# Epoxidation of Natural Rubber Studied by NMR Spectroscopy

J. H. BRADBURY, and M. C. S. PERERA,* *Chemistry Department, Australian National University, P.O. Box 4, Canberra, A.C.T. 2601, Australia*

## Synopsis

Epoxidation of natural rubber with peroxyacids in homogeneous solution ($CHCl_3$, benzene) and in latex occurs without main chain fission or isomerization of the *cis* configuration. There are two possible modes of addition of oxygen to the double bond, which gives rise to diastereoisomers in dyad structures, as shown by the occurrence of splitting of ^{13}C NMR resonances in 100% epoxidized rubber. In partially epoxidized rubber the ^{13}C NMR resonances of the methylene carbon atoms have been fully assigned using pulse sequences and lanthanide shift reagents, in terms of triad sequences. Resonances in the olefinic region of the spectrum require assignment in terms of pentad sequences whereas those from the oxirane region are much more closely spaced and are assigned using triads. Intensity measurements on the methylene carbon NMR resonances show that the epoxidation reaction is a random process in both homogeneous solution and in latex particles.

## INTRODUCTION

It is perhaps a tribute to the excellent intrinsic properties of natural rubber that relatively little commercial success has been achieved with chemically modified natural rubber. Nevertheless, the increasing cost of polymers based on the petrochemical industry is changing the economics of modified rubber, in those cases in which modifications lead to exceptional properties.[1] One such case is that of epoxidized natural rubber.[2]

Epoxidation of natural rubber and other usaturated elastomers is well known,[3-5] and the ^{13}C NMR spectra of partially epoxidized 1,4-polyisoprene and 1,4-polybutadiene have been studied.[6] Prominent signals were interpreted in terms of dyads of the *cis*-1,4-unsaturated unit and epoxidized units, but the signal assignments were not discussed in detail. The monomer sequence distribution in partly epoxidized *cis*-1,4-polybutadiene[7] and partly epoxidized *trans*-1,4-polyisoprene[8] was discussed in terms of triads and the relative intensities of the ^{13}C NMR resonances in the polymers of different epoxy content agreed with those calculated on the basis of a random distribution of epoxidized *cis*-1,4-polybutadiene and epoxidized *trans*-1,4-polyisoprene.

Tutorskii et al.[9] studied the kinetics of the reaction of polyisoprene with perbenzoic acid in benzene, chloroform, and carbon tetrachloride. The rate constant decreased with conversion, and this was explained by the inductive effect of the epoxide groups on the adjacent double bonds which would tend to produce epoxidized residues at every alternate position. However, the ^{13}C NMR results[7,8] indicate a random distribution.

* A permanent address: Rubber Research Institute of Sri Lanka, Ratmalana, Sri Lanka.

The ^{13}C NMR resonances of partly epoxidized cis-1,4-polyisoprene are more crowded together than occurred with cis-1,4-polybutadiene and trans-1,4-polyisoprene. This has limited to some degree the assignment of the ^{13}C NMR signals of partially epoxidized cis-1,4-polyisoprene given in this paper, in terms of triads of cis-1,4-unsaturated and epoxidized units. Epoxidation studies have been made both in homogeneous solution and also using latex.

## EXPERIMENTAL

### Materials

Solid natural rubber (SLR 5 grade) and centrifuged natural rubber latex (60% dry rubber content, ammonia stabilized) were obtained from Sri Lanka. Solvents and hydrogen peroxide (27.5% w/w) were analytical reagents and m-chloroperoxybenzoic acid was a technical grade obtained from Aldrich Chemical Co. Spectral grade deuterated chloroform and tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)europium(III) Eu(fod)$_3$) were used in NMR work.

### Methods

**NMR Spectroscopy.** ^{1}H NMR spectra were obtained at 270 MHz and proton decoupled ^{13}C NMR spectra were obtained at 67.89 MHz using a Bruker HX-270 spectrometer with an Oxford Instrument Co. magnet. For ^{13}C NMR spectra free induction decays were accumulated in 16 K data points, spectral width 15000 Hz, 13 ms (45°) pulse width, and 3.0 s repetition time. Spectra were determined at 298 K in CDCl$_3$ (5% w/v) with TMS as an internal standard. The solubility of the product decreased progressively with increase in epoxy content, but well-resolved ^{13}C NMR spectra were previously obtained from 60% epoxidized natural rubber, although the product swelled but was not soluble in CDCl$_3$.[10] Spectral intensities were measured by cutting out and weighing each peak area and in the case of very sharp peaks the heights of resonances were used.

Spin lattice relaxation times ($T_1$) were measured using a standard 180°–$\tau$–90° pulse sequence,[11] with $\tau \geqslant 3T_1$. $T_1$ values were determined by the method of Gerhards and Dietrich.[12]

The modified[13] INEPT (insensitive nuclei enhancement by polarization transfer) pulse sequence of Morris and Freeman[14] was used to separate methyl, methylene, methine, and quaternary carbon atoms. In an INEPT spectrum resonances from methyl and methine carbons remain in phase, those from methylene carbons are inverted and those from quaternary carbons disappear (see Fig. 6). The spectra were simplified further by addition of the lanthanide shift reagent Eu(fod)$_3$.[15]

*Determinations of viscosity and gel content.* The intrinsic viscosity (dL g$^{-1}$) was measured using a suspended-level Ubbelohde dilution viscometer at 25° in toluene.[16] Gel content was measured in benzene using a standard procedure.[17]

## Preparation of Epoxidized Rubber

**Solution Method I.** Solid natural rubber dissolved in chloroform (1.5% w/v) was stirred at 20°C for 1 h with $m$-chloroperoxybenzoic acid, using the stoichiometric amount to give a desired degree of epoxidation of double bonds. The epoxidized polymer was precipitated by pouring the reaction mixture into methanol. It was filtered, broken into small pieces, washed thoroughly with $H_2O$, and dried at 34°C.

**Solution Method II.** A 1.5% w/v solution of solid natural rubber in benzene (225 mL) was stirred at 35–40°C for 24 h with 0.7 mL of hydrogen peroxide and 0.07 mL of 98% formic acid. Samples were withdrawn at regular intervals and coagulated with methanol. The product was washed and dried as above.

**Latex Method.** Epoxidation was carried out for 18 h at 20°C with performic acid prepared *in situ* by adding 7 mL of hydrogen peroxide and 3 mL of formic acid to 5 mL of latex diluted with 10 mL of water and stabilized with 1 mL of surfactant. The product was precipitated with cold methanol, filtered, washed thoroughly with water, and dried at 34°C.

## RESULTS AND DISCUSSION

Previous work[18] has shown that epoxidation of unsaturated bonds in a polydiene with organic peracids does not cause main chain fission. This was confirmed by viscosity measurements in toluene of natural rubber and of 17, 30, and 57% epoxidized natural rubber (solution method) which gave values of $[\eta]$ of 4.44, 3.95, 4.66, and 4.23 dL g$^{-1}$, respectively.

A ring opening reaction is possible in acid solution which produces a formyl ester and an alcohol group.[19,20] The amount of acid was carefully controlled in our experiments and the $^1$H NMR spectrum in Figure 1 shows
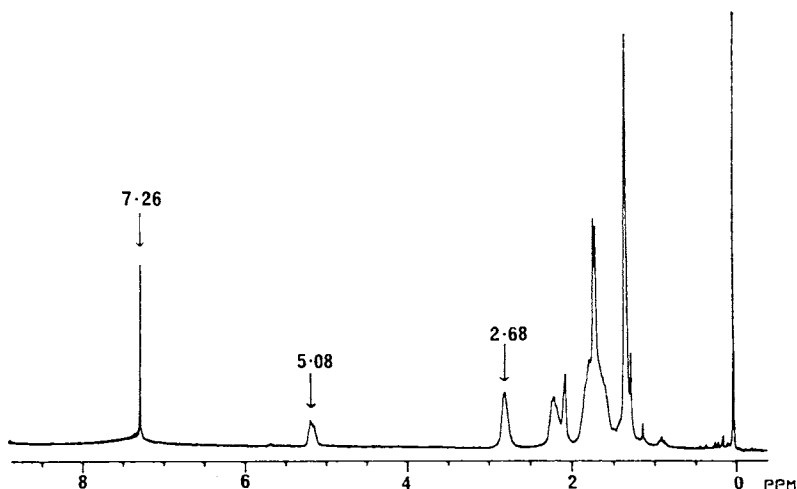


Fig. 1.  $^1$H NMR spectrum at 270 MHz in CDCl$_3$ of 65% epoxidized natural rubber. Assignments of peaks are δ 5.08, — C= C — ; δ 2.68, — C —C —;δ 1–2.5, —CH$_2$ and —CH$_3$; δ 7.26, CHCl$_3$.

no resonances at δ 8 due to the formate ester group, consistent with the absence of any ring opening reaction. However, the 30% epoxidized rubber in the latex gave a gel content of 74%, whereas the rubbers epoxidized by the solution methods (see above) were all soluble. We therefore conclude that the rubber epoxidized by the latex method is crosslinked probably by ring opening and reaction with nonrubber compounds present in the latex. This may occur by a mechanism similar to that proposed in the storage hardening of rubber.[21]

The epoxy content of epoxidized rubber was determined from the ratio of the area of the peak at δ 2.68 divided by the sum of the areas of the peaks at δ 2.68 and δ 5.08 (see Fig. 1).[22-24]

The spectrum of natural rubber shown in Figure 2 was previously assigned.[10,25] By comparison that of epoxidized rubber is clearly much more complicated. Its assignment is based on a consideration of the triad sequences of epoxy isoprene units (E) and unepoxidized isoprene units (C) shown in Figure 3. The number one carbon atom (see Fig. 2) of the middle unit in the CEC triad is represented as $C^1EC$. The rest of the carbon atoms of the middle unit are denoted respectively as $C^2EC$, $CE^3C$, $CE^4C$, and $C^5EC$, depending on the position of the particular carbon atom with respect to the double bond as shown in Figure 2. Since natural rubber is at least 99% in the *cis* form[26] and the stereochemistry of alkenes is preserved during epoxidation,[27] it is only necessary to consider the *cis* configuration of the epoxy group.

## Fully Epoxidized Natural Rubber

The assignment of the $^{13}C$ NMR spectrum of 100% epoxidized natural rubber shown in Figure 4 has been aided by use of the INEPT pulse se-
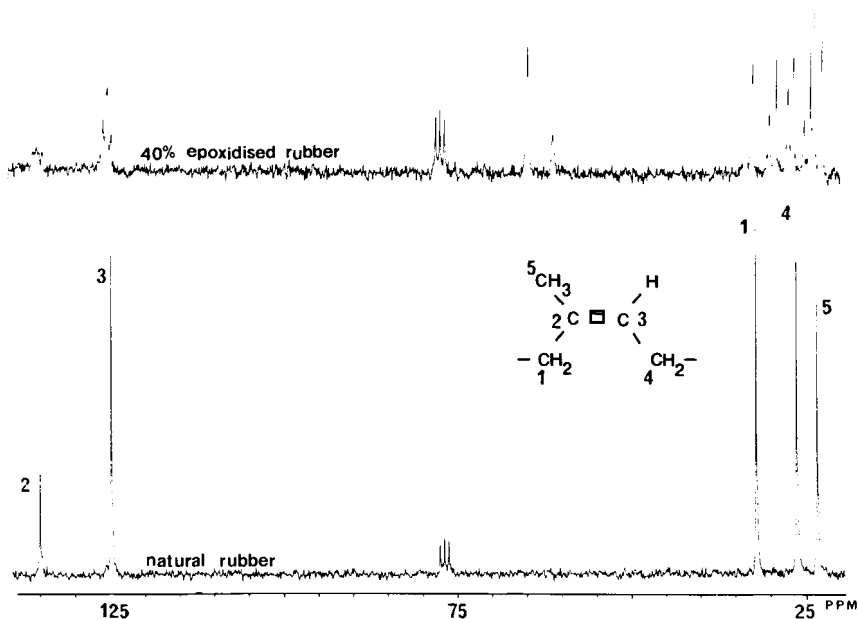


Fig. 2.  $^{13}C$ NMR spectra at 67.89 MHz of natural rubber and of 40% epoxidized natural rubber in CDCl₃. Solvent triplet at δ 77.
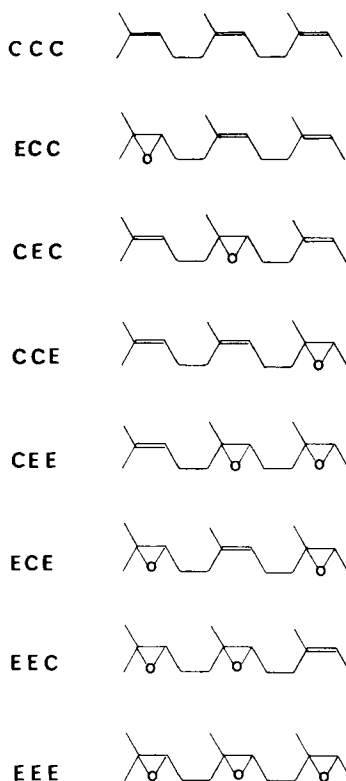
Fig. 3.   All triad sequences of epoxy isoprene units (E) and of unepoxidized isoprene units (C) in partly epoxidized natural rubber.

quence. This differentiates between the methine carbon resonances ($\delta$ 64.5, $\delta$ 64.6), and the quaternary carbon resonances at $\delta$ 60.5 and $\delta$ 61.3, the methylene peaks at $\delta$ 29.73, $\delta$ 29.76, and also at $\delta$ 24.7 and the methyl carbon resonance at $\delta$ 22.3. The two methylene resonances are distinguished
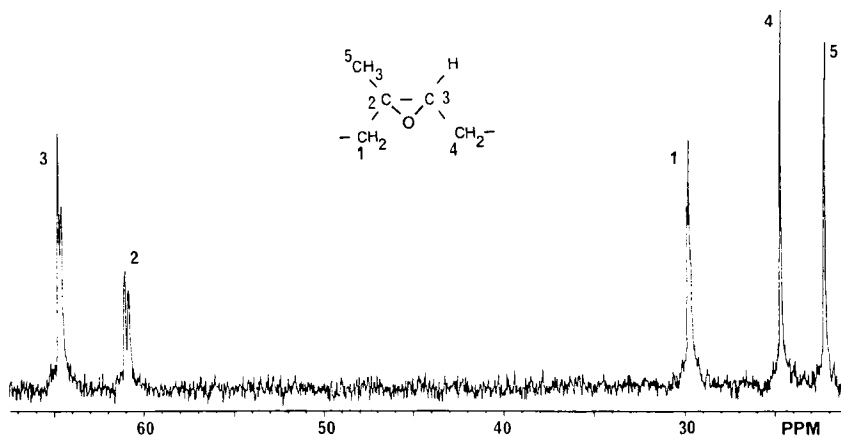


Fig. 4.   $^{13}$C NMR spectrum at 67.89 MHz of 100% epoxidized natural rubber swollen in CDCl$_3$.

by comparison with those reported for partially epoxidized polybutadiene[7] (see also Fig. 2). The splitting of the peaks arises because of the two possible modes of attachment of the epoxy group to the double bond, which gives rise to stereoisomers. Following Schilling et al.[28] it is necessary to consider the stereochemistry of two adjacent epoxidized isoprene units as shown in Figure 5. Structures a and b represent enantiomers and so do structures c
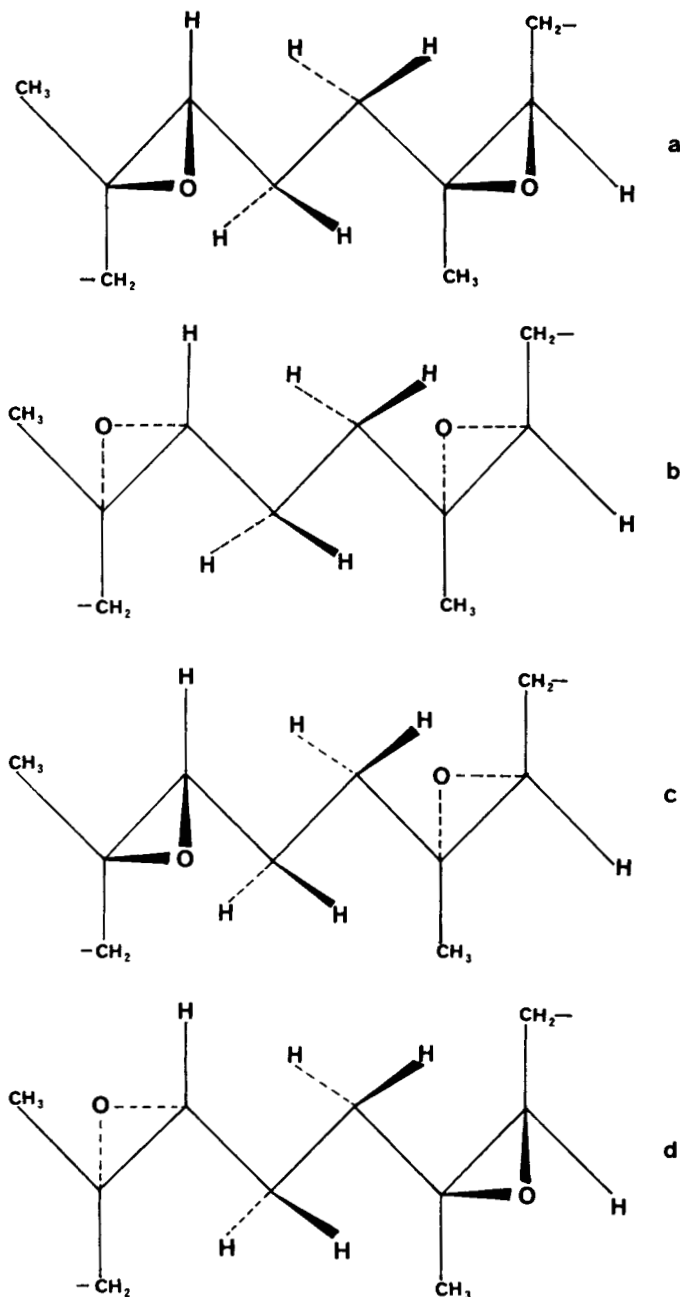


Fig. 5.   Four isomers of two adjacent oxirane units.

and d.[28] Such enantiomers a and b or c and d cannot be normally distinguished by NMR spectroscopy, but since each pair comprise diastereoisomers it will give rise to separate resonances. The splitting of the resonances of carbons 2 and 3 due to the two possible orientations of the adjacent oxirane ring is greater than that of the resonance from carbon 1 or that of resonances from carbons 4 and 5 which show no splitting.

## Partially Epoxidized Natural Rubber

**Methyl and Methylene Regions of the Spectrum.** The spectrum in Figure 6 shows that the two upfield peaks $C_5$-1 and $C_5$-2 (Fig. 7) are due to methyl carbon atoms and the remainder of the adjacent downfield resonances are due to methylene carbons. Intensities of the resonances $C_5$-1, $C_1$-3, $C_1$-4, $C_4$-3, and $C_4$-4 decrease as the level of epoxidation increases; hence they arise from $C_5$, $C_1$, and $C_4$ atoms that are adjacent to olefinic carbon atoms on both sides and their assignments are given in Table I. Intensities of resonances $C_5$-2, $C_1$-5, and $C_4$-5 increase from zero with increased level of epoxidation hence they must arise from $C_5$, $C_1$, and $C_4$ atoms that have epoxidized groups on both sides (see Table I). Intensities of the remaining
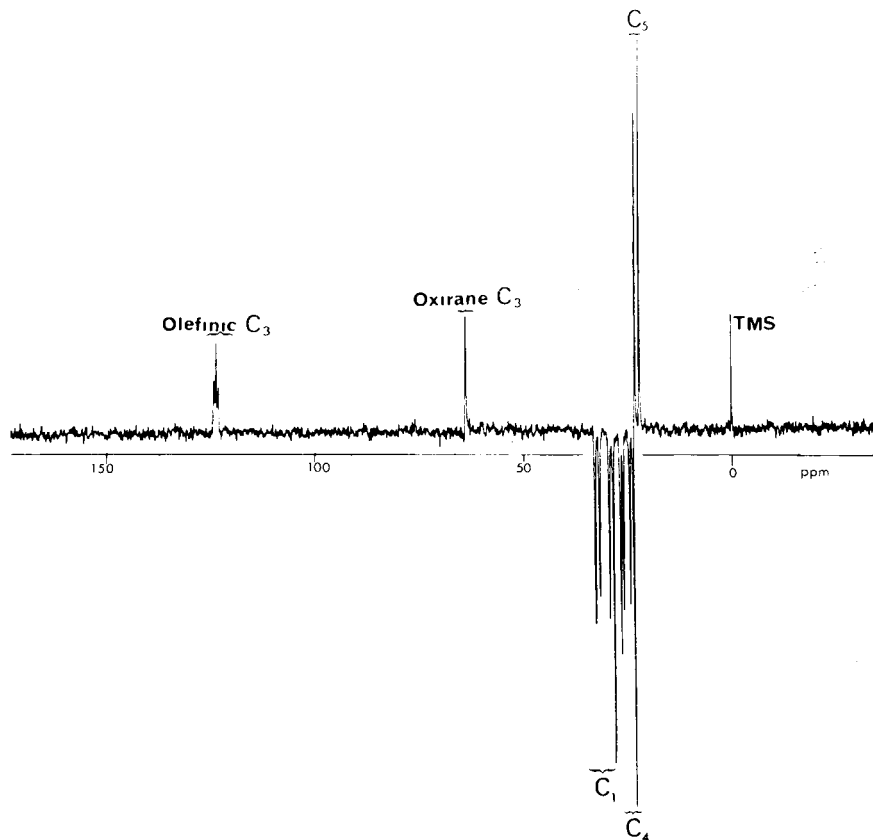


Fig. 6. ^{13}C NMR spectrum at 67.89 MHz using INEPT pulse sequence of 55% epoxidized natural rubber, showing methyl ($C_5$) and methine ($C_3$) peaks in phase, methylene peaks ($C_1$, $C_4$) inverted. The quaternary carbon ($C_2$) resonances (compare Figs. 2 and 4) have disappeared.
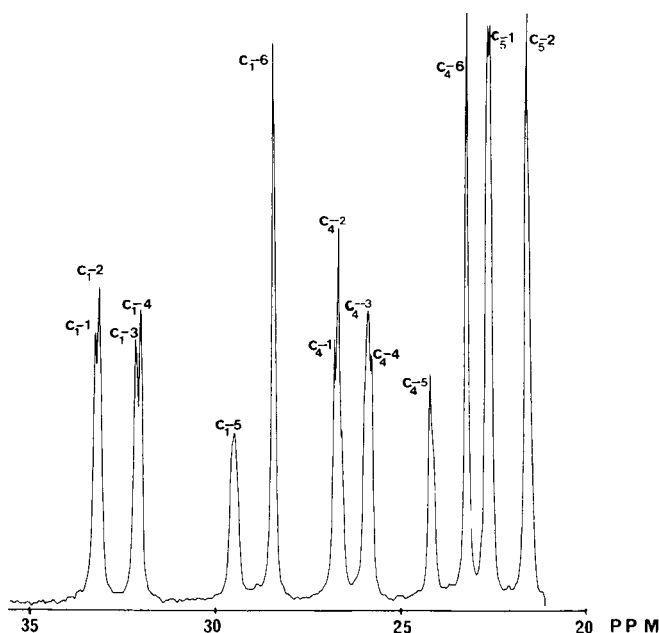
Fig. 7. Expansion of the methyl and methylene region of the $^{13}$C NMR spectrum of 40% epoxidized natural rubber.

six peaks ($C_1$-1, $C_1$-2), $C_1$-6, ($C_4$-1, $C_4$-2) and $C_4$-6 increase from zero and then decrease back to zero at 100% epoxidation. Hence they must arise from methylene carbon atoms that are not present at either 0% or 100% epoxidation.

Lanthanide shift reagent experiments were used for further analysis. Chemical shifts were measured as a function of the concentration of Eu(fod)$_3$ and results are given in Figure 8. In general, the steeper the slope of the lines, the closer is the associated carbon atom to the epoxy moiety which

TABLE I
Resonance Assignments for Methyl and Methylene Carbons (see Fig. 7)

| Resonance (see Fig. 5) | Chemical shift (ppm) | Assignments |
|---|---|---|
| $C_1$-1 | 33.31 | C$^1$EC[a] |
| $C_1$-2 | 33.21 | C$^1$EE |
| $C_1$-3 | 32.24 | C$^1$CC[a] |
| $C_1$-4 | 32.11 | C$^1$CE |
| $C_1$-5 | 29.73 | E$^1$EC,E$^1$EE |
| $C_1$-6 | 28.78 | E$^1$CC,E$^1$CE |
| $C_4$-1 | 27.15 | CE$^4$C[a] |
| $C_4$-2 | 27.07 | EE$^4$C |
| $C_4$-3 | 26.43 | CC$^4$C[a] |
| $C_4$-4 | 26.36 | EC$^4$C |
| $C_4$-5 | 24.76 | EE$^4$E,CE$^4$E |
| $C_4$-6 | 23.89 | EC$^4$E,CC$^4$E |
| $C_5$-1 | 23.43 | 5$_C$[a] |
| $C_5$-2 | 22.34 | 5$_E$[a] |

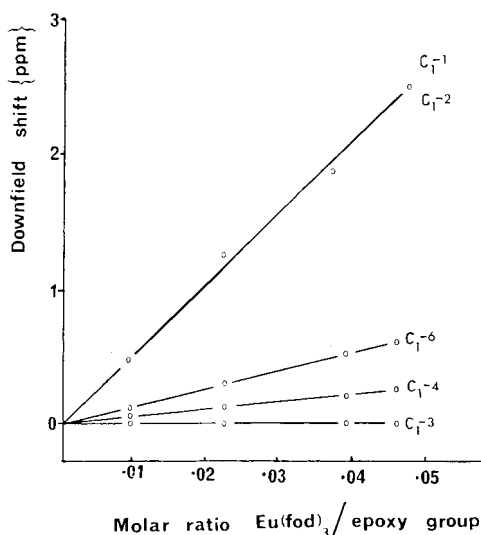[a] Assignments by Gemmer and Golub.[6]

Fig. 8. Downfield shifts of resonances from $C_1$ atoms (see Fig. 7) on addition of lanthanide shift reagent, Eu(fod)$_3$.

binds the lanthanide shift reagent, Thus, $C_1$-3 does not shift on addition of lanthanide; hence it does not have an epoxy group and is assigned to $C^1CC$, in confirmation of the assignment of Gemmer and Golub.[6] Similarly, the assignment of $C_1$-4 above to $C^1CE$ is in agreement with its small observed lanthanide shift. $C_1$-5 was also assigned above and its breadth (Fig. 7) suggests incipient splitting into two resonances thus accounting for two triads (Table I). However, it was not possible to follow its movement on addition of lanthanide because of its relatively low intensity. The distinction between the resonances yet to be assigned, viz., ($C_1$-1, $C_1$-2) and $C_1$-6 is possible, since
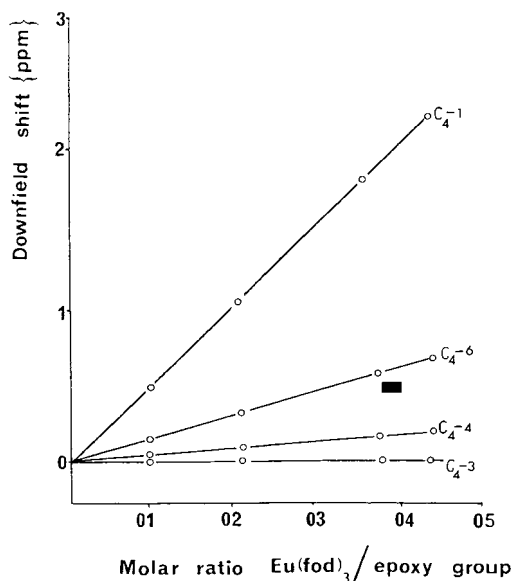


Fig. 9. Downfield shifts of resonances of the $C_4$ atoms (see Fig. 7) on addition of Eu(fod)$_3$.

the latter shifted less (Fig. 8) than the former. This shows that $C_1$-6 arises from a $C_1$ atom in which the epoxide is further away than in the case of the $C_1$-1 and $C_1$-2 resonances. This leads to the assignments in Table I for these resonances, although the assignments of $C_1$-1 and $C_1$-2 may need to be reversed. $C_1$-6, like $C_1$-5, is assigned to two carbon atoms, and these resonances may be expected to split at higher field strength.

The assignments of the $C_4$ peaks may be completed by the lanthanide shift data shown in Figure 9. The $C_4$-3 and $C_4$-4 resonances show zero shift and a small shift respectively and the assignments made above are confirmed. As with the $C_1$ resonances above, the distinction between the ($C_4$-1, $C_4$-2) and $C_4$-6 resonances is possible from shifts in Figure 9, but there is a possibility that the assignments of $C_4$-1 and $C_4$-2 may need to be reversed. The lanthanide shifts of resonances $C_5$-1 and $C_5$-2 (not shown) were also followed and these confirmed the assignments given in Table I.
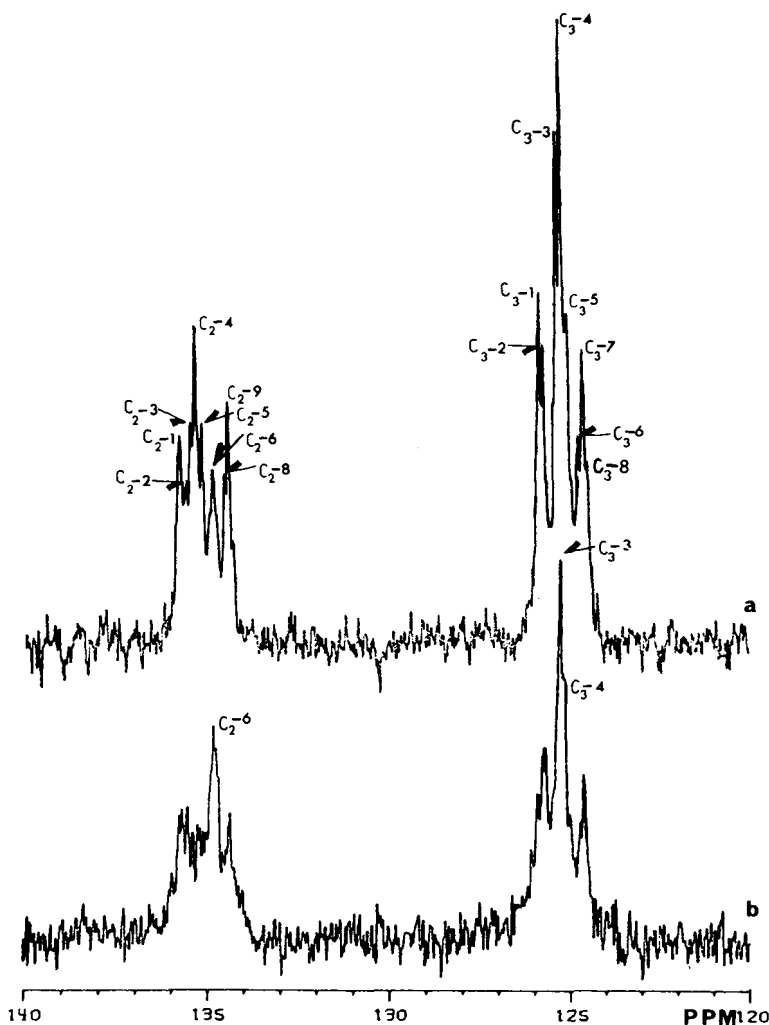


Fig. 10. Expansion of the olefinic region (see Fig. 2) of (a) 40% and (b) 64% epoxidized natural rubber.

*Olefinic Region of the Spectrum.* This region shown in Figure 2, when expanded contains eight peaks in the $C_2$ region and eight peaks in the $C_3$ region (Fig. 10). This number of peaks greatly exceeds the four peaks each for $C_2$ and $C_3$ that would be expected from a consideration of the various possible triad arrangements CCC, ECC, CCE, and ECE. As a first suggestion further splitting may be due (as in the case of 100% epoxidized rubber, see above) to two possible stereochemical arrangements of the epoxide group. However, considering ECC, the two possible isomers of EC [as shown for EE in Fig. 5(a) and 5(b)] can be readily seen to be enantiomers and would not give rise to two NMR resonances. Similarly, CCE would only produce one NMR resonance. In the triad ECE the two epoxide groups will give rise to diastereoisomers, which may give rise to different resonances. It would therefore be expected that there would be one resonance for $C_2$ and one for $C_3$ from each of CCC, ECC, and CCE and two resonances from ECE, a total of five resonances.

The additional peaks observed in the $C_2$ and $C_3$ region must be due to these carbon atoms (involved in a double bond) being sensitive to the nature of the groups attached (whether epoxy or double bond) along more than three carbon atoms of the chain. Thus pentad sequences are needed for the interpretation of resonances from $C_2$ and $C_3$ atoms, whereas only triad sequences are needed to interpret resonances from methylene carbon atoms (Table I), as was also observed by Schilling et al.[28] in partially epoxidized 1,4-polybutadiene.

Assignment of the $C_2$ and $C_3$ resonances is aided by work on partly epoxidized squalene (CCC) where assignments of ^{13}C NMR resonances were based on the observation that $T_1$ values are longer for nuclei near the end of the molecule.[29] A study of E[2]C[3]C and C[2]C[3]E showed that on replacement of C by E the resonance of the double bonded carbon atom nearest to the substituted epoxide group moved about 0.5 ppm upfield and the resonance of the adjacent (more remote) double bonded carbon atom moved about 0.5 ppm downfield.[29] The assignment given in Table II is also based on use of lanthanide shift reagents, (see Fig. 11). Resonance $C_3$-4 does not shift on addition of Eu(fod)$_3$ and hence is assigned to CCC[3]CC and $C_3$-3 which shifts by the greatest amount to EEC[3]EE. These peaks are adjacent as also found in 1,4-*trans*-polybutadiene[28] and the fact that the $C_3$-3 resonance increases

TABLE II
Resonance Assignments for Olefinic Region $C_3$ Carbon Atoms (see Fig. 10)

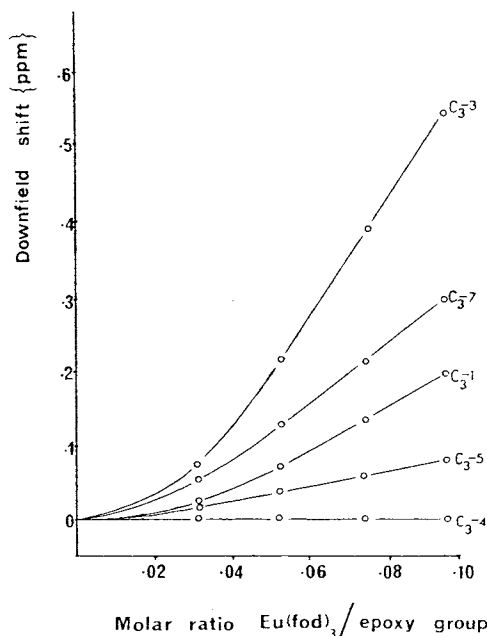| Resonance | Chemical shift (ppm) | Assignment |
|---|---|---|
| $C_3$-1 | 125.71 | CEC[3]CC |
| $C_3$-2 | 125.61 | CEC[3]CE, EEC[3]CC, EEC[3]CE |
| $C_3$-3 | 125.20 | EEC[3]EE |
| $C_3$-4 | 125.07 | CCC[3]CC[a] |
| $C_3$-5 | 124.94 | CCC[3]CE |
| $C_3$-6 | 124.65 | ECC[3]EC |
| $C_3$-7 | 124.52 | CCC[3]EC |
| $C_3$-8 | 124.41 | ECC[3]EE, CCC[3]EE |

[a] Assignments by Gemmer and Golub.[6]

Fig. 11.  Downfield shifts of resonances of $C_3$ carbon atoms (see Fig. 10) on addition of Eu(fod)$_3$.

and $C_4$-4 decreases in intensity with increase in epoxidation confirms this assignment (Fig. 10). The results obtained for the epoxidation of squalene[29] enables the assignment of $C_3$-7 to $CCC^3EC$ and $C_3$-1 to $CEC^3CC$, which is consistent with their observed lanthanide shifts. The resonances immediately adjacent to $C_3$-7, viz., $C_3$-6 and $C_3$-8, are assigned on the basis that the inclusion of one or more additional epoxide groups at a greater distance from the central group (i.e., in position 1 or 5 in the series $C^1C^2C^3C^4C^5$) would only make a very small change of the chemical shift. Likewise, the assignment of resonance $C_3$-2 rests on its similarity to $C_3$-1.

The assignment procedure for the olefinic $C_2$ region (Fig. 10) follows the same arguments that have been made for the olefinic $C_3$ region (see above). As before the $C_2$-4 peak, which does not move on addition of Eu(fod)$_3$, is assigned to $CC^2CCC$ and the fastest moving peak $C_2$-6 to $EE^2CEE$. The distance between these two peaks is greater than in the $C_3$ region (Fig. 10). The other $C_2$ assignments in Table III are based on $C_2$-4 and $C_2$-6 and arguments similar to that used for the $C_3$ region (see above) and are not therefore discussed in detail. In Tables II and III where there are multiple entries there is the possibility of ambiguity with regard to some assignments, which involve the first and fifth groups in the pentad.

**Oxirane Region of the Spectrum.** The $C_3$ resonances of the oxirane region of the spectrum (see Figs. 2 and 4), when expanded, shows a broadened singlet with some evidence of splitting (see Fig. 13). Peak separation occurs on addition of lanthanide shift reagent (Fig. 14) and $C_3$-10, the faster moving peak is assigned to EEE and $C_3$-9 to CEC (Table IV). The $C_2$ oxirane resonances show evidence of four closely placed resonances, which may be interpreted in terms of the four possible triads CEC, CEE, EEC, and EEE.
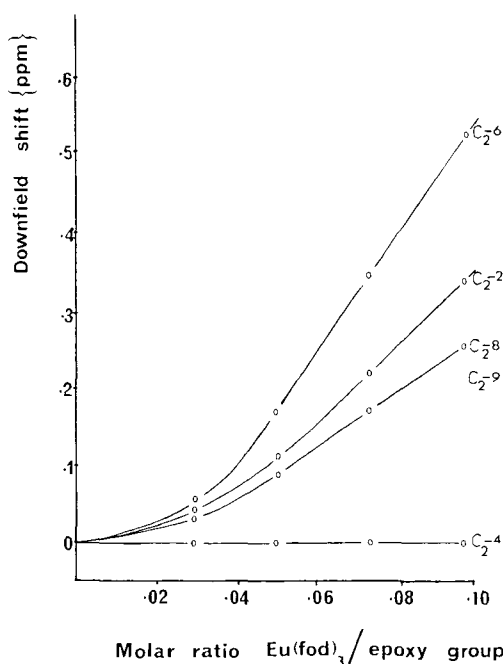
Fig. 12. Downfield shifts of resonances of $C_2$ carbon atoms (see Fig. 10) on addition of Eu(fod)$_3$.

Assignments of $C_2$-11 to CEC and $C_2$-12 to EEE are based on the decrease of the former and increase of the latter with increase in the degree of epoxidation (see Fig. 13). Unfortunately, the lanthanide shift reagent experiment (Fig. 14) was not useful because of line broadening and because all the triads show large lanthanide shifts due to strong binding to the central epoxy group of the triad.

## Monomer Sequence Distribution

It is important to determine whether the monomer sequence distribution is indicative of randon epoxidation of double bonds on treatment of natural rubber in solution or in the latex with peroxyacid. This may be determined by measurement of the amounts of each of the eight possible triads shown

TABLE III
Resonance Assignments for Olefinic Region $C_2$ Carbon Atoms (see Fig. 10)

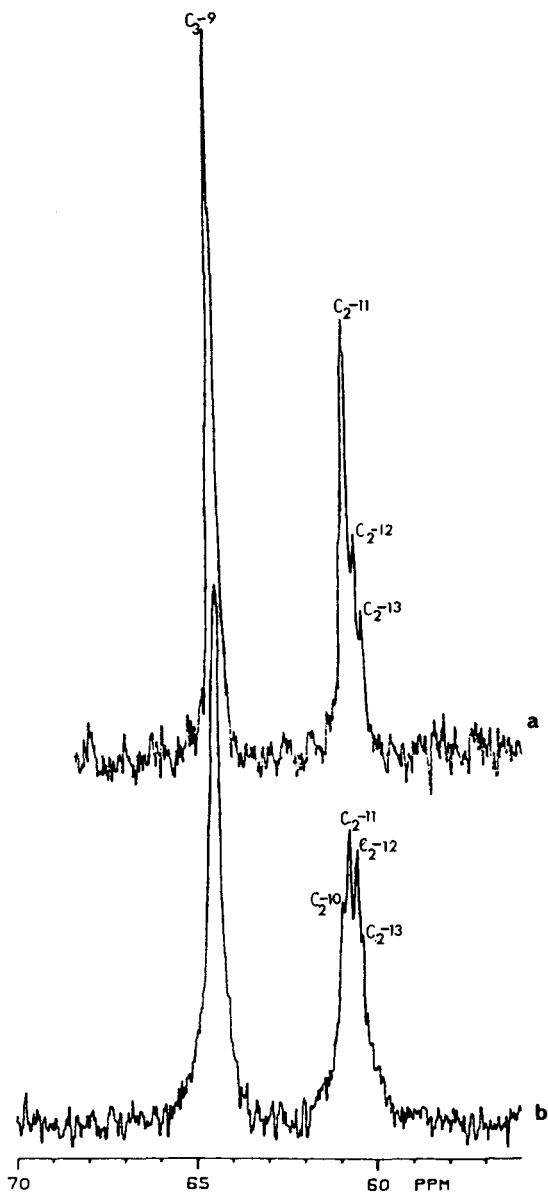| Resonance | Chemical shift (ppm) | Assignment |
|---|---|---|
| $C_2$-1 | 135.66 | CC²CEC, CC²CEE, EC²CEE |
| $C_2$-2 | 135.49 | EC²CEC |
| $C_2$-3 | 135.36 | CC²CCE |
| $C_2$-4 | 135.23 | CC²CCC, EC²CCE |
| $C_2$-5 | 135.05 | EC²CCC |
| $C_2$-6 | 134.76 | EE²CEE, EE²CEC, CE²CEE, CE²CEC |
| $C_2$-8 | 134.42 | CE²CCE |
| $C_2$-9 | 134.31 | CE²CCC, EE²CCC, EE²CCE |

Fig. 13.   Expansion of oxirane region (see Figs. 2 and 4) of (a) 40% and (b) 64% epoxidized natural rubber.

in Figure 3, which are identified by the $^{13}C$ NMR resonances of the $C_1$ and $C_4$ methylene carbon atoms (Table I and Fig. 7).

The intensities of the various resonances must be measured under conditions such that the intensity of each $^{13}C$ NMR resonance is proportional to the number of carbon atoms that produces the resonance. The first condition is complete relaxation of carbon nuclei between successive pulses, which is achieved if the repetition time (time between pulses) $> 5$ $T_1$.[30] This was determined by measurements of the $T_1$ values, which vary from 0.19 to 0.45 s (Table V). Thus a repetition time of 3 s ensured complete relaxation
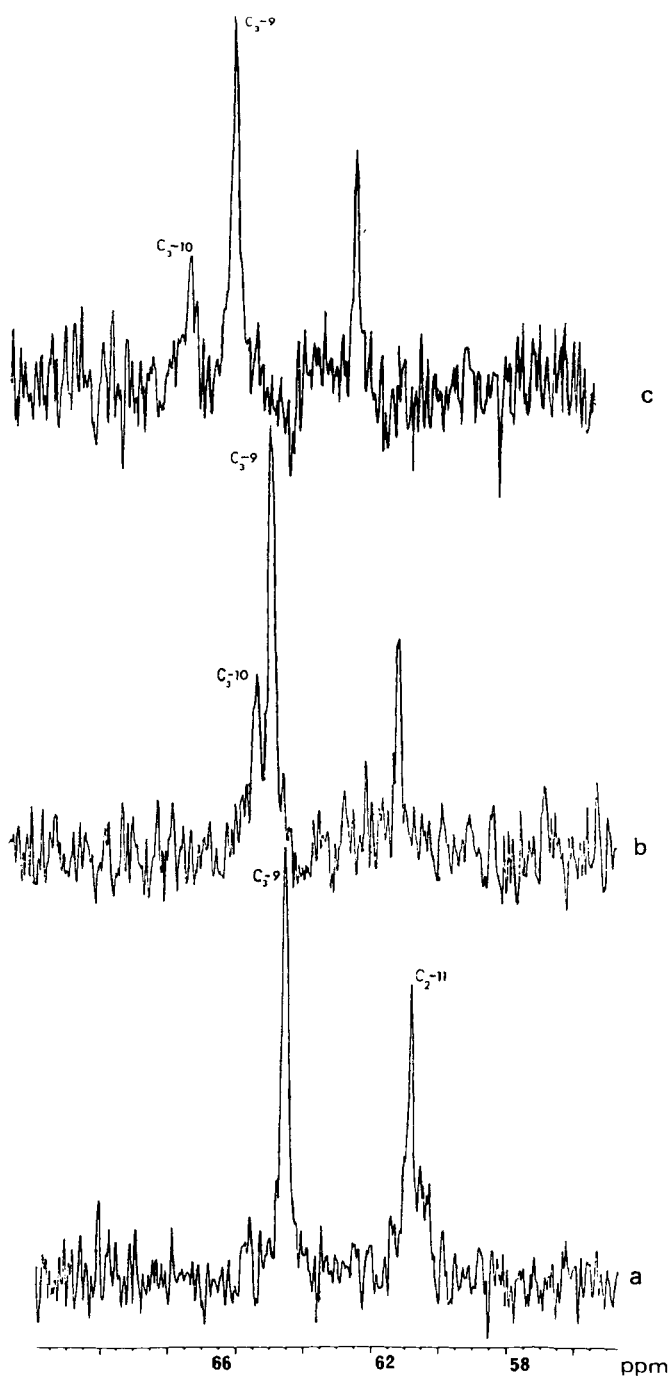
Fig. 14. $^{13}C$ NMR spectra of oxirane resonances of 40% epoxidized natural rubber on addition of Eu(fod)$_3$; molar ratio: (a) 0; (b) 0.025; (c) 0.048.

between pulses. It is noted that for both C$_1$ and C$_4$ methylene carbon atoms there is a decrease in $T_1$ in going from a CCC to an EEE triad. This indicates that the epoxidized polymer forms a more rigid structure than natural rubber, which is consistent with the great difference between their physical

TABLE IV
Resonance Assignments for Oxirane Region

| Resonance | Chemical shift (ppm) | Assignment |
|---|---|---|
| $C_2$-10 | 60.90 | $E^2EC$[a] |
| $C_2$-11 | 60.82 | $C^2EC$ |
| $C_2$-12 | 60.56 | $E^2EE$ |
| $C_2$-13 | 60.37 | $C^2EE$[a] |
| $C_3$-9 | 64.53 | $CE^3C$, $EE^3C$[b] |
| $C_3$-10 | 64.53 | $EE^3E$, $CE^3E$[b] |

[a] These assignments may need to be reversed.
[b] These assignments are doubtful.

properties. The second condition is that the nuclear Overhauser enhancement (NOE) of the proton decoupled $^{13}C$ NMR resonances is the same for each methylene carbon atom. Because the methylene carbon atoms are located in similar environments it is assumed that the NOE would be the same for all methylene carbon atoms, an assumption which has been found to be justified with another system.[30]

The results of a comparison between the theoretical calculation of occurrence of different triads assuming a random sequence distribution, and the experimentally determined values using $^{13}C$ NMR, are given in Table VI. Although the deviations from the theoretical value are perhaps slightly larger for the latex than for the solution method, it is likely that these deviations are within experimental error, given the likely errors inherent in the $^{13}C$ NMR method. Thus we have shown that epoxidation of natural rubber occurs by a random process when the reaction occurs in homogeneous solution or in rubber latex. Earlier kinetic studies in homogeneous solution indicated a nonrandom distribution,[9] but $^{13}C$ NMR studies on related systems[7,8] showed evidence of a random distribution. Burfield et al.[31] also favored random epoxidation of latex using peracetic acid and glass transition temperature studies.

There is thus considerable evidence including our own results to support the concept of a random epoxidation process both in homogeneous solution and in latex. The latter result indicates that performic acid is able to pen-

TABLE V
Spin–Lattice Relaxation Times [$T_1$ (s)] of Methylene Carbon Atoms of Partially Epoxidized Natural Rubber

| | $T_1$ (s) | | |
|---|---|---|---|
| | 30% epoxidized | 60% epoxidized | Mean |
| $C^1EC$, $C^1EE$ | 0.32 | 0.34 | 0.33 |
| $C^1CC$, $C^1CE$ | 0.34 | 0.42 | 0.38 |
| $E^1EC$, $E^1EE$ | 0.23 | 0.26 | 0.25 |
| $E^1CC$, $E^1CE$ | 0.29 | 0.31 | 0.30 |
| $CE^4C$, $EE^4C$ | 0.30 | 0.26 | 0.28 |
| $CC^4C$, $EC^4C$ | 0.39 | 0.45 | 0.42 |
| $EE^4E$, $CE^4E$ | 0.19 | 0.24 | 0.22 |
| $EC^4E$, $CC^4E$ | 0.31 | 0.37 | 0.34 |

TABLE VI
Experimentally Determined and Theoretical[a] Percentages of Occurrence of Triad Sequences in Natural Rubber Epoxidized to Different Levels by the Solution or Latex Methods

| Triad Sequence | Level of epoxidation (%) | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | 40 | | | 54 | | 64 | | |
| | Solution | Latex | Theoret | Latex | Theoret | Solution | Latex | Theoret |
| CEC, CEE | 23 | 23 | 24 | 21 | 25 | 22 | 24 | 23 |
| CCC | 20 | 19 | 22 | 8 | 9 | 4 | 6 | 4 |
| CCE | 16 | 15 | 14 | 10 | 11 | 7 | 8 | 8 |
| EEC, EEE | 18 | 15 | 16 | 28 | 31 | 44 | 39 | 42 |
| ECC | 16 | 17 | 14 | 10 | 11 | 7 | 7 | 8 |
| ECE | 11 | 11 | 10 | 17 | 14 | 16 | 17 | 15 |

[a] The theoretical percentage occurrence of a particular triad is calculated assuming random placement of epoxide groups along the chain.

etrate the latex droplet and effect epoxidation evenly throughout the droplet. From a practical point of view this is important, because it is much cheaper to epoxidize natural rubber in latex rather than in an organic solvent.

## References

1. M. Porter, *Eur. Rubber J.*, **159**, 13 (1977).

2. D. Barnard, Proc. Symp. on Powdered, Liquid and Thermoplastic Natural Rubber, Kuala Lumpur, 1981, p. 79.

3. R. Pummer and P. A. Burkard, *Ber.*, **55**, 3458 (1922).

4. C. Roux, R. Pautrat, R. Cheritat, F. Ledran, and J. C. Danjard, *J. Polym. Sci., C*, **16**, 4687 (1969).

5. Hercules Powder Co., B.P. 892361, *Chem. Abstr.*, 5748774 (1961).

6. R. V. Gemmer and M. A. Golub, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 2985 (1978).

7. O. Hayashi, T. Takahashi, H. Kurihara, and H. Ueno, *Kobunshi Ronbunshi*, **37**, 195 (1980).

8. O. Hayashi, T. Takahashi, H. Kurihara, and H. Ueno, *Polym. J. (Jpn.)*, **13**, 215 (1981).

9. I. A. Tutorskii, I. D. Khodghayeva, and B. A. Dogadkin, *Polym. Sci. USSR*, **16**, 187 (1974).

10. M. W. Duch and D. M. Grant, *Macromolecules*, **3**, 165 (1970).

11. R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.*, **48**, 3831 (1968).

12. R. Gerhards and W. Dietrich, *J. Magn. Reson.*, **23**, 21 (1976).

13. D. M. Doddrell and D. T. Pegg, *J. Am. Chem. Soc.*, **102**, 6388 (1980).

14. G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, **101**, 760 (1979).

15. A. F. Cockerill, G. L. O. Davies, R. C. Harden, and D. M. Rackham, *Chem. Rev.*, **73**, 553 (1973).

16. J. H. Bradbury, *The Physical Principles and Techniques of Protein Chemistry, Part B*, Academic, New York, 1970, p. 99.

17. P. W. Allen and G. M. Bristow, *J. Appl. Polym. Sci.*, **7**, 603 (1963).

18. I. A. Tutorskii, I. D. Khodzhaeva, and B. A. Dogadkin, *Khim. Khim. Technol., Tr. Yubileinvi Konf, Posoyashch. 70- Letiyu Inst.*, 187 (1970); *Chem. Abstr.*, **81**, 106968j (1974).

19. K. Udipi, *J. Appl. Polym. Sci.*, **23**, 3301 (1979).

20. D. Swern, G. N. Billen, T. W. Findley, and J. T. Scanlan, *J. Am. Chem. Soc.*, **68**, 1504 (1946).

21. D. R. Burfield and S. N. Gan, *J. Polym. Sci.*, **15**, 2721 (1977).

22. M. A. Golub, M. S. Hsu, and L. A. Wilson, *Rubb. Chem. Technol.*, **48**, 953 (1975).

23. A. J. Durbetaki, *Anal. Chem.,* **37**, 1231 (1965).

24. J. G. Dorsey, *Anal. Chem.,* **49**, 1144 (1977).

25. A. S. Khatchaturov, E. R. Dolinskaya, L. K. Prozenko, E. L. Abramenko, and V. A. Kormen, *Polymer,* **18**, 871 (1977).

26. M. A. Golub, *J. Am. Chem. Soc.,* **84**, 4981 (1962).

27. D. Swern, *J. Am. Chem. Soc.,* **70**, 1235 (1948).

28. F. C. Schilling, F. A. Bovey, S. Tseng, and A. E. Woodward, *Macromolecules,* **16**, 808 (1983).

29. M. E. Van Dommelen, L. J. M. Van de Ven, H. M. Buck and J. W. de Haan, *Rec. Trav. Chim. Pays-Bas,* **96**, 295 (1977).

30. J. H. Bradbury and J. G. Collins, *Cereal Chem.,* **59**, 159 (1982).

31. D. R. Burfield, K. L. Lim and K. S. Law, *J. Appl. Polym. Sci.,* **29**, 1661 (1984).