Articles

Substituent Effects of *tert*-Butyl Groups on Fluorenyl Ligand in Syndiospecific Living Polymerization of Propylene with *ansa*-Fluorenylamidodimethyltitanium Complex

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ABSTRACT: [*t*-BuNSiMe₂(2,7-*t*-Bu₂Flu)]TiMe₂ and [*t*-BuNSiMe₂(3,6-*t*-Bu₂Flu)]TiMe₂ were synthesized and characterized by elemental analysis, ¹H NMR, and single-crystal X-ray analysis. These complexes were applied for propylene polymerization using dried modified methyaluminoxane (dMMAO) as a cocatalyst at 0 and 25 °C. The introduction of *tert*-butyl substituents to the fluorenyl ligand improved the activity more than 3 times regardless of the position of the substituents. The postpolymerization testified that both catalytic systems conducted the propylene polymerization in a living manner at both 0 and 25 °C. The propagation rate increased linearly against the Al/Ti ratio from the range of 100–400 with keeping the number of polymer chains constant, which directly indicates that a larger amount of dMMAO enhanced the propagation rate. The introduction of *tert*-butyl substituents also improved the syndiospecificity: the 3,6-position was more effective than the 2,7-position, and [*t*-BuNSiMe₂(3,6-*t*-Bu₂-Flu)]TiMe₂ gave the living polypropylene with the syndiotactic triad of 0.93 and the melting point of 142 °C.

Introduction

Since the first living polymerization of propylene was reported with the V-based homogeneous catalyst in the end of 1970s,¹ much effort has been paid for developing homogeneous catalysts for living polymerization of propylene by designing the structure of complexes and controlling the polymerization conditions.^{2–14} Although stereospecific living polymerization systems are necessary to design propylene-based well-defined polymers, there are only limited examples for the stereospecific living polymerization of propylene.

The Mitsui group and Coates et al. reported that bis-(phenoxyimine)titanium derivatives combined with methylalumoxane (MAO) were effective for syndiospecific living polymerization of propylene by chain-end control to give syndiotactic polypropylene (PP)-block-poly-(ethylene-co-propylene) by sequential monomer addition.^{6–10} The Mitsui group succeeded in improving the syndiospecificity to 0.94 in syndiotactic triad (rr) by tuning the bis(phenoxyimine) ligand.¹⁰ Busico et al. reported the synthesis of isotactic PP-block-polyethylene with the Zr complex containing phenoxyamine ligand via "quasi-living polymerization", and they have recently found that the use of adamantyl-substituted phenoxy ligands not only improved isospecificity to 0.985 in isotactic pentad (mmmm) but also suppressed the monomer-induced chain transfer.¹¹ Coates et al. have

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recently reported that the bis(phenoxyketimine)titanium complex produced substantially isotactic living PP with mmmm value of 0.61 at -20 °C and gave isotactic PP-*block*-poly(ethylene-*co*-propylene).¹² These living systems realized the block copolymers composed of stereoregular PP segments. The propagation rates of propylene in these living systems were however much lower than those of common nonliving systems.

We have previously reported that Ti complex 1 (Chart 1) possessing the fluorenyldimethylsilylamido ligand conducted syndiospecific living polymerization of pro-

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Table 1. Propylene Polymerization with 2 and 3 Activated by DMMAO^a

entry	cat.	temp (°C)	Al/Ti ^b	time (min)	yield (g)	activity c	$M_{ m n}{}^d~(imes 10^4)$	$M_{ m w}/M_{ m n}^{d}$	$N^e \ (\mu { m mol})$
1	1	0	400	11	2.42	660	16.1	1.31	15
2	2	0	400	3	2.28	2279	20.8	1.65	11
3	3	0	400	3	2.32	2318	19.6	1.46	12
4	2	0	200	9	2.36	787	20.2	1.68	12
5	3	0	200	7	2.14	916	16.9	1.45	13
6	2	25	200	6	2.44	1220	19.0	1.48	13
7	3	25	200	5	2.20	1318	16.9	1.43	12

^{*a*} Polymerization conditions: heptane = 30 mL, Ti = 20 μ mol, propylene = 1 atm. ^{*b*} Molar ratio. ^{*c*} Activity in kg of PP/(mol of Ti h). ^{*d*} Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration. ^{*e*} Calculated from yield and M_n .

pylene at 0 °C, when activated by dried methylaluminoxane (dMAO) in toluene.¹³ We have investigated the solvent effects on the stereospecificity of the propylene polymerization by using 1 combined with dried modified MAO (dMMAO), which was prepared from the toluene solutions of MMAO by removing the solvent and free trialkylaluminums, and found that the syndiospecificity improved according to the decrease in the polarity of the solvent with keeping the livingness, and the PP with the rr value of 0.73 was obtained in heptane with high activity.¹⁴ The Atofina group has reported that [*t*-BuNSiMe₂(2,7-*t*-Bu₂Flu)]TiCl₂¹⁵ and [*t*-BuNSiMe₂(3,6-*t*-Bu₂Flu)]TiCl₂¹⁶ combined with MAO produced highly snydiotactic PP with high activity.

In this paper, aiming at highly syndiospecific living polymerization of propylene with high activity, we synthesized $[t-BuNSiMe_2(2,7-t-Bu_2Flu)]TiMe_2$ (2) and $[t-BuNSiMe_2(3,6-t-Bu_2Flu)]TiMe_2$ (3) (Chart 1) and applied them for propylene polymerization in heptane using dMMAO as a cocatalyst.

Experimental Section

Materials. All operations were performed under nitrogen gas using standard Schlenk techniques, and all solvents were dried by usual procedures and freshly distilled before use. The ligands of the Ti complexes and the complexes were prepared according to the literature procedure.^{16,17} The complexation of the ligands and TiCl₄ was conducted by the method reported by Resconi to directly obtain the corresponding dimethyl complexes, and the complexes were isolated as dark-red single crystals in good yields (see Supporting Information). dMMAO was prepared according to the method reported previously.¹⁸ Reserarch grade propylene (Takachiho Chemicals Co.) was purified by passing it through columms of NaOH, P₂O₅, and molecular sieves 3 Å, followed by bubbling it through a NaAlH₂Et₂/1,2,3,4-tetrahydronaphthalene solution.

Polymerization Procedure. Polymerization was performed in a 100 mL glass reactor equipped with a magnetic stirrer and carried out as the following two methods. (i) Semibatch method. At first, the reactor was charged with prescribed amounts of dMMAO and solvent (heptane). After the solution of cocatalyst was saturated with gaseous propylene under atmospheric pressure, polymerization was started by the addition of 1 mL solution of the Ti complex (20 μ mol) in heptane, and the consumption rate of propylene was monitored by a mass flow meter. (ii) Batch-type method. After a certain amount of gaseous propylene was dissolved in the heptane solution of dMMAO, polymerization was started by the addition of 1 mL solution of catalyst (20 μ mol) in heptane. Polymerization was conducted for a certain time and terminated with acidic methanol. The polymers obtained were adequately washed with methanol and dried under vacuum at 60 °C for 6 h.

Analytical Procedure. Molecular weight and molecular weight distribution of polymer obtained were determined by gel permeation chromatography with a Waters 150 CV at 140 °C using *o*-dichlorobenzene as a solvent. The parameters for universal calibration were $K = 7.36 \times 10^{-5}$, $\alpha = 0.75$ for



Figure 1. Rate-time profiles of propylene polymerization with **2** or **3** activated by dMMAO at 0 °C: (\blacksquare) **2**, (\blacklozenge) **3**.

polystyrene standard and $K = 1.03 \times 10^{-4}$, $\alpha = 0.78$ for PP samples. The ¹³C NMR spectra of PPs were measured at 130 °C on a JEOL GX 500 spectrometer operated at 125.65 MHz in the pulse Fourier transform mode. The pulse angle was 45°, and about 10 000 scans were accumulated in pulse repetition of 5.0 s. Sample solutions were prepared in 1,1,2,2-tetrachloroethane- d_2 , and the central peak of the solvent (74.47 ppm) was used as an internal reference. Differential scanning calorimetry (DSC) analyses were performed on a Seiko DSC-220. The samples were encapsulated in aluminum pans and annealed at 80 °C for 4 h to ensure sufficient time for crystallization. After annealing, the DSC curves of the samples were recorded under a nitrogen atmosphere with a heating rate of 10 °C/min from 20 to 200 °C. Diffraction measurements of X-ray were made on a Rigaku RAXIS IV imaging plate area detector with Mo K α radiation ($\lambda = 0.71059$ Å). Indexing was performed from two oscillation images, which were exposed for 5 min. The crystal-to-detector distance was 110 mm. Readout was performed with the pixel size of 100 μ m $\times \mu$ m. Neutral scattering factors were obtained from the standard source.

Results and Discussion

Propylene polymerizations were performed by **2** and **3** activated with dMMAO in heptane at 0 and 25 °C, respectively. The results are summarized in Table 1.

For comparison, the result of the nonsubstituted original complex 1 is shown in entry 1 of Table 1. 2 and 3 showed more than 3 times higher activity of 1 in the presence of dMMAO (Al/Ti = 400) and produced a large amount of polymer in a few minutes to stop the stirring (entries 2 and 3). Hence, the polymerization behaviors could not be evaluated correctly. We therefore reduced the Al/Ti ratio to 200 (entries 4 and 5).

The rate-time profiles of propylene polymerization with both systems showed the constant activity after a certain induction period until the stirring was interfered by the polymer produced.

Both systems gave high-molecular-weight PPs ($M_n > 150\ 000$) for 7 min at 0 °C. These results indicate that the propagation rate was improved by the introduction

Та	ıb	le	2.	Postpo	lymerization	of Propy	lene	with	2 and 3^a	
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				10			
cat.	propylene (g)	temp (°C)	time (min)	yield (%)	$M_{ m n}{}^b(imes 10^4)$	$M_{ m w}/M_{ m n}{}^b$	$N^{ m c}~(\mu{ m mol})$
2	0.63	0	60	100	6.5	1.56	10
2	0.63 ± 0.63	0	60 + 60	100	11.0	1.49	11
2	0.63	25	20	97	5.0	1.41	12
2	0.63 ± 0.63	25	20 + 20	95	10.2	1.43	12
3	0.63	0	60	100	5.9	1.27	11
3	0.63 ± 0.63	0	60 + 60	100	11.2	1.29	11
3	0.63	25	20	97	5.1	1.28	12
3	0.63 ± 0.63	25	20 + 20	98	10.5	1.32	12
	cat. 2 2 2 2 3 3 3 3 3 3 3	$\begin{tabular}{ c c c c c c } \hline cat. & propylene (g) \\ \hline 2 & 0.63 \\ 2 & 0.63 + 0.63 \\ 2 & 0.63 + 0.63 \\ 3 & 0.63 \\ 3 & 0.63 + 0.63 \\ 3 & 0.63 + 0.63 \\ 3 & 0.63 + 0.63 \\ \hline 3 & 0.63 + 0.63 \\ \hline 3 & 0.63 + 0.63 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	cat.propylene (g)temp (°C)time (min)2 0.63 0602 $0.63 + 0.63$ 060 + 602 0.63 25202 $0.63 + 0.63$ 2520 + 203 0.63 0603 $0.63 + 0.63$ 060 + 603 $0.63 + 0.63$ 060 + 603 $0.63 + 0.63$ 25203 $0.63 + 0.63$ 2520 + 20	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	cat.propylene (g)temp (°C)time (min)yield (%) $M_n{}^b (\times 10^4)$ 20.630601006.520.63 + 0.63060 + 6010011.020.632520975.020.63 + 0.632520 + 209510.230.63060 + 601005.930.63 + 0.63060 + 6010011.230.632520975.130.63 + 0.632520 + 209810.5	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$

^{*a*} Polymerization conditions: heptane = 30 mL, Ti = 20 μ mol, Al = 4.0 mmol. ^{*b*} Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration. ^{*c*} Calculated from yield and M_n .



Figure 2. GPC curves of polypropylenes obtained in postpolymerization: (a) **2**-dMMAO at 0 °C; (b) **2**-dMMAO at 25 °C; (c) **3**-dMMAO at 0 °C; (d) **3**-dMMAO at 25 °C.



Figure 3. 125 MHz ¹³C NMR spectra of the methyl region of polypropylenes obtained at 0 °C: (a) 1–dMMAO entry 1; (b) 2–dMMAO, entry 4; (c) 3–dMMAO, entry 5.

of *tert*-butyl groups on the Flu ligand. The raise of polymerization temperature to 25 °C improved the activity but did not affect the number of polymer chains (N) and molecular weight distributions (MWDs). The N values were about 60–65% of the Ti used, and the MWDs were around 1.5.

To investigate the living nature of the 2-dMMAO and 3-dMMAO systems, we conducted postpolymerization at 0 and 25 °C: the first-step polymerization was conducted with a certain amount of propylene for 1 h, and the second-step polymerization was continued for another 1 h after the addition of the same amount of propylene with the first step. The results are summarized in Table 2.

In both steps, the conversions were almost quantitative regardless of the complex used and polymerization temperature, and the M_n value became almost double of those of the first-step polymers with keeping the Nvalues constant.

The GPC curves of the polymers obtained are illustrated in Figure 2. The curves of second step shifted to higher molecular weight region of that of first step in each catalyst system, and no peak or shoulders were observed. The results testified that propylene polymer-

Table 3. Stereosequence Distributions and Melting Temperature for Sample Entries 1, 4, and 5 in Table 1

	stereosequence distribution ^a									
entry	mmmm	mmmr	rmmr	mmrr	$\mathbf{mmrm} + \mathbf{rmrr}$	rmrm	rrrr	mrrr	mrrm	$T_{\mathbf{m}}{}^{b}\left(^{\circ}\mathbf{C}\right)$
1	0.00	0.00	0.04	0.09	0.10	0.04	0.60	0.13	0.00	89
4	0.00	0.00	0.04	0.08	0.05	0.02	0.69	0.12	0.00	92
5	0.00	0.00	0.02	0.03	0.02	0.00	0.86	0.07	0.00	142

^a Determined by ¹³C NMR spectroscopy. ^b Melting Temperature determined by DSC.



Figure 4. ORTEP drawings of the molecular structures of 2 and 3. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are drawn at the 30% probability level.

ization proceeded in a living manner at both 0 and 25 °C regardless of the complexes employed, although the MWDs were slightly larger than that of an ideal living polymerization system. Both systems show certain induction period as shown in the rate-time profiles (Figure 1), and the large amount of produced polymers prohibited effective stirring to decrease the homogeneity of the polymerization system, which should be the reasons for the broader MWDs. The narrower MWDs with batch system in Table 2 compared with those with semibatch system in Table 1 support this assumption.

The ¹³C NMR spectra of methyl region of PPs obtained with **2** and **3** at 0 °C are shown in Figure 3. The steric pentad distributions in main chain and the melting temperatures of the polymers obtained are summarized in Table 3. The introduction of *tert*-butyl groups increased the syndiotactic pentad in the following order: **3** (0.86) > **2** (0.69) > **1** (0.60). In the enantiomorphicsite controlled syndiospecific polymerization with a C_s symmetric catalyst, two types of stereodefects should be formed: one is "rmrr" arising from the "chain migration" without monomer insertion, and the other is "rmmr" arising from the "monomer miss-insertion".¹⁹ The stereosequence distributions in Table 3 indicate that the syndiospecific propagation proceeded via enantiomorphic-site controlled mechanism.

The rmrr content was decreased in the following order: 1 (0.10) > 2 (0.05) > 3 (0.02). The decrease of

Table 4. Effect of Al/Ti Ratio on PropylenePolymerization with 3 Activated by dMMAO^a

Al/Ti ^b	time (min)	yield (g)	activity c	$M_{ m n}{}^d$ (×10 ⁴)	$M_{ m w}/M_{ m n}{}^d$	$\stackrel{N^{\rm e}}{(\mu{\rm mol})}$
100	17	1.85	326	15.2	1.48	12
200	7	2.14	916	16.9	1.45	13
400	3	2.32	2318	19.6	1.46	12

^{*a*} Polymerization conditions: heptane = 30 mL, Ti = 20 μ mol, propylene = 1 atm. ^{*b*} Molar ratio. ^{*c*} Activity in kg of PP/(mol of Ti h). ^{*d*} Number-average molecular weight and molecular weight distribution determined by GPC using universal calibration. ^{*e*} Calculated from yield and $M_{\rm n}$.

rmrr can be explained by the increase of propagation rate by the introduction of *tert*-butyl groups if the chain migration without monomer insertion is independent of the tert-butyl groups. On the other hand, the rmmr content was decreased only by **3**: 1(0.04) = 2(0.04) > $\mathbf{3}$ (0.02). These results indicate that the introduction of tert-butyl proups at the 3,6-position is effective to improve the enantioselectivity of the catalyst. As a consequence, 3 gave the PP with the highest syndiotacticity, of which melting temperature was 142 °C. These results are in good agreement with those reported by Razzavi et al. in propylene polymerization with the corresponding chloride complexes activated by MAO.^{15,16} They described the importance of 3,6-positions of the Flu ligand for proper regulation of the coordinating monomer and growing polymer chain compared to 2,7positions. The molecular structures of 2 and 3 determined by single-crystal X-ray analysis are displayed in Figure 4.

One of the characteristics of the living system is of its simple kinetics: the number of active centers can be calculated from the yield and the M_n value, and the propagation rate can be directly evaluated from the M_n value and polymerization time.

Although metallocene catalysts generally need a high Al/metallocene ratio for high activity, the reason of which is not yet clear. The effect of Al/Ti ratio on this living polymerization system was therefore investigated with 3-dMMAO under an atmospheric pressure of propylene in a semibatch system. The results are summarized in Table 4.

The polymerization time was changed according to the activity for keeping good stirring during the polymerization. The activity increased with increasing Al/Ti ratios, whereas the N value was independent of the Al/Ti. This result indicates that the high activity should come from the high propagation rate.

The propagation rates were calculated from the number-average polymerization degree P_n ($M_n/42$) and the polymerization time, and the values thus obtained are plotted against the Al/Ti value in Figure 5. The propagation rate was found to increase linearly or rather exponentially against the Al/Ti ratio. We can therefore conclude that the high Al/Ti ratio is necessary for high propagation rate but not for high initiation efficiency in the present catalyst system. The same phenomenon



Figure 5. Plots of P_n/t and N values against Al/Ti ratio in the **3**-dMMAO system.

was observed in the living polymerization of norbornene with 1-MMAO in toluene.²⁰ One plausible explanation for the rate enhancement with the larger amount of MMAO should be the neutralization of the counteranion by Lewis acidic MMAO, which promotes the separation of active ion pair composed of the Ti cation and the methyl anion abstracted by MMAO.

In summary, the introduction of the *tert*-butyl groups on the fluorenyl ligand of [*t*-BuNSiMe₂Flu]TiMe₂ at the 2,7-position ([*t*-BuNSiMe₂(2,7-*t*-Bu₂Flu)]TiMe₂, **2**) and the 3,6-position ([*t*-BuNSiMe₂(3,6-*t*-Bu₂Flu)]TiMe₂, **3**) improved the activity more than 3 times in propylene polymerization using dMMAO as a cocatalyst in heptane. The propylene polymerization proceeded in a living manner at 0 and 25 °C regardless of the position of *tert*butyl substituents, whereas the 3,6-position was more effective for the improvement of syndiospecificity. **3**–dM-MAO in heptane was found to produce the living PP with the syndiotactic triad of 0.93 and melting point of 142 °C in high activity.

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Supporting Information Available: Details of catalysts synthesis and characterization; X-ray crystallographic files in CIF format for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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