Efficient living polymerization of 1-hexene by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)-borate catalyst systems at low temperature

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Abstract

Details for 1-hexene polymerization by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) have been explored in the presence of organoboron and organoaluminum compounds. The polymerization took place in a living manner with remarkably high catalyst efficiency at $-30\,^\circ$C, when both Ph$_3$CB(C$_6$F$_5$)$_4$ and Al^{i}Bu$_3$ were used as cocatalysts under the optimized conditions. The resultant poly(1-hexene) possessed high molecular weight with narrow molecular weight distribution ($M_n = 186.5 \times 10^4$, $M_w/M_n = 1.27$). Effects of polymerization temperature and monomer concentration were explored, and the M_n values increased linearly upon the consumption of 1-hexene in all cases. Use of a mixture of Al(n-C$_8$H$_{17}$)$_3$ and Al^{i}Bu$_3$ was also found to be effective, but relatively excess amount of Al^{i}Bu$_3$ was necessary in order for this catalytic reaction to proceed efficiently.
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Keywords: Titanium; Olefin polymerization; Homogeneous catalysis; Living polymerization

1. Introduction

Design and synthesis for efficient transition metal complex catalyst towards precise, controlled olefin polymerization has attracted considerable attention not only in the field of catalysis, organometallic chemistry, but also in the field of polymer chemistry. *Nonbridged* half-metallocene type group 4 transition metal complexes of the type, Cp$'$M(L)X$_2$ (Cp$'$ = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic ligand such as OAr, NR$_2$, NPR$_3$, etc.; X = halogen, alkyl) [1–12] have been one of the promising candidates as the new type of olefin polymerization catalysts, because some of these complexes exhibited unique characteristics that are different from both ordinary metallocene type [13] and so-called 'constrained geometry' (linked half-metallocene) type catalysts [13b,14–19].

We reported that a catalyst system composed of Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**, Cp* = C$_5$Me$_5$), Al^{i}Bu$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$ exhibited significant catalytic activity for 1-hexene polymerization at $-30\,^\circ$C (under bulk polymerization conditions), affording high molecular

weight poly(1-hexene) with relatively narrow polydispersity ($M_w = 126 \times 10^4$, $M_w/M_n = 1.49$) [2c]. Moreover, the M_n value for resultant poly(1-hexene) increased upon increasing the turnover number, suggesting a possibility that the polymerization took place in a quasi-living manner [2c]. We also reported recently that the reaction of **1** with B(C$_6$F$_5$)$_3$ in toluene-d_8 gave decomposed products even at $-70\,^\circ$C, and the reaction with Ph$_3$CB(C$_6$F$_5$)$_4$ in CDCl$_3$ gave Ph$_3$CCH$_3$ without decomposition [2d]. These results are in good agreement with the result for effect of organoboron compounds as the cocatalyst, because the extremely low catalytic activity for the polymerization was observed with B(C$_6$F$_5$)$_3$ in place of Ph$_3$CB(C$_6$F$_5$)$_4$. In addition, the species generated from the reaction of **1** with Ph$_3$CB(C$_6$F$_5$)$_4$ consumed 1-hexene at $-30\,^\circ$C in CDCl$_3$, but the observed activity was extremely low compared to that in the co-presence of Al^{i}Bu$_3$ (20 turnovers after 1 h) [2d].

Although many examples of living polymerization of ethylene, propylene and 1-hexene can be seen recently [20], we still have an interest in exploring the details including roles of organoaluminum compounds as well as exploring a possibility to establish the living polymerization system. This is because, we believe, the facts through this research may also give important information for designing better

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Table 1
Polymerization of 1-hexene by **1**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system[a]

Run number	**1** (μmol)	B/Ti[b]	Al/Ti[b]	Time (min)	Polymer (yield/mg)	Activity[c]	TON[d]	M_n[e] ($\times 10^{-4}$)	M_w/M_n[e]
1	0.5	1.5	38	30	16.4	66	390	–	–
2	0.5	1.5	78	10	553.9	6650	13200	85.2	1.72
3	0.5	1.5	116	6[f]	407.1	8140	9690	82.1	1.55
4	0.25	3.0	62.5	10	84.3	2020	4010	28.8	1.81
5	0.25	3.0	125	10	187.3	4500	8920	191.7	1.66
6	0.25	3.0	250	10[f]	647.4	15540	30830	151.5	1.76
7	0.25	3.0	500	7[f]	826.9	28350	39380	160.2	1.61
8	0.25	2.0	500	10	59.1	1420	2810	14.8	1.99
9	0.25	1.5	500	10	12.7	305	605	17.8	1.37
10	0.25	–	500	10	–	–	–	–	–
11	0.25	3.0	–	10	Trace	Trace	–	–	–
12	–	–	500[g]	60	–	–	–	–	–
13	–	3.0[h]	–	10	–	–	–	–	–

[a] Reaction conditions: 1-hexene 10 ml, **1** 2.0 μmol/ml toluene, −30 °C, B = Ph$_3$CB(C$_6$F$_5$)$_4$, Al = Al^{i}Bu$_3$ (**1** was pre-treated with 2.0 eq. of Al^{i}Bu$_3$ at −30 °C for 10 min before addition into the reaction mixture).
[b] Molar ratio of Ph$_3$CB(C$_6$F$_5$)$_4$/Ti or Al^{i}Bu$_3$/Ti.
[c] Activity in kg polymer/mol Ti h.
[d] TON = molar amount of 1-hexene consumed/mol Ti.
[e] GPC data in THF vs. polystyrene standard.
[f] High exotherm was observed, and the polymerization was terminated at the initial stage.
[g] 500 μmol of Al^{i}Bu$_3$ was used.
[h] 3.0 μmol of Ph$_3$CB(C$_6$F$_5$)$_4$ was used.

catalyst for precise olefin polymerization. In this paper, we wish to introduce detailed results of 1-hexene polymerization with **1**–Ph$_3$CB(C$_6$F$_5$)$_4$ and organoaluminum catalyst system.

2. Results and discussion

2.1. Polymerization of 1-hexene by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system

2.1.1. Effect of cocatalyst

1 showed significant catalytic activity when Ph$_3$CB(C$_6$F$_5$)$_4$ or Me$_2$PhNHB(C$_6$F$_5$)$_4$ was used in the presence of Al^{i}Bu$_3$, and the extremely low activity was observed when B(C$_6$F$_5$)$_3$ was used in place of Ph$_3$CB(C$_6$F$_5$)$_4$ [2c]. As shown in Table 1, the activity increased at higher Al/Ti molar ratios (runs 1–7),[1] and the activity also increased at higher borate/Ti molar ratio when the polymerization was performed under low catalyst concentration conditions (**1**, 0.25 μmol, runs 7–9). The polymerization did not take place in the absence of Ph$_3$CB(C$_6$F$_5$)$_4$ (run 10) and trace amount of poly(1-hexene) was obtained in the absence of Al^{i}Bu$_3$ (run 11). Suitable amount of both Ph$_3$CB(C$_6$F$_5$)$_4$ and Al^{i}Bu$_3$ was thus required to optimize the polymerization conditions.

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[1] The observed catalytic activities shown in Table 1 were slightly higher than those reported previously [2c]. Probably the pretreatment of **1** with 2.0 eq. of Al^{i}Bu$_3$ increased the activity.

2.1.2. Temperature dependence in 1-hexene polymerization by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system

We chose the diluted conditions (1-hexene/n-hexane = 30/30 ml) instead of bulk polymerization conditions (1-hexene, 60 ml) as the optimized conditions, because the control of high exotherm (to keep the reaction temperature exactly at −30 °C) seemed not very easy under bulk polymerization conditions due to the high catalytic activity (7120 kg polymer/mol Ti h from Ref. [2c]). This is also because that the polymerization stopped at the initial stage due to the difficulty of stirring the reaction mixture (because of increased viscosity) under the optimized conditions shown in Table 1. A prescribed amount (3.0 ml) of the reaction mixture was removed via a syringe from the polymerization solution to examine the time course (turnover numbers, molecular weight and molecular weight distributions for resultant polymers). **1** was pretreated with 2.0 eq. of Al^{i}Bu$_3$ at −30 °C, because, as reported previously [2c], this procedure was found to be effective in exhibiting high catalytic activity with high reproducibility.

It turned out that the polymerization took place without deactivation at −30 °C, but the reaction stopped after 20 min when the polymerization was performed at 0 and −10 °C (Fig. 1). The polymerization results at −30 °C are summarized in Table 2, and the time course plots [turnover numbers (TON) versus time, plots of M_n and M_w/M_n versus TON] were shown in Fig. 2. As shown in Fig. 2a, the polymerization results at −30 °C were reproducible, and the observed catalytic activities [initial catalytic activity = 3690–3800 kg poly(1-hexene)/mol Ti h based on the initial TOF values (less than 20 min, shown in Table 4)] were
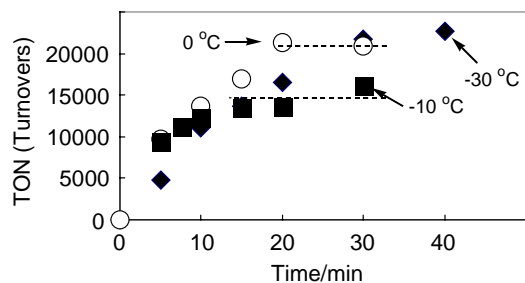
Fig. 1. Temperature dependence in 1-hexene polymerization with $Cp*TiMe_2(O-2,6-^iPr_2C_6H_3)$ (**1**)–Al^iBu_3–$Ph_3CB(C_6F_5)_4$ catalyst system. (○: 0 °C; ■: −10 °C; ◆: −30 °C). Reaction conditions: 1-hexene, 30 ml; n-hexane, 30 ml; **1**, 1.0 μmol; $Al^iBu_3/Ph_3CB(C_6F_5)_4/Ti = 500/3.0/1.0$ (molar ratio). TON (turnovers) = molar amount of 1-hexene consumed/mol Ti, −30 °C.

Table 2
Selected data in polymerization of 1-hexene by **1**–Al^iBu_3–$Ph_3CB(C_6F_5)_4$ catalyst system at −30 °C[a]

Time (min)	Polymer[b] (yield/mg)	Conversion[c] (%)	TON[d]	M_n[e] ($\times 10^{-4}$)	M_w/M_n[e]
5[f]	20.3	2.0	4830	50.1	1.64
10[f]	46.6	4.6	11100	93.7	1.36
15[f]	57.1	5.7	13600	114.5	1.37
20[f]	69.5	6.9	16500	123.9	1.35
30[f]	91.5	9.1	21800	162.8	1.33
40[f]	95.2	9.4	22700	186.5	1.27
5[g]	22.3	2.2	5310	53.7	1.49
10[g]	39.6	3.9	9430	83.6	1.44
15[g]	51.0	5.1	12100	131.1	1.36
20[g]	69.6	6.9	16600	138.7	1.36

[a] Reaction conditions: 1-hexene 30 ml, n-hexane 30 ml, **1** 1.0 μmol, $Al^iBu_3/Ph_3CB(C_6F_5)_4/Ti = 500/3.0/1.0$ (molar ratio), **1** was pre-treated with 2.0 eq. of Al^iBu_3 at −30 °C for 10 min before addition into the reaction mixture.

[b] A prescribed amount (3.0 ml) of the reaction mixture was removed via a syringe from the polymerization mixture, and the yields were based on obtained amount from the sample solution (3.0 ml).

[c] Conversion (%) of 1-hexene = polymer yields (mg)/1-hexene charged (mg).

[d] TON (turnovers) = molar amount of 1-hexene consumed/mol Ti.

[e] GPC data in THF vs. polystyrene standards.

[f] Independent runs (shown as ◆ in Fig. 2).

[g] Independent runs (shown as ▲ in Fig. 2).

higher than that obtained with **1** in the presence of MAO cocatalyst at 25 °C (621 kg polymer/mol Ti h) [2c].

It turned out that the M_n value increased upon increasing the TON value (calculated based on 1-hexene consumed per titanium (mol^{-1} Ti), this value corresponds to the polymer yield per titanium). In addition, the observed polydispersities (PDIs, M_w/M_n) were relatively narrow in all cases ($M_w/M_n = 1.27–1.37$, Table 2 and Fig. 2b).[2] Moreover,

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[2] The observed molecular weight distributions ($M_w/M_n = 1.27–1.37$) were relatively narrow, but the values were somewhat larger than those previously reported ($M_w/M_n < 1.2$). Since a linear relationship between M_n and TON values (without changing M_w/M_n value) was observed, it is thus concluded that this polymerization took place in a living man-
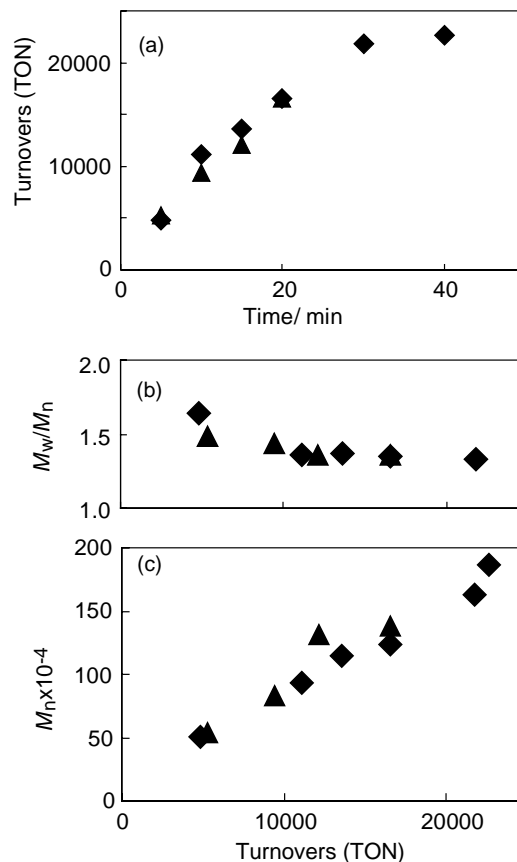

Fig. 2. 1-Hexene polymerization by **1**–Al^iBu_3–$Ph_3CB(C_6F_5)_4$ catalyst system. (a) Time course plots, (b) plots of TON vs. M_w/M_n, and (c) plots of TON vs. M_n. Plots with (◆) are same as those in Fig. 1, and plots with (▲) are the results of independent polymerization run. Reaction conditions: 1-hexene, 30 ml: n-hexane, 30 ml; **1**, 1.0 μmol; $Al^iBu_3/Ph_3CB(C_6F_5)_4/Ti = 500/3.0/1.0$ (molar ratio), −30 °C.

importantly, the resultant polymer possessed high molecular weight, and remarkably high catalyst efficiency could be thus suggested from the number of polymer chain (N) calculated based on both M_n values and polymer yields although observed M_n values are based on polystyrene standards [21].[3] These results clearly indicate that the present

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ner under these conditions. The probable reason for rather broad molecular weight distribution is due to that the rate for propagation [initial TOF = 730–753 min^{-1}, activity = 3690–3800 kg poly(1-hexene)/mol Ti h] is much higher than that for initiation.

[3] The observed M_n values were based on polystyrene standards, and it has been well known that these values can be simply converted by using Q values [M_n (by polystyrene standards) × (Q factor for poly(1-hexene), 33.1)/(Q factor for polystyrene, 41.1). According to this procedure, N values (number of polymer chain) plotted as ◆ and ▲ in Fig. 2 (and in Table 2) were 1.01–1.40 μmol and 0.97–1.25 μmol, respectively, and these values were somewhat larger than the amount of titanium catalyst used (1.0 μmol). On the other hand, it is well known that these calculated M_n values for poly(1-hexene)s by this procedure are smaller than those of the actual values (and then will afford slightly smaller N values shown above). Although attempts to determine the exact molecular weight were not made, we can suppose that this polymerization took place in a living manner with significant catalyst efficiency (almost quantitative). For related references see Ref. [21].
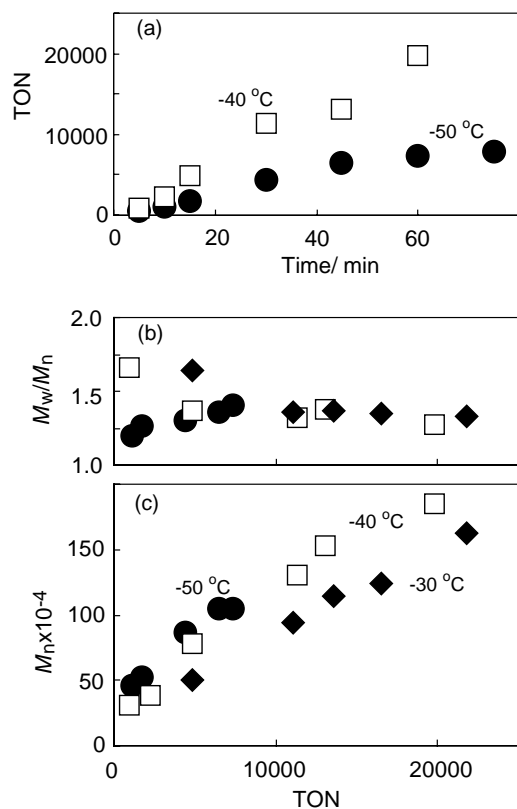
Fig. 3. Temperature dependence in 1-hexene polymerization catalyzed by 1–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system. (a) Time course plots, (b) plots of TON vs. M_w/M_n, and (c) plots of TON vs. M_n (◆: $-30\,°C$; □: $-40\,°C$; ●: $-50\,°C$). Plots with (◆) (in b and c) are adopted from Figs. 1 and 2. Reaction conditions: 1-hexene, 30 ml; n-hexane, 30 ml; 1, 1.0 μmol, Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$/Ti = 500/3.0/1.0 (molar ratio).

polymerization proceeds in a living manner with notably high catalyst efficiency. The resultant polymer possessed extremely high molecular weight with narrow polydispersity ($M_n = 186.5 \times 10^4$, $M_w/M_n = 1.27$). Taking into account these results, it is thus demonstrated that, as far as we know, the present catalyst system is a rare example for affording high molecular weight polymer by living polymerization with significant catalyst efficiency.

Fig. 3 shows results for the 1-hexene polymerization at -40 and $-50\,°C$, and the detailed results are summarized in Table 3.[4] The reaction rate decreased at lower temperature (Fig. 3a), and the observed activity at $-70\,°C$ was extremely low. The linear relationships between TON values and M_n values were observed in all cases (Fig. 3b). The percentage

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[4] A reviewer commented that M_n value seemed to reach a constant value at high TONs when the polymerization was performed at $-50\,°C$. In fact, as shown in Table 3, M_n value did not change between 45 and 60 min, although the polymer yield still increased linearly. On the other hand, it is hard to conclude only from this result (at 60 min) that some chain-transfer reaction took place, because molecular weight distribution was still narrow. Authors believe that the probable reason for the observed fact is the very low catalytic activity under these conditions. We believe that we will be able to establish a living polymerization system under higher catalyst concentration (or 1-hexene concentration) conditions.
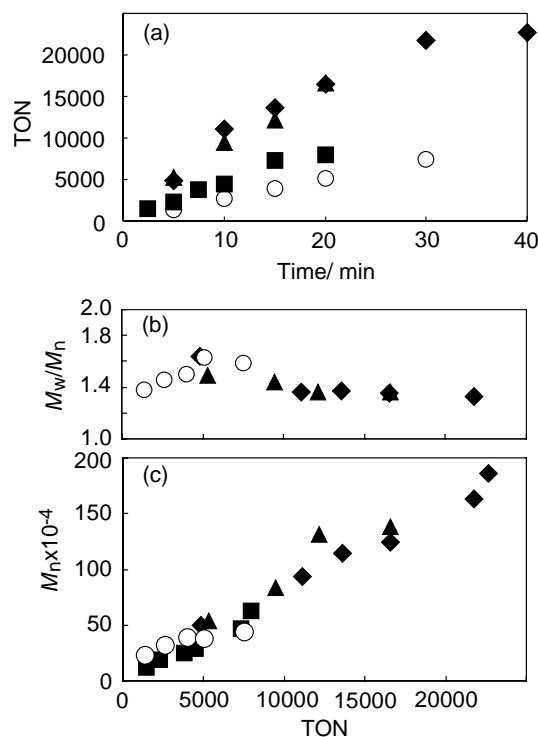

Fig. 4. Effect of monomer concentration in 1-hexene polymerization by 1–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system. (a) Time course plots, (b) plots of TON vs. M_w/M_n, and (c) plots of TON vs. M_n [1-hexene concentration = 4.00 mol/l (◆), 4.00 mol/l (▲), 2.67 mol/l (■), and 1.33 mol/l (○)]. Plots with (◆) and with (▲) are the same as those in Figs. 1 and 2. Reaction conditions: 1-hexene/n-hexane = 30/30 ml (◆, ○), 20/40 ml (■), 10/50 ml (○), 1 1.0 μmol, Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$/Ti = 500/3.0/1.0 (molar ratio), $-30\,°C$.

for catalytically-active species in the reaction mixture was found to be dependent upon the polymerization temperature employed, because the M_n values at each TON values obtained at both -40 and $50\,°C$ were higher than those at $-30\,°C$ (Fig. 3b).

2.1.3. Monomer concentration dependence

1-Hexene polymerizations using 1–Al^{i}Bu$_3$–Ph$_3$CB (C$_6$F$_5$)$_4$ catalyst system were conducted under various initial 1-hexene concentrations at $-30\,°C$, since some bridged half-metallocene type catalyst systems showed the second order dependence for the catalytic activity in propylene polymerization [20n]. As shown in Fig. 4a, the polymerization rate decreased at lower monomer concentrations. The linear relationships between M_n values and TON values were observed in all cases, and the molecular weight distributions for resultant poly(1-hexene)s were relatively narrow (Fig. 4b), suggesting that these polymerizations took place in a living manner.[5] The initial TOF values

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[5] Although a linear relationship between M_n values and TON values were observed in the polymerization at the initial 1-hexene concentration of 2.67 mol/l, the resultant M_w/M_n values were somewhat broad (1.9–2.0). Although the results were reproducible, the reason for the broad molecular weight distribution is not clear at this moment.

Table 3
Selected data in 1-hexene polymerization by **1**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system: effect of polymerization temperature[a]

Temperature (°C)	Time (min)	Polymer[b] (yield/mg)	Conversion[c] (%)	TON[d]	M_n[e] ($\times 10^{-4}$)	M_w/M_n[e]
−30	5[f]	20.3	2.0	4830	50.1	1.64
	10[f]	46.6	4.6	11100	93.7	1.36
	15[f]	57.1	5.7	13600	114.5	1.37
	20[f]	69.5	6.9	16500	123.9	1.35
	30[f]	91.5	9.1	21800	162.8	1.33
	40[f]	95.2	9.4	22700	186.5	1.27
−40	5	3.9	0.4	929	30.9	1.66
	10	9.3	0.9	2210	38.6	2.02
	15	20.5	2.0	4880	78.2	1.37
	30	47.5	4.7	11300	130.1	1.32
	45	54.8	5.4	13000	153.0	1.38
	60	83.1	8.2	19800	184.5	1.27
−50	5	1.9	0.2	452	–	–
	10	4.7	0.5	1120	45.8	1.20
	15	7.1	0.7	1690	52.4	1.26
	30	18.6	1.8	4430	86.3	1.30
	45	27.4	2.7	6520	105.2	1.36
	60	31.0	3.1	7380	105.3	1.41

[a] Reaction conditions: 1-hexene 30 ml, *n*-hexane 30 ml, **1** 1.0 μmol, Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$/Ti = 500/3.0/1.0 (molar ratio), **1** was pre-treated with 2.0 eq. of Al^{i}Bu$_3$ at −30 °C for 10 min before addition into the reaction mixture.

[b] A prescribed amount (3.0 ml) of the reaction mixture at prescribed time (shown above) was removed via a syringe from the polymerization mixture, and the yields were based on the obtained amount.

[c] Conversion (%) of 1-hexene = polymer yields (mg)/1-hexene charged (mg).

[d] TON (turnovers) = molar amount of 1-hexene consumed/mol Ti.

[e] GPC data in THF vs. polystyrene standards.

[f] Results shown in Table 2.

(calculated based on TON values at the initial stage shorter than 20 min) under various 1-hexene concentration conditions are summarized in Table 4. The first order relationship between the initial TOF values and 1-hexene concentrations was observed (Fig. 5), and the results clearly show that the polymerization rate showed first order dependence upon the monomer concentration.

2.2. A study exploring the role of Al cocatalyst in 1-hexene polymerization

Since some organoaluminum compounds are known to be effective in removing impurities (H$_2$O, oxygen, etc.) in

Table 4
Summary for initial reaction rates in 1-hexene polymerization by **1**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system[a]

Initial 1-hexene (conc./mol/l)	Initial turnover frequency (mol 1-hexene consumed/mol Ti min)
1.33	244
2.67	396
4.00	730
4.00	753
8.00[b]	1410

[a] Reaction conditions: 1-hexene + *n*-hexane total 60 ml, **1** 1.0 μmol (2.0 μmol/ml toluene), −30 °C, Al^{i}Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$/Ti = 500/3.0/1.0 (molar ratio), **1** was pre-treated with 2.0 eq. of Al^{i}Bu$_3$ at −30 °C for 10 min before addition into the reaction mixture. Detailed results are shown in Fig. 4.

[b] Cited from Ref. [2c] (under bulk polymerization conditions).

the reaction mixture, Al(*n*-C$_8$H$_{17}$)$_3$ was chosen to replace Al^{i}Bu$_3$ in some extents. The results are summarized in both Table 5 and Fig. 6.

As shown in Fig. 6a, the polymerization took place without deactivation when Al(*n*-C$_8$H$_{17}$)$_3$ was used in stead of Al^{i}Bu$_3$ (marked with ■ and ●), although the observed catalytic activities were slightly lower than those in the presence of Al^{i}Bu$_3$ (marked with ◆). As shown in Fig. 6b, a linear relationship was observed between M_n and TON values, and the polydispersities for resultant poly(1-hexene)s were relatively narrow in all cases. These results also suggest that these polymerizations proceed in a living manner. Since the activity did not decrease for low Al^{i}Bu$_3$/Ti molar ratios, removal of some impurities (so called scavenger) by aluminum
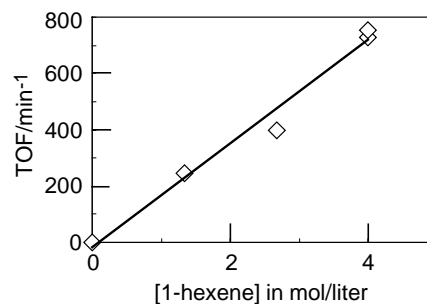

Fig. 5. Plots of initial TOF (min^{-1}) values vs. monomer concentration based on data shown in Fig. 4. TOF (turnover frequency) = TON (mol^{-1} Ti)/time (min).

Table 5
Selected data for effect of aluminum cocatalyst in 1-hexene polymerization by $\mathbf{1}$–$Ph_3CB(C_6F_5)_4$ catalyst system[a]

$Al^iBu_3/Al(n\text{-}C_8H_{17})_3/\mathbf{1}$	Time (min)	Polymer[b] (yield/mg)	Conversion[c] (%)	TON[d]	M_n[e] $(\times 10^{-4})$	M_w/M_n[e]
500/–/1.0	5[f]	20.3	2.0	4830	50.1	1.64
	10[f]	46.6	4.6	11100	93.7	1.36
	15[f]	57.1	5.7	13600	114.5	1.37
	20[f]	69.5	6.9	16500	123.9	1.35
	30[f]	91.5	9.1	21800	162.8	1.33
	40[f]	95.2	9.4	22700	186.5	1.27
300/200/1	5	22.5	2.2	5360	56.6	1.47
	10	35.4	3.5	8430	85.3	1.45
	15	40.3	4.0	9600	128.5	1.35
	20	53.3	5.3	12700	135.1	1.38
	30	61.4	6.1	14600	176.5	1.30
	40	75.5	7.5	18000	150.5	1.44
	50	86.2	8.5	20500	184.7	1.35
100/400/1	5	18.9	1.9	4500	52.4	1.57
	10	30.4	3.0	7240	129.8	1.35
	15	43.4	4.3	10300	136.9	1.39
	30	61.0	6.0	14500	185.1	1.38

[a] Reaction conditions: 1-hexene 30 ml, *n*-hexane 30 ml, $\mathbf{1}$ 1.0 μmol, $Ph_3CB(C_6F_5)_4/Ti = 3.0$, $\mathbf{1}$ was pre-treated with 2.0 eq. of Al^iBu_3 at $-30\,^\circ C$ for 10 min before addition into the reaction mixture.

[b] A prescribed amount (3.0 ml) of the reaction mixture was removed via syringe from the polymerization mixture, and the yields were based on obtained amount.

[c] Conversion (%) of 1-hexene = polymer yields (mg)/1-hexene charged (mg).

[d] TON (turnovers) = molar amount of 1-hexene consumed/mol Ti.

[e] GPC data in THF vs. polystyrene standards.

[f] Results shown in Table 2.

compound could be thus considered. On the other hand, the observed activity was extremely low if all of Al^iBu_3 was replaced with $Al(n\text{-}C_8H_{17})_3$, it is thus clear that Al^iBu_3 plays an important role in the present catalytic polymerization.

Since pre-treatment of $\mathbf{1}$ with 2.0 eq. of Al^iBu_3 at $-30\,^\circ C$ was very effective in exhibiting high catalytic activity with high reproducibility [2c] and some part of Al^iBu_3 could be replaced with $Al(n\text{-}C_8H_{17})_3$, reactions of $\mathbf{1}$ with these aluminum compounds were explored. The observed ^1H NMR showed a mixture of $\mathbf{1}$ and $Al(n\text{-}C_8H_{17})_3$, when the reaction of $\mathbf{1}$ with 1.0 eq. of $Al(n\text{-}C_8H_{17})_3$ was conducted at $-50\,^\circ C$, and no drastic change in the spectrum could be observed at both -10 and $-30\,^\circ C$. These results strongly indicate that no reaction took place between $\mathbf{1}$ and $Al(n\text{-}C_8H_{17})_3$ under these conditions.

The ^1H NMR spectrum for the reaction of $\mathbf{1}$ with 1.0 eq. of Al^iBu_3 at $-50\,^\circ C$ gave a resonance at 0.40 ppm that would be ascribed to methyl proton connected to Al (Fig. 7c). Resonances ascribed to C_5Me_5 (ca. 1.70 ppm) and titanium-methyl protons (0.75 ppm) were observed as two separate peaks (resonances slightly shifted to lower field was observed as an additional peak). The intensity for the resonance ascribed to the Ti-Me protons slightly decreased after the reaction with Al^iBu_3. Although complete explanation for the observed results may be difficult only from this result, we can at least suggest that alkyl exchange reaction or interaction between methyl group in $\mathbf{1}$ and Al^iBu_3 may take place. Since the efficiency for formation of alkyl-cationic species with the reaction of borate compounds should be influenced by the nature of alkyl species (methyl versus

isobutyl) [22], we would deduce that pre-treatment of $\mathbf{1}$ with Al^iBu_3 may give the alkyl-exchanged product that would enhance the efficiency for generating catalytically-active species for the polymerization. Taking into account these results, it is thus clear at this moment that the role of organoaluminum compounds is not only to remove impurities but also to generate catalytically-active species efficiently in the present catalytic 1-hexene polymerization.[6]

3. Experimental

3.1. General procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade of *n*-hexane and toluene (Kanto Kagaku Co. Ltd.) were transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the drybox under nitrogen flow. 1-Hexene was also stored in the

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[6] One point it is still not clear is that why relatively excess amount of Al^iBu_3 (more than 100 eq.) are required in the present catalyst system, because the catalytic activity with a mixture of $Al^iBu_3/Al(n\text{-}C_8H_{17})_3$ (2/498, molar ratio) was extremely low. We roughly assume at this moment that this would be probably due to that excess amount of Al^iBu_3 may be required for stabilizing catalytically-active species (like formation of adduct in a certain degree with the borate compound), although we do not have clear evidence for explaining this assumption.
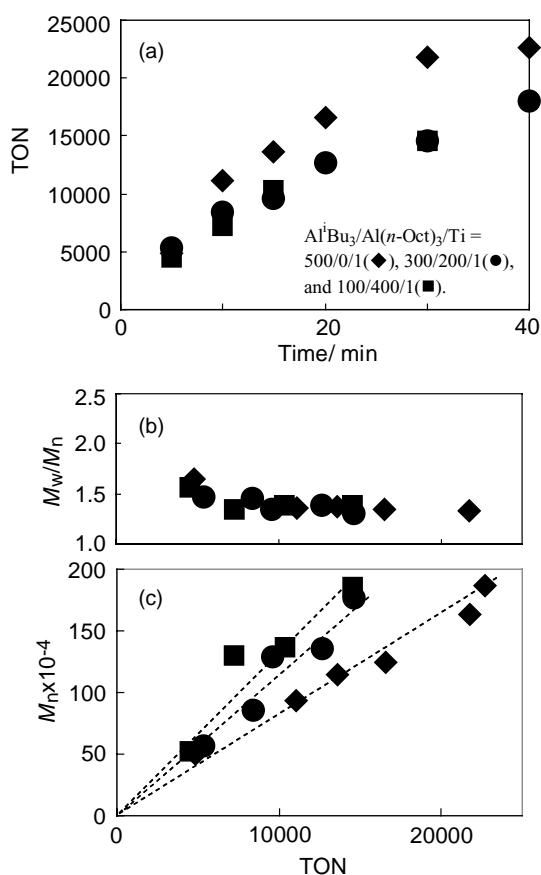
Fig. 6. Effect of organoaluminum compounds in 1-hexene polymerization by **1**–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst. Molar ratio of Al^{i}Bu$_3$/Al(n-C$_8$H$_{17}$)$_3$/Ti = 500/0/1 (◆), 300/200/1 (●), and 100/400/1 (■). (a) Time course plots, (b) plots of TON vs. M_w/M_n, and (c) plots of TON vs. M_n. Reaction conditions: 1-hexene, 30 ml; n-hexane, 30 ml, **1** 1.0 μmol, Ph$_3$CB(C$_6$F$_5$)$_4$/Ti = 3.0 (molar ratio), −30 °C.

Fig. 7. ^{1}H NMR spectra (in toluene-d_8) of (a) Al^{i}Bu$_3$ (independent run for comparison), (b) Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**), (c) **1** with 1.0 eq. of Al^{i}Bu$_3$ at −50 °C.

drybox in the presence of molecular sieves. Syntheses of Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**) was according to our previous report [2b]. Ph$_3$CB(C$_6$F$_5$)$_4$ and B(C$_6$F$_5$)$_3$ were purchased from Asahi Glass Co. Ltd., and were used as received in the drybox.

All ^{1}H NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H). All chemical shifts are given in ppm and are referenced to SiMe$_4$. All deuterated NMR solvents were stored over molecular sieves in the drybox.

^{1}H NMR experiments concerning reaction of **1** with organoaluminum compounds are as follows [2d]. Solid sample of **1** (ca. 50 mg) was added into a NMR tube capped with rubber septa, and the tube was then placed in a liquid nitrogen Dewar bath, and was then added appropriate amount of toluene-d_8 and Al^{i}Bu$_3$ or Al(n-C$_8$H$_{17}$)$_3$ (1.0 eq.) slowly via a syringe. These samples were directly placed into the NMR instrument precooled at −50 °C.

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
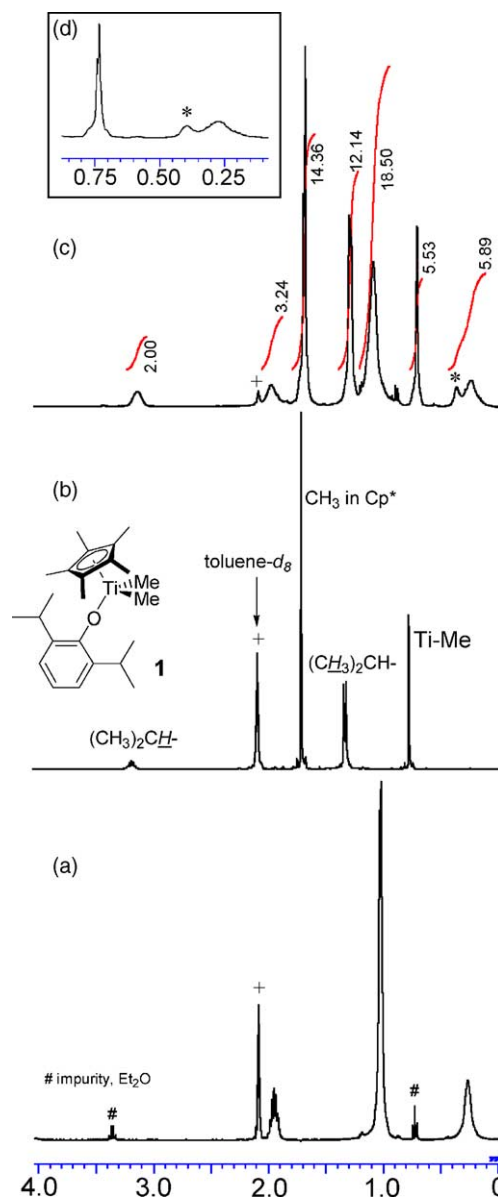
was used for GPC and were degassed prior to use. GPC were performed at 40 °C on a Shimazu SCL-10A using a RID-10A detector (Shimazu Co. Ltd.) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 ml/min). GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm, Ø) were calibrated versus polystyrene standard samples.

3.1.1. Polymerization of 1-hexene catalyzed by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)–Al^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ system

1-Hexene polymerizations described in Table 1 were performed as follows. 1-Hexene (10 ml) and prescribed amount

of Al^{i}Bu$_3$ were added into a round bottom flask (25 ml) connected to three-way valves under N$_2$. A certain amount of toluene solution containing **1** (2.0 μmol/ml-toluene) [pre-treated with 2.0 eq. of Al^{i}Bu$_3$ in advance at $-30\,^\circ$C] was added into the above solution, and the polymerization was then started by addition of borate compound dissolved in toluene (1.0 ml). The reaction mixture was stirred for pre-scribed time, 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$_2$SO$_4$, and chloroform and 1-hexene unreacted was then removed in vacuo.

Typical polymerization procedures were as follows: 1-hexene (30 ml), *n*-hexane (30 ml) and a prescribed amount of Al^{i}Bu$_3$ [and Al(n-C$_8$H$_{17}$)$_3$] 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. A toluene solution containing **1** (2.0 μmol/ml) [pre-treated with 2.0 eq. of Al^{i}Bu$_3$ at $-30\,^\circ$C] was added into the mixture, and the polymerization was then started by the addition of a prescribed amount of toluene solution containing Ph$_3$CB(C$_6$F$_5$)$_4$ (2.0 μmol/ml). A prescribed amount (3.0 ml) of the reaction mixture was removed via a syringe from the polymerization solution to monitor 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$_2$SO$_4$, and chloroform and 1-hexene unreacted was then removed in vacuo.

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