Synthesis of Terminally Aluminum-Functionalized Polypropylene

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ABSTRACT: Atactic and isotactic polypropylenes were respectively prepared with Cp_2ZrCl_2– and $Et[H_4Ind]_2ZrCl_2$–methylaluminoxane catalyst systems. These polymers were found predominantly to contain vinylidene end groups caused by β-hydrogen elimination. The vinylidene groups were caused to react with an excess amount of $(iso\text{-}C_4H_9)_2AlH$ in heptane or octane at refluxing temperatures to give quantitatively hydroaluminated polymers.

Introduction

Propene polymerization catalysts have been dramatically improved in both activity and stereospecificity, yielding new generations of highly economical production systems. More recently much effort is being made to functionalize polypropylene. Terminally functionalized polymers are expected to be useful not only to synthesize block copolymers but also to modify polymer properties.

We have already prepared terminally OH-, Cl-, and COOH-functionalized isotactic polypropylene by using $Zn(C_2H_5)_2$ as a chain-transfer reagent.[1,2]

Homogeneous Kaminsky-type catalysts are well-known to produce polypropylenes with completely different stereoregularity depending on the structure of the organotransition-metal compounds.[3] The propagation and chain-transfer reactions with these catalyst systems proceed mainly via 1,2-addition and β-hydrogen elimination or by chain transfer with the monomer, indicating that the majority of the resulting polymers possess terminal vinylidene groups.[4,5] According to Ziegler's original work, such terminal olefins can easily insert into Al–H bonds or replace the isobutyl group of isobutyl–Al compounds.[6] In this paper, therefore, an attempt was made to prepare aluminum-terminated polypropylenes (polypropylenylaluminums) by hydroalumination of polypropylene prepared with Kaminsky-type catalysts. Since Al–carbon bonds are highly reactive, such polypropylenylaluminum is expected to be an excellent precursor of a terminally functionalized polypropylene or a macromolecular cocatalyst in Ziegler–Natta polymerization.

Experimental Section

Materials. Propene (Mitsubishi Petrochemical Co.) was purified by passing through columns of NaOH, P_2O_5, and molecular sieves 3A. Bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) obtained from Tokyo Kasei Kogyo K. K. was used without further purification. Ethylenebis(tetrahydroindenyl)zirconium dichloride ($Et[H_4Ind]_2ZrCl_2$) was prepared according to the literature.[7] $Al(CH_3)_3$ (Tosoh Akzo Chemical Co.) was used without further purification. Methylaluminoxane (MAO) was prepared from hydrous aluminum sulfate and $Al(CH_3)_3$ according to the literature.[8] EtO^2H (99% ^2H) and ^2HCl (99% ^2H, 35 wt % in ^2H_2O) was obtained from MSD Isotopes and used without further purification. Research-grade toluene, heptane, and octane (commercially obtained) were dried over calcium hydride under refluxing for 24 h and distilled before use. Argon (99.9995%) was used without further purification.

Preparation of Polypropylenes. Propene polymerization was conducted with a 200-mL glass reactor or a 200-mL stainless steel autoclave equipped with a magnetic stirrer. In the case of the glass reactor, after measured amounts of toluene and MAO were added into the reactor under an argon atmosphere, propene was introduced at polymerization temperature until the solvent was saturated with propene. Polymerization was started by adding the Zr compound into the reactor. In the case of the autoclave, after measured amounts of MAO, toluene, and Zr compound were added into the reactor under an argon atmosphere, 20 L (STP) of propene monomer was condensed into the reactor at liquid-nitrogen temperature. Polymerization was started by setting the reactor at polymerization temperature. The polymerization was terminated by addition of a dilute solution of hydrochloric acid in ethanol. When using $Et[H_4Ind]_2ZrCl_2$, the precipitated polymer was filtrated and washed with plenty of ethanol. In the case of Cp_2ZrCl_2, the produced polymer (atactic) was extracted with hexane and recovered by evaporation of the solvent because the product was very sticky. Both isotactic and atactic polymers were dried in vacuo at 60 °C for 8 h.

Hydroalumination of the Terminal C═C Bonds of Polypropylenes. The terminal C═C bonds of the polypropylenes were hydroaluminated by $(iso\text{-}C_4H_9)_3Al$ or $(iso\text{-}C_4H_9)_2AlH$. After measured amounts of the polymer, solvent (heptane or octane), and $(iso\text{-}C_4H_9)_2AlH$ or $(iso\text{-}C_4H_9)_3Al$ were added into the glass reactor equipped with a condenser and a magnetic stirrer, the mixture was heated at refluxing temperatures. Although the isotactic polymer was insoluble in these solvents at room temperature, it became soluble at refluxing temperatures. The process of the hydroalumination was followed by checking the relative intensity of the resonances of the vinylidene and the aliphatic protons in the ^1H NMR spectrum: A small portion of the reaction mixture was taken out during the reaction and poured into acidic ethanol. The polymer was purified with the same procedure described above and offered to ^1H NMR measurement. The amount of isobutane in the solution was also determined by gas chromatography. The solvent peak was used as an internal standard.

Preparation of ^2H-Quenched Polypropylene. The solution of hydroaluminated polypropylene was poured into a 10% solution of ^2HCl in EtO^2H. The precipitated polymer was purified according to the usual procedures described above.

Analytical Procedures. ^1H and ^{13}C NMR spectra of samples were recorded on a JEOL EX-90 spectrometer operated at 89.45 and 22.40 MHz or a GX-500 spectrometer operated at 500.00 and 125.65 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. In ^{13}C NMR measurements, broad-band decoupling was used to remove ^{13}C–^1H couplings. The pulse angle was 45°, and 6000–8000 scans were accumulated in 8 s of pulse repetition. The spectra were obtained at room temperature or 80 °C in $CDCl_3$ or C_6D_6 solution (5 wt % for ^1H NMR and 15 wt % for ^{13}C NMR in a 5-mm-o.d. tube), using $CHCl_3$ or C_6H_6 as an internal reference (7.24 and 7.15 ppm for ^1H NMR and 77.0 and 128.0 ppm for ^{13}C NMR, respectively).

Differential scanning calorimetry (DSC) measurements were made with a Shimadzu DSC-30 under a nitrogen atmosphere. Polymer samples (ca. 3 mg) were encapsulated in aluminum pans. Samples were pretreated at 200 °C for 5 min, cooled to room temperature and scanned at 10 °C/min.

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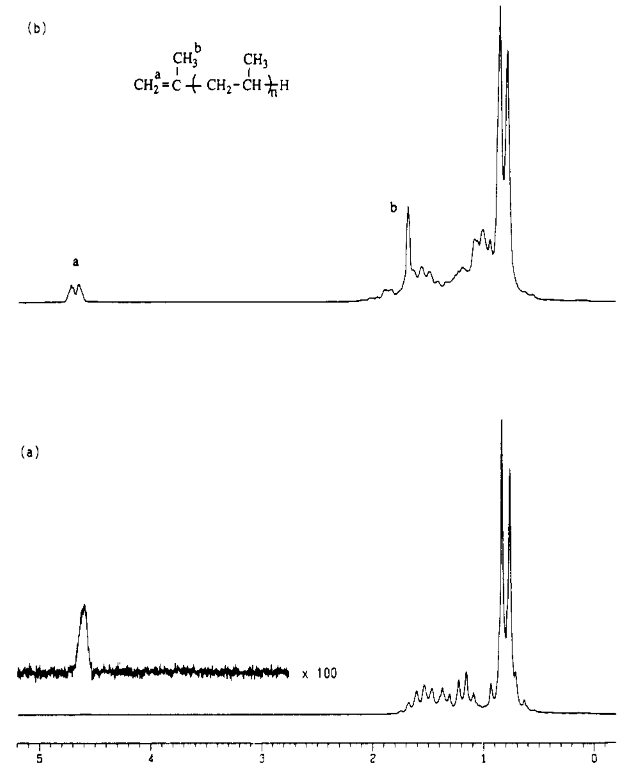


Figure 1. 90-MHz ^{1}H NMR spectra of atactic and isotactic polypropylene obtained at 20 °C: (a) isotactic, (b) atactic.

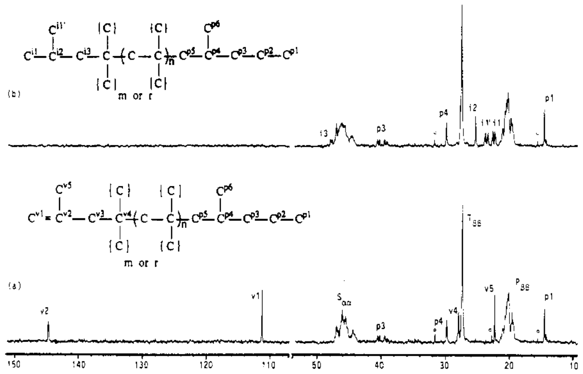


Figure 2. 22.5-MHz ^{1}H NMR spectra of atactic polypropylenes: (a) before hydroalumination, (b) after hydroalumination. (○) Peaks from *n*-hexane.

Results and Discussion

Propene Polymerization. Propene polymerization was first performed at 20 °C using isospecific (Et[H$_4$-Ind]$_2$ZrCl$_2$) and aspecific (Cp$_2$ZrCl$_2$) catalysts combined with MAO. The ^{1}H NMR spectra of the resulting polymers are reported in parts a and b of Figure 1, respectively. The strong peaks attributed to the main chain are observed between 0.5 and 2.0 ppm in both spectra. In addition, some weak peaks are observed at around 4.8 and 1.7 ppm in Figure 1b, which can be assigned to vinylidene protons and methyl protons attached to a vinylidene group, respectively. The resonances due to vinylidene protons are also observed in the expanded spectrum of Figure 1a.

The ^{13}C NMR spectra of these polymers were measured to investigate the structures in more detail. Figure 2a shows the 22.5-MHz ^{13}C NMR spectrum of the polymer obtained with Cp$_2$ZrCl$_2$. In the same figure is also reported the labeling of the carbon used in this paper. Besides the resonances attributable to main-chain carbons, several resonances are observed with the same intensities. These resonances except C^{v4} can be assigned according to the literature[5,9] to the carbons of the end groups of structure I. The v4 peak may be assigned to C^{v4} as follows: (i) The

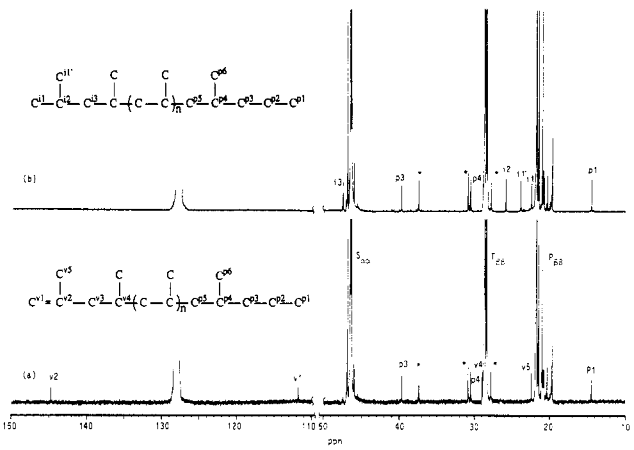
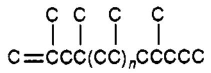


Figure 3. 125-MHz ^{13}C NMR spectra of isotactic polypropylenes: (a) before hydroalumination, (b) after hydroalumination. (*) Peaks from the tetramethylene structure.



$$\mathrm{C{=}\overset{C}{C}C\overset{C}{C}(C\overset{C}{C})_{\mathit{n}}C\overset{C}{C}CCC}$$

I

peak intensity of v4 is almost the same as those of v1, v2, and v5. (ii) v4 can be assigned to a methine carbon from the distortionless enhancement by polarization transfer (DEPT) spectra. (iii) This peak completely disappears after hydroalumination (see the following section). The resonances of both chain end groups show almost the same intensity, indicating that a chain-transfer reaction proceeds preferentially via β-hydrogen elimination or by the monomer under the present experimental conditions.

Figure 3a illustrates the expanded 125-MHz ^{13}C NMR spectrum of the polymer obtained with Et[H$_4$Ind]$_2$ZrCl$_2$, where the assignment of each resonance is also indicated. This spectrum is more simple compared with the spectrum shown in Figure 2a, probably due to the stereoregularity of the methyl groups. The resonances attributed to the carbons in initiation and termination end groups display nearly the same intensities, indicating that this polymer has also the same structure (structure I).

By assuming the polymer structure as structure I, the M_n value was calculated from the relative intensities of the vinylidene protons to the aliphatic protons in the ^{1}H NMR spectrum and those of the *n*-propyl end group to the main-chain carbons in the ^{13}C NMR spectrum. Although the M_n values estimated from ^{13}C NMR scattered to some extent depending upon the carbons used, both analytical methods gave nearly the same values (see Table I), which may again indicate that most polymer chain ends have vinylidene groups.

Besides the resonances of chain end carbons, three other weak peaks with the same intensities are observed in Figure 3a. These peaks can be assigned to a tetramethylene sequence in a main chain as reported previously.[4,10] The intensities of chain end carbons and those of tetramethylene carbons seem to be nearly the same. Taking into consideration the fact that one tetramethylene structure has two equivalent carbons (see structure II), approximately half of the polymer chains should have such a regioirregular unit on average. The corresponding reso-

$$\mathrm{-C\overset{C}{C}\overset{C}{C}CCCC\overset{C}{C}\overset{C}{C}C-}$$

II

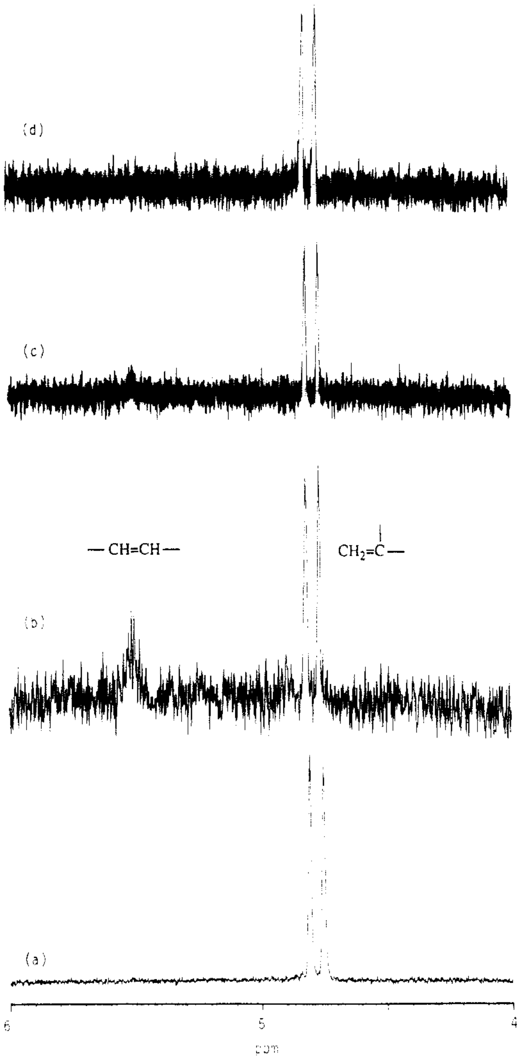
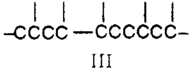


Figure 4. 500-MHz ^1H NMR spectra of polypropylenes obtained at various temperatures: (a) atactic, 0 °C, (b) isotactic, 10 °C, (c) isotactic, 15 °C, (d) isotactic, 20 °C.

nances can hardly be observed in the atactic polymer obtained with Cp_2ZrCl_2.

Polymerization of propene was conducted at various temperatures, and the produced polymers were similarly analyzed by NMR. Figure 4 shows the ^1H NMR spectra of typical polymers obtained. The amount of vinylidene protons decreased in both atactic and isotactic polymers with decreasing polymerization temperatures. However, the isotactic polymer obtained with $Et[H_4Ind]_2ZrCl_2$ at a lower temperature displays a broad peak at around 5.5 ppm, whose relative intensity to vinylidene protons increased with a decrease in the polymerization temperature. This peak might be assigned to the protons in internal C=C double bonds (Figure 4b,c).

Zambelli et al.[4] investigated the polymers obtained at 0 and 25 °C with the same catalyst system and found that the polymer produced at 0 °C contains inverted propene units (structure III), whereas the polymer produced at 25 °C contains tetramethylene sequences (structure II). Figure 5 illustrates the ^{13}C NMR spectrum of the polymer obtained at 10 °C, which displays weak peaks atrributed to the inverted propene units in addition to the peaks originated from the tetramethylene structure. Therefore, the peak at around 5.5 ppm may be derived from the protons of the 2-butenyl end groups formed by the chain transfer of 2,1-inserted propene chain ends (eq 1).



$$-C\overset{C}{\overset{|}{C}}C\overset{C}{\overset{|}{C}}-\overset{C}{\overset{|}{C}}CC\overset{C}{\overset{|}{C}}C\overset{C}{\overset{|}{C}}-$$

III

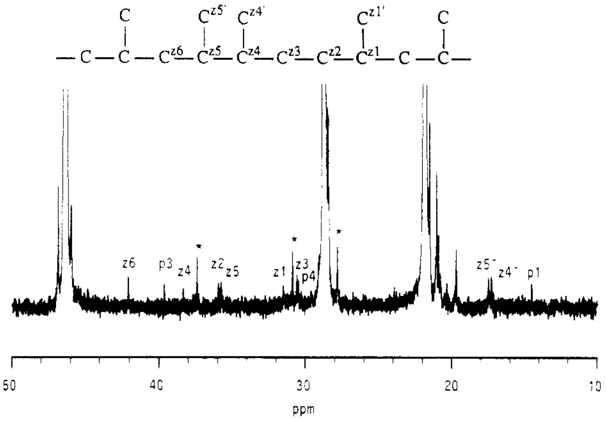
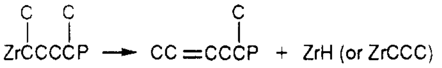


Figure 5. 125-MHz ^{13}C NMR spectrum of isotactic polypropylene obtained at 10 °C.



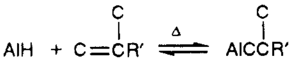
$$Zr\overset{C}{\overset{|}{C}}C\overset{C}{\overset{|}{C}}CP \longrightarrow CC{=}CC\overset{C}{\overset{|}{C}}P + ZrH\ (\text{or } ZrCCC) \qquad (1)$$

IV

Looking at the M_n values of isotactic polymer at 10 °C (run no. Z33) in Table I more carefully, one may notice that the value estimated from ^1H NMR is much higher than that estimated from ^{13}C NMR. The M_n value was recalculated considering structures I and IV. The value thus estimated (shown in parentheses in Table I) is in agreement with that estimated from ^{13}C NMR.

The steric triad distributions and the average run number of the m block determined from the intensities of the methyl carbon resonances of the spectra are summarized in Table I. The results of DSC analysis are also shown in the table. An increase in the polymerization temperature caused a decrease in the mm triad, the average run number of the m block, the melting point, and crystallinity, which agrees well with the results reported by Kaminsky et al.[3b]

Hydroalumination of Polypropylenes. Hydroalumination of polypropylene was conducted in an aliphatic hydrocarbon with $(iso\text{-}C_4H_9)_3Al$ or $(iso\text{-}C_4H_9)_2AlH$ according to the procedure described in the Experimental Section. The catalytic hydroalumination under mild conditions in a polar solvent like diethyl ether is also well-known;[11] however, we did not apply this method due to the low solubility of isotactic polypropylene in such polar solvents. Hydroalumination is a reversible reaction when the alkyl group is branched at the β-position as shown in eq 2. Ziegler used an excess amount of β-branched olefin to obtain quantitatively corresponding trialkylaluminum, and the produced alkylaluminum and unreacted olefin were separated by distillation. In this study, an excess amount of alkylaluminum was used to complete the hydroalumination of vinylidene groups in chain ends.



$$AlH + C{=}\overset{C}{\overset{|}{C}}R' \overset{\Delta}{\rightleftharpoons} AlC\overset{C}{\overset{|}{C}}R' \qquad (2)$$

The polymers which selectively have vinylidene groups (sample nos. Z29, Z31, and Z32) were chosen as starting materials. The conversion of vinylidene to aluminum-carbon bonds was calculated from the intensities of ^1H NMR spectra assuming that the disappeared methine groups are totally reduced to the corresponding alkanes.

Table I
Results of Propene Polymerization with Kaminsky–Sinn Catalysts[a]

run no.	Zr compd	polym temp (°C)	condn time (h)	yield (g)	content of C=C (mmol/g of PP)		$M_n \times 10^{-3}$ by NMR[c]		steric triad (%)					
					$-C=CH_2$	$-HC=CH-$	^1H	^{13}C	mm	mr	rr	n_m[d]	T_m (°C)	ΔH (J/g)
Z30	$Et[H_4Ind]_2ZrCl_2$	0	6	11.5					96	3	1	65	147	95
Z33	$Et[H_4Ind]_2ZrCl_2$	10	4	17.8	0.045	0.026	22.0 (14.0)[e]	12–16	93	5	2	48	143	89
Z34	$Et[H_4Ind]_2ZrCl_2$	15	1	24.1	0.16	0.019	5.4	4.7–6.1	90	7	3	27	134	79
Z29	$Et[H_4Ind]_2ZrCl_2$	20	1	39.6	0.29	nd	3.5	3.1–4.0	81	13	6	13	121	50
Z35	$Et[H_4Ind]_2ZrCl_2$	26	1	30.2	0.38	nd	2.6							
Z31[b]	Cp_2ZrCl_2	0	1	17.8	0.45	nd	2.2	2.1–2.4						
Z32	Cp_2ZrCl_2	20	3	15.3	2.1	nd	0.48	0.47–0.52						

[a] Polymerization conditions: Zr = 0.034 mmol, MAO = 10 mmol, toluene = 100 mL, C_3 = 1 atm. [b] Polymerization was conducted with a 200-mL stainless steel autoclave containing 20 L (STP) of propene. [c] M_n was calculated on the assumption that the structure of all polymer chains should be $CH_2=C(CH_3)[CH_2CH(CH_3)]_nH$. [d] Average run number of the m block; $n_m = \{[mm] + [mr]/2\}/\{[mr]/2\}$. [e] M_n calculated considering both structures, $>C=CH_2$ and $-HC=CH-$.

Table II
Results of Hydroalumination of Polypropylenes

run no.	prepolymer (g)		alkyl aluminum[a] (mmol)		C=C/Al (mol/mol)	solvent[b] (mL)	time (h)	convn to residual	
								alkane (%)	isobutane (%)
A8	Z32	0.4	$i\text{-}Bu_3Al$	1.0	0.72	nC_7 (1)	2	81	
A9	Z32	0.4	$i\text{-}Bu_2AlH$	1.0	0.72	nC_7 (1)	2	94	
A10	Z32	10.0	$i\text{-}Bu_2AlH$	25.0	0.72	nC_7 (25)	1	92	
							3	97	
							5	99	
A27	Z31	2.0	$i\text{-}Bu_2AlH$	0.32	2.8	nC_8 (7)	3		35
							6	94	8
A28	Z31	4.0	$i\text{-}Bu_2AlH$	0.86	2.1	nC_8 (14)	1	87	
							3	96	
A29	Z31	4.0	$i\text{-}Bu_2AlH$	1.4	1.3	nC_8 (16)	3	>99	
AI13	Z29	5.0	$i\text{-}Bu_2AlH$	0.52	2.8	nC_8 (25)	5	84	20
							10	89	13
							22	93	
AI15	Z29	5.0	$i\text{-}Bu_2AlH$	1.4	0.99	nC_8 (25)	1	96	
							6	>99	

[a] $i\text{-}Bu_3Al$ and $i\text{-}Bu_2AlH$ denote triisobutylaluminum and diisobutylaluminum hydride, respectively. [b] nC_7 and nC_8 denote *n*-heptane and *n*-octane, respectively. Hydroalumination was conducted under refluxing temperature.

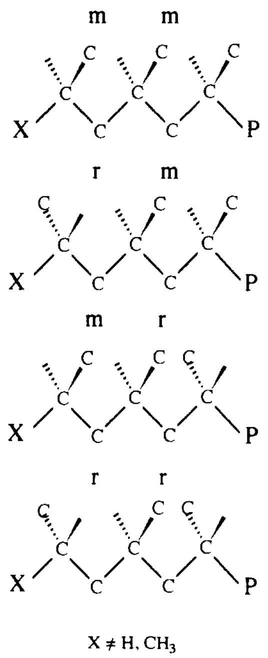
The remaining isobutyl groups were also analyzed by gas chromatography.

For convenience and preciseness of the analysis, the polymer with the lowest molecular weight polypropylene (sample no. Z32) was first exposed to hydroalumination in heptane under its refluxing temperature. The results are summarized in Table II. $(iso\text{-}C_4H_9)_2AlH$ gave a better result than $(iso\text{-}C_4H_9)_3Al$ (see run nos. A8 and A9).

The 22.5-MHz ^{13}C NMR spectrum of the hydrolyzed polymer is illustrated in Figure 2b. The ^{13}C resonances of vinylidene end groups (C^{v1}, C^{v2}, C^{v4} and C^{v5} in Figure 2a) completely disappeared and the ^{13}C resonances attributable to isobutyl end groups newly appeared. The intensities of the *n*-propyl end-group carbons are nearly equal to those of the isobutyl end-group carbons, indicating that the original polymer contained one Al–carbon bond per one polymer chain.

Atactic and isotactic polypropylenes with higher molecular weights (sample nos. Z31 and Z29) were then hydroaluminated in octane by changing the molar ratio of C=C/Al. Since 1 mol of $(iso\text{-}C_4H_9)_2AlH$ can theoretically react with 3 mol of olefins, the reaction was first carried out at the molar ratio of C=C/Al = 2.8 (run nos. A27 and AI13). The conversion increased with an increase in the reaction time and reached more than 90% after 22 h. Atactic polymer was hydroaluminated with a higher speed than isotactic polymer, which may be due to the difference in the solubility of the two polymers in solvents. When $(iso\text{-}C_4H_9)_2AlH$ was used in excess, hydroalumination proceeded much faster and the vinylidene groups were quantitatively hydroaluminated within several hours (run nos. A29 and AI15).

Chart I



In Figure 3a is illustrated the ^{13}C NMR spectrum of the hydrolyzed polymer (run no. AI15), where the resonances attributed to vinylidene end-group carbons completely disappeared and those attributable to isobutyl end-group carbons newly appeared. The intensities of the carbons of both end groups (*n*-propyl and isobutyl) are approximately the same, suggesting that the original polymer

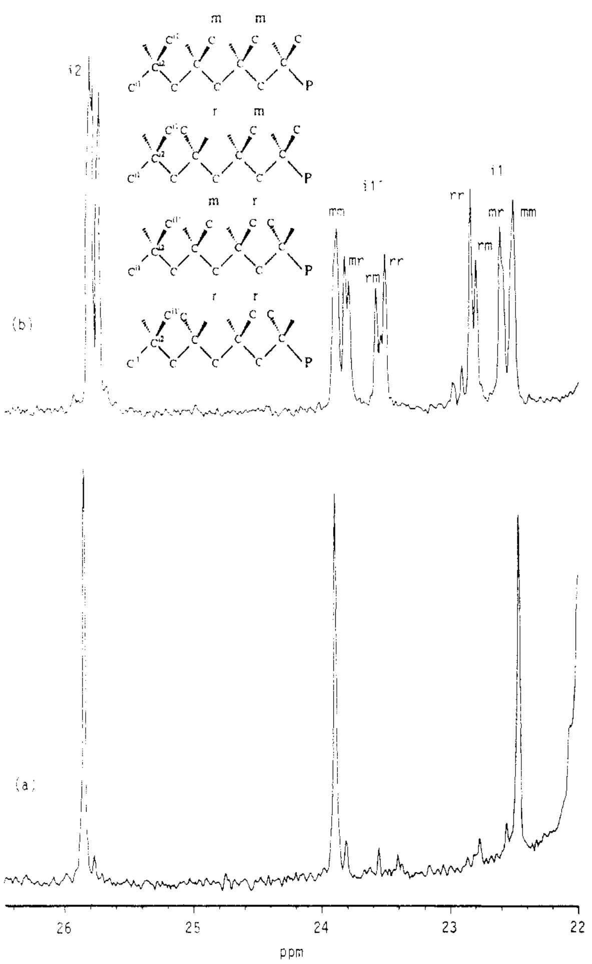


Figure 6. 125-MHz ^{13}C NMR spectra of methyl and methine carbons in isobutyl end groups: (a) isotactic, (b) atactic.

Table III
Triad Tacticity Distributions in Isotactic Polypropylene

	main chain CH_3	initiation C^{p3}	termination C^{i1}	 $C^{i1'}$
mm	81	80	88	86
mr	13	6	4	6
rm		9	6	5
rr	6	5	2	4

contained one Al–carbon bond per one polymer chain.

In Figure 6 are illustrated the expanded spectra of the methyl and methine carbons of isobutyl end groups of sample nos. A29 and AI15. The chemical shifts of the methyl carbons in polypropylene are strongly affected by the configuration of neighboring methyl groups. Taking the neighboring methyl triad into consideration, the chain end should have four different diastereomeric structures as shown in Chart I. The peaks in Figure 6 can be assigned as indicated by referring to the literature.[9] In the atactic polymer (Figure 6b), the intensities of those four peaks are almost the same, which indicates the configuration of the methyl groups is random. On the other hand, the mm peaks are very sharp in the isotactic polymer (Figure 6a).

For comparison, the stereoregularity of the initiation end was also investigated. In Figure 7 are illustrated the methine carbon (C^{p3}) of n-propyl end groups, whose chemical shift is very sensitive to the stereoregularity of the neighboring methyl groups.[9] Similar to the termination end, four peaks are observed with the same intensities in the atactic polymer, while one strong mm peak is observed together with several weak peaks in the isotactic polymer. The triad distribution of the methyl groups in main-chain, initiation, and termination chain ends was determined from these ^{13}C NMR spectra (Table III), which suggests that the stereospecificity of the catalyst does not change so much during propagation, from initiation to termination.

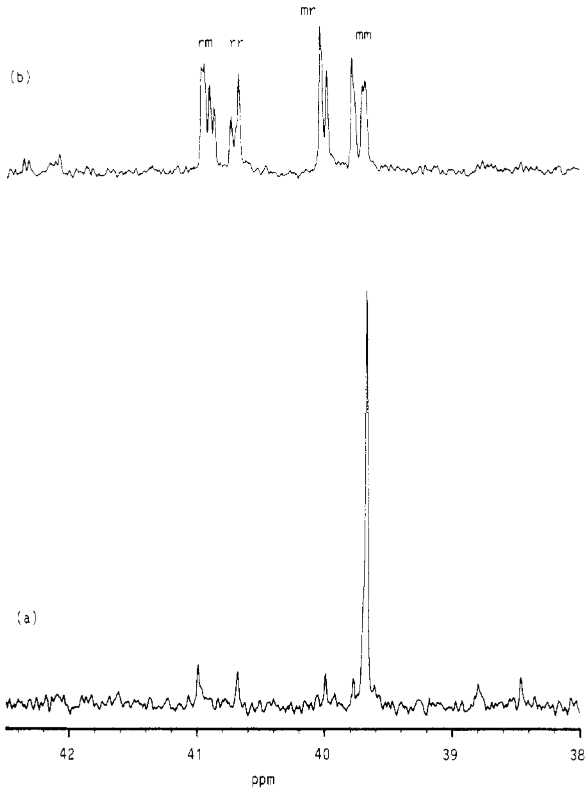


Figure 7. 125-MHz ^{13}C NMR spectra of the methine carbon of the n-propyl end group: (a) isotactic, (b) atactic.

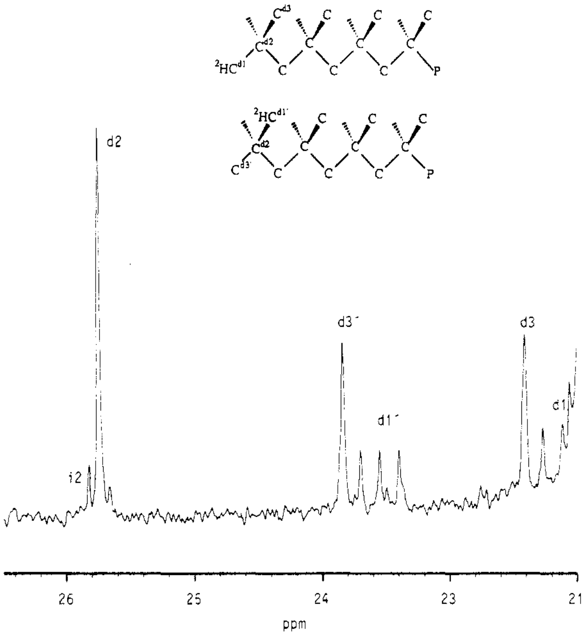
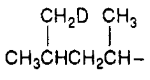


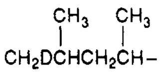
Figure 8. 125-MHz ^{13}C NMR spectrum of isotactic polypropylene quenched by EtO^2H in the methyl and methine regions of the isobutyl end group.

To get more information about the Al-terminated polymer end, AI15 was quenched by the mixture of EtO^2H and ^2HCl. The isobutyl region in the ^{13}C NMR spectrum of a ^{2}H-quenched polymer is shown in Figure 8. The intensities of both methyl carbons of the isobutyl end groups at 23.87 and 22.43 ppm decreased by approximately 50% and new triplet resonances appeared near the methyl resonances at 23.56 and 22.12 ppm with intensities comparable to those of the remaining methyl peaks. The peaks attributable to the remaining methyl groups are shifted to 23.84 and 22.41 ppm, respectively. The resonance of the methine carbon is also shifted from 25.82 to 25.75 ppm without changing the intensity. Any triplet peaks cannot be observed in the methine region. The small nondeuterated peak remaining at 25.82 ppm might be formed by isotopic impurities of H_2O. It is reported that introduction of ^2H caused the α-carbon to shift to −0.4 ppm, the β-carbon to −0.12 ppm, and the γ-carbon to −0.02 ppm, respectively.[12] The differences in the observed chemical shifts between nondeuterated and deuterated polymers are −0.31, −0.07, and −0.03 to −0.02 ppm, which are in good agreement with the expected values. These results indicate the presence of equal amounts of structures V and VI, suggesting that all the vinylidene groups were hydroaluminated and the hydroalumination of the terminal vinylidene group was highly regioselective but nonenantioselective.



$$\mathrm{CH_3\overset{\overset{\textstyle CH_2D}{|}}{C}HCH_2\overset{\overset{\textstyle CH_3}{|}}{C}H-}$$

V



$$\mathrm{CH_2D\overset{\overset{\textstyle CH_3}{|}}{C}HCH_2\overset{\overset{\textstyle CH_3}{|}}{C}H-}$$

VI

In conclusion, it was found that terminally aluminated atactic and isotactic polypropylenes can be synthesized by hydroalumination of polypropylenes prepared with Kaminsky-type catalysts. It is expected that they can be utilized to prepare terminally functionalized polypropylenes as well as polypropylene-based block copolymers. From such a viewpoint, a study on the application of these terminally Al-functionalized polymers is now being carried out and the results will be reported elsewhere.

References and Notes

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Registry No. Cp_2ZrCl_2, 1291-32-3; $(Et[H_4Ind]_2ZrCl_2$, 96363-63-2; $H_2C{=}CHCH_3$ (isotactic homopolymer), 25085-53-4; $H_2C{=}CHCH_3$ (homopolymer), 9003-07-0.