

Article

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

Received: 14 November 2019; Accepted: 16 December 2019; Published: 18 December 2019



**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  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (1)– $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (borate) catalyst in the presence of  $\text{Al}^i\text{Bu}_3/\text{Al}(n\text{-C}_8\text{H}_{17})_3$  proceeded in a quasi-living manner in *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

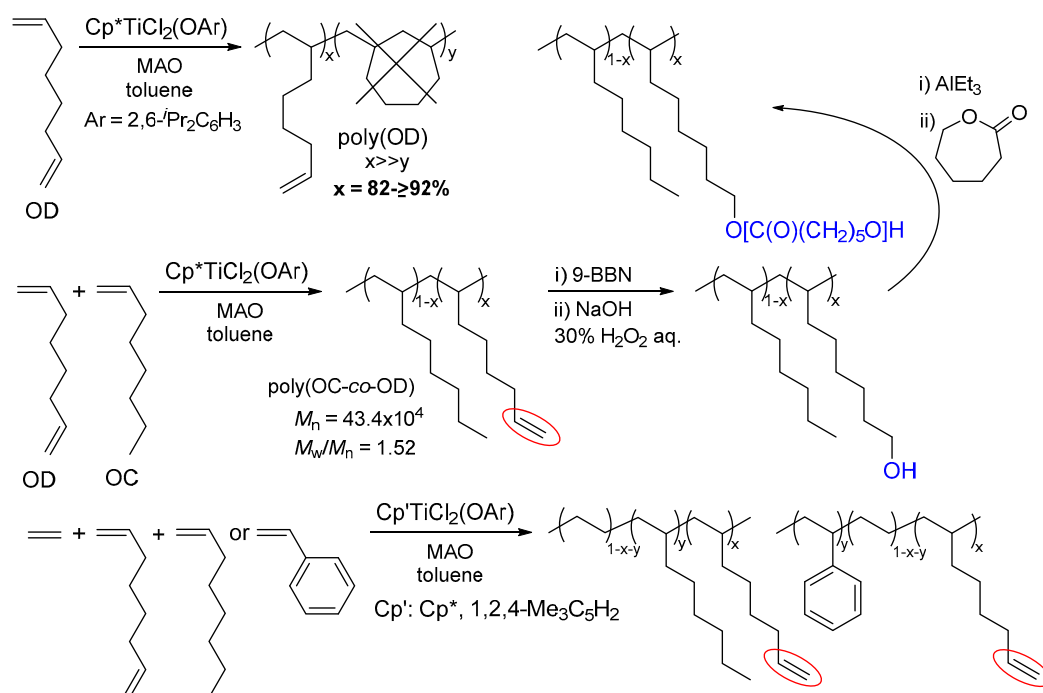
## 1. Introduction

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)s [21,25–27] by using

[2,2-(O-4-Me-6-*t*-Bu-C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>S]TiCl<sub>2</sub> (with water modified MMAO cocatalyst) [27,28], (C<sub>5</sub>HMe<sub>4</sub>)<sub>2</sub>HfCl<sub>2</sub> (under ultrahigh pressure) [25], titanium complexes with diamine bis(phenolate) ligands [26]. Synthesis of rather high molecular weights poly( $\alpha$ -olefin)s, mostly poly(1-hexene)s, using the other catalysts, have also been known [24,29–37].

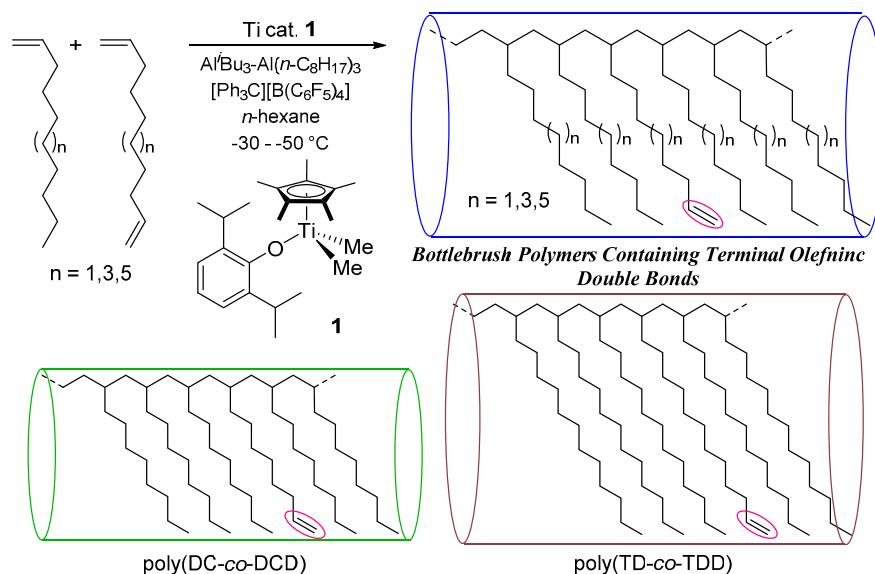
We reported that Cp\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-MAO catalyst afforded high molecular weight poly( $\alpha$ -olefin)s by polymerizations of 1-decene (DC), 1-dodecene (DD), 1-hexadecene, and 1-octadecene [21]. It was then revealed that polymerizations of DC, DD, and 1-tetradecene (TD) proceeded in a quasi-living manner in the presence of Cp\*TiMe<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1)-[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (borate) catalyst and Al cocatalysts at -30 to -50 °C, affording UHMW polymers (e.g., poly(DC): M<sub>n</sub> = 7.04 × 10<sup>5</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.37; poly(TD): M<sub>n</sub> = 1.02 × 10<sup>6</sup>, M<sub>w</sub>/M<sub>n</sub> = 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<sub>w</sub>/M<sub>n</sub>) values decreased (accompanied with decrease in the catalytic activity) with an increase in the Al(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>/Al<sup>*i*</sup>Bu<sub>3</sub> 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\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-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  $\epsilon$ -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\*TiCl<sub>2</sub>(O-2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (Cp\* = Cp\*, 1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)-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

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).



**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  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (**1**)- $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  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 *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.  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (**1**) was prepared according to our previous report [46], and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (Asahi Glass Co. Ltd., Tokyo, Japan) was used as received.

All  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV 500 spectrometer (500.13 MHz for  $^1\text{H}$ ; 125.77 MHz for  $^{13}\text{C}$ , Bruker Japan K.K., Tokyo, Japan) at 25 °C, and all chemical shifts in the spectra were recorded in ppm (reference  $\text{SiMe}_4$ ). Samples for the measurement were prepared by dissolving the polymers in 1,1,2,2-tetrachloroethane- $d_2$  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-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804, and 802, 30 cm  $\times$  8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from  $<10^2$  to  $2 \times 10^7$  MW).

Typical polymerization procedures were as follows: in the dry box, 1-decene (30.0 mL), 1,9-decadiene (0.5 mL), *n*-hexane (30.0 mL), and  $\text{Al}^i\text{Bu}_3$  and  $\text{Al}(n\text{-C}_8\text{H}_{17})_3$  (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  $\mu\text{mol/mL}$ ), which was pretreated with 2.0 eq. of  $\text{Al}^i\text{Bu}_3$  at  $-30$  °C, was then added into the mixture precooled at  $-30$  °C under  $\text{N}_2$  atmosphere. The polymerization was started by the addition of a prescribed amount of toluene solution

containing  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  ( $2.0 \mu\text{mol}/\text{mL}$ ). A certain amount ( $3.0 \text{ mL}$ ) 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  $i\text{PrOH}$  ( $150 \text{ mL}$ ) containing  $\text{HCl}$  ( $10 \text{ mL}$ ). The resultant polymer as precipitates was collected, adequately washed with  $i\text{PrOH}$ , 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],  $\text{Cp}^*\text{TiMe}_2(\text{OAr})$  (**1**,  $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ) was chosen as the catalyst precursor, and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (borate) was chosen as the cocatalyst in the presence of  $\text{Al}^i\text{Bu}_3$  and  $\text{Al}(n\text{-C}_8\text{H}_{17})_3$  [22,29]. Copolymerizations of DC with 1,9-decadiene (DCD) were conducted in  $n$ -hexane at  $-30$  to  $-50 \text{ }^\circ\text{C}$ , in the presence of Al cocatalyst  $[\text{Al}(n\text{-C}_8\text{H}_{17})_3]/\text{Al}^i\text{Bu}_3/\text{Ti} = 400/100/1.0$  (at  $-30$  and  $-40 \text{ }^\circ\text{C}$ ) or  $300/200/1.0$  (at  $-50 \text{ }^\circ\text{C}$ ), molar ratio]; the ratios were used on the basis of the homo polymerization results [22]. As reported previously [22,29,47–49], use of  $\text{Al}(n\text{-C}_8\text{H}_{17})_3$ , 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.

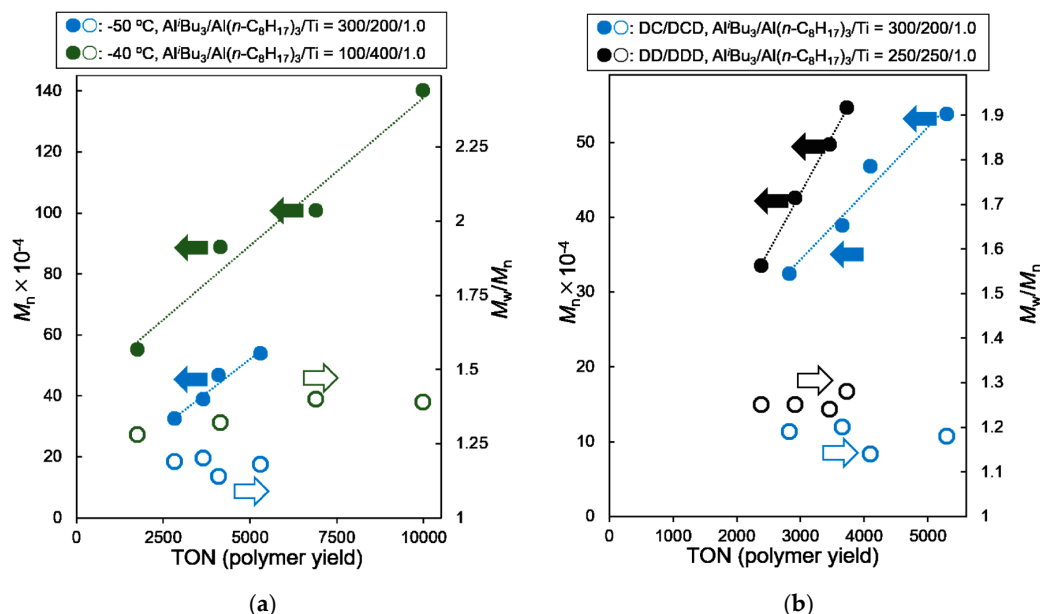
**Table 1.** Copolymerization of 1-decene (DC) with 1,9-decadiene (DCD) by  $\text{Cp}^*\text{TiMe}_2(\text{O-}2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (**1**)– $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (borate) catalyst <sup>a</sup>.

Run	$\text{Al}(n\text{-C}_8\text{H}_{17})_3/\text{Al}^i\text{Bu}_3/\text{Ti}$ <sup>b</sup>	Temp. <sup>c</sup> / $^\circ\text{C}$	Time /min	Yield <sup>c</sup> /mg	Activity <sup>d</sup>	TON <sup>e</sup>	$M_n$ <sup>f</sup> $\times 10^{-4}$	$M_w/M_n$ <sup>f</sup>	DCD <sup>g</sup> /mol%	Conv. <sup>h</sup> /%
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	6
			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

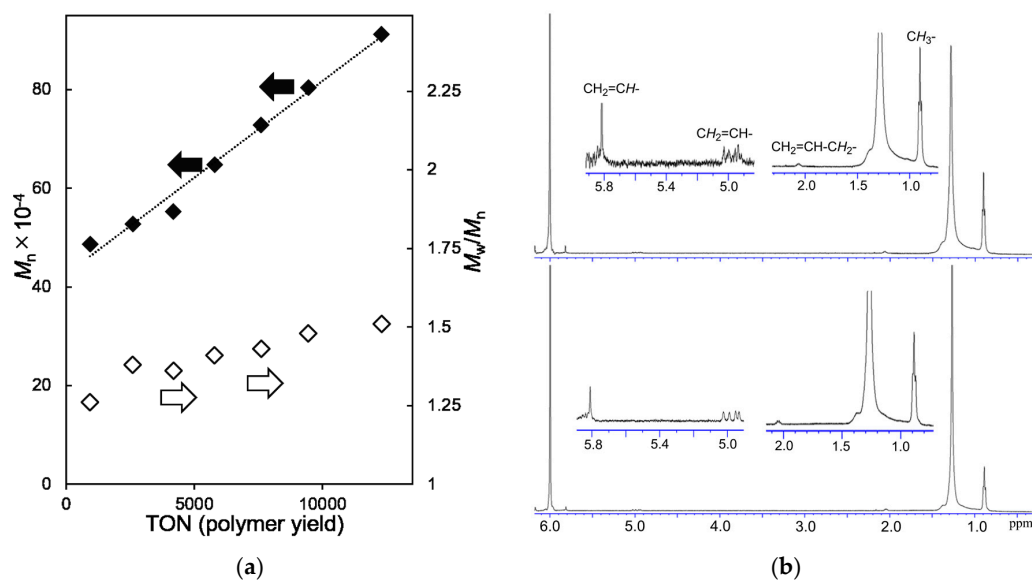
<sup>a</sup> Conditions: **1**  $1.0 \mu\text{mol}$ , 1-decene  $30.0 \text{ mL}$ , 1,9-decadiene  $0.5 \text{ mL}$ ,  $n$ -hexane  $30.0 \text{ mL}$ ,  $\text{Al}^i\text{Bu}_3/\text{Al}(n\text{-C}_8\text{H}_{17})_3/[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Ti} = 100/400/3.0/1.0$  molar ratio ( $200/300/1.0$  at  $-50 \text{ }^\circ\text{C}$ ), **1** was pretreated with  $2.0$  equiv of  $\text{Al}^i\text{Bu}_3$  at  $-30 \text{ }^\circ\text{C}$  for  $10 \text{ min}$  before addition into the mixture. <sup>b</sup> Molar ratio. <sup>c</sup> A prescribed amount ( $3.0 \text{ mL}$ ) of the solution was removed via syringe from the reaction mixture, and the yields were based on obtained amount. <sup>d</sup> Activity in  $\text{kg-polymer}/\text{mol-Ti}\cdot\text{h}$ . <sup>e</sup> TON (turnovers) = monomer consumed (mol)/mol-Ti. <sup>f</sup> GPC data in THF vs polystyrene standards. <sup>g</sup> Estimated by  $^1\text{H NMR}$  spectra. <sup>h</sup> Estimated ((DCD consumed/DCD charged)  $\times 100$ ) (conv. = conversion).

As observed in the polymerization of DC, the copolymerization of DC with DCD proceeded with high catalytic activities ( $2750\text{--}7820 \text{ kg-polymer}/\text{mol-Ti}\cdot\text{h}$  within  $20 \text{ min}$ ), even at  $-30 \text{ }^\circ\text{C}$ , affording high molecular weight polymers with rather narrow molecular weight distributions (run 1,  $M_n = 3.24 \times 10^5\text{--}7.53 \times 10^5$ ,  $M_w/M_n = 1.43\text{--}1.47$ ). The  $M_n$  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  $-40 \text{ }^\circ\text{C}$  possessed UHMW (run 2,  $M_n = 1.40 \times 10^6$  after  $45 \text{ min}$ ), with low PDI ( $M_w/M_n = 1.39$ ), and the PDI value became low when the copolymerization was conducted at  $-50 \text{ }^\circ\text{C}$  (run 3,  $M_n = 5.38 \times 10^5$ ,  $M_w/M_n = 1.18$ , after  $120 \text{ min}$  at  $-50 \text{ }^\circ\text{C}$ ). As shown in Figure 1a, linear relationships between the  $M_n$  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  $^1\text{H}$  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.** 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  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (**1**)– $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (borate) catalyst. (b) The results in DC/DCD copolymerization at  $-50\text{ }^\circ\text{C}$  were plotted for comparison. Detailed data are shown in Tables 1 and 2.



**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  $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$  (**1**)–borate catalyst. (b) Selected  $^1\text{H}$  NMR spectra (in 1,1,2,2-tetrachloroethane- $d_2$  at  $25\text{ }^\circ\text{C}$ ) 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.

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- $i$ -Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1)-[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (borate) catalyst <sup>a</sup>.

Run	Al( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub> / Al <sup><i>i</i></sup> Bu <sub>3</sub> /Ti <sup>b</sup>	Temp. /°C	Time /min	Yield <sup>c</sup> /mg	Activity <sup>d</sup>	TON <sup>e</sup>	$M_n$ <sup>f</sup> $\times 10^{-4}$	$M_w/M_n$ <sup>f</sup>	DDD <sup>g</sup> /mol%	Conv. <sup>h</sup> /%
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		
			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

<sup>a</sup> Conditions: **1** 1.0 μmol, 1-dodecene 25.0 mL, 1,11-dodecadiene 0.5 mL, *n*-hexane 35.0 mL, Al<sup>*i*</sup>Bu<sub>3</sub>/Al(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/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<sup>*i*</sup>Bu<sub>3</sub> at  $-30$  °C for 10 min before addition into the mixture. <sup>b</sup> Molar ratio. <sup>c</sup> 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. <sup>d</sup> Activity in kg-polymer/mol-Ti-h. <sup>e</sup> TON (turnovers) = monomer consumed (mol)/mol-Ti. <sup>f</sup> GPC data in THF vs polystyrene standards. <sup>g</sup> Estimated by <sup>1</sup>H NMR spectra. <sup>h</sup> Estimated ((DDD consumed/DDD charged)  $\times 100$ ).

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-tetradecadiene (TDD) by  $Cp^*TiMe_2$  (O-2,6- $i$ -Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1)-[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (borate) catalyst ( $-30$  °C) <sup>a</sup>.

Run	Time/min	Yield <sup>b</sup> /mg	Activity <sup>c</sup>	TON <sup>d</sup>	$M_n$ <sup>e</sup> $\times 10^{-4}$	$M_w/M_n$ <sup>e</sup>	TDD <sup>f</sup> /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	1220	12300	91.2	1.51	

<sup>a</sup> Conditions: **1** 1.0 μmol, 1-tetradecene 20.0 mL, 1,13-tetradecadiene 1.0 mL, *n*-hexane 40.0 mL, Al<sup>*i*</sup>Bu<sub>3</sub>/Al(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Ti = 100/400/3.0/1.0, molar ratio, **1** was pretreated with 2.0 equiv of Al<sup>*i*</sup>Bu<sub>3</sub> at  $-30$  °C for 10 min before addition into the mixture. <sup>b</sup> 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. <sup>c</sup> Activity in kg-polymer/mol-Ti-h. <sup>d</sup> TON (turnovers) = monomer consumed (mol)/mol-Ti. <sup>e</sup> GPC data in THF vs polystyrene standards. <sup>f</sup> Estimated by <sup>1</sup>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\*TiCl<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-MAO catalyst, and no resonances ascribed to protons in the internal olefins were observed (additional <sup>1</sup>H 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 Cp<sub>2</sub>ZrCl<sub>2</sub>-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 ( $M_w/M_n$ ) values has been attained by polymerization of long-chain (higher)  $\alpha$ -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\*TiMe<sub>2</sub>(O-2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1)-[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (borate) as the catalyst, in the presence of Al<sup>*i*</sup>Bu<sub>3</sub>/Al(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>. These polymerizations proceeded in a quasi-living manner in *n*-hexane at -30 to -50 °C, and linear relationships between the  $M_n$  values and the polymer yields were observed in all cases, without significant changes in the PDI ( $M_w/M_n$ ) values. The resultant poly(DC-*co*-DCD) prepared at -40 °C possessed UHMW ( $M_n = 1.40 \times 10^6$  after 45 min) with low PDI ( $M_w/M_n = 1.39$ ), and UHMW poly(TD-*co*-TDD) was also obtained in the TD/TDD copolymerization at -30 °C ( $M_n = 9.12 \times 10^5$ ,  $M_w/M_n = 1.51$ , 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  $\epsilon$ -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: <sup>1</sup>H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 25 °C) for poly(1-decene-*co*-1,9-decadiene) (run 1, after 5 min, 1,9-decadiene 8.9 mol%), Figure S2: <sup>1</sup>H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 25 °C) for poly(1-decene-*co*-1,9-decadiene) (run 2, after 10 min, 1,9-decadiene 9.1 mol%), Figure S3: <sup>1</sup>H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 25 °C) for poly(1-dodecene-*co*-1,11-dodecadiene) (run 4, after 30 min, 1,11-dodecadiene 7.7 mol%), Figure S4: <sup>1</sup>H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 25 °C) for poly(1-dodecene-*co*-1,11-dodecadiene) (run 5, after 120 min, 1,11-dodecadiene 7.5 mol%), Figure S5: <sup>1</sup>H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 25 °C) for poly(1-tetradecene-*co*-1,13-tetradecadiene) (run 6, after 30 min, 1,13-tetradecadiene 4.5 mol%), Figure S6: <sup>1</sup>H NMR spectrum (in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> at 25 °C) for poly(1-tetradecene-*co*-1,13-tetradecadiene) (run 6, after 60 min, 1,13-tetradecadiene 3.7 mol%).

**Author Contributions:** Data collection and writing reports, S.P.; project support, teaching, and supervision, W.A.; project administration, funding acquisition, conceptualization, supervision, and original draft preparation, K.N. All authors have read and agreed to the published version of the manuscript.

**Funding:** This project was partly supported by Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science (JSPS, No. 18H01982).

**Acknowledgments:** The authors would like to thank A. Inagaki, Ken Tsutsumi, and S. Komiya (Tokyo Metropolitan University) for fruitful discussions.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. Brintzinger, H.H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R.M. A Tailor-made metallocene for the copolymerization of ethene with bulky cycloalkenes. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143–1170. [[CrossRef](#)]
2. McKnight, A.L.; Waymouth, R.M. Group 4 *ansa*-cyclopentadienyl-amido catalysts for olefin polymerization. *Chem. Rev.* **1998**, *98*, 2587–2598. [[CrossRef](#)] [[PubMed](#)]
3. Britovsek, G.J.P.; Gibson, V.C.; Wass, D.F. The search for new-generation olefin polymerization catalysts: Life beyond metallocenes. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 428–447. [[CrossRef](#)]
4. Gibson, V.C.; Spitzmesser, S.K. Advances in non-metallocene olefin polymerization catalysis. *Chem. Rev.* **2003**, *103*, 283–316. [[CrossRef](#)]
5. Nomura, K.; Liu, J.; Sudhakar, P.; Kitiyanan, B. Nonbridged half-metallocenes containing anionic ancillary donor ligands: New promising candidates as catalysts for precise olefin polymerization. *J. Mol. Catal. A* **2007**, *267*, 1–29. [[CrossRef](#)]
6. Nomura, K. Half-titanocenes containing anionic ancillary donor ligands as promising new catalysts for precise olefin polymerization. *Dalton Trans.* **2009**, 8811–8823. [[CrossRef](#)]
7. Nomura, K.; Liu, J. Half-titanocenes for precise olefin polymerisation: Effects of ligand substituents and some mechanistic aspects. *Dalton Trans.* **2011**, *40*, 7666–7682. [[CrossRef](#)]
8. Makio, H.; Terao, H.; Iwashita, A.; Fujita, T. FI Catalysts for olefin polymerization—A comprehensive treatment. *Chem. Rev.* **2011**, *111*, 2363–2449. [[CrossRef](#)]
9. Nomura, K.; Zhang, S. Design of vanadium complex catalysts for precise olefin polymerization. *Chem. Rev.* **2011**, *111*, 2342–2362. [[CrossRef](#)]
10. Delferro, M.; Marks, T.J. Multinuclear olefin polymerization catalysts. *Chem. Rev.* **2011**, *111*, 2450–2485. [[CrossRef](#)]
11. Redshaw, C.; Tang, Y. Tridentate ligands and beyond in group IV metal  $\alpha$ -olefin homo-/co-polymerization catalysis. *Chem. Soc. Rev.* **2012**, *41*, 4484–4510. [[CrossRef](#)] [[PubMed](#)]
12. Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Coordinative chain transfer polymerization. *Chem. Rev.* **2013**, *113*, 3836–3857. [[CrossRef](#)] [[PubMed](#)]
13. Osakada, K. *Organometallic Reactions and Polymerization*; The Lecture Notes in Chemistry 85; Springer: Berlin/Heidelberg, Germany, 2014.
14. Hoff, R. *Handbook of Transition Metal. Polymerization Catalysts*, 2nd ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2018.
15. López-Barrón, C.R.; Tsou, A.H.; Younker, J.M.; Norman, A.I.; Schaefer, J.J.; Hagadorn, J.R.; Throckmorton, J.A. Microstructure of crystallizable  $\alpha$ -olefin molecular bottlebrushes: Isotactic and atactic poly(1-octadecene). *Macromolecules* **2018**, *51*, 872–883. [[CrossRef](#)]
16. López-Barrón, C.R.; Tsou, A.H.; Hagadorn, J.R.; Throckmorton, J.A. Highly entangled  $\alpha$ -olefin molecular bottlebrushes: Melt structure, linear rheology, and interchain friction mechanism. *Macromolecules* **2018**, *51*, 6958–6966. [[CrossRef](#)]
17. Choi, H.J.; Jhon, M.S. Polymer-induced turbulent drag reduction. *Ind. Eng. Chem. Res.* **1996**, *35*, 2993–2998. [[CrossRef](#)]
18. Brostow, W. Drag reduction in flow: Review of applications, mechanism and prediction. *J. Ind. Eng. Chem.* **2008**, *14*, 409–416. [[CrossRef](#)]
19. Ivchenko, P.V.; Nifant'ev, I.E.; Tavgorkin, A.V. Polyolefin drag reducing agents. *Petrol. Chem.* **2016**, *56*, 775–787. [[CrossRef](#)]
20. Cuenca, F.G.; Marín, M.G.; Folgueras Díaz, M.B. Energy-savings modeling of oil pipelines that use drag-reducing additives. *Energy Fuels* **2008**, *22*, 3293–3298. [[CrossRef](#)]
21. Nomura, K.; Pengoubol, S.; Apisuk, W. Synthesis of ultrahigh molecular weight polymers by homopolymerisation of higher  $\alpha$ -olefins catalysed by aryloxo-modified half-titanocenes. *RSC Adv.* **2016**, *6*, 16203–16207. [[CrossRef](#)]
22. Nomura, K.; Pengoubol, S.; Apisuk, W. Synthesis of ultrahigh molecular weight polymers with low PDIs by polymerizations of 1-decene, 1-dodecene, and 1-tetradecene by Cp\*TiMe<sub>2</sub> (O-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-borate catalyst. *Molecules* **2019**, *24*, 1634. [[CrossRef](#)]



23. Grumel, V.; Brüll, R.; Pasch, H.; Raubenheimer, H.G.; Sanderson, R.; Wahner, U.M. Homopolymerization of higher  $\alpha$ -olefins with metallocene/MAO catalysts. *Macromol. Mater. Eng.* **2001**, *286*, 480–487. [[CrossRef](#)]
24. Saito, J.; Suzuki, Y.; Fujita, T. Higher  $\alpha$ -olefin polymerization behavior of a bis (phenoxy-imine)titanium complex/*i*-Bu<sub>3</sub>Al/Ph<sub>3</sub>CB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> catalyst system. *Chem. Lett.* **2003**, *32*, 236–237. [[CrossRef](#)]
25. Fries, A.; Mise, T.; Matsumoto, A.; Ohmori, H.; Wakatsuki, Y. Polymerization of hex-1-ene by homogeneous zirconocene and hafnocene catalysts in compressed solution. *Chem. Commun.* **1996**, 783–784. [[CrossRef](#)]
26. Segal, S.; Goldberg, I.; Kol, M. Zirconium and titanium diamine bis (phenolate) catalysts for  $\alpha$ -olefin polymerization: From atactic oligo(1-hexene) to ultrahigh-molecular-weight isotactic poly (1-hexene). *Organometallics* **2005**, *24*, 200–202. [[CrossRef](#)]
27. Fujita, M.; Seki, Y.; Miyatake, T. Enhancement of productivity, molecular weight and stereoregularity of 1-butene polymerization by MAO modification. *Macromol. Chem. Phys.* **2004**, *205*, 884–887. [[CrossRef](#)]
28. Fujita, M.; Seki, Y.; Miyatake, T. Synthesis of ultra-high-molecular-weight poly ( $\alpha$ -olefin)s by thiobis(phenoxy)titanium/modified methylaluminumoxane system. *J. Polym. Sci. Part A Polym. Chem.* **2004**, *42*, 1107–1111. [[CrossRef](#)]
29. Nomura, K.; Fudo, A. Efficient living polymerization of 1-hexene by Cp\*TiMe<sub>2</sub> (O-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)-borate catalyst systems at low temperature. *J. Mol. Catal. A Chem.* **2004**, *209*, 9–17. [[CrossRef](#)]
30. Jayaratne, K.C.; Sita, L.R. Stereospecific living Ziegler-Natta polymerization of 1-hexene. *J. Am. Chem. Soc.* **2000**, *122*, 958–959. [[CrossRef](#)]
31. Domski, G.J.; Lobkovsky, E.B.; Coates, G.W. Polymerization of  $\alpha$ -olefins with pridyamidohafnium catalysts: Living behavior and unexpected isoselectivity from a C<sub>s</sub>-symmetric catalyst precursor. *Macromolecules* **2007**, *40*, 3510–3513. [[CrossRef](#)]
32. Cai, Z.; Ohmagari, M.; Nakayama, Y.; Shiono, T. Highly active syndiospecific living polymerization of higher 1-alkene with *ansa*-fluorenylamidodimethyltitanium complex. *Macromol. Rapid Commun.* **2009**, *30*, 1812–1816. [[CrossRef](#)]
33. Kotzabasakis, V.; Mourmouris, S.; Pitsikalis, M.; Hadjichristidis, N.; Lohse, D.J. Synthesis and characterization of complex macromolecular architectures based on poly( $\alpha$ -olefins) utilizing a C<sub>s</sub>-symmetry hafnium metallocene catalyst in combination with atom transfer radical polymerization (ATRP). *Macromolecules* **2011**, *44*, 1952–1968. [[CrossRef](#)]
34. Kiesewetter, E.T.; Waymouth, R.M. Octahedral group IV bis (phenolate) catalysts for 1-hexene homopolymerization and ethylene/1-hexene copolymerization. *Macromolecules* **2013**, *46*, 2569–2575. [[CrossRef](#)]
35. Nakata, N.; Toda, T.; Matsuo, T.; Ishii, A. Controlled isospecific polymerization of  $\alpha$ -olefins by hafnium complex incorporating with a *trans*-cyclooctanediyl-bridged [OSSO]-type bis (phenolate) ligand. *Macromolecules* **2013**, *46*, 6758–6764. [[CrossRef](#)]
36. Dai, S.; Zhou, S.; Zhang, W.; Chen, C. Systematic investigations of ligand steric effects on  $\alpha$ -diimine palladium catalyzed olefin polymerization and copolymerization. *Macromolecules* **2016**, *49*, 8855–8862. [[CrossRef](#)]
37. Nomura, K.; Fujita, K.; Fujiki, M. Effects of cyclopentadienyl fragment in ethylene, 1-hexene, and styrene polymerizations catalyzed by half-titanocenes containing ketimide ligand of the type, Cp\*TiCl<sub>2</sub> (N=C<sup>t</sup>Bu<sub>2</sub>). *Catal. Commun.* **2004**, *5*, 413–417. [[CrossRef](#)]
38. Nomura, K.; Liu, J.; Fujiki, M.; Takemoto, A. Facile, efficient functionalization of polyolefins via controlled incorporation of terminal olefins by repeated 1,7-octadiene insertion. *J. Am. Chem. Soc.* **2007**, *129*, 14170–14171. [[CrossRef](#)]
39. Chung, T.C. *Functionalization of Polyolefins*; Academic Press: San Diego, CA, USA, 2002.
40. Chung, T.C. Synthesis of functional polyolefin copolymers with graft and block structures. *Prog. Polym. Sci.* **2002**, *27*, 39. [[CrossRef](#)]
41. Nomura, K. New approaches in precise synthesis of polyolefins containing polar functionalities by olefin copolymerizations using transition metal catalysts. *J. Synth. Org. Chem. Jpn.* **2010**, *68*, 1150–1158. [[CrossRef](#)]
42. Franssen, N.M.G.; Reek, J.N.H.; de Bruin, B. Synthesis of functional ‘polyolefins’: State of the art and remaining challenges. *Chem. Soc. Rev.* **2013**, *42*, 5809–5832. [[CrossRef](#)]
43. Mohanty, A.D.; Bae, C. Transition metal-catalyzed functionalization of polyolefins containing C–C, C=C, and C–H bonds. *Adv. Organomet. Chem.* **2015**, *64*, 1–39.

44. Apisuk, W.; Nomura, K. Efficient terpolymerization of ethylene and styrene with 1,7-octadiene by aryloxo modified half-titanocenes—Cocatalyst systems: Efficient introduction of the reactive functionality. *Macromol. Chem. Phys.* **2014**, *215*, 1785–1791. [[CrossRef](#)]
45. Zhao, W.; Nomura, K. Copolymerizations of norbornene, tetracyclododecene with  $\alpha$ -olefins by half-titanocene catalysts: Efficient synthesis of highly transparent, thermal resistance polymers. *Macromolecules* **2016**, *49*, 59–70. [[CrossRef](#)]
46. Nomura, K.; Naga, N.; Miki, M.; Yanagi, K. Olefin polymerization by (cyclopentadienyl) (aryloxy)—Titanium (IV) complexes-cocatalyst systems. *Macromolecules* **1998**, *31*, 7588–7597. [[CrossRef](#)]
47. Nomura, K.; Fudo, A. Syndiospecific styrene polymerization by (*tert*-BuC<sub>5</sub>H<sub>4</sub>) TiCl<sub>2</sub> (O-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)—Borate catalyst system. *Catal. Commun.* **2003**, *4*, 269–274. [[CrossRef](#)]
48. Nomura, K.; Suzuki, N.; Kim, D.-H.; Kim, H.J. Effect of cocatalyst in ethylene/styrene copolymerization by aryloxo-modified half-titanocene-cocatalyst systems for exclusive synthesis of copolymers at high styrene concentrations. *Macromol. React. Eng.* **2012**, *6*, 351–356. [[CrossRef](#)]
49. Nomura, K.; Pracha, S.; Phomphrai, K.; Katao, S.; Kim, D.-H.; Kim, H.J.; Suzuki, N. Synthesis and structural analysis of phenoxy-substituted half-titanocenes with different anionic ligands, Cp\*TiX(Y)(O-2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>): Effect of anionic ligands (X,Y) in ethylene/styrene copolymerization. *J. Mol. Catal. A Chem.* **2012**, *365*, 136–145. [[CrossRef](#)]
50. Hagihara, H.; Shiono, T.; Ikeda, T. Living polymerization of propene and 1-hexene with the [*t*-BuNSiMe<sub>2</sub>Flu]TiMe<sub>2</sub>/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst. *Macromolecules* **1998**, *31*, 3184–3188. [[CrossRef](#)]
51. Fukui, Y.; Murata, M.; Soga, K. Living polymerization of propylene and 1-hexene using bis-Cp type metallocene catalysts. *Macromol. Rapid Commun.* **1999**, *20*, 637. [[CrossRef](#)]
52. Beckerle, K.; Manivannan, R.; Spaniol, T.P.; Okuda, J. Living isospecific styrene polymerization by chiral benzyl titanium complexes that contain a tetradentate [OSSO]-type bis(phenolato) ligand. *Organometallics* **2006**, *25*, 3019–3026. [[CrossRef](#)]
53. As reported previously [[21,22,29](#)], the resultant polymers do not have stereo-regularity (atactic polymers), as observed in the spectra in poly(1-hexene) [[29](#)], poly(1-decene) and poly(1-dodecene) [[22](#)] using 1-borate catalyst. Resonances ascribed to 2,1- or other insertion units could not be found, strongly suggesting that the polymerizations proceeded with (in high certainty) 1,2-insertion manner.
54. Nomura, K.; Hatanaka, Y.; Okumura, H.; Fujiki, M.; Hasegawa, K. Polymerization of 1,5-hexadiene by nonbridged half-titanocene complex—MAO catalyst system: Remarkable difference in the selectivity of repeated 1,2-insertion. *Macromolecules* **2004**, *37*, 1693–1695. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).