

## Geometrical Isomerisation of Polyisoprenes. Part 1. Occurrence and Estimation of Trans-alkene Functionality in Natural Rubber

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*A procedure to measure low levels of trans-alkene content in samples of natural rubber has been developed based on  $^1\text{H}$ -NMR spectroscopy at 400 MHz. Modification levels ranging between 0.20 mole% and 0.79 mole% have been measured in natural rubber originating from a variety of grades of Malaysian rubber. There is no general correlation between trans-alkene content and grade of natural rubber. A combination of 'spin-counting' and comparative NMR analyses has demonstrated that the sol and gel phases of natural rubber are homogeneous with both phases containing the same level of trans-alkene content.*

Natural rubber is a high molecular weight polyisoprenoid which was believed to be composed of 100% *cis*-1,4-polyisoprene<sup>1</sup>. Tanaka and co-workers<sup>2,3</sup> have shown that  $^{13}\text{C}$ -NMR spectroscopy can be used to characterise the arrangement of isomeric units in polyisoprenoids and has indicated the presence of *trans*-alkene units in lower molecular weight fractions of natural rubber.  $^{13}\text{C}$ -NMR measurements, based on the relative intensity of *trans*-alkene resonances and average degree of polymerisation, have been used to show an average of 2.0–3.9 *trans*-alkene units per polymer chain in natural rubber;  $^{13}\text{C}$ -NMR chemical shift data indicates that these units are adjacent to the  $\omega$ -terminal of each polymer chain (*i.e.* the chain end at which polymerisation is initiated, Figure 1)<sup>4</sup>.

Geometrical isomerisation in natural rubber can be induced using a variety of sulphur-based reagents<sup>1</sup> and a small increase in *trans*-1,4-polyisoprene content is sufficient to significantly change some physical properties<sup>1,5</sup>. The introduction of 2–5 mole% *trans*-alkene units into natural rubber has been used commercially to prepare 'anti-crystallising' rubber<sup>1</sup>, modified natural rubber whose vulcanisates exhibit a marked decrease in their rate of crystallisation at sub-zero temperatures. Beyond 5 mole%, the benefits of resistance to low-temperature crystallisation are outweighed by a progressive loss in tensile strength and modulus as stress-induced crystallisation is suppressed<sup>5</sup>.

A simple calculation of *trans*-alkene content, based on three isomeric units per

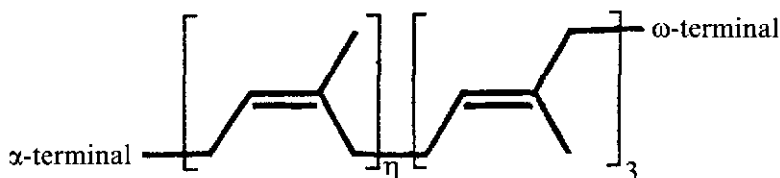


Figure 1. Polymer chain structure in natural rubber.

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polymer chain<sup>2,3,4</sup>, an average molecular weight of 200 000 and the assumption that chains are unbranched, yields a modification level of 0.10 mole%. This level of geometrical isomerisation would not be expected to be significant, but recent work by Chasset and co-workers<sup>6</sup> on variability in the low temperature crystallisation behaviour of uncured dry rubber strongly suggests that small differences in *trans*-alkene content can affect physical properties. Therefore, the measurement of low levels of *trans*-alkene content in natural rubber is important. Analytical techniques to measure the extent of geometrical isomerisation in polyisoprenoids are based on infra-red spectroscopy<sup>1,7</sup> or <sup>13</sup>C-NMR spectroscopy<sup>2,3</sup>. The infra-red technique is awkward and relatively inaccurate with a reported error of  $\pm 2$  mole% while the application of <sup>13</sup>C-NMR spectroscopy to measure *trans*-alkene content below 5 mole% is time consuming and subject to inaccuracies arising from the mode of data acquisition.

This paper describes the development of a method to accurately determine *trans*-alkene content in samples of natural rubber using <sup>1</sup>H-NMR spectroscopy.

## EXPERIMENTAL

### NMR Spectroscopy

The *trans*-alkene content of natural rubber samples was measured using <sup>1</sup>H-NMR spectroscopy at a Larmor frequency of 400 MHz on a Varian VXR-400 NMR spectrometer and 1% w/v solutions of the sol fractions in deuteriated chloroform (CDCl<sub>3</sub>). Typically, 32-128 transients were acquired at a probe temperature of 25°C using quadrature detection, double precision electronics and a spectral width of 5600 Hz. Quantitative data acquisition was ensured by the use of a pulse angle of 25° and a delay time between pulses of 4.3 s; data was acquired using 32K data points and zero-filled to 64K before Fourier transformation. All the samples were doped with a drop of deuteriated dimethylsulphoxide (d<sub>6</sub>-DMSO) to selectively shift the water resonance.

<sup>13</sup>C-NMR spectra were acquired at a Larmor frequency of 125 MHz using a Jeol GSX-500 NMR spectrometer and 3% w/v solutions of the sol fractions in CDCl<sub>3</sub>. Samples were run in the absence of spinning to prevent the formation of spectral artefacts<sup>8</sup>. <sup>13</sup>C-NMR spectra were acquired at a probe temperature of 20°C with full broadband decoupling, a pulse angle of 23°, an acquisition time of 0.54 s and a delay time between pulses of 2.5 s.

### Separation of Sol and Gel Fractions

Samples of natural rubber were adequately separated by swelling at 0.5-1.0% w/v in CDCl<sub>3</sub> for 24-48 h at 5°C. The sol fractions were separated by filtration through two layers of lens tissue followed by solvent evaporation using a stream of nitrogen and drying *in vacuo* at 50°C.

## RESULTS AND DISCUSSION

### Quantitative Measurement of *Trans*-alkene Content in Natural Rubber

Differentiation between *cis*- and *trans*-1,4-polyisoprenoids is relatively facile by <sup>1</sup>H-NMR spectroscopy at high magnetic fields due to the chemical shift difference between the methyl group resonances<sup>9</sup>; in CDCl<sub>3</sub>, *cis*-1,4-addition yields a peak at 1.68 p.p.m. while the corresponding *trans*-1,4-addition peak is found at 1.61 p.p.m. Lee<sup>10</sup> showed that for <sup>1</sup>H-NMR spectroscopy at 90 MHz, the two methyl group resonances overlapped in CDCl<sub>3</sub> and the difference in chemical shift could be increased to 0.06 p.p.m. if deuterobenzene, C<sub>6</sub>D<sub>6</sub>, was used as the NMR solvent. Deuterobenzene was not used in these studies because it is a high viscosity solvent which has a deleterious effect on peak line widths and spectral resolution<sup>11</sup>.

The measurement of trace levels of *cis-trans* isomerisation in natural rubber using <sup>1</sup>H-NMR spectroscopy and the methyl group resonances is primarily dependent upon two factors; complete resolution of

the two methyl resonances and a sufficient delay time between pulses in the NMR experiment to allow full magnetisation recovery of the methyl group signals. It has been found that the methyl group resonances can be fully resolved using 1% w/v solutions of sol fractions in  $\text{CDCl}_3$  and  $^1\text{H}$ -NMR spectroscopy at 400 MHz (Figure 2). However, the accurate measurement of *trans*-alkene content at 1 mole% or less also requires differentiation from any additional peaks found between 1.50 p.p.m. and 1.70 p.p.m. Water has a low solubility in  $\text{CDCl}_3$  and resonates between 1.52 p.p.m. and 1.55 p.p.m. according to the extent of solvent hydration<sup>12</sup> and adventitious water can be a problem in the chemical shift region of interest (Figure 2). In addition, there is

spectroscopic evidence<sup>8</sup> for the presence of a tightly-bound water fraction in samples of natural rubber which is characterised by a broad  $^1\text{H}$ -NMR resonance centred at 1.55 p.p.m. (Figure 3). Deuterated dimethylsulphoxide ( $\text{d}_6$ -DMSO) has been found to be an effective shift reagent for water and doping with  $\text{d}_6$ -DMSO shifts the water resonance to 2.0-2.2 p.p.m. leaving a relatively clean and linear baseline between 1.5 p.p.m. and 1.7 p.p.m. (Figure 2). There are a number of additional minor resonances between 1.55 p.p.m. and 1.65 p.p.m., but they are sufficiently isolated from the *trans*-alkene resonance to have no effect on quantification. The construction of a linear baseline is dependent on accurate phasing of the spectra.

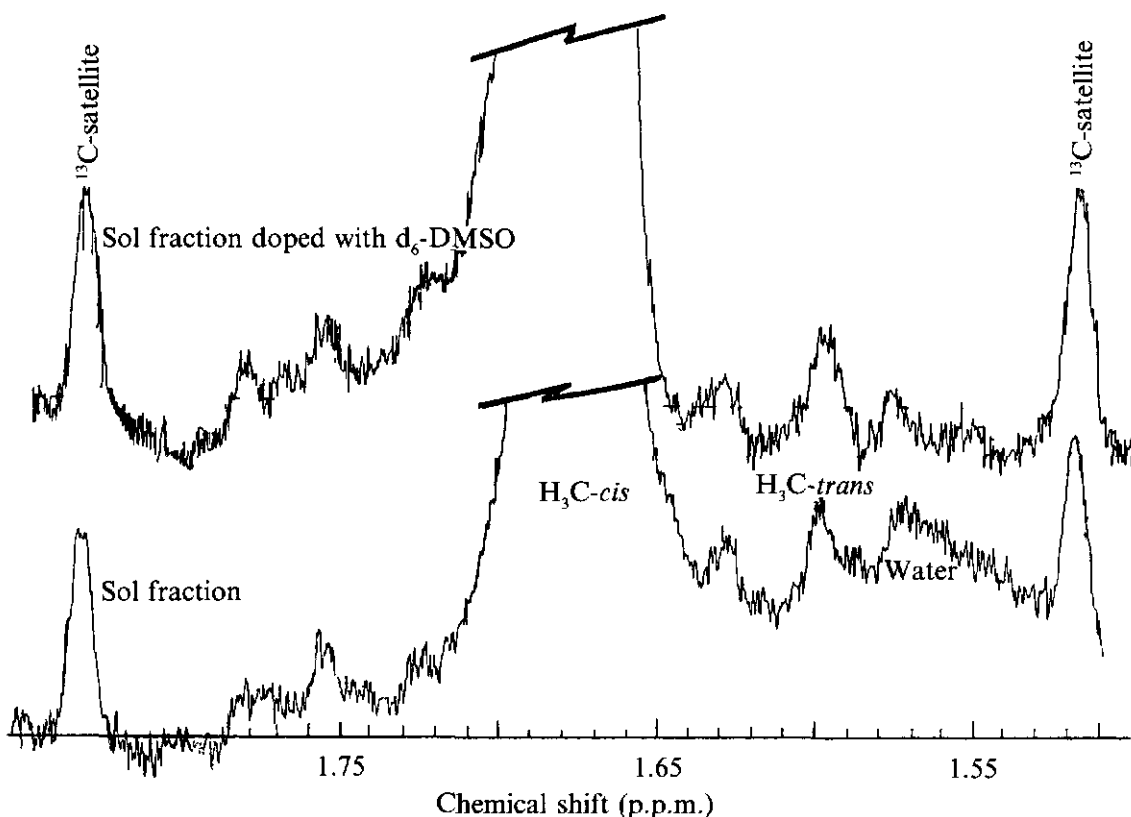


Figure 2.  $^1\text{H}$ -NMR spectroscopic discrimination between isomeric alkene units and the effect of adventitious water.

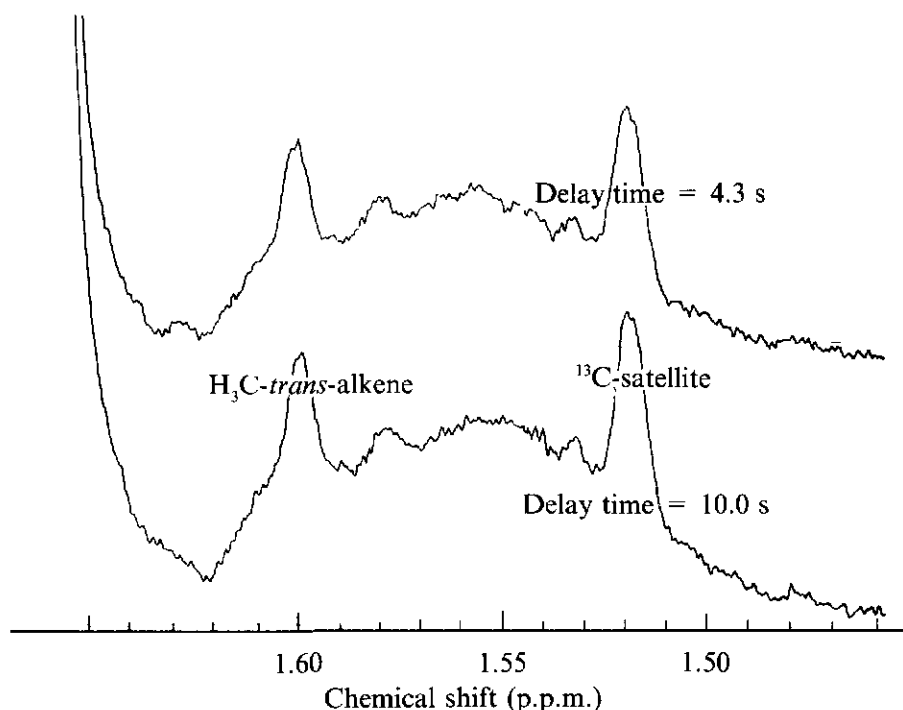


Figure 3. Effect of variation in the delay time between pulses in  $^1\text{H}$ -NMR spectra of natural rubber.

The rate of magnetisation recovery for a NMR signal after pulsed excitation is determined by the spin-lattice relaxation time ( $T_1$ ) of the resonance.  $T_1$  values can be determined by a variety of experimental techniques<sup>13</sup> and the standard inversion-recovery experiment<sup>14</sup> was used to measure a  $T_1$  value of  $1.5 \pm 0.1$  s for the methyl group protons in the *cis*-alkene units of natural rubber. The relative size of the corresponding *trans*-alkene resonance is very small (<1%) and is therefore not suitable for the accurate measurement of  $T_1$ . However, one can show using arrayed experiments (in which the delay time between pulses was varied from 1 s to 20 s through a series of acquisitions) that a delay time of 4.3 s is sufficient to allow full relaxation for the *trans*-alkene resonance (Figure 3). The two spectra presented in Figure 3 were acquired with delay times of 4.3 s and 10 s and *trans*-alkene content

measurement from these spectra gave modification levels of 0.48 mole% and 0.47 mole% respectively. These results were found to be reproducible ( $\pm 5\%$ ) over a range of samples and consequently, 4.3 s was adopted as an appropriate delay time for the acquisition of quantitative NMR data.

The analytical technique has been applied to the sol fractions derived from a selection of grades of natural rubber from Malaysia. The results of this survey (Table 1) demonstrated a wide range for *trans*-alkene content between different samples (0.20–0.79 mole%) with no obvious correlation between rubber grade and *trans*-alkene content. The identification of factors which influence the degree of geometrical isomerisation present in grades of natural rubber will be discussed in a forthcoming publication.

TABLE 1. *TRANS*-ALKENE CONTENT IN NATURAL RUBBER SAMPLES

NR grade	<i>Trans</i> -alkene content (mole%)			
SMR L <sup>a</sup>	0.50	0.44	0.34	0.51
SMR 5 <sup>a</sup>	0.24	0.36	0.42	0.79
SMR 10 <sup>a</sup>	0.40	0.36	0.37	0.51
SMR CV	0.25			
DPNR	0.23			
DPNR (CV)	0.44			
HA Latex <sup>b</sup>	0.20	0.21		

<sup>a</sup>Results for several samples<sup>b</sup>Dried rubber samples derived from HA latex concentrates by precipitation in methylated spirits and drying *in vacuo* at 50°C

### <sup>13</sup>C-NMR Spectroscopy

The characterisation of *trans*-alkene unit in natural rubber has been based solely upon <sup>1</sup>H-NMR spectroscopic evidence relative to *trans*-1,4-polyisoprenoids and confirmatory evidence was sought from another technique. It is known that *trans*-1,4-polyisoprenoids give rise to characteristic <sup>13</sup>C-NMR resonances at 16 p.p.m. and 39-40 p.p.m. and these can be used diagnostically for the detection of isomeric alkene units in natural rubber<sup>2,3,4</sup>. <sup>13</sup>C-NMR spectroscopy at 125 MHz (i.e. 500 MHz for <sup>1</sup>H-NMR spectroscopy) was used to analyse a sample of SMR 5 which was shown by <sup>1</sup>H-NMR spectroscopy to contain 0.45 mole% *trans*-alkene content. An overnight acquisition of 16 h duration provided a spectrum of sufficient signal to noise ratio to detect chemical modifications in trace amounts and spectral expansions in the chemical shift region of interest showed the presence of resonances at chemical shifts characteristic of *trans*-alkene units (Figure 4). The detection of these resonances in samples of natural rubber subjected to <sup>1</sup>H-NMR analysis provides strong evidence for *trans*-alkene units. The observation of multiple resonances in the diagnostic chemical shift regions indicates that additional *trans*-alkene resonances to those situated at the  $\omega$ -terminal of each

polymer chain<sup>2,3,4</sup> are observed in samples of bale rubber.

### Structural Homogeneity

Unpublished work<sup>8</sup> has demonstrated that <sup>1</sup>H-NMR spectroscopy is capable of observing, typically, over 90% of the NMR-active nuclei in the sol fraction and 80% of the NMR-active nuclei in the gel fraction of uncured natural rubber samples when swollen in CDCl<sub>3</sub>. Therefore, comparative <sup>1</sup>H-NMR analysis of natural rubber (whole samples *versus* sol fraction) can be used to determine the structure of both the sol and gel fractions. Application of this technique to Malaysian bale rubbers indicates, by the similarity in results for the sol fraction alone and the total sample, that natural rubber is homogeneous with respect to *trans*-alkene content (Table 2). In an exceptional case, a sample of SMR 5 (Standard Malaysian Rubber) appeared to contain significantly less *trans*-alkene in the gel phase, but this anomaly is attributable to the degree of spectral overlap between the two methyl resonances used to determine *trans*-alkene content (Figure 5). The <sup>1</sup>H-NMR spectrum for the sol fraction alone was fully resolved whereas the spectrum acquired from the unfractionated rubber had an extensively broadened resonance for the *cis*-alkene

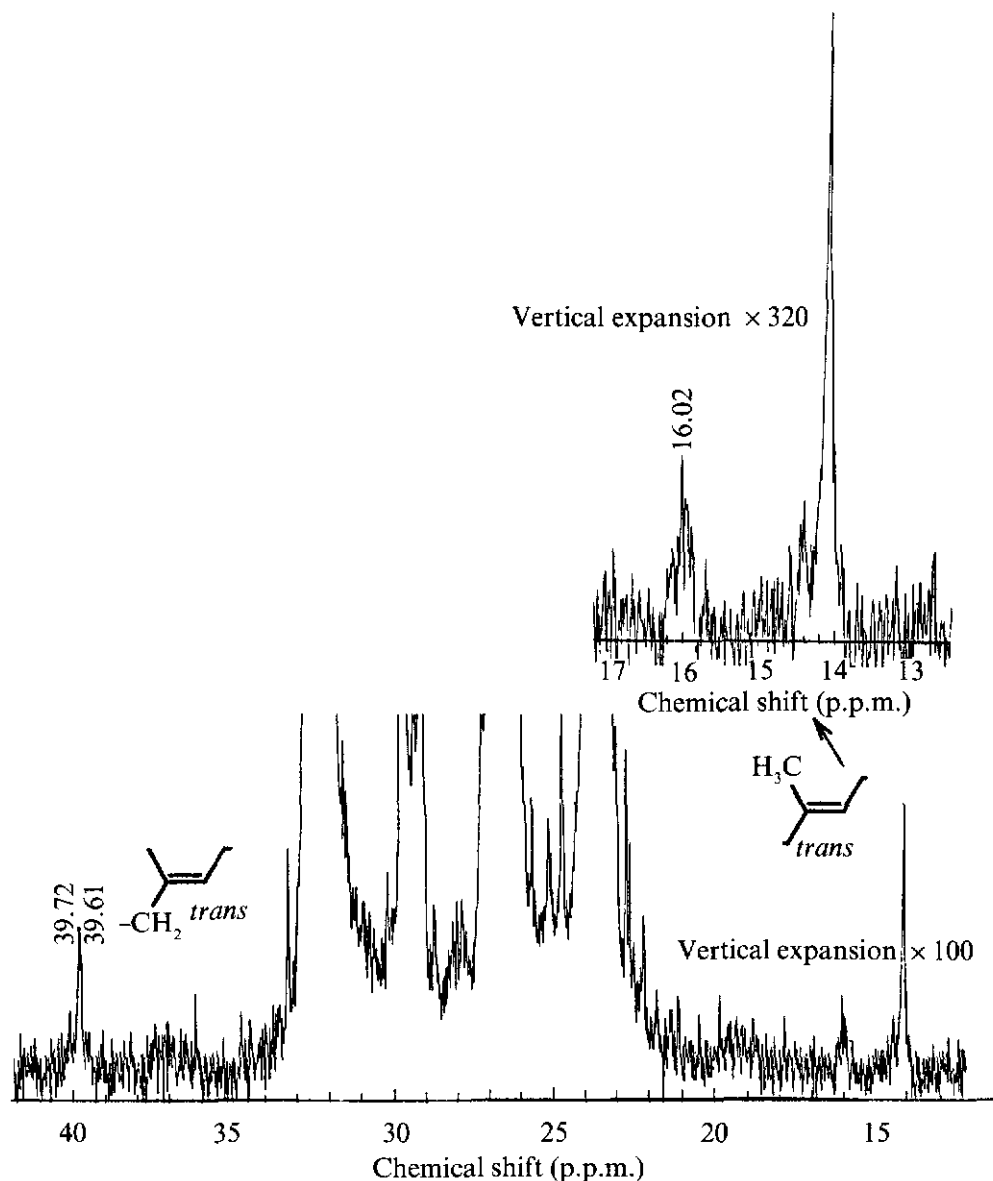


Figure 4.  $^{13}\text{C}$ -NMR confirmation of trans-alkene content in natural rubber (SMR 5).

TABLE 2. TRANS-ALKENE CONTENT FOR BOTH SOL AND GEL PHASES IN BALE GRADES OF MALAYSIAN NATURAL RUBBER

Bale grade	Trans-alkene content (mole%)	
	Sol fraction alone	Sol and gel fractions
SMR L	0.44	0.29
SMR L	0.51	0.51
SMR 5	0.42	0.41
SMR 5	0.79	0.24
SMR 10	0.40	0.30
SMR 10	0.51	0.55

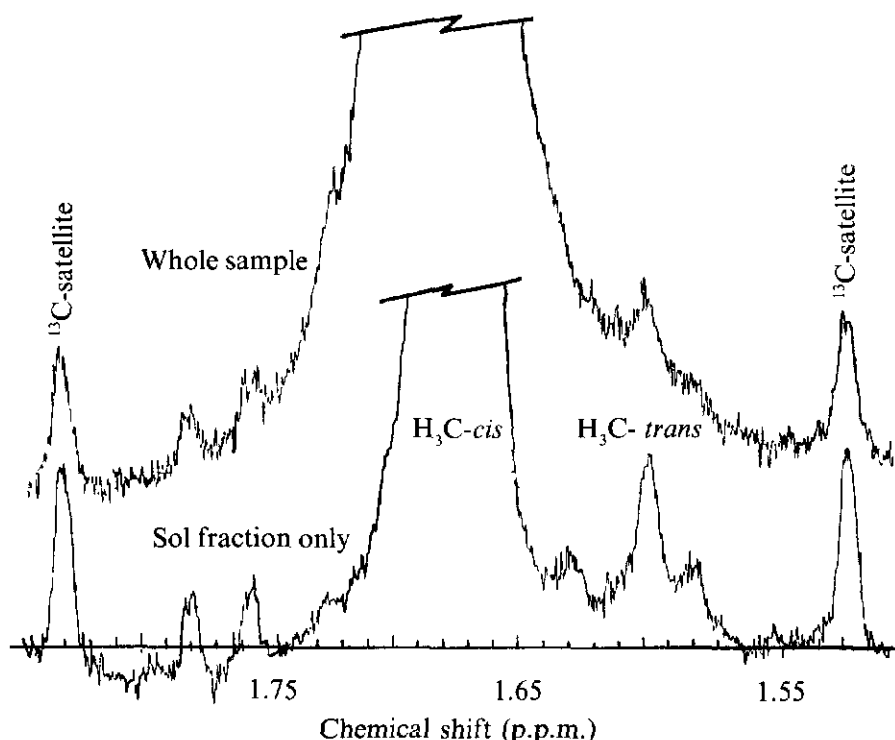


Figure 5. Comparative  $^1\text{H}$ -NMR spectra for whole and fractionated natural rubber.

methyl group. This led to severe peak overlap with the *trans*-alkene resonance and a consequent loss in accuracy (Figure 5).

#### CONCLUSION

The occurrence of *trans*-alkene units in the predominantly *cis*-1,4-polyisoprenoid structure of natural rubber has been demonstrated using  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopy.  $^1\text{H}$ -NMR spectroscopy at 400 MHz has been used to determine the *trans*-alkene content of a selection of grades of natural rubber and modification levels between 0.20 mole% and 0.79 mole% have been measured. Comparative  $^1\text{H}$ -NMR analyses of whole and fractionated samples of natural rubber demonstrate structural homogeneity for *trans*-alkene unit content between the sol and gel phases of natural rubber.

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