

Coordination Copolymerization of Butadiene and Isoprene with Rare Earth Chloride–Alcohol–Aluminum Trialkyl Catalytic Systems

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Synopsis

Butadiene and isoprene were copolymerized with $\text{LnCl}_3\text{-ROH-}\text{AlR}_3$ catalytic system. The products obtained were confirmed to be copolymers by their glass transition temperatures and characteristic pyrolytic chromatograms, etc. The equation for copolymerization rate may be expressed as $R_p = K_p(M)^2(\text{cat})$. The rate constants of copolymerization, activation energy, and monomer reactivity ratios for catalytic systems containing various rare earth elements in III-B family and different solvents were determined. It was found that the reactivity ratio of butadiene was greater than that of isoprene and r_1r_2 near 1, and the composition and microstructure of copolymers were not much affected by variation of polymerization conditions. Both monomer repeat units in the copolymers had *cis*-1,4 contents above 95%, which is a distinguishing feature of coordination polymerization with the lanthanide catalyst system.

INTRODUCTION

In the field of polymer science, copolymerization study is essential not only for investigating the nature of copolymerization process, but also for obtaining new polymers with desired properties. In order to elucidate the mechanism for the stereospecific polymerization of conjugated dienes by coordination rare-earth-based catalysts, we investigated the copolymerization of butadiene with isoprene by using lanthanide naphthenate catalyst¹ and found that both monomer repeat units in the copolymer have high *cis*-1,4 content. The copolymerization of these two monomers with neodymium stearate catalyst system in toluene was recently reported by Monakov et al.² In this paper, we report the copolymerization kinetics of butadiene and isoprene by using a highly active $\text{LnCl}_3\text{-ROH-}\text{AlR}_3$ catalytic system.³ The rare earth element, aluminum alkyl, solvent, and alcohol complex were varied, and from the resulting data the copolymerization rate, monomer reactivity ratios, and sequence distribution were calculated.

EXPERIMENTAL

Materials

Both the monomers used for copolymerization studies were of polymerization grade. Aluminum alkyl, ethyl alcohol and the solvent (hexane, etc.) were of high

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purity. Anhydrous lanthanide chloride was prepared according to the procedure of Taylor and Cartes.⁴

Copolymerization

The copolymerization of butadiene and isoprene was carried out in glass ampules which were dried thoroughly by evacuation and purging with nitrogen several times under heat before use. Catalyst, after aging for a predetermined period at 20°C, was added to the ampule containing monomer. After the introduction of solvent, the ampules were sealed and kept in a thermostat for copolymerization. The reaction was terminated by adding ethyl alcohol containing antioxidant 2,6-diisobutyl-4-methylphenol. Copolymers were dried in an evacuated oven at 40°C. Generally, the copolymerization conditions were fixed as follows: butadiene/isoprene = 6/4 (molar ratio); monomer concentration (M) = 1.25 mol/L; $\text{LnCl}_3/\text{monomer} = 2 \times 10^{-4}$ (molar ratio); $\text{AlR}_3/\text{LnCl}_3 = 30$ (molar ratio); alcohol/ $\text{LnCl}_3 = 4$ (molar ratio); 40°C.

The catalyst was prepared in the presence of a small amount of isoprene (molar ratio isoprene/ $\text{LnCl}_3 = 10$) according to Ref. 3.

Analyses of Copolymers

The intrinsic viscosity of copolymer was determined with Ubbelode viscometer in toluene at 30°C and calculated according to⁵

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln\eta_r)}}{C} \quad (1)$$

The molecular weight distribution of a copolymer was measured with GPC. (The GPC was made by us; 20°C, toluene, flow velocity 1 mL/min.) Its microstructure was determined from infrared spectra according to the following equations⁶

Butadiene:

$$\text{cis-1,4 content (\%)} = (17667 \times D_{738}/A) \times 100 \quad (2)$$

$$1,2 \text{ content (\%)} = (3673.8 \times D_{911}/A) \times 100 \quad (3)$$

$$\text{trans-1,4 content (\%)} = (4741.4 \times D_{967}/A) \times 100 \quad (4)$$

where

$$A = 17667 \times D_{738} + 3673.8 \times D_{911} + 4741.4 \times D_{967} \quad (5)$$

The D_{738} , D_{911} , and D_{967} are the optical densities for the 738 cm^{-1} , 911 cm^{-1} , and 967 cm^{-1} , respectively.

Isoprene:

$$\text{cis-1,4 content (\%)} = (145 \times D_{836} - 1.95 \times D_{890})/A' \times 100 \quad (6)$$

$$3,4 \text{ content (\%)} = (19.9 \times D_{890} - 1.79 \times D_{836})/A' \times 100 \quad (7)$$

where

$$A' = 145 \times D_{836} - 1.95 \times D_{890} + 19.9 \times D_{890} - 1.79 \times D_{836} \quad (8)$$

The D_{836} and D_{890} are the optical densities for the 836 cm^{-1} and 890 cm^{-1} , respectively.

The composition of copolymers was also determined by pyrolytic chromatography (pyrolysis followed by GLC), as there was a linear dependence of butadiene content in copolymer to that in its pyrolytic product with a deviation less than 2%. The butadiene content was evaluated according to following equation:

$$\text{butadiene (wt\%)} = \frac{0.90 \times h_{\text{Bd}}/h_{\text{Ip}}}{1 + 0.90 \times h_{\text{Bd}}/h_{\text{Ip}}} \times 100 \quad (9)$$

$$\text{butadiene (mol\%)} = \frac{1.14 \times h_{\text{Bd}}/h_{\text{Ip}}}{1 + 1.14 \times h_{\text{Bd}}/h_{\text{Ip}}} \times 100 \quad (10)$$

where h_{Bd} (or h_{Ip}) = the height of butadiene (or isoprene) peak in pyrolytic chromatogram.

RESULTS AND DISCUSSION

Verification of Copolymerization

As mentioned above, the lanthanide chloride–alcohol–aluminum alkyl catalytic system is a high active catalyst in the stereospecific polymerization of conjugated dienes. Therefore, in our case, the first problem was to clarify whether butadiene and isoprene were homopolymerized or copolymerized. It is well known that copolymers generally have only one glass transition temperature (T_g) while a mixture of homopolymers has more than one T_g . Table I lists the T_g 's of our polymerized products as measured by DSC and shows that there was only one T_g for a given copolymer composition. The T_g values decreased with increasing butadiene content in the copolymer.

The chromatograms of the pyrolysis data of the homopolymers of butadiene and isoprene, their blend, and copolymerized product are shown in Figure 1. Figure 1 demonstrates the differences in the pyrolytic chromatograms between homopolymers and their blend. Table II shows that the compositions of various copolymer fraction lie in a narrow range and the lower the butadiene content in the copolymer fraction, the lower the intrinsic viscosity. Hence, the product obtained from the copolymerization of butadiene and isoprene with the present catalyst system is indeed a copolymer.

TABLE I
Glass Transition Temperature of Copolymers Prepared from Butadiene and Isoprene (DSC Method)^a

Bd content in monomer (mol %)	Bd content in copolymer (mol %)	T_g of copolymer (°C)
100	100	-94
80	83.2	-88
70	73.4	-85
50	54.5	-77
40	45.7	-74
20	23.2	-66
0	0	-57

^a Perkin Elmer DSC-2C, heating rate = 10°C/min.

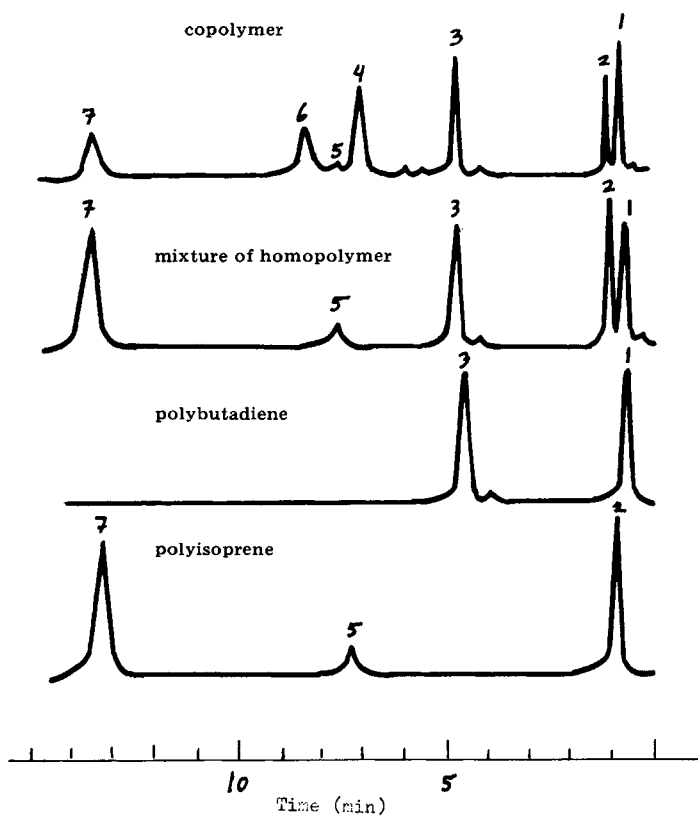


Fig. 1. The pyrolytic chromatogram of polymer: (1) $-(C_4H_6)$; (2) $-(C_5H_8)$; (3) $-(C_4H_6)_2$; (4) $-(C_4H_6-C_5H_8)$; (5) $-(C_5H_8)_2$; (6) $-(C_5H_8-C_4H_6)$; (7) $-(C_5H_8)_2$.

TABLE II
[η] and Compositions of Bd-Ip^a Copolymer and Their Fractions

Expt no.	1030	F-1	F-2	F-3	F-4	F-5	F-6	F-7
Bd content (mol %)	62.8	54.0	58.8	59.4	59.2	61.9	66.1	70.7
[η](dL·g ⁻¹)	4.52	2.57	3.49	5.93	6.70	6.72	9.72	10.32

^a Bd/Ip = 60/40 (mol %).

Copolymerization Rate and Apparent Activation Energy

Figure 2 illustrates the rate of Bd-Ip copolymerization at various temperatures with the catalysts prepared from $NdCl_3-C_2H_5OH-Al(C_2H_5)_3$ -hexane. This figure indicates that the rate is second order with respect to the total monomer concentration. The linearity of logarithm plot of copolymerization rate vs. total catalyst concentration showed that the copolymerization rate was first order with respect to the total concentration of catalyst (Fig. 3).

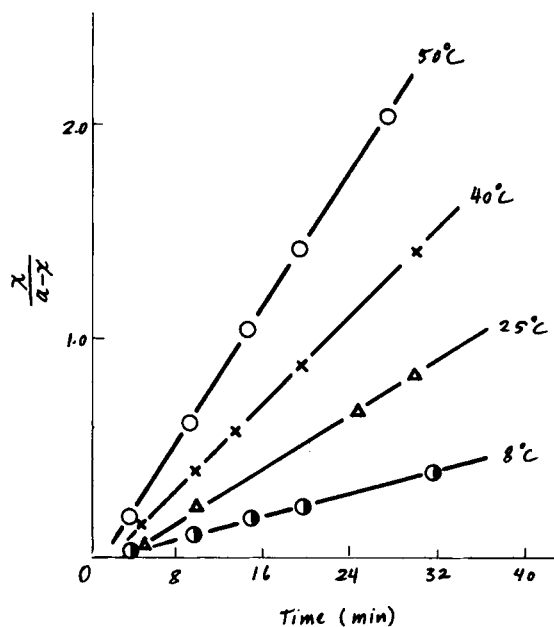


Fig. 2. Copolymerization rate of isoprene and butadiene at various temperatures. NdCl_3 - $\text{C}_2\text{H}_5\text{OH}$ - $\text{Al}(\text{C}_2\text{H}_5)_3$ -hexane; $\text{Bd}/\text{Ip} = 6/4$; $\text{NdCl}_3/\text{monomer} = 2 \times 10^{-4}$; $\text{Al}(\text{C}_2\text{H}_5)_3/\text{NdCl}_3 = 30$; $\text{C}_2\text{H}_5\text{OH}/\text{NdCl}_3 = 4$ (all ratios are molar ratios). $x = \text{yield} (\%)$, $a = 100$.

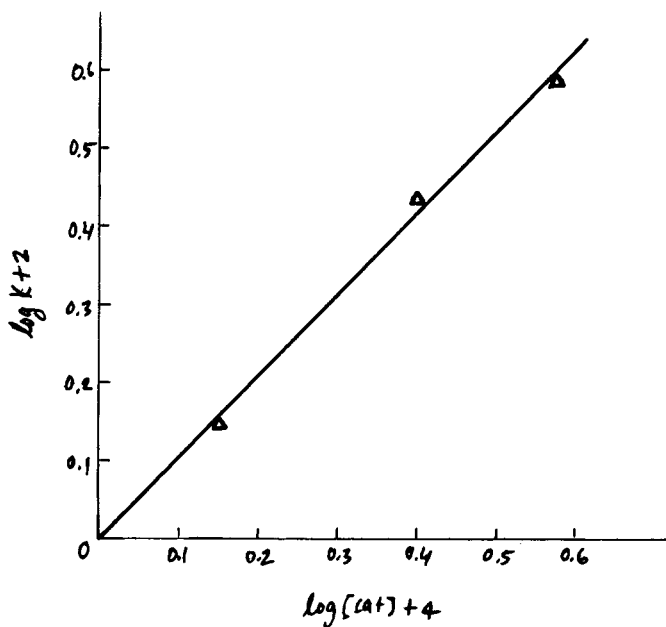


Fig. 3. Copolymerization rate vs. total concentration of catalyst temp 40°C ; other conditions conform with Figure 2.

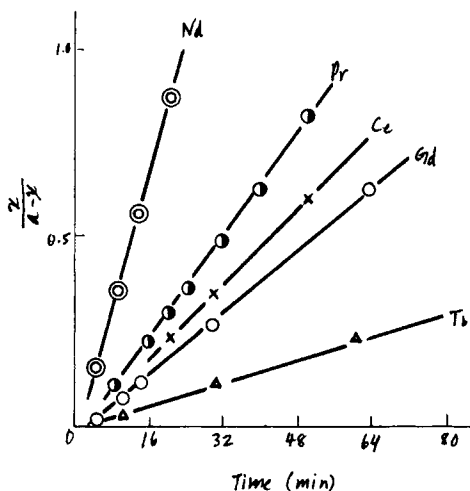


Fig. 4. Effect of rare earth element on copolymerization reaction. Conditions conform with Figure 3.

The copolymerization rate did not vary with the concentration of triethylaluminum in the range from 3.75×10^{-3} (mol/L) to 1.5×10^{-2} (mol/L) with the concentration of NdCl_3 and $\text{C}_2\text{H}_5\text{OH}$ kept constant.

Consequently, we arrived at the copolymerization rate equation as follows:

$$R_p = K_p(M)^2(\text{cat})$$

where (M) = the concentration of monomer and (cat) = the concentration of catalyst.

The effect of different rare earth elements on the catalytic activity during copolymerization is shown in Figure 4. The order of activity did not differ from that shown in both monomers homopolymerization, i.e., $\text{Nd} > \text{Pr} > \text{Ce} > \text{Gd} > \text{Tb} > \text{Dy} > \text{La} \sim \text{Ho} > \text{Y} > \text{Sm} \sim \text{Er} > \text{Tm} > \text{Lu} \sim \text{Yb} \sim \text{Sc} \sim \text{Eu}$.

Figure 5 shows the arrhenius plot of copolymerization rate with various catalytic systems vs. the reciprocal of temperature. Table III summarizes the copolymerization rates and apparent activation energies calculated from Figure 5. The data of Table III show that the copolymerization rate of different catalytic system was appreciably different. The polymerization rate with Nd-catalyst was highest, about three times greater than that with Pr-catalyst, as shown in Table III. It was pointed out in Ref. 3 that the nature of lanthanide-alcohol complex binary system and $\text{LnCl}_3\text{-ROH-AlR}_3$ ternary system was similar. The copolymerization rates determined with a number of binary systems are listed in Table IV, which showed a tendency to a moderate increase of copolymerization rate as the alkyl group in the alcohol complexed to the lanthanide ion was lengthened.

Reactivity Ratio and Sequence Distribution of the Copolymer

The reactivity ratio of butadiene and isoprene was determined according to the Fineman-Rose copolymerization equation.⁷ The polymerization conversions

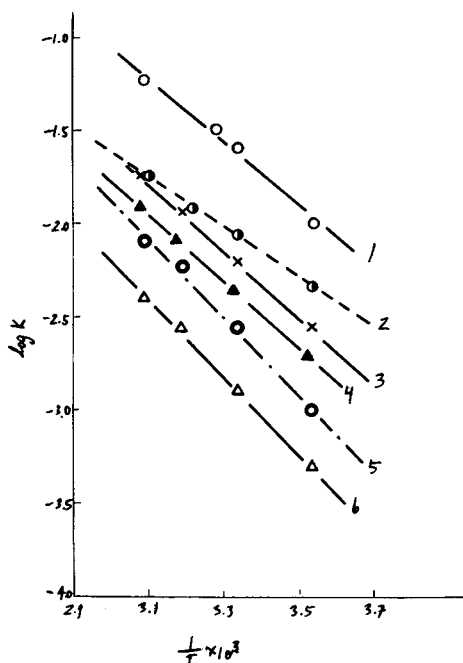


Fig. 5. Copolymerization rate of various catalytic systems: (1) $\text{NdCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3$; (2) $\text{NdCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(i\text{-C}_4\text{H}_9)_3$; (3) $\text{PrCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3$; (4) $\text{CeCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3$; (5) $\text{NdBr}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3$; (6) $\text{TbCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3$. Other conditions conform with Figure 3.

TABLE III
Apparent Activation Energy of Copolymerization of Bd and Ip with Various Catalytic Systems^a

Catalytic system	<i>K</i> , copolymerization rate $\times 10^3$				Apparent activation energy $\pm 0.5(\text{kJ}\cdot\text{mol}^{-1})$
	50°C	40°C	25°C	10°C	
$\text{NdCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3\text{-hexane}$	56.7	38.4	21.5	10.5	31.0
$\text{PrCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3\text{-hexane}$	18.5	12.3	8.2	2.8	34.3
$\text{CeCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3\text{-hexane}$	13.5	8.9	5.2	2.2	33.9
$\text{GdCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3\text{-hexane}$	10.4	6.4	2.8	1.1	41.9
$\text{TbCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3\text{-hexane}$	4.7	3.4	1.5	0.6	39.8
$\text{NdBr}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3\text{-hexane}$	6.2	4.4	2.2	1.0	34.8
$\text{NdCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(i\text{-C}_4\text{H}_9)_3\text{-hexane}$	19.2	12.4	7.6	3.8	30.6

^a Conditions conform with Figure 3.

TABLE IV
Copolymerization Rate with $\text{NdCl}_3\cdot\text{ROH-Al}(\text{C}_2\text{H}_5)_3$ Binary Systems^a

$\text{NdCl}_3\cdot\text{ROH}$	$\text{NdCl}_3\cdot\text{CH}_3\text{OH}$	$\text{NdCl}_3\cdot\text{C}_2\text{H}_5\text{OH}$	$\text{NdCl}_3\cdot n\text{-C}_3\text{H}_7\text{OH}$	$\text{NdCl}_3\cdot i\text{-C}_3\text{H}_7\text{OH}$	$\text{NdCl}_3\cdot n\text{-C}_4\text{H}_9\text{OH}$
Copolymerization rate constant $\times 10^2$ (40°C)	0.083	1.4	3.2	1.1	3.4

^a Other conditions conform with Figure 3.

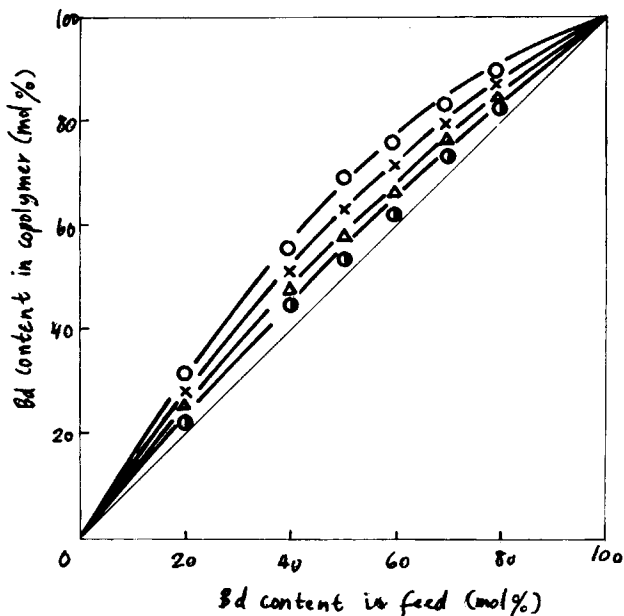
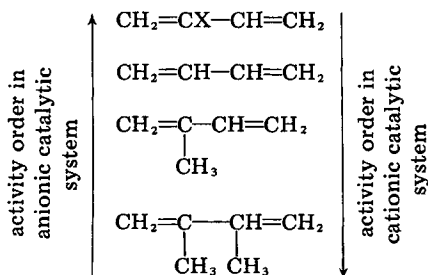


Fig. 6. The dependence of composition of copolymer on that of feed: (●) Nd, Pr, Ce; (▲) Gd; (x) La, Y; (○) H_0 , T_m . Conditions conform with Figure 3.

were controlled below 15% to meet the requirement in evaluation. Figure 6 showed the variation in composition in the copolymer obtained with various feed mixtures. In present case, no matter what kind of catalytic systems was chosen, the butadiene content in copolymer is always greater than that in the feed. Values of the reactivity ratios found with different catalytic systems and their reactivity ratio products were listed in Table V. The data show that the reactivity ratio of butadiene is higher than that of isoprene in all these catalytic systems and the product of reactivity ratios of these two monomers is remarkably close to unity, with the exception for Tb- and Tm-catalyst systems, a characteristic feature of coordination anionic copolymerization as pointed out by Natta.⁸ The product of r_1r_2 is close to 1. It suggests that the copolymers synthesized were essentially random ones which had then been verified by its sequence distribution.

It is well known⁹ that the polymerization activity order of conjugated dienes using a typical cationic or anionic system is as follows:



where X = electron with drawing group.

TABLE V
Reactivity Ratios of Bd and Ip Obtained Using a Different Rare Earth Compound as a Catalyst Component

Rare earth element	r_1 (Bd)	r_2 (Ip)	r_1r_2
La ^a	1.76	0.77	1.36
Ce	1.17	1.04	1.22
Pr	1.10	0.88	0.96
Nd	1.24	0.73	0.91
Sm ^b	1.71	1.03	1.76
Gd	1.58	0.90	1.41
Tb	1.16	0.38	0.44
Dy ^a	1.93	0.66	1.27
Ho ^a	1.90	0.44	0.84
Er ^a	1.85	0.49	0.91
Tm ^c	0.80	0.14	0.11
Lu ^c	2.41	0.55	1.33
Y ^d	1.61	0.72	1.15

^a $\text{LnCl}_3/\text{monomer} = 4 \times 10^{-4}$ mol.

^b $\text{LnCl}_3/\text{monomer} = 10 \times 10^{-4}$ mol.

^c $\text{LnCl}_3/\text{monomer} = 16 \times 10^{-4}$ mol.

^d $\text{LnCl}_3/\text{monomer} = 5 \times 10^{-4}$ mol.

This means that the activity of butadiene is higher than that of isoprene using an anionic catalyst and vice versa using a cationic catalyst. In the case of coordination polymerization, however, it is much more complicated. Generally, if the reactivity ratio of butadiene is greater than that of isoprene, the copolymerization process is assumed to be by a coordination anionic mechanism.⁹ For example, the reactivity ratio of butadiene and isoprene for a typical coordination catalyst $\text{TiI}_4\text{-Al}(i\text{-C}_4\text{H}_9)_3$ (molar ratio of Al/Ti = 1) was $r_1 = 2.8$ and $r_2 = 0.53$, respectively. Based on the data listed in Table V, we conclude that lanthanide-compounds-based catalytic systems exhibit coordination anionic mechanism in the polymerization of dienes. This mechanism was further supported by the results obtained with $\text{C}^{14}\text{H}_3\text{OH}$ and CH_3OT quenching methods in polymerization of butadiene in our laboratory.¹⁰ The radioactivity of the polymer quenched by CH_3OT is over 100 times greater than that of the polymer quenched by $\text{C}^{14}\text{H}_3\text{OH}$. The quenching process can be described as follows:

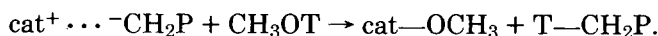


Table VI shows that the reactivity ratio was virtually constant within the temperature range of 10–50°C, and also when the molar ratio of AlR_3 to lanthanide

TABLE VI
Reactivity Ratio of Bd and Ip at Various Temperatures^a

Cat T (°C)	$\text{CeCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(\text{C}_2\text{H}_5)_3$			$\text{NdCl}_3\text{-C}_2\text{H}_5\text{OH-Al}(i\text{-C}_4\text{H}_9)_3$		
	r_1	r_2	r_1r_2	r_1	r_2	r_1r_2
10	1.20	0.89	1.07	1.33	0.89	1.18
25	1.14	0.72	0.82	1.19	0.87	1.04
40	1.25	1.07	1.34	1.13	0.68	0.77
50	1.16	1.0	1.16	1.32	0.87	1.15

^a Conditions conform with Figure 2.

TABLE VII
 Effect of AlR₃/LnCl₃ (Molar Ratio) on Reactivity Ratio of Bd and Ip

Cat Al/Ln (molar ratio)	PrCl ₃ -C ₂ H ₅ OH-Al(C ₂ H ₅) ₃			NdCl ₃ -C ₂ H ₅ OH-Al(<i>i</i> -C ₄ H ₉) ₃		
	<i>r</i> ₁	<i>r</i> ₂	<i>r</i> ₁ <i>r</i> ₂	<i>r</i> ₁	<i>r</i> ₂	<i>r</i> ₁ <i>r</i> ₂
15	1.02	0.67	0.69	1.11	0.59	0.65
30	1.09	0.88	0.96	1.13	0.68	0.77
60	1.13	0.83	0.94	1.37	1.07	1.47

^a Other conditions conform with Figure 3.

 TABLE VIII
 Reactivity Ratios of Bd and Ip Obtained Using NdCl₃-ROH-Al(C₂H₅)₃ Binary System as a Catalyst^a

Catalytic system	<i>r</i> ₁	<i>r</i> ₂	<i>r</i> ₁ <i>r</i> ₂
Ternary-NaCl ₃ -C ₂ H ₅ OH-Al(C ₂ H ₅) ₃	1.24	0.73	0.91
Binary-NdCl ₃ -C ₂ H ₅ OH-Al(C ₂ H ₅) ₃	1.24	1.09	1.35
Binary-NdCl ₃ -CH ₃ OH-Al(C ₂ H ₅) ₃	1.66	1.08	1.79
Binary-NdCl ₃ - <i>n</i> -C ₃ H ₇ OH-(C ₂ H ₅) ₃	1.46	1.37	1.99
Binary-NdCl ₃ - <i>i</i> -C ₃ H ₇ OH-Al(C ₂ H ₅) ₃	1.22	1.06	1.29
Binary-NdCl ₃ - <i>n</i> -C ₄ H ₉ OH-Al(C ₂ H ₅) ₃	1.58	1.46	2.30

^a Conditions conform with Figure 3. The components of the copolymer were determined with JEOL FX-100 ¹H-NMR.

chloride was varied (Table VII). When Al(*i*-C₄H₉)₃ was substituted for Al(C₂H₅)₃, the reactivity ratio remained unchanged.

Table VIII summarizes the reactivity ratios of the binary lanthanide chloride/alcohol complex system we obtained. It showed that the reactivity ratio of butadiene and isoprene both in the binary system and in the ternary system were similar. Hence it assures us once more that there is no difference in mechanism between the studied binary and ternary catalytic systems.

Table IX lists the sequence distribution of copolymer calculated according to the following equation. The probability of forming a sequence of *n* units of monomer M₁ is

$$(P_{M_1})_n = P_{11}^{n-1}(1 - P_{11})$$

where

$$\begin{aligned}
 P_{11} &= \frac{K_{11}(M_1^*)(M_1)}{K_{11}(M_1^*)(M_1) + K_{12}(M_1^*)(M_2)} = \frac{r_1(M_1)}{r_1(M_1) + (M_2)} \\
 &= \frac{r_1}{r_1 + (M_2)/(M_1)}
 \end{aligned}$$

On the supposition that the initial (M₁)/(M₂) = 1 in the feed mixture, the data revealed that the product obtained was a copolymer of random structure and did not vary with changing of rare earth metal element in the catalytic system, and the sequence distribution of isoprene seemed somewhat narrower than that of butadiene, having a sequence of 1 isoprene repeat unit above 50%, and sequence of 3 units only about 5%, as shown in Table IX.

TABLE IX
 Sequence Distribution of Copolymer

Cata- lytic systems	SD of butadiene (%)					SD of isoprene (%)				
	n_1	n_2	n_3	n_4	n_5	n_1	n_2	n_3	n_4	n_5
LaCl ₃	27.5	20.0	14.5	10.5	7.6	66.0	22.4	7.6	2.6	0.9
CeCl ₃	36.3	23.1	14.7	9.4	6.0	59.0	24.2	9.9	4.1	1.7
PrCl ₃	37.8	23.5	14.6	9.1	5.7	63.1	23.3	8.6	3.2	1.2
NdCl ₃	34.9	22.7	14.8	9.6	6.3	67.2	22.0	7.2	2.4	0.8
SmCl ₃	28.0	20.2	14.5	10.5	7.5	59.3	24.1	9.8	4.0	1.6
GdCl ₃	29.7	20.9	14.7	10.3	7.3	62.6	23.4	8.7	3.3	1.2
TbCl ₃	36.6	23.2	14.7	9.3	5.9	79.7	16.2	3.3	0.7	0.1
DyCl ₃	25.7	19.1	14.2	10.5	7.8	69.5	21.2	6.5	2.0	0.6
HoCl ₃	26.0	19.2	14.2	10.5	7.8	77.3	17.5	4.0	0.9	0.2
ErCl ₃	26.5	19.5	14.3	10.5	7.7	75.3	18.6	4.6	1.1	0.3
TmCl ₃	45.4	24.8	13.5	7.4	4.0	100	0	0	0	0
LuCl ₃	21.7	17.0	13.3	10.4	8.2	73.1	19.7	5.3	1.4	0.4
NdCl ₃ - CH ₃ OH	28.7	20.5	14.6	10.4	7.4	58.2	24.3	10.2	4.3	1.8
NdCl ₃ - C ₂ H ₅ OH	34.9	22.7	14.8	9.6	6.3	58.0	24.4	10.2	4.3	1.8
NdCl ₃ - <i>n</i> - C ₃ H ₇ OH	31.4	21.5	14.8	10.1	7.0	52.3	25.0	11.9	5.7	2.7
NdCl ₃ - <i>i</i> - C ₃ H ₇ OH	35.4	22.9	14.8	9.5	6.2	58.5	24.3	10.1	4.2	1.7
NdCl ₃ - <i>n</i> - C ₄ H ₉ OH	29.7	20.9	14.7	10.3	7.3	50.7	25.0	12.3	6.1	3.0

 TABLE X
 $[\eta]$ and Microstructure of Bd-Ip Copolymer Using NdCl₃-C₂H₅OH-Al(C₂H₅)₃ Catalytic System

Solvent T (°C)	$[\eta]$ (dL·g ⁻¹)	Microstructure of copolymer (%)					
		Bd repeat unit		Ip repeat unit			
		<i>cis</i> -1,4	1,2 <i>trans</i> -1,4	<i>cis</i> -1,4	3,4		
Hexane	8	6.57	97.8		2.2	99.4	0.6
	25	5.17	97.1	0.6	2.3	99.4	0.6
	40	4.76	96.8	0.5	2.7	99.4	0.6
	50	4.10	95.2	0.8	4.0	99.8	0.2
Cyclohexane	10	7.21	98.0	0.5	1.5	99.0	1.0
	25	4.67	97.2	0.6	2.2	98.7	1.3
	40	4.40	96.5	0.9	2.6	98.3	1.7
	60	4.17	93.4	1.0	5.6	97.8	2.2
Benzene	10	7.21	97.7	0.6	1.7	98.7	1.3
	25	5.99	97.2	0.6	1.8	98.5	1.5
	40	4.40	96.5	0.6	2.9	98.0	2.0
	60	3.36	94.4	0.9	4.4	97.4	2.6
Toluene	10	4.37	97.1	0.5	2.4	99.0	1.0
	25	2.56	93.9	0.8	5.3	98.6	1.4
	40	2.07	90.0	2.5	7.5	97.2	2.8
	60	1.67	84.3	5.1	10.6	94.3	5.7
Chlorobenzene	10	9.50	97.3	0.8	1.7	98.9	1.1
	25	7.79	96.9	0.8	2.3	98.6	1.4
	40	5.53	97.0	0.8	2.2	98.3	1.7
	60	4.92	96.4	1.0	2.6	97.8	2.2

TABLE XI
Effect of $\text{AlR}_3/\text{LnCl}_3$ and Bd/Ip on $[\eta]$ and Microstructure of Copolymer

Variation of ratio	$[\eta]$ ($\text{dL}\cdot\text{g}^{-1}$)	Microstructure of copolymer (%)					
		Bd repeat unit			Ip repeat unit		
		<i>cis</i> -1,4	1,2	<i>trans</i> -1,4	<i>cis</i> -1,4	3,4	
$\text{Al}(\text{C}_2\text{H}_5)_3/\text{NdCl}_3$ (molar ratio)	15	6.03	97.0	0.5	2.5	98.6	1.4
	20	5.50	96.6	0.8	2.6	98.5	1.5
	25	5.20	96.0	1.0	2.6	98.5	1.5
	30	4.76	96.8	0.5	2.7	99.4	0.6
	60	3.87	95.4	1.2	3.5	98.9	1.1
	80	3.26	94.5	1.7	3.8	98.9	1.1
Bd/Ip (molar ratio)	8/2	5.46	97.5	0.6	1.9	99.3	0.7
	6/4	4.76	96.8	0.5	2.7	99.4	0.6
	5/5	4.53	96.1	0.9	3.0	98.4	1.6
	4/6	5.00	95.6	0.7	3.7	98.4	1.6
	2/8	4.71	93.0	2.7	4.3	97.8	2.2

^a Other conditions conform with Figure 3.

TABLE XII
 $[\eta]$ and Microstructure of Copolymer Obtained in $\text{LnCl}_3\text{-ROH-}\text{AlR}_3$ Binary System

Alcohol complex	$[\eta]$ ($\text{dL}\cdot\text{g}^{-1}$)	Microstructure of copolymer (%)				
		Bd repeat unit			Ip repeat unit	
		<i>cis</i> -1,4	1,2	<i>trans</i> -1,4	<i>cis</i> -1,4	3,4
Methyl alcohol	5.45	97.1	0.5	2.4	98.5	1.5
Ethyl alcohol	5.55	96.4	0.7	2.9	98.6	1.4
<i>n</i> -Propyl alcohol	4.49	96.8	0.6	2.6	98.5	1.5
<i>n</i> -Butyl alcohol	4.02	96.3	0.7	3.0	98.6	1.4

Intrinsic Viscosity and Microstructure of Butadiene–Isoprene Copolymer

Table X summarizes the effects of copolymerization temperature and polymerization solvent on the intrinsic viscosity and microstructure of the resulting copolymer. The $[\eta]$ values of copolymers were fairly similar when hexane, cyclohexane, and benzene were used as solvents. The values were significantly greater in chlorobenzene and smaller in toluene.

The temperature, time, and the solvents studied during copolymerization do not exert much influence on the copolymer IR microstructure when all other conditions are kept the same. Both butadiene and isoprene repeat units have *cis*-1,4 contents above 95%.

As seen from Table XI, the $[\eta]$ of copolymers decreases with increasing the molar ratio of AlR_3 to NdCl_3 due to greater chain transfer reaction at higher aluminum alkyl concentration. It was observed along with the higher aluminum alkyl and isoprene concentrations in feed, a slight decrease of *cis*-1,4 content in butadiene unit occurs.

Table XII lists the $[\eta]$ and the IR microstructure of copolymer obtained with $\text{LnCl}_3\text{-ROH-}\text{AlR}_3$ binary systems. From the data one can see that the IR mi-

crostructures of copolymer are not affected by variation of alcohol complexed to metal ion, and the $[\eta]$ of copolymer shows a small decrease with increase of chain length of alkyl radical of the alcohol.

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