Articles

Cis-Specific Living Polymerization of 1,3-Butadiene Catalyzed by Alkyl and Alkylsilyl Substituted Cyclopentadienyltitanium Trichlorides with MAO[†]

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ABSTRACT: Cis-specific living polymerizations of 1,3-butadiene (BD) catalyzed by the catalyst system composed of $C_5H_4RTiCl_3$ (**4a**, R = H; **4b**, R = *n*-butyl; **4c**, R = isopropyl; **4d**, R = *tert*-butyl; **4e**, R = trimethylsilyl) with methylaluminoxane (MAO) to give polyBDs with narrow molar mass distribution and high cis content are described. Polybutadienes (polyBDs) prepared by the catalyst at −25 °C are monodispersed ($M_w/M_n = 1.04-1.05$) in all cases. From the comparison with propagation rate constants (k_p), the order of polymerization activity was as follows: **4d** > **4e** > **4c** > **4b** = **4a**. The microstructures of polyBDs were all dominated by the cis configuration. The complex **4d** having bulky *tert*-butyl group showed higher cis specicficity. Both k_ps and cis specificity in the polymerization of BD were strongly affected by the substituents introduced on the cyclopentadienyl ring.

Introduction

A simultaneous and precise control of both molecular weight and microstructure of polymer backbone has been one of the challenging targets in polybutadiene (polyBD) synthesis. High *cis*-polyBDs are known; these are useful materials as a synthetic rubber for practical purposes and are widely used in the industrial field.[1] High *cis*-polyBDs can be prepared in some ways as conventional Ziegler-type polymerizations, which is promoted by catalyst systems composed of transition metal compounds (Ti, Ni, Co, and Nd) and aluminum alkyls.[2] The Ziegler-type catalyst systems are effective to cause the polymer backbone to take a cis configuration in high levels; however, the molar mass distributions (MMD, M_w/M_n) of the obtained polyBDs are fairly broad.

In 1984, Tessié and co-workers reported that the combination of (η^3-allyl)(trifluoroacetato)nickel and chloranil promote the living polymerization of 1,3-butadiene (BD) to yield *cis*-polyBD (73% of cis content) with narrow MMD (1.20).[3] Some combinations of lanthanide metal halides or acetates with aluminum alkyls are claimed as an efficient initiator for high *cis*-1,4-polymerization (cis content > 95%) of BD with a living nature at −70 °C, but the MMD of obtained polyBDs are relatively broad (MMD > 1.7).[4]

On the other hand, anionic polymerizations initiated by lithium alkyls or sodium naphthalenide afford polyBDs with narrow MMD ($M_w/M_n < 1.1$), but the above polymerizations are less stereospecific in cis specificity.[5] Thus, it has been hardly possible to control both the cis specificity and the MMD of polyBD in high levels.

In this decade, cyclopentadienyltitanium trichloride ($C_5H_5TiCl_3$) has attracted much attention for a novel stereospecific polymerization catalyst for styrene and 1,3-conjugated diolefins.[6] For example, the $C_5H_5TiCl_3$ activated with methylaluminoxane (MAO) promotes the polymerization of BD to yield *cis*-polyBD in good yield. However, the cis content of the resulting polymer was lower than that of polyBDs prepared by the Ziegler-type catalyst. And the way to discovering a method to control polymer molecular weight has not been successful so far.

To achieve simultaneous control of both molecular weight and cis specificity in the polymerization of BD, we investigated the substituent effect introduced on the cyclopentadienyl ring. Herein, we wish to report the cis-specific living polymerization of BD catalyzed by $C_5H_4RTiCl_3$ (R = H, *n*-butyl, isopropyl, *tert*-butyl, and trimethylsilyl) with MAO catalysts, which are an efficient initiator to prepare high *cis*-polyBD with narrow MMD.

Results and Discussion

Catalyst Preparation. Five kinds of $C_5H_4RTiCl_3$ (R = H, **4a**; *n*-butyl, **4b**; isopropyl, **4c**; *tert*-butyl, **4d**; trimethylsilyl, **4e**) were employed as polymerization

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Scheme 1

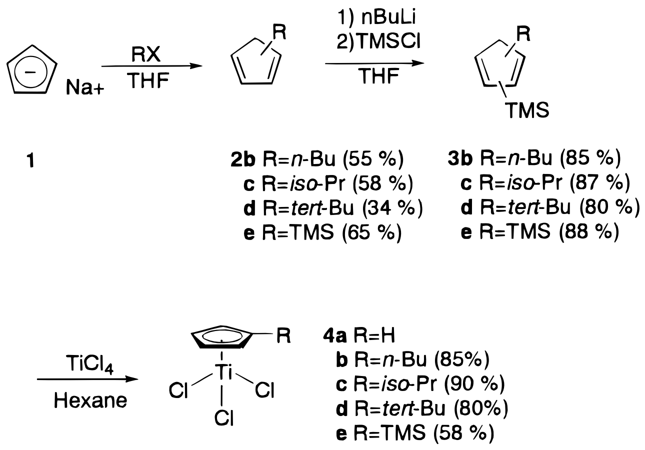

Table 1. Polymerization Results of 1,3-Butadiene Catalyzed by 4a–e/MAO Catalysts[a]

run	catalyst	$[BD]_0$ (wt %)	temp (°C)	time (h)	yield (%)	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]
1	**4a**	6.70	25	0.33	91	17.8	1.36
2	**4a**	6.47	−25	20	66.8	12.3	1.03
3	**4b**	6.50	−25	20	64.4	13.0	1.04
4	**4c**	5.07	25	0.33	94.1	10.6	1.43
5	**4c**	5.07	−5	1	82.0	17.3	1.05
6	**4c**	5.07	−25	12	70.8	13.1	1.04
7	**4d**	6.05	25	0.1	80.0	14.4	1.29
8	**4d**	6.05	−5	0.5	93.0	19.3	1.28
9	**4d**	6.44	−25	1.33	57.9	12.6	1.04
10	**4e**	6.44	25	0.25	97.0	13.3	1.82
11	**4e**	6.44	−25	7	73.5	14.1	1.04

[a] $BD_0/Ti = 100$ g/mmol (1850 mol/mol); Al/Ti = 1000 mol/mol. [b] Determined by SEC with THF as eluent, calibrated with standard polybutadiene.

catalysts for the polymerization of BD. Complexes **4b**,[7] **4c**[8], **4d**,[9] and **4e**[10] were prepared according to the method reported previously with a slight modification.

The reactions of sodium cyclopentadienide with alkyl halides or chlorotrimethylsilane were carried out in THF at 0 °C to give corresponding substituted cyclopentadienes **2b**–**e** in 55%, 58%, 34%, and 65% yield, respectively (Scheme 1). Introduction of trimethylsilyl group on the cyclopentadienyl ring of **2b**–**e** was achieved by the reaction of the lithium salt of **2b**–**e** generated by the reaction with *n*-BuLi at −78 °C and a quantitative amount of chlorotrimethylsilane to afford the corresponding disubstituted cyclopentadienes (**3b**–**e**) in good yield. Complexation of **3b**–**e** with $TiCl_4$ leading to the desired complexes (**4b**–**e**) was achieved in hexane at −78 °C. Complexes **4b**–**e** were isolated by recrystallization from hexane solution.

Polymerization of 1,3-Butadiene. Polymerizations of BD using **4a**–**e** with MAO as a cocatalyst were carried out at +25 and −25 °C in toluene under conditions of BD/catalyst (**4a**–**e**) = 1850 mol/mol and Al/Ti = 1000 mol/mol. The catalyst **4a**–**e** was aged for 5 min with MAO at room temperature before injection into the monomer solution. Polymerization results are summarized in Table 1. When the polymerization was carried out at 25 °C, the monomer was almost consumed within 30 min to afford polyBDs in good yield with relatively narrow MMD (1.36 for **4a**, 1.43 for **4c**, 1.29 for **4d**, and 1.82 for **4e**). On the other hand, when the polymerization temperature was brought down to −25 °C, although the polymerization activities naturally decreased, the MMDs of the resulting polymers became as narrow as 1.03–1.05 in all cases. Therefore, we investigated the polymerizations of BD with **4a**–**e**/MAO in detail.

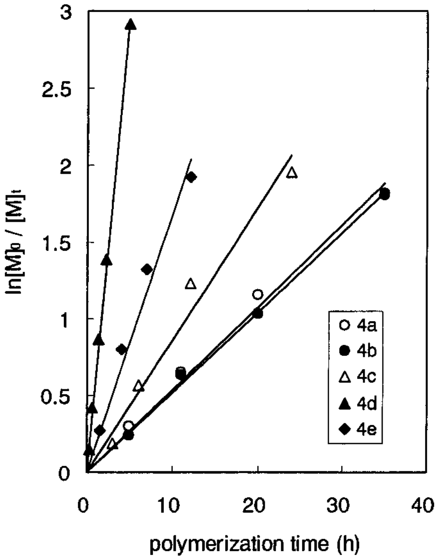

Figure 1. First-order plots of polymerizations of BD catalyzed by **4a**–**e**/MAO at −25 °C. Polymerization conditions are described in Table 1.

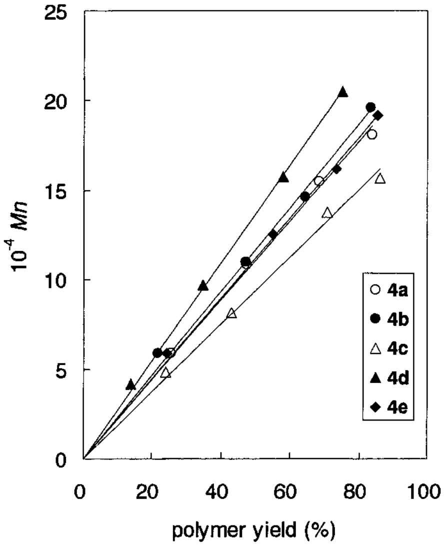

Figure 2. M_n and M_w/M_n vs polymer yield plots for polymerization of BD initiated by **4a**–**e** with MAO at −25 °C. Polymerization conditions are the same as Figure 1.

The first-order plots ($\ln[M]_0/[M]_t$ vs polymerization time) for catalysts **4a**–**e** for the polymerization at −25 °C is shown in Figure 1. In all cases, good linear relationships between $\ln [M]_0/[M]_t$ and polymerization time were obtained, which indicates that the concentration of the living ends ([LE]) remains constant during the course of the polymerization and that termination reactions such as chain transfer reaction or *β*-hydride elimination reaction should be negligible. From the results shown in Figure 2, it is clear that the number-average molecular weights (M_n) increased proportionally along with increasing polymer yields. The MMDs of resulting polymers during the course of polymerization were kept an extremely narrow range (1.03–1.06). Moreover, from the two-step polymerization results using **4d**/MAO catalyst at −25 °C shown in Figure 4, the SEC profiles of polyBD obtained at first-step polymerization (97% yield) moved to a higher molecular

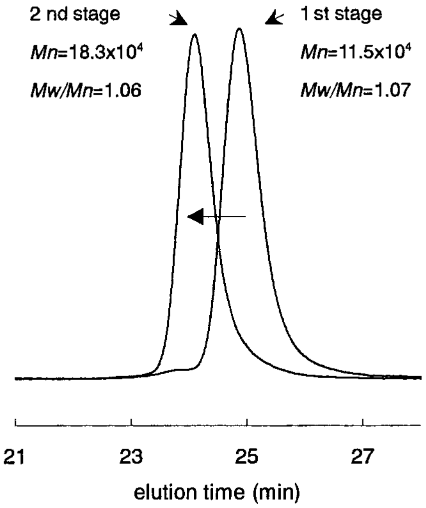

Figure 3. SEC profiles of polyBDs obtained in post-polymerization at −25 °C.

weight region (second step, 185% yield), keeping a narrow MMD.

Concerning the living polymerization characteristic, the numbers of the initiator efficiency (IE) and the propagation rate constants (k_ps) can be readily estimated by using eqs 1 and 2 , where [LE] indicates the

$$\text{IE (\%)} = 100[\text{LE}]/[\text{Ti}] \qquad (1)$$

$$\ln [\text{M}]_0/[\text{M}]_t = k_p[\text{LE}]t \qquad (2)$$

concentration of the living ends, [Ti] indicates the molar amount of whole Ti compounds used for the polymerization, $[\text{M}]_0$ indicates the initial concentration of the monomer, and $[\text{M}]_t$ indicates the monomer concentration at the stated time. The calculation results are summarized in Table 2. The k_ps were strongly affected by the catalyst structure, and the order was as follows: **4d** > **4e** > **4c** > **4b** = **4a**. The introduction of the bulky and electron-donating *tert*-butyl group on the cyclopentadienyl ring was effective for the increase of k_p. The complex **4e**, having a bulky TMS group and a weaker electron-donating character than the isopropyl group, showed a larger k_p than that of **4c**. Thus, the acceleration effect caused by introduction of a substituent in the polymerization of BD seems to depend strongly on the steric bulkiness of the substituent on the cyclopentadienyl ring.

Table 2. Initiator Efficiency (IE) and Propagation Rate Constants (k_p) in the Polymerization of 1,3-Butadiene Catalyzed by 4a−e/MAO Catalysts at −25 °C[a]

catalyst	IE (%)	$[\text{LE}]k_p$[b] (min^{-1})	k_p (L mol^{-1} min^{-1})
4a	56.6	9.0×10^{-4}	2.9
4b	51.3	8.4×10^{-4}	3.0
4c	54.7	1.4×10^{-3}	5.5
4d	47.2	9.3×10^{-3}	39.0
4e	53.0	3.0×10^{-3}	10.0

[a] Polymerization conditions were the same as Table 1. [b] [LE] means the concentration of the living ends.

Microstructure Analysis. To understand the effectiveness of introduction of substituent on the cyclopentadienyl ring for the stereospecificity in the polymerization of BD, we analyzed microstructures (*cis*-, *trans*-, and 1,2-structures) of polyBDs by ^{1}H and ^{13}C NMR measurements.

The ratios of 1,4- and 1,2-units were determined from the comparison of the peak areas with two methylene protons between the signal at about 4.9 ppm (olefinic methylene of the 1,2-insertion unit) and the signal at about 5.2 ppm (olefinic methyne of the 1,4-insertion unit) by ^{1}H NMR measurement.[11] The ratios of *cis*-/*trans*-units were determined by ^{13}C NMR from the comparison between the peak areas of methylene carbons originating from *cis*- and *trans*-units. The signal assignment was referred to the method reported by Bywater[12] and Sato[13] and was as follows: carbons originating from the *cis*-unit appeared at 27.44 ppm (neighboring 1,4-unit) and 25.10, 31.99, 32.74 ppm (neighboring vinyl unit). The carbons originating from the *trans*-unit appeared at 32.68 ppm (neighboring 1,4-unit) and 30.16, 38.20, and 38.60 ppm (neighboring vinyl unit). The expanded ^{13}C NMR spectrum of polyBD prepared with **4d**/MAO was depicted in Figure 4, and the assigned signals mentioned above were indicated in Table 4. Total ratios for each component were summarized in Table 3.

The microstructure of all polymers was dominated by the cis structure. In particular, it is worthwhile to mention that the **4d**/MAO catalyzed polymerization of BD showed higher cis specificity than that of the parent $C_5H_5TiCl_3$ (**4a**). Moreover, from the sequential analysis of the polyBD prepared with **4d**/MAO, there is no vinyl−trans linkage in the ^{13}C NMR spectrum. The cis content for each catalyst in the polymerization at −25 °C is as follows: 88.4% for **4a**, 88.2% for **4b**, 89.9% for **4c**, 93.5% for **4d**, and 92.6% for **4e**. Changing the polymerization

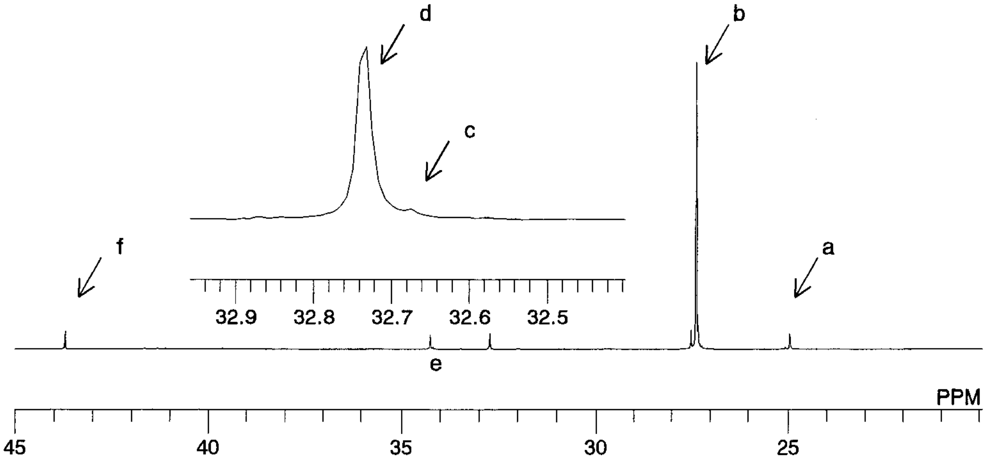

Figure 4. Expanded ^{13}C NMR (150 MHz) spectrum of polyBD prepared with **4d**/MAO catalyst at −25 °C.

Table 3. Microstructure Analyses of Polybutadienes Prepared with the Catalyst System of 4a−e/ MAO[a]

		microstructure (mol %)[b]			
catalyst	polym temp (°C)	1,4-/1,2-	*cis*-	*trans*-	1,2-
4a	25	82.0/18.0	80.4	1.6	18.0
4a	−25	89.7/10.3	88.4	1.3	10.3
4b	−25	90.6/9.4	88.2	2.4	9.4
4c	25	86.0/14.0	81.5	4.5	14.0
4c	−25	91.5/8.5	89.9	1.6	8.5
4d	25	90.3/9.7	88.3	2.0	9.7
4d	−25	93.8/6.2	93.5	0.3	6.2
4e	25	89.0/11.0	87.0	2.0.	11.0
4e	−25	93.3/6.7	92.6	0.7	6.7

[a] Polymerization conditions were the same as Table 1. [b] Microstructures were determined by ^{1}H and ^{13}C NMR.

Table 4. Signal Assignments of Polybutadiene Prepared by 4d/MAO at −25 °C

sequence	carbon[a]	signal[b]	chem shift (ppm)
C−v	4	a	25.10
C−1,4, 1,4−C	4, 1	b	27.44
T−1,4, 1,4−T	4, 1	c	32.68
1,4−v−C	1	d	32.74
1,4−V−1,4	1	e	34.26
1,4−V−1,4	2	f	42.72

[a] Carbons: 1,4-unit, $-C(1)H_2C(2)H{=}C(3)HC(4)H_2-$; 1,2-unit, $-C(1)H_2C(2)H(C(3)H{=}C(4)H_2)-$. [b] Signals are indicated in Figure 4.

temperature (from +25 to −25 °C) caused an increase in the cis content. Therefore, introduction of a substituent and changing the polymerization temperature to a lower one are effective for enhancement of both the 1,4-/1,2- ratio and cis/trans ratio. Complexes **4d,e** having a bulky substituent on the cyclopentadienyl ring showed higher cis selectivity. It seems to be that the enhancement of cis specificity is strongly dependent on the bulkiness of the substituent introduced on the cyclopentadienyl ring.

Conclusion

We demonstrated that the catalyst systems composed of $C_5H_4RTiCl_3$ (**4a−e**) with MAO promote living polymerizations of BD with high cis specificity at −25 °C. It was found that an introduction of bulky substituent is effective to increase the propagation rate constant (k_p). The cis specificity in the polymerization is controlled by the steric bulkiness of substituent introduced on the cyclopentadienyl ring and the polymerization temperature. Studies on the detailed reaction mechanism and the preparation of block copolymers leading to new materials are now in progress.

Experimental Section

General Remarks. All melting and boiling points are uncorrected. Cyclopentadienyltitanium trichloride purchased from Aldrich Chemical Co., was further purified by recrystallization from dichloromethane. MAO (30 wt % solution in toluene) was purchased from Tosoh-Akzo Co Ltd. and used without further treatment. Sodium cyclopentadienide in THF solution (2.0 mol/L) was purchased from Aldrich Chemical Co. All solvents were dried by the general manner reported previously and were distilled prior to use.[14] Other chemicals were purchased from chemical companies and were used without further purification. 1,3-Butadiene (BD) donated by Nippon Zeon (> 99.5% pure), was distilled from the container, dried by passing through a column packed with molecular sieves, and distilled over triethylaluminum prior to use.

Size exclusion chromatographic (SEC) analyses were performed on a Tosoh HLC8120 system in THF and calibrated with polybutadiene standards (Polymer Laboratories Co. Ltd.). NMR spectra were recorded at 600 MHz for ^{1}H and 150 MHz for ^{13}C on a Nippon Densi lambda spectrometer using $CDCl_3$ as the solvent, and the signals of nondeuterated chloroform were used as internal reference. High-resolution mass spectra (HRMS) were obtained on a Hitachi M-80B spectrometer at 75 eV using a direct inlet system.

Preparation of *n*-Butylcyclopentadiene (2b). To a solution of 0.2 mol of sodium cyclopenytadienide in 100 mL of dry THF was added dropwise 25.0 g (0.183 mol) of *n*-butyl bromide in 50 mL of dry THF at 0 °C with stirring under N_2 atmosphere. After the addition was completed, the resulting reaction mixture was stirred for 1 h at room temperature. The reaction was quenched by addition of a small amount of methanol and then poured into a large amount of ice/water. The organic phase was extracted with ether several times. The ether extract was washed with water and brine, dried over $MgSO_4$, and then concentrated to leave a residue. The residue was distilled under reduced pressure to give 12.16 g (55% based on *n*-butyl bromide) of *n*-butylcyclopentadiene (**2b**) as an isomeric mixture: colorless liquid; bp 44 °C/15 mmHg (lit.[15] bp 115−118 °C).

Compounds **2c−e** were prepared in a similar manner.

Isopropylclopentadiene. 2c (isomeric mixture): colorless liquid, bp 60 °C/22 mmHg (lit.[16] bp 38−43 °C/14 mmHg).

***tert*-Butylcyclopentadiene. 2d** (isomeric mixture): colorless liquid, bp 31 °C/10 mmHg (lit.[17] bp 53 °C/42 mmHg).

Trimethylsilylcyclopentadiene. 2e (isomeric mixture): colorless liquid, bp 40−45 °C/16 mmHg (lit.[18] bp 41−43 °C/16 mmHg).

Preparation of *n*-Butyltrimethylsilylcyclopentadiene (3b). To a solution of 12.16 g (0.1 mol) of **2b** in a mixed solution of 100 mL of dry THF and 100 mL of dry hexane was added dropwise 66 mL of *n*-BuLi (1.6 mol/L hexane solution) at −78 °C with stirring under N_2 atmosphere. After the addition was completed, the resulting reaction mixture was allowed to stir for 1 h at room temperature. The reaction mixture was cooled to −78 °C again, and then 11.4 g (105 mmol) of chlorotrimethylsilane was added dropwise to the reaction mixture. After the mixture was stirred for 1 h at room temperature, a small amount of methanol involving a small amount of hydrochloric acid was added to the reaction mixture and poured into a large amount of ice/water. The organic layer was extracted with hexane several times. The combined organic layer was washed with water and brine and was dried over Mg_2SO_4. THF, hexane, and other low boiling point organic materials were removed by distillation using a rotary evaporator under water aspirator vacuum to leave a residue. The residue was distilled under reduced pressure to give 16.5 g (85% based on **2b**) of *n*-butyltrimethylsilylcyclopentadiene (**3b**): a slightly pale yellow liquid, bp 68 °C/5 mmHg (lit.[19] bp 28−34 °C/0.5 mmHg).

Compounds **3c−e** were prepared in a similar manner.

Isopropyltrimethylsilylcyclopentadiene. 3c (isomeric mixture): colorless liquid, bp 49 °C/5 mmHg; IR (KBr) 960, 986, 1143, 1378, 1410, 1458, 1589, 2929, and 3043 cm^{-1}; NMR ($CDCl_3$) δ (ppm) 6.0−6.5 (3H, m), 3.22 (1H, s), 2.70 (1H, m), 1.15 (6H, d, $J = 7.3$ Hz), −0.07 (9H, s); HRMS calculated for $C_{11}H_{20}Si$ 180.1334, found 180.1336.

***tert*-Butyltrimethylsilylcyclopentadiene. 3d** (isomeric mixture): colorless liquid, bp 51 °C/5 mmHg; IR (KBr) 964, 985, 1130, 1362, 1410, 1461, 1580, 2902, 2959, and 3063 cm^{-1}; NMR ($CDCl_3$)δ (ppm) 6.0−6.6 (3H, m), 3.22 (1H, s), 1.17 (9H, s), −0.07 (9H, s); HRMS calculated for $C_{12}H_{22}Si$ 194.1491, found 194.1483.

Bis(trimethylsilyl)cyclopentadiene. 3e (isomeric mixture): a slightly pale yellow liquid, bp 75 °C/1 mmHg (lit.[10] bp 40 °C/0.1 mmHg).

Preparation of *n*-butylcyclopentadienyltitanium trichloride (4b). To a solution of 3.63 g (18.7 mmol) of **3b** in 50 mL of dry hexane was added carefully 3.37 g (17.7 mmol) of $TiCl_4$ by using a syringe at −78 °C under N_2 atmosphere, and then the colorless solution turned clear orange immediately. After 1 h, the reaction mixture was warmed to room temperature and evaporated to leave a residue. The resulting dark orange oil was cooled to −30 °C, washed with a least amount of dry pentane several times, and evaporated to leave a residue. The resulting orange solid was recrystallized from dry hexane at −30 °C to form orange plate crystals. As the melting point of **4b** was below room temperature, complex **4b** could not be isolated in a crystal form at room temperature; instead an orange viscous oil was obtained at room temperature: NMR ($CDCl_3$) δ (ppm) 6.95 (2H, t, $J = 2.7$ Hz), 6.82 (2H, t, $J = 2.7$ Hz), 2.85 (2H, t), 1.63 (2H, m), 1.38 (2H, m), 0.95 (3H, t).

Compounds **4c**−**e** were prepared in a similar manner.

Isopropylcyclopentadienyltitanium Trichloride (4c): orange prisms (hexane), mp 78.5 °C (lit.[8] mp 75 °C).

***tert*-Butylcyclopentadienyltitanium Trichloride (4d):** orange prisms (hexane), mp 59−61 °C; NMR ($CDCl_3$) δ (ppm) 7.02 (2H, t, $J = 2.7$ Hz), 6.86 (2H, t, $J = 2.7$ Hz), 1.38 (9H, s); HRMS calculated for $C_9H_{13}Cl_3Ti$ 273.9562, found 273.9605.

Trimethylsilylcyclopentadienyltitanium Trichloride (4e): yellow prisms (hexane), mp 62−63 °C (lit.[10] mp 64−64.5 °C).

Typical Procedure for the Polymerization of 1,3-Butadiene with R(cyclopentadienyl)TiCl$_3$/MAO catalyst. Aging Process. To a solution of 9.3 mL of MAO (28.3 mmol of Al) in toluene solution was added slowly via syringe a solution of 0.0283 mmol of (cyclopentadienyl)$TiCl_3$ in 0.67 mL of dry toluene. The resulting mixture was aged for 5 min at room temperature, and then that solution was cooled to −25 °C before addition to the monomer solution.

Polymerization. Polymerization was carried out by using a pressure resistant 150 mL glass ampule equipped with rubber septum to add the aged catalyst solution. To a solution of 2.83 g (28.3 mmol) of BD in 36 mL of dry toluene solution was added the aged catalyst solution above at once via syringe at −25 °C, and polymerization was conducted for the stated time at −25 °C. The clear monomer solution turned pale green immediately. Polymerization was terminated by addition of a small amount of acidic methanol containing 2,6-di-*tert*-butyl-*p*-cresol (1 wt %) as antioxidant reagent, and the resulting polymer solution was poured into a large amount of the above methanol solution. Then the crude bulk polymer was precipitated and collected. The crude polymer was dissolved again in toluene, and the catalyst ash was removed by centrifugation. The purified polymer was reprecipitated by pouring the solution into a large amount of the above methanol solution, collected, and dried under reduced pressure in vacuo at 60 °C for 12 h.

Post polymerization of BD with 4d/MAO. To a solution of 1.53 g of 1,3-butadiene in 21.0 mL of dry toluene was added the aged catalyst solution prepared from 8.5 mg (0.031 mmol) of **4d** and 10 mL (31 mmol) of MAO toluene solution at once via syringe at −25 °C. After polymerization for 6 h, a small portion of the polymerization mixture was picked up for analysis. Taking a 1 h interval before injection of the second monomer solution, a solution of 1.15 g of 1,3-butadiene in 13.9 mL of dry toluene was added to the above polymer solution. Polymerization was conducted for another 6 h and then quenched by addition of a small amount of methanol. Purification and analysis were carried out by the method mentioned above.

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