

# THE CHAIN STRUCTURE OF 1,2-POLYBUTADIENES PREPARED WITH MOLYBDENUM CATALYST SYSTEMS

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## ABSTRACT

The chain structure of 1,2-polybutadienes prepared with molybdenum catalyst systems has been studied by IR,  $^{13}\text{C}$ -NMR and  $T_g$  method, and the method to regulate the chain structure investigated. It was found that some polar additives, e.g., allyl halides, are able to regulate not only the content of 1,2-units in the polymer, but also its configuration and sequence distribution. Attempt has been made to estimate the sequence length of stereo-isomers of 1,2-units by statistical theory.

1,2-Polybutadienes possess excellent properties which are useful in many branches of the polymer industry, such as rubber, plastic, coating, adhesive, etc.<sup>[1-4]</sup>. The properties of a polymer depend primarily on its chain structure. It is of importance to investigate with modern structural analytical methods the chain structure of 1,2-polybutadienes and to seek the ways to regulate their chain structure in order to improve the physical properties and to study the mechanism of formation of 1,2-units in the polymer. In the present paper, the chain structure of 1,2-polybutadienes prepared with molybdenum catalyst systems was studied by IR,  $^{13}\text{C}$ -NMR and  $T_g$  method, and attempt was made to regulate the chain structure.

## EXPERIMENTAL

1,2-Polybutadiene samples were prepared with catalyst systems composed of a molybdenum compound and an alkoxy aluminium alkyl together with a polar additive. The microstructure of the samples was measured by Perkin-Elmer 599 IR spectrometer;  $^{13}\text{C}$ -NMR measurement was performed on JEOL FX-100 NMR Spectrometer, the resolution of the instrument was 0.2 Hz ( $5 \times 10^{-9}$ ) and the resolution in the experiment was about 0.8 Hz.  $T_g$  was determined by linear expansion method.

## RESULTS AND DISCUSSION

### 1. Chain structure of the polymer

The chain structure of 1,2-polybutadienes prepared with molybdenum catalyst systems depends on the molybdenum compound, more 1,2-units being formed when larger substituents are used in OR on the molybdenum (Fig. 1).

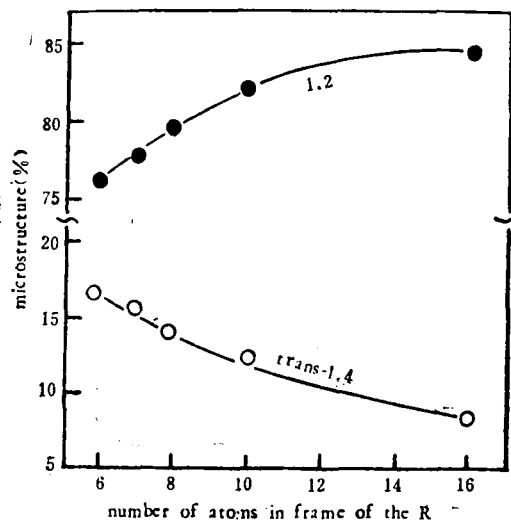


Fig. 1 Microstructure of 1,2-polybutadienes prepared with  $\text{MoCl}_5(\text{OR})_2$ - $i\text{-Bu}_2\text{AlOEt}$  as a function of the number of carbon atoms in R

The microstructure of the polymers varies also with the alkoxy substituent in the aluminum alkyl. Data for the microstructure of 1,2-polybutadienes prepared with  $\text{MoCl}_4\text{OC}_8\text{H}_{17}$ - $i\text{-Bu}_2\text{AlOR}'$  ( $\text{R}'$ =alkyl group) are given in Table 1, where it is seen that a tendency is that the larger the  $\text{R}'$  group, the higher the content of 1,2-units in the polymers.

Table 1 Microstructure of 1,2-polybutadienes prepared with  $\text{MoCl}_4\text{OC}_8\text{H}_{17}$ - $i\text{-Bu}_2\text{AlOR}'$

| $\text{R}'$ (normal alkyl) |   | $\text{C}_3\text{H}_7$ | $\text{C}_4\text{H}_9$ | $\text{C}_5\text{H}_{11}$ | $\text{C}_7\text{H}_{15}$ | $\text{C}_8\text{H}_{17}$ | $\text{C}_9\text{H}_{19}$ | $\text{C}_{10}\text{H}_{21}$ |
|----------------------------|---|------------------------|------------------------|---------------------------|---------------------------|---------------------------|---------------------------|------------------------------|
| Microstructure (%)         | V | 77                     | 82                     | 82                        | 84                        | 87                        | 86                        | 88                           |
|                            | T | 13                     | 9                      | 10                        | 9                         | 8                         | 9                         | 5                            |
|                            | C | 10                     | 9                      | 8                         | 7                         | 5                         | 5                         | 7                            |

V: 1,2-unit; T: trans-1,4-unit; C: cis-1,4-unit.

## 2. Regulation of the content of 1,2-units in the polymer

It is desirable to regulate the content of 1,2-units in the synthesis of 1,2-polybutadienes. It has been found that some of the polar additives given in Table 2 are able to exert great effect on the microstructure of 1,2-polybutadienes prepared with molybdenum catalyst systems. Allyl halides are more efficient in regulating the content of 1,2-units in the polymer, of which allyl iodide is the best for this purpose (Fig. 2). The content of 1,2-units in the polymer rises with increase in the amount of allyl halides added and 1,2-polybutadienes with a content of 1,2-units of 98% can be obtained with allyl iodide as the additive.

## 3. Analysis of the chain structure of the polymer

(1) Content of 1,2-units in the polymer Data on the microstructure in Tables 1 and 2

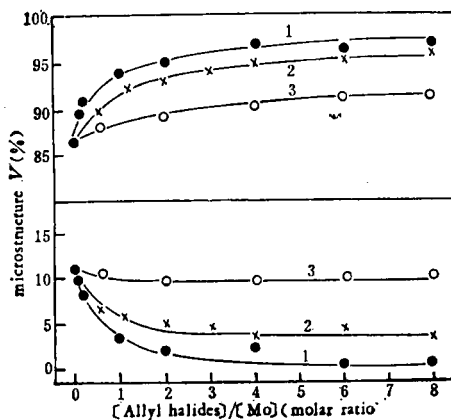


Fig. 2 Effect of allyl halides on the microstructure of the polymer  
 1.  $\text{CH}_2=\text{CH}-\text{CH}_2\text{I}$ ; 2.  $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$ ; 3.  $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ .

Table 2 Effect of additives on the microstructure of 1,2-polybutadienes catalysed by  
 $\text{MoCl}_4\text{OC}_8\text{H}_{17}-i\text{-Bu}_2\text{AlO}$  

| Additive            | [Additive]/[Mo]<br>(molar ratio) | Conversion<br>(%) | Microstructure (%) |    |    |
|---------------------|----------------------------------|-------------------|--------------------|----|----|
|                     |                                  |                   | V                  | T  | C  |
| Iodine              | 0                                | 81                | 86                 | 10 | 4  |
|                     | 0.5                              | 38                | 85                 | 11 | 4  |
|                     | 0.6                              | 36                | 87                 | 9  | 4  |
|                     | 2                                | 21                | 95                 | 3  | 2  |
|                     | 4                                | 6                 | 95                 | 4  | 1  |
| Thionyl chloride    | 1                                | 83                | 86                 | 11 | 3  |
|                     | 2                                | 75                | 78                 | 19 | 3  |
|                     | 4                                | 79                | 66                 | 26 | 8  |
|                     | 8                                | 89                | 67                 | 22 | 11 |
|                     | 10                               | 77                | 71                 | 22 | 7  |
| Hexachloropropylene | 2                                | 63                | 79                 | 11 | 10 |
|                     | 4                                | 72                | 84                 | 14 | 5  |
|                     | 6                                | 63                | 76                 | 19 | 5  |
|                     | 8                                | 59                | 74                 | 23 | 3  |
|                     | 10                               | 50                | 66                 | 15 | 19 |
| Allyl benzoate      | 4                                | 74                | 79                 | 12 | 9  |
|                     | 8                                | 64                | 76                 | 18 | 6  |
|                     | 10                               | 80                | 63                 | 23 | 14 |
| Allyl ether         | 3                                | 42                | 81                 | 11 | 8  |
|                     | 6                                | 22                | 80                 | 12 | 8  |
|                     | 10                               | 7                 | 79                 | 13 | 8  |
| Phenyl ether        | 8                                | 80                | 79                 | 14 | 7  |
|                     | 10                               | 70                | 76                 | 18 | 6  |

$[\text{Mo}]/[\text{butadiene}] = 8 \times 10^{-5}$  (molar ratio);  $[\text{Al}]/[\text{Mo}] = 16$  (molar ratio).

and Fig. 2 were measured by IR. In order to analyse more accurately the content of 1,2-units in the polymer,  $^{13}\text{C}$ -NMR and  $T_g$  method (linear expansion) were also tried, and the results by IR are given in Table 3. Results by  $^{13}\text{C}$ -NMR agree with those by IR, but the results from  $T_g$  are somewhat higher. In the  $T_g$  method the content of 1,2-units is estimated according to Bahary<sup>[5]</sup> equation,  $T_g = 91V - 106$ , an expression relating content of 1,2-units to glass temperature  $T_g$  of 1,2-polybutadienes.  $T_g$  values of 1,2-polybutadienes prepared with allyl iodide as additive are given in Table 4. The higher values from this latter method are the result of higher stereoregularity of 1,2-polybutadienes prepared with Mo catalyst (see below) as  $T_g$  of polymer with more regular chain structure is higher than that of atactic polymer with the same 1,2-content.

Table 3 1,2-Content as Measured by IR and  $^{13}\text{C}$ -NMR and from  $T_g$

| [Allyl iodide]/[Mo]<br>(molar ratio) | 0  | 0.1 | 1  | 4  | 8   | 10  |
|--------------------------------------|----|-----|----|----|-----|-----|
| IR                                   | 86 | 93  | 94 | 97 | 96  | 96  |
| $^{13}\text{C}$ -NMR                 | 91 | 93  | 94 | 96 | 97  | 97  |
| from $T_g$                           | 92 | —   | 98 | 99 | 100 | 100 |

Table 4  $T_g$  of 1,2-polybutadienes prepared with allyl iodide as additive

| [Allyl iodide]/[Mo]<br>(molar ratio) | 0   | 1   | 2   | 4   | 8   | 10  |
|--------------------------------------|-----|-----|-----|-----|-----|-----|
| $T_g$ ( $^{\circ}\text{C}$ )         | -22 | -17 | -16 | -16 | -13 | -11 |

(2) Configuration of the 1,2-units The  $^{13}\text{C}$ -NMR spectra of  $\text{CH}_2=$  in the vinyl group of the polymer are shown in Fig. 3. The assignment of the three resonance peaks with chemical shifts at 113.5, 114.0 and 114.7 ppm as isotactic 1,2-, atactic 1,2- and syndiotactic 1,2-unit, respectively, has been reported<sup>[6, 7]</sup>. From these resonance peaks the relative contents of the three 1,2-isomers in a 1,2-polybutadiene can be estimated, as shown in Table 5. It was found that with the increase of the added amount of allyl iodide the content of isotactic 1,2-unit decreases and the content of syndiotactic 1,2-units increases, while the atactic 1,2-content has little change. This shows that the allyl iodide is able to regulate not only the content of 1,2-units in the polymer but also their configuration.

Table 5 Relative content of 1,2-unit isomers in the polymer

| [Allyl iodide]/[Mo]<br>(molar ratio) | 0  | 0.3 | 1  | 4  | 8  | 10 |
|--------------------------------------|----|-----|----|----|----|----|
| isotactic (%)                        | 48 | 36  | 28 | 25 | 22 | 21 |
| syndiotactic (%)                     | 12 | 22  | 29 | 31 | 34 | 34 |
| atactic (%)                          | 40 | 42  | 43 | 44 | 44 | 45 |

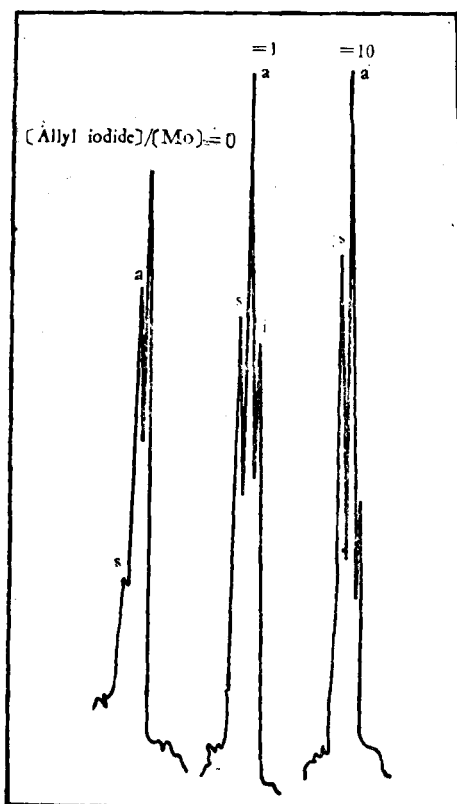


Fig. 3  $^{13}\text{C}$ -NMR spectra of  $\text{CH}_2=$  in the vinyl group of the polymer

| Peak | Chemical shift | Assignment            |
|------|----------------|-----------------------|
| i    | 113.5 (ppm)    | isotactic 1,2-unit    |
| a    | 114.0          | atactic 1,2-unit      |
| s    | 114.7          | syndiotactic 1,2-unit |

[Allyl iodide]/[Mo]=0

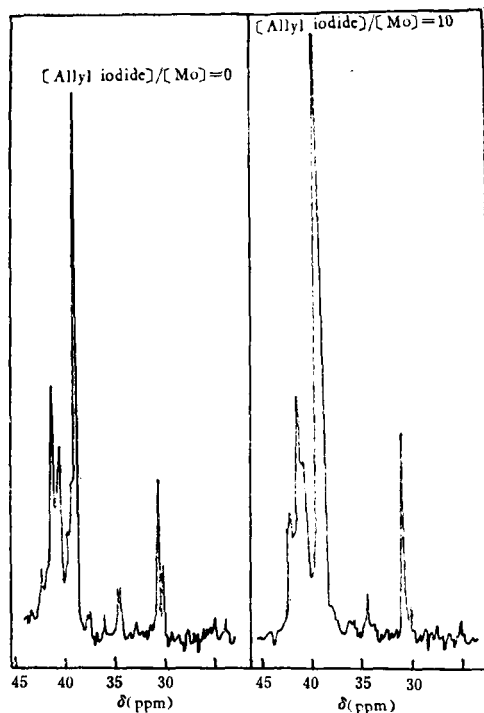


Fig. 4 Part of  $^{13}\text{C}$ -NMR spectra assigned to saturated carbons in the polymer

(3) Sequence distribution The part of  $^{13}\text{C}$ -NMR spectra assigned to saturated carbons in the polymer is shown in Fig. 4. The appearance of only resonance peaks assigned to isolated 1,4-units (24.6 ppm, cis-1,4-unit; 29.8 ppm, trans-1,4-unit) in the  $^{13}\text{C}$ -NMR spectra shows that both cis-1,4- and trans-1,4-units are mostly isolated in the polymer chain. The sequence distribution of 1,2-units in the polymer can be examined by statistic theory. If the number of 1,4-units in the polymer is small enough to be ignored, the relation between the dyads and triads of the 1,2-units that appear as random sequence distribution can be expressed as:

$$P_i = P_m \cdot P_m = P_m^2 \quad (1)$$

$$P_s = P_r \cdot P_r = P_r^2 \quad (2)$$

$$P_a = 2P_m \cdot P_r \quad (3)$$

where  $P_i$ ,  $P_s$  and  $P_a$  are generating probability or concentration of isotactic, syndiotactic and atactic triads, respectively, and  $P_m$  and  $P_r$  are generating probability of the dyads that two vinyl groups are at the same side and opposite sides of main chain in the polymer, respectively. There are the following relations among the triads:

$$P_i + P_s + P_a = 1 \quad (4)$$

$$\sqrt{P_i} = P_i + \frac{1}{2}P_a \quad (5)$$

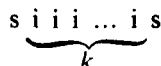
$$\sqrt{P_s} = P_s + \frac{1}{2}P_a \quad (6)$$

The randomness of sequence distribution of 1,2-units in the polymer can be examined according to Eqs. (5) and (6), and  $P_i$ ,  $P_s$  and  $P_a$ , in fact, are the relative contents of the 1,2-isomers which can be measured by  $^{13}\text{C}$ -NMR. The fact that  $\sqrt{P_i}$  and  $(P_i + \frac{1}{2}P_a)$  and  $\sqrt{P_s}$  and  $(P_s + \frac{1}{2}P_a)$  are basically equal for polymer with allyl iodide as polymerization additive (see Table 6) implies that the sequence distribution of the 1,2-isomers in the polymer is random. Then the sequence length of isotactic and syndiotactic 1,2-units in the polymer can be approached from a random distribution model by statistic principle.

Table 6 Influence of allyl iodide on sequence distribution of 1,2-units in the polymer

| [Allyl iodide]/[Mo]<br>(molar ratio) | 0    | 0.3  | 1    | 4    | 8    | 10   |
|--------------------------------------|------|------|------|------|------|------|
| $\sqrt{P_i}$                         | 0.69 | 0.60 | 0.53 | 0.50 | 0.50 | 0.45 |
| $P_i + \frac{1}{2}P_a$               | 0.68 | 0.57 | 0.50 | 0.45 | 0.45 | 0.44 |
| $\sqrt{P_s}$                         | 0.35 | 0.47 | 0.54 | 0.56 | 0.58 | 0.58 |
| $P_s + \frac{1}{2}P_a$               | 0.32 | 0.43 | 0.51 | 0.53 | 0.56 | 0.57 |

Assume isotactic 1,2-sequence having a length of  $k$ :



and its generating probability is

$$P_r^2 P_m^k \quad (7)$$

There are  $(n-1)$  dyads in a polymer chain with  $n$  units (1,4-units assumed to be negligible). Then sequence distribution function of the isotactic 1,2-unit can be expressed as

$$I_k = (n-1)P_r^2 P_m^k \quad (8)$$

In the same way, the sequence distribution function of syndiotactic 1,2-unit can be obtained as

$$S_l = (n-1)P_m^2 P_r^l \quad (9)$$

Both number and weight average sequence lengths of the stereoisomers of 1,2-units can be evaluated from the sequence distribution functions:

$$\langle M_i \rangle_n = \sum_{k=1} KI_k / \sum_{k=1} I_k = 1 / (1 - P_m) \quad (10)$$

$$\langle M_s \rangle_n = \sum_{l=1} l S_l / \sum_{l=1} S_l = 1 / P_m \quad (11)$$

$$\langle M_i \rangle_w = \sum_{k=1} K^2 I_k / \sum_{k=1} K I_k = (1 + P_m) / (1 - P_m) \quad (12)$$

$$\langle M_s \rangle_w = \sum_{l=1} l^2 S_l / \sum_{l=1} l S_l = (2 - P_m) / P_m \quad (13)$$

where  $\langle M_i \rangle$  and  $\langle M_s \rangle$  are average sequence length of isotactic and syndiotactic 1,2-units respectively, and the subscripts  $n$  and  $w$  indicate number average and weight average values for the sequence length respectively.

The results of the average sequence length of stereoisomers of 1,2-units in the polymer as obtained from the Eqs. (1) and (10)–(13) and the data in Table 5 are given in Table 7. It should be noted that the average sequence length of isotactic 1,2-unit shortens and that of syndiotactic 1,2-unit grows with the increase of the added amount of allyl iodide in the catalyst systems.  $\langle M_i \rangle_w / \langle M_i \rangle_n$  and  $\langle M_s \rangle_w / \langle M_s \rangle_n$  can be used to characterize the polydispersity of the sequence distribution of isotactic and syndiotactic isomers in 1,2-polybutadienes in same manner as the polydispersity of molecular weight of a polymer can be characterized by  $\langle M \rangle_w / \langle M \rangle_n$ . From Table 7 it can be seen that the change of  $\langle M_i \rangle_w / \langle M_i \rangle_n$  and  $\langle M_s \rangle_w / \langle M_s \rangle_n$  of the polymer with the added amount of allyl iodide is very small.

**Table 7** Average sequence length of isotactic and syndiotactic 1,2-units in the polymer and its sequence distribution

| [Allyl iodide]/[Mo]<br>(molar ratio)            | 0   | 0.3 | 1   | 4   | 8   | 10  |
|-------------------------------------------------|-----|-----|-----|-----|-----|-----|
| $\langle M_i \rangle_n$                         | 3.2 | 2.5 | 2.1 | 2.0 | 2.0 | 1.9 |
| $\langle M_s \rangle_n$                         | 1.4 | 1.7 | 1.9 | 2.0 | 2.0 | 2.2 |
| $\langle M_i \rangle_w$                         | 5.5 | 4.0 | 3.3 | 3.0 | 3.0 | 2.7 |
| $\langle M_s \rangle_w$                         | 1.9 | 2.3 | 2.8 | 3.0 | 3.0 | 3.3 |
| $\langle M_i \rangle_w / \langle M_i \rangle_n$ | 1.7 | 1.6 | 1.5 | 1.5 | 1.5 | 1.5 |
| $\langle M_s \rangle_w / \langle M_s \rangle_n$ | 1.3 | 1.4 | 1.5 | 1.5 | 1.5 | 1.5 |

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