An Efficient Gadolinium Metallocene-Based Catalyst for the Synthesis of Isoprene Rubber with Perfect 1,4-Cis Microstructure and Marked Reactivity Difference between Lanthanide Metallocenes toward Dienes As Probed by Butadiene−Isoprene Copolymerization Catalysis

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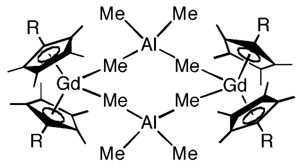
A variety of catalysts for polymerization of conjugated dienes, e.g., butadiene and isoprene, have been studied aiming at high 1,4-cis regulated polymers because such stereoregular diene polymers are expected on further manipulations to give synthetic rubber with enhanced performance in thermal and mechanical properties.[1] Indeed, the main component of natural rubber (NR) is extremely high 1,4-cis regulated polyisoprene (>99.99%, $T_g \approx -68$ °C) with high molecular weight ($M_w > 10^6$) and is one of the most important materials as elastomer used for tires and other elastic materials in large quantities. Synthetically, Li-, Ti-, and Nd-based catalyst systems have been developed as polymerization catalysts for isoprene, and some of them have already been widely used for industrial applications as polymerization catalysts.[1−6] However, the 1,4-cis selectivity of the synthetic polyisoprenes (isoprene rubber, IR) produced with these catalysts are still lower than NR (1,4-cis selectivity ≈ Li 95%, Ti and Nd 98%), and their physical properties, e.g., elasticity and tensile strength, are not satisfactory compared to those of NR.

As for related butadiene polymerization, we reported some years ago a novel catalyst system based on coordination compounds, i.e., lanthanide metallocenes with cocatalysts, which was highly effective for the 1,4-cis stereospecific polymerization of butadiene. For example, $(C_5Me_5)_2Sm[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]Sm(C_5Me_5)_2$/$[Ph_3C][B(C_6F_5)_4]$/$Al^iBu_3$ gave a polybutadiene with high 1,4-cis content (>99.5%).[7] However this samarocene-based catalyst system did not induce polymerization of isoprene under various conditions we examined. More recently, we found out that the gadolinium analogue can more efficiently catalyze the polymerization of butadiene, allowing for the synthesis of almost perfectly 1,4-cis regulated polybutadiene (>99.99%).[8] We have examined whether this gadolinium metallocene-based system is applicable to the polymerization of isoprene.

As is the case of the Sm analogue reported previously, $(C_5Me_5)_2Gd[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]Gd(C_5Me_5)_2$ (**1**)[8] alone does not induce the polymerization of isoprene. Addition of equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ to **1** was found to activate the complex, initiating the polymerization in toluene at room temperature ($[\text{isoprene}]_0/[\mathbf{1}]_0 = 1500$, 97% yield in 2 h) and producing a high molecular weight polyisoprene with a relatively narrow molecular weight distribution (MWD) ($M_n = 179\,100$, $M_w/M_n = 2.07$). The resultant polyisoprene, however, possessed a low content of 1,4-cis microstructure (1,4-cis selectivity = 32.6%, $T_g = -31.7$ °C) (run 1 in Table 1). On lowering the reaction temperature to −20 °C, the 1,4-cis selectivity slightly increased to 44.9% ($T_g = -25.9$ °C) but the reaction was too slow (22% yield in 6 days) while the MWD became broader ($M_w/M_n = 10.01$) (run 2 in Table 1). These drawbacks were further improved by a small amount of Al^iBu_3 added to the $\mathbf{1}/[Ph_3C][B(C_6F_5)_4]$ mixture. Thus, the $\mathbf{1}/[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ system very efficiently catalyzed the polymerization (full conversion in 1 h at room temperature, $[Al^iBu_3]_0/[\mathbf{1}]_0 = 10$) and gave polyisoprene with narrow MWD (1.73). The 1,4-cis selectivity of the polyisoprene under this condition was still not high, 50.8% ($T_g = -51.2$ °C) (run 3 in Table 1). Since the activity of the ternary system is much higher than the binary system, we next examined its low-temperature reactions. As expected, it exhibited good catalytic activity even at low temperatures (0 °C, 93% in 5 h; −20 °C, 88% yield in 10 h) (runs 4 and 5 in Table 1). Surprisingly, the 1,4-cis selectivity dramatically increased up to 98.7% at 0 °C ($T_g = -67.5$ °C) and reached to >99.99% at −20 °C ($T_g = -68.4$ °C). No evidence for the presence of a trace amount of 1,4-trans polymers or 3,4 polymers was observed in the ^{13}C NMR spectrum (Figure 1). To the best of our knowledge, this is the first synthetic polyisoprene with perfect cis regularity.



1: R = Me
2: R = ^{i}Pr

An improvement of the catalyst system has been attained by introducing a novel gadolinium metallocene complex, $(C_5Me_4{}^iPr)_2Gd$, in place of $(C_5Me_5)_2Gd$: $(C_5Me_4{}^iPr)_2Gd[(\mu\text{-Me})AlMe_2(\mu\text{-Me})]Gd(C_5Me_4{}^iPr)_2$ (**2**) was prepared by a similar procedure to the synthesis of **1**.[9] The 1,4-cis regulatory ability of **2** was remarkably higher than that of **1** when compared under the same conditions, e.g., the 1,4-cis selectivity at room temperature, **2** (90.0%, $T_g = -61.1$ °C) ≫ **1** (50.3%) (run 6 vs run 3 in Table 1). Already at 0 °C, $\mathbf{2}/[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ was able to give a polyisoprene with perfect 1,4-cis microstructure (>99.99%, $T_g = -69.2$ °C) in 55% yield after 5 h (Table 1, run 7).

The large difference in catalytic reactivity effected by various lanthanide metals (vide supra) have been investigated in more detail by means of butadiene/isoprene copolymerization. When the copolymerization reactions catalyzed by $\mathbf{1}/[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ were carried out with varying initial monomer feed ratios (isoprene feed = 40−90 mol %) at room temperature, butadiene−isoprene copolymers with high molecular weights ($M_n = 99\,100−67\,000$) and narrow MWDs ($M_w/M_n = 1.42−1.51$) were obtained, the isoprene content

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Table 1. Polymerization of Isoprene with Gadolinium Metallocene/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$[a]

run	catalyst	T_p (°C)	$[Al^iBu_3]_0/[Gd]_0$	time	yield (%)	microstructure[b] 1,4-cis (%)	1,4-trans (%)	3.4 (%)	M_w[c]	M_n[c]	M_w/M_n[c]	T_g (°C)[d]
1	**1**	r.t.		2 h	97	32.6	18.8	48.6	370 900	179 100	2.07	−31.7
2	**1**	−20		6 days	22	44.9	3.0	52.2	1 146 400	114 600	10.01	−25.9
3	**1**	r.t.	10	1 h	~100	50.8	12.7	36.5	112 700	65 300	1.73	−51.2
4	**1**	0	20	5 h	93	98.7	0.0	1.3	902 000	461 500	1.95	−67.5
5	**1**	−20	50	10 h	88	>99.99			1 494 500	675 000	2.21	−68.4
6	**2**	r.t.	10	1 h	70	90.0	0.3	9.7	129 500	72 300	1.79	−61.1
7	**2**	0	20	5 h	55	>99.99			1 345 100	668 200	2.01	−69.2

[a] Polymerization conditions: in toluene; $[\text{isoprene}]_0 = 1.5$ M (3.0 mL, 0.03 mol); $[Gd]_0 = 0.001$ M (11 mg, 2×10^{-5} mol). [b] Measured by ^1H NMR and ^{13}C NMR in $CDCl_3$. [c] Determined by GPC vs polystyrene standards. [d] Determined by DSC.

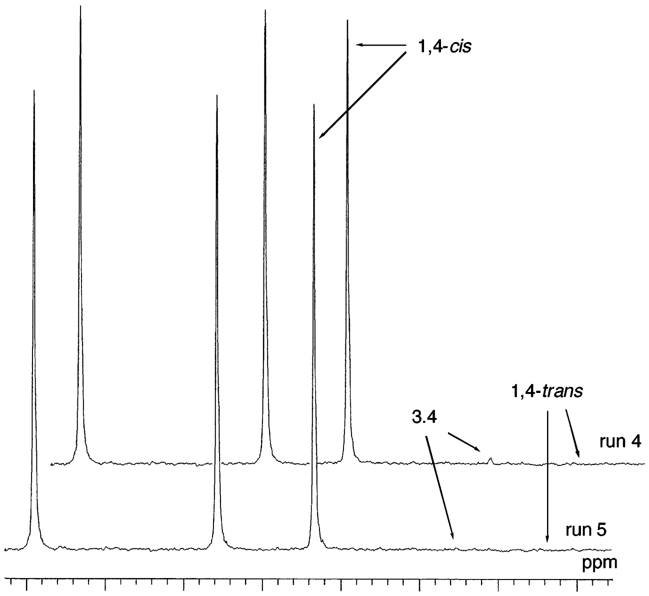

Figure 1. ^{13}C NMR spectra of the polyisoprenes obtained from runs 4 and 5 in Table 1.

of which was in the range 11.0−40.8 mol % (Table 2). The conversions were deliberately controlled at low levels (polymer yield = 19−24%) in order to evaluate the monomer reactivity ratios by applying the Fineman−Ross method,[10] $r_{\text{butadiene}} = 4.7$ and $r_{\text{isoprene}} = 0.02$, indicating that isoprene is 2 orders of magnitude less reactive than butadiene, being obtained from the above-mentioned copolymerization with by **1**/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$. The 1,4/1,2 ratio of the butadiene unit and the 1,4/3,4 ratio of the isoprene unit in the copolymers obtained at room temperature were virtually constant independent of the copolymer compositions (1,4 content of butadiene unit = 98.4−96.9%, 1,4 content of isoprene unit = 54.2−51.5%), although it slightly changed at lower polymerization temperatures (e.g., 1,4 content of butadiene unit = 99.3%, 1,4 content of isoprene unit = 68.8% at −40 °C). The T_g of these polymers varies from −104.2 to −78.9 °C, depending on the copolymer compositions, whereas T_g peaks due to homopolymers were not observed as confirmed by DSC. These results suggest that the copolymer products obtained in these reactions are random butadiene−isoprene copolymers and not mixtures of the homopolymers.

Similarly, copolymers were obtained with other lanthanide metallocene-based catalyst systems, $(C_5Me_5)_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]Ln(C_5Me_5)_2/[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ (Ln = Sm, Nd, Pr), which were similar to those obtained by the Gd analogue: $M_n = 90\,300{-}60\,000$, $M_w/M_n = 1.30{-}1.57$, 1,4 content of butadiene unit = 99.2−98.5%, 1,4 content of isoprene unit = 67.5−46.8%. The T_g values of these copolymers vary from −101.4 to −69.9 °C and are apparently related to their isoprene content. The respective monomer reactivity ratios are as follows: Sm, $r_{\text{butadiene}} = 3.8$ and $r_{\text{isoprene}} = 0.16$; Nd, $r_{\text{butadiene}} = 3.2$ and $r_{\text{isoprene}} = 0.28$; Pr, $r_{\text{butadiene}} = 2.4$ and $r_{\text{isoprene}} = 0.30$. It appears that the reactivity of isoprene as compared to that of butadiene toward a specific metal (Pr > Nd > Sm > Gd) is a function of the size of the reaction center (ionic radius: Pr > Nd > Sm > Gd). The tendency found in the present system differs from that known in ordinary lanthanide catalyst system such as $Ln(\text{naphthenate})_3/Al^iBu_3/Et_3Al_2Cl_3$, which has the disordered monomer reactivity ratios.[4] While these metallocene reaction centers prefer butadiene in general, larger metal tends to take up isoprene more frequently, although the microstructure in the resulting copolymer stays almost unchanged. It is interesting to note that, among the four lanthanide metals examined, only the Gd−metallocene complex, which is the smallest and takes isoprene most reluctantly in the copolymerization with butadiene, can catalyze homopolymerization of isoprene efficiently.

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Table 2. Copolymerization of Butadiene and Isoprene with 1/$[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$[a]

run	isoprene in feed (mol %)	time (min)	yield (%)	isoprene content in copolymer (mol %)[b]	butadiene unit microstructure[c] 1,4 (%)	1,2 (%)	isoprene unit microstructure[c] 1,4 (%)	3,4 (%)	M_w[d]	M_n[d]	M_w/M_n[d]	T_g (°C)[e]
1	40	0.5	22	11.0	98.4	1.6	53.5	46.5	149 400	99 100	1.51	−104.2
2	50	0.5	19	15.5	97.4	2.6	52.0	48.0	121 800	84 400	1.44	−99.7
3	60	1	22	19.7	97.3	2.7	54.2	45.8	112 200	79 100	1.42	−97.2
4	70	4	21	25.5	97.3	2.7	53.4	46.6	98 300	67 000	1.47	−93.2
5	80	15	24	32.9	96.9	3.1	51.5	48.5	116 800	81 400	1.44	−86.1
6	90	20	19	40.8	97.6	2.4	52.4	47.6	97 100	68 500	1.42	−78.9

[a] Polymerization conditions: in toluene; T_p = room temperature; $[Al^iBu_3]_0/[\mathbf{1}]_0 = 5$; $\{[Ph_3C][B(C_6F_5)_4]\}_0/[\mathbf{1}]_0 = 1$; $[\text{butadiene}]_0 + [\text{isoprene}]_0 = 1.33$ M (0.02 mol); $[\mathbf{1}]_0 = 1.33 \times 10^{-3}$ M (11 mg, 2×10^{-5} mol). [b] Determined from ^1H NMR spectra. [c] Measured by ^1H NMR and ^{13}C NMR in $CDCl_3$. [d] Determined by GPC vs polystyrene standards. [e] Determined by DSC.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of the polyisoprene with 1,4-cis content as high as >99.99% (run 7 in Table 1) and the butadiene–isoprene copolymer (run 2 in Table 2). DSC charts of the butadiene–isoprene copolymers (runs 1–6 in Table 2); results of the copolymerization of butadiene with isoprene by $(C_5Me_5)_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]Ln(C_5Me_5)_2/[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ (Ln = Sm, Nd, Pr); Fineman–Ross plot for the copolymerization of butadiene and isoprene with $(C_5Me_5)_2Ln[(\mu\text{-}Me)AlMe_2(\mu\text{-}Me)]Ln(C_5Me_5)_2/[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ (Ln = Gd, Sm, Nd, and Pr). This material is available free of charge via the Internet at http://pubs.acs.org.

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