Synthesis of Ultrahigh Molecular Weight Polymers Containing Reactive Functionality with Low PDI by Polymerizations of Long-Chain $\alpha$-Olefins in the Presence of Their Nonconjugated Dienes by Cp*TiMe$_2$(O-2,6-\textit{i}Pr$_2$C$_6$H$_3$)–Borate Catalyst

Kotohiro Nomura*, Sarntamon Pengoubol and Wannida Apisuk

Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami Osawa, Hachioji, Tokyo 192-0397, Japan; sarntamon@gmail.com (S.P.); wannida.ppc@gmail.com (W.A.)
* Correspondence: ktnomura@tmu.ac.jp; Tel.: +81-42-6772547

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Abstract: Copolymerizations of 1-decene (DC) with 1,9-decadiene (DCD), 1-dodecene (DD) with 1,11-dodecadiene (DDD), and 1-tetradecene (TD) with 1,13-tetradecadiene (TDD), using Cp*TiMe$_2$(O-2,6-\textit{i}Pr$_2$C$_6$H$_3$) (1)–[Ph$_3$C][B(C$_6$F$_5$)$_4$] (borate) catalyst in the presence of Al$i$Bu$_3$/Al(\textit{n}-C$_8$H$_{17}$)$_3$ proceeded in a quasi-living manner in \textit{n}-hexane at $-30$ to $-50$ °C, affording ultrahigh molecular weight (UHMW) copolymers containing terminal olefinic double bonds in the side chain with rather low PDI ($M_w/M_n$) values. In the DC/DCD copolymerization, the resultant copolymer prepared at $-40$ °C possessed UHMW ($M_n = 1.40 \times 10^6$ after 45 min) with low PDI ($M_w/M_n = 1.39$); both the activity and the PDI value decreased at low polymerization temperature ($M_n = 5.38 \times 10^5$; $M_w/M_n = 1.18$, after 120 min at $-50$ °C). UHMW poly(TD-co-TDD) was also obtained in the copolymerization at $-30$ °C ($M_n = 9.12 \times 10^5$, $M_w/M_n = 1.51$, after 120 min), using this catalyst.

Keywords: polymerization; titanium complex; catalyst; $\alpha$-olefin; nonconjugated diene; half-titanocene; borate; bottlebrush polymer

1. Introduction

Transition metal catalyzed olefin polymerization is the core technology in the polyolefin industry, and the recent progress in the catalyst development provides new possibilities for the synthesis of new polymers [1–14]. Homopolymers of long-chain (higher) $\alpha$-olefins are branched macromolecules with a high graft density, and the polymers are thus recognized as the simplest bottlebrush polymers, with their backbone and side chains consisting of alkanes [15,16]. Amorphous poly($\alpha$-olefin)s are used in hot-melt applications due to their high melt–flow rate with low density, and the ultrahigh molecular weight (UHMW) polymers possess highly entangled bottlebrush architectures and are used as drag-reducing agents (DRAs) in pipeline transport methods for crude oil and petroleum products for improvement of piping system capacity [17–20]. Recent reports revealed their melt structure, linear rheology, and interchain friction mechanism, including effect of side-chain length toward their linear viscoelastic response and melt microstructure [15,16].

However, reports for synthesis of UHMW polymers by polymerization of higher $\alpha$-olefins (1-decene, 1-dodecene, 1-tetradecene, etc.) still have been limited [15,16,21,22], probably due to their preferred $\beta$-hydrogen elimination compared to the repeated insertion of monomer with a steric bulk (of alkane branching), as seen in ordinary metallocene catalysts yielding oligomers [21,23,24]. There are several examples for synthesis of (ultra)high molecular weight poly(1-hexene) [21,25–27] by using...
[2,2-(O-4-Me-6-i-Bu-C₆H₃)₂S]TiCl₂ (with water modified MMAO cocatalyst) [27,28], (C₃HMe₅)₂HCl₂ (under ultrahigh pressure) [25], titanium complexes with diamine bis(phenolate) ligands [26]. Synthesis of rather high molecular weights poly(α-olefin)s, mostly poly(1-hexene)s, using the other catalysts, have also been known [24,29–37]. We reported that Cp’*TiCl₂(O-2,6-i-Pr₂C₆H₃)–MAO catalyst afforded high molecular weight poly(α-olefin)s by polymerizations of 1-decene (DC), 1-dodecene (DD), 1-hexadecene, and 1-octadecene [21]. It was then revealed that polymerizations of DC, DD, and 1-tetradecene (TD) with 1,9-decadiene (DCD), DD with 1,11-dodecadiene (DDD), and TD with 1,13-tetradecadiene (TDD), was also demonstrated into poly(1-octene- (synthesis of copolymers containing terminal olefinic double bonds with uniform compositions), and (borate) catalyst and Al cocatalysts at −30 to −50 °C, affording UHMW polymers (e.g., poly(DC): \( M_n = 7.04 \times 10^5 \), \( M_w/M_n = 1.37 \); poly(TD): \( M_n = 1.02 \times 10^6 \), \( M_w/M_n = 1.38 \)); the polymerizations proceeded with rather high catalytic activities (activity at −30 °C: 4120–5860 kg-poly(DC)/mol-Ti·h) [22]. The PDI (\( M_w/M_n \)) values decreased (accompanied with decrease in the catalytic activity) with an increase in the Al(n-C₈H₁₇)/Al’Bu₃ molar ratio and/or by decreasing the polymerization temperature (−40 and −50 °C). Moreover, it was demonstrated that 1,7-octadiene (OD) polymerization by Cp’*TiCl₂(O-2,6-i-Pr₂C₆H₃)–MAO catalyst afforded polymers containing terminal olefinic double bonds in the side chain without cyclization, cross-linking (Scheme 1). An introduction of polar functionality and the subsequent grafting (by living ring opening polymerization of \( \varepsilon \)-caprolactone) was also demonstrated into poly(1-octene-co-OD)s under mild conditions [38]. The method introduced a possibility for synthesis of functionalized polyolefins by incorporation of reactive functionalities, as demonstrated in the ethylene/1-octene or ethylene/styrene copolymerization in the presence of OD (synthesis of copolymers containing terminal olefinic double bonds with uniform compositions), and subsequent chemical modification under mild conditions (Scheme 1) [39–45].

Scheme 1. Polymerization of 1,7-octadiene (OD) and ethylene copolymerizations in the presence of OD, using Cp’*TiCl₂(O-2,6-i-Pr₂C₆H₃) (Cp’* = Cp’, 1,2,4-Me₃C₅H₂)–MAO catalysts [38,44].

Since, as described above, UHMW polymers are simple bottlebrush polymers prepared by polymerization of these higher \( \alpha \)-olefins via the grafting-through approach, we thus have an interest in synthesis of the UHMW polymers containing terminal olefinic double bond by copolymerization of DC with 1,9-decadiene (DCD), DD with 1,11-dodecadiene (DDD), and TD with 1,13-tetradecadiene (TDD), using 1–borate catalyst [46]. We thus, herein, wish to introduce our explored results for synthesis of

![Diagram](image-url)
new bottlebrush polymers with low PDIs containing reactive functionality in the side chain by 1–borate
catalyst in the presence of Al cocatalyst (Scheme 2).

\[\text{Scheme 2. Copolymerization of 1-decene (DC), 1-dodecene (DD), 1-tetradecene (TD) with 1,9-decadiene}
-(DCD), 1,11-dodecadiene (DDD), and with 1,13-tetradecadiene (TDD), using Cp*TiMe2(O-2,6-\text{Pr3C6}H3)
-1\text{–}[\text{Ph3C}\] [\text{B(C6F5)4}] catalyst in the presence of Al cocatalyst.\]

2. Materials and Methods

All experiments were conducted in a dry box, under a nitrogen atmosphere, unless otherwise
specified. All chemicals of reagent grade were purified by the standard purification protocols.
The \text{n}-hexane or toluene (anhydrous grade, Kanto Kagaku Co. Ltd., Tokyo, Japan) was stored in a
bottle containing molecular sieves (mixture of 3A and 4A 1/16, and 13X) in the dry box, and was used
without further purification. The 1-Decene, 1-dodecene, 1-tetradecene, 1,9-decadiene, 1.11-dodecadiene,
and 1,13-tetradecadiene (reagent grades, TCI Co., Ltd., Tokyo, Japan) were stored in bottles, in the
dry box, and were passed through an alumina short column prior to use. Cp*TiMe2(O-2,6-\text{Pr2C6}H3)
(1) was prepared according to our previous report [46], and [\text{Ph3C}\] [\text{B(C6F5)4}] (Asahi
Glass Co. Ltd., Tokyo, Japan) was used as received.

All \text{1H} and \text{13C} NMR spectra were recorded on a Bruker AV 500 spectrometer (500.13 MHz for \text{1H};
125.77 MHz for \text{13C}, Bruker Japan K.K., Tokyo, Japan) at 25 °C, and all chemical shifts in the spectra
were recorded in ppm (reference SiMe4). Samples for the measurement were prepared by dissolving
the polymers in 1,1,2,2-tetrachloroethane-\text{d}_2 solution. Gel-permeation chromatography (GPC) were
conducted for analysis of molecular weights (based on the calibration with standard polystyrene
samples as the standard procedure) and the distributions. HPLC grade THF (degassed prior to use)
was used for GPC analysis, and the GPC analysis was performed at 40 °C on a Shimadzu SCL-10A,
using a RID-10A detector (Shimadzu Co., Ltd.), using degassed prior to use in THF (containing 0.03
wt.% of 2,6-di-\text{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 <10^2 to 2 × 10^7 MW).

Typical polymerization procedures were as follows: in the dry box, 1-decene (30.0 mL),
1,9-decadiene (0.5 mL), \text{n}-hexane (30.0 mL), and Al′Bu3 and Al(\text{n-C8H17})3 (prescribed amount) were
added into a 100 mL round-bottom flask, which was connected to three-way valves. The flask
was taken out from the dry box, and a toluene solution containing 1 (2.0 \text{µmol/mL}), which was pretreated
with 2.0 eq. of Al′Bu3 at −30 °C, was then added into the mixture precooled at −30 °C under N2
atmosphere. The polymerization was started by the addition of a prescribed amount of toluene solution.
containing [Ph₃C][B(C₆F₅)₄] (2.0 μmol/mL). A certain amount (3.0 mL) of the reaction solution was taken out via a syringe from the reaction mixture, to monitor the time course; the sample solution was then quickly poured into 1PrOH (150 mL) containing HCl (10 mL). The resultant polymer as precipitants was collected, adequately washed with 1PrOH, and then dried in vacuo, for further analysis.

3. Results and Discussion

On the basis of our previous reports for polymerizations of 1-decene (DC), 1-dodecene (DD), and 1-tetradecene (TD) [22], and of 1,7-octadiene [38], Cp*TiMe₂(OAr) (1, Ar = 2,6-iPr₂C₆H₃) was chosen as the catalyst precursor, and [Ph₃C][B(C₆F₅)₄] (borate) was chosen as the cocatalyst in the presence of AlBu₃ and Al(n-C₆H₄C)₃ [22,29]. Copolymerizations of DC with 1,9-decadiene (DCD) were conducted in n-hexane at −30 to −50 °C, in the presence of Al cocatalyst [Al(n-C₆H₄C)₃]/AlBu₃/Ti = 400/100/1.0 (at −30 and −40 °C) or 300/200/1.0 (at −50 °C), molar ratio]; the ratios were used on the basis of the homo polymerization results [22]. As reported previously [22,29,47–49], use of Al(n-C₆H₄C)₃, weak reagent for alkylation, and/or chain transfer was effective to proceed without catalyst deactivation, probably not only due to a role as a scavenger, but also due to the fact that the Al alkyl would contribute to the stabilization of the catalytically active species by preventing the decomposition from further reaction with borate [50–52]. The results in the DC/DCD copolymerization are summarized in Table 1.

Table 1. Copolymerization of 1-decene (DC) with 1,9-decadiene (DCD) by Cp*TiMe₂(O-2,6-iPr₂C₆H₃) (1)–[Ph₃C][B(C₆F₅)₄] (borate) catalyst e.

| Run | Al(n-C₆H₄C)₃/AlBu₃/Ti b | Temp. /°C | Time /min | Yield /mg | Activity e | TON e | Mn f /× 10⁻⁴ | Mw/Mn f | DCD g /mol% | Conv. h /% |
|-----|--------------------------|-----------|-----------|-----------|-----------|-------|------------|--------|-----------|---------|
| 1   | 400/100/1.0              | −30       | 5         | 652       | 7820      | 4650  | 32.4       | 1.43   | 8.9       | 16      |
|     |                          |           | 10        | 796       | 4780      | 5680  | 45.3       | 1.47   | 8.4       | 17      |
|     |                          |           | 15        | 864       | 3460      | 6160  | 52.4       | 1.45   | 8.2       | 19      |
|     |                          |           | 20        | 918       | 2750      | 6550  | 75.3       | 1.43   | 8.0       | 19      |
| 2   | 400/100/1.0              | −40       | 10        | 246       | 1480      | 1760  | 55.1       | 1.28   | 9.1       | 13      |
|     |                          |           | 20        | 582       | 1750      | 4150  | 88.7       | 1.32   | 8.8       | 13      |
|     |                          |           | 30        | 966       | 1930      | 6900  | 100.7      | 1.40   | 7.8       | 19      |
|     |                          |           | 45        | 1400      | 1870      | 9990  | 140.1      | 1.39   | 5.6       | 20      |
| 3   | 300/200/1.0              | −50       | 60        | 396       | 400       | 2830  | 32.4       | 1.19   | 9.8       | 10      |
|     |                          |           | 75        | 512       | 410       | 3660  | 38.9       | 1.20   | 9.2       | 12      |
|     |                          |           | 90        | 574       | 380       | 4100  | 46.8       | 1.14   | 8.3       | 13      |
|     |                          |           | 120       | 742       | 370       | 5300  | 53.8       | 1.18   | 7.4       | 15      |

a Conditions: 1 1.0 μmol, 1-decene 30.0 mL, 1,9-decadiene 0.5 mL, n-hexane 30.0 mL, AlBu₃/Al(n-C₆H₄C)₃/[Ph₃C][B(C₆F₅)₄]/[borate] = 100/400/30/1.0 molar ratio (200/300/1.0 at −50 °C), 1 was pretreated with 2.0 equiv of AlBu₃ at −30 °C for 10 min before addition into the mixture. b Molar ratio. c A prescribed amount (3.0 mL) of the solution was removed via syringe from the reaction mixture, and the yields were based on obtained amount. d Activity in kg-polymer/mol-Ti·h. e TON (turnovers) = monomer consumed (mol/mol-Ti). f GPC data in THF vs polystyrene standards. g Estimated by 1H NMR spectra. h Estimated ((DCD consumed/DCD charged) × 100) (conv. = conversion).

As observed in the polymerization of DC, the copolymerization of DC with DCD proceeded with high catalytic activities (2750–7820 kg-polymer/mol-Ti·h within 20 min), even at −30 °C, affording high molecular weight polymers with rather narrow molecular weight distributions (run 1, Mₙ = 3.24 × 10⁵–7.53 × 10⁵, Mₘ/Mₙ = 1.43–1.47). The Mₙ value increased over the time course, without significant changes in the PDI values. It turned out that the PDI values decreased at a low temperature, with a decrease in the catalytic activity; the resultant copolymer prepared at −40 °C possessed UHMW (run 2, Mₙ = 1.40 × 10⁶ after 45 min), with low PDI (Mₘ/Mₙ = 1.39), and the PDI value became low when the copolymerization was conducted at −50 °C (run 3, Mₙ = 5.38 × 10⁵, Mₘ/Mₙ = 1.18, after 120 min at −50 °C). As shown in Figure 1a, 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, as reported in the polymerization of DC [22]. As shown in Figure 2b (shown below), the resultant copolymers contain terminal olefinic double bonds by incorporation of
DCD. The content of DCD estimated by $^1$H NMR spectra slightly decreased gradually due to rather high consumption of DCD (rather high conversion of DCD and changes in the DCD concentration in the reaction solution) during the polymerization time course. This would suggest the possibility of (rather) gradient composition, although we do not have the firm elucidation at this moment.

![Figure 1](image1.png)

Figure 1. Plots of $M_n$, $M_w/M_n$ vs polymer yields (turnover numbers, TON) in copolymerization of (a) 1-decene (DC) with 1,9-decadiene (DCD) and (b) 1-dodecene (DD) with 1,11-dodecadiene (DDD), using Cp*TiMe$_2$(O-2,6-$^t$Bu$_3$/C$_8$H$_17$)/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (borate) catalyst. (b) The results in DC/DCD copolymerization at $-50 \, ^\circ\text{C}$ were plotted for comparison. Detailed data are shown in Tables 1 and 2.

![Figure 2](image2.png)

Figure 2. (a) Plots of $M_n$, $M_w/M_n$ vs. polymer yields (turnover numbers, TON) in copolymerization of 1-tetradecene (TD) with 1,13-tetradecadiene (TDD), using Cp*TiMe$_2$(O-2,6-$^t$Pr$_2$C$_6$H$_3$) (I)–[Ph$_3$C][B(C$_6$F$_5$)$_4$] (borate) catalyst. (b) Selected $^1$H NMR spectra (in 1,1,2,2-tetrachloroethane-$d_2$) for (top) poly(DC-co-DCD) (after five min) and (bottom) poly(TD-co-TDD) (after 60 min). The resonance at 5.8 ppm would be overlapped with the satellite of the resonance at 6.0 ppm.

(a) 1-decene (DC) with 1,9-decadiene (DCD) and (b) 1-dodecene (DD) with 1,11-dodecadiene (DDD), using Cp*TiMe$_2$(O-2,6-$^t$Bu$_3$/C$_8$H$_17$) (I)–[Ph$_3$C][B(C$_6$F$_5$)$_4$] (borate) catalyst. (b) The results in DC/DCD copolymerization at $-50 \, ^\circ\text{C}$ were plotted for comparison. Detailed data are shown in Tables 1 and 2.
Table 2 summarizes results in the DD/DDD copolymerization conducted at −40 and −50 °C. As observed in the DC/DCD copolymerization, the $M_n$ value increased over the time course, without significant changes in the PDI values, and the PDI became low at −50 °C (run 5). The resultant copolymer prepared at −50 °C possessed high molecular weight with low PDI value (run 5, $M_n = 5.46 \times 10^5$, $M_w/M_n = 1.28$ after 120 min). As shown in Figure 1b, a linear relationship between the $M_n$ values and the polymer yields (turnover numbers, TON) was observed in the polymerization at −50 °C, suggesting a possibility of a quasi-living manner, as observed in the DC/DCD copolymerization.

Table 2. Copolymerization of 1-dodecene (DD) with 1,11-dodecadiene (DDD) by Cp*TiMe$_2$(O-2,6-Pr$_2$C$_6$H$_3$) (1)–[Ph$_3$C][B(C$_6$F$_5$)$_3$L] (borate) catalyst $^a$.

| Run | $\text{Al(n-C}_4\text{H}_{17})_2$/Al'Bu$_3$/Ti $^b$ | Temp. $^c$ /°C | Time/min | Yield $^c$ /mg | Activity $^d$ | TON $^c$ | $M_n/f$ $\times 10^{-4}$ | $M_w/M_n/f$ | DDD $^f$/mol% | Conv. $^h$ /% |
|-----|---------------------------------|-----------------|-----------|----------------|--------------|---------|----------------|--------------|---------------|-------------|
| 4   | 400/100/1.0                     | −40             | 20        | 828            | 2480         | 5900    | 42.6           | 1.34         | 7.9           | 17          |
|     |                                 |                 | 30        | 897            | 1790         | 6390    | 48.3           | 1.39         | 7.7           | 18          |
|     |                                 |                 | 40        | 932            | 1400         | 6640    | 51.4           | 1.38         | 6.6           | 18          |
| 5   | 250/250/1.0                     | −50             | 75        | 402            | 320          | 2390    | 33.5           | 1.25         | 7.9           | 17          |
|     |                                 |                 | 90        | 492            | 330          | 2920    | 42.6           | 1.25         | 7.7           | 10          |
|     |                                 |                 | 105       | 582            | 330          | 3460    | 49.7           | 1.24         | 7.5           | 11          |
|     |                                 |                 | 120       | 628            | 310          | 3730    | 54.6           | 1.28         | 7.5           | 12          |

$^a$ Conditions: 1 1.0 μmol, 1-dodecene 25.0 mL, 1,11-dodecadiene 0.5 mL, n-hexane 35.0 mL, Al'Bu$_3$/Al(n-C$_4$H$_7$)$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_3$L]/Ti = 100/400/3.0/1.0 molar ratio (250/250/1.0 at −50 °C), 1 was pretreated with 2.0 equiv of Al'Bu$_3$ at −30 °C for 10 min before addition into the mixture. $^b$ Molar ratio. $^c$ A prescribed amount (3.0 mL) of the solution was removed via syringe from the reaction mixture, and the yields were based on obtained amount. $^d$ Activity in kg-polymer/mol-Ti-h. $^e$ TON (turnovers) = monomer consumed (mol)/mol-Ti. $^f$ GPC data in THF vs polystyrene standards. $^h$ Estimated by $^1$H NMR spectra. $^i$ Estimated (DDD consumed/DDD charged) × 100).

Table 3 summarizes results in TD/TDD copolymerization conducted at −30 °C. Due to a difficulty of polymerization at low temperature (the n-hexane solution would be heterogeneous due to the freezing of TD), the polymerization could be conducted only at −30 °C, under rather diluted conditions. As observed in Tables 1 and 2, the $M_n$ value increased over the time course, without significant changes in the PDI values. The resultant copolymer possessed high molecular weight, with unimodal molecular weight distribution (run 6, $M_n = 9.12 \times 10^5$, $M_w/M_n = 1.51$ after 120 min). As also shown in Figure 2a, a linear relationship between the $M_n$ values and the polymer yields (turnover numbers, TON) was clearly observed. The results thus also suggest that the TD/TDD copolymerization proceeded in a quasi-living manner.

Table 3. Copolymerization of 1-tetradecene (TD) with 1,13-tetradiodecenedi (TDD) by Cp*TiMe$_2$(O-2,6-Pr$_2$C$_6$H$_3$) (1)–[Ph$_3$C][B(C$_6$F$_5$)$_3$L] (borate) catalyst (−30 °C) $^i$.

| Run | Time/min | Yield $^b$/mg | Activity $^c$ | TON $^d$ | $M_n/e$ $\times 10^{-4}$ | $M_w/M_n/e$ | TDD $^f$/mol% |
|-----|----------|---------------|--------------|----------|----------------|--------------|---------------|
| 6   | 10       | 184           | 1100         | 927      | 48.7           | 1.26         |
| 30  |          | 516           | 1030         | 2600     | 52.8           | 1.38         | 4.5           |
| 40  |          | 830           | 1110         | 4180     | 55.3           | 1.36         | 4.0           |
| 60  |          | 1150          | 1150         | 5790     | 64.8           | 1.41         | 3.7           |
| 75  |          | 1510          | 1210         | 7610     | 72.9           | 1.43         | 3.5           |
| 90  |          | 1872          | 1250         | 9440     | 80.4           | 1.48         | 3.2           |
| 120 |          | 2432          | 12300        | 91.2     | 1.51           |              |               |

$^i$ Conditions: 1 1.0 μmol, 1-tetradecene 20.0 mL, 1,13-tetradiodecenedi 1.0 mL, n-hexane 40.0 mL, Al'Bu$_3$/Al(n-C$_4$H$_7$)$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_3$L]/Ti = 100/400/3.0/1.0, molar ratio, 1 was pretreated with 2.0 equiv of Al'Bu$_3$ at −30 °C for 10 min before addition into the mixture. $^d$ 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. $^e$ Activity in kg-polymer/mol-Ti-h. $^d$ TON (turnovers) = monomer consumed (mol)/mol-Ti. $^g$ GPC data in THF vs polystyrene standards. $^h$ Estimated by $^1$H NMR spectra.
As shown in Figure 2b, the resultant polymers possessed a terminal olefinic double bond, as observed in poly(1-octene-co-1,7-octadiene) and poly(ethylene-co-1-octene-co-1,7-octadiene) [38], as well as in poly(ethylene-co-styrene-co-1,7-octadiene) [44] prepared by Cp*TiCl2(O-2,6-iPr2C6H3)–MAO catalyst, and no resonances ascribed to protons in the internal olefins were observed (additional 1H NMR spectra are shown in the Supplementary Materials) [53]. The resultant polymers are highly soluble in toluene, THF, chloroform, dichloromethane, etc., without any difficulties (as seen in poly(1,5-hexadiene) containing partial cross-linking prepared by Cp2ZrCl2-MAO catalysts even under diluted conditions [54]). The results thus suggest that the resultant polymers were poly(DC-co-DCD)s and poly(TD-co-TDD)s containing terminal olefins in the side chain, as expected on the basis of our previous results [22,38].

4. Conclusions

We have shown that synthesis of ultrahigh molecular weight (UHMW) highly branched (bottlebrush) polymers that contain terminal olefinic double bonds in the side chain with rather low PDI (Mw/Mn) values has been attained by polymerization of long-chain (higher) α-olefins (1-decene (DC), 1-dodecene (DD), and 1-tetradecene (TD)) in the presence of corresponding nonconjugated dienes (1,9-decadiene (DCD), 1,11-dodecadiene (DDD), and 1,13-tetradecadiene (TDD), respectively), using Cp*TiMe2(O-2,6-iPr2C6H3) (1)–[Ph2B(OTf)2]4 (borate) as the catalyst, in the presence of AlB12H12/Al(r-C3H7)3. These polymerizations proceeded in a quasi-living manner in n-hexane at −30 to −50 °C, and linear relationships between the Mn values and the polymer yields were observed in all cases, without significant changes in the PDI (Mw/Mn) values. The resultant poly(DC-co-DCD) prepared at −40 °C possessed UHMW (Mn = 1.40 × 106 after 45 min) with low PDI (Mw/Mn = 1.39), and UHMW poly(TD-co-TDD) was also obtained in the TD/TDD copolymerization at −30 °C (Mn = 9.12 × 105, Mw/Mn = 1.51, after 120 min). As described in the introduction, these polymers should possess highly branched bottlebrush architectures, and the present results strongly suggest a possibility of introduction of reactive functionality (terminal olefins) into the side chain (outside of the cylindrical structure). Moreover, as described in the introductory, as well as reported previously [38], an introduction of hydroxy group by treatment of the terminal olefinic double bonds with BBN and the subsequent grafting (by living ring opening polymerization of ε-caprolactone) would be possible. One issue we have not yet clarified clearly is the effect of diene monomers on the monomer reactivity ratio. We thus believe that the results could demonstrate providing new materials (functionalized polyolefin bottlebrush) based on polyolefins, and more details including further analysis and applications will be introduced in the future.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4360/12/1/3/s1. Figure S1: 1H NMR spectrum (in 1,1,2,2-tetrachloroethane-d2 at 25 °C) for poly(1-decene-co-1,9-decadiene) (run 1, after 5 min, 1,9-decadiene 8.9 mol%), Figure S2: 1H NMR spectrum (in 1,1,2,2-tetrachloroethane-d2 at 25 °C) for poly(1-decene-co-1,9-decadiene) (run 2, after 10 min, 1,9-decadiene 9.1 mol%), Figure S3: 1H NMR spectrum (in 1,1,2,2-tetrachloroethane-d2 at 25 °C) for poly(1-decene-co-1,11-decadiene) (run 4, after 30 min, 1,11-decadiene 7.7 mol%), Figure S4: 1H NMR spectrum (in 1,1,2,2-tetrachloroethane-d2 at 25 °C) for poly(1-decene-co-1,11-decadiene) (run 5, after 120 min, 1,11-decadiene 7.5 mol%), Figure S5: 1H NMR spectrum (in 1,1,2,2-tetrachloroethane-d2 at 25 °C) for poly(1-tetradecene-co-1,13-tetradecadiene) (run 6, after 30 min, 1,13-tetradecadiene 4.5 mol%), Figure S6: 1H NMR spectrum (in 1,1,2,2-tetrachloroethane-d2 at 25 °C) for poly(1-tetradecene-co-1,13-tetradecadiene) (run 6, after 60 min, 1,13-tetradecadiene 3.7 mol%).

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