

Characterisation of the Chemical Structure of Sulphur Vulcanisates of Natural Rubber Using ^1H NMR Spectroscopy¹

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^1H NMR investigation of the chemical structure of crosslink sites in rubber vulcanisates has not been considered viable because of the line-broadening effects that occur, even in the swollen state. A procedure is now described which produces high resolution ^1H NMR spectra of polymer recovered from a natural rubber gum vulcanisate and examined in solution. The vulcanisation is specifically prepared to be free from monosulphidic crosslinks and it is disrupted under mild conditions using established thiol exchange chemistry. The spectroscopic information is interpreted in terms of characteristic protons on the carbon atoms at the sulphuration site. Conditions of sample preparation are discussed in detail, as is the justification for interpretation of the data in terms of pendent thiol groups rather than pendent disulphidic groups. Spectral assignments for relevant model thiols are tabulated.

For largely historical reasons, there is more published literature on the vulcanisation chemistry of natural rubber (NR) and synthetic polyisoprene than for other elastomers. An extensive, although still incomplete knowledge base has been generated²⁻⁵. New experimentation periodically stimulates further activity and in recent years renewed interest in the detailed chemical characterisation of network sulphuration sites has been generated by the development of high resolution ^{13}C NMR techniques for the direct characterisation of solid vulcanisates⁶⁻⁹. These techniques are being applied to vulcanisates of several elastomers other than polyisoprene¹⁰⁻¹⁴.

From the standpoint of reliable chemical characterisation, there is much to be gained from a comparison of high-resolution ^{13}C and ^1H NMR spectra of the same sample, but such a comparison is not readily attainable for vulcanisates. Although natural abundance ^{13}C provides ample sensitivity for characterisation

of the polymer backbone in either solid state or solution NMR spectroscopy, the detection of crosslink reaction sites relies on the concentration effect of the solid state measurement for its results. On the other hand, ^1H NMR spectroscopy does not have the inherent limitation of isotope abundance, but line-broadening presents a serious limitation to interpretation. Spectra of solid elastomers with line widths as low as 0.2 p.p.m. have only recently been reported¹⁵.

The purpose of the present paper is to demonstrate that there is sufficient inherent sensitivity in the ^1H NMR measurement to allow the examination of sulphuration sites on polymer which has been recovered into solution after vulcanisation. For the spectra to be meaningful in comparisons with solid-state carbon work and for them to successfully complement that work in interpreting vulcanisation chemistry, the disruption of the network must be achieved under the mildest

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possible conditions. To establish the principles of the procedure, we have chosen to work with a specially prepared gum vulcanisate of natural rubber in which the network is highly polysulphidic and maturation to form monosulphidic crosslinks is essentially absent. Thiol exchange chemistry at ambient temperature produces complete dissolution of this network and, given careful attention to handling procedures, good quality ^1H NMR spectra are obtained at 400 MHz. The paper will concentrate specifically on the methodology of obtaining interpretable ^1H -NMR spectra and on comparison with relevant model compound spectra. Discussion of other issues as the absolute levels of crosslink residues, the incursion of oxidation chemistry and the extension of the approach of other vulcanisates will be deferred to a later publication.

EXPERIMENTAL

General

Natural rubber (NR) was commercial SMRL (Malaysia). The polymer microstructure was >99.7% *cis*-1,4-polyisoprene as assessed from the ^1H NMR signal at 1.60 p.p.m. for methyl protons on *trans*-1,4- units, relative to the signal for *cis*-1,4- methyl groups at 1.68 p.p.m.¹⁶ Zinc oxide and sulphur were commercial materials used as received; 2,6-di-*tert*-butyl-4-methylphenol (BHT) was Aldrich Gold Label reagent. Hexanethiol and piperidine were Aldrich Reagent grade and solvents for purification of the soluble rubber were Analytical Reagent grade. Solvents were degassed under reduced pressure in an ultrasonic bath and were subsequently saturated with nitrogen. Nitrogen was bubbled through samples of solvents for 5 min immediately before they were used.

Vulcanisate Preparation

The cyclohexylammonium salt of benzothiazole-2-thiolate (CBM) was prepared from

benzothiazole-2-thiol (MBT) and excess cyclohexylamine in acetone/diethyl ether and was recrystallised from toluene¹⁷. The vulcanisation recipe was NR (100), zinc oxide (5), CBM (2.7), sulphur (10), BHT (1). The mix was prepared as a 500 g batch on a two-roll mill and sheets (1 mm thick) were press-cured for 8 h at 80°C.

Model Thiol Synthesis

A mixture of (*Z*)- and (*E*)-2-methylpent-2-ene-1-thiols (**9** and **10**) and 2-methylpent-1-ene-3-thiol (**11**) was prepared by published procedures¹⁸, as follows. 2-Methylpent-2-enal, obtained by basic self-condensation of propanal, was reduced with lithium aluminium hydride to 2-methylpent-2-enol, which was transformed to 1-chloro-2-methylpent-2-ene (together with some 3-chloro-2-methylpent-1-ene) using phosphorus trichloride/pyridine. The mixture of thiols was obtained from the chlorides by initial reaction with thiourea followed by hydrolysis of the mixture of *S*-(2-methylpent-2-enyl) thiuronium chlorides with sodium hydroxide. Fractional distillation under reduced pressure provided samples with the methylpentene-3-thiol considerably enriched or almost completely excluded.

A mixture of (*Z*)- and (*E*)-2,6-dimethylocta-2,6-diene-5-thiols (**1** and **2**) containing a small amount of (*Z*)-2,6-dimethylocta-2,5-diene-7-thiol (**3**) was prepared by the following published reaction sequence^{19,20}. Ethyl 2-ethoxycyclopropanecarboxylate, obtained by copper-catalysed reaction of ethyl diazoacetate with ethyl vinyl ether, was reacted with methylmagnesium iodide to give 2-(2-ethoxycyclopropyl)propan-2-ol which was hydrolysed to give 4-methylpent-3-enal. Reaction of the aldehyde with 1-methylprop-1-enylmagnesium iodide²¹ gave (*E*)-2,6-dimethylocta-2,6-dien-5-ol, together with a small amount of the (*Z*)-isomer (**14**). Reaction of the dienols with thioacetic acid and the

complex of di-isopropyl azodicarboxylate with triphenylphosphine gave a mixture of isoallylic thioacetates, which were reduced to the thiols with lithium aluminium hydride.

(*Z*)-2,6-dimethylocta-2,6-diene-4-thiol (**4**), together with smaller amounts of the (*E*)-isomer (**5**) and (*E*),(*Z*)- and (*E*),(*E*)-2,6-dimethylocta-3,6-diene-2-thiols (**6** and **7**), was prepared by lithium aluminium hydride reduction of the corresponding thioacetate mixture¹⁹, which was obtained by the following reaction sequence^{19,20}. 3-Methylpent-3-en-1-ol, from reaction²¹ of 1-methylprop-1-enylmagnesium bromide with oxirane, was oxidized to the aldehyde using pyridinium chlorochromate buffered with sodium acetate. Reaction of the aldehyde with 2-methylprop-1-enylmagnesium bromide²¹ gave 2,6-dimethylocta-2,6-dien-4-ol, which with thioacetic acid and di-isopropyl azodicarboxylate/triphenylphosphine gave the mixture of isoallylic thioacetates.

2,6-Dimethyloctane-3-thiol (**8**) was prepared by UV-initiated addition of mercaptoacetic acid to 2,6-dimethyloct-2-ene, followed by hydrolysis with aqueous-ethanolic potassium hydroxide²².

The thiol structures are summarised in *Figure 1* and the high field ¹H and ¹³C NMR data are collated in *Tables 1-4*.

Recovery of Soluble Polymer

Soluble polymer was recovered from the vulcanisate by the following 'probe reagent' treatment. A solution of hexane-1-thiol (1M, 75 cm³) in piperidine was added to a sample of vulcanisate (1 g) under nitrogen at room temperature. The sample was gently agitated at intervals during 48 h, by which time complete dissolution had occurred. The solution was run slowly into methanol (375 cm³) and the precipitated polymer was collected around a clean glass rod. The polymer was rinsed with

fresh methanol (3 × 25 cm³) and re-dissolved in dichloromethane containing approx. 0.1% v/v formic acid to make a 1% w/v solution. The sample was gently agitated in a closed flask in the absence of light for 24 h and the resultant solution was filtered through two layers of lens cleaning tissue into five times its volume of methanol. The precipitated polymer was rinsed and re-dissolved in dichloromethane/formic acid, as before, and a final precipitation of filtered solution was made into acetone/water (85:15, v/v). The polymer was rinsed with acetone (3 × 25 cm³) and quickly surface-dried on filter paper. A sample (*ca.* 150 mg) was immediately weighed into deuteriochloroform containing one drop of a solution of formic acid in deuteriochloroform (10%, w/w), to make a 3% w/v solution of polymer. If dissolution was poor, additional drops of formic acid solution were added. Reprecipitated polymer was never allowed to dry before being redissolved. The deuteriochloroform solutions were stored at 0 – 4°C in the absence of light until spectra were recorded. A sample of the unvulcanised rubber mix was subjected concurrently to the same sequence of thiol treatment and polymer recovery.

Spectral Measurement

¹H NMR spectra of polymer solutions were obtained on a Varian VXR-400 spectrometer operating at 400 MHz, using tetramethylsilane as reference, and a pulse width of 23°. The spectra were obtained from a minimum of 6000 transients with a delay time of 4.3 s, giving near-quantitative conditions for the main polymer signals (*T*₁ relaxation times for the main NR signals were measured at 25°C in deuteriochloroform solution and are all <2 s). Reference spectra for model compounds were recorded on a General Electric QE300 spectrometer at 300 MHz (¹H) or 75 MHz (¹³C) or on the Varian VXR-400 spectrometer at 400 MHz (¹H) or 100 MHz (¹³C) in deuterio-

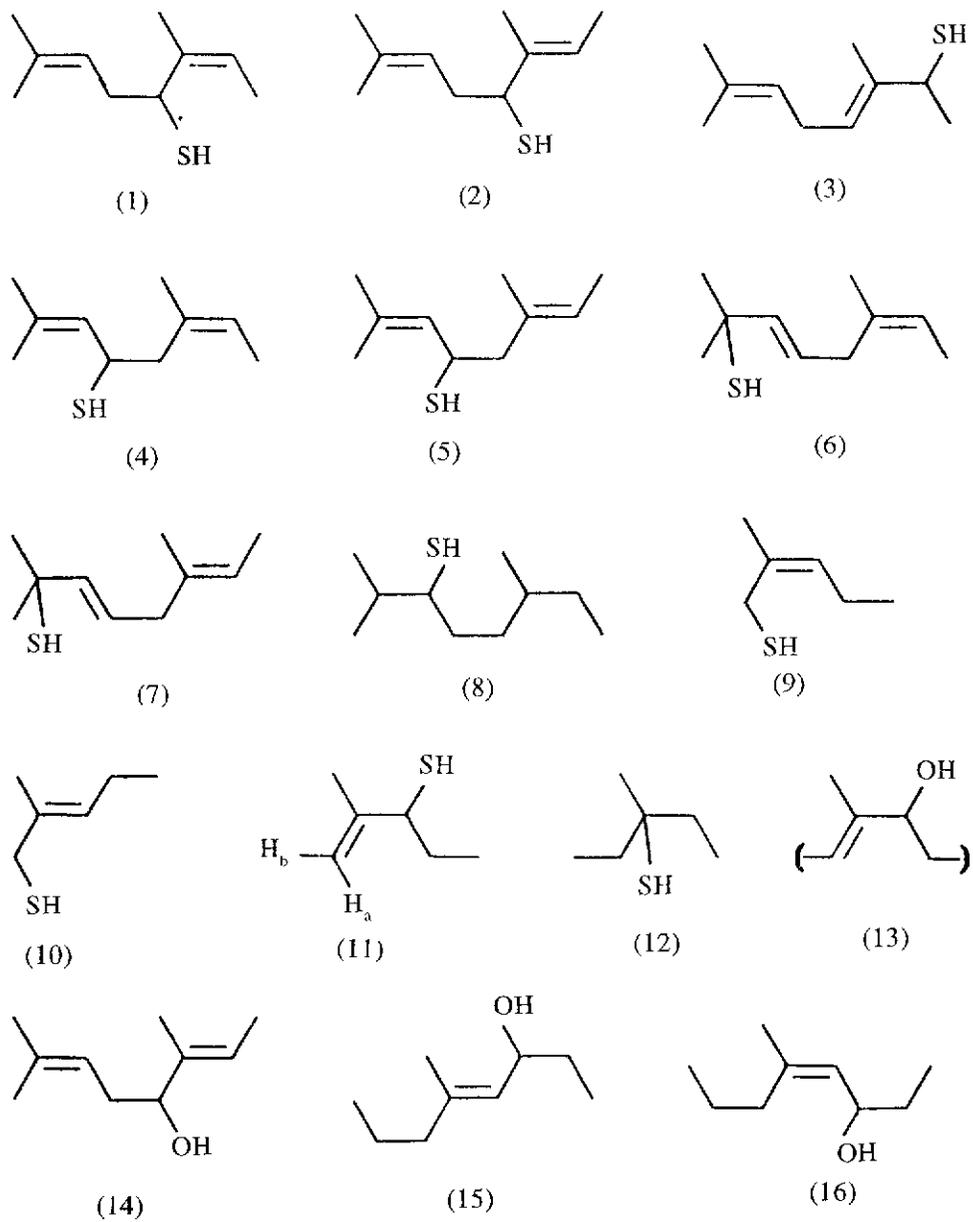


Figure 1. Model chemical structures.

TABLE 1. ¹H NMR DATA FOR (Z)- AND (E)-2,6-DIMETHYLOCTA-2,6-DIENE-5-THIOLS (1 AND 2), (Z)-2,6-DIMETHYLOCTA-2,5-DIENE-7-THIOL (3), (Z)- AND (E)-2,6-DIMETHYLOCTA-2,6-DIENE-4-THIOLS (4 AND 5), (E),(Z) AND (E), (E)-2,6-DIMETHYLOCTA-3,6-DIENE-2-THIOLS (6 AND 7), AND 2,6-DIMETHYLOCTANE-3-THIOL (8): δ (p.p.m.); COUPLING CONSTANTS (HZ)

Position	1 ^a	2 ^a	3 ^b	4 ^c	5 ^c	6 ^d	7 ^d	8 ^e
1	1.633(br s)	-	-	1.656(br s)	-	1.488(s)	1.496(s)	0.973/0.915/ 0.908
2-Me	1.700(d)	-	-	1.695(br s)	-	1.488	1.496	(3xd)
2	-	-	-	-	-	-	-	1.859/1.850 (2xdsp)
3	5.028(tsp)	5.028(tsp)	5.078(tm)	5.131(dsp)	5.094(d)	5.705(dt)	5.694(dt)	2.676/2.700 (2xp)
4	2.22-2.40(m)	-	2.70(m)	3.926(dtd)	3.89(m)	5.403(dt)	5.453(dt)	1.35-1.70(m)
5	4.017(dt)	3.486(dt)	5.302(br t)	2.327(dABq)	2.245(dABq)	2.736(d)	2.67(d)	1.3-1.6(m)
6	-	-	-	-	-	-	-	1.33(m)
6-Me	1.727(p)	1.668(p)	-	1.680(p)	-	-	-	0.870(d)
7	5.249(qq)	5.415(dqq)	3.657(p)	5.343(qq)	5.281(m)	-	-	1.15/1.33 (2xm)
8	1.61(dq)	-	1.383(d)	1.609(d)	-	-	-	0.867/0.872 (2xt)
SH	1.59(d)	1.59(d)	-	1.591(d)	-	-	-	1.125(2xd)
<i>J</i> _{1/2 Me 2}	-	-	-	-	-	-	-	6.7
<i>J</i> _{1,3}	~1.3	~1.3	~1.4	1.3	-	0	0	-
<i>J</i> _{2,3}	-	-	-	-	-	-	-	3.9/4.0
<i>J</i> _{3,4}	7	7	5.7?	9.8	9.7	15.3	15	8.7
<i>J</i> _{3,5}	0	0	-	0	0	1.5	1.5	-
<i>J</i> _{4,5}	7.7	7.5	7.0?	7.5	8	6.6	6.6	-
<i>J</i> _{5,7}	~0	0.6	-	~0	~0	~0	~0	-
<i>J</i> _{7,8}	6.9	6.7	6.9	6.8	-	-	-	7.2
<i>J</i> _{3,2 Me}	1.2	1.2	~1.4	1.3	-	0	0	-
<i>J</i> _{6,6-Me}	-	-	-	-	-	-	-	6.6
<i>J</i> _{7,6 Me}	1.3	1.3	-	1.0	-	-	-	-
<i>J</i> _{8,6-Me}	1.5	1.2	-	1.3	-	-	-	-
<i>J</i> _{CH SH}	5.0	5.0	-	3.8	-	-	-	7.2
<i>J</i> _{5a 5b}	-	-	-	13.5	-	-	-	-

^a4-H₂ and 5-H, 5-H and SH decoupled

^b7-H and 8-H₃ decoupled

^c7-H and 8-H₃, 7-H and 6-Me, 3-H and 1-H₃, 3-H and 2-Me, 3-H and 4-H, 4-H and SH, 4-H and 5-H₂ all decoupled

^d3-H, 4-H and 5-H₂ decoupled

^e1-H₃/2-Me and 2-H, 2-H and 3-H, 3-H and 4-H₃, 3-H and SH, 6-H and 6-Me, 7-H₂ and 8-H₃ all decoupled

TABLE 2. ¹³C NMR DATA FOR (Z)- AND (E)-2,6-DIMETHYLOCTA-2,6-DIENE-5-THIOLS (1 AND 2), (Z)- AND (E)-2,6-DIMETHYLOCTA-2,6-DIENE-4-THIOLS (4 AND 5), (E),(Z)- AND (E),(E)-2,6-DIMETHYLOCTA-3,6-DIENE-2-THIOLS (6 AND 7), AND 2,6-DIMETHYLOCTANE-3-THIOL (8): δ (p.p.m.)

Position	1	2	4	5	6	7	8
1		17.70	17.9	17.5?	32.2		17.1/17.3/
2-Me		25.69		25.6	32.2	-	19.1/19.3
2	133.81	133.59	132.6	132.0?	42.5		34.3/34.4 ^a
3	121.43?	121.67?	128.0	128.0?	140.1	140.6	48.3/48.4/ 48.5/48.5
4	34.88	35.24	36.3	36.6	127.2?	-	34.5/34.6 ^b
5	39.26	48.89	40.9	49.4	34.3	39.2?	33.9/34.1 ^b
6	136.83	137.30	132.9	133.1?	134.0?	-	33.3/33.6 ^a
6-Me	18.05	11.70?	23.4	15.0?	23.8?	-	20.4/20.5
7	121.19?	120.53?	122.1	121.2?	119.8?	-	29.2/29.6
8	12.94?	13.34?	13.6	13.4?	13.3	-	11.3/11.4

^{a,b}Assignments may be interchanged

TABLE 3. ¹H NMR DATA FOR (Z)- AND (E)-2-METHYLPENT-2-ENE-1-THIOLS (9 AND 10), 2-METHYLPENT-1-ENE-3-THIOL (11), AND 3-METHYLPENTANE-3-THIOL (12): δ (p.p.m.); COUPLING CONSTANTS (Hz)

Position	9 ^a	10 ^b	11 ^c	12
1	3.135 (d)	3.12 (dd)	a 4.86 (m) b 4.76 (p)	0.96 (t)
2	-	-	-	1.59/1.61 (2 × dq)
2-Me	1.80 (d)	1.72 (d)	1.78 (m)	-
3	5.18 (tm)	5.33 (tq)	3.38 (dt)	-
3-Me	-	-	-	1.29 (s)
4	2.01 (p)	2.01 (p)	1.66 (dq)	1.59/1.61 (2 × dq)
5	0.92 (t)	0.95 (t)	0.97 (t)	0.96 (t)
SH	1.42 (t)	1.39 (t)	1.57 (d)	1.47 (s)
<i>J</i> _{CH,SH}	7.6	7.6	6.1	-
<i>J</i> _{1,3}	~0	~0.5?	-	-
<i>J</i> _{3,4}	7.4	7.3	7.5	-
<i>J</i> _{4,5}	~7	7.6	~7	7.5/7.8
<i>J</i> _{3,2-Me}	1.3	1.1	-	-

^a1-H and 3-H, 1-H and SH decoupled

^b1-H and SH decoupled

^c3-H and 1-H_a, 3-H and 4-H₂, 3-H and 6-H₃, 3-H and SH all decoupled; *J*_{1a,1b} 1.5 Hz, *J*_{1a,6} 0.8 Hz, *J*_{1b,6} 1.5 Hz

TABLE 4 ^{13}C NMR DATA FOR (Z)- AND (E)-2-METHYLPENT-2-ENE-1-THIOLS (9 AND 10), 2-METHYLPENT-1-ENE-3-THIOL (11), AND 3-METHYLPENTANE-3-THIOL (12) δ (p p m)

Position	9	10	11	12
1	25.3	34.0	113.1/111.6	9.19
2	133.6	133.6	144.1/147.1	36.35
2-Me	21.9 ^a	14.0 ^b	17.5	-
3	129.0	128.7	53.1/48.3	49.11
3-Me	-	-	-	29.13
4	21.1 ^a	21.3	29.4	36.35
5	14.4	14.5 ^b	12.2	9.19

^{a,b}Assignments may be interchanged

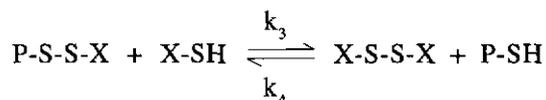
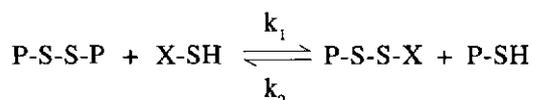
chloroform, also using tetramethylsilane as reference

RESULTS AND DISCUSSION

Thiol - disulphide Exchange

Procedures for selective cleavage of polysulphidic crosslinks and for cleavage of poly- and disulphidic crosslinks in sulphur vulcanisates have been in use for some considerable times^{23,24}. For these procedures to be reliable, the crosslinks must be transformed at least as far as pendent disulphidic groups but the further transformation to rubber-bound thiol is not essential. When this same chemistry is applied to the recovery of soluble polymer for ^1H NMR examination, the signals that are observed from protons on or adjacent to the crosslink sites will depend on whether these sites carry thiol or disulphide functionality. There is therefore a need to re-assess the thiol-disulphide equilibrium situation of thiol probe reaction conditions in terms of the expected contributions of pendent thiol and pendent disulphide.

The equilibration of reagent thiol (X-SH) with disulphidic crosslinks (P-S-S-P) can be represented by the equations



The reaction of polysulphides can be reduced to the same pair of equations *via* the elimination of one molecule of H_2S for each atom of sulphur in the crosslink in excess of two. The equilibria have been discussed by Gorin *et al*²⁵ in terms of the constants $K_1 = k_2/k_1$ and $K_2 = k_4/k_3$. For the present purposes, their algebraic relationships were replaced by an iterative numerical procedure involving individual rate constants. No differentiation between ionised and un-ionised thiol species was made because we consider that free ions do not occur under the probe reagent conditions and that the thiol is fully associated with the amine by hydrogen bonding.

The absolute values assigned to the rate constants are not important, but the relative values are. From a consideration of known equilibrium constants^{25,26}, we deduce that, where XSH is hexane-1-thiol, $k_1 \geq k_2$ and $k_3 \geq k_4$. The upper limit for the chemical crosslink concentration in a highly crosslinked poly-

isoprene network may be taken as 20 mmol/100 g rubber, which is equivalent to a homogeneous solution concentration of $2.7 \times 10^{-3} M$ for the sample weight to solvent ratio used in the present experiments. Making a simplifying assumption that $k_1 = k_3$, the results in *Figure 2* are obtained for the amounts of residual disulphidic crosslink and pendent disulphide as a function of the ratio k_1/k_2 , when the reaction has reached equilibrium. Even for a statistical distribution of products ($k_1 = k_2$), the concentration of pendent disulphide groups is only about 1% of the total crosslink sites and that of the residual crosslinks is only a very small fraction of 1%.

For a primary thiol probe reacting with a more crowded crosslink, the equilibria should be biased to further reduce the levels of pendent

disulphide and crosslink. There are therefore good grounds for interpreting the relevant 1H NMR spectral data in terms of rubber-bound thiol functionality only.

Vulcanisate Preparation

Some rationalisation of the choice of vulcanisation conditions for this study is appropriate. Polysulphidic crosslinks are associated with early stages of cure^{3,4,24} or low cure temperatures²⁷. An essentially polysulphidic network can be generated in NR by stopping an accelerated sulphur cure having a high sulphur to accelerator ratio some way before the attainment of optimum crosslinking²⁴ but the timing of such an exercise is difficult to control with sufficient precision to prevent the incursion of enough monosulphidic

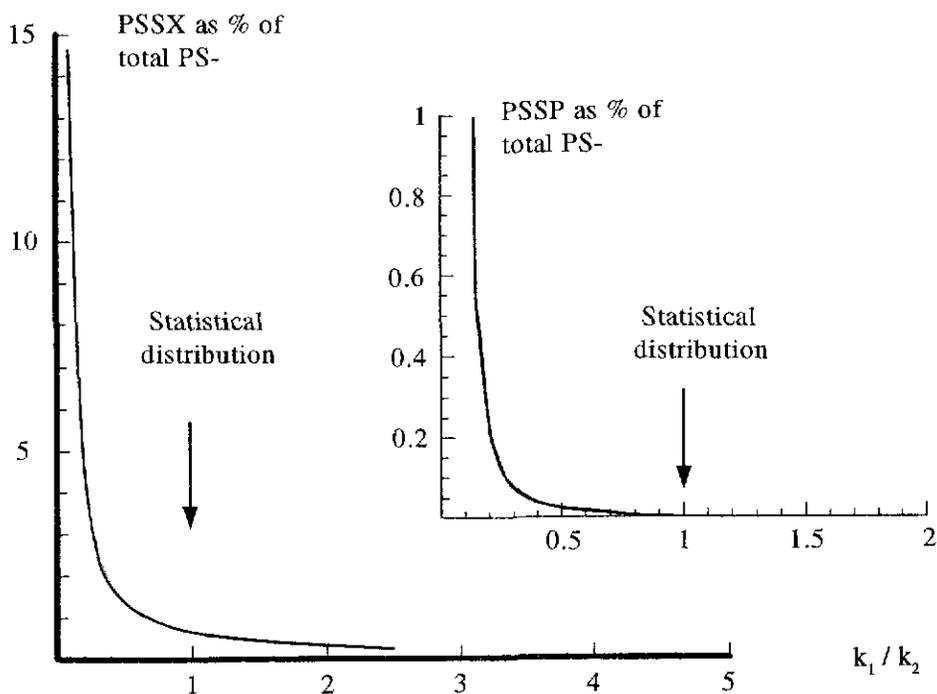


Figure 2. Dependence of residual disulphidic crosslink (PSSP) and pendent disulphide (PSSX) concentrations on the rate constant ratio k_1/k_2 .

crosslinks to prevent dissolution of the network. The cure chosen for the present work addresses these difficulties in the following ways:

- a) The cure temperature was reduced considerably to obviate difficulties of timing and also to reduce the desulphuration and thermal decomposition of polysulphidic crosslinks and polysulphidic pendent groups^{4,27,28}. The activation energies for crosslink shortening and crosslink destruction (reversion) are significantly higher than that for crosslink insertion.
- b) The unnecessarily long scorch delay of a sulphenamide cure at low temperature was dispensed with by using MBT as its amine salt. The activating effect of the amine on the rate of sulphuration of the polymer was, however, retained, giving a close resemblance to the normal sulphenamide cure chemistry.
- c) A high sulphur loading was used to encourage interaction of the active accelerator complex with elemental sulphur rather than with sulphur in polysulphidic crosslinks. The accelerator loading was also higher than normal, but the cure was not continued to an 'optimum' or 'maximum crosslinking' level. The resultant vulcanisate had a crosslink density higher than normal, but considerably less than that potentially available from the total sulphur loading.
- d) Zinc oxide was included to ensure the formation of active zinc-accelerator complexes²⁹, but fatty acid or zinc soaps were omitted on the grounds that carboxylate complexes are particularly effective at causing crosslink shortening²⁹.

These conditions should ensure that the crosslink insertion chemistry is observed with little or no side reactions. The curing behaviour is shown in *Figure 3*.

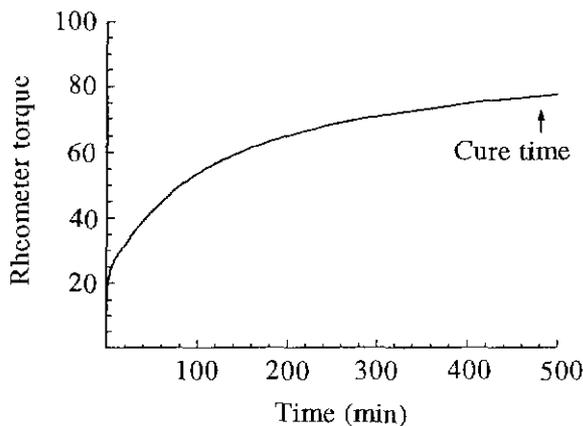


Figure 3. Gottfert elastograph at 80°C of the mix NR (100), zinc oxide (5), CBM (2.7), sulphur (10) and BHT (1).

Vulcanisate Dissolution

Samples of the vulcanisate dissolved completely in the hexanethiol probe reagent. It was, however, necessary to exercise considerable care during the subsequent purification steps to minimise reformation of gel. In particular, samples were not allowed to dry out between precipitations. Even so, occasionally some polymer was lost as loose gel before the final solution in deuteriochloroform was obtained. One reason for gel formation is that the thiol groups on the rubber, formed in the course of the dissolution process, are readily oxidised to disulphides under basic conditions. Addition of formic acid served to neutralise traces of piperidine and minimise this oxidation. A contribution to gel formation may also have arisen from secondary interactions (*e.g.* hydrogen bonding) of functional groups on the treated polymers. Piperidine (the solvent for the initial dissolution process) is not only a

good solvent for polydienes, it is also a strongly solvating and hydrogen bonding solvent. Furthermore, the hydrogen bonding characteristics of piperidine are opposite to those of chloroform or deuteriochloroform. It is therefore possible that deuteriochloroform, even in the presence of small amounts of formic acid, was less able to disrupt secondary interactions. Support for this view comes from the observation that traces of the base DABCO (1,4-diazabicyclo[2,2,2]octane) were effective in assisting dissolution in dichloromethane, although its use was inappropriate from the point of view of base catalysed oxidation of thiol groups.

Spectral Characterisation

The major features of the spectrum of the recovered polymer are shown in *Figure 4*. The very sharp singlet at 2.174 p.p.m. and the small singlet at 5.301 p.p.m. are residual acetone and dichloromethane, respectively, from the polymer recovery procedure. The signals centred at 1.68, 2.04 and 5.13 p.p.m. are from the methyl, methylene and methyne protons of unmodified *cis*-1,4-polyisoprene. Other minor signals can be detected, but the spectrum is featureless between 2.5 and 5 p.p.m. on this expansion scale. However, expansion between 3 and 4 p.p.m. (*Figure 5*) reveals several groups of signals which are not present in the spectrum of the rubber recovered from the mix before vulcanisation and are therefore directly ascribable to the products of the vulcanisation process. This chemical shift region is free from extraneous signals in raw NR and also lies largely within a window between the groups of signals at 3.9-4.2 and 2.6-2.8 p.p.m. which appear in autoxidised NR.

The accelerated sulphuration of NR is considered to occur primarily through substitution at an allylic hydrogen atom^{2,4}, as shown in *Figure 6*, where the A, B and D

nomenclature follows the practice adopted at the Malaysian Rubber Producers' Research Association. The C category is assigned to products of addition to the double bond, corresponding to the model structures **8** and **12**, but is not considered to be significant in the early stages of accelerated sulphur vulcanisation or at low cure temperatures^{2,4}. Five of the six possible allylic structures (ignoring *cis-trans* isomers) have a hydrogen atom on the site of sulphuration of the polymer chain. The sixth structure (A₂) has no such hydrogen atom but, on the basis of model sulphuration chemistry, it is expected to make very little contribution to the total crosslink sites. The data for model compounds in *Tables 1* and *2* indicate that the protons at the sulphuration sites should resonate in the chemical shift region 3-4 p.p.m., *i.e.* there is a down-field shift relative to saturated primary and secondary thiols³⁰, arising from the effect of the adjacent double bond. The signals in the expanded spectrum of the recovered rubber therefore lie in the chemical shift region anticipated for crosslink sites.

The most prominent feature of the expanded spectrum is the sharp doublet (3.14 p.p.m., 77.5 Hz) whose position and coupling constant corresponds closely to those of the protons in the thiol-substituted 1-position of model compounds **9** and **10** (**9**: 3.135 p.p.m., d, $J_{\text{CH,SH}}$ 7.6 Hz. **10**: 3.12 p.p.m., dd, $J_{\text{CH,SH}}$ 7.6 Hz, $J_{1,3}$ ~0.5 Hz). Although the model compounds **9**, **10**, and **11** are deficient in the substitution of one of the γ -carbon atoms, such substitution is of minor significance in determining the chemical shift in ¹H-NMR spectra. Thus the methyl protons *trans* to the ethyl substitution in 2-methylpent-2-ene resonate at 1.683 p.p.m. and those in the methyl group of natural rubber at 1.679 p.p.m. Similarly, the methyl protons *cis* to the ethyl substitution in 2-methylpent-2-ene resonate at 1.600 p.p.m. and those in the methyl group of *trans*-1,4-polyisoprene at

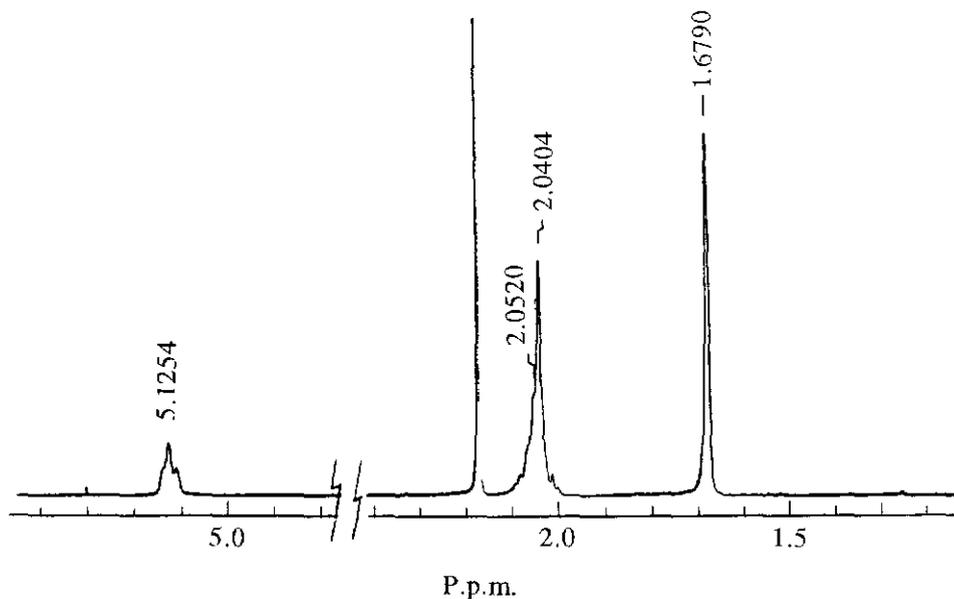


Figure 4. ^1H NMR spectrum of soluble rubber regenerated from the NR vulcanisate.

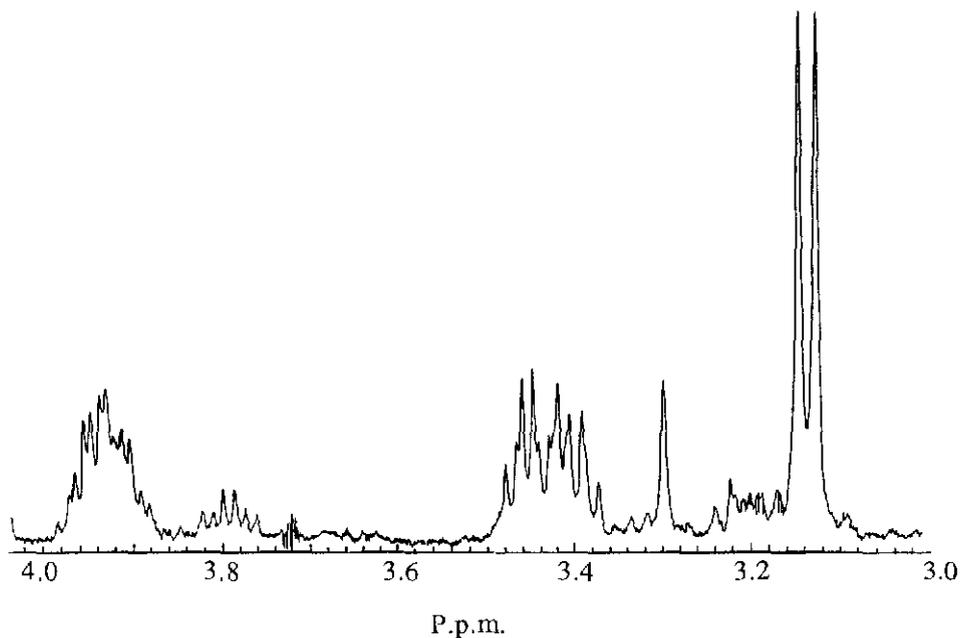


Figure 5. ^1H NMR spectrum of soluble rubber regenerated from the NR vulcanisate: protons at the sulphuration sites.

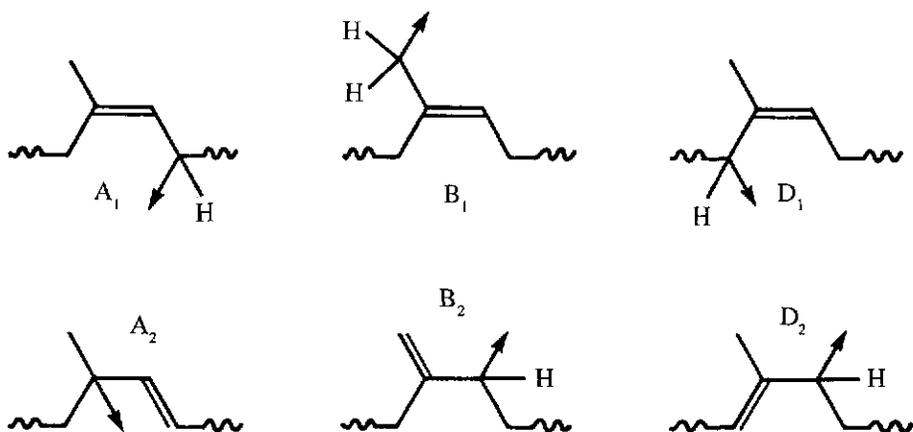


Figure 6. Structures produced by allylic substitution of *cis*-polyisoprene (11 possible structures, allowing for *cis*-*trans* isomerism).

1.599 p.p.m. The doublet at 3.14 p.p.m. can be assigned with some confidence to the *cis*- or the *trans*-B₁-thiol structures (or a mixture of the two), where sulphuration of the polymer chain has occurred at the out-of-chain methyl group. The small difference in chemical shift seen for the *cis*- and *trans*- isomers in the models is not reliably detected in the polymer spectra. In one instance, a spectrum was recorded in which some small splitting of the peaks in the 3.14 p.p.m. doublet was present but the observation appeared to be critically dependent on the conditions of measurement (solution viscosity, *etc*). An expected partner to the B₁ thiol is the isoallylic B₂ thiol, where sulphuration is at an in-chain carbon atom and the double bond has moved into the out-of-chain position. The relevant model is compound **11** (3.38 p.p.m., dt, $J_{\text{CH,SH}}$ 6.1 Hz, $J_{3,4}$ 7.5 Hz). The polymer spectrum has a complex group of peaks between 3.35 and 3.5 p.p.m. which can reasonably be interpreted as two adjacent dt structures centred at 3.399 p.p.m. (J 6.0/7.3 Hz) and 3.454 p.p.m. (J 4.6/7.5 Hz) with an additional singlet at

3.419 p.p.m. (Figure 7a). Of the two groups of signals with the expected splitting pattern, the group at 3.399 p.p.m. matches more closely the chemical shift and coupling constants of compound **11**. The assignment is not entirely unambiguous because of uncertainties, discussed below, about the exact assignment of signals from the *trans*-D₁ and -D₂ polymer-structures.

The other identifiable pattern within this complex group (3.454 p.p.m., dt, J 4.8/7.5 Hz) lies sufficiently close to the chemical shift of 5-H of compound **2** (3.486 p.p.m., dt, $J_{\text{CH,SH}}$ 5.0 Hz, $J_{4,5}$ 7.5 Hz) to suggest its identification as the *trans*-D₁ polymer structure. The splitting pattern and coupling constants support this assignment. Differentiation between *cis*- and *trans*-configurations in the pair of compounds **1** and **2** is very pronounced, and a little surprising, but given the existence of this difference, there seems little doubt that the polymer structure should be assigned as *trans*-. Signals for the *cis*-D₁ structure are expected to appear near 4.0 p.p.m., again with

a dt splitting pattern (model compound **1**: 4.017 p.p.m., dt, $J_{\text{CH,SH}}$ 5.0 Hz, $J_{4,5}$ 7.7 Hz). The polymer spectrum has a complex group of signals centred around 3.92 p.p.m. (discussed below) and a number of minor signals from 4.03 to 4.1 p.p.m. which are most probably due to alcohols or hydroperoxides arising from oxidation. There is no dt splitting pattern which can reasonably be identified with the *cis*-D₁ structure and we conclude that the structure does not make a significant contribution to the crosslinking under the vulcanisation conditions used in this work.

The best available model for the *trans*-D₂ polymer structure (isoallylic with D₁) is also compound **2** (Compound **3** may appear to be the more obvious model, but this has a methyl substituent at the site of sulphur attachment rather than an in-chain methylene group, while compound **2** has the correct structure extending as far as both γ -carbons). The *trans*-D₂-alcohol structure **13** in NR has been obtained through

singlet oxidation followed by triphenylphosphine reduction³¹. The proton on the alcoholic carbon resonates at 3.95 p.p.m.³², only 0.03 p.p.m. upfield from the corresponding proton in the model alcohol **14**, analogue of the model thiol **2**. This data indicates that compound **2** is indeed a good model for the *trans*-D₂-thiol polymer structure and that the signals should be expected at about 3.456 p.p.m. (3.486 - 0.03 p.p.m.), *i.e.* very close to those assigned to the *trans*-D₁ structure. Digital processing of the spectrum for enhanced resolution gives some grounds for believing that an additional group of signals may be present under those for the B₂ structure, but the extraction of a formal dt structural pattern is not justifiable. Thus we conclude that either the *trans*-D₁ and -D₂ dt patterns coincide at 3.454 p.p.m., or that one of them lies under the B₂ signals at 3.399 p.p.m.

The signals at 3.85–4.00 p.p.m. show additional complexity but can be interpreted

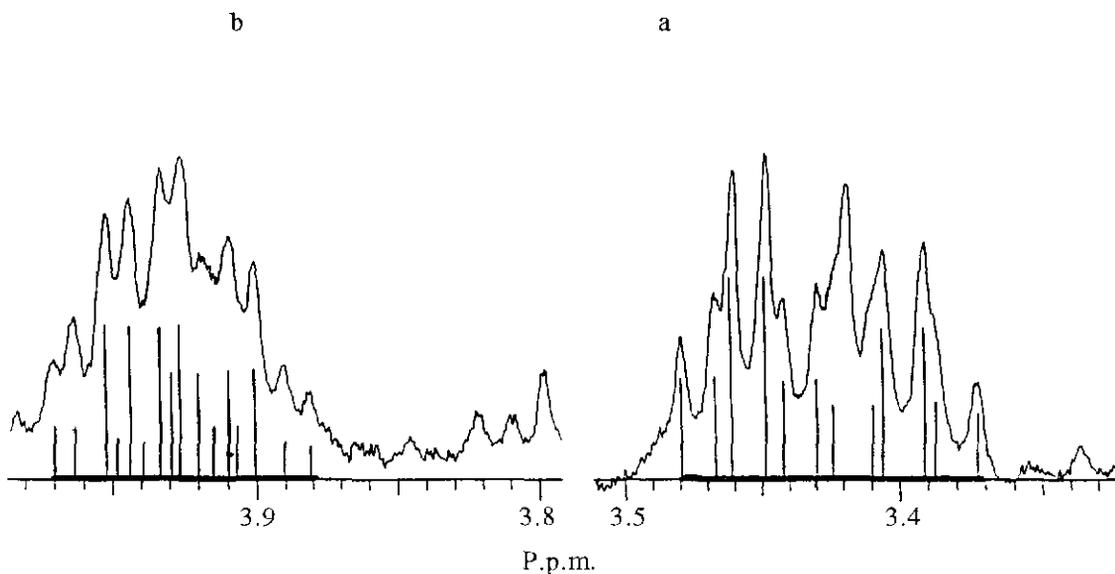


Figure 7. ¹H NMR splitting patterns of protons at (a) the B₂, *trans*-D₁ and *trans*-D₂ sites, and (b) the *cis*- and *trans*-A₁ sites.

by the following sequence of arguments. The chemical shift region is in agreement with that for the thiol-substituted 4-H of compounds **4** and **5** (**4**: 3.926 p.p.m., dtd, $J_{3,4}$ 9.8 Hz, $J_{4,5}$ 7.5 Hz, $J_{\text{CH,SH}}$ 3.8 Hz. **5**: 3.890 p.p.m., m, $J_{3,4}$ 9.7 Hz, $J_{4,5}$ 8.0 Hz, $J_{\text{CH,SH}}$ not determined), but **4** is the preferred model because it has the correct geometry at the adjacent double bond. If the 9.8 Hz and 7.5 Hz couplings are not resolved in the polymer structure, the dtd splitting pattern in the model reduces to an expected dq pattern, with the two quartets separated by the CH,SH coupling constant. On this basis, six out of eight expected signals of a double quartet can be identified at 3.939 p.p.m., J 3.0/7.3 Hz (Figure 7b). The signals at 3.909 and 3.900 p.p.m. are not part of this splitting pattern. Read in conjunction with the signals at 3.890 and 3.881 p.p.m., they can be assigned to a second dq pattern at 3.914 p.p.m., J 3.6/7.8 Hz, which does not conflict with that already described. Model compound **4** does not distinguish *cis*- and *trans*- isomerism about the double bond of the allylic thiol structure whereas such isomerism can occur in the polymer chain. The spectroscopic effect of the isomerism is expected to be small because it simply results in a change in the relative positions of the methyl and methylene groups on the γ -carbon atom. In unsubstituted polyisoprenes, the methylene protons at the A_1 site are shifted downfield by 0.03 p.p.m. when comparing the *trans*-units of *Gutta percha* (2.07 p.p.m.) with the *cis*-units of NR (2.04 p.p.m.). A similar but slightly smaller shift of 0.017 p.p.m. is observed when comparing the corresponding protons on the alcoholic carbons of the *trans*-alcohol **15** (4.294 p.p.m.) and the *cis*-alcohol **16** (4.277 p.p.m.)³³. We therefore believe that the double quartets centred at 3.914 and 3.939 p.p.m. are best ascribed to the *cis*- and *trans*- A_1 structures, respectively, in the approximate ratio 2:3.

The A_2 structures have no proton at the site of sulphuration. Based on the model compound **6**, olefinic resonances are expected at about 5.40 and 5.71 p.p.m. for the *trans*- A_2 polymer structure (the thermodynamically preferred A_2 structure). This region is downfield from the olefinic NR signal, but only very minor signals can be detected here are also present in spectra derived from the unvulcanised rubber mix. We conclude that there is little or no production of A_2 structures under our vulcanisation conditions.

Apart from very minor signals, the remaining components of the spectral region are the dt structure at 3.792 p.p.m., J 4.9/9.7 Hz, and the singlets at 3.419 and 3.299 p.p.m. These do not correspond to any of the model compound data and remain unidentified. However, their intensities vary considerably from sample to sample, unlike the signals assigned to the crosslink sites, suggesting that they arise from the sample preparation process rather than the vulcanisation. 3-H of the saturated thiol, compound **8**, resonates at 2.7 p.p.m., in the region expected for simple thiols. The polymer spectrum in this region is very complex. It is expected to contain the resonances from skipped dienes generated in the formation of D_2 , and possibly A_2 , structures (cf. compounds **3**, **6** and **7**) as well as skipped dienes and epoxides arising from autoxidation. The tertiary thiol, compound **12**, has no resonances in this region but, on the basis of model chemistry⁴, is a more likely structure. Based on this work, we are unable to exclude either saturated structure as contributing to the polymer crosslinking. Similar difficulties arise when attempts are made to substantiate the assignments of the sulphur structures by reference to the methyl, methylene and olefinic proton resonances. Information can be seen to be present but the complexity has yet to be unravelled. Two

further features should be mentioned, although full substantiation must await further publication. Firstly, there is no evidence of significant *cis-trans* isomerisation at sites removed from the sites of crosslinking and, secondly, there is evidence of significant autoxidation of the main polymer chains.

Integration of the four regions assigned to chain sulphuration sites and comparison with the olefinic and methyl protons of the unmodified isoprene units gives a total of 2.56 mol% of sulphuration sites on the polymer chain. The distribution of these sites into the main classes of crosslink termini is summarised in Table 5. The thermodynamically preferred isomers A₁ and B₁ predominate, when compared with the isoallylic isomers A₂ and B₂, under the vulcanisation conditions used in this work. However, this cannot be used directly for interpretation of sulphuration mechanisms because of the known pathway of interconversion of isoallylic in allylic di- and polysulphides at modest temperatures⁴.

the observed resonances to specific crosslink residues, but further work on a range of samples is appropriate to improve the details of these assignments. The spectra were obtained for a vulcanisate which was specifically designed to be free of monosulphidic crosslinks, in order to allow efficient recovery of polymer into solution using thiol probe chemistry. The results therefore describe the network chemistry at early stages of cure, before the incursion of substantial amounts of maturation chemistry. The extent to which the experimental technique can be extended towards technological curing conditions and the comparison of crosslink density as assessed by the ¹H NMR spectroscopy with that determined by more traditional procedures are topics of current investigation.

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TABLE 5. SULPHURATION SITES PER 100 REPEAT UNITS OF POLYISOPRENE CHAIN (mol%) FOR SOLUBLE RUBBER RECOVERED FROM VULCANISATION

Site designation	A ₁	D ₁ ,D ₂	B ₂	B ₁
Range of δ (p.p.m.)	3.85 – 4.0	3.43 – 3.50	3.35 – 3.43	3.10 – 3.17
Amount (mol%)	0.97	0.56	0.41	0.61

CONCLUSIONS

¹H NMR spectra of soluble polymer recovered from a sulphur-vulcanised NR network can be obtained with sufficient sensitivity and resolution to allow the tentative assignment of the structure of sulphuration sites in some detail. Data on relevant model thiols indicate that sites of allylic sulphuration result in resonances in the 3 to 4 p.p.m. region of the spectrum. Analogous resonances are detected in the recovered polymer and are absent from polymer in the mix prior to vulcanisation. Substantial progress has been made in assigning

(*Z*)- and (*E*)-2,6-dimethylocta-2,6-diene-5-thiol, and to Messrs. A. Wilkinson and J. Matharoo, for assistance with the experimental work. We also thank the Materials Characterisation Group at MRPRA for recording the NMR spectra of some of the model compounds, University College London for the use of the VXR-400 spectrometer, and the Board of the Malaysian Rubber Producers' Research Association for permission to publish this work.

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