

^{13}C -NMR STUDY ON THE CHAIN TERMINAL STRUCTURE OF POLY-1,3-PENTADIENE POLYMERIZED WITH RARE EARTH CATALYST

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ABSTRACT

The sequence distribution and the terminal structures of poly-1,3-pentadiene chains obtained by rare earth catalyst and effect of polymerization temperature on microstructure of the polymer have been investigated by ^{13}C -NMR method. According to experimental results it was supposed that terminal active growing chain of the polymer would be four types of anti- and syn- η^3 -allyl structures. When polymerization temperature was reduced, the content of *cis*-1,4-poly-1,3-pentadiene increases. It can be explained by isomerization between anti- and syn- η^3 -allyl. The process forming *trans*-1,2 unit instead of 3,4-unit were also described.

INTRODUCTION

The mechanism of diene polymerization with rare-earthbased catalyst has been studied^[1-2]. Based on the research of configuration of diene polymer obtained with rare earth catalyst at various monomer concentrations it was supposed that anti-syn isomerization would occur during the chain propagation and the isomerization level depends on the monomer structure and addition manner. In this paper, the sequence distribution and the terminal structures of the poly-1,3-pentadiene obtained with $\text{NdCl}_3 \cdot 3\text{C}_2\text{H}_5\text{OH}-\text{Al}(\text{C}_2\text{H}_5)_3$ catalytic system at various polymerization temperatures and high catalyst concentrations are investigated by ^{13}C -NMR. According to the chain terminal structures of the polymer, the possible structures of the growing chain ends in 1,3-pentadiene polymerization are proposed and the influence of polymerization temperature on *cis*- and *trans*-contents in the polymer is explained. The results provide a favourable experimental evidence for polymerization mechanism described previously^[2].

EXPERIMENTAL

Materials

1,3-pentadiene was prepared as described previously^[3]. Heptane used as polymerization solvent was purified by distillation and dried with active Al_2O_3 . Absolute ethyl alcohol was analytically pure reagent. All chemicals were dried with active Al_2O_3 before use. $\text{Al}(\text{C}_2\text{H}_5)_3$ was pure grade. Anhydrous NdCl_3 was prepared according to the literature [4].

Catalyst was prepared as follows: Into a pre-dried tube containing several glass beads a weighed quantity of anhydrous NdCl_3 was introduced, followed by a calculated quantity of ethyl alcohol solution in heptane. Then the mixture was shaken for several minutes and a calculated quantity of $\text{Al}(\text{C}_2\text{H}_5)_3$ (mole ratio of $\text{Al}/\text{Nd} = 40$) was added. The mixture was aged for at least 12

hr. before polymerization.

Polymerization

Polymerization runs were carried out in a cylindrical glass vessel which was dried, evacuated and then filled with pure dry nitrogen before use. Solvent and monomer were introduced first, followed by a measured amount of the catalyst suspension as described above. Polymerization reaction was running in the water-bath kept at a constant temperature. In order to obtain low molecular weight polymer, low monomer concentration (0.1 mol./L) and high catalyst level (mole ratio of monomer/Nd = 10) were used. The polymerization was quenched by adding a small amount of absolute ethyl alcohol (mole ratio of ROH/Me = 10). Then the contents of the reaction vessel were poured into a large excess of absolute ethyl alcohol containing a small amount of hydrochloric acid. The coagulated polymer was repeatedly washed with pure absolute alcohol and finally dried under vacuum below 50°C.

Polymer analysis: The ^{13}C -NMR spectra of poly-1,3-pentadiene in CDCl_3 were recorded at 25 MHz and 50°C on a JEOL-FX-100FT spectrometer. Chemical shifts were referred to TMS added as an internal standard. All spectra were proton noise decoupled and obtained with double precision accumulation and multiple scans with pulse repetition time of 1.5 sec., pulse width 5 μs and data point 4k, window 3.

RESULTS AND DISCUSSION

The ^{13}C -NMR spectrum of poly-1,3-pentadiene prepared at 50°C is shown in Fig.1. The peak assignments were based on the chemical shift parameters obtained previously^[5]. The chemical shifts, relative intensities of the peaks and their assignments are listed in Table 1.

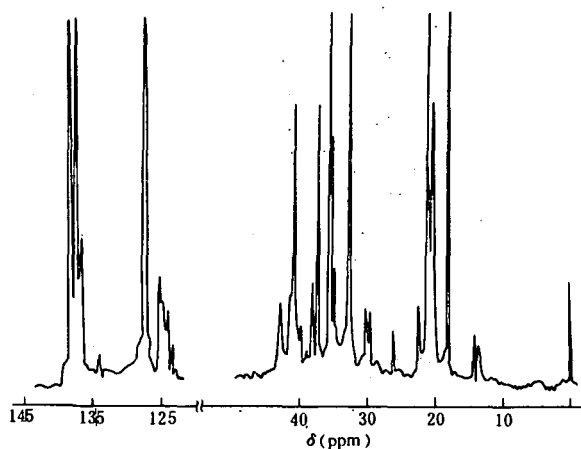


Fig.1 ^{13}C -NMR spectrum of poly-1,3-pentadiene

The microstructure contents of poly-1,3-pentadiene obtained at different polymerization temperature were calculated based on the ^{13}C -NMR data. The results are listed in Table 2. As shown in Table 2, the *cis*-1,4 content of the polymer decreases but the *trans*-1,4 as well as 1,2-unit increase with rising polymerization temperature. The influence of polymerization temperature on polymer configuration shows the fact that the isomerization equilibrium constant between the anti- and syn- η^3 -allyls is dependent on polymerization temperature. Because syn- η^3 allylic

Table 1 Assignments and relative intensities of the ¹³C-NMR peaks

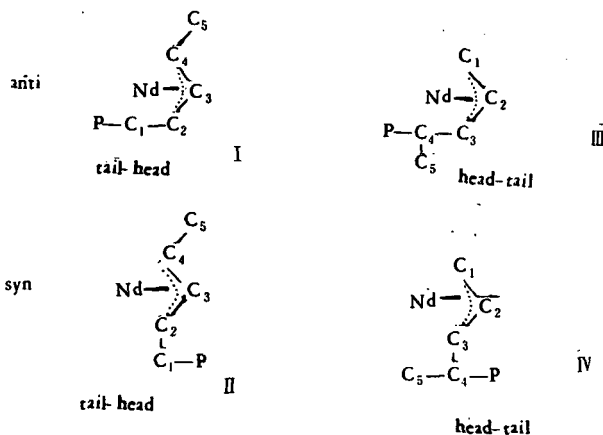
Peaks number	Chemical Obs.	shift(ppm) Cal.	Relative intensities	Assignment
1	13.41	13.38	0.78	$C_2^* - C = C - \underset{\substack{ \\ C}}{C} -$
2	14.04	13.90	0.83	$C^* - C - C = C - C -$
3	17.94	17.90	8.18	$V_3, C_1^* - C = C - \underset{\substack{ \\ C}}{C} -$
4	20.24	20.28	5.76	(1,4T) ₃ 1,4
5	20.58	20.68	3.00	(1,4T) ₃ 1,2
6	20.89	20.72	17.64	(1,4C) ₃ 1,4 C - C ₂ [*] - C = C - C -
7	21.99	21.60	1.56	(1,4C) ₃ 1,2
8	25.65	25.85	1.12	C - C ₁ [*] - C = C - C -
9	27.83	28.39	0.80	(4,1C) ₁ 1,4
10	29.25	30.08	1.21	(1,4C) ₄ 1,2 1,4
11	29.71	30.18	1.13	(1,4C) ₄ 1,2 1,2
12	32.36	32.36	14.03	(1,4C) ₄ 1,4
13	32.83	33.09	1.08	4,1 1,2 (1,4C) ₁
14	33.61	33.49	0.88	1,2 1,2 (1,4C) ₁
15	33.92	33.75	1.08	(4,1T) ₁ 1,4
16	34.46	34.66	1.74	(1,4T) ₄ 1,2 1,4
17	35.01	35.06	3.64	(1,4T) ₄ 1,2 3,4
18	35.24	35.24	12.31	1,4(1,4C) ₁
19	36.88	36.95	8.07	(1,4T) ₄ 1,4 1,4(1,2) ₂ 1,2
20	37.66	37.75	1.81	1,2(1,2) ₂ 1,2
21	38.60	38.45	0.90	1,4 1,2(1,4T) ₁
22	39.22	39.10	1.44	1,2 1,4(1,2) ₂ 1,4
23	40.39	40.20	8.15	1,4(1,4T) ₁ 1,2(1,2)1,4
24	40.86	40.70	1.44	1,2(1,2) ₁ 1,2
25	42.57	42.50	1.42	1,4(1,2) ₁ 1,2 1,4

Table 2 Effect of polymerization temperature on microstructures of poly-1,3-pentadiene

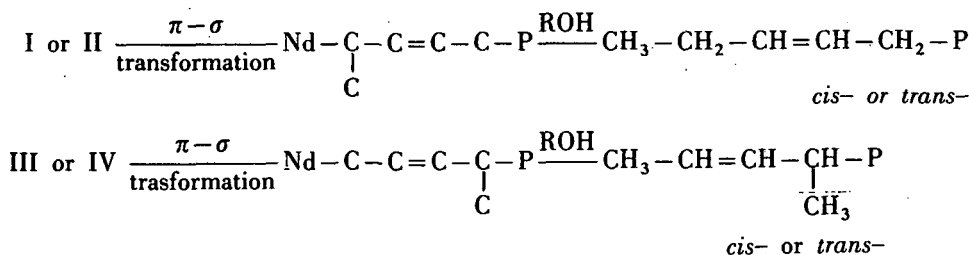
Polymerization temperature(°C)	Microstructures of the polymer (%)		
	<i>cis</i> -1,4	<i>trans</i> -1,4	<i>trans</i> -1,2
0	74.17	8.16	17.67
20	72.07	9.37	18.56
50	53.13	24.24	22.63

compound is thermodynamically more stable than anti-one, the lower polymerization temperature is in favor of the formation of anti- η^3 allyl, leading to higher contents of *cis*-1,4-Poly-1,3-pentadiene.

We have proposed growing chain end in diene polymerization with Nd-based catalyst exhibits η^3 -allyl character^[2]. Obviously, the insertion of a monomer between the growing chain end and the transition metal would have predominantly two manners, either head to tail or tail to head. The propagating species could exist in four possible structures:

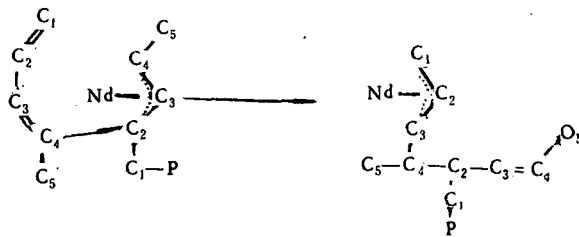


When the propagating species of the above structures were terminated by alcohol, the following reaction would occur:



These polymer chain ends were detected by the ^{13}C -NMR as shown in Table 3. It is reasonable to believe that the four types of η^3 -allylic active chain ends are present in the polymerization of 1,3-pentadiene. The results are in agreement with the previous conclusion^[2].

As shown in Table 2, *trans*-1,2 units were observed in poly-1,3-pentadiene. It could be formed from growing species I or II as follows:



The fact that *cis*-1,2 units were not detected in the poly-1,3-pentadiene reveals that C₅-methyl in the growing species I or II only exists in syn-configuration as above mentioned scheme I or II. 3,4-units were not found in the poly-1,3-pentadiene. It is possible that stereo-hindrance caused by C₅-methyl in active species III or IV does not favor the attachment of monomer C₃ atom.

Table 3 ¹³C-NMR peaks associated with the polymer chain ends

Chemical		Structures of the polymer chain ends				
shift (ppm)		$\begin{array}{c} \text{C}_5 \\ \\ \text{C}_1 - \text{C}_2 = \text{C}_3 - \text{C}_4 - \end{array}$			$\text{C}_1 - \text{C}_2 - \text{C}_3 = \text{C}_4 - \text{C}_5 -$	
		C ₁	C ₂	C ₁	C ₂	C ₃
<i>cis</i>	Obs.	13.14	122.66	14.04	20.89	133.18
	Model ^[6]	12.99	122.46	13.90	20.79	
	Cal.	13.38	121.67			130.17
<i>trans</i>	Obs.	17.94	123.28	14.04	25.65	133.18
	Model ^[6]	17.95	123.00	14.10	25.79	132.01
	Cal.	17.90	123.28	13.90	25.85	131.26

Keywords:

Poly-1,3-pentadiene; Terminal structures; Diene polymerization; polymerization mechanism; Sequence distribution.

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