^{13}C-NMR STUDY ON THE EQUIBINARY (cis-1,4;1,2) POLYBUTADIENE POLYMERIZED WITH IRON CATALYST

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ABSTRACT

The (cis-1,4 and 1,2) polybutadiene polymerized with iron catalyst was investigated by ^{13}C-NMR. Assignments have been made on the spectra for all peaks of the aliphatic and olefinic carbons using chemical shift corrective terms together with Furukawa parameters. The relative intensities of peaks were calculated from the Bernoulli distribution of cis-1,4 and 1,2 units.

Quantification of cis-1,4 and 1,2 contents, sequence distribution, alternation pattern of cis-1,4 and 1,2 units, and the chain propagation mechanism were discussed as a result of the detailed study of the spectra.

INTRODUCTION

As shown in the previous papers[1], equibinary (cis-1,4 and 1,2) polybutadiene with good performance was prepared with Fe catalyst of high activity. ^{13}C-NMR studies on equibinary polybutadienes prepared with Co or Mo catalyst[2-5] have been reported in the literature.

In the present work the chain structure of polybutadienes prepared with Fe catalyst was studied with ^{13}C-NMR. Spectra show that there are eleven resonance peaks in the aliphatic carbon part and nine in olefinic carbon part. These resonance peaks were assigned by applying Randall's method[6] with corrected Furukawa's parameters. It was confirmed that the polymer obtained is a random copolymer of 1,4 and 1,2 enchainments, the distribution of which deviated from the Bernoulli distribution but tended to be the first order Markov distribution.

The content and the sequence distribution of 1,2- and cis-1,4 units in the polymer were discussed quantitatively.

EXPERIMENTAL

1. *Conditions of polymer preparation*

Al $(i\text{-}Bu)_3$, 0.04 ml; Fe $(acac)_3/L=1$ (L, a nitrogen ligand); Fe, 5×10^{-6} mol; butadiene, 2.5×10^{-2} mol; benzene, 10 ml; polymerization temp., 10°C for 3 hr. The polymer contained cis-1,4, 44.7%; 1,2, 55.3% determined by IR.

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2. ^{13}*C-NMR measurement*

The ^{13}C-NMR spectra recorded from FX-100 NMR (JEOL. Ltd., Japan) at the observation frequency: 25.2 MHz; spectra width: 4000 Hz; impulse width: 5μs (ca. 45°); sampling time: 1.5 sec.; accumulation times: 2000. Sample used in the measurement contained ca. 10% polymer in CCl_4.

RESULTS AND DISCUSSION

1. ^{13}*C-NMR spectra*

Figure 1 (a) gives the resonance peaks for the aliphatic carbons of the polymer. If the polybutadiene was high in cis-1,4 content, a characteristic peak would appear at 27.3 ppm; and if it was high in 1,2-content, a few resonance peaks would appear at 39 ppm. But many resonance peaks as shown in Figure 1 indicate that 1,2 and cis-1,4 units are interbonded.

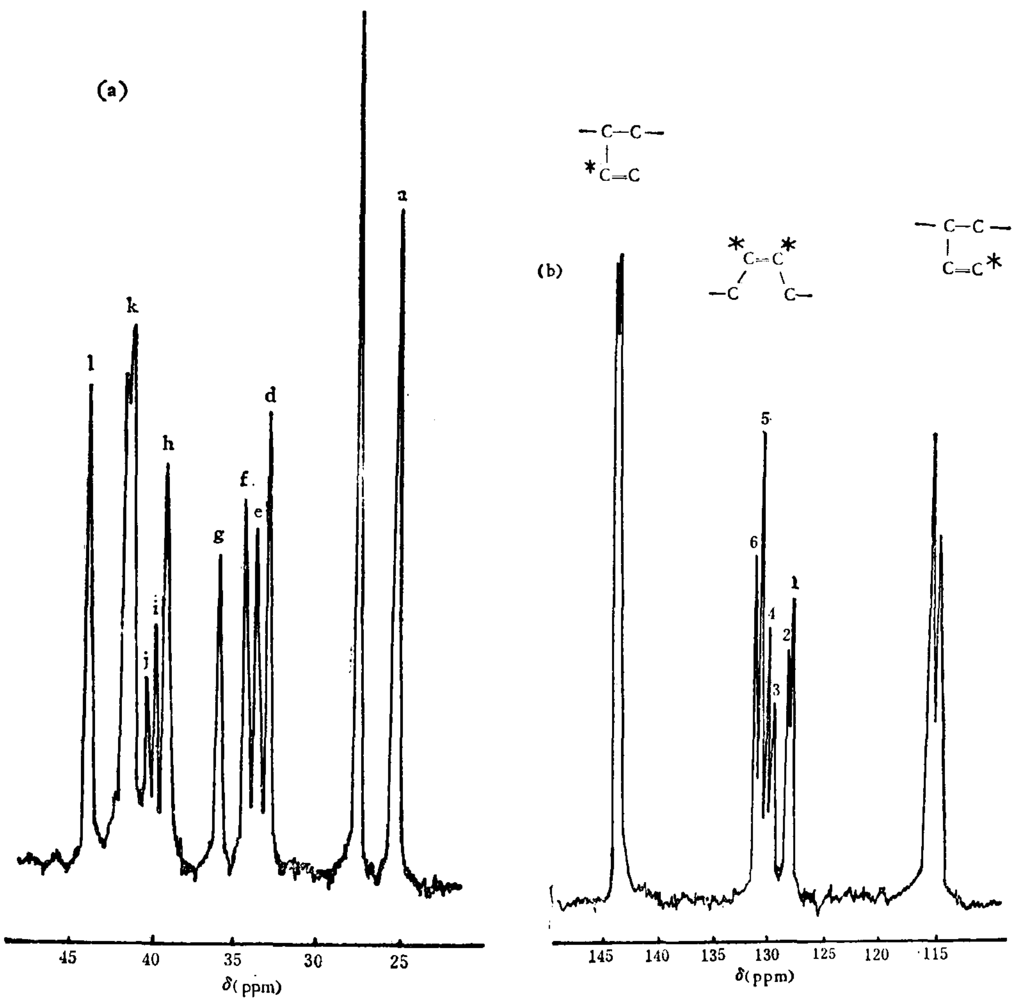


Fig. 1 ^{13}C-NMR spectra of (cis-1,4; 1,2) polybutadiene: (cis-1,4, 44.7%; 1,2, 55.3%)
(a) aliphatic portion; (b) olefinic portion.

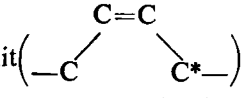
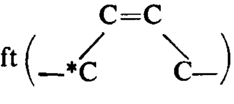
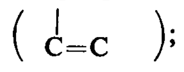
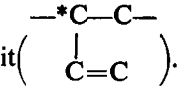
This implied that aliphatic carbons are situated in a variety of chemical environment. The eleven resonance peaks were marked as a,b,d,e,f,g,h,i,j,k and 1 respectively.

Figure 1 (b) shows the resonance peaks of olefinic carbons in the polymer. The resonance peaks near 114 ppm are the characteristic carbon signal for vinyl terminal bonded to the chain of polybutadiene, while the peaks near 140 ppm are that for the other carbon atom of vinyl group; and the peaks near 130 ppm are the contribution of olefinic carbon in the cis–double bond of the chain of polybutadiene. Originally, there should be only one resonance peak from cis–1,4 polybutadiene. After a certain amount of vinyl group bonded to the chain it gives rise to an increase of peaks such as 1,2,3,4,5,6 etc.

2. *Assignment of resonance peaks*

(1) Aliphatic carbon portion: The addition of a butadiene monomer to a growing polymeric chain can give rise either to a cis–1,4 or to 1,2–unit in our catalyst system. In most cases, the 1,2–unit exists as head–to–tail joining in polymerization chain. If the growth of chain is a perfect stochastic process, the sequence arrangement should be many and varied in forms. According to Grant[7] the equation for calculating chemical shift is

$$\delta_c\,(K) = A + \sum_l B_l N_{Kl}.$$

Since the carbon atom is influenced by all five adjacent carbons, 47 sequences could be arranged, as shown in Table 1. In the sequences C* is used to express the aliphatic carbon on the right side of cis–1,4 unit ; *C as that on the left ; V* the secondary carbon in 1,2–unit ; and *V the tertiary carbon in 1,2–unit . According to the parameters used by Furukawa, the chemical shifts were calculated according to the following equation:

$$\delta_c(K) = A + \sum_l B_l N_{Kl} + C_K$$

where δ_c (K) is the chemical shifts of K carbon, A is a constant; B_l are the parameters away from various positions of K carbon; N_{Kl} is the number of carbon away from various positions of K carbon; C_K is the parameter of characteristic structure for K carbon itself (belonging to aliphatic carbon). These parameters are given in Table 2.

In Table 2, 2° represents the secondary carbon atom adjacent to the tertiary carbon, 3′ the tertiary carbon, 2° (3′) the contribution of chemical shift of the tertiary carbon relative to the secondary carbon, 3′ (2°) the contribution of chemical shift of the secondary carbon relative to the adjacent tertiary one. The tertiary carbon here refers in particular to the α position of vinyl group, C (α) is expressed as the contribution of chemical shift of cis–double bond relative to the secondary carbon in α–position, and C (γ2°) as the contribution of chemical shift of cis–double bond relative to the secondary carbon in γ–position.

From Table 1 it is seen that the chemical shift of each resonance peak calculated from Furukawa's parameters are mostly in agreement with the values in literature[3], with the exception of the chemical shifts of the two peaks, i,j, which are different. After recalculation, it is confirmed that the value in literature was mistaken.

Table 1 ^{13}C–NMR chemical shifts of binary (cis–1,4; 1,2) polybutadiene (aliphatic portion)

Peak	Assign.	Chem. shift (ppm)			Intensity (I)		
		Oos.	Cal.	Rev.	Cal. (%)	Obs. (%)	Equation (I)
a	$\mathrm{c\ v{\cdot}\underline{c}\ v}$	24.9	26.5	24.9	12.9	12.2	$KN_{\mathrm{vcv}}+K\sum_{i=0}^{n}N_{\mathrm{vc(c)_icv}}$
	$\mathrm{v\ v\ v{\cdot}\underline{c}\ v}$		26.6	25.0			
	$\mathrm{c\ v\ v{\cdot}\underline{c}\ v}$		26.6	25.0			
	$\mathrm{c\ v\ v{\cdot}\underline{c}\ c}$		26.5	24.9			
	$\mathrm{c\ v{\cdot}\underline{c}\ c}$		26.4	24.8			
	$\mathrm{v\ v\ v{\cdot}\underline{c}\ c}$		26.5	24.9			
b	$\mathrm{v\ c{\cdot}\underline{c}\ c}$	27.3	28.6	27.0	18.8	15.7	$2K\sum_{i=0}^{n}(i+1)N_{\mathrm{vc(c)_icv}}$
	$\mathrm{c\ \underline{c}{\cdot}\ c\ v}$		28.6	27.0			
	$\mathrm{v\ \underline{c}{\cdot}\ c\ c}$		28.6	27.0			
	$\mathrm{v\ c{\cdot}\underline{c}\ v}$		28.7	27.1			
	$\mathrm{c\ c{\cdot}\underline{c}\ v}$		28.7	27.1			
	$\mathrm{v\ \underline{c}{\cdot}\ c\ v}$		28.6	27.0			
	$\mathrm{c\ c{\cdot}\underline{c}\ c}$		28.6	27.0			
d	$\mathrm{v\ \underline{c}{\cdot}\ v\ c}$	32.7	34.2	32.6	5.8	8.8	$KN_{\mathrm{vcv}}+K\sum_{i=0}^{n}N_{\mathrm{vc(c)_icv}}$ $-K\sum_{i=0}^{n}N_{\mathrm{cv(v)_ivc}}=KN_{\mathrm{cvc}}$
	$\mathrm{c\ \underline{c}{\cdot}\ v\ c}$		34.2	32.6			
e	$\mathrm{v\ \underline{c}{\cdot}\ v\ v\ c}$	33.4	34.6	33.0	7.1	6.5	$K\sum_{i=0}^{n}N_{\mathrm{cv(v)_ivc}}$
	$\mathrm{c\ \underline{c}{\cdot}\ v\ v\ c}$		34.6	33.0			
	$\mathrm{v\ \underline{c}{\cdot}\ v\ v\ v}$		34.6	33.0			
	$\mathrm{c\ \underline{c}{\cdot}\ v\ v\ v}$		34.6	33.0			
f	$\mathrm{c\ \underline{v}{\cdot}\ c\ v}$	34.1	35.8	33.7	5.8	6.8	KN_{cvc}
	$\mathrm{c\ \underline{v}{\cdot}\ c\ c}$		35.8	33.7			
g	$\mathrm{c\ v\ \underline{v}{\cdot}\ c\ v}$	35.7	36.2	34.6	7.1	6.0	$K\sum_{i=0}^{n}N_{\mathrm{cv(v)_ivc}}$
	$\mathrm{v\ v\ \underline{v}{\cdot}\ c\ v}$		36.2	34.6			
	$\mathrm{c\ v\ \underline{v}{\cdot}\ c\ c}$		36.2	34.6			
	$\mathrm{v\ v\ \underline{v}{\cdot}\ c\ c}$		36.2	34.6			

(Table 1 cont'd)

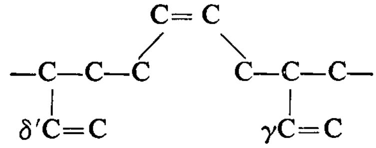
Peak	Assign.	Chem. shift (ppm) Obs.	Chem. shift (ppm) Cal.	Chem. shift (ppm) Rev.	Intensity (I) Cal. (%)	Intensity (I) Obs. (%)	Intensity (I) Equation (1)
h	c v·$\underline{\text{v}}$ v c	38.9	39.7	38.1	7.6	7.5	$K\sum_{i=0}^{n} iN_{\mathrm{cv(v)}_i\mathrm{vc}}$
	c v·$\underline{\text{v}}$ v v		39.8	38.2			
	c v v·$\underline{\text{v}}$ v c		39.8	38.2			
	v v v·$\underline{\text{v}}$ v v		39.9	38.3			
	c v v·$\underline{\text{v}}$ v v		39.9	38.3			
i	c $\underline{\text{v}}$· v c	39.7	41.4	39.3	3.2	4.6	KN_{cvvc}
j	c $\underline{\text{v}}$· v v c	40.0	41.8	39.7	3.9	3.5	$K\sum_{i=0}^{n} N_{\mathrm{cv(v)}_i\mathrm{vc}}$
	c $\underline{\text{v}}$· v v v		41.8	39.7			
k k$_1$	v v $\underline{\text{v}}$· v v c	41.0 ~ 41.5	42.2	40.6	21.9	19.2	$K\sum_{i=0}^{n} iN_{\mathrm{cv(v)}_i\mathrm{vc}}$
	c v $\underline{\text{v}}$· v v c		42.2	40.6			
	v v $\underline{\text{v}}$· v v v		42.2	40.6			
	c v $\underline{\text{v}}$· v c		41.8	40.2			
	v v $\underline{\text{v}}$· v c		41.8	40.2			
k$_2$	c v v·$\underline{\text{v}}$ c		42.0	40.4			$2K\sum_{i=0}^{n} N_{\mathrm{cv(v)}_i\mathrm{vc}}$
	v c·$\underline{\text{v}}$ v c		41.9	40.3			
	v v v·$\underline{\text{v}}$ c		42.0	40.4			
	c c·$\underline{\text{v}}$ v c		41.9	40.3			
	v c·$\underline{\text{v}}$ v v		42.0	40.4			
	c v·$\underline{\text{v}}$ c		41.9	40.3			
	c c·$\underline{\text{v}}$ v v		42.0	40.4			
l	c c·$\underline{\text{v}}$ c	43.6	44.1	42.5	5.8	9.1	KN_{cvc}
	v c·$\underline{\text{v}}$ c		44.1	42.5			

Table 2 Chemical shift parameters ppm

A	B_l	C_K	
−2.6	α 9.1	2°(3′)	−1.3
	β 9.4	3′(2°)	−2.3
−4.2 (this work)	γ-2.5	C(α)	−1.6
	δ 0.3	C(γ2°)	−0.5 (this work)
	ε 0.1		

By comparison of the calculated values with the observed ones, it was found that the departure of the peaks, j,k, and the relative position of peaks, d,e,f,g are not good enough. The difference between values of chemical shift calculated is too small for f,g peaks, but too large for e,f peaks. On the other hand, all the calculated values of resonance peaks are higher than the observed ones. We considered that this arose from the systematic error of the instrument and the internal standard used. In order to make the calculated values consistent with the observed values, a value of -4.2 ppm for constant A and a factor of -0.5 ppm (Table 2) for an additional structure correction C ($\gamma 2^{\circ}$) have been adopted and recalculated. At the same time the observed values are listed using CCl_4 as the internal standard (96.00 ppm). By this treatment, the revised values are in agreement with the observed values reasonably. C ($\gamma 2^{\circ}$) which we introduced indicates the influence of cis–double bond on the $—CH_2—$ in the adjacent 1,2 unit. This carbon is located in the γ position of cis–double bond, perhaps it is the result of steric effect. After above revision, the departure of j,k peaks has been satisfactorily fitted and the relative position of f peak has been also adjusted. This makes a better coincidence with the calculated values and the experimental facts. Consequently, the problem of assignment of each resonance peak has been settled.

(2) Olefinic carbon portion: Under the influence of vinyl group in the adjacent 1,2 unit the cis–double bond in the principal chain of polybutadiene splitted up into six peaks. Taking the parameters $\gamma = -1.60$, $\delta = +0.48$, $\gamma' = +0.48$, $\delta' = -0.365$,



according to K. F. Elgert[4], and corrected with the high cis–1,4 polybutadiene olefinic carbon signal as 129.40 ppm, the results are shown in Table 3. From Table 3 it could be seen that the observed values and the calculated ones are in good coincidence in which the fifth peak is an overlap of various sequence signals. Hence the intensity is higher.

3. *The numerical value expression for spectrum signal*

From the assignment of each resonance peak given in Table 1 the mathematical expression for corresponding signal intensity was obtained.

$$I_{\mathrm{d}} = KN_{\mathrm{vcv}} + K\sum_{i=0}^{n} N_{\mathrm{vc(c)_{i}cv}} - K\sum_{i=0}^{n} N_{\mathrm{cv(v)_{i}vc}}$$

$$I_{\mathrm{c}} = K\sum_{i=0}^{n} N_{\mathrm{cv(v)_{i}vc}} \quad I_{\mathrm{a}} = KN_{\mathrm{vcv}} + K\sum_{i=0}^{n} N_{\mathrm{vc(c)_{i}cv}}$$

It could be easily seen that $I_{\mathrm{d}} + I_{\mathrm{e}} = I_{\mathrm{a}}$, $I_{\mathrm{i}} + I_{\mathrm{j}} = I_{\mathrm{g}}$, etc. From IR data the relative intensity for each resonance peak was calculated according to Bernoulli distribution, i.e. the calculated values in Table 1. They fulfiled the above equations. This indicates that the 47 sequences are perfect and the attributions are resonable. On the other hand, Randall considered that in ^{13}C–NMR quantitative researches of most polymers the NOE effect might be ignored. In this way, a reliable basis is provided for quantitative analysis of the chain structure in (cis–1,4; 1,2) polybutadiene. By normalization treatment for all aliphatic carbon signal intensities, from the percentage of cis–1,4 and 1,2 unit aliphatic carbon signal intensity, its quantity could be obtained conveniently. For instance, the equation for calculating the content of cis–1,4 structure unit from aliphatic carbon spectrum would be

$$C\% = \frac{\sum_{\alpha} I_{\alpha}}{\sum_{\beta} I_{\beta}} \times 100\%$$

in which a,b,d,e were taken as α and a,b,d,e,f,g,h,i,j,k_1,k_2 and l as β. Similar results could be also achieved from olefinic carbon spectrum as shown in Table 4.

The pattern of sequence distribution of polymer chain structure is an important aspect for the research of chain structure. It conduces to probe into the polymerization mechanism. As mentioned above, the signal intensity in Table 1 was expressed as relative value through normalization, while the calculated values were obtained according to Bernoulli distribution treatment from IR data. The data of olefinic carbon in Table 3 were treated on the basis of Bernoulli distribution. It is emphasized especially on the treatment of the triad information by taking the cis-1,4 structural unit as the center.

Table 3 ^{13}C-NMR chemical shifts of (cis-1,4; 1,2) polybutadiene (olefinic portion)

Peak	Sequence	Chem. shift (ppm)		Intensity (%)	
		Obs.	Calc.	Obs.	Calc.
1	v c• v	127.45	127.44	0.160	0.153
2	c c• v	127.76	127.80	0.132	0.124
3	v c• c	129.05	129.04	0.106	0.124
4	c •c• c	129.40	129.40	0.146	0.200
5	c •c v	129.87	129.87	0.256	0.247
	v •c c		129.87		
6	v •c v	130.33	130.36	0.200	0.153

Table 4 Structural data obtained by different methods

Structure	^{13}C-NMR (%)		IR (%)
	Aliph. spec.	Olef. spec.	
1,2	56.7	52.8	55.2
cis-1,4	43.3	47.2	44.7

Following the Randall's definition the number of triad taking 1,2-structure unit as the center could be deduced from the expression

$$N_{vvv} = \frac{1}{2K}(I_h + I_{k_1}); \quad N_{vvc} = \frac{1}{2K}(I_g + I_i + I_j + I_{k_2});$$

$$N_{cvc} = \frac{1}{2K}(I_f + I_l)$$

thereby the relative concentration of triad could be calculated. The figures in Table 5 and the observed values of signal intensity in Table 1 and Table 3 together give the characteristics of sequence structure for (cis–1,4; 1,2) polybutadiene catalyzed by iron system. The data listed in Table 5 show that all sequence distribution of polymer chain deviates from Bernoulli's distribution. These are undoubtful experimental facts. By comparison of the observed values in Table 5 with the values from both theories especially from the number-average sequence lengths, a deviation from the Bernoulli distribution could also be found distinctly, but there is a definite tendency to approach the first order Markov distribution.

Table 5 Sequence distribution (triad) and number-average sequence length

Sequence	Exp.	Bernoulli $p_v=0.559$	Markov–1 $p_{vc}=0.488$
v v v	0.308	0.313	0.262
v v c	0.411	0.493	0.500
c v c	0.280	0.194	0.250
L_v	2.06	2.27	2.05

From Table 1 and Figure 1 (a), it is shown clearly that the peak "b" is the characteristic peak of high cis-polybutadiene. The peak "b" would disappear for perfect alternation sequence, and only the a,d,f and 1 peaks left; but for segmented block sequence, the height of b,h and k peaks would be remarkable and that of a, d, f, l peaks would be relatively lowered. Actually all the 11 peaks appeared in the spectrum with comparable intensities. In order to characterize quantitatively the degree of alternation of polymer chain the definition of A_v as a numerical index is as following: $A_v=(I_f+I_l)/\sum_r I_r$, in which f,g,h,i,j,k and 1 were taken as r. It is apparent that for segmented polymers, f,l will vanish, and $A_v=0$; for alternated polymers, $A_v=1$. The values of A_v will vary with the compositions for random copolymers. We have calculated the value of A_v with variations of the 1,2– structural unit content according to Bernoulli distribution. The result is depicted by the solid line in Figure 2. Evidently, if the polymer chain possesses a higher alternated degree, A_v would situate above the $A_v \sim V$ line. On the contrary, with lower alternation, A_v would situate below the line. Therefore, the difference between the degree of alternation for polymer chain could be reflected, and similarly, it could also be obtained from the number-average sequence length of 1,2 structure unit. For Mo–polybutadiene reported in literature[3], L_v is 2.48, while for the corresponding polymers with same composition and entirely following the Bernoulli distribution, the L_v is 2.21. But for Fe-polybutadiene, L_v is 2.06, and the corresponding one with same composition and entirely following the Bernoulli distribution, L_v is 2.31. As the number-average sequence length increases, the alternated degree of polymer chain decreases. Obviously, the two kinds of polybutadiene chain possess different degree of alternation. Generally, the higher the content of 1,2 structural unit, the longer the number-average sequence length L_v, while conversely, the shorter the L_v. The experimental result in this report is just the opposite. For low 1,2-content of Mo–polybutadiene, the length of the number-average sequence is rather long, while for high 1,2 content of Fe-polybutadiene, it is fairly short. The opposite tendency of the degree

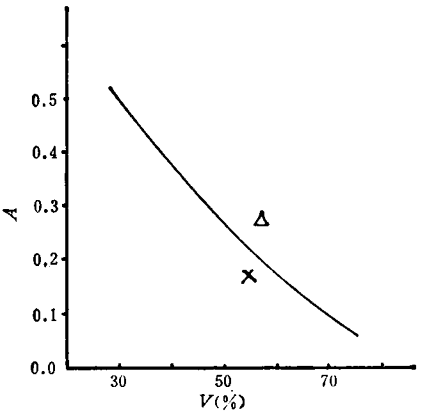


Fig. 2 Relation between A_V and content of 1,2 units
—×— Mo polybutadiene; —△— Fe polybutadiene.

of alternation for polymer chain might result from the role of the catalytic system.

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