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Stereospecific Polymerization of 1,3-Butadiene with Samarocene-Based Catalysts[1]

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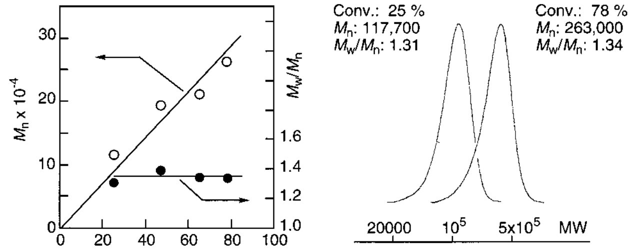
Selective 1,4-*cis* polymerization of 1,3-butadiene (BD) is of much importance, since the resulting high *cis*-poly(BD)s can find wide applications as synthetic rubbers.[3] Industrially, catalyst systems such as $TiI_4/I_2/Al(i\text{-}Bu)_3$, $CoCl_2{\cdot}Py/AlEt_2Cl/H_2O$, $Ni(OCOR)_2/AlEt_3/BF_3OEt_2$, and $NdCl_3/EtOH/Al(i\text{-}Bu)_3$ have been used for the production of poly(BD)s which have high 1,4-*cis* contents (94−98%), but the molecular weight and molecular weight distribution (MWD $\approx$ 3−4) of the resulting polymers in these systems cannot be well controlled.[4] As homogeneous catalysts which can better control molecular weight, d-block transition metal metallocene/MAO catalyst systems such as $CpTiCl_3$/MAO, Cp_2TiCl/MAO, Cp_2VCl/MAO, and Cp_2Ni/MAO have been reported. However, all these systems showed considerably lower 1,4-*cis* selectivity (79−91%).[5] We report herein an extremely active, lanthanide-based single-site catalyst system, which can effect both high 1,4-*cis* selectivity and "living" control on the molecular weight of the polymer products.

Single-component lanthanide metallocene complexes, such as $(C_5Me_5)_2LnR$ (R = H or alkyl) or $(C_5Me_5)_2Sm(THF)_2$ (**1**),[6] are known to be efficient catalysts or precatalysts for polymerization of ethylene and methyl methacrylate in a living way to give monodispersed high molecular weight polymers in good yields.[7] However, these complexes are almost completely unreactive for polymerization of dienes due to easy formation of stable η^3-allyl complexes, which appear to be somewhat of a thermodynamic sink.[7a] For example, the reaction of **1** with BD yields a stable dimeric samarium(III) μ-allyl complex, $[(C_5Me_5)_2Sm(\mu\text{-}\eta^3\text{-}CH_2CHCHCH_2\text{-})]_2$, which is not active for polymerization of BD.[8] We have found out, however, that when a cocatalyst such as MMAO (MMAO is modified methylaluminoxane containing isobutylaluminoxane) is present, the lanthanide metallocene complex **1** can efficiently polymerize BD.

Thus, the divalent samarium complex **1** with MMAO as a cocatalyst ([MMAO]/[**1**] = 200) induced rapid polymerization of BD at 50 °C in toluene, with the conversion of 2500 equiv of BD reaching to 65% in 5 min (TON: 20 000 BD-mol/Sm-mol·h) (run 1, Table 1).[9] The resulting poly(BD) possesses a very high 1,4-*cis* microstructure (98.8%),[10] high molecular weight (M_n = 400 900), and narrow MWD (M_w/M_n = 1.82).[10] The samarocene(III) methyl complex $(C_5Me_5)_2Sm(Me)(THF)_2$ (**2**)[11] was also active for the polymerization of BD when treated with MMAO, giving selectively 1,4-*cis*-poly(BD) (98.0%) with high molecular weight (M_n = 1 257 800) and narrow MWD (M_w/M_n = 1.69) (run 2, Table 1). The combination of the samarocene(III) chloride complex $(C_5Me_5)_2Sm(Cl)(THF)$ (**3**)[12] with MMAO showed no activity under the same conditions (run 3, Table 1), which is in contrast to what has been previously observed in the case of group 4 metallocene chloride/MAO systems.[13]



(a) (b)

Figure 1. Plots of M_n and M_w/M_n vs BD conversion for polymerization with $\mathbf{1}/Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$ in toluene at 50 °C under N_2. $[BD]_0$ = 2.5 M (2.5 × 10^{-2} mol); $[\mathbf{1}]_0$ = 0.001 M, (1.0 × 10^{-5} mol); $[Al(i\text{-}Bu)_3]_0/[\mathbf{1}]_0$ = 10; $[B]_0/[\mathbf{1}]_0$ = 1.

In place of MMAO, $Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$[14] can also be used as a cocatalyst for **1**. The three-component catalyst system effects smooth polymerization of BD without an induction period. The M_n of the resulting poly(BD) increases in direct proportion to monomer conversion, and at every conversion the microstructure of the poly(BD) has constantly high 1,4-*cis* content (94.2−95.0%) and narrow MWD (M_w/M_n = 1.31−1.39) (Figure 1a,b). Thus, the present catalytic system is "living" to a large extent. Other alkylaluminum compounds, such as $AlMe_3$ and $AlEt_3$, are also effective and have great influence on the microstructure of the poly(BD) products (runs 1−3, Table 2), although the catalytic activity (TON: 10 000−13 900) is not much affected.

Since the reaction of **1** with excess $AlMe_3$ has been well-known to give $(C_5Me_5)_2Sm[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2Sm(C_5Me_5)_2$ (**4**),[11] which appears to be a complex closely related to our present catalytic system, its reactivity toward BD was also examined. Complex **4** or $\mathbf{4}/[Ph_3C][B(C_6F_5)_4]$ did not show activity for the polymerization.[15] However, addition of a slight excess (≥1 equiv) of $AlMe_3$ to $\mathbf{4}/[Ph_3C][B(C_6F_5)_4]$ (i.e., $\mathbf{4}/AlMe_3/[Ph_3C][B(C_6F_5)_4]$) brought about rapid polymerization. Similar to what was observed in the case of $\mathbf{1}/AlR_3/[Ph_3C][B(C_6F_5)_4]$, the kind of alkylaluminum in the $\mathbf{4}/AlR_3/[Ph_3C][B(C_6F_5)_4]$

Table 1. Polymerization of 1,3-Butadiene with Samarocene/MMAO[a]

					microstructure[c]					
run	samarocene	time	yield (%)	TON[b]	1,4-*cis* (%)	1,4-*trans* (%)	1,2 (%)	M_w[d]	M_n[d]	M_w/M_n[d]
1	**1**	5 min	65	20 000	98.8	0.5	0.7	730 900	400 900	1.82
2	**2**	15 min	86	8 900	98.0	0.9	1.1	2 125 500	1 257 800	1.69
3	**3**	24 h	no polymerization							

[a] Polymerization conditions: in toluene; T_p = 50 °C; $[BD]_0$ = 2.5 M (2.5 × 10^{-2} mol); $[Sm]_0$ = 0.001 M (1.0 × 10^{-5} mol); $[MMAO]_0/[Sm]_0$ = 200. [b] TON = BD-mol/Sm-mol·h. [c] Measured by ^1H NMR and ^{13}C NMR in $CDCl_3$. [d] Determined by GPC against polystyrene standard.

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Table 2. Polymerization of 1,3-Butadiene with Samarocene/AlR_3/$[Ph_3C][B(C_6F_5)_4]$[a]

					microstructure[c]					
run	samarocene	AlR_3	yield (%)	TON[b]	1,4-*cis* (%)	1,4-*trans* (%)	1,2 (%)	M_w[d]	M_n[d]	M_w/M_n[d]
1	**1**[e]	$AlMe_3$	88	13 900	51.2	45.9	2.9	515 200	310 400	1.66
2	**1**[e]	$AlEt_3$	65	10 000	70.0	27.1	2.9	173 800	123 000	1.41
3	**1**[e]	$Al(i\text{-}Bu)_3$	78	12 200	95.0	2.2	2.8	352 500	263 000	1.34
4	**4**[f]	$AlMe_3$	95	29 100	57.5	39.2	3.3	433 900	275 800	1.57
5	**4**[f]	$AlEt_3$	98	29 600	83.8	12.9	3.3	670 300	378 100	1.77
6	**4**[f]	$Al(i\text{-}Bu)_3$	94	28 400	90.0	6.8	3.2	670 000	429 500	1.56
7	**4**[g]	$Al(i\text{-}Bu)_3$	65	320	>99.5	<0.1	0.4	1 300 900	702 900	1.85

[a] Polymerization conditions: in toluene; $[BD]_0 = 2.5$ M (2.5×10^{-2} mol); $[Sm]_0 = 0.001$ M (1.0×10^{-5} mol); $[B]_0/[Sm]_0 = 1$. Runs 1−6: $T_p = 50$ °C unless otherwise noted. [b] TON = BD-mol/Sm-mol·h. [c] Measured by ^{1}H NMR and ^{13}C NMR in $CDCl_3$. [d] Determined by GPC against polystyrene standard. [e] $[AlR_3]_0/[Sm]_0 = 10$, polymerization time = 10 min. [f] $[AlR_3]_0/[Sm]_0 = 3$, polymerization time = 5 min. [g] Polymerization was carried out at −20 °C for 5 h; $[AlR_3]_0/[Sm]_0 = 3$.

system showed great influence on the microstructure of the poly(BD) products but did not affect the catalytic activity (TON: 28 400−29 600) (runs 4−6, Table 2). It is also noteworthy that the **4**/AlR_3/$[Ph_3C][B(C_6F_5)_4]$ system is more active than **1**/AlR_3/$[Ph_3C][B(C_6F_5)_4]$ system (runs 1−3 vs 4−6, Table 2) and can efficiently induce the polymerization even at low temperature. Moreover, when the polymerization reaction was carried out at low temperature, a dramatic increase in the 1,4-*cis* content of the poly(BD) products has been observed. For example, when **4**/$Al(i\text{-}Bu)_3$/$[Ph_3C][B(C_6F_5)_4]$ was used as a catalyst, poly(BD) product with 1,4-*cis* content of as high as >99.5% has been obtained at −20 °C (run 7, Table 2).

In summary, the stereospecific polymerization of BD with a lanthanocene-based system has been achieved for the first time by using MMAO or AlR_3/$[Ph_3C][B(C_6F_5)_4]$ as a cocatalyst. Extremely high 1,4-*cis* selectivity, well-controlled polymerization behavior ("living" polymerization), and high activity have been accomplished with this new catalytic system. Further studies on the mechanistic aspects and on the polymerization of other monomers with this and related lanthanocene-based systems are under progress.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of polybutadiene with 1,4-*cis* content higher than 99.5% (run 7, Table 2). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) This work was presented in part at the following meetings. (a) The 76th National Meeting of the Chemical Society of Japan, Yokohama, Japan, March 1999; paper 2H105. (b) The 48th Annual Meeting of the Society of Polymer Science, Kyoto, Japan, May 1999; paper IIPa023: Kaita, S.; Hou, Z.; Wakatsuki, Y. *Polym. Prepr. Jpn.* **1999**, *48*, 221.

(2) Special Postdoctoral Researcher under the Basic Science Program of RIKEN.

(3) For a review, see: Porri, L.; Giarrusso, A. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 4, pp 53−108.

(4) For examples, see: (a) Saltman, W. M.; Link, T. H. *Ind. Eng. Chem. Prod. Res. Dev.* **1964**, *3*, 199. (b) Gippin, M. *Ind. Eng. Chem. Prod. Res. Dev.* **1962**, *1*, 32. (c) Ueda, K.; Yoshimoto, T.; Hosono, J.; Maeda, K.; Matsumoto, T. *Kogyo Kagaku Zasshi* **1963**, *66*, 1103. (d) Yang, J.; Hu, J.; Feng, S.; Pan, E.; Xie, D.; Zhong, C.; Ouyang, J. *Sci. Sin. (Engl. Ed.)* **1980**, *23*, 734. (e) Hsieh, H. L.; Yeh, H. C. *Rubber Chem. Technol.* **1984**, *58*, 117.

(5) (a) Oliva, L.; Longo, P.; Grassi, A.; Ammendola, P. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 519. (b) Ricci, G.; Italia, S.; Giarrusso, A.; Porri, L. *J. Organomet. Chem.* **1993**, *451*, 67. (c) Ricci, G.; Bosisio, C.; Porri, L. *Makromol. Chem., Rapid Commun.* **1996**, *17*, 781. (d) Ricci, G.; Panagia, A.; Porri, L. *Polymer* **1996**, *37*, 363. (e) Endo, K.; Matsuda, Y.; Aoki, S. *Polym. Prepr. Jpn.* **1993**, *42*, 282.

(6) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941.

(7) (a) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091. (b) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (c) Yasuda, H.; Yamamoto, H.; Yokota, K.; Miyake, S.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 4908. (d) Yasuda, H.; Furo, M.; Yamamoto, H.; Miyake, S.; Kibino, N. *Macromolecules* **1992**, *25*, 5115. (e) Yamashita, M.; Ihara, E.; Yasuda, H. *Macromolecules* **1995**, *29*, 1798.

(8) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.

(9) The catalytic activity was strongly dependent on the [MMAO]/[**1**] ratio. The polymerization did not occur at the ratio of [MMAO]/[**1**] < 50. When more than 500 equiv of MMAO was used, the catalytic activity decreased compared to that in the case of [MMAO]/[**1**] = 200. The use of PMAO (ordinary methylaluminoxane) instead of MMAO gave a polymer with lower 1,4-*cis* content under the same conditions.

(10) The microstructure of the poly(BD) products was measured 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-BD 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*-BD unit), 32.7 (1,4-*trans*-BD unit), 127.7−131.8 (1,4-BD unit), 113.8−114.8 and 143.3−144.7 (1,2-BD 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 [Shodex GPC System-11; detector, RI (RI-71); column, GPC KF-508L × 2; temperature, 40 °C; eluent, THF; polystyrene standard].

(11) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423.

(12) Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614.

(13) It has been well-known that the reaction of group 4 metallocene chlorides with MAO generates the corresponding metallocene alkyl cations which are similarly active as those formed in the metallocene alkyl/MAO systems. For examples, see: (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (c) Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: Weinheim, 1996. The fact that the $(C_5Me_5)_2Sm(Cl)(THF)$/MMAO system shows no activity for the polymerization of BD might be due to the difficulty of alkylation of $(C_5Me_5)_2Sm(Cl)(THF)$ by MMAO under the present conditions.

(14) (a) Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1991**, *10*, 840. (b) Ewen, J. A.; Elder, M. J.; Jones, R. L.; Haspeslagh, L.; Atwood, J. L.; Bptt, S. G.; Robinson, K. *Makromol. Chem., Macromol. Symp.* **1991**, *48/49*, 253. (c) Chien, J. C. W.; Tsai, W. M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570. (d) Pellecchia, C.; Longo, P.; Proto, A.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 265.

(15) It was established that none of **1**/$Al(i\text{-}Bu)_3$, **1**/$[Ph_3C][B(C_6F_5)_4]$, or $Al(i\text{-}Bu)_3$/$[Ph_3C][B(C_6F_5)_4]$ showed activity under the same conditions.

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