Isoprene Polymerization with (η₃-C₃H₅)₂Ceci₅Mg₂(Tmed)₂/Alkylaluminum

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ISOPRENE POLYMERIZATION WITH (η^3-C$_3$H$_5$)$_2$CeCl$_5$Mg$_2$(tmed)$_2$/ALKYLALUMINUM

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ABSTRACT

(η^3-C$_3$H$_5$)$_2$CeCl$_5$Mg$_2$(tmed)$_2$ combined with HAl(i-Bu)$_2$ or Al(i-Bu)$_3$ can initiate the polymerization of isoprene with about 50% of the cis-1,4 microstructure contained in the polymer. The insertion reaction of isoprene occurring between Ce^{3+} and η^3-allyl was identified by NMR techniques.

INTRODUCTION

In our study of the polymerization mechanism of conjugated dienes with rare earth metal coordination catalysts, the η^3-allyl rare earth metal complex was considered to be the active center [1, 2]. Because of their instability and sensitivity

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TABLE 1.   Isoprene Polymerization[a] with
$(\eta^3\text{-}C_3H_5)_2CeCl_5Mg_2(tmed)_2/HAl(i\text{-}Bu)_2$

Al/Ce (molar ratio)	Conversion, %	Microstructure, %		
		cis-1,4	trans-1,4	3,4-
0.5	0	—	—	—
2	0	—	—	—
4	9.8	50.2	46.5	3.3
20	17.2	53.0	45.7	1.3

[a]Conditions: [Ce] = 1.5×10^{-4} mol; isoprene, 6 mL; 50°C; 2 h.

to air and water, these kinds of complexes are very difficult to synthesize or isolate directly from the polymerization system. Up to now, no sound evidence for the mechanism has been found. In order to study the above mechanism with the η^3-allyl rare earth metal model complex, we synthesized $[Li(2.5D)][Y(\eta^3\text{-}C_3H_5)_4]$ (D = dioxane) and studied the polymerization mechanism of isoprene catalyzed by the complex [3, 4]. Although $CH_2{=}CH{-}CH_2{-}$ was found at the polymer ends, this complex was not a good model complex because it contained lithium.
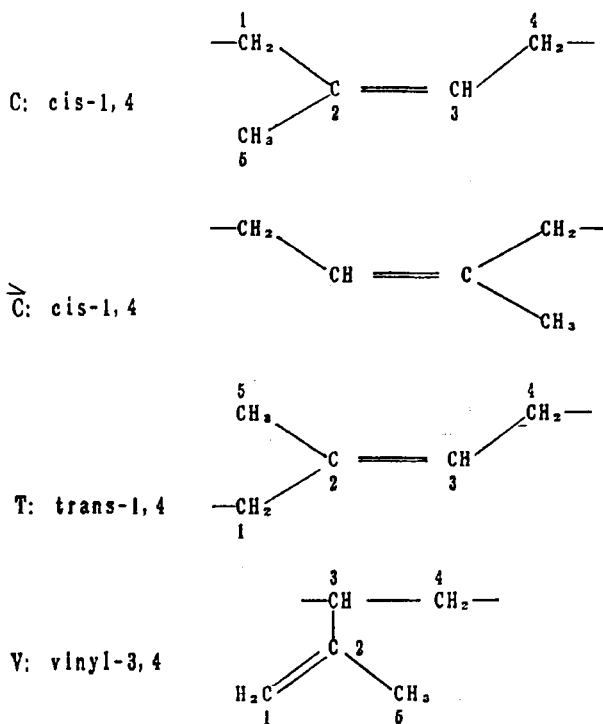
SCHEME 1. Structures of polymer chain.

TABLE 2. Isoprene Polymerization[a] with
$(\eta^3\text{-}C_3H_5)_2CeCl_5Mg_2(tmed)_2/Al(i\text{-}Bu)_3$

Al/Ce (molar ratio)	Conversion, %	Microstructure, %		
		cis-1,4	trans-1,4	3,4-
0.5	0	—	—	—
2	Trace	—	—	—
4	100	45.9	53.2	0.9
20	88.2	55.5	41.8	2.7

[a]Conditions as in Table 1.

One of the authors reported the synthesis and the crystal structure of $(\eta^3\text{-}$ $C_3H_5)_2CeCl_5Mg_2(tmed)_2$ [5] (tmed $= N,N,N',N'$-tetramethyl ethylene diamine). In this complex, the allyls coordinated to Ce^{3+}, and Ce^{3+} and Mg^{2+} bonded by Cl bridges. $MgCl_2$ cannot polymerize dienes. Therefore, this complex was a good model complex of the active centers mentioned above. In the present paper we report the polymerization of isoprene with $(\eta^3\text{-}C_3H_5)_2CeCl_5Mg_2(tmed)_2$/alkylaluminum and the mechanism of isoprene polymerization.

EXPERIMENTAL

Measurements

^{13}C-NMR and DEPT ^{13}C-NMR [6] spectra were recorded with a Unity-400 spectrometer. Chemical shifts of polymer were referenced to tetramethylsilane added as the internal standard using chloroform-d_1 as solvent. The microstructure of polyisoprene was determined with ^{13}C-NMR according to peak height measurement by Randall's method [7].

Polymerization Procedures

All the polymerization procedures were carried out under argon. $(\eta^3\text{-}$ $C_3H_5)_2CeCl_5Mg_2(tmed)_2$ was prepared in 1×10^{-4} mol/mL toluene. Al(i-Bu)$_3$ and HAl(i-Bu)$_2$ were dissolved in toluene with a concentration of 1×10^{-3} mol/mL. Components of the polymerization were added by syringe techniques. Polymerization was terminated with 1:1 HCl. The polymer precipitated with alcohol was dried in vacuum at 50°C.

Preparation of Low Molecular Weight Polyisoprene

Isoprene (1.36 g) was polymerized by $(\eta^3\text{-}C_3H_5)_2CeCl_5Mg_2(tmed)_2$/Al(i-Bu)$_3$ [Al/ Ce = 4 (molar ratio), Al(i-Bu)$_3$ = 6×10^{-4} mol] at 50°C. Ten minutes later the polymerization was terminated with D_2O. The polymer precipitated with alcohol and containing a small amount of 1:1 HCl was dissolved in chloroform and repre-
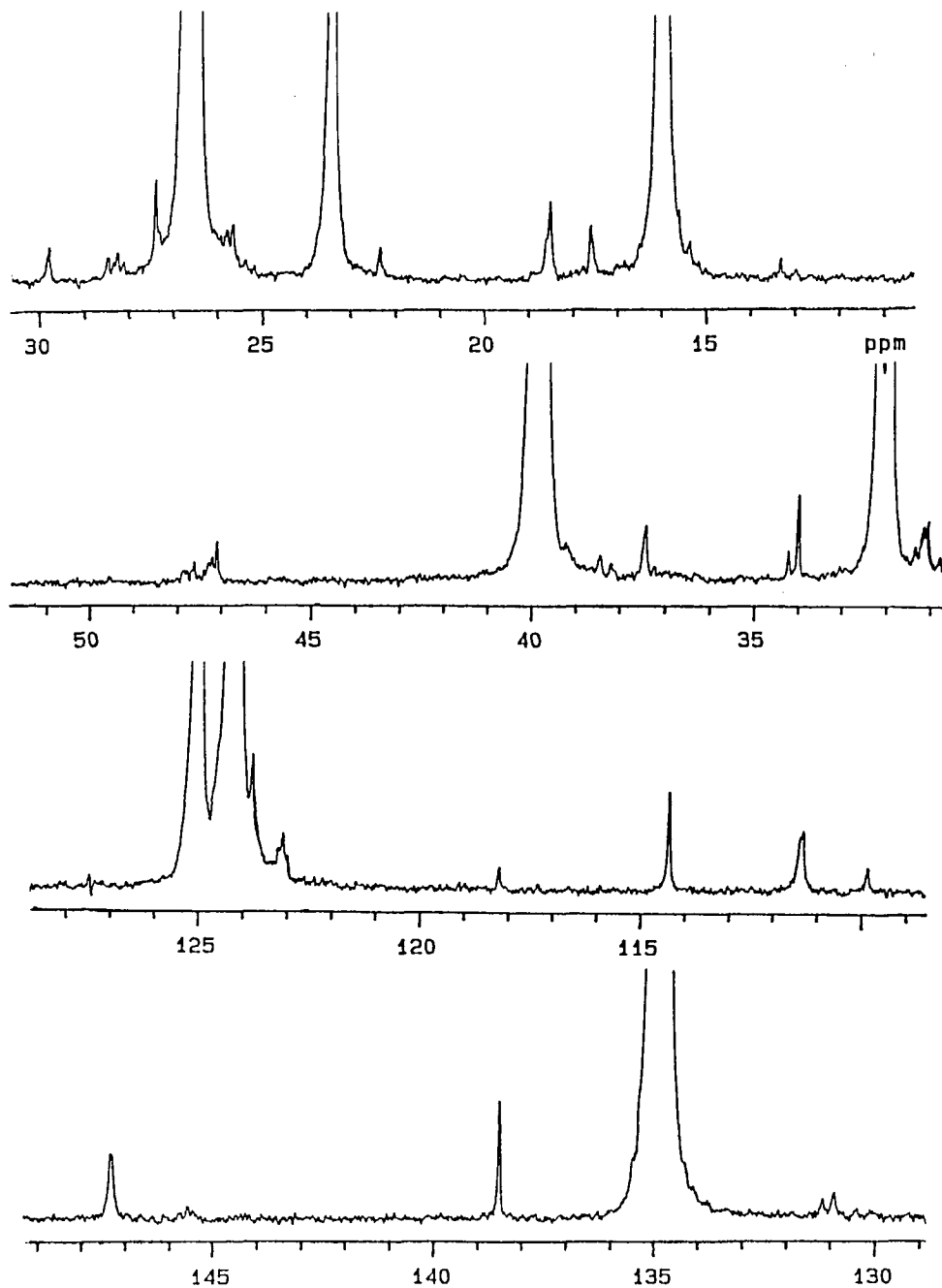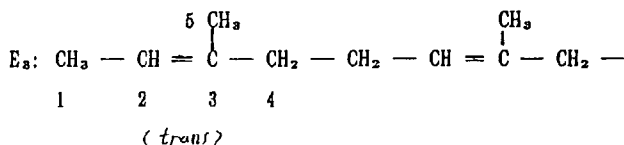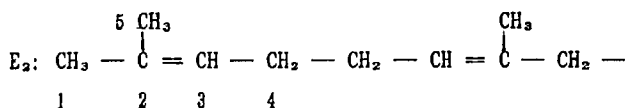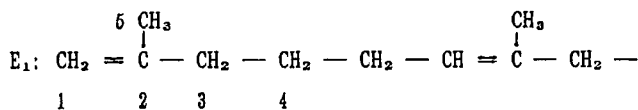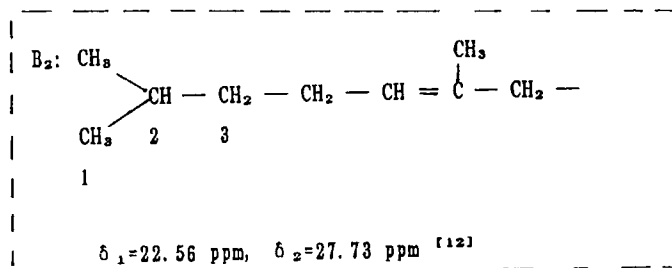
FIG. 1.   Proton noise-decoupled ^{13}C-NMR spectra of polyisoprene. Measuring condi-
tions: Acquisition time, 0.35 s; delaying time, 7.6 s; pulse width, 8 μs; accumulating 3776
times.

$$B_1: \quad CH_2= CH - CH_2 - CH_2 - CH \rightleftharpoons \overset{\overset{\displaystyle CH_3}{|}}{C}-CH_2 -$$

$$\qquad\qquad 1 \quad\quad 2 \quad\quad 3 \quad\quad 4 \quad\quad 5$$

$$B_2: \quad \overset{CH_3}{\underset{CH_3}{\diagdown}} CH - CH_2 - CH_2 - CH \rightleftharpoons \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2 -$$

$$\qquad\qquad\qquad\qquad 2 \qquad 3$$

$$\qquad\qquad 1$$

$$\delta_1 = 22.56 \text{ ppm}, \quad \delta_2 = 27.73 \text{ ppm} \quad [12]$$

$$E_1: \quad CH_2 \rightleftharpoons \overset{\overset{\displaystyle 5 \; CH_3}{|}}{C} - CH_2 - CH_2 - CH_2 - CH \rightleftharpoons \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2 -$$

$$\qquad\qquad 1 \qquad\quad 2 \qquad 3 \qquad 4$$

$$E_2: \quad CH_3 - \overset{\overset{\displaystyle 5 \; CH_3}{|}}{C} = CH - CH_2 - CH_2 - CH \rightleftharpoons \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2 -$$

$$\qquad\qquad 1 \qquad\quad 2 \qquad 3 \qquad 4$$

$$E_3: \quad CH_3 - CH \rightleftharpoons \overset{\overset{\displaystyle 5 \; CH_3}{|}}{C} - CH_2 - CH_2 - CH \rightleftharpoons \overset{\overset{\displaystyle CH_3}{|}}{C} - CH_2 -$$

$$\qquad\qquad 1 \qquad\quad 2 \qquad 3 \qquad 4$$

$$(trans)$$
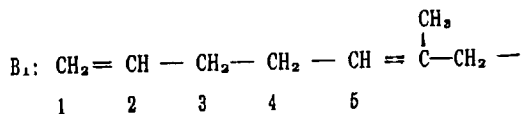
SCHEME 2. Terminal ends of polyisoprene.

cipitated by alcohol. The polymer was purified three times and dried in vacuum at 50°C over 24 hours.

RESULTS AND DISCUSSION

Catalytic Properties of $(\eta^3\text{-}C_3H_5)_2CeCl_5Mg_2(tmed)_2$

Because of the coordination saturation of Ce^{3+}, $(\eta^3\text{-}C_3H_5)_2CeCl_5Mg_2(tmed)_2$ cannot polymerize isoprene alone under the experimental conditions. But combined with $HAl(i\text{-}Bu)_2$, it can initiate the polymerization of isoprene with low activity

CH,CH$_3$

CH$_2$
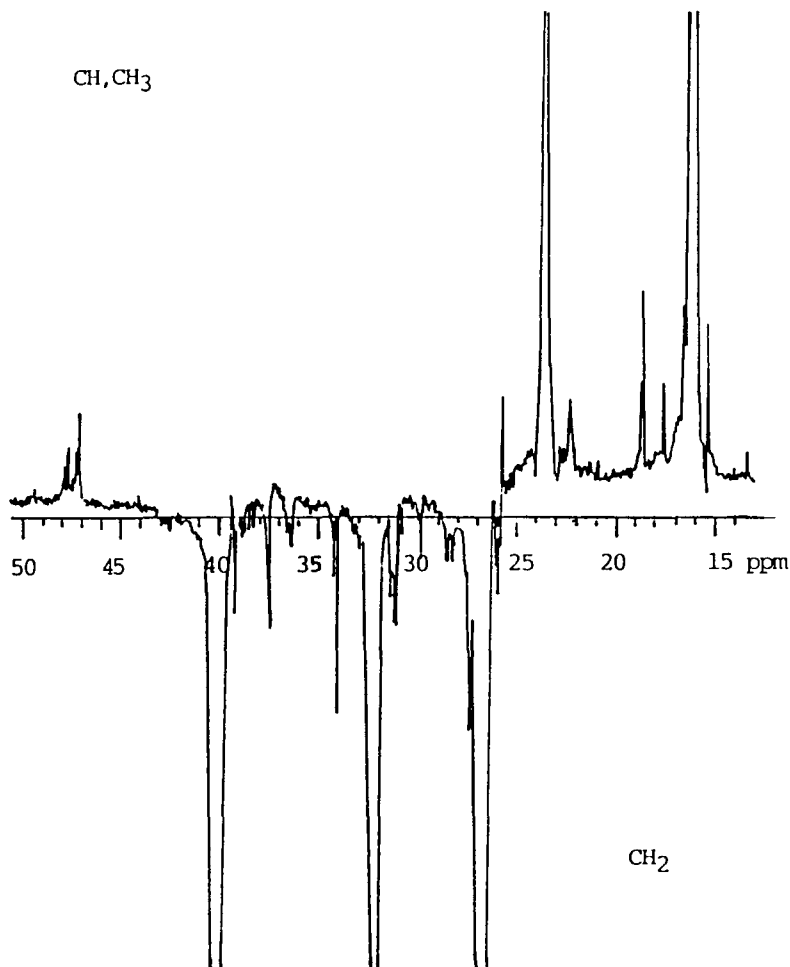
FIG. 2.   DEPT ^{13}C-NMR spectrum of polyisoprene for saturated carbons.

described in Table 1. By adding HAl(i-Bu)$_2$ to the polymerization system, (η^3-C$_3$H$_5$)$_2$CeCl$_5$Mg$_2$(tmed)$_2$ changed from orange to white while releasing propene, and the bond of η^3-allyl and Ce^{3+} disappeared. About 50% cis-1,4 microstructure (Scheme 1) was contained in the polyisoprene.

Upon adding Al(i-Bu)$_3$ to the polymerization system catalyzed by (η^3-C$_3$H$_5$)$_2$CeCl$_5$Mg$_2$(tmed)$_2$ (Al/Ce $\geq$ 2 molar ratio), the entire system became homogeneous and orange-yellow, and no gas was released. As can be seen from Table 2, the Al(i-Bu)$_3$ system was much more active than the HAl(i-Bu)$_2$ system. The microstructure of the polymer was nearly the same as that of the system described above.

FIG. 3. DEPT ^{13}C-NMR spectrum of polyisoprene for unsaturated carbons.
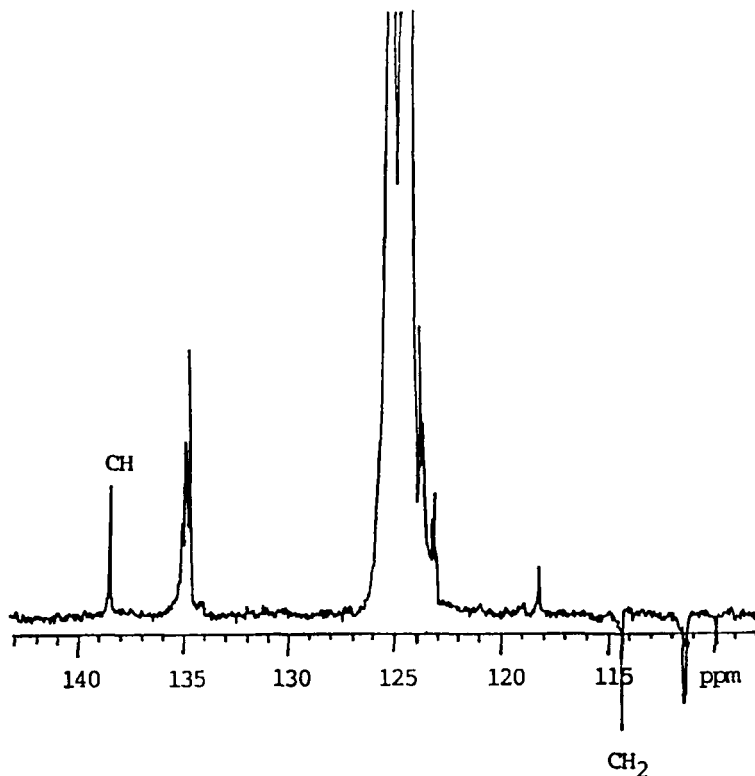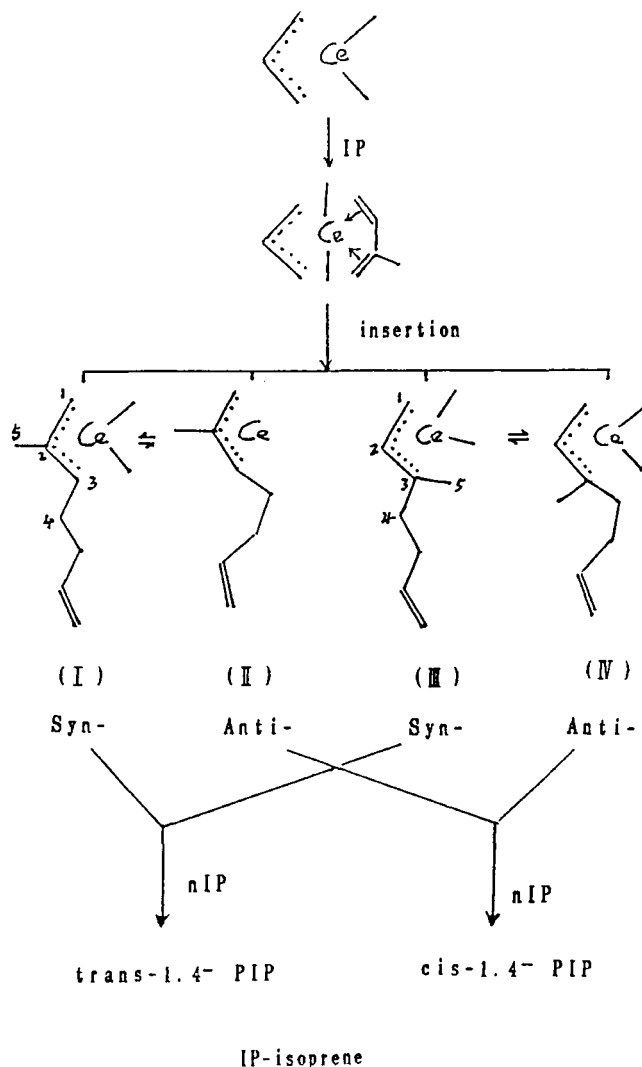
Polymerization Mechanism of Isoprene with (η^3-C$_3$H$_5$)$_2$CeCl$_5$Mg$_2$(tmed)$_2$/Al(*i*-Bu)$_3$

The ^{13}C-NMR spectra of low molecular weight polyisoprene prepared with (η^3-C$_3$H$_5$)$_2$CeCl$_5$Mg$_2$(tmed)$_2$/Al(*i*-Bu)$_3$ are shown as Fig. 1. All of the peaks of the polymer chains were assigned by referencing to previously reported values [8–11], and the chemical shifts of polymer ends were assigned according to the values of model compounds [12] and calculation results based on Dorman's parameters [13] (Table 3). As shown in Scheme 2, four kinds of polymer ends were found. E$_1$, E$_2$, and E$_3$ are derived from isoprene after the termination of polymerization, and B$_1$ is from the allyls after the insertion reaction of isoprene occurring between η^3-allyl and Ce^{3+}. All the assignments were further supported by DEPT ^{13}C-NMR spectra (Figs. 2 and 3). The appearance of two chemical shifts of C$_2$ from the E$_2$ end may be caused by the different linkages between the polymer chain and E$_2$.

It is noteworthy that no B$_2$ end was found in the polymer, and this indicates that Al(*i*-Bu)$_3$ may only act as a Lewis acid and that Ce^{3+} was not alkylated by

SCHEME 3.   Mechanism of isoprene polymerization.

Al(i-Bu)$_3$. By adding Al(i-Bu)$_3$ to the polymerization system, the electron density of the active center Ce^{3+} decreased through the coordination of N and Cl to Al, and the activity increased.

According to the microstructure (cis-1,4: 33.8%; $trans$-1,4: 64.8%; 3,4: 1.4%) of polyisoprene and the polymer ends, the mechanism of isoprene polymerization can be briefly described by Scheme 3. Monomer isoprene coordinated to Ce^{3+} and inserted between η^3-allyl and Ce^{3+} gives four types of active centers (I to IV) and the B$_1$ end. Types I and II were in equilibrium (syn- $\rightleftharpoons$ $anti$-), as were Types III and IV. The active centers all kept an η^3-allyl structure during polymerization. Types II and IV gave a cis-1,4 microstructure, and Types I and III gave a $trans$-1,4

TABLE 3. Assignments of ^{13}C-NMR Spectra of Polyisoprene

| Signals | Chemical shifts | | | Relative intensity[a] |
	Obs	Ref	Assignments	
1	15.94	15.76	c, t T_5 c, t	100
2	18.51	18.74	c, t V_5 c, t	2.1
3	23.40	23.38	c, t C_5 c, t	52.3
4	26.38	26.36	C_4c	16.6
5	26.54	26.55	T_4c	57.6
6	26.66	26.69	T_4t	68.8
7	28.21	28.21	V_4t	1.2
8	28.47	28.77	$C_4\vec{c}$	1.1
9	29.77	29.89	vC_1	1.2
10	31.06		cV_4t	1.5
11	31.14	31.15	cV_4c	1.4
12	31.35	31.50	$\vec{c}C_1$	1.0
13	31.96	31.95	tC_1	38.7
14	32.24	32.08	cC_1	13.5
15	34.21	33.36	cT_4v	1.0
16	37.43	37.39	vT_1	1.4
17	39.73	39.70	tT_1	75.3
18	40.02	39.91	cT_1	36.6
19	47.11	47.07	tV_3 c, t	1.1
20	47.64	47.79	cV_3 c, t	0.7
21	111.33	111.29	cV_1c	1.3
22	111.39	111.42	cV_1v	1.2
23	123.09	123.00	vC_3v	1.0
24	124.23	124.65	c, tT_3 c, t	63.8
25	125.04	125.00	c, tC_3 c, t	30.5
26	134.68	134.55	tT_2c	63.2
27	134.92	134.68	tC_2t	39.7
28	135.08	135.10	cC_2c	17.3
29	147.31	147.22	cV_2v	1.4
30	147.35	147.50	cV_2c	1.3
31	13.30	13.32	C_1 (E_3)	0.7
32	15.40	15.52	C_5 (E_3)	0.7
33	17.60	17.66	C_5 (E_2)	1.6
34	22.34	22.40	C_5 (E_1)	1.0
35	25.65	25.74	C_1 (E_2)	1.3
36	27.40	28.04	C_4 (E_2)	2.9
37	34.00	34.03	C_3 (B_1)	2.2
38	38.46	38.09	C_3 (E_1)	0.7
39	109.87	109.76	C_1 (E_1)	0.5
40	114.36	114.20	C_1 (B_1)	2.1
41	118.20	118.44	C_2 (E_3)	0.4
42	123.78	125.15^{cal}	C_5 (B_1)	2.3
43	130.93	131.29	C_2 (E_2)	0.5
44	131.20	131.29	C_2 (E_2)	0.4
45	138.54	139.24	C_2 (B_1)	2.6

[a]Based on the height of Peak 1 as 100.

microstructure. When monomer attacked site "3" of Type I or II, a 3,4 microstructure was produced. Polymer ends E_1 and E_2 were produced from the attack of C_3 and C_1 of Types I and II by H^+ during termination, and E_3 from the attack of C_1 of Types III and IV by H^+. To our surprise, no deuterium signals were observed in the NMR spectra. (See Table 3.)

In summary, this paper gives direct evidence for the η^3-allyl polymerization mechanism of diene polymerization with rare earth metal coordination catalysts.

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