

## Progress in Coordination Polymerization by Rare Earth Catalysts\*

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### Abstract

Rare earth catalysts represent an unprecedented case where either butadiene, isoprene or mixtures of butadiene and isoprene can be polymerized to elastomers with high content of *cis*-isomer and good properties.

As high as 98% *cis*-polyacetylene films with metallic sheen can be prepared by rare earth catalysts at room temperature. Rare earth catalysts are excellent as high *cis*-stereospecific polymerization catalysts for acetylenes.

High molecular weight polyepoxides can also be prepared by rare earth catalysts.

### Introduction

China has abundant resources of rare earths. This challenges our interest in investigating rare earth compounds as coordinating catalysts in coordination polymerization. Early in the 1960s, we suggested a rare earth compound as a butadiene polymerization catalyst for the first time. Ziegler–Natta catalysts first described in the literature did not include rare earth elements in Group IIIB. A new ‘family’ of rare earth coordination catalysts with fairly high activity and high stereospecificity in polymerization of conjugated dienes has been developed since then. Rare earth catalysts represent an unprecedented case where either butadiene, isoprene or mixtures of butadiene and isoprene can be polymerized to elastomers with high content of the *cis*-isomer and good properties.

Since 1981 we have been extending the study of rare earth coordination catalysts toward polymerization of acetylene, phenylacetylene and some terminal alkynes. As high as 98% *cis*-polyacetylene film with metallic sheen can be prepared by these new catalysts at room temperature. The results of the study show that rare earth catalysts are excellent as high *cis*-stereospecific polymerization catalysts for acetylenes.

Very recently we have succeeded in preparing high molecular weight polyepoxides such as polyethylene oxide, and polypropylene oxide by rare earth catalysts. Thus a new area of coordination polymerization has been opened. This article describes briefly the progress in coordination polymerization by rare earth catalysts.

### Diene Polymerization

Linear polybutadiene with a high proportion of the *cis*-isomer with molecular weight from  $10^4$  to  $10^6$  and molecular weight distribution from 3–10 can be prepared with rare earth catalysts. These polybutadienes have the following features: excellent compounding behavior; high tensile strength of the vulcanizates and better cold flow resistance. Linear polyisoprene of high molecular weight ( $[\eta] = 10$  dl/g,  $M = 2 \times 10^6$ ) and varying molecular weight distribution ( $M_w/M_n = 2-10$ ) could be obtained. Properties of the polyisoprene gum, compound and vulcanizate are comparable to the corresponding properties of the Ti-catalyzed polyisoprene.

The rare earth coordination catalysts used initially in butadiene polymerization were a binary system composed of rare earth chlorides ( $\text{LnCl}_3$ ; Ln, Y, La, Ce, Pr, Nd, Sm, Gd, Er and  $\text{AlR}_3$  (R = Et, *i*-Bu; Ln = lanthanide) [1]. It was found that the stereospecificity of these catalysts was high, yet their catalytic activity was rather low. The adoption of rare earth  $\beta$ -diketone chelates such as  $\text{NdB}_3$ ,  $\text{NdBTA}$ ,  $\text{NdTTA}$ ,  $\text{PrB}_3$ ,  $\text{PrTTA}$ ,  $\text{YB}_3$ ,  $\text{YBTA}$  and  $\text{LaBTA}$  instead of the chloride made the catalyst system a homogeneous one and with a somewhat higher activity [2]. Throckmorton modified the catalyst system from binary to a ternary one—cerium octanoate— $\text{AlR}_3$ —halide which showed higher polymerization activity [3].

In the 1970s we Chinese chemists developed three-component systems including lanthanide naphthenate, lanthanide carboxylate or lanthanide phosphonate together with aluminum alkyl and a halide-containing compound. These catalysts are used for butadiene (Bd) polymerization, for isoprene (Ip) polymerization, for 2,4-hexadiene and for Bd–Ip copolymerization. Subsequently, it was found that

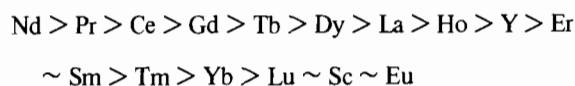
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the addition of an appropriate amount of an alcohol to the original lanthanide chloride–aluminum alkyl binary system led to greatly enhanced activity without any decrease in stereospecificity [4]. Further investigation revealed that the lanthanide halide first reacts with the alcohol added to form an alcoholate which then reacts with  $AlR_3$  to form an active catalyst. Thus a new efficient binary system of  $RCl_3 \cdot 3(\text{alcohol})$ –aluminum alkyl was established [4]. Since 1980 many new binary systems composed of aluminum alkyl and the following rare earth compounds have been developed:  $NdCl_3 \cdot 3P_{350}$  [5];  $NdCl_3 \cdot 3TBP$  [6];  $LnCl_3 \cdot 4DMSO$  [7];  $LnCl_3 \cdot nHMPA$  [8];  $LnCl_3 \cdot 2THF$  [9];  $Nd(i-OPr)_3 \cdot nCl_n$  [10];  $(CF_3COO)_2NdCl \cdot Et_2O$  or  $(CF_3COO)_2NdCl \cdot EtOH$  [11];  $NdCl_3 \cdot 1.5Py$ ,  $NdCl_3 \cdot 1.5DPy$ ,  $NdCl_3 \cdot 2HMTA$ ,  $NdCl_3 \cdot 2Phen$  and  $NdCl_3 \cdot 3EDA$ , etc.,  $NdCl_3 \cdot N$ -containing complexes [12];  $C_5H_5LnCl_2 \cdot nTHF$  ( $C_5H_5$  = cyclopentadienyl,  $Ln = Ce, Pr, Nd, Gd$  and  $Y$ ,  $n = 0, 1, 2, 3$ ) and  $C_5H_5LnCl_2 \cdot HCl \cdot 2THF$  ( $Ln = Pr$  and  $Nd$ ) [13];  $C_9H_7LnCl_2 \cdot (C_4H_8O)_x$  ( $Ln = Nd, Pr, Gd$  and  $Sm$ ;  $C_9H_7$  = indenyl,  $C_4H_8O$  = tetrahydrofuran,  $x = 0, 1, 2$ ) [14]. Some polymer-supported rare earth catalysts have been developed recently [15, 16].

The role of different rare earth elements in the stereospecific polymerization of dienes can be generalized as follows: the stereoregularity of polydienes obtained with different rare earth elements is nearly the same and reflects the similarity in chemical nature of 4f orbital electrons in all rare earth elements. On the other hand, the activity of the rare earth catalysts in diene polymerization varies from one to another within the series. This indicates the difference in complexing ability due to the electronic structure or the number of 4f orbital electrons in each kind of element in the series.

Both polybutadiene and polyisoprene with high *cis*-1,4 content can be obtained by the same rare earth catalyst, as shown in Table I. This is one of the characteristics of the rare earth catalyst system.

The catalytic activity of various individual rare earth compounds with the same ligand shows the same trend in relative activity in diene polymerization with the following three different catalyst systems:  $Ln(naph)_3-Al(i-Bu)_3-Al_2Et_3Cl_3$ ;  $LnCl_3-AlEt_3-EtOH$ ;  $LnCl_3 \cdot (TBP)_3-Al(i-Bu)_3$ . That is, the activity decreases in the following order:



For the active catalysts, the rare earth elements remain in the trivalent state, as evidenced by chemical analyses and spectrophotometric studies. On the other hand, elements having very low or no polymerization activity, such as Sm and Eu, show reduction to bivalency accompanied by a color change. Two explanations have been suggested for the different activities of the elements maintaining their trivalent state: one considers the activity difference as a result of difference in energy change during the formation of a bond between the diene and rare earth ions [6]; the other suggests that the difference in  $Ln-C$  bond strength affects the inserting activity of the monomer.

It is well known that the number of vacant sites on the active metal ion and the distribution of its electron density, *i.e.* bond polarity and bond strength of the coordination complex, can be changed by varying the ligands coordinated to it and the type of aluminum alkyl used, which in turn influences the activity and stereospecificity of the catalyst thus prepared. The effects of ligand groups and alkyl groups in

TABLE I. Microstructure of Polydienes Prepared with Catalysts Containing Different Rare Earth Elements

Rare earth element	Polybutadiene <sup>a</sup>			<i>cis</i> -1,4-Polyisoprene		3,4-Polyisoprene	
	<i>cis</i> -1,4	<i>trans</i> -1,4	1,2	(a)	(b)	(a)	(b)
La	97.2	2.1	0.7	94.1	94.2	5.9	5.8
Ce	97.2	2.1	0.7	94.8	93.6	5.2	6.7
Pr	97.2	2.2	0.6	94.9	93.9	5.1	6.1
Nd	97.3	2.2	0.5	94.7	95.0	5.1	5.0
Sm	98.0	1.6	0.4	96.7	94.6	3.3	5.4
Gd	97.3	2.2	0.5	96.8	96.0	3.2	4.0
Tb	97.9	1.6	0.5	97.2	95.2	2.8	4.8
Dy	97.5	1.9	0.6	97.2	95.2	2.8	4.8
Ho	96.7	2.8	0.5	97.4	95.5	2.6	4.5
Er	93.0	6.1	0.9	97.4	94.7	2.6	5.3
Tm	90.6	8.7	0.7	97.6		2.4	
Yb	97.1	2.6	0.3	98.0		2.0	

<sup>a</sup> $LnCl_3$  catalyst.

<sup>b</sup> $Ln(naph)_3$  catalyst.

TABLE II. Effect of Components in the Catalytic System on the Polymerization of Isoprene

Catalyst component	Yield (%)	[ $\eta$ ] (dl/g)	Microstructure of polyisoprene		
			<i>cis</i> -1,4	<i>trans</i> -1,4	3,4
NdX <sub>3</sub> + C <sub>2</sub> H <sub>5</sub> OH + Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>					
X = F			95.2	0	4.8
Cl	84	5.7	96.2	0	3.8
Br	42	6.6	93.7	0	6.3
I	5	5.8	90.5	0	9.5
NdL <sub>3</sub> + Al( <i>i</i> -Bu) <sub>3</sub> + Al <sub>2</sub> Et <sub>3</sub> Cl <sub>3</sub>					
L = Nd(AA) <sub>3</sub> ·2H <sub>2</sub> O	58	5.0	94.1	0	5.9
Nd(BA) <sub>3</sub> ·2H <sub>2</sub> O	60	6.4	94.5	0	5.5
Nd(P <sub>204</sub> ) <sub>3</sub>	96	3.5	94.7	0	5.3
Nd(naph) <sub>3</sub>	82		95	0	5.0
Nd(naph) <sub>3</sub> + Al <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> Cl <sub>3</sub> + AlR <sub>3</sub>					
R = Al(CH <sub>3</sub> ) <sub>3</sub>	20	6.28	94	0	6
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	41	7.10	95	0	5
Al( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	66	7.81	94	0	6
Al( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> H	70	4	94	0	6

aluminum alkyl on the polymerization activity, molecular weight and microstructure of polyisoprene are illustrated in Table II.

The activity sequences of NdCl<sub>3</sub>·N-containing complexes for butadiene polymerization in combination with various alkyl aluminum are different, as summarized as follows [12]:

(i) in combination with AlEt<sub>3</sub>, the activity decreases in the following order: EDA > THF > *i*-PrOH > Py > HMTA > DPy ≫ Phen

(ii) in the case of Al(*i*-Bu)<sub>3</sub>: EDA ≈ THF > *i*-PrOH > HMTA > DPy > Py ≫ Phen

(iii) in combination with HAl(*i*-Bu)<sub>2</sub>: Phen > THF > *i*-PrOH > EDA > HMTA > Py > DPy

That is, NdCl<sub>3</sub>·3EDA forms very highly active systems with both AlEt<sub>3</sub> and Al(*i*-Bu)<sub>3</sub>, while NdCl<sub>3</sub>·2Phen is active only with HAl(*i*-Bu)<sub>2</sub> as a cocatalyst.

Another characteristic of rare earth coordination catalysts is that the high *cis* stereospecificity of polybutadiene and polyisoprene is quite indifferent to the changes in composition and the relative proportion of the catalyst components, as well as other polymerization conditions used in the process.

Kinetic studies on the rare earth catalyzed polymerization of diene have been carried out by Chinese scientists [17–21], as well as Russian scientists [22]. Only a few points from the results will be mentioned. The equation of the butadiene polymerization rate generally can be described as:

$$V = k[\text{Ln}][\text{Al}]^n[\text{M}] \quad \text{or} \quad R_p = k_p[\text{C}^*][\text{M}]$$

where [Ln] = concentration of rare earth catalyst; [Al] = concentration of alkyl aluminum; [M] = concentration of monomer;  $R_p$  = rate of propagation;  $k_p$  = rate constant of propagation; [C\*] = concentra-

tion of active species. In the case of AlEt<sub>3</sub>,  $n = 1/2$ ; with Al(*i*-Bu)<sub>3</sub>  $n = 1$ ; and  $n = 1/3$  in the case of Al(*i*-Bu)<sub>2</sub>H. For isoprene polymerization the following rate equation has been established:  $R_p = k_p[\text{M}][\text{Cat}]^{1.75}$ ,  $E = 7.5$  kcal/mol [21];  $E = 9.0$  kcal/mol [19]. The number of active species of the Nd(naph)<sub>3</sub> and NdCl<sub>3</sub> systems in butadiene polymerization, determined by tritiated methanol quenching, kinetic and retarding agent methods amounts to 0.6–10 mol% of Nd, while in Ti catalyst systems generally it is only about 0.5%.

Tritiated and <sup>14</sup>C-labelled methanol (CH<sub>3</sub>OT and <sup>14</sup>CH<sub>3</sub>OH) quenching techniques have been used for determining the number of active centers in butadiene polymerization with the neodymium compound—Al(*i*-Bu)<sub>2</sub>Cl—AlR<sub>3</sub> systems [17]. It was found that the specific radioactivity of the polymer quenched by CH<sub>3</sub>OT was over 100 times greater than that of the polymer quenched by <sup>14</sup>CH<sub>3</sub>OH. This result suggests that the polymerization of diene by rare earth coordination catalysts follows an anionic coordination mechanism. The mechanism was further supported by the change of composition of butadiene–isoprene copolymer with rare earth catalysts [23].

It has been reported that under certain conditions isoprene polymerization with a Nd(naph)<sub>3</sub>—Al(*i*-Bu)<sub>3</sub>—Al<sub>2</sub>Et<sub>3</sub>Cl<sub>3</sub> catalyst proceeded by a 'living' polymerization mechanism. This means that the molecular weight of polymer increases proportionally with increasing conversion; molecular weight distribution of the polymer remains unchanged during polymerization. The termination and transfer of the growing polymer chain are almost entirely absent and a block copolymer can be prepared [24]. Recently,

the above mentioned phenomenon has been found also in butadiene polymerization with  $\text{NdCl}_3 \cdot i\text{PrOH}-\text{Al}(i\text{-Bu})_3$  binary catalyst. That is, the molecular weight of polybutadiene increased with polymerization time or conversion, while the number of macromolecules per mol of Nd remained constant, indicating the absence of a chain transfer and termination at polymerization temperatures below  $-30^\circ\text{C}$ . Block copolymers were formed under the given conditions [25].

Rare earth catalysts have a long lifetime of activity. Experimental data indicate that their catalytic activity is retained unchanged even after aging 40 days. In the absence of a solvent, the mixture of rare earth catalyst components after being heated to  $150-180^\circ\text{C}$  under reduced pressure for 1 h is still active for diene polymerization and keeps its high stereospecificity. This indicates that the thermal stability of the rare earth metal-carbon bond is relatively high [26].

Rare earth active species for diene polymerization from the following catalyst systems have been isolated.

*The  $(\text{CF}_3\text{COO})_2\text{LnCl} \cdot \text{EtOH}-\text{AlEt}_3$  or  $(\text{CF}_3\text{COO})_2\text{LnCl} \cdot 2\text{THF}-\text{AlEt}_3$  Systems*

Six Ln- (Ln = La, Ce, Pr, Nd, Sm and Eu) and Al-containing bimetallic complexes have been isolated from the titled homogeneous catalyst by Jin *et al.* [27]. These complexes alone can function as active catalysts in the polymerization of butadiene or isoprene giving the same regularity and stereospecificity of polymerization as the binary system.

*The Ternary  $(i\text{-PrO})_3\text{Nd}-\text{AlEt}_3-\text{AlEt}_2\text{Cl}$  System and Binary  $(i\text{-PrO})_2\text{NdCl}-\text{AlEt}_3$  System*

Shan *et al.* [28] have obtained a single crystal from the titled ternary system. The crystal was confirmed by a four-circle diffractometer study to have the following parameters of a triclinic unit cell space group *PT*:  $a = 15.195 \text{ \AA}$ ,  $b = 15.263 \text{ \AA}$ ,  $c = 13.749 \text{ \AA}$ ,  $\alpha = 90.01^\circ$ ,  $\beta = 95.123^\circ$ ,  $\gamma = 82.65^\circ$ ,  $V = 3149.5 \text{ \AA}^3$ ,  $Z = 1$ . It is a dimer of the polynuclear Nd-Al bimetallic complex with a formula of  $[\text{Al}_3\text{Nd}_6(\mu\text{-Cl})_6(\mu_3\text{-Cl})_6(\mu_2\text{-Et})_9\text{Et}_5(i\text{-PrO})_2]_2$ . The single crystal has high activity and stereospecificity for catalysed polymerization of butadiene. An active bimetallic complex Nd-Al was also isolated from the titled binary catalyst system.

The copolymerization of butadiene and isoprene was first investigated by using lanthanide naphthenate systems and was found unique in that both butadiene and isoprene monomer moieties in the copolymers are in a high *cis*-1,4 configuration, in contrast to copolymerizations with Co- or Ti-based catalysts, where usually only one of the comonomers polymerizes to a high *cis*-1,4 configuration while the other is polymerized to a lower *cis*-1,4 content than

in its homopolymerization [29]. The copolymerization was also carried out by a Nd stearate system [30]. Shen *et al.* have studied the copolymerization kinetics of butadiene and isoprene by using highly active  $\text{LnCl}_3-\text{EtOH}-\text{AlR}_3$  catalyst systems with the variation of rare earth element, aluminum alkyl, solvent and alcohol complex [31]. The microstructure of copolymers so prepared is not affected materially by the composition of the monomer mixtures, while the microstructures of copolymers prepared with Ti or Co catalysts change tremendously with the content of the comonomer. The Al/Ln molar ratio, polymerization temperature and type of solvent also do not exert much influence on the microstructure of the copolymer. Both butadiene and isoprene repeat units in copolymer have *cis*-1,4 contents above 95%. The butadiene-isoprene copolymers have excellent low temperature properties.

The rate of the butadiene-isoprene copolymerization reaction with  $\text{NdCl}_3$  system is second-order with respect to the total monomer concentration and is first-order with respect to the total concentration of catalyst. The orders of activity of catalysts containing various rare earth elements do not differ from that shown in both monomer homopolymerization. Values of the reactivity ratios found with different catalysts and their reactivity ratio products are listed in Table III. These results further confirm that the copolymerization reaction proceeds by a coordination anionic mechanism. The relationship between the value of  $n$  in  $\text{Nd}(i\text{-PrO})_{3-n}\text{Cl}_n$  and the reactivity ratio of butadiene and isoprene with the binary catalyst  $\text{Nd}(i\text{-PrO})_{3-n}\text{Cl}_n\text{AlEt}_3$  has been studied [32].

TABLE III. Reactivity Ratios of Butadiene (Bd) and Isoprene (Ip) Obtained Using a Different Rare Earth Compound as a Catalyst Component

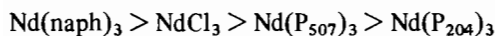
Rare earth element	$r_1$ (Bd)	$r_2$ (Ip)	$r_1 r_2$
La <sup>a</sup>	1.76	0.77	1.36
Ce	1.17	1.04	1.22
Pr	1.10	0.88	0.96
Nd	1.24	0.73	0.91
Sm <sup>b</sup>	1.71	1.03	1.76
Gd	1.58	0.90	1.41
Tb	1.16	0.38	0.44
Dy <sup>a</sup>	1.93	0.66	1.27
Ho <sup>a</sup>	1.90	0.44	0.84
Er <sup>a</sup>	1.85	0.49	0.91
Tm <sup>c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

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

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

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

Factors affecting the copolymerization reaction of ethylene and butadiene with rare earth coordination catalysts such as variation of the monomer ratio, aluminum alkyl, ligand and rare earth element have been investigated [33]. It was found that the catalytic activity of various ligands and rare earth elements in copolymerization have the following order:



and  $\text{Pr} > \text{Nd} > \text{Gd} > \text{Dy} > \text{La} > \text{Er}$ .

This order agrees with that of ethylene polymerization [34], but differs from that of diene polymerization. The copolymers contain long ethylene-ethylene sequences and a *cis*-1,4 butadiene unit [33].

The polymerization of 1,3-pentadiene [35, 36], 2,4-hexadiene [37] and 2,3-dimethyl-1,3-butadiene with rare earth coordination catalysts have also been reported.

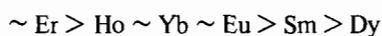
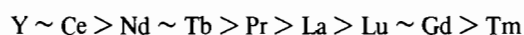
### Alkyne Polymerization

Polyacetylene (PA) is the simplest conjugated polymer and arouses considerable interest because of its metallic conductivity ( $10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ ) possessed by doping. Polyacetylene has *cis*- and *trans*-isomers. Both *cis*- and *trans*-PA can be doped. The *cis*-polymer is more elastic, flexible and easy to process. Furthermore, the doping effect of the *cis*-polymer is even greater than that of the *trans* one. Therefore, efforts have been made to synthesize high *cis* content PA recently. The commonly used catalysts for preparing high *cis* content PA are  $\text{Ti}(\text{OBu})_4\text{-AlEt}_3$  ( $-78^\circ\text{C}$ ) and  $\text{Co}(\text{NO}_3)_2\text{-NaBH}_4$  ( $-80^\circ\text{C}$ ). Shen *et al.* for the first time have investigated the stereospecific polymerization of acetylene by using rare earth coordination catalysts [38]. Thus a new 'family' of coordination catalysts based upon rare earth compounds for the high *cis* content acetylene polymerization at room temperature have been developed and a new variety of PA-rare earth PA results. We have carried out a systematic and detailed study. These

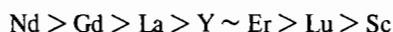
studies include catalysts, polymerization process, kinetics, mechanism, electrochemical properties, structure and the fabrication of rare earth PA cells.

The *cis* contents of PA obtained by all rare earth catalysts composed of naphthenate and phosphonate with aluminum alkyl are listed in Table IV. It is seen that the *cis* content of PA obtained by the  $\text{Ln}(\text{P}_{204})_3$  system is somewhat lower than that of  $\text{Ln}(\text{naph})_3$ -catalyzed PA. Rare earth naphthenates combined with  $\text{Al}(\text{i-Bu})_3$  systems are the best catalysts to synthesize easily and conveniently high *cis* content PA with metallic appearance at room temperature [39]. The variation of polymerization parameters, such as polymerization temperature and molar ratio of aluminum alkyl to the rare earth compound, have no significant effect on the microstructure of the PA [39].

The catalytic activity on the PA film yield with the  $\text{Ln}(\text{naph})_3\text{-Al}(\text{i-Bu})_3$  system at  $30^\circ\text{C}$  decreased in the following order:



Nevertheless, in the  $\text{Ln}(\text{P}_{204})_3$  system the catalytic activity has the following sequence:



It is postulated that the activity may be related to the radii of the rare earth ions and the hardness of the ionic hard-soft acid [40].

Addition of an appropriate third component not only facilitates the formation of silvery PA film and raises the polymer yield, but it also can raise the *cis* content of PA. The effectiveness on addition of a third component (donor) is in the following order in the  $\text{Ln}(\text{P}_{204})_3\text{-Al}(\text{i-Bu})_3$  system [41]:

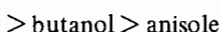
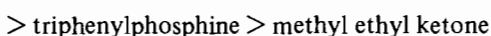
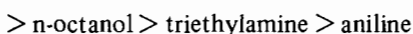
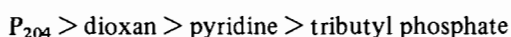
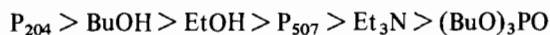


TABLE IV. The *cis* Content of Polyacetylene (%)

Rare earth	$\text{Ln}(\text{naph})_3$	$\text{Ln}(\text{P}_{204})_3$	Rare earth	$\text{Ln}(\text{naph})_3$	$\text{Ln}(\text{P}_{204})_3$
Sc	96.0	96.0 <sup>a</sup>	Gd	96.1	84.0
Y	96.2	88.5	Tb	96.0	91.1
La	95.0	92.2	Dy	95.8	96.1
Ce	92.4	83.5	Ho	96.6	83.4
Pr	96.0	94.9	Er	96.7	89.4
Nd	96.9	92.2	Tm	96.0	85.5
Sm	95.3	86.3	Yb	93.6	79.5
Eu	88.0	76.4	Lu	90.9	83.7

<sup>a</sup>Polymerization temperature  $0^\circ\text{C}$ .

The effectiveness of a third component in raising the yield of PA film with the  $\text{Nd}(\text{i-OPr})_3\text{-Al}(\text{i-Bu})_3$  system has the following order [42]:



Polyacetylenes obtained by rare earth coordination catalysts are silvery grey films with a metallic luster and are not soluble in organic solvents or inorganic acids and bases. It is worth noting that PA so obtained is comparatively stable and isomerizes only slowly when it is stored in air at room temperature.

The electron spin resonance spectra of PA show that the polymers are paramagnetic and their unpaired electron concentrations and  $g$  values are about  $10^{16}$  spins/g and  $2.0028 \pm 0.0001$  respectively. The differential scanning calorimetry of the PA so obtained reveals the existence of two exothermic peaks at 195–200 °C and 375–380 °C, and one endothermic peak at 460 °C which are attributed to *cis-trans* isomerization, hydrogen migration, crosslinkage and decomposition of PA. These temperatures are higher than that of  $\text{Ti}(\text{OBu})_4$ -catalyzed PA, thus also reflecting the thermal stability of rare earth polyacetylene. The X-ray diffraction patterns of these PA reveal that the specimens are crystalline polymers characterized by an intense and sharp reflection at a Bragg angle between  $2\theta = 23.1\text{--}23.3^\circ$ . The crystallinity of scandium-catalyzed PA is about 70% [43]. A clear spot diagram, typical of a single crystal, in the electron diffraction pattern was observed in  $\text{Nd}(\text{P}_{507})_3$ -catalyzed polyacetylene [44]. The scanning and transmission electron micrograph images of rare earth catalyzed PA show clearly discernible fibrillar morphology. They consist of a fleece of randomly oriented fibers with diameters of 200–650 Å and of indefinite length, depending on the catalyst and polymerization conditions used [45].

In order to have more insight into the characteristics of these catalyst systems, the kinetics and mechanism of polymerization of acetylene in rare earth coordination catalysts were investigated [40]. It was shown that the initial rate of the reaction is first-order with respect to the overall concentration of catalyst and the pressure of acetylene in the system. The active species was assumed to be deactivated by a bimolecular mechanism. According to the results and arguments, an anionic coordination mechanism for acetylene polymerization in rare earth coordination catalysts has been proposed.

The electrical resistivity of rare earth PA with high *cis* content is  $10^{8-10}$  ohm cm. Therefore, pristine PA film is an organic semiconductor or insulator, but it can be doped either chemically or electrochemically. The electrical conductivities of iodine-doped PA was raised 11 to 12 orders of magnitude to the metallic conducting regime [46]. The iodine complexes of PA also have been characterized by IR, DSC, X-ray and

SEM. Recently we have investigated the doping of rare earth PA with  $\text{FeCl}_3$ . The highest conductivity obtained for  $\text{FeCl}_3$ -doped *cis*-PA reaches a little over  $1000 \text{ ohm}^{-1} \text{ cm}^1$ . The average drop in conductivity of the samples  $[\text{CH}(\text{FeCl}_4)_{0.0555}]_x$  and  $[\text{CH}(\text{FeCl}_4)_{0.0508}]_x$  is only approximately 0.5% and 0.8% per day [47, 48]. It seems  $\text{FeCl}_3$ -doped rare earth PA has the most stable conductivity. A systematic study of the chemical doping of rare earth PA films with all 15 lanthanide chlorides has also been carried out by us [49]. The conductivities of *cis*- and *trans*-rare earth PA films increase 1–3 orders after doping with  $\text{LnCl}_3$ . No significant difference is observed among the PA films doped with various 15 rare earth chlorides. This may be due to the similarity in structure of all  $\text{LnCl}_3$  compounds. These doped films can be used as substrates for the redoping with  $\text{FeCl}_3$  or  $\text{I}_2$  to prepare films having high and more stable conductivities. The electrochemical doping of rare earth PA employing organic and aqueous electrolytes and the electrochemistry of several PA batteries have been studied [50, 51]. The study revealed that the rare earth PA could be utilized as the cathode of a battery either in an aqueous or organic electrolyte solution. The aqueous PA battery can be utilized as a primary battery.

Polymer composite films of rare earth PA and various elastomers (butadiene styrene rubber, natural rubber, *cis*-1,4-polybutadiene and ethylene-propylenediene terpolymer) which showed higher toughness, tensile strength and resistance to oxygen attack have been synthesized [52].

The rare earth naphthenates of Y, Sc, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, in combination with trialkyl aluminum, were found for the first time to be active for phenylacetylene polymerization by Shen *et al.* [53–55]. Two kinds of polymer of phenylacetylene are obtained. One is a yellow or dark yellow powder with low ( $\bar{M}_n = 1000$ ) to moderate ( $\bar{M}_n = 4000$ ) molecular weights, which dissolves in common organic solvents and exhibits a low degree (28%) of crystallinity. The other polymer is a dark red solid and is insoluble in common organic solvents at room temperature, but slowly dissolves in *o*-dichlorobenzene at 135 °C. The red polyphenylacetylene is in a *cis-cisoidal* configuration and has 45% crystallinity [53–55].

Recently we have developed a method for polymerizing phenylacetylene and forming films simultaneously by the  $\text{Nd}(\text{naph})_3\text{-Al}(\text{i-Bu})_3$  system [56]. The polyphenylacetylenes so obtained are yellow, orange and red films. They have a high *cis* content, high molecular weight and high softening point. A detailed study on polymerization of phenylacetylene by rare earth coordination catalysts is progressing.

The polymerization of alkyl substituted, terminal acetylenes was first carried out at 20 °C using rare

TABLE V. Polymerization of 1-Alkynes by Sc and Nd Systems<sup>a</sup>

Monomer	State of polymer	Sc(naph) <sub>3</sub>		Nd(naph) <sub>3</sub>	
		Conversion (%)	$M_n$ ( $\times 10^{-4}$ )	Conversion (%)	$M_n$ ( $\times 10^{-4}$ )
1-Hexyne	yellow, rubbery solid	95	2.4	100	3.5
1-Pentyne	yellow, rubbery solid	96	2.3	100	3.7
3-Methyl-1-pentyne	light yellow solid	32	1.5	38	3.0
4-Methyl-1-pentyne	yellow solid	56	1.2	63	2.6
3-Methyl-1-butyne	light yellow solid	27	0.8	29	0.8
Phenylacetylene	orange-red solid	46		40	

<sup>a</sup>Reaction conditions: C<sub>2</sub>H<sub>5</sub>OH/Ln(naph)<sub>3</sub> 3(molar ratio); Al(i-Bu)<sub>3</sub>/Ln(naph)<sub>3</sub> 7.5(molar ratio); (M) 1.0 mol/l; 20 °C; 24 h.

earth naphthenates with tri-isobutyl aluminum or triethyl aluminum as the catalyst in cyclohexane or chlorobenzene by Shen *et al.* [54, 55]. The monomers 1-hexyne, 1-pentyne, 3-methyl-1-pentyne, 4-methyl-1-pentyne and isopropylacetylene gave light yellow occasionally elastomeric polymers, in very high yields in some cases. Membrane osmometric measurements revealed that the molecular weights of some polymers obtained are in the 80 000–170 000 range, which is extremely high for polymers of substituted acetylenes. These polymers were studied by ultraviolet, infrared and NMR spectrometry. The states, conversion and molecular weights of the polyalkynes obtained with the Sc(naph)<sub>3</sub>–Al(i-Bu)<sub>3</sub> and Nd(naph)<sub>3</sub>–Al(i-Bu)<sub>3</sub> systems are shown in Table V. It is seen from the data that the scandium catalytic system shows activity as high as the neodymium system. It is apparent that the position of the methyl group with respect to the triple bond strongly affects the rate of polymerization of the monomer. The lowest conversions for both catalysts were obtained with 3-methyl-1-butyne, in which steric hindrance would be expected to be the greatest. All the polyalkynes dissolved readily in aliphatic and aromatic hydrocarbons and other organic solvents. The infrared spectra of these polymers revealed that *trans* double bonds appear to be minimal in these polymers, whereas strong *cis* absorption is observed in all cases. These results show that rare earth coordination catalysts are good catalysts capable of promoting polymerization of alkynes to high molecular weight, *cis-cisoid* polymers in high yields.

### Alkylene Oxide Polymerization

Polyalkylene oxides or polyepoxides are polymers with versatile uses, which have been known and used for many years. Until now there has been no information about the ring-opening polymerization of epoxides such as ethylene oxide, propylene oxide and epichlorohydrin by using rare earth catalysts. Very recently we have discovered for the first time that the

rare earth coordination catalysts can induce the ring-opening polymerization of epoxides to give high molecular weight polyalkylene oxides with a high polymerization rate and a high final conversion [57]. Thus a new and important development has been exploited. The research into the ring-opening polymerization of epoxides by rare earth coordination catalysts is now progressing successfully in my group.

### Conclusions

The discovery of rare earth coordination catalysts in stereospecific polymerization not only contributes to the development of Ziegler–Natta catalysts and coordination polymerization from the usual d-orbital transition elements to elements involving f-orbitals, which poses new problems in coordination polymerization having theoretical significance, but also shows the potential catalytic activities of rare earths in producing new varieties of polydienes, polyethylene, polyacetylene, polyphenylacetylene, polyalkylalkynes, polyethylene oxide, polypropylene oxide and polyepichlorohydrin, etc., with characteristic properties. Therefore rare earth coordination polymerization could be expected to be one of the research frontiers of rare earth chemistry and polymer science to be producing much more fruitful products.

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