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Synthesis of Aluminum-Terminated Polypropylene by a $MgCl_2$-Supported $TiCl_4$ Catalyst Combined with Al(*i*-Bu)$_3$ as Cocatalyst

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Chain-transfer reactions in propene polymerization by Ziegler−Natta catalysts mainly occur via transmetalation of a growing polymer chain to alkylmetals 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. In some catalyst systems, one of these transfer reactions selectively occurs. We have previously prepared terminally-functionalized isotactic polypropylenes from the Zn-terminated polymer obtained by the $TiCl_3$−$AlEt_2Cl$−$ZnEt_2$ catalyst[1] and from the vinylidene-terminated polymer obtained by the *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)$ZrCl_2$−methylaluminoxane catalyst via hydrometalations.[2]

However, it is said that both of these transfer reactions should concurrently occur in commercial $MgCl_2$-supported titanium catalysts. In this paper, an attempt was made to obtain aluminum-terminated PP in high yields by a $MgCl_2$-supported $TiCl_4$ catalyst combined with Al(*i*-Bu)$_3$ as cocatalyst as well as a hydroalumination reagent.

Experimental Section. Materials. Propene (from Mitsubishi Petrochemical Co.) was purified by passing through columns of $CaCl_2$, P_2O_5, and molecular sieves 3A. $TiCl_4$ (from Toho Titanium Co.) and Al(*i*-Bu)$_3$ (from Tosoh Akzo Chemical Co.) were used without further purification. Research-grade hexane, heptane, and decane (commercially obtained) were dried over calcium hydride under refluxing from 24 h and distilled before use. Nitrogen of 99.9995% and oxygen 99.7% (from Nihon Sanso Co.) were used after passing through a 3A molecular sieve column. The Ti content in the catalyst determined by inductively coupled plasma spectrometry (Seiko SPS-1500 VR) was 1.76 wt %.

Preparation of Catalyst. Catalyst preparation was performed in a 1-L three-necked flask equipped with a condenser and a magnetic stirrer. To 100 mL of decane were added continuously 5 g (52.5 mmol) of $MgCl_2$ and 20 mL of neat $TiCl_4$. Diisobutyl phthalate (DIBP) (8.4 mmol) was dropped into the mixture at 90 °C, and then the mixture was allowed to react at 100 °C for 2 h with vigorous stirring. After the reaction mixture was cooled, the solid product was separated, washed several times with 300 mL of hexane to remove $TiCl_4$, and dried under vacuum.

Polymerization Procedure. Propene polymerization was conducted in a 200-mL glass reactor equipped with a magnetic stirrer. After measured amounts of decane and Al(*i*-Bu)$_3$ were added into the reactor under a nitrogen atmosphere, propene was introduced at the polymerization temperature until the solvent was saturated with propene. Polymerization was started by adding the catalyst into the reactor and performed at 80 °C for 2 h. The polymerization was terminated by addition of a dilute solution of hydrochloric acid in ethanol. The precipitated polymers were filtered out, washed with plenty of ethanol, and dried under vacuum at 60 °C for 6 h. The obtained polymers were fractionated with boiling heptane to give isotactic (heptane-insoluble) and atactic (heptane-soluble) polypropylene. Both fractions were dried under vacuum at 60 °C for 6 h. The weight fraction of heptane-insoluble fraction was 47 wt %.

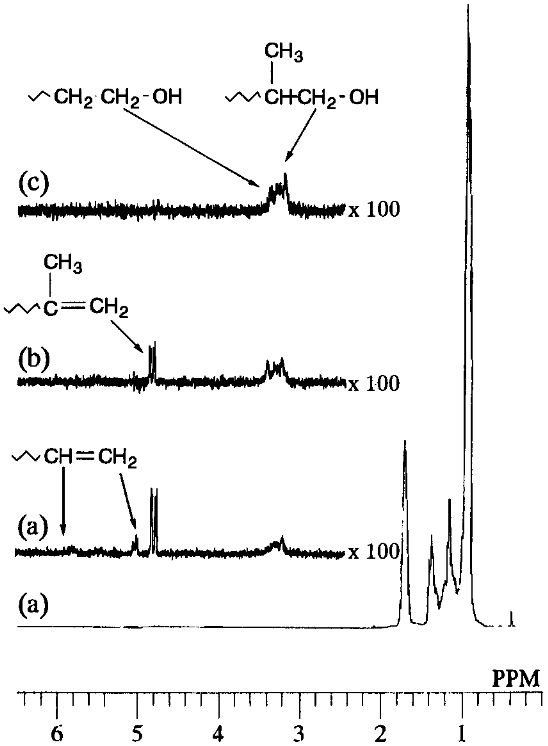

Figure 1. 400-MHz ^1H NMR spectra of heptane-soluble fractions obtained with the $MgCl_2$/$TiCl_4$−Al(*i*-Bu)$_3$ catalyst at 80 °C: quenched by oxygen before (a) and after (b) heating at 120 °C and after heating at 120 °C under reduced pressure (c).

Preparation of Hydroxy-Terminated PP. After the propene polymerization, the reaction mixture was divided into two parts under a nitrogen atmosphere. One part was directly brought into contact with oxygen gas at room temperature for 1 h followed by addition of hydrochloric acid solution in ethanol (path A). The other part was heated for 2 h with or without adequate evacuation and then brought into contact with oxygen gas at room temperature (path B). The precipitated polymers were purified as described above. Progress of the hydroalumination was followed by the relative intensities of the resonances of vinylidene, vinyl, and hydroxy-terminated methylene to the alipathic protons in the ^1H NMR spectrum.

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. In ^1H NMR measurements, the pulse angle was 45°, and 100−500 scans were accumulated in 10 s of pulse repetition. 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. Effect of Heat Treatment on the Chain-End Structures of Polypropylene by a $TiCl_4/MgCl_2-Al(i\text{-}Bu)_3$ Catalyst after Quenched with Oxygen[a]

	chain-end propene units in mol %					
	APP			IPP		
heat treatment	$CH_2{=}C(CH_3)-$	$CH_2{=}CH-$	$HOCH_2CH_2-$	$CH_2{=}C(CH_3)-$	$CH_2{=}CH-$	$HOCH_2CH_2-$
none	0.14	0.05	0.12	0.03	0.02	(0.02)[e]
yes[b]	0.06	n.d.[d]	0.19			
yes[c]	trace	n.d.	0.28	trace	n.d.	(0.06)[e]

[a] Oxidation conditions: room temperature for 1 h by O_2 bubbling. [b] Heated at 120 °C for 2 h. [c] Heated at 120 °C for 2 h with adequate evacuation. [d] Not detected. [e] Precise values could not be obtained due to the low signal/noise ratio.

Gel-permeation chromatography (GPC) of the polymers was performed on a Waters 150 C equipped with a Shodex 80M/S column at 140 °C and *o*-dichlorobenzene as solvent. The molecular weights were determined by a universal calibration technique as follows: heptane-soluble fraction, $M_n = 12\,000$, $M_w/M_n = 5.0$; heptane-insoluble fraction, $M_n = 24\,000$, $M_w/M_n = 8.1$.

Results and Discussion. Chain-End Structures of PP before Hydroalumination (Path A). After the polymerization, the slurry was cooled to room temperature and quenched by oxygen to convert Al−polymer bonds to hydroxyl groups.

The ^{1}H NMR spectrum of the heptane-soluble fractions (APP) are 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 protons, respectively. The result indicates that both the chain transfer to $Al(i\text{-}Bu)_3$ and β-hydrogen elimination occur in the present system. The weaker resonance at around 5.0 ppm assignable to vinyl protons suggests that 2,1-insertion occasionally occurs followed by β-hydrogen elimination of the methyl group.

Resonances of vinyl, vinylidene, and hydroxymethylene groups were observed also in the heptane-insoluble fraction (IPP), although the intensities of the peaks were very weak because of the high molecular weight of IPP (Figure 2a).

From the above results, the following mechanism of chain-transfer reaction may be applied to the present propene polymerization (Scheme 1). The propagation proceeds mainly via 1,2-addition. β-Hydrogen elimination of a growing polymer chain to monomer or to the active center produces terminal vinylidene groups.

On the other hand, transmetalation of the growing polymer chain to alkylaluminum as cocatalyst gives terminal Al−carbon bonds which are converted to hydroxyl groups by oxygen. A small amount of terminal vinyl groups seems to be produced from the occasional 2,1-inserted propagation chain end via β-hydrogen elimination of the methyl group. The absence of internal olefins indicates that the β-hydrogen elimination selectively occurs on the methyl group. The result is in contrast to that of the *rac*-ethylenebis(4,5,6,7-tetrahydroindenyl)$ZrCl_2$−methylaluminoxane catalyst, which predominantly gives internal olefins from the 2,1-inserted chain end.[3]

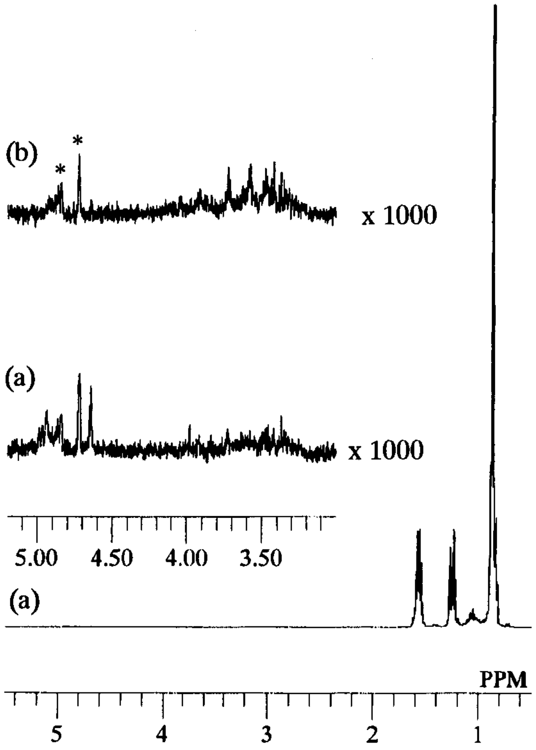
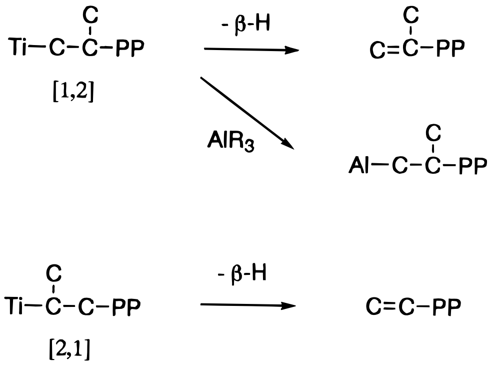


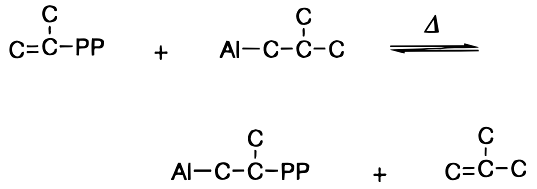
Figure 2. 400-MHz ^{1}H NMR spectra of heptane-insoluble fractions obtained with the $MgCl_2/TiCl_4-Al(i\text{-}Bu)_3$ catalyst at 80 °C: quenched by oxygen before heating (a) and after heating at 120 °C under reduced pressure (b). (*) Resonances of impurities.

Scheme 1



Preparation of Al-Terminated Polypropylene (Path B). Kashiwa et al. reported that the chain transfer by $AlEt_3$ predominantly occurred in propene polymerization at 100 °C by the $MgCl_2$/dioctyl phthalate/$TiCl_4-AlEt_3$/diphenyldimethoxysilane catalyst.[4] However, it has been proved that the present catalyst gives both aluminum-terminated and vinylidene-terminated PP with a small amount of vinyl-terminated PP under these polymerization conditions. Therefore, an attempt was made to introduce aluminum−carbon bonds at all the termination chain ends by hydroalumination. The catalytic hydroalumination under mild conditions in a polar solvent like diethyl ether is well-known;[5] however, the method was not applied to this system because of the low solubility of IPP in such polar solvents.

Hydroalumination of vinylidene groups by $Al(i\text{-}Bu)_3$ is reversible, as shown in eq 1. In this paper, therefore, an excess amount of $Al(i\text{-}Bu)_3$ was used as cocatalyst to shift the equilibrium to the right.



$$C{=}\overset{C}{C}{-}PP + Al{-}C{-}\overset{C}{C}{-}C \overset{\Delta}{\rightleftharpoons} Al{-}C{-}\overset{C}{C}{-}PP + C{=}\overset{C}{C}{-}C \quad (1)$$

After the propene polymerization, half of the slurry was heated at 120 °C for 2 h to hydroaluminate the vinyl and vinylidene groups by the Al(*i*-Bu)$_3$. The resulting mixture was cooled to room temperature and quenched by oxygen to convert Al−polymer bonds to hydroxyl groups. The ^{1}H NMR spectrum of APP obtained after the heating is shown in Figure 1b, where the resonances of vinyl protons disappeared completely and those of vinylidene protons were significantly weakened. On the other hand, the intensity of hydroxymethylene protons was increased accompanied with the appearance of hydroxymethylene peaks derived from the vinyl groups. According to eq 1, the removal of isobutene should promote the hydroalumination of the terminal vinylidene groups. Actually, the resonance of the terminal vinylidene groups disappeared almost completely by adequate evacuation during the heating (Figures 1c and 2b).

The contents of the terminal vinylidene, vinyl, and hydroxyl group were calculated from the relative intensities of these protons to the main chain protons in the ^{1}H NMR spectra. The results are summarized in Table 1. It was proved that the aluminum-terminated IPP and APP were selectively obtained when Al(*i*-Bu)$_3$ was used as cocatalyst followed by the heat treatment under reduced pressure.

In conclusion, aluminum-terminated APP and IPP were obtained in high yields by a MgCl$_2$-supported TiCl$_4$ catalyst combined with Al(*i*-Bu)$_3$ as cocatalyst as well as a hydroalumination reagent. It is expected that various terminally-functionalized PP or PP-based block copolymers could be synthesized by applying this method.

References and Notes

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