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Random- and Block-Copolymerization of 1,3-Butadiene with Styrene Based on the Stereospecific Living System: $(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2/Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$[1]

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Random-copolymers of 1,3-butadiene (butadiene) and styrene are utilized commercially as styrene−butadiene rubbers (SBR). Being produced via radical or anionic polymerization, the stereocontrol of the polybutadiene microstructures has not been possible in these systems.[3,4] Since 1,4-*cis*-polybutadiene microstructure is essential in butadiene rubber (BR), a number of works have been devoted to the synthesis of SBR with high 1,4-*cis*-polybutadiene microstructures (e.g., $Co(acac)_2/AlEt_2Cl/H_2O$, $Ni(OCOR)_2/AlEt_3/BF_3OEt_2$, $Ln(OCOR_3)/Al(i\text{-}Bu)_3/AlEt_2Cl$ (Ln = Pr, Nd, Gd, Dy, and Yb), $Nd(OCOR_3)/Al(i\text{-}Bu)_3/CCl_4$, and $CpTiCl_3/MAO$) (1,4-*cis* selectivity = 73−94%).[5] Though this aim has been partially fulfilled in some systems, the fatal problem of the polymers obtained by these transition metal catalysts is their very low molecular weights ($M_w \sim 10^4$) and broad molecular weight distributions (MWDs) ($M_w/M_n \approx 2-10$).

Herein, we report that the Sm(III)/Al(III) heterobimetallic complex $(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2$ (**1**),[6] in combination with $Al(i\text{-}Bu)_3$ and $[Ph_3C][B(C_6F_5)_4]$,[7] can act as an excellent catalyst system for the 1,4-*cis* stereospecific living homopolymerization of butadiene (1,4-*cis* selectivity = 99.0%, $M_w/M_n = 1.20-1.23$). As an immediate application of the stereospecific and living nature of this system, block-copolymerization of butadiene and styrene has been performed and thereby block-copolymer with 1,4-*cis*-polybutadiene microstructure as high as 99.0% has been realized. Furthermore, we have demonstrated that random butadiene−styrene copolymers with high contents of the 1,4-*cis*-polybutadiene microstructure (up to 95.1%), as well as high molecular weights ($M_w > 10^5$) and relatively narrow MWDs ($M_w/M_n = 1.41-2.23$), have been achieved for the first time. Although the performance was not so good as in the present system, a similar Sm-catalyzed system for the "living" stereospecific homopolymerization of butadiene has been described in our previous paper.[8] Because of rather low activity toward styrene of the previous catalyst, however, the random copolymerization of butadiene−styrene is useful only in the present catalytic system.

As shown in Figure 1a, the $\mathbf{1}/Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$ system induced a smooth polymerization of butadiene in toluene at −20 °C ($[\text{butadiene}]_0 = 1.0$ M; $[\text{butadiene}]_0/[\mathbf{1}]_0 = 200$; $[Al(i\text{-}Bu)_3]_0/[\mathbf{1}]_0 = 3$; $\{[Ph_3C][B(C_6F_5)_4]\}_0/[\mathbf{1}]_0 = 1$) without an induction period. The conversion reached to 95% in 20 min, and the MWDs of the resulting polymers remained narrow throughout the reaction ($M_w/M_n = 1.20-1.23$) (Figure 1b).[9,10] To examine the living nature of this polymerization system, a second feed of butadiene was added to the reaction mixture when most of the initial charge of butadiene had been consumed (95% conversion in 20 min). After the second addition, a smooth second-phase polymerization took place again, and the conversion reached to 183% (83% consumption of the added butadiene) in an additional 20 min (Figure 1a). The M_n increased in direct proportion to monomer conversion throughout the two-step polymerization reactions, while the MWDs remained unimodal and narrow ($M_w/M_n = 1.20-1.24$) (Figure 1b,c). These results show that the $\mathbf{1}/Al(i\text{-}Bu)_3/$

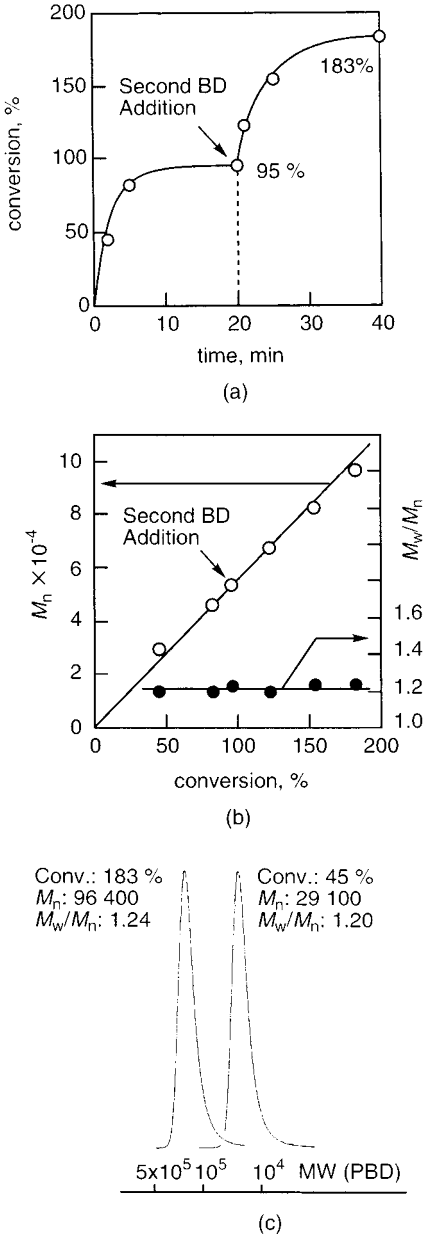

Figure 1. Monomer addition experiment for polymerization of butadiene with $\mathbf{1}/Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$ in toluene at −20 °C. $[\text{butadiene}]_0 = [\text{butadiene}]_{add} = 1.0$ M (1.0×10^{-2} mol); $[\mathbf{1}]_0 = 0.005$ M (5.0×10^{-5} mol); $[Al(i\text{-}Bu)_3]_0/[\mathbf{1}]_0 = 3$; $\{[Ph_3C][B(C_6F_5)_4]\}_0/[\mathbf{1}]_0 = 1$. The M_w, M_n, and M_w/M_n were determined by GPC against polybutadiene standards.

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Table 1. Random-Copolymerization of 1,3-Butadiene and Styrene with 1/Al(*i*-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$]^a

	styrene in feed			microstructure			styrene content in copolymer			
run	(mol %)	time (h)	yield (%)	1,4-*cis* (%)	1,4-*trans* (%)	1,2 (%)	(mol %)^b	M_w ^{c}	M_n ^{c}	M_w/M_n ^{c}
1	40	0.5	21	94.6	4.4	1.0	4.6	142 000	101 000	1.41
2	50	1	22	95.1	3.9	1.0	7.2	124 800	78 600	1.59
3	60	6	20	91.7	7.2	1.1	11.4	124 200	73 900	1.69
4	70	12	23	87.4	11.7	0.9	19.1	67 800	38 700	1.75
5	80	50	21	80.3	18.7	1.0	33.2	52 200	23 400	2.23

^{a} Polymerization conditions: in toluene; $T_p = 50$ °C; [butadiene]$_0$ + [styrene]$_0$ = 6.0 M (3.0×10^{-2} mol); [**1**]$_0$ = 0.006 M (3.0×10^{-5} mol); [Al(*i*-Bu)$_3$]$_0$/[**1**]$_0$ = 3; {[Ph$_3$C][B(C$_6$F$_5$)$_4$]}$_0$/[**1**]$_0$ = 1. ^{b} Measured by ^{1}H NMR and ^{13}C NMR in CDCl$_3$. ^{c} Determined by GPC against polystyrene standard.

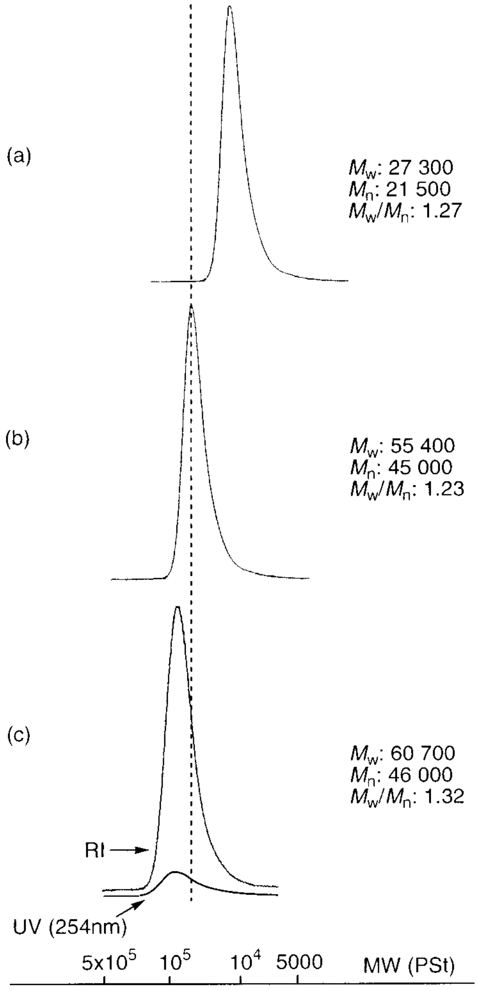

Figure 2. MWD curves obtained in block-copolymerization of butadiene and styrene with **1**/Al(*i*-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] in toluene at −20 °C. [butadiene]$_0$ = [styrene]$_0$ = 0.5 M (5.0×10^{-3} mol); [**1**]$_0$ = 0.005 M (5.0×10^{-5} mol); [Al(*i*-Bu)$_3$]$_0$/[**1**]$_0$ = 3; {[Ph$_3$C][B(C$_6$F$_5$)$_4$]}$_0$/[**1**]$_0$ = 1. The M_w, M_n, and M_w/M_n were determined by GPC against polystyrene standards throughout the first and second block.

[Ph$_3$C][B(C$_6$F$_5$)$_4$] system is an excellent living system for the polymerization of butadiene.[11] Moreover, at every conversion the resultant polybutadiene possesses a constantly very high 1,4-*cis* microstructure (e.g., 1,4-*cis*:1,4-*trans*:1,2 = 99.0:0.6:0.4 at 183% conversion), showing that this living polymerization reaction is 1,4-*cis* stereospecific.[12]

The reactivity of the living end group in the butadiene polymerization toward styrene monomer was then investigated.[13] At first, butadiene was polymerized with **1**/Al(*i*-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] in toluene at −20 °C with [butadiene]$_0$ = 0.5 M and [butadiene]$_0$/[**1**]$_0$ = 100. Under this condition, the monomer conversion reached to 55% in 1 min and to 98% in 10 min. The MWDs remained unimodal and narrow (M_w/M_n = 1.27, 1 min; 1.23, 10 min), while the M_n increased with increase of the monomer conversion ($M_n = 21\,500 \rightarrow 45\,000$) (Figure 2a,b).[14] Styrene monomer was then added to the reaction mixture ([styrene]$_0$/[**1**]$_0$ = 100), and the mixture was stirred at −20 °C for an additional 5 h to yield a butadiene−styrene copolymer (styrene content = 5.5 mol %) with a high 1,4-*cis*-polybutadiene microstructure (99.0%) as determined by ^{1}H NMR and ^{13}C NMR spectroscopy. The MWD curve of the copolymer was unimodal and narrow (M_w/M_n = 1.32) and shifted to a higher molecular weight region (M_n = 46 000).[14] The UV (254 nm)-detected MWD curve, which is sensitive to the styrene unit, was in harmony with the RI-detected MWD curve (Figure 2c). These results suggest that the resulting polymer is not a mixture of the homopolymers but a true butadiene−styrene block-copolymer. It should be mentioned that, to our knowledge, the most successful highly *cis*-butadiene−styrene block-copolymers have been those produced by [(η^3-allyl)(trifluoroacetato)-nickel]/chloranil and reported to have 1,4-*cis*-polybutadiene microstructures of at most 89.5%.[15]

When the copolymerization reactions of butadiene with styrene were carried out at various initial monomer feed ratios with **1**/Al(*i*-Bu)$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] in toluene at 50 °C, random butadiene−styrene copolymers (styrene content = 4.6−33.2 mol %) with high contents of the 1,4-*cis*-polybutadiene microstructure (95.1−80.3%), high molecular weights (M_w = 142 000−52 200; M_n = 101 000−23 400), and relatively narrow MWDs (M_w/M_n = 1.41−2.23) were obtained (Table 1).[16] The polymer yields were deliberately controlled at a low level in order to evaluate the monomer reactivity ratios (i.e., $r_{\text{butadiene}} = 16.9$ and $r_{\text{styrene}} = 0.4$) by applying the Fineman−Ross method.[17] The polybutadiene microstructure varied with styrene content in the copolymer, it can be explained on the basis of the concept of backbiting coordination for the 1,4-*cis* selectivity mechanism in which the penultimate styrene unit inhibits the 1,4-*cis* control of the terminal butadiene unit.[18] The MWD value increased with increasing styrene content in copolymer possibly owing to the lack of living character in the incorporation of styrene. The ^{13}C NMR spectroscopy spectra of the polymer products showed typical signals of the random butadiene−styrene sequences (e.g., 25.2 and 35.8 ppm for 1,4-*cis*-butadiene−styrene sequence; 30.8 and 40.2 ppm for 1,4-*trans*-butadiene−styrene sequence),[18b−d] while the RI-detected MWD curves were unimodal and in harmony with the UV (254 nm)-detected MWD curves. These results all suggest that the copolymer products obtained in these reactions are random butadiene−styrene copolymers and not mixtures of the homopolymers.

In summary, we have shown that the block-copolymerization of butadiene and styrene with high 1,4-*cis*-polybutadiene microstructure is possible by use of $(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2/Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$, because this system can effect an excellent living and 1,4-*cis* stereospecific polymerization of butadiene itself. Importantly, this catalyst system can also give random butadiene−styrene copolymers with relatively high contents of the 1,4-*cis*-polybutadiene microstructure with great improvement in molecular weight as compared to the known related systems. Further studies on the application of this catalyst system to the polymerization and copolymerization of other monomers are under progress.

Supporting Information Available: The ^1H NMR and ^{13}C NMR spectra of the 1,4-*cis*-polybutadiene in Figure 1 and the ^{13}C NMR spectrum of a random-copolymer of 1,3-butadiene and styrene (run 4, Table 1). 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 48th Symposium of the Society of Polymer Science, Niigata, Japan, Oct 1999; paper IIB01: Kaita, S.; Hou, Z.; Wakatsuki, Y. *Polym. Prepr. Jpn.* **1999**, *48*, 221. (b) The 49th Annual Meeting of the Society of Polymer Science, Nagoya, Japan, May 2000; paper IIE07: Kaita, S.; Hou, Z.; Wakatsuki, Y. *Polym. Prepr. Jpn.* **2000**, *49*, 211.

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

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(5) (a) Gehrke, K.; Harwart, M. *Plast. Kautsch.* **1993**, *40*, 356. (b) Anzai, S.; Irako, K.; Onishi, A.; Furukawa, J. *Kogyo Kagaku Zasshi* **1969**, *72*, 2081. (c) Kaita, S.; Kobayashi, E.; Sakakibara, S.; Aoshima, S.; Furukawa, J. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34*, 3431. (d) Oehme, A.; Gebauer, U.; Gehrke, K. *Macromol. Rapid Commun.* **1995**, *16*, 563. (e) Zambelli, A.; Proto, A.; Longo, P.; Oliva, P. *Macromol. Chem. Phys.* **1994**, *195*, 2623.

(6) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423. Although this compound was isolated as a tetrameric form $(C_5Me_5)_2Sm[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2Sm(C_5Me_5)_2$ in solid state, it has an equilibrium with the dimeric form "$(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2$" in solution. For simplicity, the dimeric form "$(C_5Me_5)_2Sm(\mu\text{-}Me)_2AlMe_2$" is used in this paper.

(7) The reaction of **1** with $[Ph_3C][B(C_6F_5)_4]$ gave a Sm(III) cationic complex $[(C_5Me_5)_2Sm][B(C_6F_5)_4]$, but this complex did not induce the polymerization of butadiene. Addition of a slight excess (≥2 equiv) of $Al(i\text{-}Bu)_3$ brought about rapid polymerization, suggesting that an alkylaluminum species must be involved in the active species. Details will be reported elsewhere in due course.

(8) Kaita, S.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 9078.

(9) The MWD became broader when the reaction was carried out under a higher monomer concentration conditions (e.g., $M_w/M_n = 1.85$ at $[\text{butadiene}]_0 = 2.5$ M; $[\text{butadiene}]_0/[\mathbf{1}]_0 = 2500$). See ref 8.

(10) 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), UV (UV-41); column, GPC KF-508L × 2; temperature, 40 °C; eluent, THF]. The calibration curves were established with polybutadiene standards.

(11) The number of the initiator efficiency was roughly estimated to be 20.0% by the comparison between the observed M_n values and the calculated values.

(12) The microstructure of the resulting polybutadienes was measured by ^1H NMR and ^{13}C NMR spectroscopy (JNM EX-300) in $CDCl_3$ in a similar way as previously described in ref 8.

(13) $\mathbf{1}/Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$ promoted the polymerization of styrene in toluene at 50 °C ($[\text{styrene}]_0 = 3.0$ M, $[\text{styrene}]_0/[\mathbf{1}]_0 = 500$, yield = 16% for 24 h, $M_n = 7900$, $M_w/M_n = 1.54$, $rr = 61\%$), but the polymerization did not exhibit a living nature.

(14) The M_w, M_n, and M_w/M_n were determined by GPC against polystyrene standards.

(15) Hadjiandreou, P.; Julémont, M.; Teyssié, P. *Macromolecules* **1984**, *17*, 2455.

(16) A typical copolymerization procedure is given below (run 2, Table 1). **1** (3.0×10^{-5} mol, 17 mg), $Al(i\text{-}Bu)_3$ (9.0×10^{-5} mol, 0.9 mL of 0.1 M in toluene), and $[Ph_3C][B(C_6F_5)_4]$ (3.0×10^{-5} mol, 28 mg) were placed in a glass pressure reactor and dissolved in 1.0 mL of toluene in a glovebox. The reaction was taken out from the glovebox, and then butadiene (1.5×10^{-2} mol, 0.81 g) and styrene (1.5×10^{-2} mol, 1.7 mL) were added into the solution at −78 °C. The total volume of the reaction mixture was adjusted to 5.0 mL. Rapid stirring of the polymerization mixture was maintained at 50 °C for 1 h. 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) as a stabilizer agent. The precipitated polymer was isolated by decantation, washed by methanol, and then dried under a reduced pressure at 60 °C for 12 h.

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