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Regioirregular Polypropene Prepared with SiO_2-Supported Titanium Catalysts

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ABSTRACT: Silica-supported titanium catalysts were prepared either by treatment of a silica-supported $TiCl_4$ with alkylaluminum under very mild conditions or by supporting $CpTiCl_3$ on silica. These catalysts gave polypropene with a high content of insertion errors mostly in blocks of 2,1-oriented propene units. From the copolymerization of propene with a small amount of ^{13}C-enriched ethene, it was also found that ethene is incorporated in the copolymer next to the propene unit with 2,1-orientation.

Introduction

The high-performance $MgCl_2$-supported titanium chloride catalysts are generally used for commercial polypropene production. EP and EPDM copolymers, however, are mostly produced with vanadium-based homogeneous catalysts due to their capability to give good elastomer.[1,2]

One of the differences between vanadium- and titanium-based catalysts in olefin polymerization is regiospecificity arising from different insertion mechanisms. Vanadium-based catalysts propagate propene polymerization by a 2,1-insertion mechanism to produce a syndiotactic or atactic polymer with a large amount of chemical inversion,[3,4] whereas polymerization with titanium-based heterogeneous catalysts proceeds by 1,2-insertion mechanism to give an isotactic or atactic polymer without insertion errors.[5] Even homogeneous catalysts developed by Kaminsky and Sinn produce polypropene with few chemical inversions.[5,6]

We recently pointed out that silica- (SiO_2-) supported $TiCl_4$ catalysts easily form $TiCl_3$ clusters on the surface of silica by cleavage of Ti–O(SiO_2) bonds during the reaction with alkylaluminum compounds used as cocatalyst.[7]

More recently, we found that the $TiCl_4/SiO_2$ catalyst, which is pretreated with $Al(i\text{-}C_4H_9)_3$ under very mild conditions, gives polypropene with a high content of chemical inversion. The catalyst system composed of a SiO_2-supported $CpTiCl_3$ and methylalumoxane (MAO) was also found to give polypropene with a very high content of chemical inversion. The regioirregular enchainment structure of these polymers was analyzed in some detail by ^{13}C NMR. Inversion of propene units in poly(ethene–propene) was also investigated by using ^{13}C-enriched ethene.

Experimental Part

Materials. Propene was supplied by Mitsubishi Petrochemical Co. Ethene-*1,2-*^{13}C (92.1 atom % ^{13}C) was purchased from MSD Isotopes. Anhydrous $MgCl_2$ was supplied from Toho Titanium Co. Silica gel (Grade 952, SA = 319 m^2/g) was purchased from Fuji Davison Co. $Al(C_2H_5)_3$, $Al(i\text{-}C_4H_9)_3$, and methylalumoxane (MAO) were supplied from Tosoh Akzo Chemical Co. $TiCl_4$ was commercially obtained and used without further purification. $CpTiCl_3$ (Cp = cyclopentadienyl) was prepared according to the literature.[8] *n*-Heptane and toluene used as solvents were purified according to the usual procedure.[9,10]

Preparation of Catalysts. The silica gel was calcined in a vacuum at 800 °C for 3 h. $TiCl_4$ solution (20 cm^3; 1 M) in *n*-heptane was added to 3 g of the calcinated silica gel. The mixture was stirred for 3 h at room temperature. After filtration and washing several times with plenty of *n*-heptane, the solid was dried in a vacuum at 60 °C for 3 h to obtain $TiCl_4/SiO_2$ (Cat-I). To prepare Cat-II, 1 g of Cat-I was treated with $Al(i\text{-}C_4H_9)_3$ (0.2 M in *n*-heptane, Al/Ti = 2 (mole ratio)) at −78 °C for 30 min, followed by washing with *n*-heptane to remove the excess alkylaluminum compound. Cat-III ($CpTiCl_3/SiO_2$) was prepared by the reaction of calcinated silica gel (3 g) with $CpTiCl_3$ (20 cm^3 of 0.1 M solution in toluene) at 100 °C for 3 h, followed by washing with plenty of toluene. The $TiCl_4/MgCl_2$ catalyst was prepared according to the procedure reported previously.[11] The contents of titanium in catalysts were determined by atomic absorption spectrometry (Shimadzu AA-6105).

ESR Measurements of the Catalysts. The ESR spectra were taken in a quartz tube of 3-mm i.d. at room temperature with a Varian E-12 spectrometer with 100-kHz field modulation. 1,1-Diphenyl-2-picrylhydrazyl (DPPH) and Mn^{2+} doped on MgO were used to determine amounts of Ti^{3+} (ESR active) and *g* values, respectively.

Polymerization and Analysis of the Polymers. Polymerization was carried out in a 100-cm^3 stainless-steel autoclave equipped with a magnetic stirrer. Polymerization was stopped by quenching with 10% HCl solution in methanol. Each of the polymers was extracted with boiling ODCB (*o*-dichlorobenzene) for 10 h to remove the catalyst residue. The polymer was then fractionated with boiling *n*-heptane for 10 h to determine the isotacticity index (II). ^{13}C NMR spectra of the polymers were recorded at 120 °C using a JEOL GX-270 spectrometer operating at 67.20 MHz. The samples were dissolved in 1,2,4-trichlorobenzene/benzene-d_6 (9/1 by volume).

Results and Discussion

The silica-supported catalyst ($TiCl_4/SiO_2$, Cat-I) was prepared with $Al(i\text{-}C_4H_9)_3$ at −78 °C followed by washing with *n*-heptane to obtain the modified catalyst (Cat-II). The color of catalyst changed from light yellow to dark brown, suggesting that Ti^{4+} was at least partly reduced to Ti^{3+}. For polymerization of propene, Cat-I was used in combination with $Al(i\text{-}C_4H_9)_3$ as cocatalyst. The results obtained are summarized in Table I.

Polypropene prepared with Cat-I combined with $Al(i\text{-}C_4H_9)_3$ contains about 20% isotactic polymer (boiling *n*-heptane-insoluble part). Cat-II, however, was found to produce predominantly atactic polymer with a higher activity as compared with Cat-I. The contents of Ti and Al in Cat-I, Cat-I′ (Cat-I + $Al(i\text{-}C_4H_9)_3$ at 40 °C, followed by washing with *n*-heptane), and Cat-II′ (Cat-I + $Al(i\text{-}C_4H_9)_3$ at −78 °C, followed by washing with *n*-heptane) measured by atomic absorption spectrometry were 1.8, 0; 1.4, 0; and 1.8, 1.8 wt %, respectively, indicating that the titanium chloride once anchored by a chemical bond at the silica skeleton was partly extracted by the reaction with $Al(i\text{-}C_4H_9)_3$ at 40 °C as suggested previously.[12] However, it is not clear whether the aluminum compounds

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Table I
Typical Results of Propene Polymerization with SiO_2-Supported $TiCl_4$ Catalysts[a]

run no.	catalyst	cocatalyst	activity (g of PP/g of Ti per h)	II[b] (%)
1	Cat-I	$Al(i\text{-}Bu)_3$	270	18.2
2	Cat-II		1820	3.5

[a] Polymerization conditions: 0.1-dm^3 autoclave, amount of propene 0.3 mol, catalyst [Ti] = 0.1 mmol, heptane volume 25 cm^3, 40 °C, 1 h. [b] Isotactic index determinded by fractionation with boiling *n*-heptane.

Table II
Quantitative Analysis of Ti^{3+} by ESR

catalyst	treatment conditions[a] with $Al(i\text{-}C_4H_9)_3$	Ti^{3+}(ESR)/Ti(total) (%) before Py[b]	Ti^{3+}(ESR)/Ti(total) (%) after Py[c]
Cat-I′	40 °C, 10 min	4.2	14.5
Cat-II′	−78 °C, 30 min	12.5	13.6

[a] Catalyst ($TiCl_4/SiO_2$) was treated under given conditions, followed by washing with *n*-heptane and drying in vacuo at room temperature. [b,c] ESR spectra were taken before and after adsorption of pyridine, respectively.

Table III
Microstructure of Polypropene

polymer no.[a]	triad[c] (%) [mm]	[mr]	[rr]	chem inversn[d] (%)
1 (C_7-S)[b]	41.8	32.7	25.5	7.5[e]
2 (C_7-S)[b]	41.7	34.8	23.5	9.1[f]

[a] Polymer numbers are from run numbers in Table I. [b] C_7-S denotes the boiling *n*-heptane-soluble part. [c,d] Estimated from the methyl and methine carbon peaks of the ^{13}C NMR spectra, respectively. [e] $M_n = 2.7 \times 10^3$, $M_w = 7.0 \times 10^4$. [f] $M_n = 2.6 \times 10^3$, $M_w = 8.8 \times 10^4$.

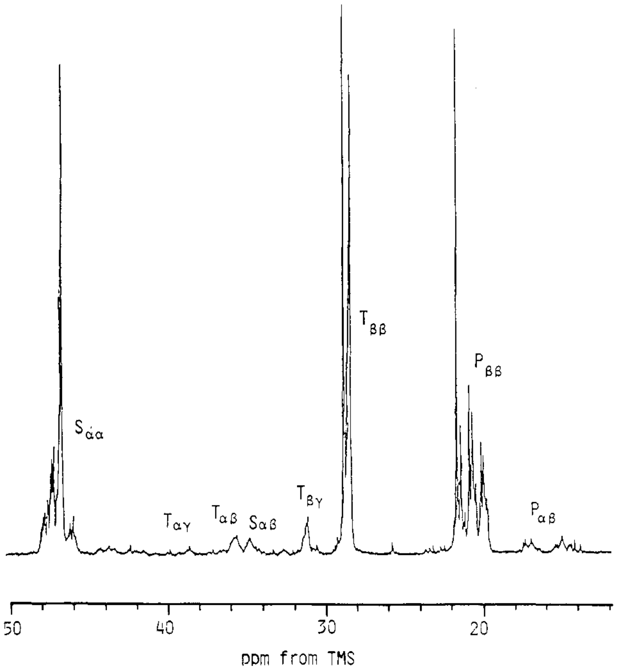


Figure 1. ^{13}C NMR spectrum of polypropene (*n*-heptane-soluble part) prepared with Cat-II (polymer 2).

left in Cat-I′ and Cat-II′ are associated with the titanium species or not. The paramagnetic $TiCl_3$ (Ti^{3+}) species show an ESR signal with *g* value 1.943.[13,14] The Ti^{3+} species in clusters are known to be ESR-silent, but they become ESR-active by adsorbing such strong electron-donor compounds as pyridine, acetonitrile, and $P(CH_3)_3$.[15,16] The ESR spectra were, therefore, taken before and after adsorption of pyridine vapor. The results are summarized in Table II.

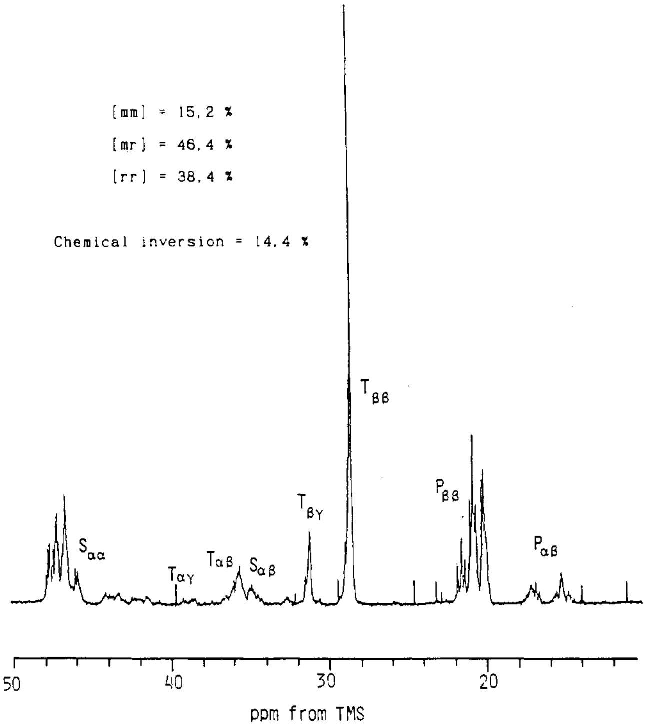


Figure 2. ^{13}C NMR spectrum of polypropene prepared with Cat-III (polymer 4).

Table IV
Results of Propene Polymerization with Cat-III–MAO and $CpTiCl_3$–MAO

run no.	catalyst	Ti (mmol)	cocatalyst	Al/Ti (mol/mol)	activity (g of PP/g of Ti per h)	II (%)
3	Cat-III[b]	0.05	MAO	10	1720	0
4		0.05		40	2050	0[c]
5		0.02		100	1795	0
6		0.05	$Al(i\text{-}C_4H_9)_3$	10	71	~4
7	$CpTiCl_3$	0.05	MAO	40	52	~3
8		0.01		450	54	nd[d]

[a] Polymerization conditions: 0.1-dm^3 autoclave, amount of toluene 20 cm^3, propene 0.3 mole, 40 °C, 2 h. [b] $CpTiCl_3/SiO_2$ (titanium content 1.37 wt %). [c] $M_n = 5.1 \times 10^3$, $M_w = 10.8 \times 10^4$. [d] Not determined due to very low yield.

Table V
Calculation of *x*

peak no.	chem shift[a] (ppm)	C type[a]	peak intens (calcd)[b] type-A	type-B	total
A	38, 48	$T_{\alpha\gamma}$	x	0	x
B	35, 49	$T_{\alpha}\beta$	x	$2(1-x)$	$2-x$
		r_1-$S_{\gamma\alpha\beta\delta}$	0	$2(1-x)$	$2(1-x)$
	34, 62	m_1-$S_{\gamma\alpha\beta\delta}$	0		
C	30, 34	$T_{\beta\gamma}$	x	$2(1-x)$	$2-x$

peak no.	rel peak intens obsd (Cat-II)[c]	obsd (Cat-III)[c]	calcd
A	1.0	1.0	x
B	15.7	18.6	$4-3x$
C	8.4	9.8	$2-x$
x(approx)	0.22	0.18	

[a] From refs 14 and 15. [b] Calculated by considering the contributions of type-A and type-B (in Scheme I) to each peak. [c] Observed from the ^{13}C NMR spectra (Figure 3).

The amounts ESR-active Ti^{3+} in the original Cat-I′ and Cat-II′ were 4.2 and 12.5%, respectively. Adsorption of pyridine caused a marked increase in the amount of ESR-

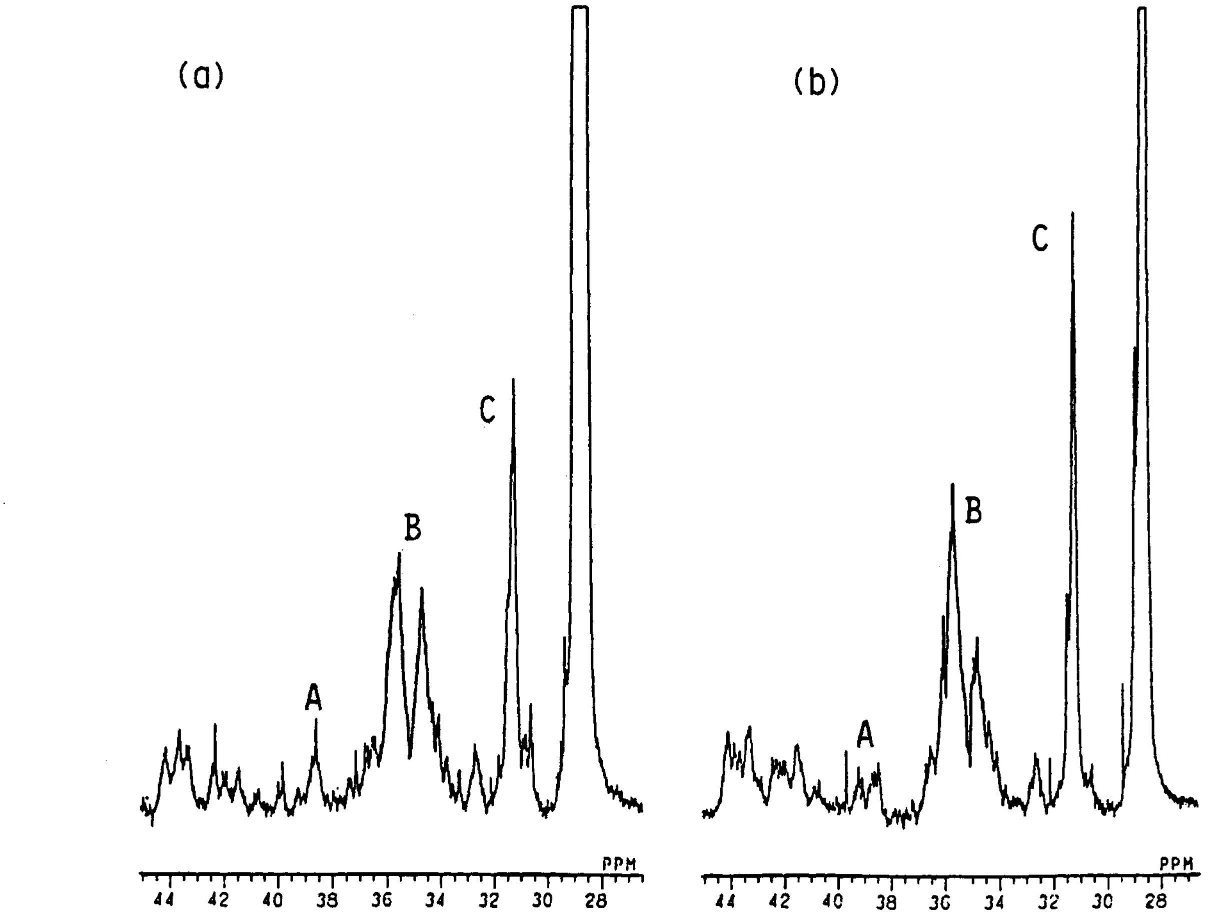


Figure 3. Extended spectra of (a) Figure 1 and (b) Figure 2.

active Ti^{3+} only in Cat-I′, indicating that the majority of the Ti^{3+} species in Cat-I′ is present in clusters. As mentioned above, the cleavage of $Ti-O(SiO_2)$ bonds takes place by the reaction with $Al(i\text{-}C_4H_9)_3$ at 40 °C, resulting in the formation of $TiCl_3$ clusters by coagulation of the dissociated titanium compounds. The $TiCl_3$ clusters thus formed on the silica gel might produce some amount of isotactic polypropylene, whereas most of the titanium species in Cat-II′ are supposed to be anchored to the hydroxyl groups of silica gel. The amount of ESR-active Ti^{3+} species was, however, limited to approximately 15% even in Cat-II′. We need much more additional data to speculate the oxidation state (Ti^{3+} or Ti^{4+}) of active titanium in the present catalysts.

The atactic polymers obtained with Cat-I-$Al(i\text{-}C_4H_9)_3$ and Cat-II were analyzed by ^{13}C NMR. Figure 1 shows a typical ^{13}C NMR spectrum with assignments.[17,18] The amount of chemical inversion, defined in a general concept, was first calculated from the following equation. The results obtained are shown in Table III together with the triad distributions.

$$\text{chem inversn } (\%) = \frac{[T_{\beta\gamma}]}{[T_{\beta\beta}] + [T_{\beta\gamma}] + [T_{\alpha\beta}] + [T_{\alpha\gamma}]} \times 100$$

The triad distributions of these atactic polymers are not so different from those obtained with the common $TiCl_4/MgCl_2-Al(C_2H_5)_3$ catalyst system. However, there is a big difference in the amount of chemical inversion; i.e., the contents of chemical inversion in the present polymers are as high as those in the atactic polymers obtained with homogeneous vanadium catalysts.

Then, a SiO_2-supported $CpTiCl_3$ catalyst (Cat-III) was prepared according to the procedure described in the Experimental Part, and polymerization of propene was carried out with it using either ($Al(i\text{-}C_4H_9)_3$ or MAO as cocatalyst. Propene polymerization was also carried out using a homogeneous $CpTiCl_3$–MAO catalyst system for reference. The polymerization results and the ^{13}C NMR spectrum of a typical polymer are shown in Table IV and Figure 2. The Cat-III-MAO catalyst system selectively gave atactic polymer with a very high content of chemical inversion as expected, where the activity was almost the same as with that of Cat-II (Table I).

Two types of mechanisms can be assumed for the enchainment structures as shown in Scheme I. Regiocontrol is recovered to the original 1,2-addition immediately after the occurrence of chemical inversion (2,1-addition) in type-A, whereas several propene units are continuously incorporated in the polymer with 2,1-orientation to form a blocky structure in type-B.

It is possible to estimate the amounts of type-A and type-B from the methine carbon peaks ($T_{\alpha\gamma}$, $T_{\alpha\beta}$, and $T_{\beta\gamma}$) in the extended ^{13}C NMR spectra (Figure 3). If the contributions of both type-A and type-B to those regioirregular units are assumed to be x and $1 - x$, each peak intensity can be calculated using the relation shown in Table V. Thus, the obtained values of x were approximately 0.22 and 0.18 for Cat-II and Cat-III, from comparison of the intensities between calculated using the above method and observed in the ^{13}C NMR spectra. Therefore, these polymers are considered to have some segments of continued 2,1-oriented propene units. Since the recovery of regiocontrol from 2,1- to 1,2-addition is sterically not easy, the subsequent insertion of propene may have a chance to proceed with the same 2,1-orientation even though it is a slow process.

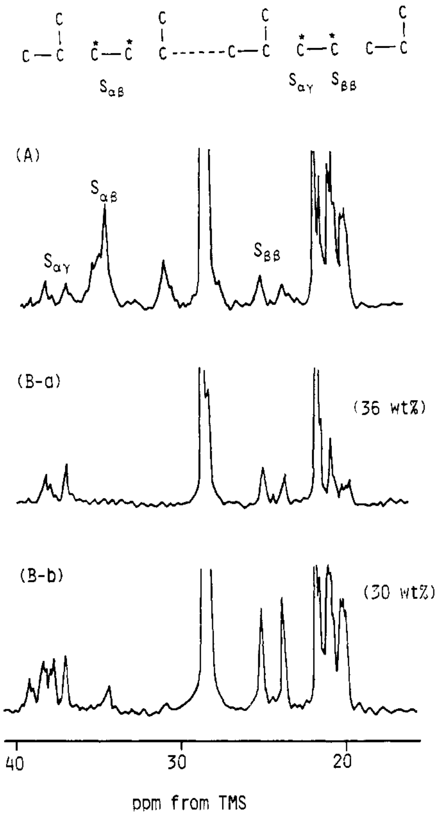
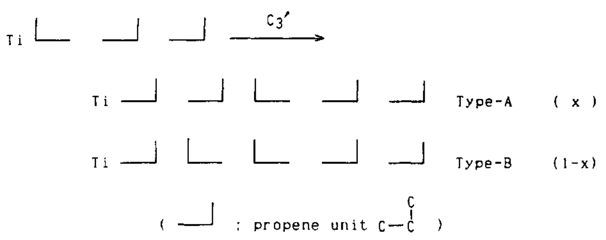
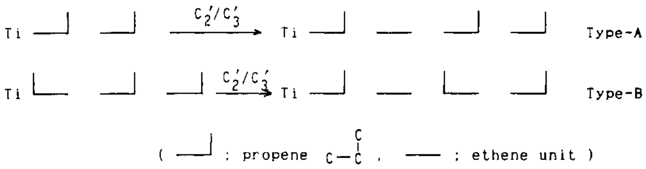


Figure 4. ^{13}C NMR spectra of EP copolymers with low amounts of 1,2-^{13}C-enriched ethene obtained with (A) Cat-II and (B) $TiCl_4/MgCl_2-Al(C_2H_5)_3$: (a) *n*-heptane soluble and diethyl ether insoluble and (b) diethyl ether soluble fractions.

Scheme I



Scheme II



To give better insight, copolymerization of propene with a small amount of 1,2-^{13}C-enriched ethene was performed by using Cat-II as well as a common $TiCl_4/MgCl_2-Al(C_2H_5)_3$ catalyst system, and the arrangement of propene units in the neighborhood of the isolated ethene unit was investigated from the ^{13}C NMR spectra. The copolymer prepared with the $TiCl_4/MgCl_2-Al(C_2H_5)_3$ catalyst system was fractionated into three parts by extraction with boiling diethyl ether and boiling *n*-heptane due to its heterogeneity. Figure 4 shows the ^{13}C NMR spectra of the crude copolymer obtained with Cat-II (A) and of the fractionated copolymers obtained with the common catalyst (B-a, B-b). Copolymer B-a displays strong signals in the $S_{\beta\beta}$ and $S_{\alpha\gamma}$ regions but no signal in the $S_{\alpha\beta}$ region, indicating that the isolated ethene units (C^*-C^*) are exclusively located between two propene units with the same orientation, head–tail and head–tail (structure A in Scheme II). Even the ether-soluble part (B-b) shows a very weak $S_{\alpha\beta}$ peak. These results may be attributed to less insertion errors even in the presence of ethene.

In contrast, the $S_{\alpha\beta}$ signal is much stronger than the $S_{\beta\beta}$ or $S_{\alpha\gamma}$ signal for the copolymer prepared with Cat-II, which indicates that the isolated ethene unit is predominantly located between two propene units arranged with the opposite orientation (structure B in Scheme II). Namely, ethene is added more frequently next to the 2,1-oriented propene unit than to the normal 1,2-oriented one. It may be considered, therefore, that the addition of propene after the occurrence of insertion error is a very slow step. Consequently, ethene has more opportunity to be added next to the 2,1-arranged propene unit. The propene monomer coming next to the ethene unit may be easily added with 1,2-orientation due to less steric hindrance.

In conclusion, we have found that highly regioirregular polypropene can be produced even with the titanium-based catalysts. However, additional experiments are necessary to discuss the active species in detail.

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Registry No. $H_2C{=}CHCH_3$, 115-07-1; $H_2C{=}CH_2$, 74-85-1; $TiCl_4$, 7550-45-0; $Al(i\text{-}C_4H_9)_3$, 100-99-2; $CPTiCl_3$, 1270-98-0; $MgCl_2$, 7786-30-3; $H_2C{=}CHCH_3$ (homopolymer), 9003-07-0; $Al(C_2H_5)_3$, 97-93-8; $(H_2C{=}CHCH_3)(H_2C{=}CH_2)$ (copolymer), 9010-79-1.