NMR Studies of Irregular Structures in Polyisoprene

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ABSTRACT: Irregular structures of synthetic polyisoprenes and natural rubber were studied by
^{1}H and ^{13}C NMR spectroscopy. In synthetic polyisoprene, only the (3,4) unit was observed besides
the regular structure, but in natural rubber, it was not observed. The (3,4) unit content, which has an
important effect upon the properties of the polymer, decreased as the molecular weight increased. In
the ^{1}H NMR spectrum of synthetic polyisoprene dissolved in CCl_4, the $=CH_2$ proton signal of the
(3,4) unit was separated into two peaks. The higher-field peak was assigned to a terminal (3,4) unit
and the lower-field peak to an inner (3,4) unit. The terminal (3,4) unit content of the polymer
suggested that there are branches in the polymer chain. The ^{13}C NMR spectrum of hydrogenated
isoprene oligomer indicated that the polymerization of isoprene propagated by the (4,1) addition and
there is a considerable amount of the (3,4) unit at the chain end in the (4,3) structure.
    KEY WORDS   NMR / Polyisoprene / Irregular Structure / (3,4) Unit /
        Branching /

Synthetic polyisoprene (PIP) varies widely in its physical properties compared with natural rubber. The main structural unit in synthetic PIP is identical with that in natural rubber, although a very small amount of irregular structure exists in the former. An irregular structure, such as (3,4) unit, has considerable effect upon crystallization velocity, and mechanical properties such as the tensile strength and tear resistance of the polymer.[1] Thus to the relationship between the structure of a synthetic PIP and its physical properties, an attempt was made to identify the irregular structure in a synthetic PIP in detail. Hydrogenated isoprene oligomers were also investigated in order to obtain information on the mechanism of isoprene polymerization.

EXPERIMENTAL

The synthetic PIP polymer samples examined in this study were obtained from the Kuraray Isoprene Chemical Co. The PIP examined were (1) a cis-1,4-polyisoprene prepared with an Al–Ti catalyst, and (2) a trans-1,4-polyisoprene prepared with an Al–V catalyst. All samples were purified by precipitation from a benzene solution with acetone. Isoprene oligomers were extracted from trans-PIP with acetone and were hydrogenated by a Pd–C catalyst in hexane.
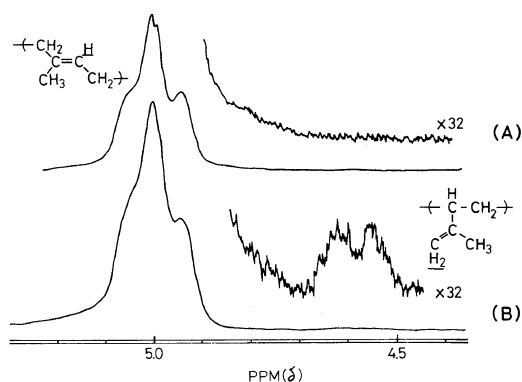
The PIP's and the hydrogenated oligomers were dissolved in CCl_4 in the NMR experiments unless stated otherwise. ^{1}H NMR spectra were recorded on a Varian HA-100 NMR spectrometer equipped with a Varian CAT 1024 time averaging computer. ^{13}C NMR measurements were carried out in part on a Varian HA-100 instrument equipped with a Fourier Transform accessory and were made at 30°C in CCl_4 (about 25% w/v). ^{13}C-enriched methyl iodide in a capillary was used as an external hetero nuclear lock signal. Chemical shifts were referenced to TMS added as an internal standard. All ^{13}C NMR spectra were measured under the condition of noise decoupling.

RESULTS AND DISCUSSION

^{1}H NMR Spectra of PIP's

^{1}H NMR spectra of olefinic protons in natural trans rubber (balata) and synthetic trans-PIP in CCl_4 solution are shown in Figure 1. These spectra were obtained after an accumulation of about 400 times.

In the spectrum of natural rubber (Figure 1A), no signal can be observed except that of methine protons in the (1,4) unit, while in the spectrum of synthetic *trans*-PIP (Figure 1B), two additional peaks can be observed in the olefinic region. There are two clear peaks in the (3,4) unit region in the spectrum of synthetic *cis*-PIP shown in Figure 2, while in the spectrum of natural rubber, no olefinic methylene peak can be observed. These facts indicate that there is a very small amount of irregular structure in the synthetic PIP in addition to the (1,4) unit which is regular in structure. The (1,2) units and the (3,4) units are possibly produced in the polymerization of isoprene. The α-CH₃ proton peak re-

sonated at about $\delta = 0.93$ can be observed in PIP by ¹H NMR if there are (1,2) units in the polymer. Such a peak is not observed in the polymer used in this study.

Most of the irregular structures in PIP are (3,4) units. The quantitative measurements of the (3,4) unit by ¹H NMR have already been reported by Chen[2] and Golub.[3] But these authors did not study the detailed assignments of the doublet at $\delta = 4.6$ ppm corresponding to $C = CH_2$ protons. As shown in Figure 3, one or two peaks were observed in methylene region of the (3,4) unit depending on the solvent used. In the CCl₄ solution, two peaks were clearly observed and the relative intensity of the peaks varied according to the species of polymerization catalysts and molecular weight as shown in Figure 4 and Figure 5. These two peaks correspond to two kinds of olefinic groups.

Elucidation of the Structures by Using Model Compounds

In order to decide the structures corresponding to the two peaks observed in methylene region of the (3,4) unit, a model compound was investigated. 2-Methyl-1-pentene was chosen as a model compound of terminal (3,4) unit in the polymer chain, and D-limonene was chosen as a model compound of an inner (3,4) unit. Referring the Sadtler Standard Spectra, the methylene proton chemical shift of each

Figure 1. The olefinic region of the time-averaged ¹H NMR spectra of PIP in CCl₄ solution: (A) natural *trans*; (B) synthetic *trans*.
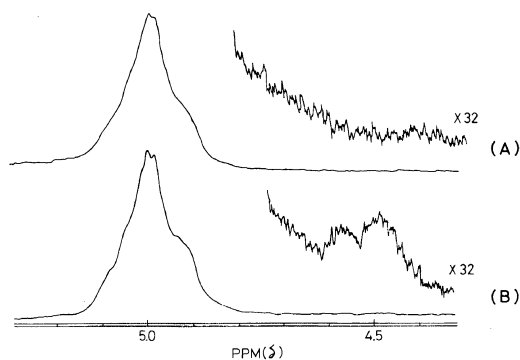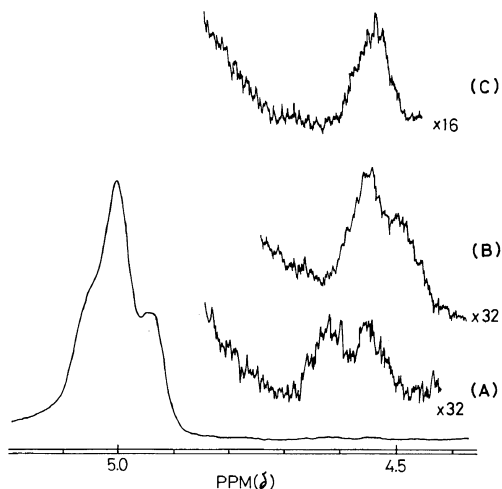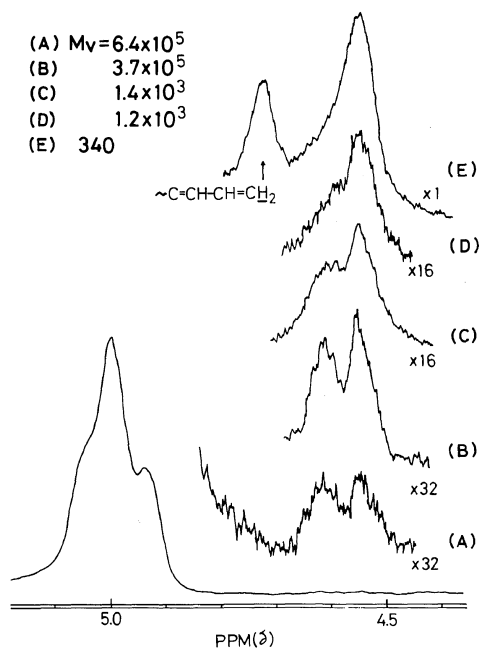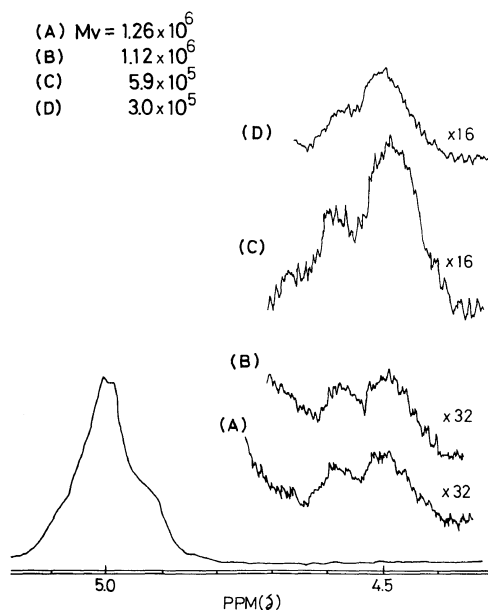

Figure 2. The olefinic region of the time-averaged ¹H NMR spectra of PIP in CCl₄: (A) natural *cis*; (B) synthetic *cis*.

Figure 3. The olefinic region of the ¹H NMR spectra of *t*-PIP in various solvents: (A) CCl₄; (B) CDCl₃; (C) C₆D₆.

(A) $M_v = 6.4 \times 10^5$
(B) 3.7×10^5
(C) 1.4×10^3
(D) 1.2×10^3
(E) 340

$\sim C=CH-CH=C\underline{H}_2$

(E) ×1
(D) ×16
(C) ×16
(B) ×32
(A) ×32

5.0   4.5
PPM(δ)

Figure 4. The olefinic region of the ^{1}H NMR spectra of various t-PIPs in CCl$_4$.

(A) $M_v = 1.26 \times 10^6$
(B) 1.12×10^6
(C) 5.9×10^5
(D) 3.0×10^5

(D) ×16
(C) ×16
(B)
(A) ×32
×32

5.0   4.5
PPM(δ)

Figure 5. The olefinic region of the ^{1}H NMR spectra of various cis-PIPs in CCl$_4$.

isopropenyl group was resonanced at $\delta = 4.61$ ppm (2-methyl-1-pentene) and at $\delta = 4.69$ ppm (D-limonene). The terminal methylene signal of D-limonene in a field lower than the terminal methylene signal of 2-methyl-1-pentene by 8 Hz. This result is roughly in accordance with the separation into two peaks in the polymer spectrum (about 7 Hz). That is the (3, 4) unit is at the terminal, and methylene ($=CH_2$) resonance may be observed in a higher field.

Dependence of (3,4) Unit Content on Molecular Weight

The methylene region in the (3,4) unit of the spectra is shown in Figure 4 for the samples with different molecular weights. The higher-field peak of the two methylene signals, namely the terminal (3,4) unit content decreases relatively and conversely the inner (3,4) unit content assigned to the lower-field peak increases, with the increase in molecular weight. Therefore, the NMR spectra in Figure 4 suggest that the ratio of the number of inner units of a polymer chain to that of the terminal unit increases relatively as the molecular weight becomes larger. The NMR spectra of several cis-PIP's of various molecular weights also show that an increase in molecular weight causes a decrease in the intensity of the higher-field peak and a relative increase of the lower peak. These spectra are shown in Figure 5. The average molecular weight of the samples shown in Figures 4 and 5 and the content of these (3,4) units are summarized in Tables I and II. These tables also

Table I. Average molecular weights and the 3,4-content for various $trans$-polyisoprene

Sample	M_v	3,4-Content %		
		Low[a]	High[b]	Total
K–PIP[d]	6.4×10^5	0.22	0.21	0.43
P–PIP[d]	3.7×10^5	0.44	0.51	0.95
OL 1[e]	1.4×10^3	1.32	1.66	2.98
OL 2[e]	1.2×10^3	0.55	1.20	1.75
IP 5	340	2.6	11.8	14.4
NR[c]		0.0	0.0	0.0

[a] Low-field peak.
[b] High-field peak.
[c] Natural rubber.
[d] Molecular weight (MW) determined by GPC.
[e] MW determined by VPO.

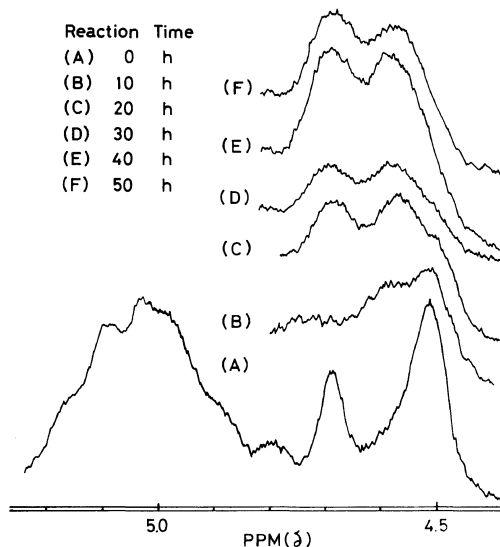**Table II.** Average molecular weights and the 3,4-content for various *cis*-polyisoprene

Sample	M_v	3,4-Content %		
		Low[a]	High[b]	Total
10A-5	1.24×10^6	0.22	0.39	0.61
3A-5	1.12×10^6	0.15	0.35	0.50
5A-5	5.6×10^5	0.39	0.77	1.16
8A-3	3.0×10^5	0.24	0.71	0.95
NR[c]		0.0	0.0	0.0

[a] Low-field peak.
[b] High-field peak.
[c] Natural rubber.
[d] *MW* determined by GPC.

Figure 6. The olefinic region of the ^{1}H NMR spectra of IP pentamer obtained by hydrogenation for the periods of time indicated.

show that the total amount of the (3,4) units increases with decrease in molecular weight. Comparing the molecular weight of each polymer with the content of the high-field peak of the (3,4) unit assigned to the terminal methylene, it is suggested that these polymers have a branching structure. When the number-average degree of polymerization of commercial *cis*- and *trans*-synthetic-PIP is estimated roughly as 10^4, the extent of branching the (3,4) units terminal is as much as 10 per molecule.

Hydrogenation of the Isoprene Oligomer

On the fractionated isoprene pentamer, the methylene peak of the isopropenyl group of the (3,4) units at each reaction time of hydrogenation was measured by ^{1}H NMR and the spectra are shown in Figure 6. As the reaction proceeds, the terminal methylene of (3,4) unit assigned to the higher-field peak is hydrogenated first. The inner (3,4) unit on the pentamer is covered with the terminal methylene peak before the reaction, but its peak becomes relatively larger as the terminal methylene of (3,4) unit is hydrogenated. Since the Pd–C catalyst used in the hydrogenation reaction has no selectivity, it is natural that the terminal of the isoprene oligomer should be hydrogenated first. By using ^{13}C NMR, the microstructures (especially the chain end structure) of the hydrogenated trimer and tetramer were investigated. The observed and calculated ^{13}C NMR stick spectra of the hydrogenated trimer and tetramer are shown in Figures 7 and 8, respectively. The

^{13}C chemical shift of each carbon atom in the trimer and the tetramer was calculated according to the method of Lindeman and Adams.[4] First, the ^{13}C chemical shift of the trimer observed was compared with the calculated value based on possible structures, which were designed assuming that about 15 mol% of (3,4) units is contained in the IP pentamer, and that the (3,4) units in the IP oligomer is located more at a chain end than in an inner part of the IP chain. The calculated spectra of (B) and (D) in Figure 7 were compared with the observed spectra, while those of (A) and (C) were excluded because of the large differences with the observed spectrum. The ^{13}C chemical shift of the terminal methyl carbon of (3,4) unit was calculated as *ca.* 17 ppm (from TMS) on (B), while the observed value was *ca.* 11 ppm. Thus, the ^{13}C NMR spectrum of (B) was not so coincident with the observed spectrum. On the other hand, the spectrum of (D) was quite similar to the observed one, where in the calculated chemical shift of the terminal methyl carbon agreed with the observed value. But the spectrum of (D) did not show perfect agreement with the observed spectrum, since the double bonds in the trimer are not completely hydrogenated. It is seen from the structure of (D) that two addition reaction types of $(4,1)_3$ and $(4,1)_2(4,3)$ are possible. On the basis of the above
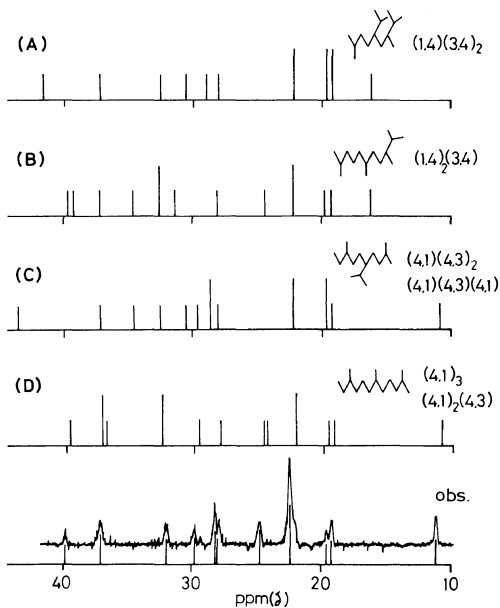
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Figure 7. The ^{13}C NMR stick spectra of the hydrogenated IP trimer observed and calculated.

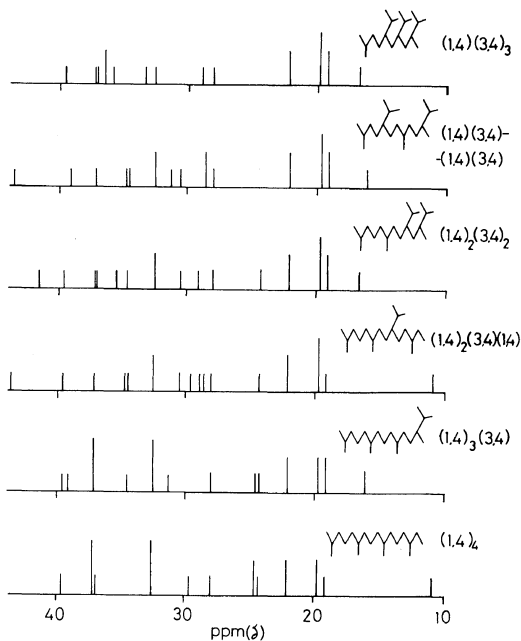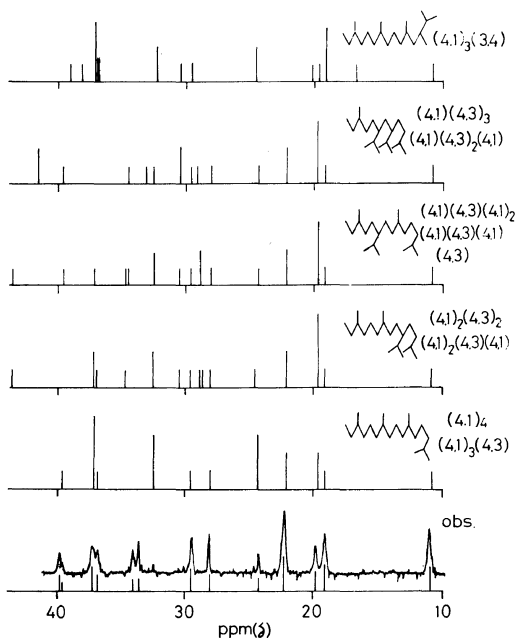**Fig. 8-b.** The calculated ^{13}C NMR spectra of the hydrogenated IP tetramer.

Fig. 8-a. The ^{13}C NMR stick spectra of the hydrogenated IP tetramer observed and calculated.

facts, it is suggested that the structure of the trimer consists mainly of (4,1) (4,1) (4,3).

On the tetramer, the observed ^{13}C NMR stick spectrum was compared with the calculated spectra (Figure 8-a and 8-b). It is also probable on the tetramer that the IP chains propagate in the (4,1) structure rather than in the (1,4) structure, and that the (3,4) unit exists in the (4,3) structure at the chain terminal. The mechanism of IP propagation in the (4,1) structure has been reported by Morton et al.[5]

CONCLUSION

In natural rubber, the (3,4) unit is not observed, while it is contained in synthetic rubber to the extent of ca. 0.4%. By ^{1}H NMR spectrum analysis of isopropenyl methylene of the (3,4) unit, the higher-field peak ($\delta = 4.56$ ppm) was assigned to a terminal (3,4) unit, and the lower-field peak to an inner (3,4) unit. The (3,4) unit content of polyisoprene decreases with increase in its molecular weight. Quantitative analysis of the terminal (3,4) unit shows that synthetic PIP has about one branch per 1000 monomer units. The ^{1}H and ^{13}C NMR spectra of the hydrogenated isoprene oligomers suggest that the

polymerization of isoprene propagates in the (4,1) structure, and that the (3,4) unit exists more at the end part than in the inner part of the chain of (4,3) structure.

REFERENCES

1. K. W. Scott, G. S. Trick, R. H. Mayer, W. M. Saltman, and R. M. Pierson, *Rubber Plast. Age*, **39**, 175 (1961).
2. H. Y. Chen, *Anal. Chem.*, **34**, 1793 (1962).
3. Q. T. Pham, *J. Polym. Sci.*, *B*, **8**, 723 (1970).
4. L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).
5. M. Morton, R. D. Sanderson, R. Sakata, and L. A. Falvo, *Macromolecules*, **6**, 186 (1973).