Synthesis of Ultrahigh Molecular Weight Polymers with Low PDIs by Polymerizations of 1-Decene, 1-Dodecene, and 1-Tetradecene by Cp*TiMe₂(O-2,6-iPr₂C₆H₃)–Borate Catalyst

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Abstract: Polymerizations of 1-decene (DC), 1-dodecene (DD), and 1-tetradecene (TD) by Cp*TiMe₂(O-2,6-iPr₂C₆H₃) (I)–[Ph₃C][B(C₆H₄F₅)₃] (borate) catalyst have been explored in the presence of Al cocatalyst. The polymerizations of DC and DD, in n-hexane containing a mixture of Al/iBu₃ and Al(n-C₆H₁₇)₃, proceeded with high catalytic activities in a quasi-living manner, affording high molecular weight polymers (activity 4120–5860 kg-poly(DC)/mol-Ti-h, Mₙ for poly(DC) = 7.04–7.82 × 10⁵, after 20 min at −30 °C). The PDI (Mₘ/Mₙ) values in the resultant polymers decreased upon increasing the ratio of Al(n-C₆H₁₇)₃/iBu₃ with decreasing the activities at −30 °C. The PDI values also became low when these polymerizations were conducted at low temperatures (−40 or −50 °C); high molecular weight poly(DD) with low PDI (Mₙ = 5.26 × 10⁵, Mₘ/Mₙ = 1.16) was obtained at −50 °C. The TD polymerization using 1–borate–Al/iBu₃ catalyst (conducted in n-hexane at −30 °C) afforded ultrahigh molecular weight poly(TD) (Mₙ = 1.02 × 10⁶, Mₘ/Mₙ = 1.38), and the PDI values also decreased with increasing the Al(n-C₆H₁₇)₃/iBu₃ ratio.

Keywords: polymerization; titanium complex; catalyst; α-olefin; half-titanocene; borate

1. Introduction

Design of molecular catalysts for olefin polymerization has been considered as an important subject in synthesis of new polymers with specified functions. The recent progress in the catalyst developments provides new possibilities [1–17]. Although crystalline isotactic polypropylene has been widely used in our daily life, use of amorphous poly(α-olefins) (APAOs) showed less attention due to their inherent stickiness and softness. APAOs possess high melt-flow rate with low density, and are used in hot melt applications, these also improve adhesion on wood and polypropylene, and improve the free-flowing ability of their granules. It has been known recently that ultrahigh molecular weight poly(α-olefin)s can be used as drag reducing agents (DRAs) in pipeline transport methods for crude oil and petroleum products, because of their ability to reduce pumping power and increase piping system capacity [18–21]. Moreover, poly(α-olefin)s with alkyl chain length greater than six have bottlebrush architecture (branched macromolecules with a high graft density along their backbone) [22–25], and are the simplest bottlebrush polymers, with their backbone and side chains consisting of alkanes.

As shown below (Table 1), polymerization of α-olefin (1-hexene, 1-octene, 1-decene, etc.) by ordinary metalloocene catalysts gave oligomers [26–28]. Several examples [28–33] were known for synthesis of (ultra)high molecular weight poly(1-hexene) by using [2,2-(O-4-Me-6-iBu-C₆H₃)$_2$Si]TiCl$_2$ (in the presence of specified modified MMAO) [31,32], or (C₅HMe$_4$)$_2$HfCl$_2$ (under ultrahigh
pressure) [29]. One example was known for synthesis of isotactic poly(1-hexene)s with ultrahigh molecular weights by titanium complexes containing diamine bis(phenolate) ligands [30]. Several examples were also known for synthesis of poly(α-olefin)s with rather high molecular weights [27,34–42]. However, synthesis of ultrahigh molecular weight polymers by polymerization of higher α-olefins (1-decene, 1-dodecene, 1-tetradecene, etc.) still have been limited [28], probably due to their tendency to undergo β-hydrogen elimination before subsequent/repeated insertion.

We recently reported synthesis of high molecular weight poly(α-olefin)s by polymerizations of 1-decene, 1-dodecene, 1-hexadecene, and 1-octadecene by Cp*TiCl₂(O-2,6-Pr₂C₆H₄)–MAO catalyst [28], and the $M_n$ values in the resultant polymers were higher than those prepared by [Me₂Si(C₅Me₅)](N'Bu)TiCl₂ and Cp₂ZrCl₂ (Table 1) [28]. Moreover, Cp*TiMe₂(O-2,6-Pr₂C₆H₄) (1)–[Ph₃C][B(C₆F₅)₄] (borate) catalyst showed the higher catalytic activities, affording ultrahigh molecular weight poly(1-octene)s and poly(1-dodecene)s (Table 1) [28]. On the other hand, we also reported that 1-hexene polymerization by 1-borate catalyst proceeded in a quasi-living manner under certain conditions to afford ultrahigh molecular weight poly(1-hexene) ($M_n > 1.0 \times 10^6$) [33]. Therefore, we herein present synthesis of high molecular weight polymers by polymerizations of 1-decene (DC), 1-dodecene (DD), and 1-tetradecene (TD) with low PDI ($M_w/M_n$) values using 1-borate catalyst in the presence of Al cocatalyst (Scheme 1).

| Catalyst | α-Olefin | Cocatalyst | Time/min | TON | Activity | $M_n$ | $M_w/M_n$ |
|----------|----------|------------|----------|-----|----------|------|----------|
| Cp*TiCl₂(O-2,6-Pr₂C₆H₄) | OC | MAO | 30 | 9950 | 2240 | 501000 | 1.42 |
| Cp*TiCl₂(O-2,6-Pr₂C₆H₄) | DD | MAO | 30 | 4120 | 1390 | 525000 | 1.35 |
| Cp*TiMe₂(O-2,6-Pr₂C₆H₄) | OC | borate | 20 | 7080 | 2380 | 1970000 | 2.04 |
| Cp*TiMe₂(O-2,6-Pr₂C₆H₄) | DD | borate | 20 | 3730 | 1880 | 1320000 | 1.99 |
| [Me₂Si(C₅Me₅)(N'Bu)]TiCl₂ | OC | MAO | 30 | 4810 | 1080 | 292000 | 1.64 |
| [Me₂Si(C₅Me₅)(N'Bu)]TiCl₂ | DD | MAO | 30 | 2060 | 690 | 351000 | 1.33 |
| Cp₂ZrCl₂ | OC | MAO | 30 | 21300 | 4790 | 4100 | 1.55 |
| Cp₂ZrCl₂ | DD | MAO | 30 | 15400 | 5190 | 5000 | 1.57 |

*Conditions (MAO cocatalyst): Complex 1.0 μmol, α-olefin 5.0 mL, d-MAO (prepared by removing toluene and AlMe₃ from ordinary MAO) 2.0 mmol, 25 °C; Conditions (borate cocatalyst): Complex 1 0.25 μmol, olefin 5.0 mL, −30 °C, AlBu₃/[Ph₃C][B(C₆F₅)₄]/Ti 500/3.0/1.0 (molar ratio). b TON (turnover number) = [mmol of α-olefin reacted]/[mmol of Ti]. c Activity = kg-polymer/mol-Ti·h. d Gel-permeation chromatography (GPC) data THF vs. polystyrene standards.

Scheme 1. Polymerization of 1-decene (DC), 1-dodecene (DD), and 1-tetradecene (TD) using Cp*TiMe₂(O-2,6-Pr₂C₆H₄) (1)–[Ph₃C][B(C₆F₅)₄] catalyst in the presence of Al cocatalyst.

2. Results and Discussion

2.1. Polymerization of 1-Decene and 1-Dodecene by Cp*TiMe₂(O-2,6-Pr₂C₆H₄) (1)–Borate Catalyst

On the basis of our previous report in 1-hexene polymerization [33], polymerizations of 1-decene (DC) using Cp*TiMe₂(O-2,6-Pr₂C₆H₄) (1)–[Ph₃C][B(C₆F₅)₄] (borate) catalyst were conducted in $n$-hexane in the presence of Al cocatalyst (Al/Ti = 500, molar ratio) with different Al($n$-C₈H₁₇)$_₃$/AlBu₃ ratios at −30 °C. Use of Al($n$-C₈H₁₇)$_₃$, which should be the weak reagent for alkylation and/or chain
transfer, but plays a role as a scavenger, was effective in the 1-hexene polymerization to proceed without catalyst deactivation [33]. The similar effect was also observed in the syndiospecific styrene polymerization using (1-BuC₆H₄)₃TiCl₂(O-2,6-Pr₂C₆H₃)–[PhN(H)Me₂]–[B(C₆F₅)₃] catalyst [43]. Use of a mixture of Al(n-C₈H₁₇)₃/Al′Bu₃ cocatalyst was also effective for exclusive obtainment of copolymers with high styrene contents in the ethylene/styrene copolymerization even at high temperature [44,45]. It was assumed that the Al alkyl would also play a role to stabilize the catalytically active species for the subsequent decomposition by reacting with borate [46–48].

As shown in Table 2, the polymerization of DC at −30 °C (runs 1–3) proceeded with high catalytic activities (4120–5860 kg-polymer/mol-Ti·h after 20 min) without significant catalyst deactivation to afford high molecular weight poly(DC)s (Mn = 7.04–7.82 × 10⁵), and the Mn values increased over time course without increasing the PDI (Mw/Mn) values. It turned out that the PDI values decreased upon increasing the Al(n-C₈H₁₇)₃/Al′Bu₃ molar ratio, whereas the catalytic activity decreased with increasing the ratio (runs 1–3). As shown in Figure 1a (shown below), rather linear relationships between the Mn values and the polymer yields (turnover numbers, TON) were observed, suggesting that these polymerizations proceeded in a (quasi) living manner.

Table 2. 1-Decene polymerization by Cp*TiMe₂(O-2,6-Pr₂C₆H₃) (1)–borate catalyst. a

| Run | Allo-C₈H₁₇₃/Al′Bu₃/[Ti | Temp/°C | Time/min | Polymer Yield/mg | Activity a | Mw/Mn × 10⁻⁴ | TON c | Mn/Mw d |
|-----|----------------------|---------|----------|------------------|------------|--------------|--------|---------|
| 1   | 2500                 | −30     | 5        | 926              | 11100      | 6600         | 40.1   | 1.52    |
| 10  | 1664                 | −30     | 15       | 1162             | 6970       | 8280         | 58.2   | 1.57    |
| 20  | 1852                 | −30     | 20       | 1782             | 5120       | 12170        | 76.4   | 1.52    |
| 2   | 2000/1000            | −30     | 10       | 992              | 1300       | 1780         | 31.9   | 1.26    |
| 15  | 1454                 | −30     | 15       | 1708             | 5120       | 12170        | 76.4   | 1.52    |
| 20  | 1708                 | −30     | 20       | 1708             | 5120       | 12170        | 76.4   | 1.52    |
| 3   | 400/100              | −30     | 10       | 92               | 4130       | 2380         | 40.1   | 1.32    |
| 15  | 1052                 | −30     | 15       | 1372             | 4130       | 2380         | 40.1   | 1.32    |
| 4   | 400/100              | −40     | 10       | 250              | 1930       | 1740         | 31.9   | 1.26    |
| 15  | 1488                 | −40     | 15       | 200              | 1630       | 2910         | 39.0   | 1.30    |
| 20  | 602                  | −40     | 20       | 1810             | 4290       | 47.7         | 1.25   |        |
| 30  | 976                  | −40     | 30       | 1950             | 6960       | 56.9         | 1.25   |        |
| 45  | 1228                 | −40     | 45       | 1640             | 8750       | 63.4         | 1.29   |        |
| 60  | 1620                 | −40     | 60       | 1620             | 11500      | 66.8         | 1.29   |        |
| 5   | 300/2000             | −30     | 15       | 230              | 1000       | 1294         | 36.2   | 1.10    |
| 30  | 400                  | −30     | 30       | 230              | 1000       | 1294         | 36.2   | 1.10    |
| 45  | 506                  | −30     | 45       | 300              | 680        | 3610         | 43.1   | 1.21    |
| 60  | 534                  | −30     | 60       | 530              | 530        | 3810         | 44.6   | 1.13    |
| 75  | 558                  | −30     | 75       | 450              | 400        | 450          | 45.5   | 1.13    |
| 90  | 582                  | −30     | 90       | 390              | 4150       | 45.5         | 1.16   |        |
| 105 | 652                  | −30     | 105      | 370              | 4650       | 46.1         | 1.14   |        |
| 120 | 684                  | −30     | 120      | 340              | 4880       | 46.5         | 1.15   |        |

a Conditions: Complex 1: 1.0 μmol, 1-decene (30 mL) and n-hexane total 60 mL (initial 1-decene concentration 2.64 M), [Ph₃C] [B(C₆F₅)₃]/Ti = 3.0 (molar ratio), 1 was pre-treated with 2.0 eq. of Al′Bu₃ at −30 °C for 10 min. b Molar ratio of Al(n-C₈H₁₇)₃/Al′Bu₃/Ti. c A prescribed amount (3.0 mL) of the reaction mixture was removed via syringe from the mixture, and the yields were based on obtained amount. d Activity in kg-polymer/mol-Ti·h. e TON (turnovers) = molar amount of 1-decene consumed/mol-Ti. f GPC data in THF vs. polystyrene standards.

It also turned out that the PDI values became low when the polymerization was conducted at −40 °C (run 4), with decreasing the activity [activity after 20 min: 4120 kg-polymer/mol-Ti·h (run 3, at −30 °C) vs. 1810 (run 4, at −40 °C)]. As shown in Figure 1a, a relatively good linear relationship between the Mn values and the polymer yields consistent with rather low PDI values (Mw/Mn = 1.25–1.30) clearly suggest that the polymerization proceeded in a (quasi) living manner. Moreover, the PDI value became low (Mw/Mn = 1.13–1.21) when the polymerization was conducted at −50 °C. The Mn value in the resultant polymers increased over time course consistent with low PDI values—high molecular weight poly(DC) with low PDI (Mn = 4.65 × 10⁵, Mw/Mn = 1.15, run 5) was thus obtained after 2 h.

Similarly, as shown in Table 3, the polymerization of DD at −30 °C (runs 6–8) proceeded with high catalytic activities (5020–8950 kg-polymer/mol-Ti·h after 20 min) without significant catalyst deactivation to afford high molecular weight poly(DD)s (Mn = 4.84–6.74 × 10⁵), and the Mn values increased over time course without increasing the PDI (Mw/Mn) values. The PDI values decreased
upon increasing the Al(n-C8H17)3/Al'Bu3 molar ratio, whereas the catalytic activity decreased with increasing the ratio. As also shown in Figure 1b (shown below), rather linear relationships between the M_n values and the polymer yields (turnover numbers, TON) suggest that these polymerizations also proceeded in a (quasi) living manner.

| Run | Al(η-C8H17)3/Al'Bu3/Ti | Temp/°C | Time/min | Polymer Yield/mg | Activity/TON·μmol·Ti·h | M_n/×10^-4 | M_w/M_n |
|-----|------------------------|---------|----------|------------------|-------------------------|-------------|----------|
| 6   | (500)                  | -30     | 5        | 600              | 7200                    | 3570        | 34.8     | 1.58    |
|     |                        |         | 10       | 1236             | 7420                    | 7340        | 48.0     | 1.66    |
|     |                        |         | 15       | 2288             | 9150                    | 13600       | 59.2     | 1.60    |
|     |                        |         | 20       | 2842             | 8950                    | 17700       | 67.4     | 1.68    |
| 7   | (800)                  | -30     | 5        | 4480             | 5340                    | 2640        | 32.9     | 1.52    |
|     |                        |         | 10       | 9300             | 5580                    | 5530        | 41.2     | 1.53    |
|     |                        |         | 15       | 1752             | 7010                    | 10400       | 48.8     | 1.58    |
|     |                        |         | 20       | 2094             | 6280                    | 12400       | 55.4     | 1.61    |
| 8   | (1000)                 | -30     | 5        | 398               | 4780                    | 2570        | 36.1     | 1.56    |
|     |                        |         | 10       | 668              | 4010                    | 4000        | 45.4     | 1.52    |
|     |                        |         | 15       | 1204             | 4820                    | 7150        | 44.7     | 1.52    |
|     |                        |         | 20       | 1674             | 5020                    | 9950        | 48.4     | 1.54    |
| 9   | (1000)                 | -40     | 10       | 304              | 1820                    | 1810        | 35.3     | 1.25    |
|     |                        |         | 15       | 428              | 1710                    | 2540        | 39.3     | 1.22    |
|     |                        |         | 20       | 574              | 1720                    | 3410        | 40.9     | 1.25    |
|     |                        |         | 30       | 654              | 1310                    | 3890        | 42.7     | 1.26    |
|     |                        |         | 45       | 682              | 910                      | 4050        | 43.1     | 1.27    |
|     |                        |         | 60       | 910              | 910                      | 5410        | 45.2     | 1.29    |
| 10  | (2000)                 | -30     | 60       | 229              | 330                      | 8410        | 25.3     | 1.18    |
|     |                        |         | 75       | 259              | 430                      | 4000        | 31.2     | 1.17    |
|     |                        |         | 90       | 291              | 390                      | 4150        | 40.8     | 1.11    |
|     |                        |         | 105      | 326              | 370                      | 4650        | 48.1     | 1.18    |
|     |                        |         | 120      | 342              | 340                      | 4880        | 52.6     | 1.14    |

* Conditions: Complex I 1.0 μmol, 1-dodecene (35 mL) and n-hexane total 60 mL (initial 1-dodecene concentration 2.63 M), [Ph3C][B(C6F5)4]/Ti = 3.0 (molar ratio), I was pre-treated with 2.0 eq. of Al'Bu3 at -30 °C for 10 min.

b Molar ratio of Al(η-C8H17)3/Al'Bu3/Ti. A prescribed amount (3.0 mL) of the reaction mixture was removed via syringe from the mixture, and the yields were based on obtained amount. c Activity in kg-polymer/mol-Ti·h. d TON (turnovers) = molar amount of 1-dodecene consumed/mol-Ti. e GPC data in THF vs. polystyrene standards.

It was also revealed that the PDI values became low when the polymerization was conducted at -40 °C (run 9), although the catalytic activity decreased at -40 °C [activity after 20 min: 5020 kg-polymer/mol-Ti·h (run 8, at -30 °C) vs. 1720 (run 9, at -40 °C)]. As shown in Figure 1b, a relatively good linear relationship between M_n value and the polymer yield consistent with rather low PDI values (M_w/M_n = 1.22–1.29) clearly suggests that the polymerization proceeded in a (quasi) living manner. Moreover, the PDI value became low (M_w/M_n = 1.11–1.18) when the polymerization was conducted at -50 °C. The M_n value in the resultant polymers increased over time course consistent with low PDI values; high molecular weight poly(DD) with low PDI (M_n = 5.26 × 10^5, M_w/M_n = 1.14) could be thus obtained after 2 h.

As shown in Figure 1, good linear relationships between the M_n values and the polymer yields (TONs) were observed without increasing the PDI values in all cases, suggesting that these polymerizations proceeded in a (quasi) living manner. In particular, the polymerizations at -40 °C afforded polymers with low PDI values, the results thus strongly indicate a possibility of living polymerization under these conditions. The resultant poly(DD)s showed similar thermal property (melting temperature (T_m) = -24 °C) to those prepared by Cp*TiCl2(O-2,6-Pr2C6H3)–MAO catalyst [28], whereas T_m values increased upon increasing methylene units in the alkyl side chain (poly(1-hexadecane) = 26 °C, poly(1-octadecene = 42 °C) due to called side chain crystallization [28].
shown in Figure 2a. These results clearly suggest that these polymerizations proceed in a (quasi) living manner and good linear relationships between the activity decreased with decreasing the Al/Mn ratios are summarized in Table 4. Plots of $n_{\text{w}}/n_{\text{m}}$ values and the polymer yields were thus obtained, as shown in Figure 2a.

In particular, the polymerizations at $-30 \, ^\circ\text{C}$ (run 9), although the catalytic activity thus obtained after 2 h.

Figure 1. Plots of $M_n$, $M_w/M_n$ vs. polymer yields (turnover numbers, TON) in (a) 1-decene (DC) and (b) 1-dodecene (DD) polymerization using Cp*TiMe$_2$(O-2,6-iPr$_2$C$_6$H$_3$) (I)–borate catalyst. Detailed data are shown in Tables 2 and 3.

2.2. Polymerization of 1-Tetradecene by Cp*TiMe$_2$(O-2,6-iPr$_2$C$_6$H$_3$) (I)–Borate Catalyst

Polymerizations of 1-tetradecene (TD) polymerizations using 1–[Ph$_3$C][B(C$_6$F$_5$)$_2$] (borate) catalyst were conducted in $n$-hexane in the presence of Al cocatalyst with different Al'Bu$_3$/Al(n-C$_8$H$_{17}$)$_3$ molar ratios at $-30 \, ^\circ\text{C}$. In order to avoid freezing of the reaction mixture at $-30 \, ^\circ\text{C}$ (due to melting temperature of TD, ca. $-12 \, ^\circ\text{C}$), rather diluted conditions compared to those for DC, DD polymerizations (TD 20 mL in $n$-hexane total 60 mL) were chosen. The results conducted under various Al'Bu$_3$/Al(n-C$_8$H$_{17}$)$_3$ molar ratios are summarized in Table 4. Plots of $M_n$, $M_w/M_n$ vs. polymer yields (turnover numbers, TON) in the polymerization are also shown in Figure 2a.

It turned out that, as observed in polymerizations of DC and DD, these polymerizations proceeded without significant decreases in the catalytic activities (based on polymer yields), whereas the observed activity decreased with decreasing the Al'Bu$_3$/Al(n-C$_8$H$_{17}$)$_3$ molar ratios. The $M_n$ values in the resultant polymers increased upon increasing the polymer yields (over time course) with consistent PDI values, and good linear relationships between the $M_n$ values and the polymer yields were thus obtained, as shown in Figure 2a. These results clearly suggest that these polymerizations proceed in a (quasi) living manner. It also turned out that the $M_n$ values after certain turnovers increased upon decreasing the Al'Bu$_3$/Al(n-C$_8$H$_{17}$)$_3$ molar ratios (eg. $M_n = 7.83 \times 10^5$ (14,400 turnovers, run 11) vs. $M_n = 7.34 \times 10^5$ (15,900 turnovers, run 12) vs. $M_n = 5.26 \times 10^5$ (14,300 turnovers, run 13)) along with decreasing the PDIs. The results thus suggest an increase of percentage of catalytically active species in situ upon increasing the ratio of Al(n-C$_8$H$_{17}$)$_3$, although we could not estimate the exact number of catalytically active species at this moment (because the $M_n$ values were estimated on gel-permeation chromatography (GPC) trace vs. polystyrene standards). Poly(TD) with ultrahigh molecular weight ($M_n = 1.02 \times 10^6$, $M_w/M_n = 1.38$) could be thus obtained in the polymerization using 1–borate-Al'Bu$_3$ catalyst (run 11, after 2 h).
Table 4. Polymerization of 1-tetradecene by Cp*TiMe$_2$(O-2,6-Pr$_2$C$_6$H$_3$) (I)–borate catalyst (−30 °C). *

| Run | Al(n-C$_5$H$_5$)$_2$/Al/BU$_3$/Ti | Time/min | Polymer Yield /mg | Activity $^d$ | TON $^e$ | $M_w/M_n$ $^f$ |
|-----|----------------------------------|----------|-------------------|----------------|---------|----------------|
| 11  | 1/500                            | 5        | 376               | 4510           | 2680    | 31.7           | 1.34           |
|     |                                  | 10       | 480               | 2880           | 3420    | 34.1           | 1.37           |
|     |                                  | 20       | 602               | 1810           | 4290    | 43.0           | 1.32           |
|     |                                  | 30       | 944               | 1890           | 6730    | 52.7           | 1.35           |
|     |                                  | 45       | 1034              | 1380           | 7370    | 65.1           | 1.41           |
|     |                                  | 60       | 1734              | 1730           | 12400   | 74.8           | 1.41           |
|     |                                  | 75       | 2016              | 1610           | 14400   | 78.3           | 1.38           |
|     |                                  | 90       | 2396              | 1600           | 17100   | 82.2           | 1.43           |
|     |                                  | 105      | 2778              | 1580           | 19800   | 90.0           | 1.41           |
|     |                                  | 120      | 3132              | 1570           | 22300   | 101.6          | 1.38           |
| 12  | 200/300                          | 20       | 202               | 610            | 1140    | 31.0           | 1.28           |
|     |                                  | 30       | 502               | 1000           | 3580    | 42.5           | 1.32           |
|     |                                  | 45       | 1000              | 1330           | 7130    | 53.5           | 1.32           |
|     |                                  | 60       | 1662              | 1660           | 11800   | 62.9           | 1.34           |
|     |                                  | 75       | 2232              | 1790           | 15900   | 73.4           | 1.28           |
|     |                                  | 90       | 2738              | 1850           | 19700   | 75.7           | 1.28           |
|     |                                  | 105      | 2980              | 1700           | 21200   | 82.5           | 1.31           |
|     |                                  | 120      | 3044              | 1520           | 21700   | 89.6           | 1.36           |
| 13  | 400/100                          | 45       | 458               | 920            | 3260    | 30.6           | 1.25           |
|     |                                  | 75       | 1464              | 1170           | 10400   | 40.5           | 1.20           |
|     |                                  | 90       | 1750              | 1170           | 12500   | 47.3           | 1.23           |
|     |                                  | 105      | 2000              | 1140           | 14300   | 52.6           | 1.21           |
|     |                                  | 120      | 2292              | 1500           | 16300   | 59.7           | 1.25           |

* Reaction conditions: Complex 1, 1.0 μmol, total volume of 1-tetradecene (20 mL) and n-hexane = 40 mL, [Ph$_6$C][BF$_4$]$_2$/Ti = 3.0 (molar ratio), I was pre-treated with 2.0 eq. of Al/BU$_3$ at −30 °C for 10 min. $^b$ Molar ratio of Al(n-C$_5$H$_5$)$_2$/Al/BU$_3$/Ti. $^c$ A prescribed amount (3.0 mL) of the reaction mixture was removed via syringe from the mixture, and the yields were based on obtained amount. $^d$ Activity in kg-polymer/mol-Ti h. $^e$ TON (turnovers) = molar amount of 1-decene consumed/mol-Ti. $^f$ GPC data in THF vs. polystyrene standards.

Figure 2b shows selected $^{13}$C NMR spectra (in CDCl$_3$ at 25 °C) for poly(DC) and poly(DD). It is clear that the resultant polymers do not have stereo-regularity (atactic polymers) [49], and as observed in the spectra in poly(1-hexene) [50], resonances ascribed to 2,1- or other insertion units could not be found. The results strongly suggest that these polymerizations proceeded with (in high certainty) 1,2-insertion manner.

Figure 2. (a) Plots of $M_w$, $M_w/M_n$ vs. polymer yields (turnover numbers, TON) in 1-tetradecene (TD) polymerization using Cp*TiMe$_2$(O-2,6-Pr$_2$C$_6$H$_3$) (I)–borate catalyst. Detailed data are shown in Table 4. (b) $^{13}$C NMR spectrum (in CDCl$_3$ at 25 °C) for poly(1-decene) (top, sample, run 1) and poly(1-dodecene) (bottom, sample, run 10).
3. Materials and Methods

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 toluene (Kanto Kagaku Co. Ltd., Tokyo, Japan) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the drybox, and was used without further purification. Reagent grades 1-decene (TCI Co., Ltd., Tokyo, Japan), 1-dodecene (TCI Co., Ltd.), 1-tetradecene (TCI Co., Ltd.) were stored in bottles in the drybox and were passed through an alumina short column prior to use. Syntheses of Cp*TiMe$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (I) was according to our previous report [50]. Ph$_3$CB(C$_6$F$_3$)$_4$ was purchased from Asahi Glass Co. Ltd., and was used as received in the drybox.

All $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV 500 spectrometer (500.13 MHz for $^1$H; 125.77 MHz for $^{13}$C), and all chemical shifts are given in ppm and are referred to SiMe$_4$. $^{13}$C NMR spectra for the resultant polymers were recorded with proton decoupling, and the pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was about 6000. The polymer samples for analysis were prepared by dissolving the polymers in CDCl$_3$ solution, and the spectra was measured at 25 °C. Molecular weights and the molecular weight distributions of the resultant polymers were measured by gel-permeation chromatography (GPC). HPLC grade THF was used for GPC and was degassed prior to use. GPC was performed at 40 °C on a Shimadzu SCL-10A using a RID-10A detector (Shimadzu Co. Ltd.) in THF (containing 0.03 wt. % of 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 diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from <10$^3$ to 2 × 10$^7$ MW) were calibrated versus polystyrene standard samples. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Typical polymerization procedures were as follows: 1-decene (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 °C. A toluene solution containing 1 (2.0 μmol/mL) [pre-treated with 2.0 eq. of Al$^i$Bu$_3$ at −30 °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$_3$)$_4$ (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 poured into $^i$PrOH (150 mL) containing HCl (10 mL). The resultant polymer was collected and was adequately washed with $^i$PrOH and then dried in vacuo.

4. Conclusions

We have shown that polymerizations of 1-decene (DC), 1-dodecene (DD), and 1-tetradecene (TD) using Cp*TiMe$_2$(O-2,6-$^i$Pr$_2$C$_6$H$_3$) (I)−[Ph$_3$C][B(C$_6$F$_3$)$_4$] (borate) catalyst proceeded with high catalytic activities, affording (ultra)high molecular weight polymers. The polymerizations of DC and DD, in n-hexane containing a mixture of Al$^i$Bu$_3$ and Al(n-C$_8$H$_{17}$)$_3$ at −30 °C, proceeded with high catalytic activities (4120−5860 kg-poly(DC)/mol-Ti-h) without catalyst deactivation, affording high molecular weight polymers ($M_n$ for poly(DC) = 7.04−7.82 × 10$^5$ after 20 min). The PDI ($M_w/M_n$) values were affected by the ratio of Al(n-C$_8$H$_{17}$)$_3$/Al$^i$Bu$_3$ as well as the polymerization temperature. Synthesis of high molecular weight poly(DC) with low PDI ($M_n$ = 5.26 × 10$^5$, $M_w/M_n$ = 1.16) could be attained at −50 °C. The TD polymerization using 1-borate−Al$^i$Bu$_3$ catalyst (conducted in n-hexane at −30 °C) also afforded ultrahigh molecular weight poly(TD) ($M_n$ = 1.02 × 10$^6$, $M_w/M_n$ = 1.38). The results presented here are rare demonstrations for successful synthesis of (ultra)high molecular weight bottlebrush poly(α-olefin)s with narrow molecular weight distributions by polymerization of higher α-olefins, which proceeded in a (quasi) living manner. The fact should be important for synthesis of new polyolefins as well as design of efficient molecular catalysts for olefin polymerization.
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**Sample Availability:** Samples of the compounds are available from the authors.