

Monomer Unit Sequence Distribution in Partly-Epoxidized *trans*-1,4-Polyisoprene

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ABSTRACT: The monomer unit sequence distribution in partly epoxidized *trans*-1,4-polyisoprene was determined by the ^{13}C NMR spectrometry available. Epoxidation of polymer was carried out by peracid prepared *in situ* from hydrogen peroxide and a small amount of formic acid, and the epoxy content in the modified polymer was determined by ^1H NMR. The ^{13}C NMR spectra of the partly epoxidized *trans*-1,4-polyisoprene exhibited new signals both in the olefinic and aliphatic carbon regions, in addition to the signals due to the original *trans*-1,4-polyisoprene. Each signal, except for the methyl carbon signals, was interpreted in terms of the dyad or triad of *trans*-1,4 and epoxidized units, taking into consideration the results from the signal assignments made by off-resonance decoupling techniques and lanthanide shift reagent experiments. The monomer unit sequence distribution in partly epoxidized *trans*-1,4-polyisoprene determined by ^{13}C NMR agreed very closely with that calculated on the basis of the random distribution of *trans*-1,4 and epoxidized isoprene units. These results suggest that the site of the epoxy group formed is not affected by such groups previously formed in polyisoprene.

KEY WORDS Epoxidation / *trans*-1,4-Polyisoprene / ^{13}C NMR / Sequence Distribution / Olefinic Carbon / Off-Resonance Decoupling / Shift Reagent / Random /

Carbon-13 nuclear magnetic resonance spectroscopy has been intensively utilized in the study of the monomer sequence distribution of various polydienes.¹⁻⁹ Some reports have been published on the sequence distribution of 3,4 and 1,4 units or *cis*-1,4- and *trans*-1,4-isoprene units in polyisoprenes.¹⁰⁻¹⁵ As for chemically-modified polymers, however, few ^{13}C NMR investigations have been made both on the reaction site and the sequence distribution of modified and unmodified units.¹⁶⁻¹⁸ Gemmer and Golub¹⁹ reported the ^{13}C NMR spectra of partly epoxidized 1,4-polyisoprenes and 1,4-polybutadienes, and interpreted the prominent signals in terms of the dyad of *cis*-1,4 units and epoxidized units, though the signal assignments were not discussed in detail.

Previously, we studied the epoxidation of polybutadiene by organic peracid, and determined the monomer unit sequence distribution in the partly epoxidized *cis*-1,4-polybutadiene by proton-

decoupled ^{13}C NMR spectra.²⁰⁻²¹ It is of interest that the relative intensities of the carbon signals in the polymers of different epoxy content were almost identical with those calculated on the basis of the random distribution of *cis*-1,4 and epoxidized butadiene units. Our attention was then directed to the study of partly-epoxidized polyisoprene by ^{13}C NMR. The ^{13}C NMR spectrum of partly-epoxidized *cis*-1,4-polyisoprene exhibited a very complicated resonance pattern due to the overlapping of methylene and methyl carbon signals.^{19,22}

In this paper, we attempt to make an assignment of the ^{13}C NMR signals of partly-epoxidized *trans*-1,4-polyisoprene in terms of the triad of *trans*-1,4 and epoxidized units, in contrast to the work done by Gemmer *et al.* and further the sequence distribution of the units and the reaction site is discussed.

EXPERIMENTAL

Epoxidation

A natural *trans*-1,4-polyisoprene, *gutta percha*, consisting exclusively of the *trans*-1,4 structure,¹ was used in this study and was purified by repeated precipitation from a chloroform solution with methanol. Epoxidation was carried out *in situ* by peroxy formic acid as follows: a solution of *trans*-1,4-polyisoprene (3.41 g; 0.05 mol monomer unit) and 2,6-di-*t*-butyl-*p*-cresol (0.1 g) as a polymer stabilizer in 200 ml of benzene was heated to 35°C and mixed with 60 mmol of 30% aq hydrogen peroxide and a small amount of formic acid (15 mmol). The solution was stirred at the same temperature for 1 to 10 h. The epoxidized polymer was obtained by pouring the reaction mixture into methanol to precipitate the product.

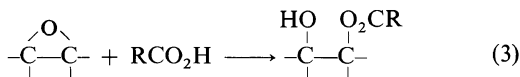
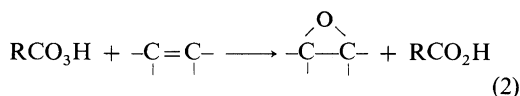
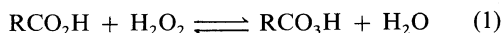
¹H and ¹³C NMR experiments

¹H NMR spectra were obtained at room temperature on ca. 5% solution of polymers in CDCl₃, using a JEOL C-60 HL spectrometer. Chemical shifts of the signals were measured in ppm relative to tetramethylsilane (TMS).

The ¹³C NMR spectra were obtained at 25.1 MHz, using a JEOL JNM-PS/PFT 100 spectrometer equipped with a Fourier transform accessory. The ¹³C NMR spectrum was measured at 50°C in CDCl₃ (approximately 8 w/v%), under the condition of a 13.0 μs (45°) pulse width, using TMS as the internal standard. The spectra were recorded as proton noise-decoupling with multiple scans at a pulse-repetition time of 3.0 s or as off-resonance decoupling at a pulse-repetition time of 1.0 s. The relative intensities of the signals in the ¹H NMR and ¹³C NMR spectra were determined by cutting out and then weighing each peak area in the Xerox copies of the spectra. When the cutting out of peak areas was not practicable, signal intensities were taken to be proportional to signal heights.

RESULTS AND DISCUSSION

It is known that the epoxidation of unsaturated bonds in a polydiene with organic peracid does not degrade the polymer²³ but is accompanied by a ring-opening reaction,²⁴⁻²⁷ (eq 1, 2, and 3),



We have already reported the epoxidation of polybutadiene under mild reaction conditions, such as low temperature and using a small amount of formic acid, enabling the reaction to be easily carried out with very few additional reactions.^{20,21} In the epoxidation of *trans*-1,4-polyisoprene, the same reaction conditions as mentioned above for polybutadiene were employed.

The ¹H NMR spectrum of the partly-epoxidized *trans*-1,4-polyisoprene indicates that the signals are assignable to the protons of the unmodified monomer unit and to the epoxidized unit produced in the reaction, and confirms that the ring-opening

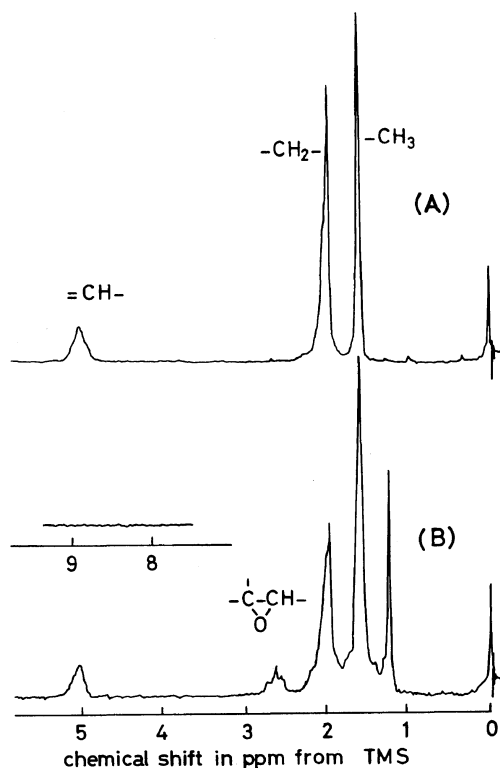


Figure 1. ¹H NMR spectra of (A) *trans*-1,4-polyisoprene and (B) partly epoxidized polymer; degree of epoxidation, 39%.

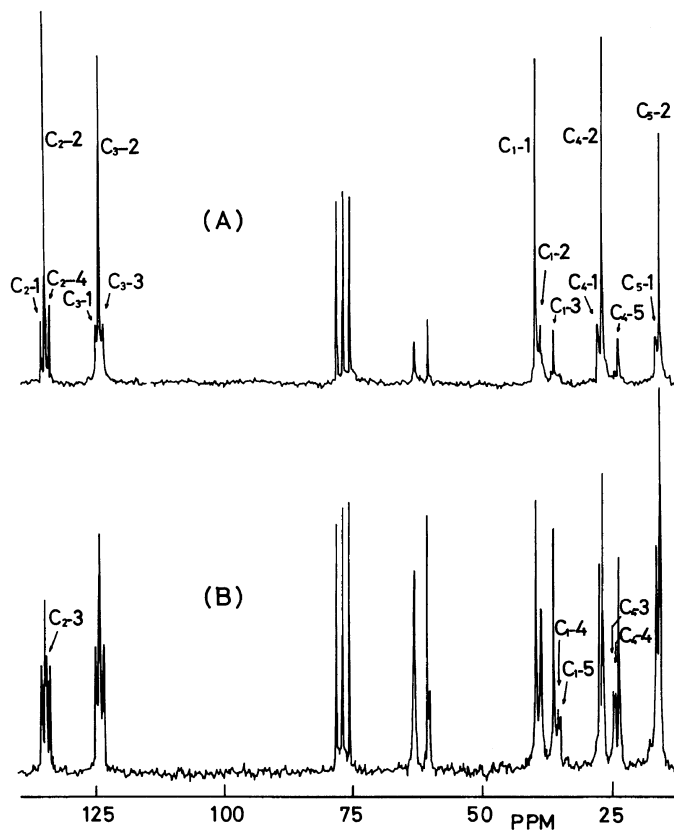


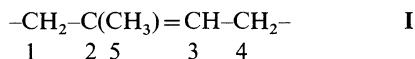
Figure 2. Proton-decoupled ^{13}C NMR spectra of partly-epoxidized *trans*-1,4-polyisoprene. Repetition time of 45° pulses is 3.0 s. Chemical shift scale in ppm from TMS. Degree of epoxidation (%): A, 17; B, 39. The signals are assigned in Tables I and II.

reaction is negligible since no signals appeared in the region of the formyloxy proton around 8 ppm. The signals at 5.08 and 2.68 ppm, assigned to the olefinic and epoxy methine protons, were used for calculating the epoxy content of the polymer by eq 4, (Figure 1),

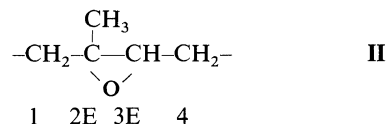
$$\text{Degree of epoxidation} = \frac{\text{Peak area at 2.68 ppm}}{\text{Peak area at 5.08 and 2.68 ppm}} \quad (4)$$

The ^{13}C NMR spectra of the partly-epoxidized *trans*-1,4-polyisoprenes containing various amounts of epoxidized units in the polymer are shown in Figures 2–4. For conveniently discussing the procedure for making assignment of signals, the signals were labeled as shown in the Figures. The triplet at *ca.* 77 ppm is due to CDCl_3 .

The five signals at 134.90 ($\text{C}_2\text{-2}$), 124.37 ($\text{C}_3\text{-2}$), 39.80 ($\text{C}_1\text{-1}$), 26.87 ($\text{C}_4\text{-2}$), and 16.08 ($\text{C}_5\text{-2}$) correspond to carbons of *trans*-1,4-polyisoprene, and were assigned to the C_2 , C_3 , C_1 , C_4 , and C_5 carbons of *trans*-1,4-polyisoprene in the order of increasing magnetic field.¹ The symbols for the carbon atoms are denoted as follows:



With the epoxidation of the reactant polymer, the 1,4-unit is converted to the structure **II**:



Unlike the simple ^{13}C NMR spectra of partly-

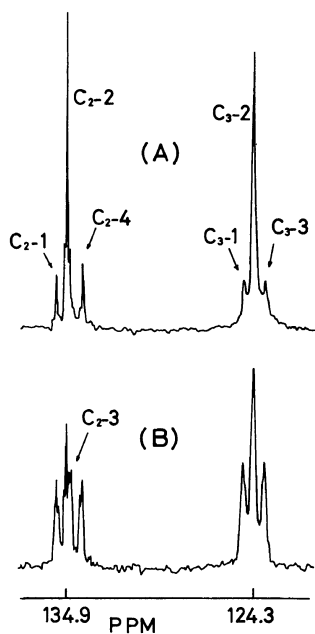


Figure 3. Carbon-13 NMR expanded spectra of the olefinic carbon regions of partly epoxidized *trans*-1,4-polyisoprenes. The samples used are the same as in Figure 2. Degree of epoxidation (%): A, 17; B, 39. The signals are assigned in Table I.

epoxidized 1,4-polybutadiene,²¹ more complicated signals could be observed in the ¹³C NMR spectra of partly-epoxidized *trans*-1,4-polyisoprene. The spectra exhibited many peaks of lesser intensity than those attributable to the unepoxidized isoprene units. Their intensities increase with an increase in the epoxy units in the polymer. This fact suggests that the peaks (C₂-1, C₂-3, C₂-4), (C₃-1, C₃-3), (C₁-2—C₁-5), (C₄-1, C₄-3—C₄-5), and C₅-1 arise from carbons of epoxidized isoprene units or from carbons of unepoxidized isoprene units affected by adjacent epoxidized units in the polymer.

Similar notations in ref 21 are used in this paper. The possible triad sequences are, T ⊕ T, E ⊕ T, T ⊕ E, E ⊕ E. T ⊕ T, E ⊕ T, T ⊕ E, and E ⊕ E, where T represents a *trans*-1,4-isoprene unit (I) and E represents an epoxidized isoprene unit (II). Thus T ⊕ T indicates an epoxidized isoprene unit adjacent to *trans*-1,4-isoprene units. Similarly T¹ ⊕ T represents a C₁ carbon in the T ⊕ T triad. Also, ¹⊕, ²⊕, ⊕³, ⊕⁴, ⁵⊕, ¹⊕, ²⊕, ⊕³, ⊕⁴ and ⁵⊕ represent the C₁, C₂, C₃, C₄, C₅ carbons

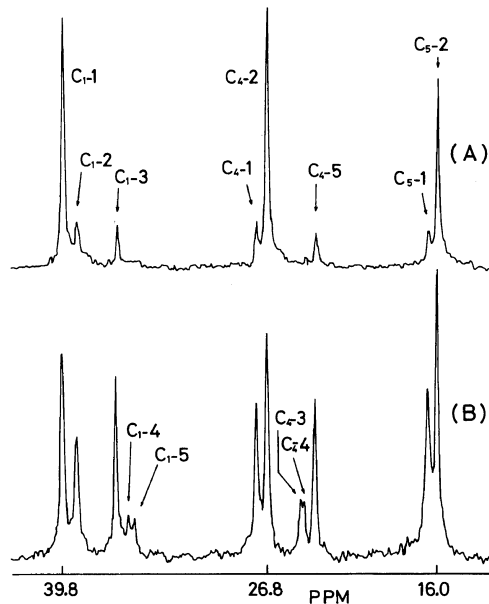


Figure 4. Carbon-13 NMR expanded spectra of the methylene and the methyl carbon regions of partly-epoxidized *trans*-1,4-polyisoprenes. The samples used are the same as in Figure 2. Degree of epoxidation (%): A, 17; B, 39. The signals are assigned in Table II.

in an unreacted *trans*-1,4-isoprene unit and in an epoxidized unit respectively. In referring to the relative position of the carbons in a unit, we use the numbers 1, 2, and 5 on the left shoulder and 3, 4 on the right shoulder of T or E.

In the present study, we assumed only the *trans* configuration for the epoxy group in the polymer, since Swern and his coworkers²⁸⁻³⁰ proved that the epoxidation of alkenes results in *syn* addition, and consequently, the stereochemistry of the alkenes is maintained in the product.

Off-resonance Decoupling

The assignment of the ¹³C NMR signals to quaternary, tertiary, and methyl carbons was confirmed by the off-resonance decoupling method. The ¹³C NMR spectrum in Figure 5 (A) shows the off-resonance decoupled signals of the epoxidized *trans*-1,4-polyisoprene of 48% epoxy content. Figure 5 (B) shows the proton-decoupled ¹³C NMR spectrum of the same polymer. The two upfield peaks C₅-1 and C₅-2 near 16 ppm can be readily assigned to the branching methyl carbons, since

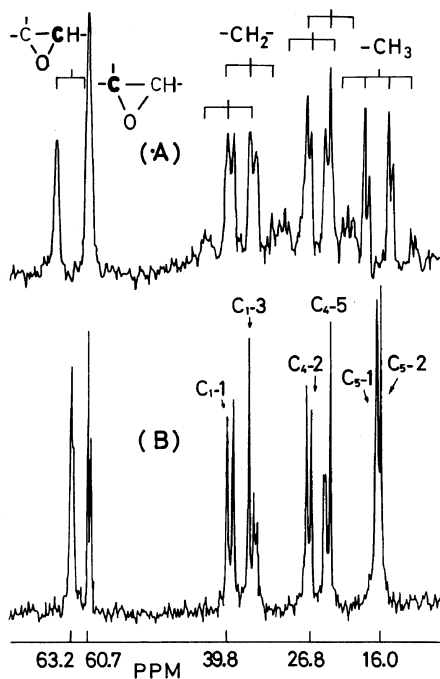


Figure 5. Carbon-13 NMR spectra of the aliphatic and the epoxy carbon regions of partly-epoxidized polyisoprene. Degree of epoxidation 48%. (A) off-resonance decoupling NMR spectrum; repetition time 1.0 s, 10,000 scans. (B) proton-decoupled NMR spectrum; repetition time, 3.0 s, 3,000 scans. Chemical shift scale in ppm from TMS.

these peaks split into quartets by off-resonance decoupling, indicating the presence of three directly-bonded protons. The signals at 60.65 and 60.26 ppm for which large proton couplings are absent, can be assigned to the epoxy ring carbon (C_{2E}) which has a methyl group, because this carbons remained singlet in off-resonance decoupling in the absence of a directly-bonded proton. The signal at 63.21 ppm (C_{3E}) however, split into doublets and one of these overlapped with the signal of C_{2E} . The intriguing order of the chemical shifts of C_{2E} and C_{3E} , which is opposite to that of the corresponding olefinic C_2 and C_3 , was reported by Gemmer and Golub.¹⁹

Lanthanide Shift Reagent Experiments

The remaining signals in the spectrum were assigned on the basis of the results of lanthanide shift reagent (LSR) experiments. The polymer in Figure 2 (A) contains small amounts of epoxidized units. Figures 6 and 7 indicate variations in the

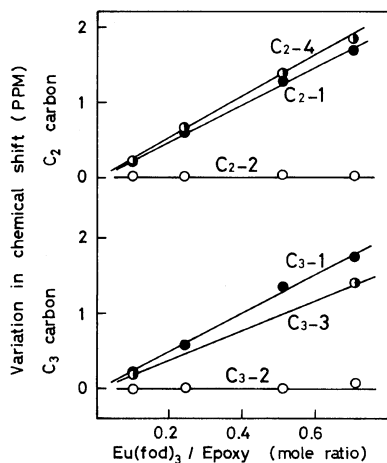


Figure 6. Variation in chemical shift of different olefinic carbons in partly-epoxidized *trans*-1,4-polyisoprene with increasing concentration of $\text{Eu}(\text{fod})_3$. Degree of epoxidation, 17%. The symbols are the same as in Figure 3.

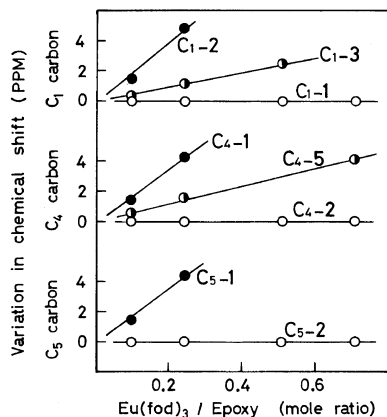


Figure 7. Variation in the chemical shift of different methylene and methyl carbons in partly-epoxidized *trans*-1,4-polyisoprene with increasing concentration of $\text{Eu}(\text{fod})_3$. Degree of epoxidation, 17%. Symbols are the same as in Figure 4.

carbon chemical shifts of the epoxidized polymer with the addition of tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) europium (III) [$\text{Eu}(\text{fod})_3$] to the NMR sample. The chemical shift was measured as a function of the added $\text{Eu}(\text{fod})_3$ concentration to determine how close the carbons are to the epoxy moieties;^{31,32} the steeper the slope, the closer the associated carbon to the epoxy moiety. These LSR experiments helped in the

Table I. Signal assignments of olefinic carbons

Signal	Chemical shift	
	ppm	
C₂ carbon		
C ₂ -1	135.48	T ² ⊕ E
C ₂ -2	134.90	T ² ⊕ T
C ₂ -3	134.78	E ² ⊕ E
C ₂ -4	134.04	E ² ⊕ T
C₃ carbon		
C ₃ -1	124.92	T ⊕ ³ E
C ₃ -2	124.30	T ⊕ ³ T, E ⊕ ³ E
C ₃ -3	123.68	E ⊕ ³ T

^a Symbols for the carbons are as follows: for T (*trans*-1,4

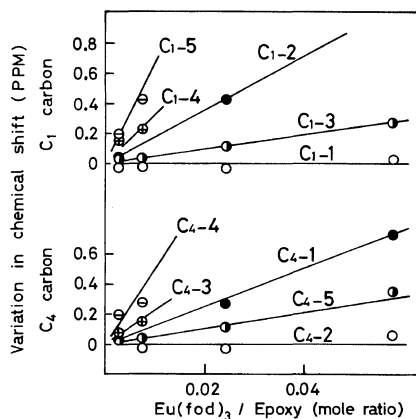
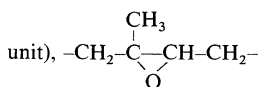
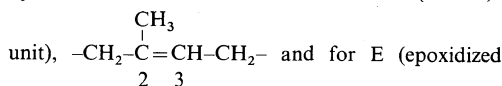


Figure 8. Variation in chemical shift of different methylene carbons in partly epoxidized *trans*-1,4-polyisoprene with increasing concentration of $\text{Eu}(\text{fod})_3$. Degree of epoxidation, 39%. The symbols are the same as in Figure 4.

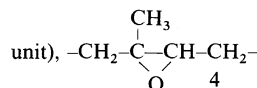
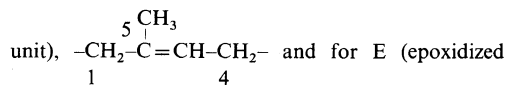
assignment of puzzling signals.

The signals of the olefinic carbons (C_2 and C_3) were assigned to one of the four T centered triad sequences of *trans*-1,4 and epoxidized units shown in Table I, based on the results derived from Figure 6. This assignment pattern for olefinic carbons was previously observed for partly epoxidized *cis*-1,4-

Table II. Signal assignment for methylene and methyl carbons

Signal	Chemical shift	
	ppm	
C₁ carbon		
C ₁ -1	39.80	T ¹ ⊕ T, T ¹ ⊕ E
C ₁ -2	38.87	T ¹ ⊕ T, E ¹ ⊕ E
C ₁ -3	36.38	E ¹ ⊕ T, E ¹ ⊕ E
C ₁ -4	35.65	T ¹ ⊕ E
C ₁ -5	35.30	E ¹ ⊕ T
C₄ carbon		
C ₄ -1	27.53	T ⊕ ⁴ T, E ⊕ ⁴ E
C ₄ -2	26.83	T ⊕ ⁴ T, E ⊕ ⁴ T
C ₄ -3	24.70	E ⊕ ⁴ T
C ₄ -4	24.58	T ⊕ ⁴ E
C ₄ -5	23.80	T ⊕ ⁴ E, E ⊕ ⁴ E
C₅ carbon		
C ₅ -1	16.70	⁵ ⊕
C ₅ -2	16.08	⁵ ⊕

^a Symbols for the carbons are as follows: for T (*trans*-1,4



polybutadiene.²¹ Since the chemical shift variations in C_2 -1 and C_2 -4 are not very different (Figure 6), no accurate assignment can be expected presently. An attempt to separate the signal assignable to E ⊕³ E from the C_3 -2 signal consisting mainly of T ⊕³ T proved unsuccessful even in LSR experiments for reasons not clear to us, though this assignment is considered to be pertinent.

In the less epoxidized polymer, the T ⊕ T triad was remarkably predominant next to the T ⊕ T triad, and C_1 -2, C_4 -1, C_5 -1 signals could be assigned to the carbons in the epoxidized unit, ¹ ⊕, ⊕⁴ and ⁵ ⊕, respectively, using the data in Figure 7. On the other hand, C_1 -3 and C_4 -5 signals could be assigned to the carbons in a *trans*-1,4 unit adjacent to an epoxidized unit, E¹ ⊕ and ⊕⁴ E, respectively. The intensities of the C_1 -2 and C_4 -5 signals are similar in the less epoxidized polymer, and this is also the same for the C_1 -3 and C_4 -1 signals. These correlations are considered strong evidence in

Table III. Signal intensities for olefinic carbons

Signal ^a	Intensities/%					
	Observed by C-13 NMR			Calculated from random assumption ^b		
	Sample a	Sample b	Sample c	Sample a	Sample b	Sample c
C₂ carbon						
C ₂ -1	13.5	21.4	24.2	14.1	20.6	23.8
C ₂ -2	70.1	58.5	51.9	71.8	58.8	52.4
C ₂ -3						
C ₂ -4	16.4	20.1	23.9	14.1	20.6	23.8
C₃ carbon						
C ₃ -1	14.6	20.6	23.7	14.1	20.6	23.8
C ₃ -2	70.5	57.2	51.9	71.8	58.8	52.4
C ₃ -3	14.9	22.2	24.4	14.1	20.6	23.8

^a The symbols are the same as in Figure 3. Signals are assigned in Table I.

^b The degree of epoxidation was determined by ¹H NMR spectrum. Degree of epoxidation (%): a, 17; b, 29; c, 39.

support of these assignments.

Variation in the chemical shifts of the epoxidized polymer with 39% epoxy content is indicated in Figure 8. The intensity of the pair signals C₁-4, C₁-5 and C₄-3, C₄-4, whose intensity ratios are similar and independent of the epoxy content of the polymer, increases with an increase in epoxy content. This suggests that these signals are related to the carbons in the epoxidized unit; these carbons are the C₁ and C₄ carbons of either the E (E) T or T (E) E triads.²¹ The assignment of these pair signals was confirmed by LSR experiments, although there was no remarkable difference in chemical shift variation.

There appeared five signals in each of the C₁ and C₄ methylene carbon regions in the spectrum and no relationship was found in their intensities between the two groups of the signals. The assignment of the methylene carbons in terms of the dyad or triad of *trans*-1,4 units and epoxidized units is summarized in Table II, which includes the assignment of the C₅ carbons.

A more detailed observation of the ¹³C NMR spectra showed that signals in the C₂ carbon region split into some weak intensity peaks. These splits are thought to be caused by certain long range sequences and/or steric effects, and are remarkable when the polymer contains a great number of

epoxidized units. But, the methyl carbon signals observed were insensitive to sequence distribution, and could be attributed only to the mono-ads of epoxidized or *trans*-1,4 units. It is not clear as yet as to why the neighbouring carbons C₂ and C₅ depend on the subsequent unit in a different manner. In some cases, especially concerning to the C₅ and C_{2E} signals, each signal splits into a number of weak peaks by the addition of Eu(fod)₃.

Monomer Sequence Distribution

Each monomer unit in these epoxidized polyisoprenes consists of five carbon atoms which give rise to different types of monomer sequences. This fact enables us to understand the monomer-unit sequence distribution of modified polymers if reliable quantitative analysis of ¹³C NMR spectra is possible. Significant uncertainty in the quantitative analysis of proton-decoupled ¹³C NMR spectra arises from different Nuclear Overhauser Enhancements (NOE). In the present study, however, this problem is not likely to be serious, because methyl (C₅), methylene (C₁, C₄), and olefinic carbons (C₂, C₃) are located in the same environment. Furthermore, we tried to make reliable quantitative analysis by operating the NMR apparatus at a rather long pulse-repetition time of 3.0 s.

Table IV. Signal intensities of methylene and methyl carbons

Signal ^a	Intensities/%					
	Observed by C-13 NMR			Calculated from random assumption ^b		
	Sample a	Sample b	Sample c	Sample a	Sample b	Sample c
C₁ carbon						
C ₁ -1	67.8	51.2	35.7	68.9	50.4	37.2
C ₁ -2	14.0	18.5	21.6	12.2	17.1	20.4
C ₁ -3	13.2	22.2	27.2	14.1	20.6	23.8
C ₁ -4	2.5	4.0	8.2	2.4	6.0	9.3
C ₁ -5	2.6	4.1	7.3	2.4	6.0	9.3
C₄ carbon						
C ₄ -1	14.1	20.8	21.6	12.2	17.1	20.4
C ₄ -2	70.9	49.4	35.5	68.9	50.4	37.2
C ₄ -3	1.9	5.2	9.4	2.4	6.0	9.3
C ₄ -4	2.0	5.2	9.1	2.4	6.0	9.3
C ₄ -5	11.1	19.4	24.4	14.1	20.6	23.8
C₅ carbon						
C ₅ -1	18.3	29.5	37.5	17.0	29.0	39.0
C ₅ -2	81.7	70.5	62.5	83.0	71.0	61.0

^a The symbols are the same as in Figure 4. Signals are assigned in Table II.

^b The degree of epoxidation was determined by ¹H NMR spectrum. Degree of epoxidation (%): a, 17; b, 29; c, 39.

The fractions of the triad sequences determined from the relative intensities in each carbon region are summarized in Tables III and IV, along with the theoretical sequences calculated on the assumption of random distribution in *trans*-1,4 and epoxidized units. Remarkable agreement between experimental and theoretical values supports not only the validity of the assignments but also that differences in the NOE factor and the effect of spin-lattice relaxation time of carbons may be overlooked.

These assumptions can be justified in various ways. The populations of E ⊕ T are equal to those of T ⊕ E: the fractions of E² ⊕ T and E ⊕ T³ are equal to those of T² ⊕ E and T ⊕ T³E, respectively.

A random distribution of *trans*-1,4 and epoxidized units found by spectroscopical work explains why the epoxy groups introduced into polymers do not control the reaction site where a new epoxy group can be formed.

We previously observed the same situation in the epoxidation of polybutadienes.²¹ It is interesting that methyl groups which account for the structural

difference between polybutadiene and polyisoprene do not affect the unit sequence distribution of the epoxidized polymers at all.

In this paper, we do not refer to those signals assigned to the epoxy carbons and the multiplicity in the C₂ carbon in detail. However, it may be expected that further study on the ¹³C NMR of epoxidized polyisoprenes will make clearer both the epoxy configuration and long-range sequences.

The results of this investigation show that carbon-13 NMR spectroscopy affords an extremely sensitive means for studying the reaction site and the monomer-unit sequence distribution of modified polymers.

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