

Effect of cocatalyst in 1-hexene polymerization by $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ complex

Kotohiro Nomura*, Takashi Komatsu, Miho Nakamura, Yukio Imanishi

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

Received 18 May 2000; accepted 6 July 2000

Abstract

Since $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2**) exhibited higher initial catalytic activity than $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**1**) for 1-hexene polymerization in the presence of MAO, the effect of cocatalyst for the polymerization was investigated at low temperature (0 to -30°C). The use of $\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ was found to be effective to improve the activity and a notable increase in the activity was obtained if **2** was pre-treated with 2 equivalent of Al^iBu_3 in advance. TON (Turnover number) of 18 100 (activity: 5710 kg-polymer/mol-Ti h) could be attained after 16 min under the optimized conditions and the M_n value for the resultant poly(1-hexene) increased upon the consumption of 1-hexene suggesting the possibility of living polymerization. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Olefin polymerization; Titanium complex; Borate cocatalyst; 1-Hexene

1. Introduction

Olefin polymerization by homogeneous catalysis has been one of the most attractive subjects in the field of both organometallic chemistry and polymer chemistry [1–7]. There are thus a lot of reports concerning this subject to design the efficient catalyst precursor, however only a few reports have been known concerning olefin polymerization with non-bridged half-metallocene type group 4B transition metal complex catalysts [8–16].

We reported recently that $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$, **1**) showed high catalytic activity not only for ethylene polymerization but also for ethylene/1-butene copolymerization in the presence of cocatalyst [8,9]. We also reported the effect of cyclopentadienyl fragment not only for the catalytic

activity in 1-hexene polymerization [10,11] but also on monomer reactivities and monomer sequence distributions in ethylene/ α -olefin copolymerization [12]. In this paper we wish to introduce our explored results concerning effect of cocatalyst for 1-hexene polymerization using $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ complex.

2. Experimental section

2.1. General procedure

All experiments were carried out under a nitrogen atmosphere in a vacuum atmosphere drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Toluene for the polymerization was distilled over sodium and benzophenone under nitrogen atmosphere and was stored in a Schlenk tube in the drybox in the presence of molecular sieves (mixture of 3A and

* Corresponding author. Tel.: +81-743-72-6041;
fax: +81-743-72-6049.
E-mail address: nomurak@ms.aist-nara.ac.jp (K. Nomura).

4A 1/16, and 13X). Reagent grade of 1-hexene was also stored in the drybox in the presence of molecular sieves. Syntheses of $\text{Cp}^*\text{Ti}(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{X}_2$ [$\text{X} = \text{Cl}$ (**1**), Me (**2**)] were according to our previous report [9]. Toluene and AlMe_3 in the commercially available methylaluminoxane (PMAO-S, 9.5 wt.% (Al) toluene solution, Tosoh Akzo Co.) were removed and dried *in vacuo* in the drybox and used as a white solid [17–19].

All ^1H - and ^{13}C -NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H ; 100.40 MHz, ^{13}C). All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed and all spectra were obtained in the solvent indicated at 25°C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves.

Molecular weights and the molecular weight distributions of the poly(1-hexene)s were measured by means of gel-permeation chromatography (GPC). HPLC grade THF was used for GPC and were degassed prior to use. GPC were performed at 40°C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 ml/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm \times 8.0 mm \varnothing) were calibrated versus polystyrene standard samples.

2.2. Typical procedure for polymerization of 1-hexene catalyzed by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**1**)-MAO system

1-Hexene (5 ml) and prescribed amount of MAO were added to a round bottom flask (25 ml) connected to three-way valves under N_2 and the polymerization was started by the addition of a toluene solution (2.5 ml) containing the catalyst (5.0 μmol). The reaction mixture was stirred for prescribed time at room temperature and the polymerization was terminated with the addition of EtOH. The reaction product was extracted with CHCl_3 that was washed with HCl aqueous solution and then rinsed with water. The chloroform extract was dried over Na_2SO_4 , and chloroform and 1-hexene remained was then removed *in vacuo*.

Polymerization of 1-hexene in the presence of $\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ (Figs. 1–3) was typically

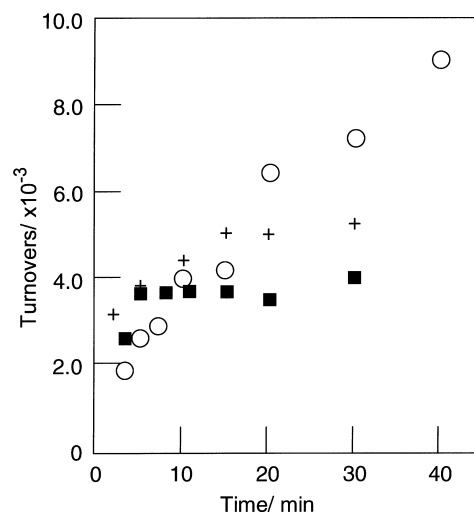


Fig. 1. Time course plot for polymerization of 1-hexene catalyzed by $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2**) - $\text{Al}^i\text{Bu}_3\text{-Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ system. Polymerization conditions: **2** 3.0 μmol (2.0 $\mu\text{mol}/\text{ml}$ toluene), $\text{Ti}/\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4 = 1/500/1.5$ (molar ratio), 1-hexene 50 ml, at 25°C (+), 0°C (■) and -30°C (○).

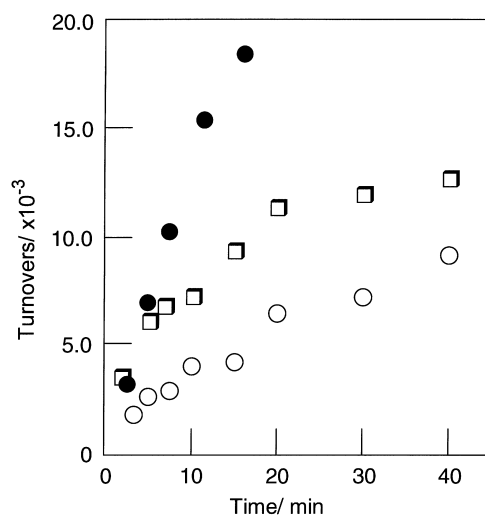


Fig. 2. Time course plot for polymerization of 1-hexene catalyzed by $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**2**) - $\text{Al}^i\text{Bu}_3\text{-Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ system at 30°C. Effect of pre-treatment of **2** with 2 equivalent of Al^iBu_3 [without pre-treatment (○), at 0°C for 10 min (□), at -30°C for 10 min (●)]. Polymerization conditions: **2** 3.0 μmol (2.0 $\mu\text{mol}/\text{ml}$ toluene), $\text{Ti}/\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4 = 1/500/1.5$ (molar ratio), 1-hexene 50 ml.

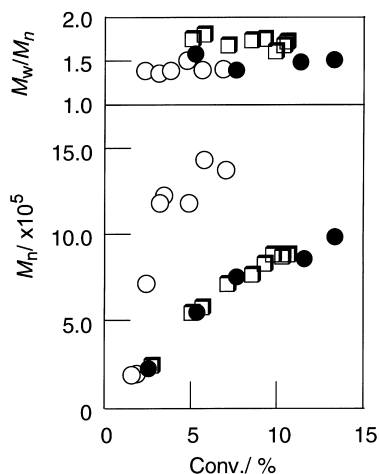


Fig. 3. Plot of M_n vs. conversion in polymerization of 1-hexene catalyzed by $Cp^*TiMe_2(O-2,6-iPr_2C_6H_3)_2$ (**2**)- Al^iBu_3 - $Ph_3CB(C_6F_5)_4$ system at $-30^\circ C$. Effect of pre-treatment of **2** with 2 equivalent of Al^iBu_3 [without pre-treatment (\circ), at $0^\circ C$ for 10 min (\square), at $-30^\circ C$ for 10 min (\bullet)]. (same polymerization conditions in Fig. 2)].

performed as follows: 1-hexene (50 ml) and a prescribed amount of Al^iBu_3 was added into a 100 ml round-bottom flask connected to three-way valves under N_2 , the solution was then cooled to $-30^\circ C$. The polymerization was started by the addition of a prescribed amount of toluene solution containing $Ph_3CB(C_6F_5)_4$ ($2.0 \mu mol/ml$) into the above solution soon after the addition of a toluene solution containing **2** ($2.0 \mu mol/ml$). A certain amount (3–10 ml) of the reaction mixture was removed via syringe from the mixture to examine the time course and the sample solution was then quickly added ethanol to terminate the reaction. The reaction product was extracted with $CHCl_3$ which was washed with HCl aqueous solution and then rinsed with water. The chloroform extract was dried over Na_2SO_4 , and chloroform and 1-hexene remained was then removed *in vacuo*.

3. Results and discussion

3.1. Polymerization of 1-hexene by

$Cp^*Ti(O-2,6-iPr_2C_6H_3)_2X_2$ -MAO catalyst

1-Hexene polymerization by **1**-MAO catalyst proceeded at significant rate at beginning but the rate

gradually decreased with a consumption of monomer and the observed activity increased upon the addition of MAO [activity in 1-hexene polymerization at $25^\circ C$: 314 kg-polymer/mol-Ti h ($Al/Ti = 500$) < 536 ($Al/Ti = 1000$) < 728 ($Al/Ti = 2000$, run 2)]¹ and the Al/Ti molar ratio of 2000 seemed to be more suited in this catalysis. The catalytic activity decreased at $0^\circ C$ (92 kg-polymer/mol-Ti h, Table 1), and the resultant polymer was atactic poly(1-hexene) by ^{13}C NMR [9,11].

It was revealed that **2** exhibited higher catalytic activity than **1** (activity: 7210 turnovers by **2** and 2890 turnovers by **1**, 10 min at $25^\circ C$, Table 1). This is an interesting contrast to the case of ethylene polymerization in which **2** exhibited slightly lower activity than **1** in the presence of MAO cocatalyst [activity in ethylene polymerization: 1240 kg-PE/mol-Ti h (by **1**) versus 718 kg-PE/mol-Ti h (by **2**), ethylene 4 kg/cm², $60^\circ C$, 1 h] [8]. However, the reaction did not take place or rapid decrease in the activity was observed after 10 min in the 1-hexene polymerization by **2**-MAO catalyst.

The activity by **2** was higher than **1** even at $0^\circ C$ (550 turnovers after 30 min by **1** and 740 turnovers after 15 min by **2**, Table 1), and the reaction proceeded at constant rate until at least 15 min. The polymerization result was reproducible under these conditions as shown in Table 1. Although, the molecular weight for the resultant poly(1-hexene) increased with the consumption of 1-hexene in the 1-hexene polymerization by **1** at room temperature (runs 1, 2 and 4), no clear time course dependences were observed in the polymerization by **2** (runs 5–10). The reason for the difference in the activity between **1** and **2** as well as in the polymerization behavior was not clear at this moment.

3.2. Hexene polymerization by $2-Al^iBu_3/Ph_3CB(C_6F_5)_4$ catalyst system

Since the catalytic activity on 1-hexene polymerization by **1**-MAO catalyst showed the extremely low activity at $0^\circ C$ (92 kg-polymer/mol-Ti h, Table 1), also since the activity slightly improved by using **2**, we explored the possibility to find a more active catalyst system especially at low temperature. We chose **2**, not only because **2** would be more suited as a cata-

¹ Part of these results are cited from [11].

Table 1
Polymerization of 1-hexene by Cp*Ti(O-2,6-*i*-Pr₂C₆H₃)X₂ [X = Cl(**1**), Me (**2**)]-MAO catalyst^a

Run no.	Complex	Temperature (°C)	Time (min)	Polymer (yield/mg)	Activity ^b	TON ^c	M _w ^d (×10 ⁻⁴)	M _w /M _n ^d
1	1	25	10	243	1460	2890	45.1	1.81
2	1	25	30	364	728	4330	69.4	1.62
3	1	0	30	46	92	550	57.6	1.51
4	1	25	60	410	410	4870	74.2	1.79
5	2	25	10	607	3640	7210	42.7	1.83
6	2	25	15	621	2480	7380	44.1	1.95
7	2	25	20	613	1840	7290	46.7	1.86
8	2	0	10	41	250	490	34.0	1.53
9	2	0	15	62	250	740	33.8	1.66
10	2	0	15	60	240	710	37.5	1.59

^a Reaction conditions: α-olefin 5 ml, **1** or **2** 1.0 μmol (2 μmol/ml-toluene), MAO white solid (Al/Ti = 2000, molar ratio), 25°C.

^b Polymerization activity (kg-polymer/mol-Ti h).

^c TON (turnover number = molar amount of 1-hexene reacted/mol-Ti).

^d GPC data in THF vs. polystyrene standard.

lyst precursor than **1** especially with a combination of Ph₃CB(C₆F₅)₄ cocatalyst but also because **2** would be also more suited to examine the possibility of living polymerization.

Table 2 summarizes the preliminary results concerning the effect of cocatalyst for 1-hexene polymerization. The observed catalytic activity was negligible if Al^{*i*}Bu₃/B(C₆F₅)₃ was used as the cocatalyst. On the other hand, a notable improvement in the activity was observed if the reaction was performed in the presence of both Al^{*i*}Bu₃ and Ph₃CB(C₆F₅)₄. Molar ratio of Al/Ti was also found to be an important factor for this reaction to proceed at remarkable rate (runs 15–18, Table 2).

Fig. 1 shows the time course plot for 1-hexene polymerization by **2** in the presence of Al^{*i*}Bu₃ and Ph₃CB(C₆F₅)₄ at various reaction temperature. The rapid decrease in the activity was observed if the reaction was conducted at 0 and 25 °C and these would be due to the deactivation of catalytically active species. On the other hand, the reaction was found to proceed without the decrease at –30°C.

It should be noted that a remarkable increase in the activity was observed if **2** was pre-treated with 2 equivalent of Al^{*i*}Bu₃ at low temperature (0 and –30°C) in advance as shown in Fig. 2. The selected data in these polymerizations are summarized in Table 3. Pre-treatment at –30°C would be more

Table 2
Polymerization of 1-hexene by Cp*TiMe₂(O-2,6-*i*-Pr₂C₆H₃) (**2**)-cocatalyst systems^a

Run no.	2 (μmol)	Cocatalyst (cocatalyst/Ti) ^b	Al/Ti ^b	Temperature (°C)	Time (min)	Polymer (yield/mg)	Activity ^c	M _w ^d (×10 ⁻⁴)	M _w /M _n ^d
11	0.5	Ph ₃ CB(C ₆ F ₅) ₄ (1.5)	250	25	10	827	9920	93.6	1.77
12	0.5	Ph ₃ CB(C ₆ F ₅) ₄ (1.5)	250	–20	5	407	9770	104	1.51
13	1.0	Me ₂ PhNHB(C ₆ F ₅) ₄ (1.5)	250	–20	15	355	2840	132	1.59
14	0.5	B(C ₆ F ₅) ₃ (1.5)	250	0	30	Trace	–	–	–
15	0.5	Ph ₃ CB(C ₆ F ₅) ₄ (1.5)	125	–30	30	Trace	–	–	–
16	0.5	Ph ₃ CB(C ₆ F ₅) ₄ (1.5)	250	–30	30	116	464	74.6	1.52
17	0.5	Ph ₃ CB(C ₆ F ₅) ₄ (1.5)	375	–30	30	158	632	75.2	1.55
18	0.5	Ph ₃ CB(C ₆ F ₅) ₄ (1.5)	500	–30	30	161	644	76.2	1.72

^a Reaction conditions: 1-hexene 10 ml (run 14, 5 ml; runs 15–18, 3 ml), **2** 2 μmol/ml-toluene, Al^{*i*}Bu₃.

^b Molar ratio of cocatalyst/Ti and Al/Ti.

^c Polymerization activity (kg-polymer/mol-Ti h).

^d GPC data in THF vs. polystyrene standard.

Table 3

Selected data for 1-hexene polymerization by Cp^*TiMe_2 ($\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$) (**2**) - $\text{Al}^i\text{Bu}_3\text{-Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ catalyst systems at -30°C^a

Run no.	Pre-treatment conditions ^b	Time (min)	TON ^c ($\times 10^{-3}$)	M_w^d ($\times 10^{-4}$)	M_w/M_n^d
19	None	5	2.69	74.6	4.08
		7	2.89	101	1.44
		10	4.08	162	1.34
		20	6.44	181	1.51
		30	7.23	203	1.40
20	0°C , 2 min	2	3.49	61.1	2.28
		7	6.73	104	1.79
		15	9.31	119	1.67
		20	11.35	133	1.72
		30	12.02	145	1.74
21	-30°C , 2 min	2.5	3.41	49.9	2.26
		5	7.50	91.1	1.57
		7.5	10.26	109	1.42
		11	15.62	126	1.49

^a Reaction conditions: 1-hexene 50 ml, **2** $3.0\ \mu\text{mol}$ ($2.0\ \mu\text{mol}/\text{ml}$ -toluene), -30°C , $2/\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4 = 1.0/500/1.5$ (molar ratio), see Section 2 for more detailed conditions.

^b Pre-treatment conditions of **2** with 2 equivalent of Al^iBu_3 .

^c TON (turnover number = molar amount of 1-hexene reacted/mol-Ti).

^d GPC data in THF vs. polystyrene standard.

suited in order for this polymerization to proceed efficiently and turnover number (TON) of 18 100 could be attained after 16 min even at -30°C . The resultant poly(1-hexene) has relatively high molecular weight with unimodal molecular weight distribution ($M_w = 1.50 \times 10^6$, $M_w/M_n = 1.53$).

Fig. 3 shows M_n versus conversion plot based on the results summarized in Table 3. It is interesting to note that the M_n value for the resultant polymer increased linearly with the increase of conversion of 1-hexene under these limited reaction conditions. However, the role of Al^iBu_3 as well as the activation mechanism has not been clear at this moment.

We have shown that a notable increase in the catalytic activity for 1-hexene polymerization by **2** at low temperature of -30°C could be attained by selecting a suitable cocatalyst, $\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ and the pre-treatment of **2** with 2 equivalent of Al^iBu_3 at -30°C was found to be effective to improve the activity. The more details including the role

of pre-treatment and the effect of cocatalyst is now under investigation.

Acknowledgements

The part of this research is supported by Grant-in-Aid for Encouragement of Young Scientists from the Ministry of Education, Science, Sports and Culture of Japan (No. 11750677). K.N. would like to express his heartfelt thanks to Tosoh Akzo Corporation for donating MAO (PMAO-S). K.N. and T.K. would also like to express their thanks to Dr. Naofumi Naga (Nara Institute of Science and Technology) for discussion.

References

- [1] K.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 1143.
- [2] W. Kaminsky, *Macromol. Chem. Phys.* 197 (1996) 3903.
- [3] W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* 127 (1997) 143.
- [4] J. Suhm, J. Heinemann, C. Wörner, P. Müller, F. Stricker, J. Kressler, J. Okuda, R. Mülhaupt, *Macromol. Symp.* 129 (1998) 1.
- [5] A.L. McKnight, R.M. Waymouth, *Chem. Rev.* 98 (1998) 2587.
- [6] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 429.
- [7] H.G. Alt, A. Köppl, *Chem. Rev.* 100 (2000) 1205.
- [8] K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, *Organometallics* 17 (1998) 2152.
- [9] K. Nomura, N. Naga, M. Miki, K. Yanagi, *Macromolecules* 31 (1998) 7588.
- [10] K. Nomura, T. Komatsu, Y. Imanishi, *J. Mol. Catal. A* 152 (2000) 249.
- [11] K. Nomura, T. Komatsu, Y. Imanishi, *J. Mol. Catal. A* 159 (2000) 127.
- [12] K. Nomura, K. Oya, T. Komatsu, Y. Imanishi, *Macromolecules* 33 (2000) 3187.
- [13] J.C. Stevens, D.R. Neithamer, *UP Patent* 5,064,-802 (1991).
- [14] Q. Wang, R. Quyoum, D.J. Gills, M.-J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, *Organometallics* 15 (1996) 693.
- [15] S.A.A. Shah, H. Dorn, A. Voigt, H.W. Roesky, E. Parisini, H.-G. Schmidt, M. Noltemeyer, *Organometallics* 15 (1996) 3176.
- [16] D.W. Stephan, J.C. Stewart, F. Guérin, R.E.v.H. Spence, W. Xu, D.G. Harrison, *Organometallics* 18 (1999) 1116.
- [17] N. Ishihara, Y. Takakura, T. Miura, *JP Kokai*, H6-329714 (1994).
- [18] C. Sista, R. Hathorn, T.J. Marks, *J. Am. Chem. Soc.* 114 (1992) 1112.
- [19] L. Resconi, S. Bossi, L. Abis, *Macromolecules* 23 (1990) 4489.