Living Polymerization of Propene and 1-Hexene with the [*t*-BuNSiMe$_2$Flu]TiMe$_2$/B(C$_6$F$_5$)$_3$ Catalyst

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ABSTRACT: Polymerization of propene was conducted by [*t*-BuNSiMe$_2$Flu]TiMe$_2$-based catalysts at −50 °C in the presence of trioctylaluminum. When B(C$_6$F$_5$)$_3$ was used as a cocatalyst, polymer yield monotonically increased with increasing polymerization time. The polypropene obtained showed narrow molecular weight distribution, and the number average molecular weight of the polymer linearly increased against the polymer yield. In addition, the number of polymer chains, which was approximately a half the number of Ti used, was almost constant during the polymerization. The living nature of the [*t*-BuNSiMe$_2$Flu]TiMe$_2$ catalyst depended on polymerization temperature and cocatalyst. Deactivation occurred at 0 °C or even at −50 °C when Ph$_3$CB(C$_6$F$_5$)$_4$ was used in place of B(C$_6$F$_5$)$_3$. ^{13}C NMR analysis of the polymer indicated that the living polymerization proceeded highly regiospecifically via 1,2-insertion to give syndiotactic-rich polymer. Polymerization of 1-hexene with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/B(C$_6$F$_5$)$_3$ also proceeded in a living manner at −50 °C, and highly regioregular and syndiotactic-rich polymer was obtained.

Introduction

A living polymerization system, in which neither chain transfer reaction nor deactivation occurs, affords polymers with predictable molecular weights and narrow molecular weight distributions. The living polymerization techniques have also attracted much attention because of their usefulness for synthesis of terminally functionalized polymers and block copolymers. Development of homogeneous single-site catalysts for α-olefin polymerization has enabled us to control the stereoregularity and the regioregularity of polyolefins. However, there are only a few examples for living polymerization of propene with homogeneous catalysts. V(acac)$_3$/AlEt$_2$Cl (acac = acetylacetonate or its analog) had been known as a homogeneous catalyst that performs living polymerization of propene.[1] The living polymerization requires a low temperature and produces syndiotactic polymer by a chain-end-controlled mechanism.

Recently, Brookhart et al.[2] reported that living polymerization of α-olefins (propene, 1-hexene, and 1-octadecene) proceeded at −10 °C with Ni-diimine catalyst. The poly(α-olefin)s obtained contained fewer branches than expected from sequential 1,2-insertion. They suggested that 2,1-insertion of the α-olefin should be predominant during the propagation and that metal migration to the terminal carbon should result in 1,*ω*-enchainment. McConville et al.[3] reported that living polymerization of a higher α-olefin (1-hexene, 1-octene, and 1-decene) was also achieved by chelating diamido complexes of titanium at 23 °C to give regioregular polymers. Schrock et al.[4] also reported the living polymerization of 1-hexene by a zirconium complex that contains the tridentate diamido ligand.

As described above, several living polymerization systems for α-olefins have been recently found. It seems that the N-based ligands play an important role in living polymerization of α-olefins by the transition metal catalysts. However, precise control of regiospecificity and stereospecificity has not been achieved.

In 1990, Bercaw and Okuda reported a new type of metallocene complex that contains the N-based ligand attached to cyclopentadiene derivatives.[5,6] The monocyclopentadienyl-amido complexes have been found to be highly efficient catalysts for the synthesis of LLDPE and the ethylene/styrene copolymerization.[7−9] We have previously studied syndiospecific polymerization of propene with the [η^1:η^5-*tert*-butyl(dimethylfluorenylsilyl)amido]dimethyltitanium ([*t*-BuNSiMe$_2$Flu]TiMe$_2$)-based catalyst at 40 °C.[10] The results indicated that the chain transfer to MAO was predominant in this system. Therefore, we conducted propene polymerization with [*t*-BuNSiMe$_2$Flu]TiMe$_2$ (**1**) using a boron compound as a cocatalyst and found that living polymerization proceeded at −50 °C when B(C$_6$F$_5$)$_3$ was used as a cocatalyst. This paper reports the preliminary results of the polymerization.

Experimental Section

Materials. Propene (from Mitsubishi Chemical Co.) was purified by bubbling through a NaAlH$_2$(*i*-Bu)$_2$/1,2,3,4-tetrahydronaphthalene solution. Triphenylcarbenium tetrakis(pentafluorophenyl)borate (Ph$_3$CB(C$_6$F$_5$)$_4$), tris(pentafluorophenyl)borane (B(C$_6$F$_5$)$_3$), and trioctylaluminum (AlOct$_3$) (from Tosoh-Akzo Chemical Co.) were used without further purification. Research-grade toluene and 1-hexene commercially obtained were dried by refluxing over calcium hydride for 12 h, distilled, and collected over 4A molecular sieves.

Synthesis of [*t*-BuNSiMe$_2$Flu]TiCl$_2$. All the syntheses were carried out under N$_2$ by using standard Schlenk techniques. *t*-BuNHSiMe$_2$C$_{13}$H$_9$ was prepared according to the literature.[11] To a solution of *t*-BuNHSiMe$_2$C$_{13}$H$_9$ (4.51 g, 15.3 mmol) in hexane (40 mL) was added *n*-BuLi (23.5 mL of a 1.55 M solution in hexane) by syringe at −78 °C. After warming to room temperature, the mixture was stirred for 3 h and then the solvent was removed to obtain Li$_2$[*t*-BuNSiMe$_2$Flu]. A solution of the dilithium salt in THF (60 mL) was added to a suspension of TiCl$_3$·3THF (5.38 g, 14.5 mmol) in THF (60 mL) at −78 °C. The mixture was stirred for one night and warmed to room temperature spontaneously. To the mixture was

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added solid $PbCl_2$ (4.25 g, 15.3 mmol), and the resulting mixture was stirred for 2 h.[12] The solvent was removed, and the residue was extracted with toluene (3 × 50 mL). Then the extract was filtered, and the toluene was evaporated to give a crude product. The crude product was extracted with pentane (3 × 100 mL). The extract was then filtered and evaporated to give [*t*-BuNSiMe$_2$Flu]TiCl$_2$ as a dark red solid (4.50 g, 10.9 mmol, 75%). ^{1}H NMR ($CDCl_3$): 7.78 (dd, 1H, $C_{13}H_8$), 7.29 (m, 4H, $C_{13}H_8$), 6.77 (ddd, 1H, $C_{13}H_8$), 6.46 (ddd, 1H, $C_{13}H_8$), 6.21 (dd, 1H, $C_{13}H_8$), 1.60 (s, 9H, C(CH_3)$_3$), 0.49, −0.04 (s, 3 H, Si(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): 143.2, 141.2, 136.6, 136.2 (C10−13 of $C_{13}H_8$), 126.3, 124.8, 122.3, 121.5, 120.4, 119.6, 117.2, 116.6 (C1−8 of $C_{13}H_8$), 108.9 (C9 of $C_{13}H_8$), 63.7 (*C*(CH$_3$)$_3$), 35.1 (C(*C*H$_3$)$_3$), 2.30, 0.56 (Si(*C*H$_3$)$_2$).

Synthesis of [*t*-BuNSiMe$_2$Flu]TiMe$_2$ (1). To a solution of [*t*-BuNSiMe$_2$Flu]TiCl$_2$ (4.50 g, 10.9 mmol) in diethyl ether (100 mL) was added MeLi (21.0 mL of a 1.04 M solution in ether) by syringe at −40 °C. The mixture was stirred for 1 day and warmed to ambient temperature (below 20 °C) spontaneously. The solvents were removed, and the residue was extracted with hexane (3 × 50 mL). To the hexane solution was added MeMgBr (3.0 mL of a 3.0 M solution in ether), and the resulting mixture was stirred for 2 h at ambient temperature. The solvents were removed, and the residue was extracted with hexane (3 × 50 mL). The hexane solution was concentrated and cooled overnight to −78 °C to give [*t*-BuNSiMe$_2$Flu]TiMe$_2$ as yellow-orange microcrystals (1.82 g, 4.91 mmol, 45%). ^{1}H NMR ($CDCl_3$): 8.12 (dd, 2H, $C_{13}H_8$), 7.67 (dd, 2H, $C_{13}H_8$), 7.45 (ddd, 2H, $C_{13}H_8$), 7.30 (ddd, 2H, $C_{13}H_8$), 1.42 (s, 9H, C(CH_3)$_3$), 0.83 (s, 6H, Si(CH_3)$_2$), −0.45 (s, 6H, Ti(CH_3)$_2$). ^{13}C NMR ($CDCl_3$): 134.5, 128.8 (C10−13 of $C_{13}H_8$), 127.6, 127.5, 124.6, 123.3 (C1−C8 of $C_{13}H_8$), 81.6 (C9 of $C_{13}H_8$), 58.8 (*C*(CH$_3$)$_3$), 55.7 (Ti(*C*H$_3$)$_2$), 34.2 (C(*C*H$_3$)$_3$), 5.7 (Si(*C*H$_3$)$_2$). Anal. Calcd for $C_{21}H_{29}NSiTi$: C, 67.91; H, 7.87; N, 3.77. Found: C, 68.03; H, 7.87; N, 3.89.

Polymerization Procedure. Polymerization of propene was conducted in a 100 mL glass reactor by batchwise operation at −50 °C. To a reactor was added toluene (total volume = 30 mL), and it was stirred in a ethanol bath equipped with a cryostat. Gaseous propene was introduced and liquefied at −50 °C. After addition of AlOct$_3$, the polymerization was started by successive introduction of the complex **1** and cocatalyst. The polymerization was quenched by addition of HCl/methanol solution. The polymer obtained was washed several times with methanol and dried under vacuum at 60 °C. Polymerization of 1-hexene was also conducted according to the same procedure except for feeding the monomer by a syringe.

Analytical Procedure. Molecular weights and molecular weight distributions of PPs were determined by a Waters 150C at 140 °C using *o*-dichlorobenzene as solvent. As parameters for universal calibration, $K = 1.38 \times 10^{-4}$ and $\alpha = 0.70$ (for PS standard) and $K = 1.00 \times 10^{-4}$ and $\alpha = 0.74$ (for PP samples) were employed. Molecular weights and molecular weight distributions of poly(1-hexene) were determined using a PS standard without universal calibration. ^{13}C NMR spectra were recorded at 120 °C on a JEOL GX-500 spectrometer operated at 125.65 MHz in pulse Fourier transform mode. The pulse angle was 45°, and about 1000 scans were accumulated with pulse repetitions of 3.3 s. Sample solutions were made in tetrachloroethane-d_2 up to 10 wt %. The central peak of tetrachloroethane-d_2 (74.47 ppm) was used as an internal reference.

Results and Discussion

Propene Polymerization. Results of propene polymerization with **1** using $Ph_3CB(C_6F_5)_4$ or $B(C_6F_5)_3$ as a cocatalyst are summarized in Table 1. Numbers of polymer chains (*N*) were calculated from the polymer yield and the M_n value. The *N* value was almost constant during the polymerization with both $B(C_6F_5)_3$ and $Ph_3CB(C_6F_5)_4$. The result suggests that chain transfer reactions did not occur in either polymerization system. Furthermore, the polypropene obtained with $B(C_6F_5)_3$ shows a narrow molecular weight distribution ($M_w/M_n \approx 1.2$).

Table 1. Results of Propene Polymerization with [*t*-BuNSiMe$_2$Flu]TiMe$_2$-Based Catalyst at −50 °C[a]

run	cocatalyst	time (h)	yield (g)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]	*N* (mmol)[c]
1	$Ph_3CB(C_6F_5)_4$	2	0.13	2.78	1.92	4.8
2	$Ph_3CB(C_6F_5)_4$	4	0.17	2.87	2.12	6.0
3	$Ph_3CB(C_6F_5)_4$	6	0.21	2.68	2.08	7.8
4	$Ph_3CB(C_6F_5)_4$	10	0.24	4.62	1.59	5.2
5	$Ph_3CB(C_6F_5)_4$	16	0.28	4.14	1.52	6.7
6	$B(C_6F_5)_3$	2	0.04	0.21	1.40	17.7
7	$B(C_6F_5)_3$	4	0.10	0.54	1.25	18.6
8	$B(C_6F_5)_3$	8	0.18	0.98	1.17	18.9
9	$B(C_6F_5)_3$	10	0.21	1.06	1.17	19.7
10	$B(C_6F_5)_3$	16	0.38	1.99	1.15	19.3

[a] Polymerization conditions: Ti = B = 40 μmol, AlOct$_3$ = 800 μmol, toluene = 30 mL, C_3H_6 = 3.5 g, temp = −50 °C. [b] Determined by GPC using a PS standard with universal calibration. [c] Number of polymer chains calculated from yield and M_n.

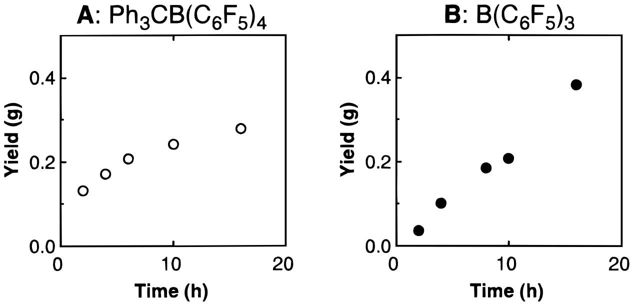

Figure 1. Polymer yield as a function of reaction time for propene polymerization with **1**: (A) $Ph_3CB(C_6F_5)_4$ as a cocatalyst; (B) $B(C_6F_5)_3$ as a cocatalyst.

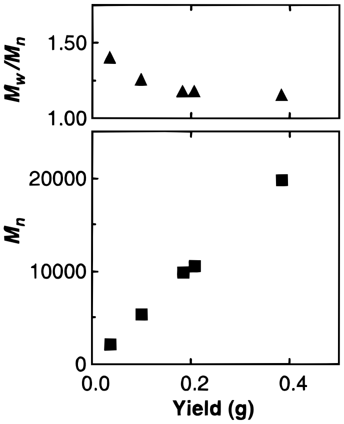

Figure 2. Number average of molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polypropene obtained with **1**/$B(C_6F_5)_3$ as a function of polymer yield.

Figure 1 shows the plots of polymer yield as a function of polymerization time. The polymer yield linearly increased with increasing polymerization time when $B(C_6F_5)_3$ was used. However, an increase of polymer yield showed saturation behavior when $Ph_3CB(C_6F_5)_4$ was used. These results indicate that the deactivation occurred during the polymerization with **1**/$Ph_3CB(C_6F_5)_4$ but not with **1**/$B(C_6F_5)_3$.

Figure 2 shows the plots of number-average molecular weight (M_n) and M_w/M_n values as a function of polymer yield in the **1**/$B(C_6F_5)_3$ system. The M_n value linearly increased against the polymer yield, and the narrow M_w/M_n value was kept during the polymerization.

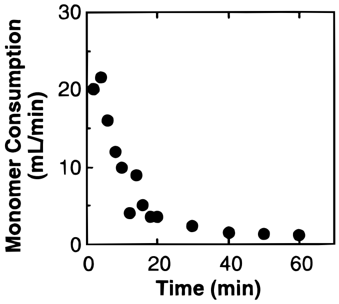

Figure 3. Propene consumption as a function of polymerization time observed in the polymerization with **1**/B(C_6F_5)$_3$. Polymerization conditions: [Ti] = [B] = 40 mmol, temp = 0 °C, [AlOct$_3$] = 800 mmol.

Table 2. Effects of AlOct$_3$ on Propene Polymerization with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/B(C_6F_5)$_3$ Catalyst at −50 °C

run	amt of Al (μmol)	time (h)	yield (g)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]	N (mmol)[c]
8	800	8	0.18	0.98	1.17	18.9
11	2000	8	0.32	1.28	1.17	25.2
12	4000	8	0.44	1.66	1.19	26.4
13	4000	16	0.82	2.30	1.30	35.5

[a] Polymerization conditions: Ti = B = 40 μmol, toluene = 30 mL, C_3H_6 = 3.5 g, temp = −50 °C. [b] Determined by GPC using a PS standard with universal calibration. [c] Number of polymer chains calculated from yield and M_n.

Therefore, there is no doubt that the living polymerization of propene proceeded with the **1**/B(C_6F_5)$_3$ catalyst at −50 °C.

The N value listed in Figure 1 indicates that about a half of Ti in the **1**/B(C_6F_5)$_3$ catalyst were active for the living polymerization. In the **1**/Ph$_3$CB(C_6F_5)$_4$ catalyst, however, only about 15% of Ti turned to be active species, which were gradually deactivated. The above results show that the efficiency of initiation and the stability of active species strongly depends on the boron compounds used.

The living nature of the **1**/B(C_6F_5)$_3$ catalyst seems to depend on polymerization temperature. Therefore, propene polymerization with the **1**/B(C_6F_5)$_3$ catalyst was conducted at 0 °C under an atmospheric pressure of propene, and the amount of consumed propene was measured by a flow meter. Figure 3 shows the plots of monomer consumption as a function of polymerization time. The activity was reduced by a factor of 10 within the initial 30 min. The result indicates that even the **1**/B(C_6F_5)$_3$ catalyst was deactivated at a higher temperature.

McConville et al. reported that some kind of diamidotitanium complex, which conducts the living polymerization of α-olefins combined with B(C_6F_5)$_3$ as a cocatalyst, evolves methane in the absence of monomer and becomes inactive for olefin polymerization.[13] A similar mechanism might be applied to the deactivation of the **1**/B(C_6F_5)$_3$ catalyst at higher temperatures.

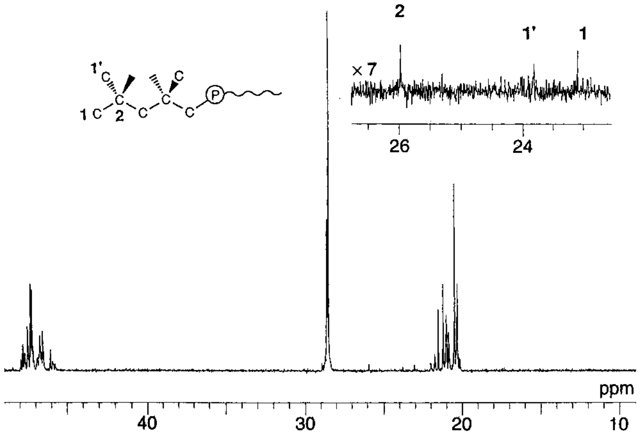

Figure 4. 125 MHz ^{13}C NMR spectrum of polypropene obtained with **1**/B(C_6F_5)$_3$ (run 7).

We used AlOct$_3$ in order to scavenge small amounts of impurities in monomer or solvent, such as oxygen and water. However, it is plausible that AlOct$_3$ takes part in the polymerization such as initiation and chain transfer reactions. Therefore, propene polymerization was conducted in the presence of various concentrations of AlOct$_3$. Table 2 shows the results of the polymerization. The polymer yield and the M_n value increased with increasing concentration of AlOct$_3$ (runs 8, 11, and 12). The result indicates that the alkylaluminum enhances the rate of chain propagation. A plausible explanation for the rate enhancement is that AlOct$_3$ interacts with the counteranion of the cationic active Ti species to improve coordinative unsaturation of the Ti species.

On the other hand, the N value also slightly increased with increasing aluminum concentration. When the polymerization time was doubled in the presence of 4000 mmol of AlOct$_3$ (runs 12 and 13), the M_n value was not doubled, although the polymer yield was approximately doubled. In addition, the M_w/M_n value and the N value increased with increasing polymerization time. Therefore, it seems that the chain transfer to AlOct$_3$ was not negligible at such a higher concentration of alkylaluminum.

Structure of Living Polypropene. We have previously investigated the microstructures of polypropene obtained with [*t*-BuNSiMe$_2$Flu]TiMe$_2$-based catalysts at 40 °C.[10] The ^{13}C NMR spectra of the polymers indicated that the polymerization proceeded via 1,2-insertion, and the catalyst system was highly regiospecific. It was also found that the syndiotactic-rich polypropene was obtained by chain-end control.

Figure 4 shows the ^{13}C NMR spectrum of “living” polypropene (obtained with run 7). The living polymerization system was also proved to be highly regiospecific because any resonances assignable to regioirregular units were not observed in the spectrum. In addition to three major resonances of the main chain carbons, three minor resonances were observed at 23–26 ppm. These resonances are assignable to the isobutyl structure of the chain end.[14] On the assumption that both the initiation and the termination chain ends are isobutyl structures, the M_n value was calculated from the intensities of these resonances. The value, 6100, almost agreed with that determined by GPC (5400). These results indicate that the living polymerization also proceeded via 1,2-insertion of propene, as shown in Scheme 1.

Table 3 lists steric pentad fractions determined from relative intensities of the methyl group in main chain, which split to nine peaks due to the stereoregularity. The “living” polypropene obtained at −50 °C was syndiotactic-rich; however, the syndiotacticity was slightly lower than that of the polypropene obtained at 40 °C. The pentad intensities calculated by Bernoullian statistical equations for chain-end-controlled syndiospecific polymerization are also listed in Table 3. The values considerably fit to the observed ones when polymeriza-

Scheme 1

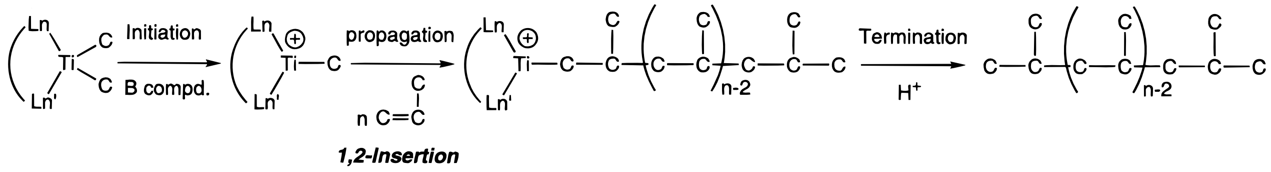

Table 3. Calculated and Measured Steric Pentad Distributions of Polypropene Obtained with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/B(C$_6$F$_5$)$_3$

		40 °C[a]		−50 °C (run 7)	
pentad	Bernoullian	found[b]	calcd[c]	found[b]	calcd[c]
(r)	P		0.74		0.70
mmmm	$(1-P)^4$	0.00	0.00	0.01	0.01
mmmr	$2P(1-P)^3$	0.02	0.03	0.04	0.04
rmmr	$P^2(1-P)^2$	0.04	0.04	0.07	0.04
mmrr	$2P^2(1-P)^2$	0.08	0.07	0.14	0.09
mmrm + rmrr	$2P(1-P)^3 + 2P^3(1-P)$	0.22	0.24	0.17	0.24
mrmr	$2P^2(1-P)^2$	0.08	0.07	0.10	0.09
rrrr	P^4	0.30	0.30	0.24	0.24
mrrr	$2P(1-P)^3$	0.21	0.21	0.17	0.21
mrrm	$P^2(1-P)^2$	0.05	0.04	0.05	0.04

[a] From ref 10. [b] Determined by ^{13}C NMR spectroscopy. [c] Calculated by the Bernoullian statistical method for chain-end-controlled syndiospecific polymerization.

Table 4. Results of 1-Hexene Polymerization with [*t*-BuNSiMe$_2$Flu]TiMe$_2$/B(C$_6$F$_5$)$_3$ Catalyst at −50 °C[a]

run	time (h)	yield (g)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]	N (mmol)[c]
14	16	0.11	0.55	1.12	20.4
15	24	0.18	1.08	1.07	17.1
16	36	0.20	1.21	1.08	16.7
17	48	0.32	1.72	1.09	18.8
18	72	0.44	2.60	1.10	17.0

[a] Polymerization conditions: Ti = B = 40 μmol, AlOct$_3$ = 800 μmol, toluene = 5 mL, 1-hexene = 10 mL, temp = −50 °C. [b] Determined by GPC using a PS standard. [c] Number of polymer chains calculated from yield and M_n.

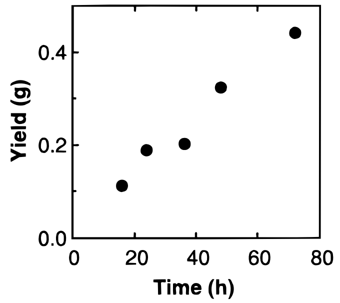

Figure 5. Polymer yield as a function of reaction time for 1-hexene polymerization with **1**/B(C$_6$F$_5$)$_3$.

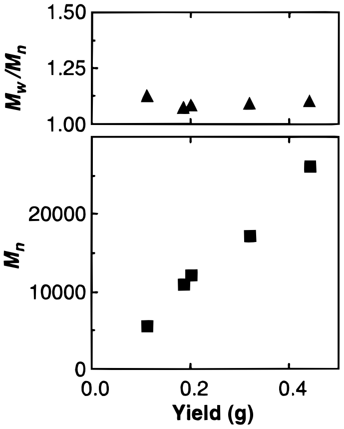

Figure 6. Number average of molecular weight (M_n) and molecular weight distribution (M_w/M_n) of poly(1-hexene) obtained with **1**/B(C$_6$F$_5$)$_3$ as a function of polymer yield.

tion was conducted at 40 °C. However, the discrepancy increases at −50 °C. Especially, the observed intensities of rmmr and mmrr were much larger than the calculated values and that of mmrm + rmrr was less than the calculated one. The structures of rmmr and mmrr are considered as predominant stereodefects in enantiomorphic-site-controlled syndiospecific polymerization due to the miss-selection of the prochiral face of propene.[15] On the other hand, the stereodefect of rmrr is characteristically observed in the chain-end-controlled polymerization, although the defect can be also produced in the enantiomorphic-site-controlled polymerization due to the miss-migration of the propagating chain.

Considering the symmetry of the Ti complex together with the above results, it seems that the syndiospecific polymerization of propene proceeds by the enantiomorphic-site control at −50 °C, although the syndiospecificity was very low. Further investigation should be necessary to clarify the mechanism.

1-Hexene Polymerization. Polymerization of 1-hexene was conducted with the **1**/B(C$_6$F$_5$)$_3$ catalyst at −50 °C, and the results are summarized in Table 4. It was found that the poly(1-hexene)s showed a narrow molecular weight distribution ($M_w/M_n = 1.1$), and the N value was almost constant during the polymerization. In Figure 5 the polymer yield is plotted against polymerization time. The yield linearly increased with increasing polymerization time. Figure 6 shows the plots of M_n and M_w/M_n as a function of the polymer yield. The M_n value also increased linearly against the polymer yield, and the M_w/M_n value was kept narrow during the polymerization. Therefore, it was found that living polymerization of 1-hexene also proceeded with the **1**/B(C$_6$F$_5$)$_3$ catalyst at −50 °C.

Structure of Living Poly(1-hexene). The structure of "living" poly(1-hexene) was investigated by ^{13}C NMR spectroscopy. Figure 7 shows the spectrum of poly(1-hexene) obtained in run 18. Any resonances assignable to regioirregular units were not observed. The fact proved that the **1**/B(C$_6$F$_5$)$_3$ catalyst system maintains the high regiospecificity in the 1-hexene polymerization.

The resonances of main chain carbons and the methylene carbon connected to the main chain were split to several peaks due to the stereoregularity of the polymer (a, b, and c illustrated in Figure 7).[16] Since the splitting of these resonances is not enough to estimate the steric triad or pentad fractions, it is difficult to elucidate the mechanism of steric control in 1-hexene polymerization as compared with the propene polymerization. However, these resonances indicate that the poly(1-hexene) obtained with **1**/B(C$_6$F$_5$)$_3$ at −50 °C was also syndiotactic-rich, similar to the polypropene.

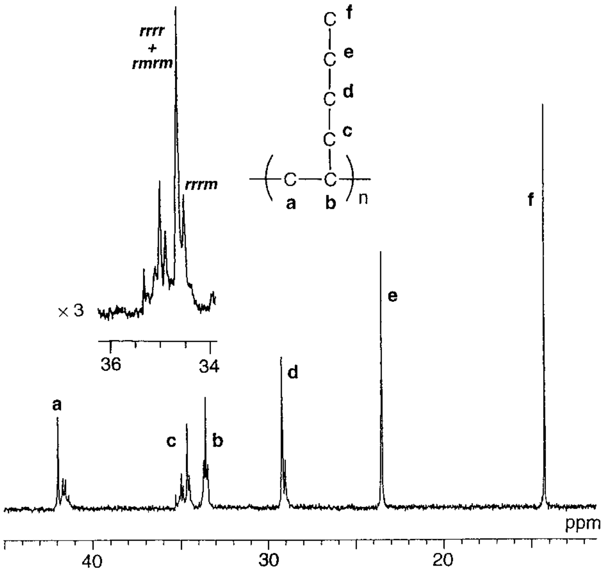

Figure 7. 125 MHz ^{13}C NMR spectrum of poly(1-hexene) obtained with **1**/B(C_6F_5)$_3$ (run 18).

Conclusion

Propene polymerization was conducted by [*t*-BuNSiMe$_2$Flu]TiMe$_2$ (**1**) combined with B(C_6F_5)$_3$ or Ph$_3$CB(C_6F_5)$_4$ as a cocatalyst in the presence of AlOct$_3$. Living polymerization of propene proceeded at −50 °C when B(C_6F_5)$_3$ was used. Addition of a large excess of AlOct$_3$ increased the propagation rate, whereas the chain transfer reaction was induced by AlOct$_3$. The ^{13}C NMR spectrum of polypropene obtained indicated that the living system was highly regiospecific and produced syndiotactic-rich polymer. Living polymerization of 1-hexene also proceeded at −50 °C with the **1**/B(C_6F_5)$_3$ catalyst. The ^{13}C NMR spectroscopy revealed that the poly(1-hexene) obtained was also highly regioregular and syndiotactic-rich.

This is the first example of highly regiospecific living polymerization of propene with the half-sandwich metallocene catalyst. It can be expected to control both the regiospecificity and the stereospecificity in living polymerization of propene by means of design of the amido-type half-titanocenes.[17] Furthermore, the excellent capability of amido-type half-titanocenes for copolymerization might allow us to synthesize various living copolymers.

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