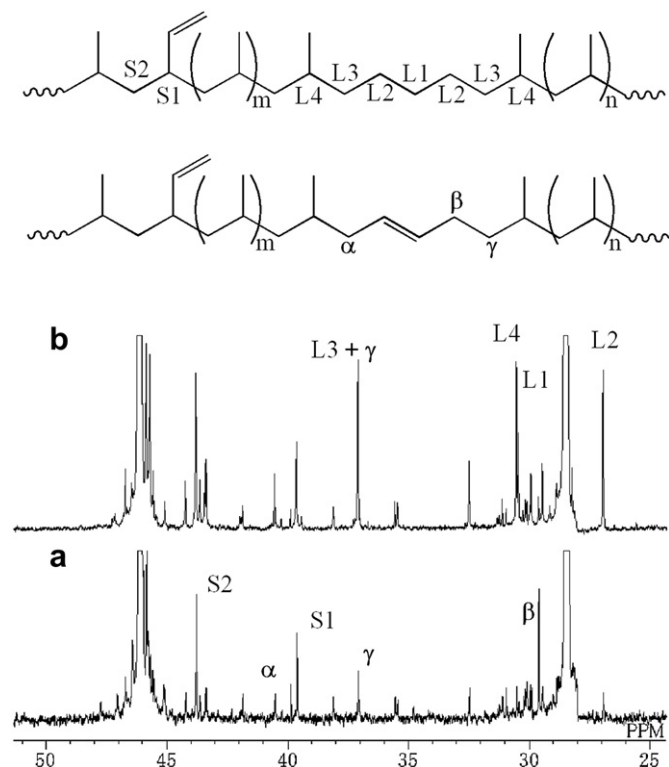
<sup>d</sup> Calculated from  $^1\text{H}$  NMR spectra.

<sup>e</sup> Selectivity for 1,2-BD unit (%) against summation of 1,2-BD, 1,4-BD and H-1,4-BD units.

<sup>f</sup> Selectivity for H-1,4-BD unit (%) against summation of 1,4-BD and H-1,4-BD units.

<sup>g</sup> Measured by DSC.

<sup>h</sup> Mole fraction of all units derived from butadiene monomer in each copolymer.



**Fig. 3.**  $^{13}\text{C}$  NMR spectra of poly(propylene-*ran*-1,3-butadiene) obtained with **4Ph**/MMAO system (Table 1). a) Without DiBAL-H (entry 1), b) with DiBAL-H 0.01 mol (entry 2).

All the zirconocenes employed conducted the copolymerization with and without DiBAL-H, but the activity strongly depended on the zirconocene structure as follows.

Without DiBAL-H: **2Me** > **1-Ind** > **Et-Ind** > **4Ph**  $\approx$  **Bz**

With DiBAL-H: **1-Ind**  $\geq$  **2Me** > **4Ph**  $\approx$  **Et-Ind**  $\approx$  **Bz**

The rate enhancement by the addition of DiBAL-H was observed in **Bz**, **4Ph**, and **1-Ind**, among which the increase of  $M_n$  was

observed in **Bz** and **4Ph**. All the polymers obtained possessed the MWD values of approximately two indicating the uniformity of the active species.

The mole fractions of butadiene units and the butadiene contents in the copolymers were determined by  $^{13}\text{C}$  NMR as described above and summarized in Table 2. The addition of DiBAL-H hardly affected the butadiene contents, which decreased in the following order: **4Ph** > **Bz**  $\geq$  **Et-Ind**  $\geq$  **1-Ind** > **2Me**  $\approx$  0. On the other hand, DiBAL-H change the mole fraction of butadiene units in **4Ph** and **Bz**: 1,4-BD was changed to hydrogenated 1,4-BD. In these catalysts, the  $M_n$  values increased accompanied by the increase of the activity as described above. The decrease of 1,4-BD was observed also in the **2Me** system accompanied by decrease of the activity and the  $M_n$  value. The activity and the  $M_n$  value of the **2Me** system without DiBAL-H were however one-order in magnitude higher than those of the **4Ph** and **Bz** systems and the butadiene content in the copolymer obtained by **2Me** seems to be too small to discuss in detail. The effect of DiBAL-H on  $M_n$  was not observed for **1-Ind** and **Et-Ind** which were characterized by low 1,2-BD selectivity (entry 8 and 10). PPBD produced by various isospecific catalysts showed melting points around 140–160 °C which indicated isotactic structures in PPBD.

The effect of alkylaluminum on the copolymerization was then investigated with **Bz** which was most largely affected among the zirconocenes employed by the addition of DiBAL-H. The alkylaluminums used were diethylaluminum hydride (DEAL-H), diisobutylaluminum hydride (DiBAL-H), triethylaluminum (TEAL) and triisobutylaluminum (TiBAL). The results are summarized in Table 3. The additions of DEAL-H, DiBAL-H and TiBAL increased the  $M_n$  value as well as the activity, whereas the decrease of 1,4-BD accompanied by the formation of hydrogenated 1,4-BD was observed only by DEAL-H and DiBAL-H. On the other hand, the addition of TEAL decreased both the activity and the  $M_n$  value accompanied by a slight increase of 1,4-BD.

The effect of the amount of DiBAL-H added was investigated in the **Bz** system. The activity and the  $M_n$  value are plotted against the amount of DiBAL-H in Fig. 4. Both values show very similar dependency on the amount of DiBAL-H and show the maximum which was more than three times larger than those without DiBAL-H. This result strongly suggests that the increase of activity should be ascribed to the increase of propagation rate.

If the hydroalumination of the carbon–carbon double bonds in the polymer proceed during the copolymerization, the vinyl group

**Table 2**  
Additive effects of DiBAL-H on propylene-1,3-butadiene copolymerization using isospecific zirconocene catalysts.<sup>a</sup>

Entry	Cat	DiBAL-H (mol)	Yield (g)	Rsp <sup>b</sup>	$M_n^c$ ( $\times 10^3$ )	MWD <sup>c</sup>	Mole fraction <sup>d</sup>				S 1 <sup>e</sup> (%)	S 2 <sup>f</sup> (%)	$T_m^g$ (°C)
							All BD <sup>h</sup>	1,2-BD	1,4-BD	H-1,4-BD			
1	<b>Bz</b>	Non	0.07	12	19.3	1.9	0.6	0.44	0.13	0	77	0	147
2	<b>Bz</b>	0.01	0.19	31	66.9	2.0	0.6	0.34	0.03	0.24	56	89	149
3	<b>4Ph</b>	Non	0.08	13	35.7	2.4	2.2	1.43	0.76	0	65	0	138
4	<b>4Ph</b>	0.01	0.20	33	62.6	1.7	2.0	1.22	0.16	0.65	60	80	139
5	<b>2Me</b>	Non	1.07	178	196	2.9	0.2	0.08	0.08	0	50	0	153
6	<b>2Me</b>	0.01	0.42	106	175	2.2	0.1	0.07	0.01	—	88	—	158
7	<b>1-Ind</b>	Non	0.36	59	45.6	1.9	0.4	0.11	0.33	0	25	0	149
8	<b>1-Ind</b>	0.01	0.67	111	36.5	1.8	0.4	0.10	0.32	0	24	0	150
9	<b>Et-Ind</b>	Non	0.20	33	25.0	2.1	0.5	0.07	0.40	0	15	0	142
10	<b>Et-Ind</b>	0.01	0.19	32	14.7	2.1	0.6	0.06	0.52	0	10	0	144

<sup>a</sup> Polymerization conditions: solvent (toluene) = 40 mL, Cat = 2  $\mu\text{mol}$ , MMAO = 4.0 mmol, 0 °C, 3 h, propylene concentration 1.8 mol L<sup>-1</sup>, butadiene concentration 90 mmol L<sup>-1</sup>.

<sup>b</sup> kg-polymer mol-Zr<sup>-1</sup> h<sup>-1</sup>.

<sup>c</sup> Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration.

<sup>d</sup> Calculation from  $^1\text{H}$  NMR spectra.

<sup>e</sup> Selectivity for 1,2-BD unit (%) against summation of 1,2-BD, 1,4-BD and H-1,4-BD units.

<sup>f</sup> Selectivity for H-1,4-BD unit (%) against summation of 1,4-BD and H-1,4-BD units.

<sup>g</sup> Measured by DSC.

<sup>h</sup> Mole fraction of all units derived from butadiene monomer in each copolymer.

**Table 3**  
Additive effect of aluminium compounds on propylene-1,3-butadiene copolymerization.<sup>a</sup>

Entry	Al	Yield (g)	Rsp <sup>b</sup>	M <sub>n</sub> <sup>c</sup> (×10 <sup>3</sup> )	MWD <sup>c</sup>	Mole fraction <sup>d</sup>				S 1 <sup>e</sup> (%)	S 2 <sup>f</sup> (%)	T <sub>m</sub> <sup>g</sup> (°C)
						All BD <sup>h</sup>	1,2-BD	1,4-BD	H-1,4-BD			
1	Non	0.07	12.4	19.3	1.9	0.6	0.44	0.13	0	77	0	147
2	DEAL-H	0.16	26.7	36.1	1.7	0.8	0.45	0.004	0.34	57	99	148
3	DiBAL-H	0.19	31.0	66.9	2.0	0.6	0.34	0.03	0.24	56	89	149
4	TEAL	0.03	4.3	8.1	2.0	0.6	0.43	0.21	—	67	0	145
5	TiBAL	0.12	20.0	23.9	2.1	0.5	0.38	0.14	0	73	0	148

<sup>a</sup> Polymerization conditions: solvent (toluene) = 40 mL, **Bz** = 2 μmol, MMAO = 4.0 mmol, 0 °C, 3 h, propylene concentration 1.8 mol L<sup>-1</sup>, butadiene concentration 90 mmol L<sup>-1</sup>.

<sup>b</sup> kg-polymer mol-Zr<sup>-1</sup> h<sup>-1</sup>.

<sup>c</sup> Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration.

<sup>d</sup> Calculated from <sup>1</sup>H NMR spectra.

<sup>e</sup> Selectivity for 1,2-BD unit (%) against summation of 1,2-BD, 1,4-BD and H-1,4-BD units.

<sup>f</sup> Selectivity for H-1,4-BD unit (%) against summation of 1,4-BD and H-1,4-BD units.

<sup>g</sup> Measured by DSC.

<sup>h</sup> Mole fraction of all units derived from butadiene monomer in each copolymer.

(1,2-BD) should be hydroaluminated more easily than the internal vinylene group. However, the increase of DiBAL-H did not change the mole fraction of 1,2-BD but selectively decreased that of 1,4-BD (Fig. 5). Therefore, the possibility of the hydroalumination after the copolymer formation can be excluded.

To get more information on the role of DiBAL-H, the copolymer obtained by **4Ph** in the presence of DiBAL-H was terminated with deuterated methanol (CH<sub>3</sub>OD). The <sup>13</sup>C NMR spectrum of the copolymer thus obtained is shown in Fig. 6 together with that of the methanol quenched one. The resonances of L1, L2 and L3 carbons assignable to hydrogenated 1,4-BD unit split and shifted to higher field by CH<sub>3</sub>OD-quenching: the resonance of L1 almost disappeared due to the direct deuteration and the deuteration of the neighboring L2; the resonance of L2 dramatically decreased due to the direct deuteration and the deuteration of the neighboring L1; the resonance of L3 slightly weakened and made a shoulder due to the deuteration of the neighboring L2.

## 2.2. Discussion

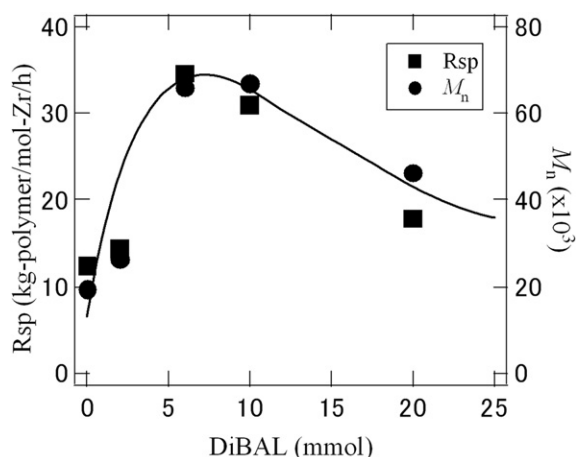
The plausible copolymerization scheme based on the above results is illustrated in Scheme 1. 1,2-Insertion of butadiene monomer forms a vinyl branch and continues the copolymerization. Whereas 2,1-coordination of butadiene led to 1,4-insertion of butadiene and forms stable π-allyl chain end with Zr center (A) which retards the insertion of successive propylene monomer.

Dialkylaluminium hydride hydroaluminates the π-allyl complex and transforms it to alkyl-Zr species (B) which can accept the successive propylene insertion (C). Hence deuterium was introduced at L1 or L2α position (D) by the CH<sub>3</sub>OD-termination.

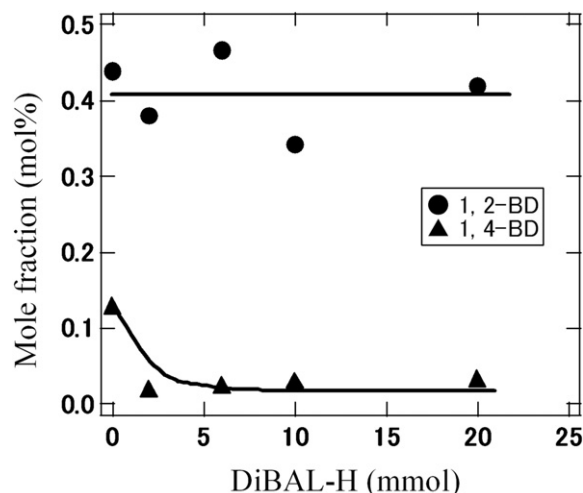
The total mole fractions of butadiene units and the mole fractions of 1,2-BD were not significantly affected by the addition of aluminium hydrides (Tables 2 and 3), indicating that the aluminium hydrides did not change the reactivity ratio of the monomers as well as the regioselectivity of butadiene insertion.

Both the activity and the M<sub>n</sub> value were increased by DEAL-H, DiBAL-H and TiBAL in the following order, DiBAL-H > DEAL-H > TiBAL, whereas they were decreased by TEAL. The phenomena can be interpreted as follows.

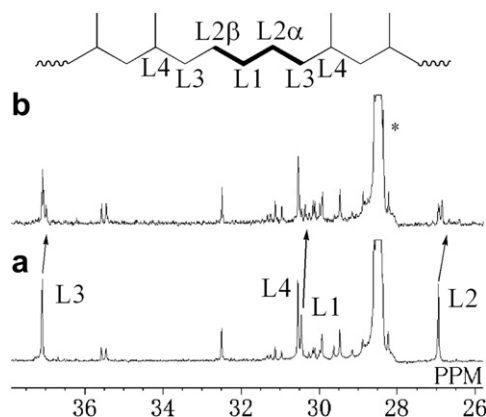
Fink et al. reported the additive effects of trialkylaluminium on propylene polymerization with Me<sub>2</sub>Si(2-Me-benz[e]Ind)<sub>2</sub>ZrCl<sub>2</sub>/MAO at 25 °C [12]. They replaced a part of MAO with trimethylaluminium (TMAL), TEAL, TiBAL, and tributylaluminium (TBAL) keeping the total Al concentration constant, and found that an appropriate amount of TiBAL and TBAL enhanced the activity by about two times while TMAL and TEAL monotonously decreased the activity according to the amounts added. They interpreted the deactivation with TMAL and TEAL by the formation of inactive binuclear species, [Me<sub>2</sub>Si(2-Me-benz[e]Ind)<sub>2</sub>Zr(μ-R)<sub>2</sub>AlR<sub>2</sub>]<sup>+</sup>, and the rate enhancement with TiBAL and TBAL by the complexation of free TMAL in MAO, which prevents the formation of the inactive



**Fig. 4.** Effects of DiBAL-H amount on Rsp and M<sub>n</sub> of poly(propylene-*ran*-1,3-butadiene) obtained with **Bz**/MMAO system.



**Fig. 5.** Effects of DiBAL-H amount on mole fractions of 1,2-BD and 1,4-BD of poly(propylene-*ran*-1,3-butadiene) obtained with **Bz**/MMAO system.



**Fig. 6.**  $^{13}\text{C}$  NMR spectra of poly(propylene-*ran*-1,3-butadiene) obtained with **4Ph**/MMAO system. a) Quenched with methanol, b) quenched with deuterized methanol.

binuclear species. On the other hand, we investigated the additive effects of various trialkylaluminiums (TMAL, TEAL, TiBAL and tryoctylaluminium (TOAL)) in propylene polymerization with [*t*-BuNSiMe<sub>2</sub>(C<sub>5</sub>Me<sub>4</sub>)]TiMe<sub>2</sub> activated by TMAL-free MAO (dried MAO) and observed the rate enhancement by TiBAL and TOAL but the rate depression with Me<sub>3</sub>Al and Et<sub>3</sub>Al [13]. Since we used TMAL-free MAO, we ascribe the rate enhancement by TiBAL and TOAL to their selective coordination to the counter ion resulting in the separation of the active ion pair and the rate depression by TMAL and TEAL to the formation of the binuclear species.

In the present copolymerization of propylene and butadiene, DiBAL-H not only transforms dormant  $\pi$ -allyl Zr species to active alkyl-Zr species by hydroalumination but also coordinates the counter anion to effectively enhance the activity. In the case of DEAL-H, the effect of transformation of  $\pi$ -allyl Zr species is compensated with the formation of inactive bimetallic species. Therefore, DiBAL-H is most effective additive to enhance activity and molecular weight.

Since the poly(propylene-*ran*-1,3-butadiene) obtained in the presence of dialkylaluminium hydride possesses alkylaluminium in main chain, the cleavage of the aluminium–carbon bond with oxygen was attempted to directly introduce hydroxyl group into PP main chain. The oxidation was conducted after the propylene-1,3-butadiene copolymerization using **4Ph**, and the  $^1\text{H}$  NMR spectra of

the copolymers before and after the oxidation are shown in Fig. 7. The resonances of hydroxyl groups were observed at 3.4–3.5 ppm after the oxidation (Fig. 7b). The intensities of two types of hydroxyl groups derived from aluminium–carbon bond were approximately the same and the summation of mole fractions of the hydroxy groups was almost equal to that of 1,4-BD in the copolymer synthesized without DiBAL-H indicating that hydroalumination of  $\pi$ -allyl Zr center and/or the oxidation of  $\pi$ -allyl Al bond was not regioselective but quantitative. On the other hand, the mole fraction of 1,2-BD did not change before and after the oxidation, which indicates that the hydroalumination of the vinyl group in the copolymer did not occur during the copolymerization.

### 3. Summary

Isospecific zirconocene catalysts /MMAO/aluminium hydride system produced PP copolymer with up to 99% of selectivity as side vinyl group to all double bonds in it. Aluminium hydrides were selectively incorporated into copolymer main chain and proposed reaction scheme was certified by deuterized methanolysis result. Oxidative cleavage of Al–carbon bond led to introduce hydroxy group into PP main chain.

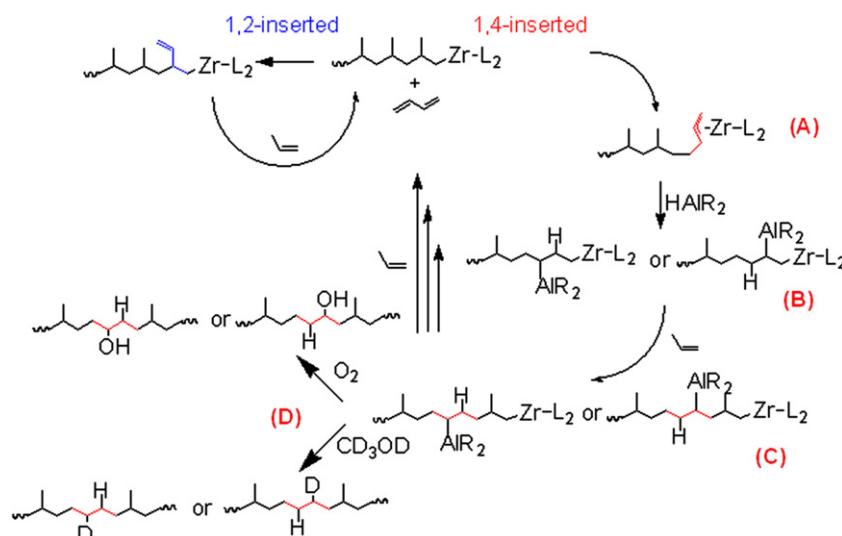
### 4. Experimental

#### 4.1. Materials

Metallocene catalysts commercially obtained from Boulder Scientific Company, and modified methylaluminoxane (MMAO) toluene solution (6.6%) and other aluminium compounds purchased from Tosoh-Finechem. Co., were used without further purification. Propylene (commercial grade, 99.8%) was dehydrated by passing it through a dehydration column of Moisture Filter CP17971. 1,3-Butadiene donated from Zeon Co. (>99.5%) was dried over CaH<sub>2</sub> and distilled before use. Oxygen was purchased from Nippon Sanso Co. (>99.9%) and used as received. Other chemicals commercially obtained were purified according to the usual procedures.

#### 4.2. Polymerization procedure

Standard propylene copolymerization with 1,3-butadiene was conducted in a 100-mL stainless steel autoclave by batch-



**Scheme 1.** Proposed reaction scheme of propylene copolymerization with 1,3-butadiene with isospecific metallocene catalysts/MMAO /dialkylaluminium hydride.

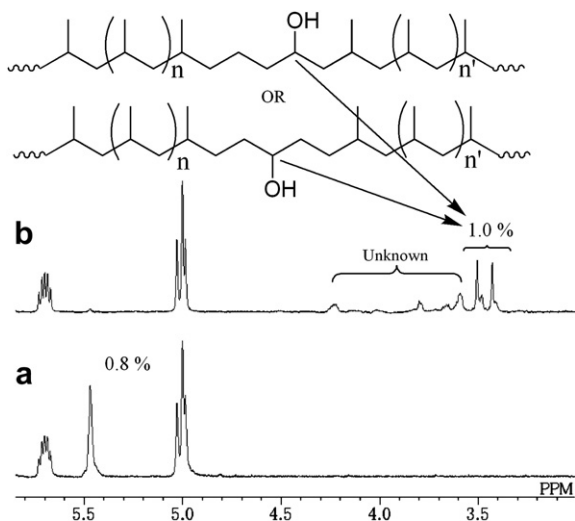


Fig. 7.  $^1\text{H}$  NMR spectra of poly(propylene-*ran*-1,3-butadiene) obtained with **4Ph**/MMAO system. a) Quenched with methanol, b) oxidized after copolymerization.

wise operation at  $0^\circ\text{C}$ . Toluene solutions of MMAO and the catalyst, toluene as the solvent, a toluene solution of 1,3-butadiene and alkylaluminium solution were added to the reactor in this order. The autoclave was cooled with liquid nitrogen and then gaseous propylene, the amount of which was measured by a mass flow meter, was introduced into the reactor. Copolymerization started by setting the reactor at the polymerization temperature. The polymerization was stopped by adding an HCl/methanol solution after remaining monomers had been purged. The polymer was precipitated in methanol, washed with methanol several times, collected by filtration and finally dried under vacuum at  $60^\circ\text{C}$ .

#### 4.3. Oxidative reaction procedure

Copolymer solution in which remained monomers were purged after copolymerization was treated with oxygen gas at room temperature in 15 min. Sodium hydroxide ethanol/water solution was injected slowly and solution was heated to  $60^\circ\text{C}$  followed by hydroxy peroxide aqueous solution addition. After 8 h heat treatment, it was poured into acidic methanol and polymer was collected by filtration, which was dried under vacuum at  $60^\circ\text{C}$ .

#### 4.4. Analytical procedures

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded at  $120^\circ\text{C}$  on a JEOL JNM-LA600 spectrometer operated at 600.05 MHz and 150.80 MHz, respectively, in pulse Fourier-transform mode. The spectra were obtained in 1,1,2,2-tetrachloroethane- $d_2$  using 1,1,2,2-tetrachloroethane (6.0 ppm for  $^1\text{H}$  NMR) and 1,1,2,2-tetrachloroethane- $d_2$  (74.0 ppm for  $^{13}\text{C}$  NMR) as internal references, respectively.

Molecular weights and molecular weight distributions of the polymers were determined by a PL-GPC210 equipped with PLgel  $10\ \mu\text{m}$  MIXED-B LS at  $140^\circ\text{C}$  using *o*-dichlorobenzene as the solvent. Molecular weights were calibrated with monodispersed polystyrene standards and converted to polypropylene molecular weights by  $K$  and  $\alpha$  values,  $1.03 \times 10^{-4}$  and 0.780, respectively.

Differential scanning calorimetry (DSC) measurements were performed on Seiko Instruments Inc. DSC 6200, and recorded the second heating cycle from  $-50^\circ\text{C}$  to  $200^\circ\text{C}$  at a  $10^\circ\text{C}/\text{min}$  rate.

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