Pronounced Enhancement Brought in by Substituents on the Cyclopentadienyl Ligand: Catalyst System $(C_5Me_4R)_2Sm(THF)_x$/MMAO ($R = Et, {}^iPr, {}^nBu$, TMS; MMAO = Modified Methylaluminoxane) for 1,4-Cis Stereospecific Polymerization of 1,3-Butadiene in Cyclohexane Solvent

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ABSTRACT: The C_5Me_4R-ligated samarocene(II) complexes, $(C_5Me_4R)_2Sm(THF)_x$ (**1**, R = Me; **2**, R = Et; **3**, $R = {}^iPr$; **4**, $R = {}^nBu$, **5**; R = TMS; $x = 1$ or 2), in combination with modified methylaluminoxane (MMAO) were examined in cyclohexane with respect to their catalytic performances for the polymerization of butadiene. Complexes **2**−**5** showed considerable promotion in both catalytic activity and regularity of the resulting polymer as compared to parent **1**: activity, **3** ≫ **5** ∼ **4** > **2** > **1**; 1,4-cis selectivity at 50 °C, **3** ∼ **5** (98.6%) > **4** (97.5%) > **2** (97.1%) > **1** (96.2%). The system **3**/MMAO showed an excellent catalytic activity even at very low catalyst concentration ($[\text{butadiene}]_0/[\text{Sm}]_0 = 150\,000$), where the turnover number (TON) reached about 115 600 butadiene-mol/(Sm-mol h) at 50 °C (78% polymer yield in 1 h). At room temperature, the polymerization reaction in cyclohexane using **3**/MMAO catalyst gave polybutadiene with extremely high 1,4-cis selectivity of 99.1% in reasonable rate (polymer yield = 87%, in 10 min) while the performance by **1**/MMAO was 97.8% in 1,4-cis selectivity and 12% in polymer yield under the same reaction conditions.

Introduction

In butadiene polymerization chemistry, stereo- and regiospecific polymerization is of crucial importance in not only academic but also industrial areas. Particularly, 1,4-cis regulated polybutadiene exhibits excellent elastic properties and has been manufactured in large quantities as synthetic rubber (high-cis butadiene rubber: high-cis BR). Various polymerization catalysts that give higher-cis BR have been developed aiming at improved thermal and mechanical properties of the resulting BR.[1] A recent successful example is neodymium compound/AlR_3 catalyst systems that realize high 1,4-cis content (∼98%) with high polymerization activity in *n*-hexane.[2] Though such Nd catalysts have already been applied to industrial processes, the molecular weight distribution (MWD) of the polybutadiene cannot be well-controlled ($M_w/M_n \gg 2.0$). With recent progress in sophisticated applications of BR, development of polymeric materials, which have even better thermal and mechanical properties, has been strongly desired. As one of the promising means for achieving the object, there have been attempts to produce BR with both high 1,4-cis content and narrow MWD, preferably using a catalyst with high polymerization activity. In 2000, Miyazawa et al. reported that a half-metallocene complex-based catalyst system $C_5H_4{}^tBuTiCl_3$/MAO afforded polybutadiene with moderately high 1,4-cis selectivity (93.5%) and a sharp MWD (1.04) when polymerized at low temperatures (polymer yield = 57.9% at −25 °C, TON = 800 butadiene-mol/(Ti-mol h)).[3] Shiono et al. proposed in 2002 a simple catalyst system $CoBr_2$/MAO which produced polybutadiene with high 1,4-cis content (98.2%) and narrow MWD (1.3) (polymer yield = 13.0% at 0 °C, TON = 1170 butadiene-mol/(Co-mol h)).[4] A neodymium-based mixture $Nd(C_3H_5)_2Cl{\cdot}1.5THF$/HIBAO (HIBAO = hexaisobutylaluminoxane) was also reported to be a good system for the 1,4-cis specific living-like polymerization of butadiene (1,4-cis selectivity = 95−98%, MWD = 1.12−1.46, TON = 1300−24 600 butadiene-mol/(Nd-mol h) at 35 °C) by Taube et al.[5] The solvent used in all of these three works was toluene.

We already reported in 1999 that the divalent samarocene complex $(C_5Me_5)_2Sm(THF)_2$ (**1**) when mixed with MMAO (MMAO = modified methylaluminoxane containing isobutylaluminoxane) induced rapid polymerization of butadiene in toluene, giving high 1,4-cis regulated polybutadiene (98.8%) with relatively narrow MWD (1.82).[6,7] Though these values and its catalytic activity ($[\text{butadiene}]_0/[\text{Sm}]_0 = 2500$, TON = 20 000 butadiene-mol/(Sm-mol h) at 50 °C) show this system to be potentially one of the best of the known catalysts, it still needs to be improved to meet the requirement from industries. In particular, the toluene solvent (aromatic solvents) is not preferable from the perspective of environment in the future if large-scale application is to be considered. In aliphatic solvents, however, the catalytic activity and stereoregularity of **1**/MMAO are not high enough to compete with the conventional catalyst systems currently employed in mass production (although some processes still use toluene). We therefore decided to modify the samarocene complex by simply substituting a larger alkyl group for one of the methyl

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Table 1. Polymerization of 1,3-Butadiene with Samarocene/MMAO in Cyclohexane

run	cat.	$[\text{butadiene}]_0/[\text{Sm}]_0$	time (min)	yield (%)	TON[f]	microstructure[g] 1,4-cis (%)	1,4-trans (%)	1,2 (%)	M_w[h]	M_n[h]	M_w/M_n[h]
1[a]	**1**	1500	10	21	1870	96.2	1.5	2.3	377 000	212 600	1.77
2[a]	**2**	1500	10	67	5960	97.1	1.0	1.9	571 100	309 000	1.85
3[a]	**3**	1500	5	~100	17 800	98.6	0.6	0.8	651 200	354 000	1.84
4[a]	**4**	1500	10	88	7820	97.5	0.9	1.6	581 500	325 500	1.79
5[a]	**5**	1500	10	91	8090	98.6	0.6	0.8	481 000	256 300	1.88
6[b]	**3**	10000	10	~100	60000	98.8	0.4	0.8	1 279 800	643 900	1.99
7[c]	**3**	25000	10	89	133300	98.8	0.4	0.8	1 413 200	722 600	1.96
8[d]	**3**	150000	60	78	115600	99.1	0.2	0.7	633 100	323 000	1.96
9[e]	**3**	10000	10	87	52400	99.1	0.2	0.7	1 783 600	901 100	1.98
10[e]	**1**	10000	10	12	7110	97.8	0.5	1.7	903 700	454 600	1.99

[a] Cyclohexane = 40 mL; T_p = 50 °C; butadiene = 2.00 g (0.037 mol); samarocene = 2.5×10^{-5} mol; $[\text{MMAO}]_0/[\text{Sm}]_0 = 100$. [b] Cyclohexane = 40 mL; T_p = 50 °C; butadiene = 6.75 g (0.125 mol); **3** = 7 mg (1.25×10^{-5} mol); $[\text{MMAO}]_0/[\text{Sm}]_0 = 500$. [c] Cyclohexane = 40 mL; T_p = 50 °C; butadiene = 6.75 g (0.125 mol); **3** = 3 mg (5.0×10^{-6} mol); $[\text{MMAO}]_0/[\text{Sm}]_0 = 1250$. [d] Cyclohexane = 360 mL; T_p = 50 °C; butadiene = 80 g (1.48 mol); **3** = 6 mg (1.00×10^{-5} mol); $[\text{MMAO}]_0/[\text{Sm}]_0 = 100$; $[\text{Al}^i\text{Bu}_3]_0/[\text{Sm}]_0 = 400$; $[\text{Al}^i\text{Bu}_2\text{H}]_0/[\text{Sm}]_0 = 15$. [e] Polymerization was carried out at room temperature; other conditions were same as run 6. [f] Turnover number (TON) = butadiene-mol/(Sm-mol h). [g] Measured by ^{1}H NMR and ^{13}C NMR in $CDCl_3$. [h] Determined by GPC vs polystyrene standards.

groups of the pentamethylcyclopentadienyl ligand and examine its catalytic performance in cyclohexane solvent. The effect turned out to be dramatic: the $(C_5Me_4\text{-}^i\text{Pr})_2\text{Sm(THF)}$/MMAO system was found to be particularly active while exhibiting very high-cis regularity (up to 99.1%) and relatively narrow MWDs (1.86−1.99).

Experimental Section

General Procedure. All manipulations were carried out under an atmosphere of dry and oxygen-free argon using the Schlenk technique or under a nitrogen atmosphere in a glovebox (Mbraun Co., Ltd.). Tetrahydrofuran (THF), diethyl ether, cyclohexane, hexane, and toluene were distilled from sodium/benzophenone ketyl and degassed two times by the freeze−thaw method. ^{n}BuLi and 2,3,4,5-tetramethyl-2-cyclopenten-1-one were purchased from Kanto Chemical Co., Inc. Trimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane [$C_5Me_4(\text{TMS})H$; TMS = trimethylsilyl] and KH were purchased from Aldrich Chemical Co. MMAO (modified methylaluminoxane containing isobutylaluminoxane: 5.8 wt % solution in toluene) was purchased from Tosoh Finechem Co., Ltd., and used without further purification. 1,3-Butadiene (Takachiho Chemical Industrial Co., Ltd.) was purified before use by passing through a Dryclean column and a Gasclean GC-XR column (Nikka Seiko Co., Ltd.). $\text{SmI}_2(\text{THF})_2$,[8] $(C_5Me_5)_2\text{Sm(THF)}_2$ (**1**),[9] $(C_5Me_4Et)_2\text{Sm(THF)}_2$ (**2**),[10] and $(C_5Me_4{}^i\text{Pr})_2\text{Sm(THF)}$ (**3**)[11] were synthesized according to the literature.

$(C_5Me_4{}^n\text{Bu})_2\text{Sm(THF)}$ (4). $C_5Me_4{}^n\text{BuH}$ was synthesized by the reaction of 2,3,4,5-tetratamethyl-2-cyclopenten-1-one (5.0 g, 36 mmol) with ^{n}BuLi (50 mmol) and yielded as a pale yellow viscous liquid (4.9 g, 76%). $C_5Me_4{}^n\text{BuH}$ (4.5 g, 25 mmol) was added dropwise to a slurry of KH (1.0 g, 25 mmol) in THF (100 mL) under an atmosphere of argon, and the reaction was allowed to stir for 12 h. $C_5Me_4{}^n\text{BuK}$ is insoluble in THF and was washed with hexane and isolated as a white powder (2.9 g, 54%). In the glovebox $\text{SmI}_2(\text{THF})_2$ (2.7 g, 5.0 mmol) and $C_5Me_4{}^n\text{BuK}$ (2.3 g, 10.5 mmol) were added in THF (60 mL) and stirred for 4 h. The solvent was removed in vacuo, and then toluene (100 mL) was added to the flask. The reaction mixture was allowed to stir for additional 12 h at room temperature. Filtration and removal of solvent yielded a purple oily product. It was dissolved in hexane, and the solvent was carefully evaporated to yield **4** as a purple-brown powder (0.37 g, 13%). ^{1}H NMR (C_6D_6): δ 33.01 (s, 4H, THF), 14.59 (s, 4H, THF), 8.95 (s, 6H, CH_3), 8.17 (s, 12H, C_5Me_4), 7.98 (s, 4H, CH_2), 2.91 (s, 4H, CH_2), −2.88 (s, 12H, C_5Me_4), −3.41 (s, 4H, CH_2).

$(C_5Me_4\text{TMS})_2\text{Sm(THF)}$ (5). A similar procedure as above using $C_5Me_4(\text{TMS})H$ (2.5 mL, 11 mmol) and KH (0.5 g, 12 mmol) yielded $C_5Me_4(\text{TMS})K$ as a white powder (2.0 g, 76%). In the glovebox $\text{SmI}_2(\text{THF})_2$ (1.1 g, 2.0 mmol) and $C_5Me_4(\text{TMS})K$ (1.0 g, 4.4 mmol) were added in THF (50 mL) and stirred overnight. The reaction mixture was filtered, and the solvent was slowly evaporated to yield **5** as brown crystals (0.9 g, 75%). ^{1}H NMR (C_6D_6): δ 19.10 (s, 18H, TMS), 10.08 (s, 12H, C_5Me_4), 5.94 (s, 4H, THF), −3.81 (s, 4H, THF), −9.52 (s, 12H, C_5Me_4). Crystal data for **5**: $C_{28}H_{50}OSi_2Sm$, F_w = 609.21, monoclinic, space group $P2_1/c$, a = 18.025(3), b = 11.098(2), c = 15.938(3) Å, α = 90°, β = 104.926(3)°, γ = 90°, V = 3080.6(9) Å^3, Z = 4, D_c = 1.314 g cm^{-3}, R = 0.0745, R_w = 0.1555 for 8566 independent reflections with $I > 2\sigma(I)$. The elemental analysis was measured after drying in vacuo, and then the solvent THF was removed. Anal. Calcd for $C_{24}H_{42}Si_2Sm$: C, 53.66; H, 7.88. Found: C, 52.90; H, 7.87.

X-ray Crystallographic Studies. The crystal was manipulated in the glovebox under a microscope mounted on the glovebox window and was sealed in thin-walled glass capillary. Data collection was performed at 293 K on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structure was solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. Hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance.

Polymerization. A typical polymerization procedure is given below (run 7 in Table 1): Via manipulation in a glovebox, **3** (3 mg, 5.0×10^{-6} mol) and MMAO (3.3 mL, 6.25×10^{-3} mol) were mixed in a glass pressure reactor and dissolved in cyclohexane (40 mL). The reactor was taken out from the glovebox, and then butadiene (6.75 g, 0.125 mol) was added into the solution at −20 °C. Rapid stirring of the polymerization mixture was maintained for 10 min at 50 °C. The polymerization was terminated by pouring the mixture into a large quantity of methanol containing a small amount of hydrochloric acid (ca. 0.5 M) and butylhydroxytoluene (BHT), which works as a stabilizing agent. The precipitated polymer was isolated by decantation, washed by methanol, and dried under a reduced pressure for 6 h at 70 °C.

Polymer Analysis. The microstructure of the polybutadiene products was determined by ^{1}H NMR and ^{13}C NMR spectroscopy (JNM EX-300) in $CDCl_3$. ^{1}H NMR: δ 4.8−5.2 (=CH_2 of 1,2-butadiene unit), 5.2−5.8 (−CH= of 1,4-BD unit and −CH= of 1,2-BD unit). ^{13}C NMR: δ 27.4 (1,4-*cis*-butadiene unit), 32.7 (1,4-*trans*-butadiene unit), 127.7−131.8 (1,4-butadiene unit), 113.8−114.8, and 143.3−144.7 (1,2-butadiene unit). The weight-average molecular weight (M_w), the number-average molecular weight (M_n), and the molecular weight distribution (M_w/M_n) of the polymers were measured by GPC [TOSOH HLC-8220 GPC; column, Super HZM-H × 3; temperature, 40 °C; eluent, THF; polystyrene standards].

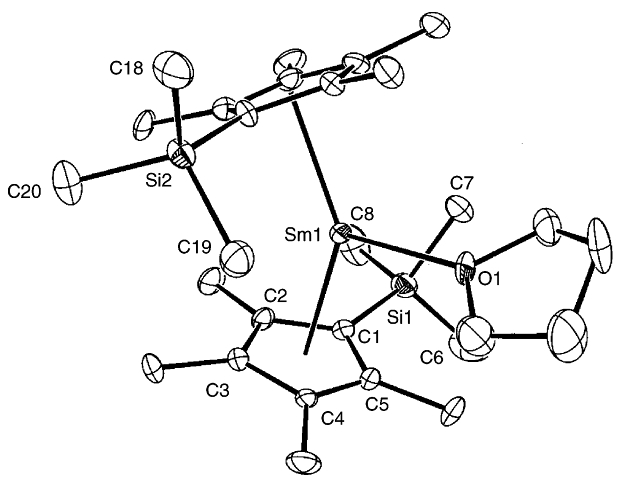
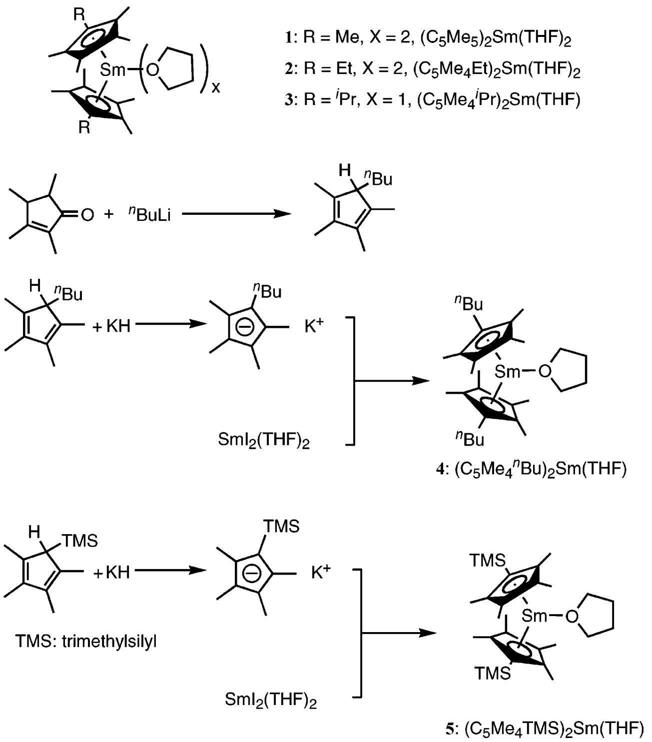


Figure 1. ORTEP drawing of **5** with hydrogen atoms omitted for clarity. Selected bond angle (deg): Cnt(1)−Sm(1)−Cnt(2) = 142.2. Selected bond distances (Å): Sm(1)−O(1) = 2.58(5), Sm(1)−C(1) = 2.742(8), Sm(1)−C(2) = 2.787(7), Sm(1)−C(3) = 2.856(8), Sm(1)−C(4) = 2.848(7), Sm(1)−C(5) = 2.770(8), Sm(1)···C(8) = 3.36, Sm(1)···C(19) = 3.66.

Scheme 1



Results and Discussion

Synthesis and Structure of Divalent Samarocene Complexes. Of the C_5Me_4R-ligated samarocene(II) complexes of the formula $(C_5Me_4R)_2Sm(THF)_x$, **1**−**3** are known compounds while **4** and **5** can be readily synthesized in a straightforward manner similar to that for **3**, as shown in Scheme 1. Complex **4** was isolated as the monosolvate form $(C_5Me_4{}^nBu)_2Sm(THF)$, which was characterized by the ^1H NMR spectrum to be free from impurities.[12] Although structural characterization and elemental analysis of complex **4** were not successful because of poor quality of the crystals, the solid-state structure of **5** was fully analyzed by crystallographic studies (Figure 1). The overall structural feature is almost the same as $(C_5Me_4{}^iPr)_2Sm(THF)$ (**3**). The (ring centroid)−Sm−(ring centroid) angle in **5** (142.2°), which is almost the same as that of **3** (141.6°), is significantly larger than the corresponding angle in $(C_5Me_5)_2Sm(THF)_2$ (**1**) (136.7°) and $(C_5Me_5)_2Sm(THF)$ (**1′**) (138.5°)[13] presumably due to larger steric bulk of the two Cp rings in **3** and **5**. The $Sm-C_5Me_4R$ bond distances in **5** (average 2.816 Å) are comparable with those of corresponding bond distances in **3** (average 2.80(3) Å) and **1′** (average 2.816(4) Å). One of the methyl groups of SiMe3 is located close to Sm (Sm···C(8), 3.36 Å vs Sm···C(19), 3.66 Å), suggesting some agostic interaction.

Polymerization. The polymerizations of butadiene catalyzed by the **1**−**5**/MMAO ($[MMAO]_0/[Sm]_0 = 100$) systems are compared in runs 1−5 of Table 1, which were carried out at 50 °C in cyclohexane with $[butadiene]_0/[Sm]_0 = 1500$. Runs 1−5 produced similar polymers in terms of molecular weight (M_n = 212 600−354 000) and relatively narrow MWDs (M_w/M_n = 1.77−1.88). However, the catalytic activity showed marked difference: **3** (TON = 17 800 butadiene-mol/(Sm-mol h)) ≫ **5** (8090) ∼ **4** (7820) > **2** (5960) > **1** (1870). It seems that the catalyst precursor having a bulky ligand shows a low catalytic activity since the monomer is difficult to attack the reaction center; however, the above trend is approximately reciprocal to the bulkiness of the substituent R. That is, the primary factor that accelerates the reaction appears to be the electron-donating ability of R rather than the steric effect. The regularity of the resulting polymer was also strongly dependent on the substituent R: **3** ∼ **5** (1,4-cis selectivity = 98.6%) > **4** (97.5%) > **2** (97.1%) > **1** (96.2%). Recently, we reported $[(C_5Me_5)_2Ln][B(C_6F_5)_4]/Al^iBu_3$ systems (Ln = Gd, Nd, Pr) as butadiene polymerization catalysts, where Gd gave a polybutadiene that possessed a higher 1,4-cis microstructure [1,4-cis selectivity at 50 °C: Gd (97.5) > Nd (91.3) > Pr (90.2); ionic radius: Gd < Nd < Pr].[14] These two results suggest that the catalyst precursor that provides crowded reaction center can control the conformation of the propagating chain end.

Overall, **3** is the best catalyst precursor among the complexes examined in the present study. To assess its catalytic activity, runs 6−8 were performed, changing the $[butadiene]_0/[Sm]_0$ value increasingly large and keeping other conditions as before. The polymerization yield of ∼100% was still obtained in 10 min when the $[butadiene]_0/[Sm]_0$ ratio was 10 000 (run 6; cf. run 3), and consequently, the TON increased to 60 000. Even though the $[butadiene]_0/[Sm]_0$ ratio was further increased to 25 000 (run 7) or as high as 150 000 (run 8), yields of polymer were satisfactory, e.g., attaining 78% in 1 h in the latter case. It is noteworthy that the 1,4-cis selectivity of polybutadiene obtained in runs 6−8 stays similar to, or a little better than, those of the polymer from run 3 while MWDs are still below 2.0. When the polymerization reaction using this catalyst system was carried out at room temperature (run 9) with other conditions similar to those of run 6, the polybutadiene was obtained in a high yield, 87% in 10 min, i.e., TON = 52 400 butadiene-mol/(Sm-mol h). In sharp contrast, the room temperature reaction catalyzed by **1**/MMAO under the same conditions afforded polybutadiene only in 12% yield (run 10).

In conclusion, the catalytic performance of the samarocene complex $(C_5Me_4R)_2Sm(THF)_x$ can be remarkably improved by simply substituting an ^iPr group for one of the methyl groups of each Cp ring, providing one of the best catalyst systems for butadiene polymerization that operate in aliphatic solvents. Their applications for related lanthanocene-based catalyst systems as well as the mechanistic aspects are now under investigation.

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Supporting Information Available: ^{1}H NMR spectra of the samarocene complexes **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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