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Epoxide Groups in Natural Rubber. II.
^{13}C-NMR Study of Undegraded Natural Rubbers

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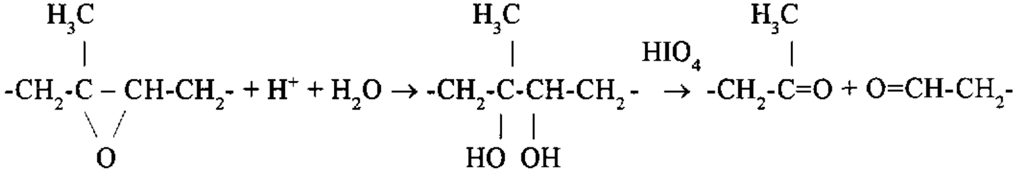
The level of epoxide groups on the natural rubber main-chain molecule is examined by ^{13}C-NMR spectroscopy. The results show that while all the rubber samples contain trans *isoprene units, purified rubbers from fresh latices contain no detectable amount of epoxide groups. This is also found to be the case for fractionated rubbers of different molecular weights, rubber samples of different clonal origin as well as rubbers isolated from different zones of centrifuged fresh latex. Nevertheless, of the six commercial solid rubber samples examined, SMR L and SMR 10 were found to contain trace amount of* cis *epoxide, the levels of which are similar to that of* trans *isoprene units. It is concluded that natural rubber has no detectable amount of epoxide groups on the main-chain molecule.*

Natural rubber has been reported to contain substantial amount of epoxide groups on the main-chain molecule. These groups were first suspected to be an integral part of the rubber molecule when a reduction of the rubber molecular weight was observed after treating acid hydrolysed natural rubber with periodic acid[1]. The reactions involved were visualised in *Scheme 1*.



$$\text{-CH}_2\text{-}\underset{\diagdown\ \diagup \atop O}{\overset{H_3C}{\overset{|}{C}}\text{ – CH}}\text{-CH}_2\text{-} + H^+ + H_2O \rightarrow \text{-CH}_2\text{-}\underset{|\atop HO}{\overset{H_3C}{\overset{|}{C}}}\text{-}\underset{|\atop OH}{CH}\text{-CH}_2\text{-} \xrightarrow{HIO_4} \text{-CH}_2\text{-}\overset{H_3C}{\overset{|}{C}}\text{=O} + \text{O=CH-CH}_2\text{-}$$

Scheme 1

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It was further demonstrated that the amount of epoxide groups can be estimated by HBr titration[2]. Based on this method, the epoxide groups were found to be in the region of 45 mmol/kg–75 mmol/kg or 0.3%–0.5% mol/mol of isoprenic unit. The HBr titration of the rubber fractions of different molecular weights revealed that the epoxide groups were concentrated in the higher molecular weight fractions[3].

The presence of epoxide groups in low molecular weight fractions of natural rubber from commercial latex has also been shown by ^{13}C-NMR technique[4]. The level of these groups were found to be in the range of 15 mmol/kg–20 mmol/kg or 0.10%–0.14% mol/mol of isoprenic unit. Despite this, no epoxide groups have been detected by the same technique in the low molecular weight fractions of the rubber obtained from fresh latices. Since epoxide groups were reported to be concentrated in the high molecular weight fraction and these fractions constitute the major part of the rubber in terms of weight ratio, it is therefore imperative to study the whole fraction of the rubber so that the presence of these groups in the polymer can be ascertained. The results of this study are presented in this paper.

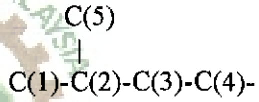
MATERIALS AND METHODS

Purified natural rubber was prepared by enzymatic treatment of fresh latex followed by centrifugation as described elsewhere[5]. Fractionation of the purified natural rubber was carried by adding methanol to the rubber/toluene solution in the usual manner. To obtain rubbers from different zones of centrifuged latex, the ultracentrifuged latex was frozen in a freezer and then separated into cream, serum (C-serum) and bottom (B-serum) fractions. Serum fraction was concentrated under reduced pressure at room temperature before precipitating out the rubber in ethanol. Commercial solid rubber samples were used without further purification.

^{13}C-NMR measurements were performed on deuterated chloroform solution of the rubbers with tetramethylsilane (TMS) as internal standard by using a JEOL FX-200 NMR spectrometer under the conditions described previously[6]. All NMR samples were prepared under nitrogen atmosphere to minimise the oxidative degradation of the rubbers during measurement.

RESULTS AND DISCUSSION

Previous ^{13}C-NMR study has shown that the C2 and C3 in the *cis* epoxide group in partially epoxidised natural rubber resonate at 60.7 p.p.m. and 64.5 p.p.m., while those in the *trans* epoxide resonate at 60.6 p.p.m. and 63.2 p.p.m. respectively[6]. The carbon atoms of the isoprene or epoxidised isoprene units are designated as follows:



$$\overset{\displaystyle C(5)}{\overset{|}{\text{C(1)-C(2)-C(3)-C(4)-}}}$$

The presence of *trans* isoprene units in natural rubber at the level of two groups per linear chain or 0.07% mol/mol of isoprenic unit, assuming the degree of polymerisation of 3000, has been confirmed by ^{13}C-NMR[7]. This level is much lower than those of naturally occurring epoxide groups in natural rubber reported so far *i.e.* 0.1%–0.5% mol/mol of isoprenic unit[8]. The ^{13}C-NMR signals, which are due to C1 and C5 in the *trans* isoprene units, can be used as references to detect low level of epoxide groups in natural rubber. In other words, failure to observe any ^{13}C-NMR signals due to epoxide groups would imply that the concentration of these groups is below two groups per chain. In the present study, all ^{13}C-NMR spectral accumulations of the rubber samples were carried out until the signals of the *trans* isoprene appeared.

Figures 1(a)–(c) show the ^{13}C-NMR spectra of purified whole natural rubbers obtained from three different clones, *i.e.* PR 107, RRIM 501 and RRIM 600. While the signals which are due to C5 and C1 in the *trans* isoprene were clearly observed at 16.0 p.p.m. and 39.8 p.p.m., respectively, no signals due to epoxide groups were found in these samples. Since epoxides have been reported to be concentrated in the high molecular weight fraction, the rubber from RRIM 600, a clone which has been reported to produce high amounts of epoxide groups in the rubber[3], was fractionated for further investigation. The results are indicated in *Figures 2(a)–(c)*. These results clearly show that all the fractionated rubbers contain no significant amounts of epoxide groups. The signals which are due to C1 and C5 in the *trans* isoprene, on the other hand, were again observed in all the spectra of the fractionated rubber samples. The signal intensity of methylene carbon of fatty acids at 29.7 p.p.m. was found to increase with decreasing molecular weight of the rubber samples. This indicates that the fatty acids are located at the chain terminal. This has been reported previously[9].

Since the rubber samples used in the present study were purified *via* centrifugation, it is tempting to suggest that certain fractions of the rubber molecules, which may contain epoxide groups, such as those in serum and bottom fractions, were discarded in the process of purification. In view of this, an ultracentrifuged fresh latex of RRIM 600 origin was carefully divided into cream, serum and bottom fractions. The rubber in each of these fractions was anlaysed by ^{13}C-NMR and the results are presented in *Figures 1(c)*, *3(a)*, and *3(b)*. Among the three samples, the bottom fraction was found to contain the highest amount of fatty acids while the serum fraction, the lowest. The spectra of all the three samples show the signals due to C1 and C5 of the *trans* isoprene. However, no signals due to epoxide groups were detected in these samples. It is, therefore, clearly demonstrated that natural rubber obtained from fresh latex contains no significant amount of epoxide groups.

It may be of interest to examine commercial natural rubbers because high processing temperature of the rubbers might lead to the formation of epoxide groups in the polymer *via* a radical route. *Figures 4(a)–(f)* show the ^{13}C-NMR spectra of six commercial natural rubbers. Of these samples examined, only SMR L and SMR 10 were found to contain trace amount of *cis* epoxide groups, the levels of which are similar to those of the *trans* isoprene units. Previous report has demonstrated that oxidative degradation of natural rubber produces much higher *cis* epoxide than *trans* epoxide as by-products[6]. Therefore, the trace amount of epoxide groups detected in these two samples are probably derived from the same mechanism. The SMR 10 sample was fractionated and the high molecular weight fraction was further examined by a high resolution ^{13}C-NMR spectrometer operating at 125 MHz. *Figure 5* shows the ^{13}C-NMR spectrum of the rubber sample accumulated for 50 000 scans. While the signals due to *trans* isoprene units were clearly found in this spectrum, the signals due to epoxide groups were not detected.

The presence of naturally occurring epoxide groups in natural molecule has been reported[1–4].

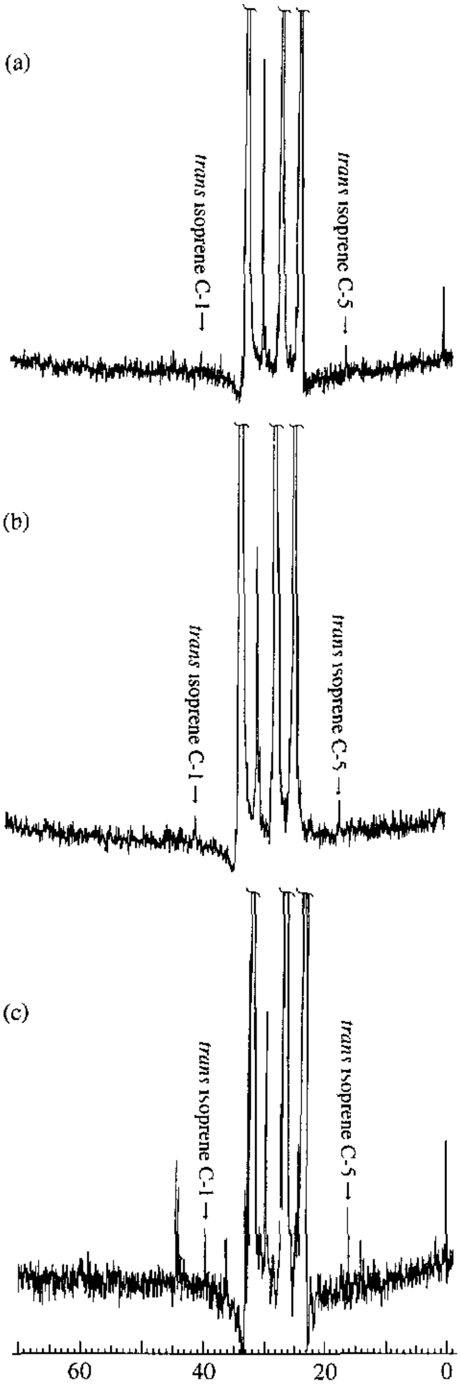


Figure 1 ^{13}C-NMR spectra of purified natural rubbers (a) PR 107, (b) RRIM 501, and, (c) RRIM 600

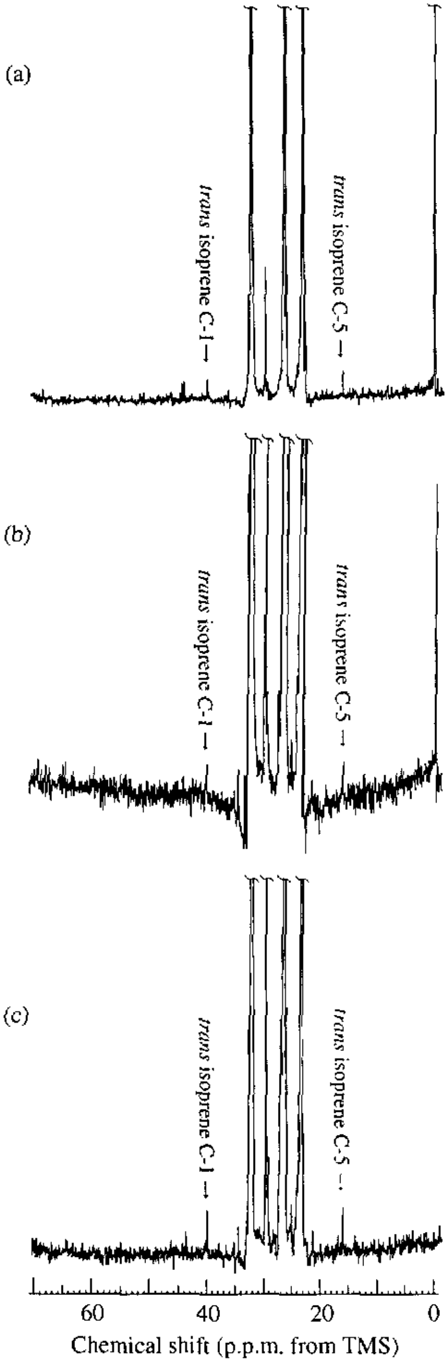


Figure 2. ^{13}C-NMR spectra of purified fractionated natural rubbers. (a) $\overline{M}_n = 1.1 \times 10^6$, (b) $\overline{M}_n = 6.1 \times 10^5$, and (c) $\overline{M}_n = 0.7 \times 10^5$m ($\overline{M}_n$values were determined by osmometry technique).

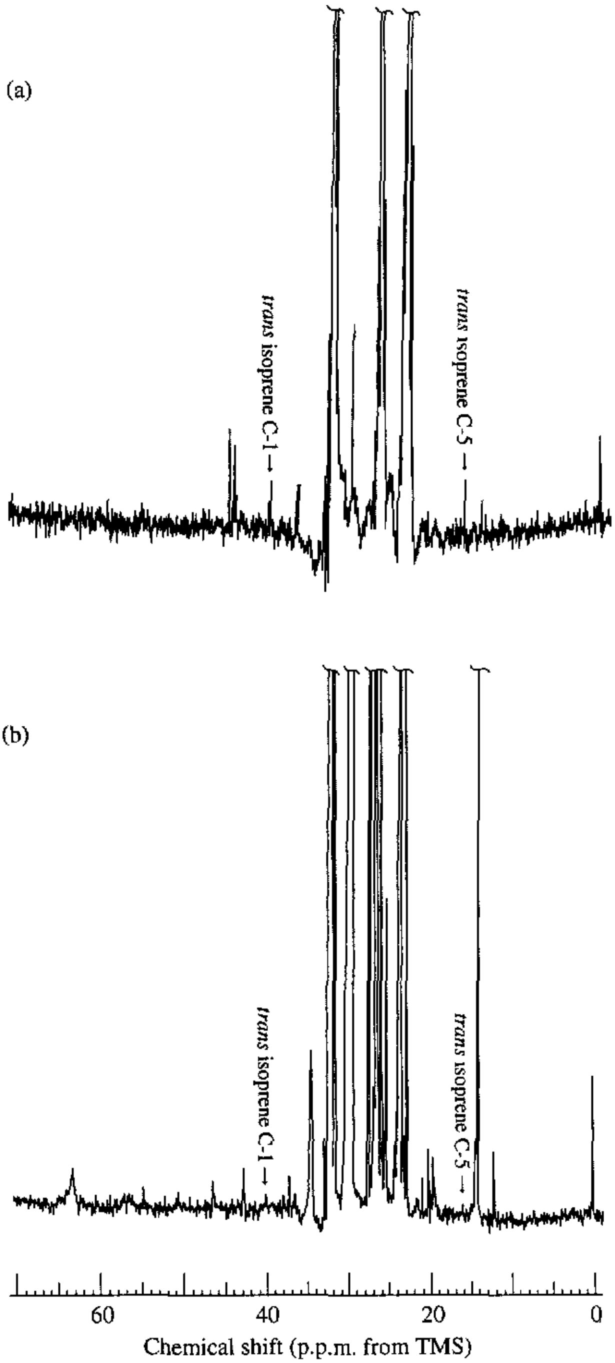


Figure 3. ^{13}*C-NMR spectra of natural rubbers from ultracentrifuged latex.*
(a) Serum fraction (C-serum), and (b) bottom fraction (B-serum)
Note: Cream fraction is given in figure 1(c).

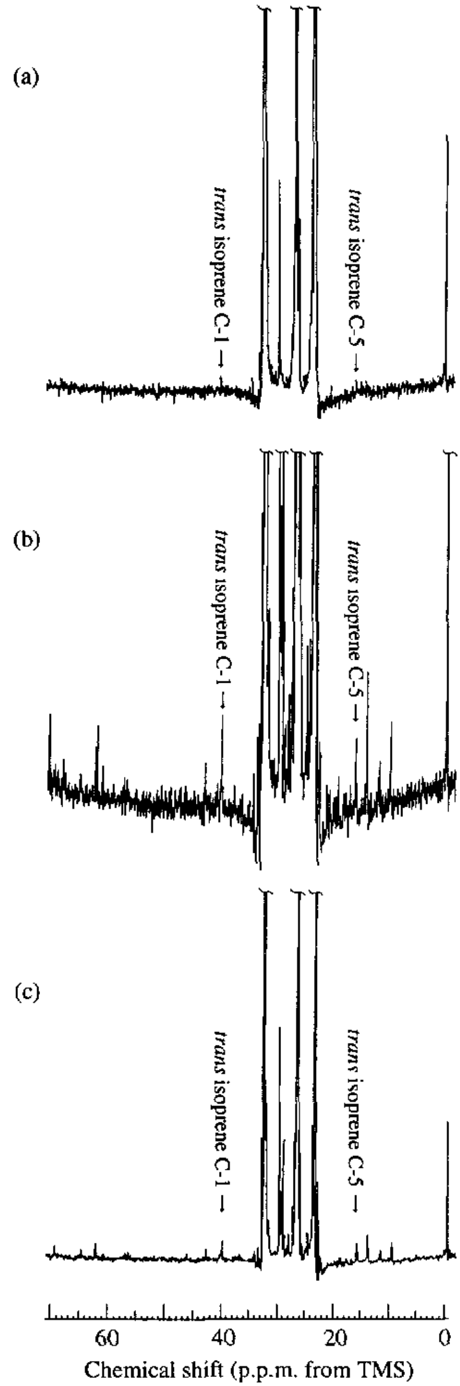


Figure 4. ^{13}C-NMR spectra of commercial dry natural rubbers.
(a) DPNR, (b) DPNR CV, (c) SMR CV.

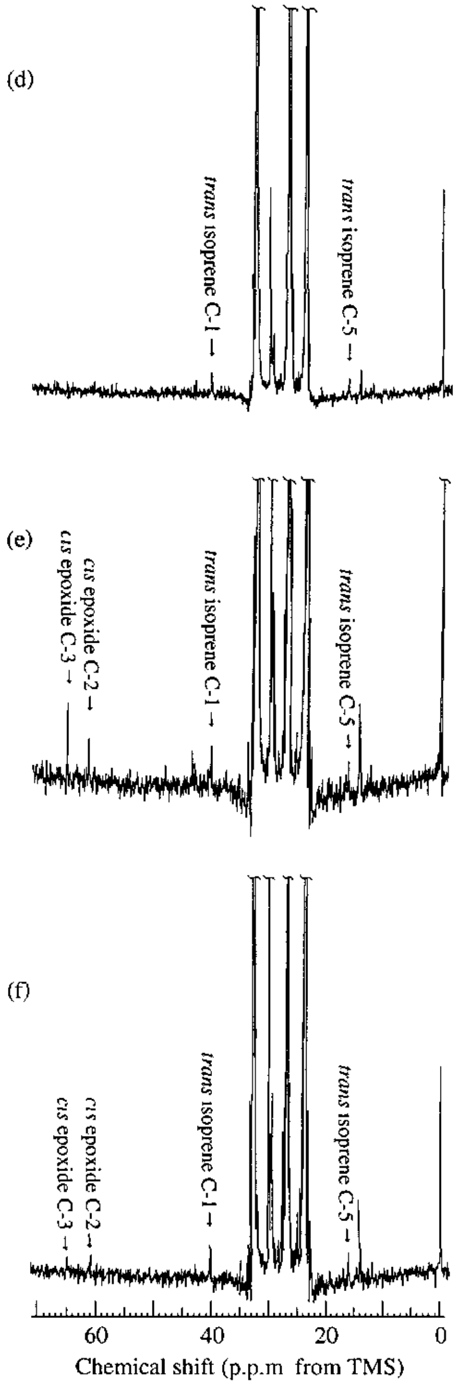


Figure 4. ^{13}C-NMR spectra of commercial dry natural rubbers (d) SMR 5, (e) SMR L, and (f) SMR 10.

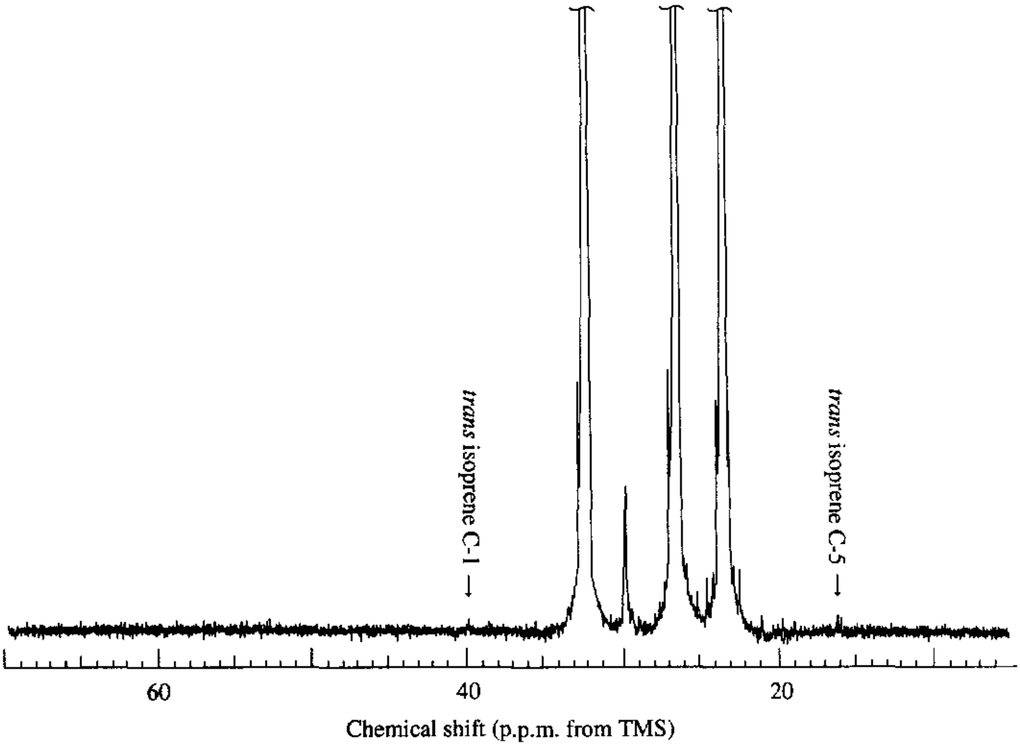


Figure 5. ^{13}C-NMR spectrum of high molecular weight fraction of SMR 10.

However, the techniques employed in these studies such as radiotracer[1] and titration[2,3], to detect epoxide groups are non-specific which can easily lead to erroneous interpretation, particularly when there are many complex naturally occurring non-rubber materials present in the natural rubber. Based on the results of the present study, it is concluded that the level of epoxide groups in undegraded natural rubber, if any, is well below the level of naturally occurring *trans* isoprene unit.

CONCLUSION

The presence of epoxide groups in undegraded natural rubbers has been investigated by ^{13}C-NMR spectroscopy. There is no detectable amount of epoxide groups found in the purified rubber samples from different latices. This indicates that natural rubber contains no naturally occurring epoxide groups on the main-chain molecule. Trace amount of epoxide groups detected in certain commercial dry rubbers are probably due to low level of degradation of the rubber molecule during processing or long term storage.

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