Syndiospecific Polymerization of Propene with [*t*-BuNSiMe$_2$Flu]TiMe$_2$-Based Catalysts by Chain-End Controlled Mechanism

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Introduction. Control of microtacticity is one of the most important subjects in propene polymerization. Generally two mechanisms are proposed for production of stereoregular polypropene (PP). One is an enantiomorphic-site-controlled mechanism, and the other is a chain-end-controlled mechanism.

In the enantiomorphic-site-controlled mechanism, steric control is caused by the chirality of the catalyst. Isospecific polymerization by the enantiomorphic-site-controlled mechanism has been investigated in both heterogeneous Zieglar-Natta[1] and homogeneous ansa−metallocene catalysts. The development of the ansa−metallocene catalysts has elucidated the nature of iso-[2] and syndiospecific[3] polymerization by the enantiomorphic-site-controlled mechanism.

In the chain-end-controlled mechanism, steric control arises from the asymmetric configuration of the propagating chain-end. Syndiospecific polymerization of propene by homogeneous V-based catalysts[4−6] have been investigated in detail, where the chain propagation proceeded *via* secondary (2,1) insertion of propene into a V−C bond. Isospecific polymerization by a chain-end-controlled mechanism was reported for the first time by Ewen.[2] Then Cp$_2$TiPh$_2$/methylaluminoxane (MAO) catalyst gave isotactic-rich PP at low temperature (below 0 °C). The chain propagation proceeded *via* primary (1,2-) insertion of propene into M−C bonds in the metallocene catalyst.[7] These results suggest that the insertion mode (1,2- or 2,1-) affects the stereospecificity of the catalyst.

According to literature reported by Erker and Fritze, however, syndiotactic-rich polypropene was obtained with the (C$_5$H$_4$*i*-Pr)$_2$TiX$_2$ (X = Cl, Ph)/MAO catalyst at 10 °C.[8] In addition, Resconi et al. reported that the Cp*$_2$MCl$_2$ (M = Zr, Hf)/MAO catalyst produced syndiotactic poly(1-butene) at low temperature.[9]

Several papers reported that PP obtained by heterogeneous Ti-based catalysts contained PP with syndiotactic sequences.[10−13] Kakugo et al.[14] isolated the syndiotactic-rich polymer from PP obtained with the TiCl$_3$/AlEt$_2$Cl catalyst and proposed syndiospecific propagation by a chain-end-controlled mechanism *via* 1,2-insertion. Busico et al.[15,16] described a similar mechanism in MgCl$_2$-supported TiCl$_4$ catalysts. Thus, it has not been sufficiently clarified as to how the stereospecific polymerization proceeds by a chain-end-controlled mechanism in the Ti-based catalysts.

We have recently found that [η^1:η^5-*tert*-butyl(dimethylfluorenylsilyl)amido]dimethyltitanium ([*t*-BuNSiMe$_2$Flu]TiMe$_2$) complex gave syndiotactic-rich PP by a chain-end-controlled mechanism using either MAO or boron compounds as the cocatalyst. This paper reports the preliminary results of the polymerizations.

Experimental Part. The [*t*-BuNSiMe$_2$Flu] ligand was prepared according to the literature procedure.[17] [*t*-BuNSiMe$_2$Flu]TiCl$_2$ was synthesized by the reaction of the dilithium ligand salt with TiCl$_3$(THF)$_3$, followed by PbCl$_2$ oxidation.[18] The dimethyl complex was obtained as a yellow-orange oily solid by reaction of methyllithium (1.02 M in ether) with the dichloride complex in toluene at −78 °C.

Propene polymerizations were conducted in a 100 mL stainless steel autoclave using toluene as a solvent.

^{13}C NMR spectra of PPs were recorded at 120 °C on a JEOL GX-500 spectrometer in pulse Fourier transform mode. Sample solutions were made in tetrachloroethane-d_2 up to 10% by weight. Molecular weights and molecular weight distributions were determined by Waters 150C at 140 °C using *o*-dichlorobenzene as the solvent.

Results and Discussion. Propene polymerizations were conducted at 40 °C with [*t*-BuNSiMe$_2$Flu]TiMe$_2$ using MAO, [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$, or B(C$_6$F$_5$)$_3$ as a cocatalyst. The results are summarized in Table 1. Polymer yield and molecular weight depended on the cocatalyst used. However, all the obtained PPs were syndiotactic-rich (rr ≈ 0.6), although the microtacticities were slightly dependent upon the kind of cocatalyst. A similar syndiotactic-rich PP was also obtained with [*t*-BuNSiMe$_2$C$_5$Me$_4$]TiCl$_2$/MAO catalyst (CGC).[19] Canich proposed a chain-end-controlled mechanism for the syndiospecific polymerization with CGC type catalysts.[20]

The result remarkably differs from that obtained with the corresponding Zr complex: several papers reported that the stereospecificity of the [*t*-BuNSiMe$_2$Flu]ZrX$_2$ (X = Cl, Me) catalyst was strongly dependent on the cocatalyst used.[21,22]

In order to investigate whether the syndiospecific polymerization proceeded by the chain-end-controlled or the enantiomorphic-site-controlled mechanism, triad analysis was carried out. As shown in Table 1, the triad analysis of all the samples fit the chain-end-controlled mechanism. Theoretical intensities from the Bernoullian statistical equations for chain-end-controlled syndiospecific polymerization also fit the observed intensities (Table 2). It is noteworthy that the chain-end-controlled syndiospecific polymerization proceeded at such a high temperature.

Homogeneous V-based catalysts are well-known to give a syndiotactic PP at low temperature (*ca.* −50 °C) by a chain-end-controlled mechanism. The polymerization mechanism in VCl$_4$/AlR$_2$Cl and V(acac)$_3$/AlR$_2$Cl (R = alkyl group) catalysts was studied in detail by Zambelli et al.[5] and Doi et al.,[6] respectively. They described that the chain propagation in the V-based systems proceed *via* secondary (2,1) insertion of propene into V−C bonds.

Recently, Ni-based diimine complexes reported by Brookhart et al.[23] have attracted much attention, because they perform living polymerization of α-olefins below −10 °C.[21] Zambelli et al.[25] reported that the (1,2-bis(2,6-diisopropylphenyl)ethylenediimine)nickel dibromide (**1**)/MAO catalyst afforded a syndiotactic PP at −78 °C by a chain-end-controlled mechanism. In the ^{13}C NMR spectrum of PP obtained with the **1**/MAO/Al(^{13}CH$_3$)$_3$ catalyst, they detected ^{13}C-enriched isobutyl end groups which were formed by primary (1,2) insertion of propene in the initiation step.[26]

In order to clarify the insertion mode of propene in the present system, the structure of obtained PPs were investigated in detail by ^{13}C NMR. No resonance

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Table 1. Triad Fraction and Triad Mechanistic Model Tests of ^{13}C NMR Spectra of the Methyl Region for Polypropenes Obtained with [*t*-BuNSiMe$_2$Flu]TiMe$_2$[a]

					triad fractions			triad tests[c]	
run	cocatalyst	yield (g)	M_n[b] ($\times 10^{-3}$)	M_w/M_n[b]	mm	mr	rr	4[mm][rr]/[mr]^2	2[mm]/[mr]
1	MAO	3.0	1.8(2.1)[d]	2.5	0.05	0.32	0.64	1.2	0.29
2	Ph$_3$CB(C$_6$F$_5$)$_4$	1.4	68.4	1.6	0.07	0.34	0.59	1.3	0.38
3	B(C$_6$F$_5$)$_3$	1.6	45.1	1.6	0.07	0.39	0.55	0.93	0.33

[a] Polymerization conditions. Run 1: Ti = 20 μmol, [Al]/[Ti] = 400 mol/mol, C$_3$H$_6$ = 3.3 g, toluene = 30 mL, 40 °C, 1 h. Runs 2 and 3: Ti = B = 40 μmol, Al(*n*-octyl)$_3$ = 800 μmol, C$_3$H$_6$ = 3.3 g, toluene = 30 mL, 40 °C, 4 h. [b] Determined by GPC using the PS standard with universal calibration. [c] 4[mm][rr]/[mr]^2 = 1 for chain-end control, 2[mm]/[mr] = 1 for enantiomorphic-site control. [d] Determined by ^{13}C NMR.

Table 2. Calculated (Bernoullian) and Measured Steric Pentad Distributions of Polypropenes Obtained with [*t*-BuNSiMe$_2$Flu]TiMe$_2$

		r	mmmm	mmmr	rmmr	mmrr	mrmm + rmrr	rmrm	rrrr	rrrm	mrrm
run		P	$(1-P)^4$	$2P(1-P)^3$	$P^2(1-P)^2$	$2P^2(1-P)^2$	$2P(1-P)^3 + 2P^3(1-P)$	$2P^2(1-P)^2$	P^4	$2P(1-P)^3$	$P^2(1-P)^2$
1	found[a]		0.00	0.02	0.03	0.07	0.20	0.05	0.38	0.21	0.04
	calcd[b]	0.78	0.00	0.02	0.03	0.06	0.22	0.06	0.37	0.21	0.03
2	found		0.00	0.02	0.04	0.09	0.19	0.07	0.38	0.19	0.02
	calcd	0.77	0.00	0.02	0.03	0.06	0.23	0.06	0.36	0.21	0.03
3	found		0.00	0.02	0.04	0.08	0.22	0.08	0.30	0.21	0.05
	calcd	0.74	0.00	0.03	0.04	0.07	0.24	0.07	0.30	0.21	0.04

[a] Determined by ^{13}C NMR. [b] Calculated by Bernoullian statistical method.

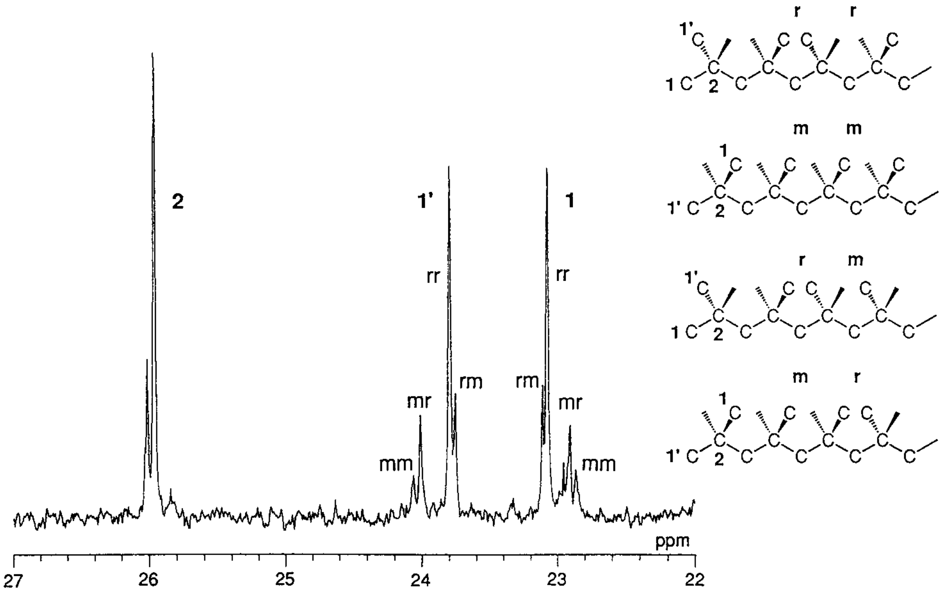


Figure 1. ^{13}C NMR spectrum (125 MHz) of polypropene obtained with the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/MAO catalyst: the isobutyl chain-end region.

assignable to regioirregular units could be observed in the spectra. The result indicates that the [*t*-BuNSiMe$_2$-Flu]TiMe$_2$ catalyst is highly regiospecific, independent of the cocatalyst. Waymouth et al.[27] reported that the CGC gave the syndiotactic-rich PP with a significant amount of regioirregular units.

In the spectrum of PP obtained with [*t*-BuNSiMe$_2$-Flu]TiMe$_2$/MAO, the resonances of isobutyl end groups were observed. However, other saturated and unsaturated structures (such as *n*-propyl, vinylidene, vinyl, and so on) were not detected in the spectrum. The expanded spectrum of the isobutyl chain-end region is shown in Figure 1. The resonances could be assigned according to the literature[28] as follows. The two methyl groups of the isobutyl chain end are not equivalent. One which occupies the "erythro-like" position to the neighboring methyl group is observed at around 23 ppm, and the other which occupies the "threo-like" position is observed at around 24 ppm. Each peak further splits to four peaks depending upon the configurations of methyl groups of the neighboring three propene units (mm, mr, rm, and rr). The relative intensities of these four peaks indicated that the chain end is also syndiotactic-rich.

The molecular weight was calculated from the relative intensity between the isobutyl chain ends and the main chain, on the assumption that both initiation and termination chain ends have the isobutyl structure. The calculated value (2.1 × 10^3) agrees with that obtained by GPC (1.8 × 10^3). The result suggests that the isobutyl group predominantly exists at both the initiation and termination chain ends. The number of polymer chains calculated from the polymer yield and the molecular weight (75 mol/mol of Ti) indicates that most of the polymer chains were terminated by some chain transfer reaction.

The plausible polymerization mechanism which can afford the isobutyl structure at both chain ends is illustrated in Scheme 1. In the initiation step, two cases can be considered for the formation of isobutyl initial ends. One is the primary (1,2) insertion of propene to the Ti$-$CH$_3$ bond followed by propagation with primary insertion. The other is the secondary (2,1) insertion to

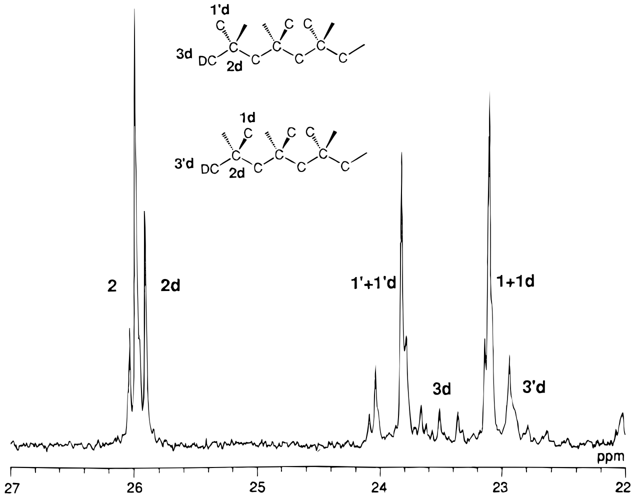
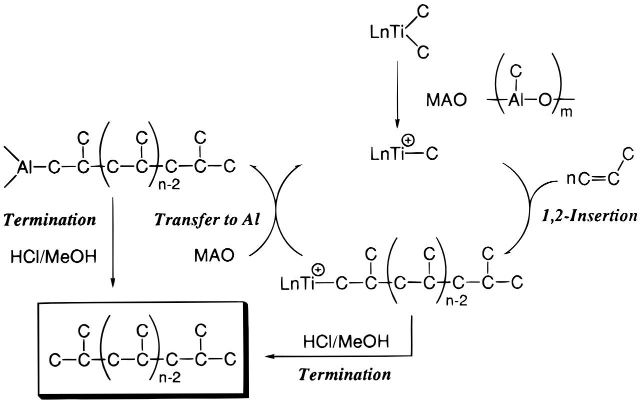


Figure 2. ^{13}C NMR spectrum (125 MHz) of D-quenched polypropene obtained with the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/MAO catalyst: the isobutyl chain-end region.

Scheme 1. Plausible Mechanism of Propene Polymerization with the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/MAO Catalyst



the Ti–H bond followed by propagation with secondary insertion. The latter case is inadequate in this catalyst system because the unsaturated chain ends such as the vinylidene and propenyl group have hardly been observed. The unsaturated chain ends and the Ti–H bond should be formed in pairs as a result of the β-H elimination from the propagating chain to the Ti species or propene monomer.[29] Therefore, it is most probable that the chain transfer to MAO predominantly occurs to provide the Ti–CH$_3$ bonds. The fact that the low molecular weight PP was obtained only by using MAO supports the mechanism described above. If the catalyst system maintains the regioselectivity of 1,2-insertion during propagation, the terminal isobutyl ends are provided by hydrolysis of the Al–CH$_2$CH(CH$_3$)CH$_2$– bonds as well as the Ti–CH$_2$CH(CH$_3$)CH$_2$– bonds.

To detect the Al-terminated chain end, the polymerization with the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/MAO catalyst was quenched by the mixture of EtOD and DCl. Figure 2 shows the isobutyl region in the ^{13}C NMR spectrum of the D-quenched PP. New triplet resonances appeared near the two methyl groups at around 23.5 ppm and around 22.8 ppm. These resonances can be assigned to the deuterated carbons (3-*d* and 3′-*d*) as shown in Figure 2 according to the literature.[30] In addition, the new resonances which can be assigned to β-deuterated carbons (2-*d*) also appeared in the methine region.

The relative intensity of the deuterated methine and nondeuterated methine (2) indicates that most chain ends were Al-terminated. The intensities of 3′-*d*'s resonances were weaker than that of 3-*d*'s resonances, which suggests that the propagation chain end transferred by Al–Me is also syndiotactic-rich.

These results indicate that the syndiospecific polymerization by the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/MAO catalyst proceeds *via* 1,2-insertion of propene from initiation to termination.

Supporting Information Available: Details of catalyst synthesis and NMR analysis (5 pages). Ordering information is given on any current masthead page.

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