Polymerization of propylene with [*t*-BuNSiMe₂Ind]TiMe₂–MAO catalyst systems

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Abstract

ansa-Indenylamidodimethyltitanium complex ([*t*-BuNSiMe₂Ind]TiMe₂: **1**) was synthesized by one-pot reactions starting from the ligand, MeLi and TiCl₄. The structure of **1** was determined by X-ray crystallography and the results obtained revealed that the indenyl ligand coordinate to titanium in an η^4-tendency. Propylene polymerization was conducted with **1** in toluene or heptane as solvent at $0\,^\circ\mathrm{C}$ in the presence of dried methylaluminoxane (MAO) or dried modified MAO (MMAO), which was prepared from the toluene solutions of MAO or MMAO by removing free trialkylaluminium contained. Polymerization behavior was investigated from the consumption rate of propylene in a semi-batch system. The dried MAO/toluene system showed the highest activity without any deactivation. The produced polymer in the dried MAO/toluene system had the highest molecular weight and narrowest molecular weight distribution. The number-average molecular weight of the polymer increased almost linearly with increasing polymerization time accompanied by narrowing molecular weight distribution from 1.42 to 1.37 and the number of polymer chains was almost constant. Thus, it was found that quasi-living polymerization of propylene proceeded. The ¹³C NMR measurement indicated that **1**-dried MAO/toluene produced poly(propylene) with isotactic triad of 40%.
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1. Introduction

During the first half of the 1990s, a new class of homogeneous Ziegler–Natta catalysts, named *ansa*-monocyclopentadienylamido (CpA) catalysts, was developed by the researchers of Dow [1] and Exxon [2]. These group 4 CpA catalysts [3] consist of the ligand system first prepared by Bercaw [4] and Okuda [5] for organoscandium, organoiron and organotitanium complexes. The CpA catalysts have been found to be highly efficient catalysts for the synthesis of linear low-density polyethylene and ethylene/styrene copolymer [1,2,6]. Several researchers reported the influence of the ligand in CpA catalysts on the stereospecificity and the regiospecificity of propylene polymerization [7].

Living polymerization is of great use for controlling the molecular weight and molecular weight distribution of polymer as well as for synthesizing block copolymers and chain-end functionalized polymers. The recent development of organometallic catalysts has realized the synthesis of stereoregular polyolefins with living polymerization [8]. V(acac)₃/AlEt₂Cl (acac = acetylacetonate and its analogues) had been known as a homogeneous catalyst which performs living polymerization of propylene below $-40\,^\circ\mathrm{C}$ and produces syndio-enriched polymers [9]. Fujita and co-workers [10] and Coates and co-workers [11] have recently reported a highly syndiospecific living polymerization of propylene with bis(salicylaldiminato)titanium complexes-methylaluminoxane (MAO) catalyst systems. We have previously reported that [*t*-BuNSiMe₂Flu]TiMe₂ activated with B(C₆F₅)₃ produced syndiotactic-enriched poly(propylene) (PP) at $-50\,^\circ\mathrm{C}$ in a living manner [12a] and that the replacement of B(C₆F₅)₃ with trialkylaluminium (Me₃Al,

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^{i}Bu$_3$Al)-free MAO, named dried MAO and dried modified MAO (MMAO), raised the living polymerization temperature up to 0 °C accompanied by the improvement of syndiospecificity [12b,e]. On the other hand, in the same polymerization conditions, almost atactic PP was produced with [ArN(CH$_2$)$_3$NAr]TiMe$_2$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) and [*t*-BuNSiMe$_2$(C$_5$Me$_4$)]TiMe$_2$ in a living and quasi-living manner, respectively [12c,d]. These results suggest the potentiality of dried MAO and dried MMAO as a cocatalyst for living polymerization with CpA and other dimethyltitanium complexes.

Isospecific living polymerization of propylene is one of the topics in the field of single-site Ziegler–Natta catalysts. Busico et al. reported the synthesis of isotactic PP-*block*-poly(ethylene) via "quasi-living polymerization" by a Zr-complex of amine-bis(phenolate) ligand activated with [HMe$_2$NPh][B(C$_6$F$_5$)$_4$] at 25 °C, which was reported as a living polymerization catalyst for higher α-olefins by Kol and co-workers [13] using the reaction product of ^{i}Bu$_3$Al with 2,6-di(*tert*-butyl)phenol as a scavenger [14].

We have recently prepared [*tert*-butyl(dimethylindenylsilyl)amido]dimethyltitanium ([*t*-BuNSiMe$_2$Ind]TiMe$_2$: **1**) complex as a single-crystal and found that **1** promoted quasi-living polymerization of propylene in toluene at 0 °C when dried MAO was used as a cocatalyst to give isotactic-enriched PP. This paper reports the preliminary results of the polymerization.

2. Experimental part

2.1. Material

Dried MAO and dried MMAO were prepared from the toluene solutions of MAO and MMAO donated from Tosoh-Finechem Co. Ltd. as reported previously [12b,c]. Research grade propylene (Takachiho Chemicals Co.) was purified by passing it through columns of NaOH, P$_2$O$_5$, and molecular sieves 3A, followed by bubbling it through a NaAlH$_2$Et$_2$/1,2,3,4-tetrahydronaphthalene solution. All solvents were commercially obtained and dried by standard methods.

2.2. Synthesis of [t-BuNSiMe$_2$Ind]TiMe$_2$ (**1**) [7c,15]

To a solution of *t*-BuNHSiMe$_2$Ind (Ind = C$_9$H$_6$, 3.47 g, 14.1 mmol) in Et$_2$O (100 mL) was slowly added excess MeLi (77.0 mL of a 0.92 M solution in Et$_2$O) at room temperature and the mixture was stirred for 5 h. TiCl$_4$ (1.50 mL, 13.8 mmol) was diluted in 80 mL of pentane. A solution of the dilithium salt in Et$_2$O was added to the TiCl$_4$ solution at room temperature (exothermic reaction). The resulting dark green-yellow suspension was stirred overnight at room temperature. After the solvent was removed, the residue was extracted with pentane (80 mL) and the pentane solution was decanted. To

the pentane solution was added MeMgBr (3.0 mL of a 3.0 M solution in ether), and the resulting mixture was stirred for 5 h at room temperature. After the solvent was removed, the residue was extracted with pentane (80 mL). The pentane solution was concentrated and cooled overnight at −30 °C to give **1** as brown microcrystals (0.682 g, 2.12 mmol, 19.7%).

2.3. Polymerization procedure

Polymerization was performed in a 100 mL glass reactor equipped with a magnetic stirrer. After 30 mL of solvent was placed in the reactor at 0 °C, the solvent was saturated with an atmospheric pressure of propylene. Polymerization was started by successive addition of prescribed amounts of co-catalyst and catalyst. Propylene was supplied during the polymerization for keeping the pressure constant, and the consumption rate of propylene was monitored by a mass flow meter. 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.

2.4. Analytical procedures

Molecular weight and molecular weight distribution of PPs obtained were determined by gel permeation chromatography (GPC) with a Waters 150CV 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 polystyrene standards and $K = 1.03 \times 10^{-4}$, $\alpha = 0.78$ for PP samples. The ^{13}C NMR spectra of PPs were measured at 120 °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 5000 scans were accumulated in pulse repetition of 5.0 s. Sample solution was prepared in 1,1,2,2-tetrachloroethane-d_2 up to 10 wt.%. The central peak of 1,1,2,2-tetrachloroethane-d_2 (74.47 ppm) was used as internal reference.

2.5. X-ray structure determination

Single crystals were mounted on glass fibers. Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ = 0.71069 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 μm × 100 μm. Neutral scattering factors were obtained from the standard source [16]. In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made [17].

The structural analysis was performed on an IRIS O2 computer using the teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan [18]. An empirical absorption correction was also made [19]. The structures were solved by a combination of the

direct methods (SHELXS-86) [19] and Fourier synthesis (DIRDIF94) [20]. Least-squares refinements were carried out using SHELXL-97 [19] (refined on F^2) linked to teXsan. All the non-hydrogen atoms were refined anisotropically. The methyl hydrogen atoms except the hydrogen atoms attached to the carbon atoms sitting on a crystallographic mirror plane were refined using riding models, and the other hydrogen atoms were fixed at the calculated positions.

3. Results and discussion

3.1. Structure of [t-BuNSiMe₂Ind]TiMe₂ (1)

The complex **1** was first prepared by Amor and Okuda as a yellow oil [15]. We synthesized **1** using one-pot reactions reported by Resconi et al. [7c] and isolated it as brown microcrystals. The single-crystal X-ray diffraction analysis of **1** was performed, and the crystallographic data and the structure obtained are shown in Table 1 and Fig. 1, respectively. The selected bond lengths of **1** are summarized in Table 2.

Table 1
Crystallographic data and parameters for **1**

	1 (Ind)
Formula	$C_{17}H_{27}NSiTi$
Formula weight	321.39
Crystal system	Triclinic
Space group	P-1(#2)
a (Å)	9.169(4)
b (Å)	9.351(3)
c (Å)	11.325(7)
α (°)	91.76(1)
β (°)	113.01(1)
γ (°)	91.35(1)
V (Å³)	892.6(6)
Z	2
$F(000)$	344
Dcalcd (g cm⁻³)	1.196
μ (cm⁻¹)	0.538
Max. 2θ (°)	55
No. of reflections observed	7280
No. of parameters refined	188
$R1$[a]	0.0590
$wR2$[b]	0.1810
No. of obsd reflns ($I > 2\sigma(I)$)	3498

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o|$.
[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2
Selected bond lengths (Å) for **1**

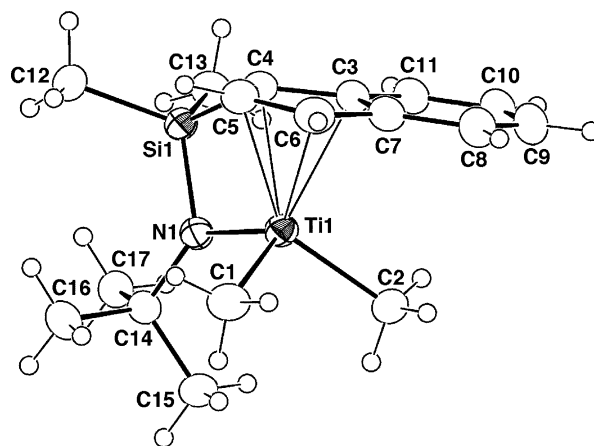|	
Ti(1)–C(1)	2.109(2)
Ti(1)–C(2)	2.121(2)
Ti(1)–C(3)	2.421(2)
Ti(1)–C(4)	2.307(2)
Ti(1)–C(5)	2.346(2)
Ti(1)–C(6)	2.479(3)
Ti(1)–C(7)	2.546(2)
Ti(1)–N(1)	1.936(2)
Ti(1)–Si(1)	2.888(1)

Fig. 1. ORTEP drawing of **1**. The thermal ellipsoids are drawn at the 30% probability level.

The corresponding Ti–C bond lengths of the tetramethyl-cyclopentadienyl (Cp*) derivative **2**, in which the Cp* group coordinate to Ti with an η^5-manner [1,3], are as follows: Ti(1)–C(3) = Ti(1)–C(5) = 2.350 Å; Ti(1)–C(4) = 2.283 Å; Ti(1)–C(6) = Ti(1)–C(7) = 2.463 Å.[1] The comparison of the bond lengths between **1** and **2** indicates that the Ti(1)–C(6) and Ti(1)–C(7) lengths of **1** were about 0.016 and 0.083 Å longer than those of **2**. These results suggest that the indenyl ligand coordinates to titanium in an η^3- or η^4-manner rather than in an η^5-manner.

3.2. Propylene polymerization

Propylene polymerization was conducted in toluene and heptane at $0\,°C$ by **1** using dried MAO or dried MMAO as a cocatalyst with a semi-batch system, and the rates of propylene consumption are plotted against polymerization time in Fig. 2.

When toluene was used as solvent, the dried MAO system showed a steady consumption rate whereas the dried MMAO system deactivated quickly. The dried MMAO/heptane system showed almost the same consumption rate of the dried MAO/toluene system in the initial stage, but the rate gradually decreased with increasing polymerization time. These results indicate that deactivation occurred irrespective of the solvent when dried MMAO was used. The dried MAO/heptane system hardly showed the activity, which should be due to the low solubility of dried MAO in heptane (entry 2) [12c].

The results of polymerization and GPC analysis are summarized in Table 3. Numbers of polymer chains (N) are calculated from the polymer yield and the M_n value and also shown in Table 3.

When dried MAO was used in toluene, the highest molecular weight (M_n) polymer was produced with the narrowest

[1] The crystallographic data of **2**: $C_{17}H_{33}NSiTi$, F.W. = 327.44 g mol⁻¹, triclinic, space group $Pnma$ (#62), $a = 11.868(2)$ Å, $b = 13.398(2)$ Å, $c = 12.232(1)$ Å, $V = 1945.0(5)$ Å³, $Z = 4$, $D_c = 1.118$ g cm⁻³, $R = 0.0840$, $R_w = 0.211$, for 1669 independent reflections with $I > 2\sigma(I)$.
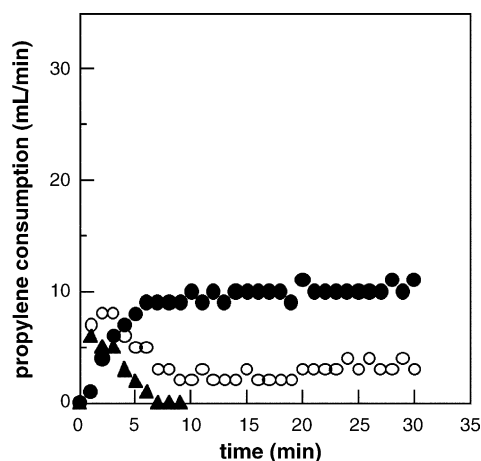
Fig. 2. Rate-time profiles of propylene polymerization with **1** at 0 °C: dried MAO/toluene (●), dried MMAO/toluene (▲), dried MMAO/heptane (○).

molecular weight distribution (MWD) of $M_w/M_n = 1.38$ (entry 1). Considering the fact that the steady polymerization rate was observed, the dried MAO/toluene system should have a living character. On the other hand, the dried MMAO/toluene system gave the lowest M_n polymer with the slightly broad MWD (entry 3), which should be ascribed to the deactivation. In the dried MMAO/heptane system, the steady rate was observed after the initial rapid deactivation, which caused the broadest MWD (entry 4).

To confirm the living nature of the **1**-dried MAO/toluene system, the dependence of M_n and M_w/M_n values on polymerization time was investigated. The results are summarized in Table 4.

The N value was almost constant, which indicates that chain transfer reaction did not occur in this system. In Fig. 3 are plotted the M_n and M_w/M_n values against the polymerization time using the data summarized in Table 4.

The M_n value linearly increased in proportion to the polymerization time and the narrow MWD was maintained during the polymerization.

As illustrated in Fig. 4, the GPC curve shifted to the higher molecular weight region with increasing polymerization time from entry 1 to 7 and the MWD value slightly decreased. These results clearly indicate that **1** promoted quasi-living polymerization at 0 °C when dried MAO was used in toluene. The initiation efficiencies determined by the N value were about 70%.

Table 4
Results of propylene polymerization with **1**-dried MAO in toluene at 0 °C[a]

Entry	Time (min)	Yield (g)	$M_n{}^{b}$ ($\times 10^4$)	$M_w/M_n{}^{b}$	N^c (μmol)
1	30	0.67	4.89	1.38	14
5	40	0.75	5.50	1.42	14
6	60	1.38	7.09	1.41	19
7	80	1.40	9.26	1.37	15

[a] Polymerization conditions: toluene = 30 mL, Ti = 20 μmol, dried MAO = 8.0 mmol, propylene = 1.0 atm.
[b] Determined by GPC using universal calibration.
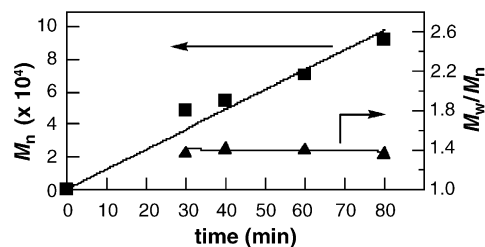[c] Number of polymer chains calculated from yield and M_n.

Fig. 3. Plots of M_n (■) and M_w/M_n (▲) vs. polymerization time in propylene polymerization with **1**-dried MAO at 0 °C in toluene.

3.3. Structure of poly(propylene)

The ^{13}C NMR spectrum of the PP obtained in entry 1 is shown in Fig. 5.

Weak resonances attributable to regioirregular structures are observed around 16, 31, 36, 38 and 44 ppm (Fig. 5A)
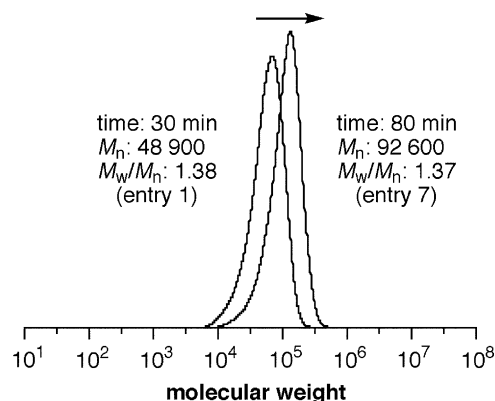

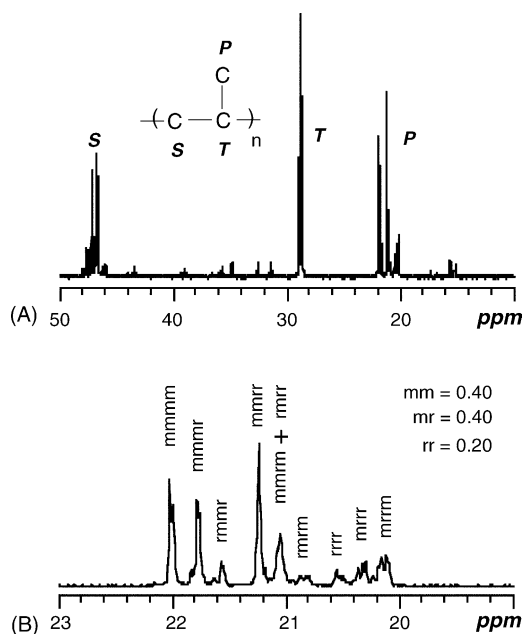Fig. 4. GPC curves of PPs obtained with **1**-dried MAO at 0 °C in toluene.

Table 3
Effect of cocatalyst and solvent on propylene polymerization with **1** at 0 °C[a]

Entry	Cocatalyst	Solvent	Time (min)	Yield (g)	Activity[b]	$M_n{}^{c}$ ($\times 10^4$)	$M_w/M_n{}^{c}$	N^d (μmol)
1	Dried MAO	Toluene	30	0.67	67.2	4.89	1.38	14
2	Dried MAO	Heptane	30	Trace				
3	Dried MMAO	Toluene	9	0.03	10.0	0.53	1.61	5.7
4	Dried MMAO	Heptane	30	0.16	15.7	2.14	9.60	7.5

[a] Polymerization conditions: solvent = 30 mL, Ti = 20 μmol, Al = 8.0 mmol, propylene = 1.0 atm.
[b] Activity = kg PP mol Ti^{-1} h^{-1}.
[c] Determined by GPC using universal calibration.
[d] Number of polymer chains calculated from yield and M_n.

Fig. 5. The 125 MHz ^{13}C NMR spectrum of a PP obtained with **1**-dried MAO at 0 °C in toluene: (A) aliphatic region, (B) expansion of the methyl region (entry 1).

as reported previously [7b,c]. The triad analysis of the methyl region (Fig. 5B) showed that the produced polymer was isotactic-enriched (mm = 40%, mr = 40%, rr = 20%). The "mm" content of the **1**-dried MAO system in toluene at 0 °C was slightly higher than the value reported previously with the same complex activated by MAO (mm = 25–27%) [7c]. Furthermore, the stereoregularity of the present system was almost the same as that of the [*t*-BuNSiMe₂ (4,7-Me₂Ind)]TiMe₂–MAO system at 50 °C (mm = 40%, mr = 39%, rr = 21%) [7c].

In summary, [*t*-BuNSiMe₂Ind]TiMe₂ effected quasi-living polymerization of propylene at 0 °C when Me₃Al-free MAO was used as a cocatalyst in toluene, and gave PP with isotactic triad of 40%.

Acknowledgements

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