

# STUDY ON SEQUENCE DISTRIBUTION OF 3, 4-POLYISOPRENE BY $^{13}\text{C}$ -NMR

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## ABSTRACT

Isoprene can be polymerized with  $\text{Fe}(\text{acac})_3$ -phen- $\text{AlEt}_3$  catalyst system into a polymer mainly containing 3, 4-unit and capable of crystallizing to some extent. The  $^{13}\text{C}$ -NMR spectra of 3, 4-polyisoprene synthesized with Fe-catalyst system were investigated, and the sequence distribution of *cis*-1, 4, *trans*-1, 4 and 3, 4-units and the amount of head-to-head and tail-to-tail linkages of 1, 4 and 3, 4-units were discussed. Results showed that the contents of *cis*-1, 4, *trans*-1, 4 and 3, 4-unit calculated from different carbon types were satisfactorily identical, indicating correct assignments of these peaks.

Isoprene can incorporate into polymer chain in four different isomeric structures, i.e., *cis*-1, 4, *trans*-1, 4, 1, 2- and 3, 4-units, the relative amounts are depending on catalyst system and polymerization conditions used. The properties of polyisoprene are affected not only by the amount but also by the distribution of these isomeric units along the polymer chain. Therefore, their contents and sequence distribution have been investigated quantitatively by  $^{13}\text{C}$  NMR technique<sup>[1,2,3]</sup>.

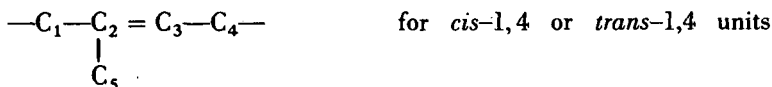
In a previous work<sup>[4]</sup>, one of the authors showed that isoprene can be polymerized with  $\text{Fe}(\text{acac})_3$ -phen- $\text{AlR}_3$  catalyst system into a polymer mainly containing 3, 4-unit and capable of crystallizing to some extent. This paper will report some new results on this polymer.

## EXPERIMENTAL

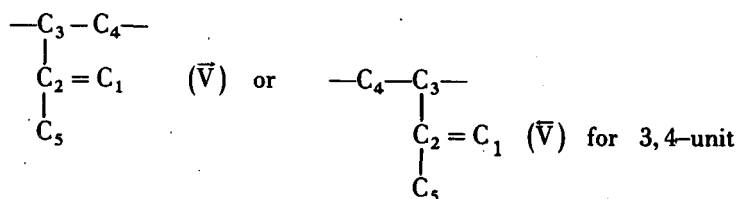
The 3, 4-polyisoprene was prepared with  $\text{Fe}(\text{acac})_3$ -phen- $\text{AlEt}_3$  catalyst according to previous method [4].  $^{13}\text{C}$  NMR spectra of the 3, 4-polyisoprene in  $\text{CDCl}_3$  were obtained at 25.0 MHz, On a JEOL-FX-100 FT Spectrometer at 50°C, chemical shifts were referred to TMS. All the spectra were proton noise decoupled, with double precision accumulation 8000 times. pulse repetition time 1.5s, pulse width 5  $\mu\text{s}$  (45°), data point 4K, window 3.

## RESULTS AND DISCUSSION

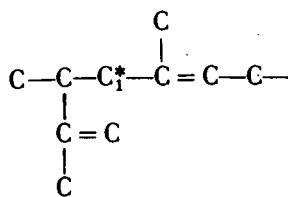
In order to label the position of a particular carbon atom in a given sequence, the *i*'th carbon atom of *cis*-1, 4 (C), *trans*-1, 4 (T) and 3, 4-(V) units is designated by *C<sub>i</sub>*, *T<sub>i</sub>* and *V<sub>i</sub>* respectively (*i* = 1, 2, 3, 4, 5) as shown in the following:



and



Thus, the notation  $\bar{\text{V}}\text{C}_1$ , for example, stands for the first carbon atom ( $\text{C}_1^*$ ) of the *cis*-1,4 unit in the following chain sequence structure:



Polyisoprene containing *cis*-1,4, *trans*-1,4 and 3,4-unit exhibits complicated  $^{13}\text{C}$  NMR spectra due to various types and sequence of carbon atoms, as shown in Figure 1.

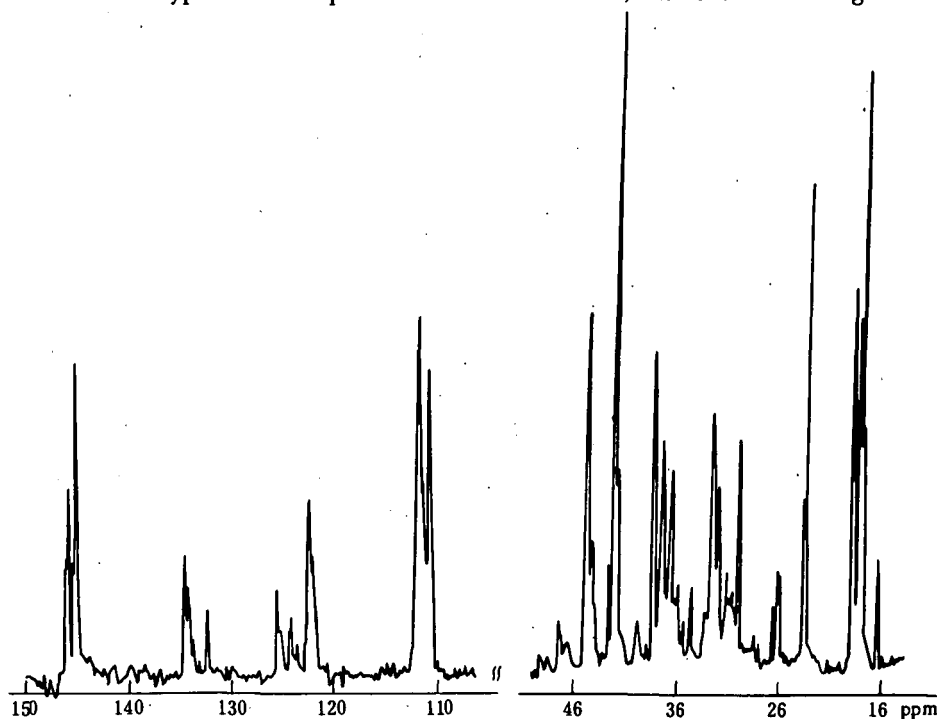


Fig. 1  $^{13}\text{C}$  NMR spectra of 3,4-polyisoprene

In the present paper, we will assign these peaks and calculated 3,4-unit content and sequence distribution on the basis of  $^{13}\text{C}$  NMR data.

#### Calculation of chemical shift

Grant et al.<sup>[5]</sup> have shown that the chemical shift  $\delta_{(k)}$  of the  $k$ 'th carbon atom in linear saturated hydrocarbon can be expressed by the following equation:

$$\delta_{(k)} = B + \sum N_{ki} A_i \quad (1)$$

The constant  $B$  is equal to the chemical shift of methane,  $Nki$  is the number of carbons at the  $i$ 'th position relative to the  $k$ 'th carbon and  $Ai$  is the chemical shift parameter associated with the  $i$ 'th carbon atom. The five  $Ai$  values ( $\alpha, \beta, \gamma, \delta$  and  $\epsilon$ ) are given in Table 1. Dorman et al.<sup>[6]</sup> reported that a double bond in a mono-olefin had influence only on the chemical shift of  $\alpha$  aliphatic carbon and had little effect on that of  $\beta$  aliphatic carbon. Therefore, it can be presumed that the chemical shift of an aliphatic carbon in polyisoprene is influenced by the adjacent double bond in the same monomer unit, while the double bonds in the next or more distant monomer units have little, if any, effect. The magnitude of influence by a double bond, i. e. shift factor  $C_1(\alpha)$ ,  $C_4(\alpha)$ ,  $T_1(\alpha)$  and  $T_4(\alpha)$  can be determined by comparing the observed signal position with that calculated according to eq. 1. For example, from the difference of the experimental shift 32.16ppm and the predicted value 39.9ppm of the signal  $cc,c$ , the parameter  $C_1(\alpha)$  is obtained, which means the correction for methylene carbon atoms with 1,1-disubstituted olefinic carbon atom in  $\alpha$ -position. From the difference of 26.11ppm and 25.2ppm for experimental and calculated positions of  $C_4C$  signal, the parameter  $C_4(\alpha)$  is determined which means a correction for methylene carbon atoms with a monosubstituted olefinic carbon in  $\alpha$ -position. From the signal of tertiary carbon atoms  $VVV_3VV$  in 3,4-block sequence the difference of the experimental position at 42.34ppm and the predicted position at 54.5ppm yields the parameter  $3'(2^\circ)$ , which means the correction for tertiary carbon atoms with an olefinic vinyl carbon in  $\alpha$ -position bound to a secondary carbon atom. For the same reason, parameter  $2'(3^\circ)$  can be determined. We also introduce a parameter  $C(r^2)$  to express the influence of *cis*-double bond on  $CH_2$  carbon atom in  $\gamma$ -position. Thus, chemical shift of the  $k$ 'th carbon can be calculated by

$$\delta_{(k)} = B + \sum NkiAi + NjAj + \text{correct term} \quad (2)$$

The value of these parameters were also listed in Table 1

Table 1 Chemical shift parameters (ppm) for the calculation of chemical shifts in 3,4-polyisoprene

|            |                  |                       |                       |
|------------|------------------|-----------------------|-----------------------|
| $B = -2.6$ | $Ai$             | $Ai$                  |                       |
|            | $\alpha = 9.1$   | $C_1(\alpha) = -7.74$ | $3'(2^\circ) = -6.08$ |
|            | $\beta = 9.4$    | $C_4(\alpha) = 0.91$  | $2'(3^\circ) = -0.82$ |
|            | $\gamma = -2.5$  | $T_1(\alpha) = 0.14$  | $C(r^2) = -0.5$       |
|            | $\delta = 0.3$   | $T_4(\alpha) = 1.2$   |                       |
|            | $\epsilon = 0.1$ |                       |                       |

For the calculating chemical shift of the olefinic carbon in *cis*-1,4/3,4 polyisoprene we used the chemical shift parameters of *cis*-1,4/1,2-polybutadiene<sup>[7]</sup> and satisfactory results have been obtained.

## ASSIGNMENT AND SEQUENCE DISTRIBUTION OF THE PEAKS

### 1. Assignment of methyl peaks

In  $^{13}C$  NMR spectra of methyl carbon in high 3,4-polyisoprene seven peaks were observed, They were tentatively assigned as shown in Table 2.

Table 2 Assignment and relative intensities of methyl carbon peaks

| Peak N | Chemical shift (ppm) | Assignment                         | Relative intensities (%) |
|--------|----------------------|------------------------------------|--------------------------|
| 1      | 16.13                | $\text{T}_3$                       | 4.10                     |
| 2      | 17.61                | $\text{VV}_3\text{V}(\text{morr})$ | 7.66                     |
| 3      | 17.92                | $\text{VV}_3\text{V}(\text{morr})$ | 23.28                    |
| 4      | 18.08                | $\text{CV}_3\text{V}$              | 15.05                    |
| 5      | 18.78                | $\text{CV}_3\text{C}$              | 18.67                    |
| 6      | 23.38                | $\text{CC}_3\text{C}$              | 22.81                    |
| 7      | 23.62                | $\bar{\text{V}}\text{C}_3\text{C}$ | 8.41                     |

The occurrence of two peaks at 17.61 and 17.92ppm might be due to different steric tacticities, however, it is not possible to give their correct assignments since pure 3,4-polyisoprene is not available now. As far as we know, assignment of the peak at 23.62ppm has not been reported in literature, we conclude that it comes from  $\bar{\text{V}}\text{C}_3\text{C}$  sequence with head-to-head linkage.

## 2. Assignment of methylene and methine carbon peaks

The signals of methylene ( $\text{CH}_2$ ) carbon atoms in *cis*-1,4 and *trans*-1,4 block sequence can be found easily at  $\text{C}_1$ :32.16,  $\text{C}_4$ :26.11,  $\text{T}_1$ :40.14 and  $\text{T}_4$ :26.42ppm respectively. Although the  $^{13}\text{C}$  NMR spectrum of pure 3,4-polyisoprene is not available at present, it can be shown that the resonances of secondary carbons ( $\text{V}_4$ ) and tertiary carbons ( $\text{V}_3$ ) in 3,4-block sequences must be assigned to  $\text{V}_4$ :38.36 and  $\text{V}_3$ :42.34ppm respectively. Assignments of the other peaks have been made by the comparison of experimental chemical shift values with those calculated by using Fig2. The results are listed in Table 3.

Table 3 Assignments and relative intensities of methylen and methine carbon peaks

| Peak No. | Chemical shift (ppm) |       | Assignment               | Relative intensities (%) |
|----------|----------------------|-------|--------------------------|--------------------------|
|          | obs.                 | cal.  |                          |                          |
| 8        | 26.11                | —     | $\text{C}_4\text{C}$     | 7.07                     |
| 9        | 26.42                | —     | $\text{T}_4\text{T}$     | 1.83                     |
| 10       | 28.30                | 28.91 | $\text{C}_4\text{C}_4$   | 0.77                     |
| 11       | 30.17                | 29.96 | $\text{VC}_1\text{CV}$   | 6.11                     |
| 12       | 30.79                | 30.88 | $\text{CV}_4\text{C}$    | 1.91                     |
| 13       | 31.34                | 31.68 | $\text{VV}_4\text{C}$    | 2.45                     |
| 14       | 32.16                | —     | $\text{CC}_1$            | 4.23                     |
| 15       | 32.58                | 32.59 | $\text{CC}_4\text{VC}$   | 4.13                     |
| 16       | 32.82                | 32.69 | $\text{CC}_4\text{VV}$   | 6.57                     |
| 17       | 33.36                | 32.98 | $\text{CT}_4\text{VV}$   | 1.90                     |
| 18       | 34.69                | 34.58 | $\text{CV}_4\text{V}$    | 2.03                     |
| 19       | 35.47                | 35.46 | $\text{CVC}_1$           | 1.02                     |
| 20       | 36.09                | 36.05 | $\text{VVC}_1$           | 2.01                     |
| 21       | 36.80                | 36.56 | $\text{CV}_4\text{VC}$   | 2.07                     |
| 22       | 37.65                | 37.64 | $\text{CV}_4\text{VV}$   | 5.85                     |
| 23       | 38.36                | —     | $\text{VV}_4\text{VVV}$  | 8.24                     |
| 24       | 40.04                | —     | $\text{CT}_1$            | 1.42                     |
| 25       | 42.10                | 42.20 | $\text{VCVV}_3\text{VC}$ | 4.42                     |
| 26       | 42.34                | —     | $\text{VVV}_3\text{VV}$  | 16.31                    |
| 27       | 42.96                | 43.04 | $\text{CV}_3\text{C}$    | 2.79                     |
| 28       | 44.67                | 44.34 | $\text{CVV}_3\text{C}$   | 4.88                     |
| 29       | 45.22                | 44.44 | $\text{VVV}_3\text{C}$   | 9.13                     |
| 30       | 47.79                | 46.44 | $\text{CV}_3\text{C}$    | 2.86                     |

Data in Table 3 show that some new peaks in  $^{13}\text{C}$  NMR spectra of Fe-catalyzed 3,4-polyisoprene can be observed such as, peak No. 18, 19, 20 and 27, which arise from head-to-head or tail-to-tail linkage of *cis*-1,4/3,4 sequences. In the previous work<sup>[1]</sup> the two peaks at 37.55 and 32.67 ppm were assigned to different configuration sequence (*m,r*) in the 3,4-block polyisoprene but we suppose these peaks are due to different sequence. Because there are head-to-head or tail-to-tail linkages and the 3,4-block sequences are not long in the 3,4-polyisoprene prepared with Fe-catalyst, its degree of crystallinity is low.

### 3. Assignment of olefinic carbon peaks

In the olefinic region, it was shown in the previous work<sup>[8]</sup> that intensities of the two peaks at 109.74 and 145.52 ppm increased with increasing *trans*-1,4 content, so they would be assigned to carbon  $V_1$  and  $V_2$  in *tVt* sequence. But these peaks are not observed now, indicating low *trans*-1,4 content in Fe-catalyzed 3,4-polyisoprene. For the same reason, two peaks at 111.20 and 147.50 ppm are attributed to carbons  $V_1$  and  $V_2$  in *cVc* sequence and peaks at 112.10, 112.36, 146.51 and 146.75 ppm should correspond to carbons  $V_1$  and  $V_2$  in different steric tacticities in block 3,4-units. Assignments and chemical shifts of olefinic carbon peaks are listed in Table 4.

Table 4 Assignment and relative intensities of olefinic carbon peaks

| Peak No. | Chemical shift (ppm) |        | Sequence                             | Relative intensities (%) |
|----------|----------------------|--------|--------------------------------------|--------------------------|
|          | obs.                 | cal.   |                                      |                          |
| 31       | 111.20               |        | $\text{CV}_1\text{C}$                | 8.05                     |
| 32       | 111.42               |        | $\text{CV}_1\text{V}$                | 10.95                    |
| 33       | 112.10               |        | $\text{VV}_1\text{V}(\text{m or r})$ | 6.92                     |
| 34       | 112.36               |        | $\text{VV}_1\text{V}(\text{m or r})$ | 12.72                    |
| 35       | 122.46               | 122.46 | $\text{VT}_3\text{C}$                | 2.42                     |
| 36       | 123.00               | 123.09 | $\text{VC}_3\text{V}$                | 4.35                     |
| 37       | 123.28               | 123.40 | $\text{CC}_3\text{V}$                | 6.28                     |
| 38       | 125.00               | 125.00 | $\text{CC}_3\text{C}$                | 1.29                     |
| 39       | 125.35               | 125.48 | $\text{VC}_3\text{C}$                | 2.25                     |
| 40       | 126.55               | 125.96 | $\text{VC}_3\text{V}$                | 4.83                     |
| 41       | 133.57               | 133.98 | $\text{VC}_2\text{V}$                | 2.42                     |
| 42       | 135.10               | 135.10 | $\text{CC}_2\text{C}$                | 1.45                     |
| 43       | 135.50               | 135.50 | $\text{VT}_2\text{C}$                | 2.58                     |
| 44       | 135.67               | 135.58 | $\text{VC}_2\text{C}$                | 3.22                     |
| 45       | 136.06               | 136.06 | $\text{VC}_2\text{V}$                | 4.35                     |
| 46       | 146.51               |        | $\text{VV}_2\text{V}(\text{m or r})$ | 10.95                    |
| 47       | 146.75               |        | $\text{VV}_2\text{V}(\text{m or r})$ | 4.02                     |
| 48       | 147.22               |        | $\text{CV}_2\text{V}$                | 6.60                     |
| 49       | 147.50               |        | $\text{CV}_2\text{C}$                | 4.35                     |

### CONTENTS OF 3,4-UNITS

The contents of 3,4-unit can be calculated from the relative peak intensities either of methyl carbon or of methylene and methine carbon peaks or of olefinic ones. Results are listed in Table 5.

It can be seen in Table 5 that contents of 3,4-, *cis*-1,4 and *trans*-1,4 units calculated from different carbons are satisfactorily identical, showing that the assignments of these peaks are correct. However, content of *trans*-1,4 unit calculated from  $\text{CH}_3$  carbon are lower than others. This is due to longer spin-lattice relaxation time ( $T_1$ ) of *trans*-1,4  $\text{CH}_3$  carbon atoms compared with *cis*-1,4 ones.

**Table 5** Isomeric unit contents calculated, with different  $^{13}\text{C}$  NMR peaks

| Peaks                | Content(%) |       |      |
|----------------------|------------|-------|------|
|                      | V          | C     | T    |
| methyl               | 64.66      | 31.24 | 4.10 |
| methylene<br>methine | 62.94      | 31.91 | 5.15 |
| olefinic             | 64.56      | 30.44 | 5.00 |

**Keywords:** $^{13}\text{C}$ -NMR ; 3,4-Polyisoprene; Sequence distribution; Diene polymerization; Fe-catalyst**REFERENCES**

- [1] Sato, H.; Ono, A. and Tanaka, Y., *Polymer*, **1977**, 18, 580.
- [2] Tanaka, Y. and Sato, H., *Polymer*, **1976**, 17, 412.
- [3] Gronski, W.; Murayama, N. and Cantow, H. J., *Polymer*, **1976**, 17, 359.
- [4] Sun Qing, M.S. Thesis of Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, **1984**.
- [5] Grant, D.M. and Paul, Z.G., *J. Am. Chem. Soc.*, **1964**, 86, 2984.
- [6] Dorman, D. E., Jautelat, M. and Roberts, J. D., *J.Org.Chem.*, **1971**, 36, 2757.
- [7] Elgert, K.T., *Polymer*, **1975**, 16, 154.
- [8] 龚志、谢德民、王佛松, 高分子通讯 (*Polymer Communications*), in Press.