

POLYMERIZATION MECHANISM OF DIENES WITH HOMOGENEOUS RARE EARTH CATALYSTS*

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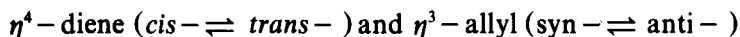
ABSTRACT

The reaction mechanisms of diene polymerization with homogeneous rare earth catalyst are studied by means of the spectra of ^1H -NMR, one- and two- dimensions ^{13}C -NMR. Based on the data of above NMR spectra, it is proposed that the polymerization reaction proceeds according to the following mechanism: η^4 -diene (*cis* $\rightleftharpoons$ *trans*) and η^3 -allyl (*syn* $\rightleftharpoons$ *anti*).

It has been continuously concerned that what the polymerization mechanism of rare earth coordination catalyst is, since its discovery, and there were some tentative ideas for it. But their main foundations came from the research on the coordination catalysts of 3d group transition metals, therefore they are short of many experimental proofs. For example, all the catalyst systems that consist of rare earth compound, AlR_3 and Lewis acid are called coordination polymerization catalyst, but so far the so-called "coordination" has not been experimentally proved. Some of researchers^[1,2], have explained some of experimental results by the aid of π -allyl mechanism of 3d group elements. However, is there any π -allyl rare earth complex in that system? What is the coordination pattern of monomer, and which is the insertional site of the monomer in $\text{Ln}-\text{C}$ or $\text{Ln}-\text{H}$ bond? What are the patterns of propagation, transformation and termination of polymer chain and what are the deciding factors to dominate microstructure and molecular structure of the polymer? and the like.

In recent years we have investigated on diene polymerization reactions with homogeneous systems, $(\text{CF}_3\text{CO}_2)_2 \text{LnCl} \cdot \text{EtOH} - \text{Al}(\text{i-Bu})_2 \text{H}$ ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Nd}, \text{Pr}, \text{Sm}, \text{Tb}$ and Ho), by means of ^1H -NMR, one- and two-dimensional ^{13}C -NMR spectra, and have obtained some experimental evidences for the aforementioned polymerization mechanism.

In this paper, it is proposed that the polymerization reaction carries out according to the following mechanism:



1. The site of active point

It is only observed in ^1H -NMR spectra that $\text{Ln}-\text{H}$ bond signals appeared in $^6\text{Nd}-\text{H} = -6.14$ and -16.63ppm (Fig. 1) but without any $\text{Ln}-\text{C}$ signal in solution of the catalyst reaction in ^{13}C -NMR spectra. When the monomer is added in the solution the $\text{Ln}-\text{H}$ signal disappeared, at the same time CH_3 -terminal resonance

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appeared at $\delta_{\text{CH}_3} = 17.97$ ppm in ^{13}C -NMR spectra^[3]. In addition, isobutylene is released from the catalyst reaction solution.

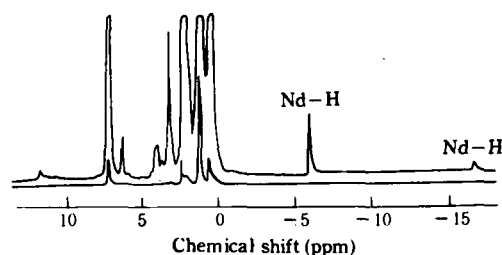
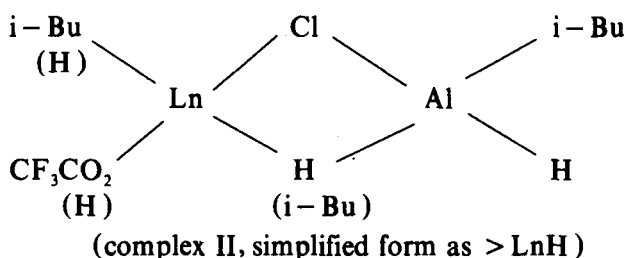


Fig.1 ^1H -NMR spectra of $(\text{CF}_3\text{CO}_2)_2 \text{NdCl} \cdot \text{EtOH} - (\text{i-Bu})_2 \text{AlH}$ system

For the above results it is considered that the site of the active point is the $\text{Ln}-\text{H}$ bond, and on the basis of the structure of the complex I^[4], active centre of the following structure is suggested:



2. The proofs of coordination polymerization

From the data of chemical shifts of proton-noise-decoupled ^{13}C -NMR spectra and coupling constants $^1J_{\text{CH}}$ (Table 1), we can see the chemical shifts of CH_2 , C, CH, CH_2 and CH_3 are in connection with *cis*- and *trans*-configuration of isoprene but they are neither the chemical shifts of polyisoprene nor that of isoprene monomer.

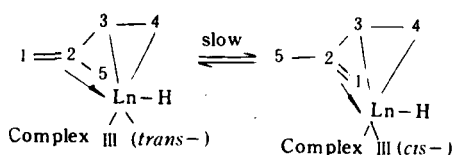
Table 1 Chemical shifts (δ , ppm) and coupling constant ($^1J_{\text{CH}}$, Hz) complex III^{a)}

Ln	Complex III	C-1		C-2	C-3		C-4		C-5
		δ	$^1J_{CH}$	δ	δ	$^1J_{CH}$	δ	$^1J_{CH}$	δ
Sc	<i>trans</i> -	108.0	-	172.1	47.3	-	16.2	-	18.0
	<i>cis</i> -	109.8	-	150.5	53.1	-	-	-	17.0
Y	<i>trans</i> -	108.0	155	172.5	47.3	126	16.3	112	18.2
	<i>cis</i> -	109.9	154	150.7	53.3	126	24.5	111	17.2
Tb	<i>trans</i> -	108.1	-	171.3	-	-	-	-	18.2
	<i>cis</i> -	109.9	-	150.8	53.1	-	-	-	17.1
Ho	<i>trans</i> -	108.1	-	172.5	47.3	-	16.4	-	18.2
	<i>cis</i> -	109.9	-	150.8	53.4	-	24.5	-	17.0
	I_p	116.5	156	142.2	139.7 ,	151	113.2 ,	154 ,	17.6

a) Error of the δ and $^1J_{\text{CH}}$ are 0.1 ppm and 0.3 Hz respectively.

It is further indicated that π -bond nature between C_1 and C_2 do not vary but both of the C_3 and C_4 have the feature of σ -bond. In addition, the two-dimensional ^{13}C -NMR spectra indicate that slow isomerization exists in the process between the configurations of η^4 -*cis*- and η^4 -*trans*-isoprene^[5].

Thus it can be considered that the monomers coordinated forward to active centres before polymerization. The configuration of the monomer coordination is shown in the following scheme:



3. Insertion reaction of the monomer

Table 2 shows the five pairs of chemical shifts and coupling constants for eight kinds of Ln polymerization systems similar to Fig. 2. The results of Table 2^[6] and the spectra of two-dimensional ¹³C-NMR (Fig. 3)^[5] indicate that C₃ and C₄ are inserted in Ln-H bond. It is possibly easy to open the unstable structure of cyclopropane formed by C₃, C₄ and Ln, and then the η^3 -syn- and η^3 -anti-crotyl complex are formed by the rapid isomerizations of η^4 -trans- and η^4 -cis-isoprene respectively, in which a slow isomerization occurs between the η^3 -syn- and η^3 -anti-complex (see Fig. 3).

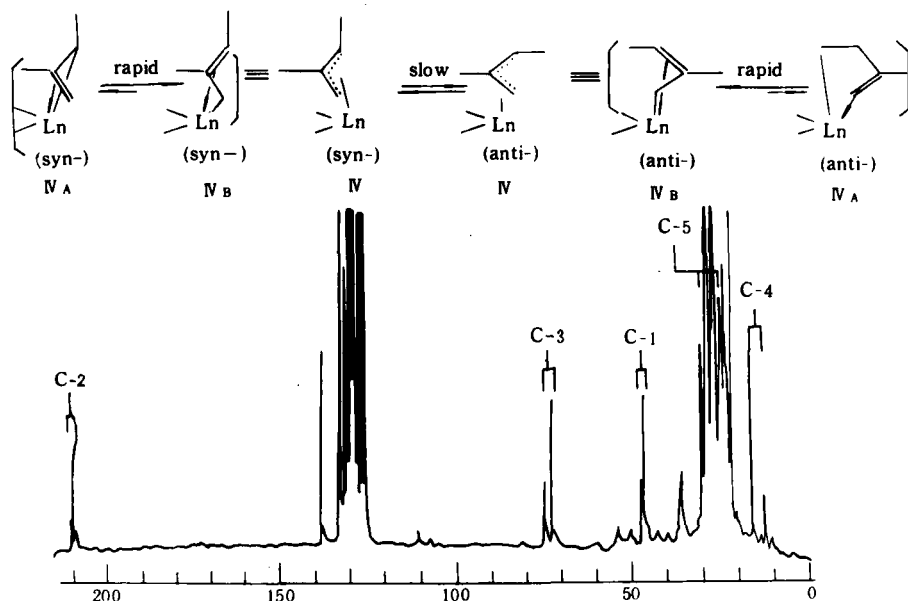


Fig.2 Proton-noise-decoupled ¹³C-NMR spectrum of (CF₃CO₂)₂ · YCl · EtOH · Al(i-Bu)₂H-I_p system (Y/I_p = 2, molar ratio)

4. Propagation reaction of polymer chain

As above the coordinated monomers are inserted in Ln-H bond and complexes IV_A are formed, and then complexes IV_B are formed by the isomerization. In this time, the monomers are mainly inserted in the C₁-Ln bonds due to steric effect and then *cis*-1, 4-polymers are formed. 3, 4-polymers are obviously formed when the monomers are inserted in C₃-Ln bonds.

If the coordinations of the following monomers exist, the C₁ and C₂ in monomers will insert forward to Ln-H bond in V(*cis*-), then the following complex VI should

Table 2 δ and $^1J_{CH}$ of η^3 -allyl complexes (ppm, Hz)

Ln	Complex IV	C-1		C-2		C-3		C-4	C-5
		δ	$^1J_{CH}$	δ	$^1J_{CH}$	δ	$^1J_{CH}$	δ	δ
Sc	syn-	46.2	-	209.2	-	72.4	-	16.2	29.8
	anti-	46.9	-	210.0	-	74.8	-	12.8	24.5
Y	syn-	46.1	131	209.2	-	72.6	144	16.2	30.0
	anti-	47.1	131	210.5	-	74.8	142	12.8	24.7
La	syn-	46.1	-	209.2	-	72.3	-	16.0	29.7
	anti-	46.8	-	210.0	-	74.5	-	12.7	-
Pr	syn-	46.2	-	209.3	-	72.4	-	16.2	29.7
	anti-	-	-	-	-	-	-	-	-
Nd	syn-	46.2	-	209.6	-	72.6	-	16.2	30.0
	anti-	47.1	-	210.6	-	74.6	-	12.8	24.7
Sm	syn-	46.1	-	209.2	-	72.3	-	16.0	29.7
	anti-	46.8	-	210.0	-	74.7	-	12.7	-
Tb	syn-	46.4	-	209.6	-	72.6	-	16.3	30.1
	anti-	47.1	-	210.4	-	74.9	-	12.9	-
Ho	syn-	46.1	-	209.5	-	72.4	-	16.1	29.9
	anti-	46.9	-	210.3	-	74.8	-	12.7	24.5
Y ^{a)}	syn-	36.5	134	183.4	144	84.5	142	13.6	-

a) Syn- η^3 -crotyl.

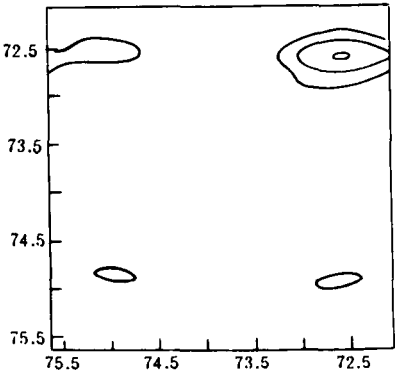
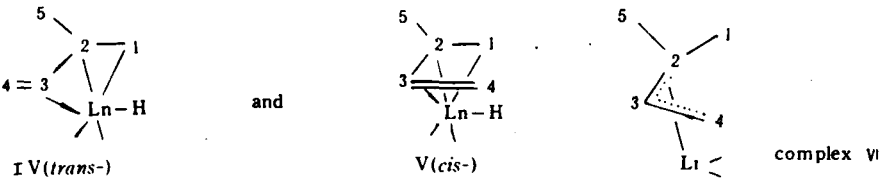


Fig.3 Two-dimension ^{13}C -NMR spectra of Fig.2 sample



be formed. However the three kinds of complexes, V (*trans*-), V (*cis*-) and VI, are not observed in the ^{13}C -NMR spectra of polymerization systems and there is no 1, 2-polymer in the obtained polymers which only contain *cis*-1, 4—80%, *trans*-1, 4—14%, and 3, 4—6%.

The chemical shifts of syn- and anti-active chain and that of the starting struc-

ture of active chain are shown as the following (Fig.4 and Table 3)^[6].

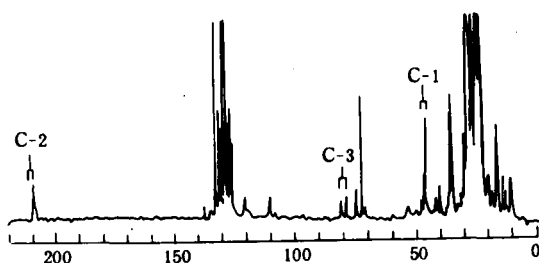
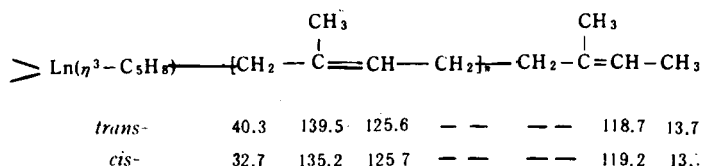


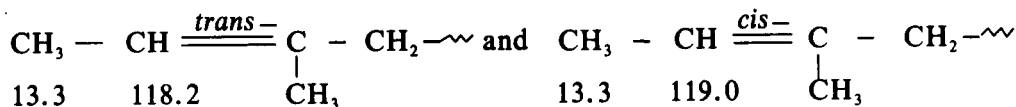
Fig.4 ^{13}C -NMR spectrum of $(\text{CF}_3\text{CO}_2)_2\text{TbCl} \cdot \text{EtOH} - \text{Al}(\text{i-Bu})_2\text{H} - \text{I}_p$ system

Table 3 δ of η^3 -allyl of activated chain (ppm)

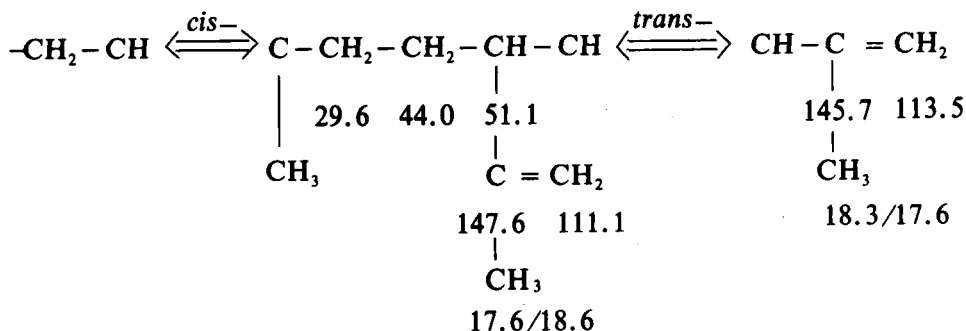
Ln	C-1		C-2		C-3	
	Syn-	Anti-	Syn-	Anti-	Syn-	Anti-
Sc	46.2	46.9	208.6	210.0	78.6	81.1
Y	46.1	47.1	208.6	210.4	78.8	81.1
La	46.1	46.8	208.4	210.0	78.5	80.9
Nd	46.2	47.1	209.0	210.4	78.8	81.1
Tb	46.4	47.1	208.9	210.4	78.8	81.1
Sm	46.1	46.8	—	210.0	78.8	80.9

5. Termination reaction of polymer chain

When the polymerization system is terminated by deuterium oxide, it is found that not only the starting chain of the polymer,



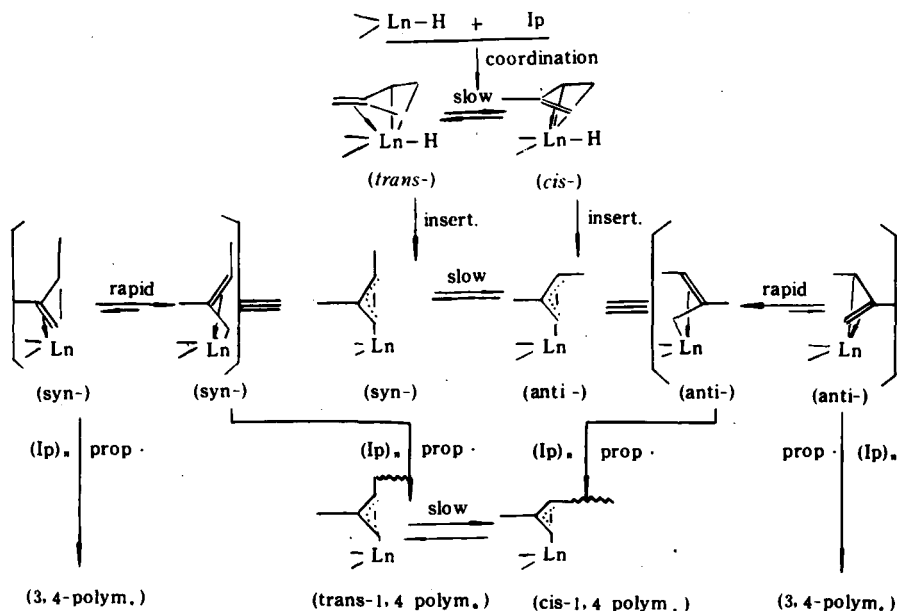
but also the following terminal chain are present^[7], which are probably formed by



allylic C₄ hydrogen elimination of the active chain end of a 1, 4-polymer with some 3, 4-content^[8].

It is hardly believed that the deuterium signal was not found within the observing range of S/N. The reason is probably relevant to the existence of excessive AIR₃ in the polymerization system.

To sum up, the reaction mechanism of the isoprene (or butadiene) polymerization with the homogeneous catalyst system, (CF₃CO₂)₂LnCl · EtOH - Al(i-Bu)₃H, can be described as the following scheme:



Keywords:

Reaction mechanism; Diene coordination polymerization; Homogeneous rare earth catalyst; η^4 -diene, η^3 -allyl.

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