Novelty of Vinylidene-Terminated Polypropylene Prepared by a $MgCl_2$-Supported $TiCl_4$ Catalyst Combined with $AlEt_3$ as Cocatalyst

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ABSTRACT: Propene polymerization was conducted by a $MgCl_2$/diisobutyl phthalate/$TiCl_4$ catalyst combined with $AlEt_3$ as cocatalyst. The polymerization was quenched by oxygen gas, and the polymer was fractionated into atactic and isotactic parts with boiling heptane. Each part was analyzed by ^1H NMR. The spectra showed the resonances of vinylidene, vinyl, and hydroxymethylene groups, whose intensities were strongly dependent on the polymerization temperature and the stereoregularity. Raising the polymerization temperature increased the intensity of the hydroxymethylene group in both parts. The relative intensity of the hydroxymethylene to that of the vinylidene group was much higher in the atactic parts. These results suggest that the rates of β-hydrogen transfer and transfer by $AlEt_3$ should be affected by the stereospecificity of the active species as well as polymerization conditions. Heat treatment at 120 °C in the presence of 1-octene quantitatively converted the terminal aluminum−carbon bond to a vinylidene group.

Introduction

Isotactic polypropylene (PP) is one of the most important plastics, of which production systems including polymerization catalysts have been progressing since the great findings of Ziegler and Natta. Recently much effort has been aimed at functionalization of PP. Terminally-functionalized polymers are useful not only for improvement of polymer properties but also for the synthesis of block copolymers. Terminally-functionalized polymer can be obtained either by using a living polymerization system or by chain-transfer reactions. However, the latter is a preferred method from a practical point of view, because the reaction to prepare the terminally-functionalized polymers is catalytic.

Chain-transfer reactions in propene polymerization by Ziegler−Natta catalysts mainly occur via transmetalation of a growing polymer chain to alkyl metals as cocatalyst and/or β-hydrogen transfer of the growing polymer chain to monomer or to the active center. The reactions give metal-terminated and vinylidene-terminated polymers, respectively.

For example, $TiCl_3{-}AlEt_xCl_{3-x}{-}ZnEt_2$ catalyst selectively gives Zn-terminated isotactic PP, which could be converted to various functional groups[1−5] and a polar polymer segment.[6] On the other hand, some zirconocene catalysts selectively give vinylidene-terminated isotactic and atactic PPs.[7,8] Such vinylidene groups are also useful for the synthesis of terminally-functionalized PPs[9−12] and PP-based block copolymers.[9,13,14]

In propene polymerization by commercial $MgCl_2$-supported $TiCl_4$ catalysts, however, both of these transfer reactions would occur concurrently. We have previously reported that PP obtained by a $MgCl_2$-supported $TiCl_4{-}Al(i\text{-}Bu)_3$ catalyst was terminated by Al−C, vinylidene, or a vinyl group.[15] Heat treatment caused hydroalumination of the terminal C═C bonds by reaction with $Al(i\text{-}Bu)_3$ used as cocatalyst. This gave terminally Al-functionalized PP in high yields.

In this paper, an attempt was made to prepare vinylidene-terminated PP by the $MgCl_2$-supported $TiCl_4$ catalyst using $AlEt_3$ as cocatalyst by means of dehydroalumination of Al−C bonds.

Experimental Section

Materials. Propene (from Mitsubishi Petrochemical Co.) was purified by passing it through columns of $CaCl_2$, P_2O_5, and 3A molecular sieves. $TiCl_4$ (from Toho Titanium Co.) and $AlEt_3$ (from Tosoh Akzo Chemical Co.) were used without further purification. Research-grade decane (commercially obtained) was dried by refluxing it over calcium hydride for 24 h, distilled, and collected over 3A molecular sieves. Nitrogen of 99.9995% purity and oxygen of 99.7% purity (from Nihon Sanso Co.) were used after they were through a 3A molecular sieve column.

A $MgCl_2$-supported $TiCl_4$ catalyst which contained diisobutyl phthalate as an internal Lewis base was synthesized as reported previously.[1] The Ti content in the catalyst determined by inductively coupled plasma spectrometry (Seiko SPS-1500 VR) was 1.76 wt. %.

Polymerization Procedure. Propene polymerization was conducted in a 200-mL glass reactor equipped with a magnetic stirrer. After measured amounts of decane (100 mL) and $AlEt_3$ (5 mmol) were added into the reactor under nitrogen atmosphere, propene was introduced at polymerization temperature until the solvent was saturated with propene. After the polymerization, the reaction mixture was divided into two parts under nitrogen atmosphere. One part was brought directly in contact with oxygen gas at room temperature for 1 h. The other part was heated for 2 h in the absence or presence of 1-octene (1 mL) and then brought into contact with oxygen gas at room temperature. The reaction mixtures were poured into 500 mL of ethanol acidified with ca. 1 mL of concentrated hydrochloric acid. The precipitated polymers were washed with plenty of ethanol and dried under vacuum at 60 °C for 6 h. The polymers were fractionated with boiling heptane to give isotactic (heptane-insoluble) and atactic (heptane-soluble) PP. Both fractions were dried under vacuum at 60 °C for 6 h.

Analytical Procedures. ^1H NMR spectra of samples were recorded on a JEOL EX-400 spectrometer operated at 399.65 MHz in the pulse Fourier transform (FT) mode. The pulse angle was 45°, and about 300 scans were accumulated in pulse repetitions of 10 s. The spectra were obtained at 80 or 130 °C in benzene-d_6 or 1,1,2,2-tetrachloroethane-d_2 solution (5 wt % in a 5-mm-o.d. tube), using benzene or 1,1,2,2-tetrachloroethane as internal reference (7.15 and 5.90 ppm, respectively).

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Table 1. Results of Propene Polymerization with a $TiCl_4/MgCl_2-AlEt_3$ Catalyst[a]

			M_n[d] (× 10^{-4})		M_w/M_n[d]		N[e]	
temp. (°C)	activity[b]	II[c]	APP[f]	IPP[g]	APP	IPP	APP	IPP
80	2.5	53.6	0.8	2.1	4.3	5.3	15.0	5.7
40	3.5	60.3	1.3	3.1	4.6	7.4	12.9	5.4

[a] Polymerization conditions: catalyst = 30 mg, $AlEt_3$ = 5 mmol, decane = 100 mL, propene = atmospheric pressure. [b] kg of PP/(g-of Ti h). [c] Weight fraction of boiling-heptane-insoluble part. [d] Number average molecular weight and polydispersity determined by GPC. [e] Number of polymer chains calculated from the polymer yield and the M_n value. [f] Boiling-heptane-soluble part. [g] Boiling-heptane-insoluble part.

Gel-permeation chromatography (GPC) analysis of the polymers was performed on a Waters 150 C equipped with a Shodex 80M/S column at 140 °C and *o*-dichlorobezene as solvent. The molecular weights were determined by a universal calibration technique.

Results and Discussion

Propene Polymerization. Propene polymerization was performed in decane at 40 or 80 °C for 2 h under an atmospheric pressure of propene by using $AlEt_3$ as cocatalyst. The isotactic indexes (IIs) of polymers were obtained by extraction with boiling heptane. The results are summarized in Table 1. Catalyst activities and IIs were higher when the polymerization reaction was done at 40 °C. The number-average molecular weight (M_n) of the produced polymers decreased with an increase of polymerization temperature in both heptane-soluble (APP) and heptane-insoluble (IPP) fractions.

The number of polymer chains was calculated from the polymer yields and the M_n value. The obtained values were much higher than the amount of Ti used. Taking into consideration the fact that only part of the supported Ti is active for propene polymerization with $MgCl_2$-supported $TiCl_4$ catalysts, the result indicates that chain-transfer reactions frequently occurred in the present system.

Chain-End Structures of PP. In order to investigate the chain-transfer reactions in this system, the polymerization slurry was directly brought into contact with oxygen gas after polymerization at room temperature to convert Al−polymer bonds to hydroxyl groups. The ^1H NMR spectrum of APP obtained at 40 °C is illustrated in Figure 1a. In addition to the resonances of main chain protons from 0.8 to 1.8 ppm, weak resonances are observed at around 3.3 and 4.8 ppm. These resonances can be assigned to hydroxymethylene and vinylidene groups, respectively. In the case of IPP obtained under the same conditions, vinylidene groups were observed together with a trace amount of hydroxymethylene groups (Figure 2a).

Methylene protons in the racemic dyad are equivalent and appear at around 1.1 ppm. However, methylene protons in the meso dyad are not equivalent; one appears at around 1.4 ppm, and the other appears at around 0.9 ppm.[2] Therefore, the stereoregularity of PP can be evaluated by ^1H NMR.[3] The resonance at 1.1 ppm in Figure 1a indicates the presence of syndiotactic structures in APP. On the other hand, Figure 2a shows no resonance at 1.1 ppm, and the resonances of methylene at 1.4 ppm and methine at 1.6 ppm are almost the same intensity. These results support the isotactic structure of IPP.

Figure 3a shows the ^1H NMR spectrum of APP when the polymerization was carried out at 80 °C. In addition to vinylidene and hydroxymetylene groups, a weak resonance assignable to vinyl protons appears at around 5.0 ppm. The ^1H NMR spectrum of IPP obtained under the same polymerization conditions also shows the resonances of hydroxymethylene and vinylidene protons, although the resonance of vinyl protons is not clear due to the high molecular weight of IPP, as shown in Figure 4a. Similar spectra were also obtained when A(i-Bu)$_3$ was used as cocatalyst.[15]

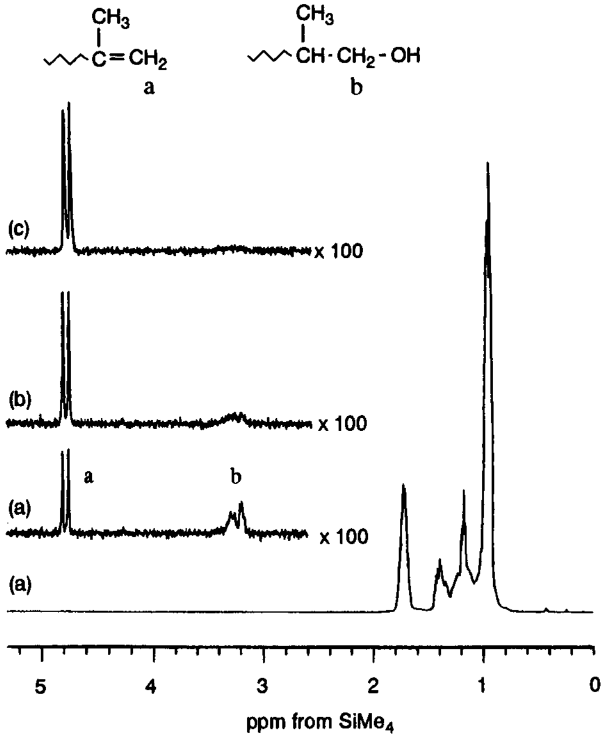


Figure 1. 400 MHz ^1H NMR spectra of heptane-soluble fractions obtained with the $MgCl_2/TiCl_4-AlEt_3$ catalyst at 40 °C: quenched by oxygen before (a) and after (b) heating, and after heating in the presence of 1-octene (c).

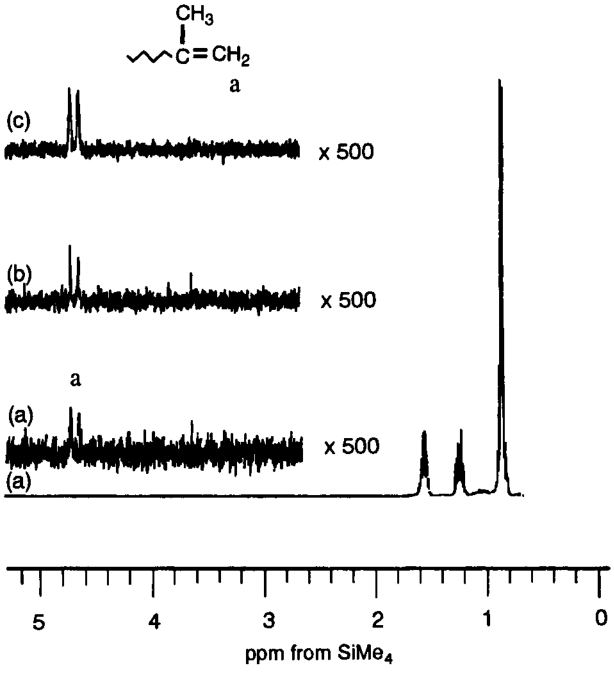


Figure 2. 400 MHz ^1H NMR spectra of heptane-insoluble fractions obtained with the $MgCl_2/TiCl_4-AlEt_3$ catalyst at 40 °C: quenched by oxygen before (a) and after (b) heating, and after heating in the presence of 1-octene (c).

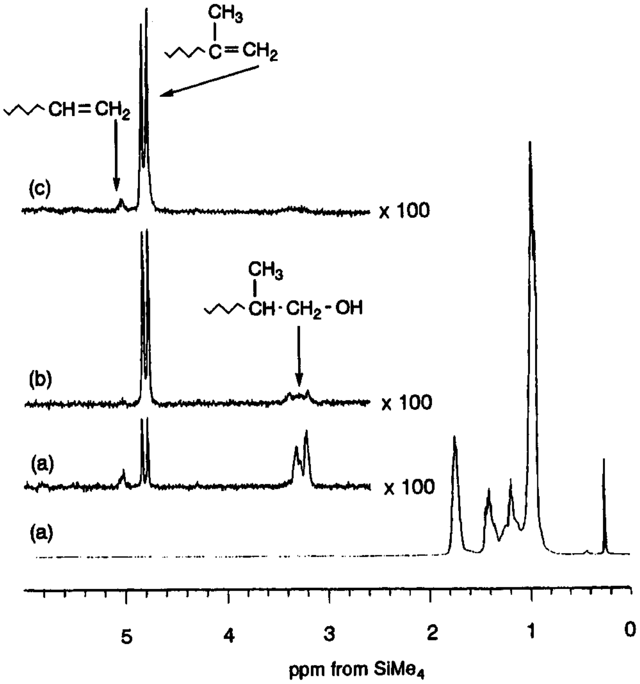


Figure 3. 400 MHz ^{1}H NMR spectra of heptane-soluble fractions obtained with the $MgCl_2/TiCl_4-AlEt_3$ catalyst at 80 °C: quenched by oxygen before (a) and after (b) heating, and after heating in the presence of 1-octene (c).

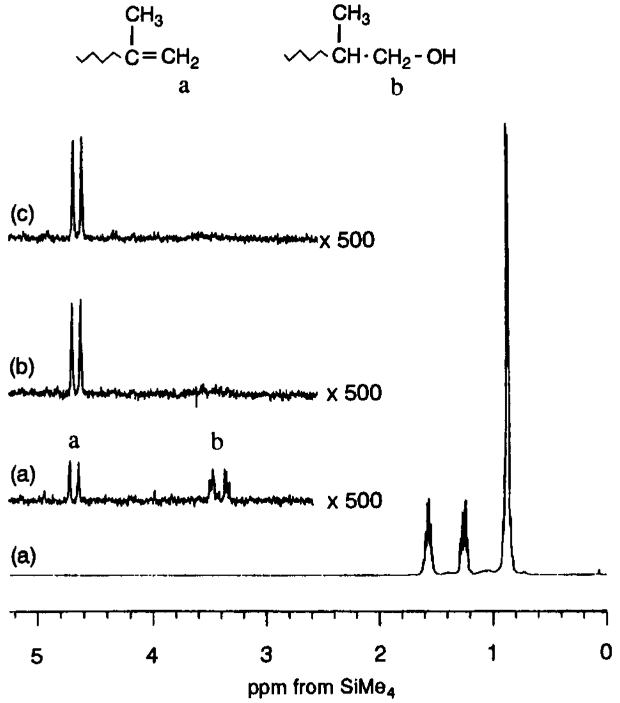
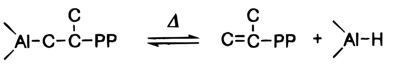


Figure 4. 400 MHz ^{1}H NMR spectra of heptane-insoluble fractions obtained with the $MgCl_2/TiCl_4-AlEt_3$ catalyst at 80 °C: quenched by oxygen before (a) and after (b) heating, and after heating in the presence of 1-octene (c).

These results indicate that both β-hydrogen transfer and transfer to $AlEt_3$ occurred in this system.

Preparation of Vinylidene-Terminated PP. It has been proved that the present catalyst gave both Al-terminated and vinylidene-terminated PP with a small amount of vinyl-terminated PP, of which amounts were strongly dependent on polymerization temperature and the stereoregularity of the polymer. Therefore, an attempt was made to introduce C=C bonds at all the termination chain-ends by dehydroalumination. The dehydroalumination easily occurs at temperatures higher than 100 °C when the alkyl group is branched at the β-position to aluminum, as shown in eq 1.[19]



$$>\text{Al-C-}\overset{\text{C}}{\text{C}}\text{-PP} \overset{\Delta}{\rightleftharpoons} \text{C=}\overset{\text{C}}{\text{C}}\text{-PP} + >\text{Al-H} \qquad (1)$$

The ^{1}H NMR spectra obtained after heating the Al-terminated polymers are shown in Figures 1b, 2b, 3b, and 4b. The heat treatment significantly weakened the resonances of hydroxymethylene protons and increased those of vinylidene protons. In Figure 3b, the vinyl protons also disappeared because the Al–H derived from the Al-terminated PP hydroaluminated the terminal vinyl group.

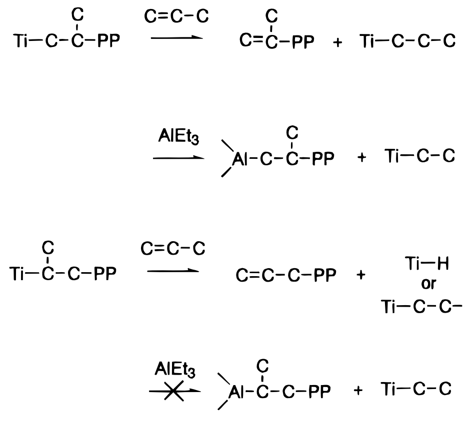
According to eq 1, trapping the Al–H bond with a linear α-olefin would shift the equilibrium to the right. Actually the resonance of the hydroxymethylene groups derived from the Al–C bonds disappeared almost completely by addition of 1-octene during the heating (Figures 1c, 3c and 4c). The hydroalumination of the vinyl group was also prohibited by 1-octene, as shown in Figure 3.

The amounts of the terminal vinylidene, vinyl, and hydroxyl groups were calculated from the relative intensities of these protons relative to those of the main chain ones in the ^{1}H NMR spectra. The results are summarized in Table 2. It was confirmed that C=C-terminated APP and IPP were selectively obtained when $AlEt_3$ was used as cocatalyst followed by the heat treatment in the presence of 1-octene. The total amounts of chain-end structures before and after heating are almost equal, which suggests that oxidation of the Al-terminated PP should be quantitative.

Plausible Chain-Transfer Reactions. It was proved that PPs obtained with the $MgCl_2/TiCl_4-AlEt_3$ catalyst possessed vinylidene-terminated and Al-terminated groups. The increase of the vinylidene group after heat treatment indicates that the 1,2-inserted propagation chain-end is chain-transferred not only by β-hydrogen abstraction but also by $AlEt_3$.

A small amount of terminal vinyl group observed at 80 °C seems to be produced from an occasional 2,1-inserted propagation chain-end via β-hydrogen abstraction of the methyl group. The absence of internal olefins after heat treatment suggests that the 2,1-inserted chain-end could not transfer to $AlEt_3$.

On the basis of these results, a plausible chain-transfer process in the present polymerization system is proposed as shown in eq 2. The propagation proceeds mainly via 1,2-addition. β-Hydrogen transfer of a



$$\begin{aligned}
&\text{Ti-C-}\overset{\text{C}}{\text{C}}\text{-PP} \xrightarrow{\text{C=C-C}} \text{C=}\overset{\text{C}}{\text{C}}\text{-PP} + \text{Ti-C-C-C}\\
&\xrightarrow{\text{AlEt}_3} >\text{Al-C-}\overset{\text{C}}{\text{C}}\text{-PP} + \text{Ti-C-C}\\
&\hspace{22em}(2)\\
&\text{Ti-}\overset{\text{C}}{\text{C}}\text{-C-PP} \xrightarrow{\text{C=C-C}} \text{C=C-C-PP} + \begin{matrix}\text{Ti-H}\\ \text{or}\\ \text{Ti-C-C-C}\end{matrix}\\
&\xrightarrow[\times]{\text{AlEt}_3} >\text{Al-}\overset{\text{C}}{\text{C}}\text{-C-PP} + \text{Ti-C-C}
\end{aligned}$$

Table 2. Effect of Heat Treatment on the Chain-End Structures of Polypropylene Formed by a $TiCl_4/MgCl_2-AlEt_3$ Catalyst after Quenched with Oxygen[a]

		Chain-end propene to total propene units in mol %[b]					
		APP			IPP		
polym temp (°C)	heat treatment	$CH_2{=}C(CH_3)$	$CH_2{=}CH$	$HOCH_2CH_2$	$CH_2{=}C(CH_3)$	$CH_2{=}CH$	$HOCH_2CH_-$
80	none	0.13	0.03	0.33	0.04	trace	0.05
80	yes[c]	0.41	nd[e]	0.08	0.09	nd	nd
80	yes[d]	0.47	0.03	trace	0.09	nd	nd
40	none	0.14	nd	0.16	0.05	nd	trace
40	yes[c]	0.24	nd	0.07	0.06	nd	nd
40	yes[d]	0.30	nd	trace	0.06	nd	nd

[a] Oxidation conditions: room temperature for 1 h by O_2 bubbling. [b] Determined by ^1H NMR. [c] Heated at 120 °C for 2 h. [d] Heated at 120 °C for 2 h in the presence of 1-octene. [e] Not detected.

growing polymer chain to monomer or to the active center produces vinylidene-terminated PP, while transfer to $AlEt_3$ gives Al-terminated PP.

The relative intensities of the chain-end groups to those of the main-chain monomer units summarized in Table 2 indicate the relative rate of each chain transfer to propagation. The content of the hydroxymethylene group increased with an increase in polymerization temperature, while that of the vinylidene group was almost constant. Polymerization temperature affects the rate constants of chain transfer and propagation as well as the monomer concentration. Therefore, the increase of $AlEt_3$ transfer can be interpreted as a higher activation energy for $AlEt_3$ transfer and/or a lower monomer concentration. Kashiwa et al. reported that the chain transfer to $AlEt_3$ predominantly occurred in propene polymerization at 100 °C by the $MgCl_2$/dioctyl phthalate/$TiCl_4-AlEt_3$/diphenyldimethoxysilane catalyst.[20]

The independence of the vinylidene content on polymerization temperature suggests that the rates of β-hydrogen transfer and propagation have the same dependency on temperature and monomer concentration. Thus, it seems that β-hydrogen transfer of a growing polymer chain occurs not to the active center but to the propene monomer.

The relative intensities of the hydroxymethylene and the vinylidene groups in APP and IPP indicate that the relative rate of $AlEt_3$ transfer to β-hydrogen transfer depended on the stereospecificity of the active sites. Under the present polymerization conditions, $AlEt_3$ transfer was predominant in aspecific sites at 80 °C, while β-hydrogen transfer was prevailing in isospecific sites at 40 °C.

Conclusion

Propene polymerization with a $MgCl_2$-supported $TiCl_4-AlEt_3$ catalyst was quenched with oxygen to convert the Al-terminated chain-ends to hydroxyl-terminated ones. The chain-end structures of the polymers were investigated in detail by ^1H NMR, which indicates that the transfers to $AlEt_3$ and propene monomer occurred concurrently. The oxygen-quenching method was proven to be useful to investigate chain-transfer reaction in Ziegler–Natta polymerization. Heat treatment in the presence of 1-octene before oxygen-quenching gave C=C-terminated APP and IPP in high yields. These C=C-terminated PPs are expected to be a precursor of functionalized-PP- and PP-based block copolymers.

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