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Butadiene Polymerization Catalyzed by Lanthanide Metallocene−Alkylaluminum Complexes with Cocatalysts: Metal-Dependent Control of 1,4-Cis/Trans Stereoselectivity and Molecular Weight

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ABSTRACT: A series of bimetallic complexes composed of lanthanide metallocene and trimethylaluminum, $Cp^*_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2LnCp^*_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$, Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Tm, Yb, Lu), were prepared, and the ability to catalyze polymerization of butadiene in the presence of cocatalysts, AlR_3 (R = Me, ^{i}Bu) and $[Ph_3C][B(C_6F_5)_4]$, was studied as a function of the 11 different lanthanide metal species and the kind of alkylaluminum in the cocatalyst. Both catalytic activity and microstructure of polybutadiene depended strongly on the kind of lanthanide metal and the trialkylaluminum. The Gd complex in combination with $Al^i Bu_3/[Ph_3C][B(C_6F_5)_4]$ was extremely active and gave perfectly 1,4-cis regulated polybutadiene at −40 °C. In contrast, the Ce complex with almost similar cocatalysts, $AlMe_3/[Ph_3C][B(C_6F_5)_4]$, yielded polybutadiene having a very high content of 1,4-trans microstructure (1,4-trans selectivity = 93.8%). With the Al/Ln ratio was 3−5, the polymerization systems, in which the alkylaluminum worked as an activator, showed somewhat living-like nature; the M_n of the resulting polybutadiene increased in proportion to monomer consumption, while the molecular weight distribution stayed narrow throughout the reactions. In the presence of a large amount of monomer, molecular weight of polybutadiene was conveniently controlled by additional excess alkylaluminum, which functioned as a chain transfer agent.

Introduction

During the past decade, homogeneous “single-site” catalysts have attracted considerable interest in the area of butadiene polymerization because they can control molecular weight, molecular weight distribution (MWD), and stereoselectivity of the polymer in a way that conventional heterogeneous Ziegler−Natta catalysts are unable to achieve. Most of these complexes are d-block transition metal metallocene or half-metallocene derivatives, e.g., $CpTiCl_3$/methylaluminoxane (MAO) ($Cp = \eta^5\text{-}C_5H_5$), which produce polybutadiene with relatively high 1,4-cis selectivity and narrow MWD.[1−8] In contrast to ethylene polymerization, in which lanthanide metallocene−alkyl species alone can be a substitute for Cp_2MCl_2/MAO (M = group IV metals) type Kaminsky catalysts, metallocenes of f-block trivalent metals are almost completely invalid for the homopolymerization of butadiene due to the easy formation of the relatively stable metallocene−η^3-allyl complexes.[9,10] Since 1999, however, we have developed lanthanide metallocene-based complexes that can initiate butadiene polymerization, the success of which owes largely to the use of appropriate cocatalysts. An example of such catalyst/cocatalyst mixture that motivated us to initiate the present work is a combination of $Cp^*_2Sm[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2SmCp^*_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$), with two cocatalysts, Al^iBu_3 and $[Ph_3C][B(C_6F_5)_4]$,[11] which catalyzes living-like polymerization to give high yields of polybutadiene with an excellent 1,4-cis stereospecificity (1,4-cis selectivity = 99.0%, M_w/M_n = 1.20−1.23).[12] On investigating a similar Gd complex, we successfully isolated the cationic complex $[Cp^*_2Gd][B(C_6F_5)_4]$, which in combination with Al^iBu_3 showed extremely high catalytic activity and produced perfectly 1,4-cis-regulated (>99.9%) polybutadiene at −78 °C.[13] These observations prompted us to investigate in detail the central metal influence in this catalytic system. We have therefore prepared Ce, Tb, Dy, Ho, Tm, Yb, and Lu complexes of the type $Cp^*_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2LnCp^*_2$. Using this series of 11 different lanthanide-complex analogues, including Pr, Nd, Sm, and Gd complexes communicated previously, we have systematically compared their catalytic behavior toward butadiene polymerization under precisely the same reaction conditions. The cocatalysts were a combination of AlR_3 (R = ^{i}Bu, Me) and $[Ph_3C][B(C_6F_5)_4]$, the role of the latter being apparently in situ formation of cationic species $[Cp^*_2Ln][B(C_6F_5)_4]$[13] (Scheme 1).

Scheme 1

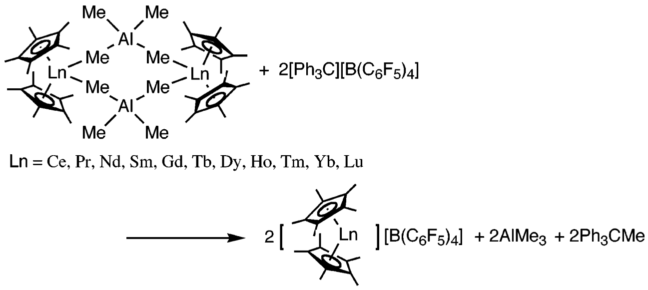

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Table 1. Polymerization of 1,3-Butadiene with $Cp^*_2Ln[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2LnCp^*_2/Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$[a]

			microstructure[b]				
run	lanthanide	yield (%)	1,4-cis (%)	1,4-trans (%)	1,2 (%)	M_n[c]	M_w/M_n[c]
1	Ce	15	38.8	59.8	1.4	12 800	1.24
2	Pr	28	55.3	43.9	0.8	22 800	1.27
3	Nd	63	65.9	32.5	1.6	40 100	1.24
4	Sm	~100	86.0	13.2	0.8	59 800	1.36
5	Gd	~100	97.3	2.0	0.7	82 500	1.32
6	Tb	~100	96.2	3.0	0.8	96 400	1.39
7	Dy	~100	95.3	2.9	1.8	94 600	1.53
8	Ho	~100	96.6	1.6	1.8	108 900	1.32
9	Tm	~100	87.5	4.7	7.8	98 700	1.58
10	Yb	no					
11	Lu	54	87.7	2.5	9.8	95 800	1.66
12[d]	Gd	~100	>99.9			113 700	1.70

[a] Conditions: in toluene; total volume = 20 mL; polymerization temperature = 25 °C; time = 15 min; butadiene = 0.54 g (1×10^{-2} mol); Ln = 5×10^{-5} mol; $[Al^iBu_3]_0/[Ln]_0 = 5$; $\{[Ph_3C][B(C_6F_5)_4]\}_0/[Ln]_0 = 1$. [b] Measured by ^1H NMR and ^{13}C NMR in $CDCl_3$. [c] Determined by gel permeation chromatography vs polystyrene standards. [d] Polymerization temperature = −40 °C; time = 5 h.

Table 2. Polymerization of 1,3-Butadiene with $Cp^*_2Gd[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2GdCp^*_2/Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$[a]

				microstructure[b]				
run	$[butadiene]_0/[Gd]_0$	time	yield (%)	1,4-cis (%)	1,4-trans (%)	1,2 (%)	M_n[c]	M_w/M_n[c]
1[d]	10 000	15 min	~100	98.6	0.1	1.3	699 700	2.17
2[e]	100 000	6 h	88	98.6	0.2	1.2	818 200	2.00
3[f]	500 000	20 h	88	98.8	0.1	1.1	788 200	1.70

[a] Conditions: in toluene; polymerization temperature = 25 °C; $\{[Ph_3C][B(C_6F_5)_4]\}_0/[Gd]_0 = 1$. [b] Measured by ^1H NMR and ^{13}C NMR in $CDCl_3$. [c] Determined by gel permeation chromatography vs polystyrene standards. [d] Total volume = 15 mL; butadiene = 2.70 g (0.05 mol); Gd = 5.0×10^{-6} mol; $[Al^iBu_3]_0/[Gd]_0 = 25$. [e] Total volume = 45 mL; butadiene = 6.75 g (0.125 mol); Gd = 1.25×10^{-6} mol; $[Al^iBu_3]_0/[Gd]_0 = 250$. [f] Total volume = 400 mL; butadiene = 67.5 g (1.25 mol); Gd = 2.5×10^{-6} mol; $[Al^iBu_3]_0/[Gd]_0 = 1200$.

Results and Discussion

Preparation of $Cp^*_2Ln[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2LnCp^*_2$ Complexes. The Sm complex $Cp^*_2Sm[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2SmCp^*_2$ was first isolated by Evans et al. from the reaction of the divalent samarocene $SmCp^*_2(THF)_2$ and $AlMe_3$.[14] In our previous communication,[13] we described a more general synthetic route to this type of complexes starting from the reaction of $LnCl_3$ with 2 equiv of Cp*Li, addition of MeLi to the resulting $Cp^*_2LnCl_2Li$, followed by treatment with $AlMe_3$ (Ln = Pr, Nd, Sm, Gd). Applying this methodology, we have newly prepared similar complexes in which Ln = Ce, Tb, Dy, Ho, Tm, Yb, and Lu as described in the Experimental Section. Aside from radioactive Pm, we did not try to prepare the La analogue. Similar complexes of Eu could not be obtained by this procedure mainly because of poor solubility of the intermediate complexes.

Polymerization of Butadiene Using Al^iBu_3 as the Alkylaluminum Component. None of the Ln(III)−Al bimetallic complexes $Cp^*_2Ln[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2LnCp^*_2$ induce polymerization of butadiene. Only when the complex is successively treated with an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ and then with 3−5 M excess Al^iBu_3 does the mixture initiate polymerization with the exception of the Yb complex, which was totally inactive. Table 1 summarizes the results of polymerization carried out in toluene at 25 °C ($[butadiene]_0/[Ln]_0 = 200$). The polybutadienes formed possessed high molecular weights (number-average molecular weight: $M_n = 108\,900-12\,800$) and relatively narrow MWDs ($M_w/M_n = 1.24-1.66$, M_w: weight-average molecular weight). The yields of the polymer reached full conversion in 15 min with the Sm, Gd, Tb, Dy, Ho, and Tm catalysts, i.e., with the metals that are in the middle of the lanthanide element series (runs 4−9), while with earlier lanthanide metals such as Ce, Pr, and Nd complexes the yields were moderate to poor under the same reaction conditions (15−63%). Although the Yb-containing system had no activity (run 10), the catalyst with Lu gave a yield of 54% (run 11). Among those lanthanide elements that give full conversion under this condition (Sm−Tm), the catalytic activity of the Gd complex is extraordinarily high, and full conversion was attained under lower catalyst concentration ($[butadiene]_0/[Gd]_0 = 10\,000$) in 15 min (run 1 in Table 2). Though it takes 20 h at 25 °C, an even much larger amount of butadiene ($[butadiene]_0/[Gd]_0 = 500\,000$) can be polymerized with this catalyst system in 88% yield (run 3 in Table 2). This is in sharp contrast with more ordinary systems based on lanthanide catalysts such as $LnCl_3/EtOH/AlEt_3$ or $Ln(OCOCCl_3)_3/Al^iBu_3/AlEt_2Cl$, in which Nd is the most active for the butadiene polymerization among the lanthanide metals.[15,16] The microstructures of the polymers obtained are highly dependent on the central metals, as shown in Figure 1. With Ce, the 1,4-trans structure predominates over 1,4-cis by ca. 20%, though the situation is overturned with neighboring Pr. As the metal gets heavier, the 1,4-cis structure steadily increases, reaching 97% for the Gd complex, while the 1,4-trans decreases compensating

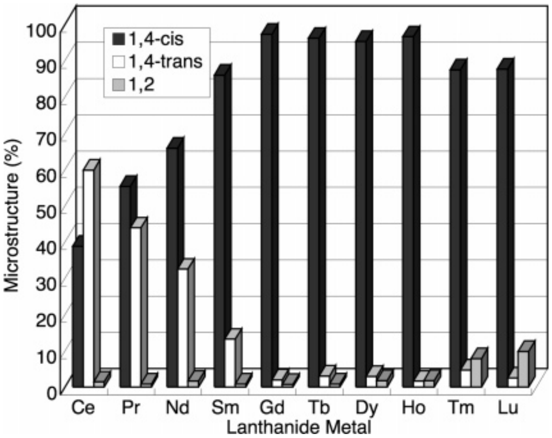

Figure 1. Microstructure of polybutadiene catalyzed by $Cp^*_2Ln[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2LnCp^*_2/Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$. Conditions: in toluene; total volume = 20 mL; polymerization temperature = 25 °C; butadiene = 0.54 g (1×10^{-2} mol); Ln = 5×10^{-5} mol; $[Al^iBu_3]_0/[Ln]_0 = 5$; $\{[Ph_3C][B(C_6F_5)_4]\}_0/[Ln]_0 = 1$.

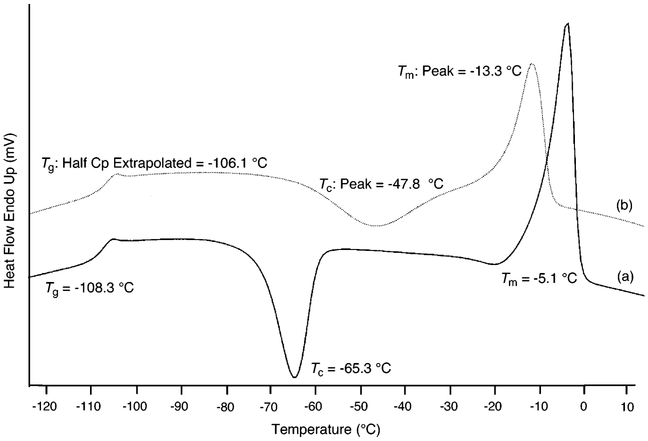

Figure 2. Differential scanning calorimeter (DSC) charts of the polybutadienes: (a) run 12, 1,4-cis selectivity >99.9%; (b) run 5, 1,4-cis/1,4-trans/1,2 = 97.3/2.0/0.7 in Table 1.

for it. Metals heavier than Gd give basically high-cis polymer also, but two of the heaviest ones, Tm and Lu, show some extent of 1,2-vinyl polymerization (5−9%), leading to lower 1,4-cis content of 87−88%. From the perspective of synthetic rubber production, the Gd, Tb, Dy, and Ho complexes are favored (1,4-cis selectivity ≥ 95.3%). Since it has been believed that a slight increase of 1,4-cis content in polybutadiene leads to great improvement in elastic properties,[17] Gd may well be the best choice (run 5 in Table 1). Toluene appears for the best solvent for the polymerization. In aliphatic solvents like cyclohexane and *n*-hexane, the 1,4-cis selectivity affected by the Gd catalyst system becomes lower [97.3% (toluene) > 91.6% (cyclohexane) > 88.7% (*n*-hexane)], although activity does not differ too much from that in toluene (full conversion in 15 min) under the conditions described in Table 1. Extremely high catalytic activity of the Gd complex enabled us to carry out the polymerization at low temperatures and thereby prepare polybutadiene with much higher 1,4-cis content. As listed in Table 1 (run 12), the polymerization takes place even at −40 °C and reaches full conversion in 5 h, resulting in virtually perfect selectivity for the 1,4-cis microstructure. The crystallization temperature (T_c = −65.3 °C) and the melting temperature (T_m = −5.1 °C) of this purely 1,4-cis structured polybutadiene (Figure 2, curve a) are distinctively different from those of “high-cis” (1,4-cis content 97.3%, T_c = −47.8 °C, T_m = −13.3 °C) polybutadiene sample (Figure 2, curve b), which was obtained by the polymerization at 25 °C (run 5 in Table 1).

Polymerization of Butadiene Using $\mathbf{AlR_3}$ ($\mathbf{AlR_3 = Al^{\mathit{i}}Bu_2H}$, $\mathbf{AlEt_3}$, or $\mathbf{AlMe_3}$) as the Alkylaluminum Component. When alkylaluminum AlR_3 was employed in place of $\mathrm{Al^{i}Bu_3}$ in the above-mentioned Gd system, i.e., when the catalyst/cocatalyst combination was $\mathrm{Cp^*{}_2Gd[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2GdCp^*{}_2/AlR_3/[Ph_3C][B(C_6F_5)_4]}$, smooth polymerization also took place in good yields (82% to full conversion in 30 min, depending on AlR_3) under a similar condition to that shown in Table 1 ($[AlR_3]_0/[Ln]_0$ = 5). However, the 1,4-cis selectivity was strongly affected by the bulkiness of the alkylaluminum, $\mathrm{Al^{i}Bu_3}$ (97.3%) > $\mathrm{Al^{i}Bu_2H}$ (96.1%) > $AlEt_3$ (73.9%) > $AlMe_3$ (60.2%). These effects have been observed with other lanthanide metal complexes.[11] The resulting polybutadiene had high molecular weight (M_n = 100 000−10 300) regardless of the kind of AlR_3 and lanthanide metals, but the MWD was somewhat variable (M_w/M_n = 1.32−2.50) depending on the lanthanides. The MWD’s became more averaged and sharp when a smaller amount of AlR_3 was used, e.g., $[AlMe_3]_0/[Ln]_0$ = 3. Table 3 summarizes the polymerization reactions carried out in toluene at 25 °C, which were catalyzed by various lanthanide metal complexes, $\mathrm{Cp^*{}_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2LnCp^*{}_2}$, with the fixed cocatalyst combination $\mathrm{AlMe_3/[Ph_3C][B(C_6F_5)_4]}$, where the aluminum lanthanide ratio was 3. Comparison of the data in Table 3 with those in Table 1 demonstrates that the molecular weight and MWD of the polymers are much the same (M_n = 144 200−29 500, M_w/M_n = 1.25−1.88), but the yields of the polymer are somewhat lower even in 30 min with the Sm, Gd, Tb, Dy, Ho, Tm, and Lu complexes, whereas those for Ce, Pr, and Nd complexes are improved. However, the most dramatic change brought about by the substitution of $AlMe_3$ for $\mathrm{Al^{i}Bu_3}$ is the microstructure of the polybutadiene, i.e., the marked increase of 1,4-trans structure as a whole in expense of 1,4-cis as graphically illustrated in Figure 3. In particular, the selectivity to 1,4-trans polymerization is enhanced when the lighter lanthanide metal complex is used as the catalyst, reaching 93.8% in the case of Ce (1,4-cis/1,4-trans/1,2 = 4.9/93.8/1.3, run 1 in Table 2). As expected, the high-trans polymer thus obtained had plastic properties (T_m = 88.6 and 49.3 °C).

Molecular Weight Control Affected by Alkylaluminum in Gd and Nd Catalyst Systems. We have already reported that the polymerization of butadiene with $\mathrm{Cp^*{}_2Sm[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2SmCp^*{}_2/Al^{i}Bu_3/[Ph_3C][B(C_6F_5)_4]}$ catalyst system shows living-like nature at −20 °C ($[Sm]_0$ = 0.005 M, $[\text{butadiene}]_0/[Sm]_0$ = 200, M_w/M_n = 1.20−1.23).[12] A similar behavior of the Nd analogue, $\mathrm{Cp^*{}_2Nd[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2NdCp^*{}_2/Al^{i}Bu_3/[Ph_3C][B(C_6F_5)_4]}$, was observed at 25 °C under the following conditions; $[Nd]_0$ = 0.005 M, $[\mathrm{Al^{i}Bu_3}]_0/[Nd]_0$ = 3, $\{[Ph_3C][B(C_6F_5)_4]\}_0/[Nd]_0$ = 1, and $[\text{butadiene}]_0/[Nd]_0$ = 500. The monomer conversion reached 42% in 2 min and 98% in 5 min. The MWD remained unimodal and narrow (M_w/M_n

Table 3. Polymerization of 1,3-Butadiene with $\mathbf{Cp^*{}_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2LnCp^*{}_2/AlMe_3/[Ph_3C][B(C_6F_5)_4]}$[a]

			microstructure[b]				
run	lanthanide	yield (%)	1,4-cis (%)	1,4-trans (%)	1,2 (%)	M_n[c]	M_w/M_n[c]
1	Ce	35	4.9	93.8	1.3	38 000	1.41
2	Pr	72	9.6	89.6	0.8	56 000	1.25
3	Nd	87	13.8	85.2	1.0	65 000	1.25
4	Sm	80	33.2	65.2	1.6	71 600	1.46
5	Gd	76	59.7	38.8	1.5	111 500	1.59
6	Tb	43	72.4	26.6	1.4	91 200	1.84
7	Dy	69	56.0	41.1	2.9	144 200	1.88
8	Ho	48	64.8	32.5	2.7	72 000	1.60
9	Tm	4	47.8	46.8	5.4	29 500	1.60
10	Yb	no					
11[d]	Lu	24	40.9	50.0	9.1	43 400	1.82

[a] Conditions: in toluene; total volume = 20 mL; polymerization temperature = 25 °C; time = 30 min; butadiene = 0.54 g (1 × 10^{-2} mol); Ln = 5 × 10^{-5} mol; $[AlMe_3]_0/[Ln]_0$ = 3, $\{[Ph_3C][B(C_6F_5)_4]\}_0/[Ln]_0$ = 1. [b] Measured by ^1H NMR and ^{13}C NMR in $CDCl_3$. [c] Determined by gel permeation chromatography vs polystyrene standards. [d] Time = 24 h.

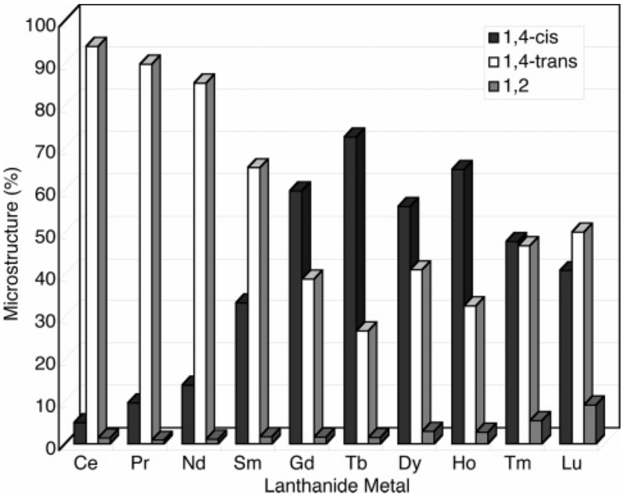

Figure 3. Microstructure of polybutadiene catalyzed by $Cp^*_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2LnCp^*_2/AlMe_3/[Ph_3C][B(C_6F_5)_4]$. Conditions: in toluene; total volume = 20 mL; polymerization temperature = 25 °C; butadiene = 0.54 g (1×10^{-2} mol); Ln = 5×10^{-5} mol; $[AlMe_3]_0/[Ln]_0 = 3$; $\{[Ph_3C][B(C_6F_5)_4]\}_0/[Ln]_0 = 1$.

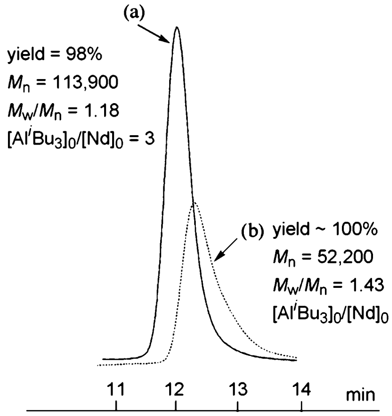

Figure 4. Molecular weight distribution (MWD) curves obtained by $Cp^*_2Nd[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2NdCp^*_2/Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$ in toluene at 25 °C. $[Nd]_0 = 0.005$ M, $\{[Ph_3C][B(C_6F_5)_4]\}_0/[Nd]_0 = 1$, $[butadiene]_0/[Nd]_0 = 500$. (a) $[Al^iBu_3]_0/[Nd]_0 = 3$, time = 5 min, yield = 98%, $M_n = 113\,900$, $M_w/M_n = 1.18$; (b) $[Al^iBu_3]_0/[Nd]_0 = 10$, time = 5 min, yield ~100%, $M_n = 52\,200$, $M_w/M_n = 1.43$.

= 1.13, 2 min; 1.18, 5 min), while the M_n increased with increase of the monomer conversion ($M_n = 69\,300 \rightarrow 113\,900$) (Figure 4a). Investigating such Nd-catalyzed living-like polymerization, we noticed that the $[Al^iBu_3]_0/[Nd]_0$ ratio strongly affects the molecular weight of the polymer. On increasing the $[Al^iBu_3]_0/[Nd]_0$ ratio from 3 to 10, for example, the MWD curve shifted to lower molecular weight region with somewhat broader MWD ($M_n = 52\,200$, $M_w/M_n = 1.43$, Figure 4b). This indicates that Al^iBu_3 not only works as an activator but also plays a role of a chain transfer agent when added in excess amounts. In the case of Gd analogue, the reaction at lower temperature was necessary to study its behavior because the catalytic activity was extremely high; typical conditions are polymerization temperature = −30 °C, $[Gd]_0 = 0.002$ M, $[butadiene]_0/[Gd]_0 = 500$, and $[Al^iBu_3]_0/[Gd]_0 = 3$. Under such conditions, the polymerization was slow and requires 30 min to reach 87% conversion. The M_n of the resulting polybutadiene increased in proportion to monomer consumption, while the MWD remained narrow throughout the reaction ($M_w/M_n = 1.19-1.27$, Figure 5). For the practical use of this system, molecular weight should be controlled under much higher $[butadiene]_0/[Cat]_0$ condition and at high conversion. As expected, addition of a large amount of Al^iBu_3 was found to be effective for this purpose. Table 2 (run 1) shows that M_n was controlled to ca. 700 000 ($M_n = 699\,700$) when the $[butadiene]_0/[Gd]_0$ ratio was 10 000, by addition of 25 M excess of Al^iBu_3 ($[Al^iBu_3]_0/[Gd]_0 = 25$) despite the rapid polymerization (~100% conversion in 15 min at 25 °C). At higher $[butadiene]_0/[Gd]_0$ ratio of 100 000 (run 2, $M_n = 818\,200$) and even 500 000 (run 3, $M_n = 788\,200$), the M_n were kept almost unchanged by addition of 250 and 1200 M excess of Al^iBu_3, which functioned as a chain transfer agent.

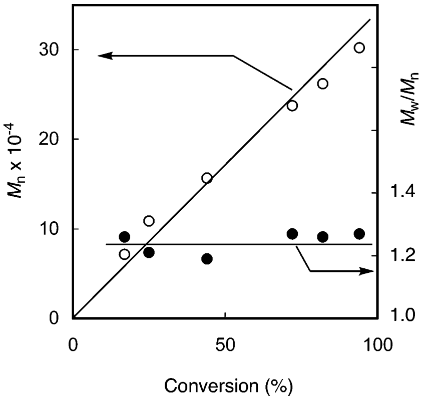

Figure 5. Plots of number-average molecular weight (M_n) and M_w/M_n vs butadiene conversion for polymerization with $Cp^*_2Gd[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2GdCp^*_2/Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$ in toluene at −30 °C. $[Gd]_0 = 0.002$ M, $[Al^iBu_3]_0/[Gd]_0 = 3$; $\{[Ph_3C][B(C_6F_5)_4]\}_0/[Gd]_0 = 1$, $[butadiene]_0/[Gd]_0 = 500$.

Conclusion. The lanthanide metallocenes $Cp^*_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2LnCp^*_2$ (Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Tm, Yb, Lu) with cocatalysts can initiate the polymerization of butadiene with varied catalytic activities and microstructures depending on the kind of lanthanide metal. Furthermore, cocatalyst AlR_3 also affects the performances of the polymer characteristics by taking a role in the formation of active species and a transfer agent. By altering these catalyst components, the molecular weights and stereospecificity of polybutadiene can be controlled at will, allowing the synthesis of polybutadienes with elastic or plastic properties. After all, the lanthanocene catalyst systems can control freely the microstructure of the producing polybutadiene, i.e., high 1,4-cis (>99.9%) to high 1,4-trans (93.8%) polybutadiene, by the choice of metal, cocatalyst, and polymerization conditions.

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.). $Cp^*_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2LnCp^*_2$ (Ln = Pr, Nd, Sm, Gd, Yb, and Lu) were synthesized as described previously.[11,13] Anhydrous $LnCl_3$ (99.9%) (Ln = Ce, Tb, Dy, Ho, Tm) and $[Ph_3C][B(C_6F_5)_4]$ (99%) were purchased from Strem Co., Ltd. and Tosoh Finechem Co., Ltd., respectively, and used without further purification. MeLi (1.0 M in diethyl ether), ^nBuLi (2.6 M in hexane), $AlMe_3$ (1.0 M in hexane), and 1,2,3,4,5-pentamethylcyclopentadiene (90%+) were purchased from Kanto Chemical Co., Inc. Al^iBu_3 (97%+, neat) and Al^iBu_2H (98%+, neat) were purchased from Tosoh Finechem Co., Ltd. LiCp* was prepared from 1,2,3,4,5-pentamethylcyclopentadiene and ^nBuLi in hexane. 1,3-Butadiene (99%+, 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.). Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium/benzophenone ketyl and degassed two times by the freeze−thaw method.

$Cp^*_2Ce[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]_2CeCp^*_2$. A suspension of $CeCl_3$ (1.23 g, 5.0 mmol) and LiCp* (1.46 g, 10.5 mmol) in THF (50 mL) was refluxed for 5 h and stirred overnight at 60 °C. The solvent was removed in vacuo, and the residue was extracted with hexane and then filtered. The solvent was evaporated to dryness, and then the resulting white solid of $Cp*_2CeCl_2Li$ was dissolved in toluene (150 mL). Then, MeLi (10 mL of 1.0 M in diethyl ether, 10 mmol) was added to the solution at −78 °C and gradually allowed to warm to room temperature over the next 12 h. The solvent was removed in vacuo, and the residue was extracted with toluene and then filtered. $AlMe_3$ (10 mL of 1.0 M in hexane, 10 mmol) was added to the filtrate and stirred overnight at room temperature. The reaction mixture was filtered, and the solvent was slowly evaporated to yield the complex as pink microcrystals (725 mg, 29%). ^1H NMR (C_6D_6): δ 3.9 (s, 60H, Cp*), −1.3 (s, 12H, (μ-Me)Al*Me*$_2$), −34.0 (s, 12H, (μ-*Me*)AlMe$_2$). In a similar way, $Cp*_2Ln[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2LnCp*_2$ (Ln = Tb, Dy, Ho, and Tm) were prepared from $LnCl_3$. Tb: white microcrystals, yield 47%; Dy: green microcrystals, yield 22%; Ho: off-white microcrystals, yield 20%; Tm: green microcrystals, yield 41%. The ^1H NMR spectra of these complexes were not observed due to paramagnetism. Yb: purple microcrystals, yield 72%; δ 5.3 (s, 60H, Cp*), 4.1 (s, 12H, (μ-Me)Al*Me*$_2$), −27.8 (s, 12H, (μ-*Me*)AlMe$_2$). Lu: off-white microcrystals, yield 78%; δ 1.8 (s, 60H, Cp*), −0.3 (s, 12H, (μ-Me)Al*Me*$_2$), −0.4 (s, 12H, (μ-*Me*)AlMe$_2$).

Polymerization. A typical polymerization procedure is given below: Via manipulation in a glovebox, $Cp*_2Gd[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2GdCp*_2$ (26 mg, 5.0×10^{-5} mol), Al^iBu_3 (2.5 mL of 0.1 M solution in toluene, 2.5×10^{-4} mol), and $[Ph_3C][B(C_6F_5)_4]$ (47 mg, 5.0×10^{-5} mol) were mixed in a glass pressure reactor and dissolved in toluene (16.5 mL). The reactor was taken out from the glovebox, and then butadiene (0.54 g, 1.0×10^{-2} mol) was added into the solution at −40 °C. Then, the reactor moved to water bath of 25 °C, and rapid stirring of the polymerization mixture was maintained for 15 min. 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 60 °C. Polymer yield ~100%, 1,4-cis/1,4-trans/1,2 = 97.3/2.0/0.7, M_n = 82 500, M_w/M_n = 1.32.

Polymer Analysis. The microstructure of the polybutadiene products was determined by ^1H NMR (300 MHz) and ^{13}C NMR spectroscopy (75 MHz) (JNM EX-300) in $CDCl_3$. ^1H NMR: δ 4.8−5.2 ($=CH_2$ of 1,2-butadiene unit), 5.2−5.8 ($-CH=$ of 1,4-butadiene unit and $-CH=$ of 1,2-butadiene 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 gel permeation chromatography (GPC) [TOSOH HLC-8220 GPC; three columns of Super HZM-H; temperature, 40 °C; eluent, THF; flow rate, 0.35 mL/min; the columns were calibrated against 13 standard polystyrene samples (M_n = 5 480 000−500, M_w/M_n < 1.15)]. The glass transition temperature (T_g), the crystallization temperature (T_c), and the melting temperature (T_m) of the polymers were measured by a differential scanning calorimeter (DSC) at 40 °C/min cooling or heating rate (Perkin-Elmer PYRIS Diamond DSC). The sample was first cooled to −150 °C and returned to 200 °C, and then the second cooling and heating scans were recorded.

Supporting Information Available: Results of the polymerization of 1,3-butadiene with $(C_5Me_5)_2Gd[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]Gd(C_5Me_5)_2/AlR_3/[Ph_3C][B(C_6F_5)_4]$: (1) the effect of solvent (toluene, cyclohexane, *n*-hexane) and (2) the effect of AlR_3 (Al^iBu_3, Al^iBu_2H, $AlEt_3$, $AlMe_3$); ^1H NMR and ^{13}C NMR spectra of the polybutadiene with 1,4-cis content as high as >99.9% (run 12 in Table 1), 1,4-cis/1,4-trans/1,2 = 97.3/2.0/0.7 (run 5 in Table 1), and 1,4-cis/1,4-trans/1,2 = 4.9/93.8/1.3 (run1 in Table 3); the differential scanning calorimeter (DSC) chart of the polybutadiene produced by $Cp*_2Ce[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]_2CeCp*_2/AlMe_3/[Ph_3C][B(C_6F_5)_4]$: 1,4-cis/1,4-trans/1,2 = 4.9/93.8/1.3 (run1 in Table 3). This material is available free of charge via the Internet at http://pubs.acs.org.

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