^{1}H n.m.r. study on the sequence length of polysulphide linkages in the copolymer of chloroprene and sulphur

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The sulphur rank distribution and the structures of chloroprene units in the chloroprene-sulphur copolymer have been investigated in detail by proton nuclear magnetic resonance spectroscopy (^{1}H n.m.r.). Two factors, the sulphur rank and the structures of chloroprene units, which complicate the spectrum, were elucidated by modification of the copolymer structure through partial and full reductions of the polysulphide linkages. The populations of the chloroprene units with different structures adjacent to the sulphur units were found to be different from those of the homosequence. It was found that the major sulphur unit in the copolymer is octasulphide, the next disulphide and the least common are the other polysulphides composed of 3–7 sulphur atoms. No evidence of monosulphide was found.

(Keywords: polychloroprene; copolymer; polysulphide linkage; sulphur rank distribution; proton nuclear magnetic resonance spectroscopy)

INTRODUCTION

It is well known that most radical polymerizations, at relatively low temperatures, are inhibited or strongly retarded by the presence of elemental sulphur or oxygen[1–4]. Carbon radicals in general react very readily with elemental sulphur to yield a polysulphenyl radical of rather low reactivity. It has been suggested that the relative reactivity of the $RS_8\cdot$ radical through the propagation to termination reactions is less than that of $R\cdot$ radicals, where M and $R\cdot$ are the monomer and the propagating radical, respectively.

$$RS_8\cdot + R\cdot \rightarrow RS_8R \text{ (termination)}$$

$$RS_8\cdot + M \rightarrow R\cdot \text{ (propagation)}$$

At relatively high temperatures near the floor temperature of elemental sulphur (159°C), copolymerization has been reported to occur for some olefins with elemental sulphur by thermal initiation. High-temperature reactions are complicated and no unique mechanism has yet been reported, although both free-radical and cationic mechanisms have been suggested[5,6].

Chloroprene and sulphur, on the contrary, are copolymerized readily by a free-radical mechanism at lower temperatures[7]. It has been suggested that sulphur has no effect on the polymerization rate in emulsion systems. There is no inhibition and no retardation, and the polysulphenyl radical can continue growth. Earlier studies on sulphur-modified polychloroprene have revealed that sulphur neither acts as a chain transfer agent nor does it react with the double bond in the polymer[8,9]. From the chemical analysis, it may be postulated that the copolymer has, in part, the following structure:

$$\sim CH_2\text{–}CCl{=}CH\text{–}CH_2\text{–}S_x\text{–}CH_2\text{–}CCl{=}CH\text{–}CH_2\sim$$
$$(x = 2 \sim 6)$$

Coleman[10] has suggested from Raman spectra that sulphur units incorporated in the copolymer are linear polysulphides. This was, however, only a report on the structure of the copolymer studied by spectroscopic methods. There still remain some unresolved questions such as: how is the sulphur incorporated into the polychloroprene chain, and is the sulphur incorporated as linear S_8 or smaller sulphur fragments? The purpose of the present paper is to investigate these problems using ^{1}H n.m.r. spectroscopy.

The structures of the sulphur units and the chloroprene units adjacent to the sulphur units were investigated in the present study. The distribution of the sulphur rank, that is the sequence length of sulphur monomeric unit in the chain, was also examined in detail. The ^{1}H n.m.r. spectrum of this copolymer is, however, complicated because of extensive spectral overlapping of multiplets of similar chemical shifts with each other. ^{1}H n.m.r. spectra were assigned with reference to those of the copolymer reduced under several conditions and also to the homonuclear two-dimensional spectra.

EXPERIMENTAL

Copolymerization (sample A)

Monomeric chloroprene (supplied by Denki Kagaku Kogyo Co. Ltd, Japan) was distilled in a nitrogen atmosphere under reduced pressure just before use. Its purity was confirmed to be 99.8% by gas chromatography. Chloroprene (100 g, 1.13 mol) and sulphur (10 g, 3.91×10^{-2} mol) were radically polymerized with an initiator, 2,2′-azobis-2,4-dimethyl valeronitrile (0.5 g), at 55°C ± 0.1°C in benzene (160 g). After 7 h reaction the reaction mixture was poured into a large volume of methanol containing a trace of antioxidant, 2,6-di-tertbutyl-4-methylphenol. The conversion of chloroprene was 44%. To about 10 wt% of the

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Table 1 Reduction conditions

Sample	Initial charge (g)		Yield (g)	Molar ratio; Ph_3P/S
	Copolymer	Ph_3P		
C	6.88	0.53	4.69	0.19
D	6.50	0.72	4.74	0.28
E	6.04	0.93	4.14	0.39
F	6.51	1.58	3.57	0.61
G	5.37	2.20	3.03	1.03

benzene solution of the copolymer, 20 wt % methanol was added and then left overnight in the dark at 5°C. Precipitated sulphur was removed by decantation. The copolymer, reprecipitated from benzene solution by an addition of methanol, was freeze-dried from the benzene solution. The copolymer was stored at −60°C prior to the reductions and various measurements.

Reductions (samples B–G)

The copolymer (sample A) was reduced by two different methods.

Method 1. The copolymer (10.0 g) was dissolved in toluene (70 cm^3) and methanol (15 cm^3) was added to the solution. Zinc powder (3.0 g) was suspended in the solution at 40°C under vigorous stirring. Hydrochloric acid (12 mol l^{-1}, 12 cm^3) was added dropwise to the solution for 1 h. After 8 h at 40°C, the reaction mixture was left overnight at 5°C. The separated toluene layer was decanted and then washed several times with distilled water in order to remove the $ZnCl_2$. The reduced copolymer (sample B), precipitated by an addition of methanol, was freeze-dried from the benzene solution.

Method 2. To a solution of the copolymer (sample A) in the mixed solvent of benzene (100 cm^3) and methanol (20 cm^3) triphenylphosphine was added under a nitrogen atmosphere at 15°C. After 2 h methanol was added to the reaction mixture to precipitate the reduced copolymer (samples C–G), which was freeze-dried from benzene solution and stored at −60°C prior to the measurements. The reduction conditions, yields and the molar ratios of sulphur in the copolymer to triphenylphosphine are summarized in *Table 1*.

Characterizations

^{1}H n.m.r. spectra were observed in deuterochloroform ($CDCl_3$) at 27°C using a JEOL GX-400 spectrometer operated at a proton frequency of 400 MHz. Polymer concentrations were about 0.10 g cm^{-3} for all samples. Tetramethylsilane (TMS) was used as an internal standard for chemical shifts. Transients (32) were accumulated using a 45° pulse and a pulse interval of 7 s. Peak areas of the well-separated signals in the spectra were determined using the intensities computed by the standard software package for integration attached to the spectrometer.

The proton two-dimensional *J*-correlated (COSY) experiment was performed with the standard $90°–t_1–90°–t_2$ pulse sequence. A total of 112 scans was accumulated for each t_1 value with a repetition time of 1.9 s. The data matrix consisted of 256 spectra of 1024 data points each and was zero filled to 256 by 1024 points covering 2750 Hz in both dimensions.

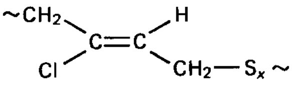
The proton two-dimensional *J*-resolved experiments were performed with the $90°–t_1/2–180°–t_1/2–t_2$ pulse sequence. A total of 8 scans was accumulated for each t_1 value with a repetition time of 2.4 s. The sweep widths were 3000 Hz in the chemical shift dimension and 50 Hz in the coupling constant dimension. The data matrix consisted of 64 spectra each of 8192 data points.

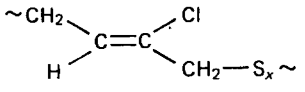
The total sulphur contents of the samples were determined by flask combustion and barium perchlorate titration[11]. The amounts of free-sulphur and triphenylphosphine sulphide as contaminants in the samples were determined using a Toyo Soda HLC-803D HPLC system equipped with Shodex A-801 and A-802 (Showa Denko K.K., Japan) mixed polystyrene gel columns, a detector with fixed-wavelength (254 nm) differential ultra-violet rays and tetrahydrofuran as eluent. The weight-average molecular weights (M_w) of the samples were determined by using the same h.p.l.c. system, but in this case the refractive detector and two Shodex A-80M (Showa Denko K.K., Japan) mixed polystyrene gel columns were used. Total sulphur, free-sulphur and triphenylphosphine sulphide contents and M_w values are summarized in *Table 2*.

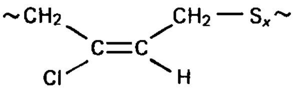
RESULTS AND DISCUSSION

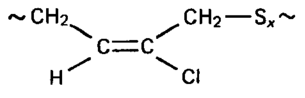
In *Figure 1* the ^{1}H n.m.r. spectrum of the copolymer is shown (sample A). Two main resonance regions, 5.1–6.0 and 1.9–3.0 ppm are assigned to the olefinic and methylenic protons, respectively. Detailed assignments of the spectrum of chloroprene homopolymer have been established by Petiaud and Pham including those corresponding to structural irregularities[12]. Signals in the region 1.0–1.9 ppm correspond to the initiator fragment (1-cyano-1,3-dimethylbutyl) bonded to the polymer terminals. The signals from the olefinic protons of the chloroprene unit adjacent to the sulphur unit are observed partly in the region 5.65–5.80 ppm.

The most useful region is 3.45–3.90 ppm, where the signals from the protons of methylene groups directly bonded to sulphur ($–\underline{CH}_2–S_x–$) appeared. These signals show lower-field shifts, the magnitudes of which depend on the sulphur rank, χ (ref. 13). Besides sulphur rank, chemical shifts are also affected by the existence of head and tail isomers and *trans* and *cis* isomers of the predominant 1,4-units, as illustrated below.


tail-*trans*


head-*trans*


tail-*cis*


head-*cis*

The contents of the other structural irregularities, namely, the 1,2- and 3,4- units adjacent to the sulphur units are considered to be negligible analogous to the homopolymer in which their contents are 1.4 % and 1.3 %, respectively (polymerization temperature was 57°C)[14].

Relative intensity of $-\underline{CH}_2-S_x-$ is 1.98% for sample A, indicating that the content of sulphur units per chloroprene unit in the copolymer is about 0.02. Information concerning the number of sulphur units per chloroprene unit, sulphur rank distribution of sulphur units, and the structures of the chloroprene units adjacent to the sulphur units can be obtained from these signals.

In order to eliminate the effect of sulphur rank on the chemical shifts of the methylenic protons, polysulphide linkages were reduced to the thiol using Zn+HCl as reductant as follows:

$\sim CH_2-{=}CH-CH_2-S_x-CH_2-CCL{=}CH-CH_2\sim$
(sample A)$\rightarrow$

$\sim CH_2-CCl{=}CH-CH_2-SH + HS-CH_2-CCl{=}CH-$
$CH_2\sim$ (sample B)

The spectrum of sample B is shown in *Figure 2*. The signals for $-\underline{CH}_2-S_x-$ which appeared in the region 3.45–3.90 ppm in *Figure 1* completely disappeared, indicating that the reduction was almost complete. The 2D *J*-resolved spectrum indicates that the signals for $-\underline{CH}_2-$SH consist of one doublet and three triplets. The doublet is assigned to $=CCl-\underline{CH}_2-SH$ and the triplets to $=CH-\underline{CH}_2-SH$. These signals are assumed to be reflected by the structures of chloroprene units adjacent to the sulphur units before reduction. Only the existence of *cis* and *trans* isomers of $=CH-\underline{CH}_2-SH$ moiety is insufficient to explain the appearance of three triplets.

Table 2 Contents of total and free sulphur and triphenylphosphine sulphide and molecular weights[a]

Sample	Total sulphur (%)	Free sulphur (%)	$Ph_3P{=}S$ (%)	$\bar{M}_w$[b]
A	4.87	0.75	n.d.	5.4×10^4
B	1.25	n.d.	n.d.	1.4×10^4
C	3.25	n.d.	n.d.	5.3×10^4
D	2.91	n.d.	n.d.	4.9×10^4
E	2.59	n.d.	n.d.	5.3×10^4
F	2.25	n.d.	n.d.	4.7×10^4
G	1.69	n.d.	2.83	3.1×10^4

[a] n.d.: not detected
[b] Calibrated by polystyrene standard samples

The COSY spectrum of sample B is shown in *Figure 3*. The crosspeaks (the peaks distant from the diagonal) in the spectrum indicate the existence of *J*-coupled protons. *Figure 3* clearly indicates the *J*-couplings of $=CH-\underline{CH}_2-$SH with olefinic and thiol protons. For instance, the 3.265 ppm centred methylene triplet is *J*-coupled with both the 1.620 ppm centred thiol and the 5.727 ppm centred methine triplets. In general, the *cis* olefinic proton against the chlorine atom should appear in a lower field

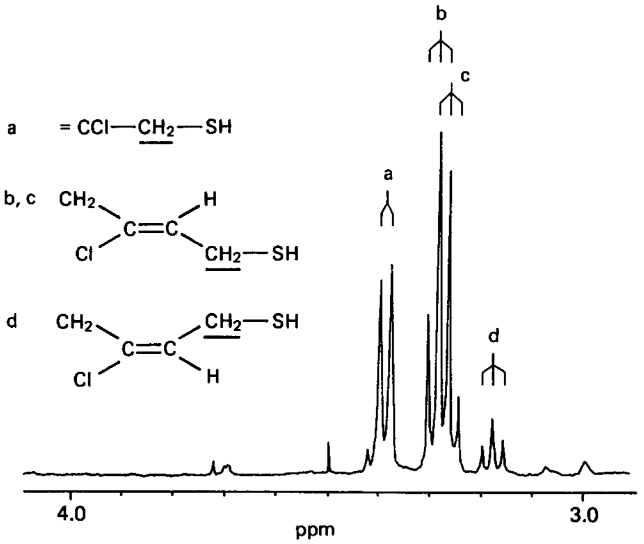


Figure 2 ^{1}H n.m.r. spectrum of sample B in the region 3.0–4.0 ppm measured in $CDCl_3$

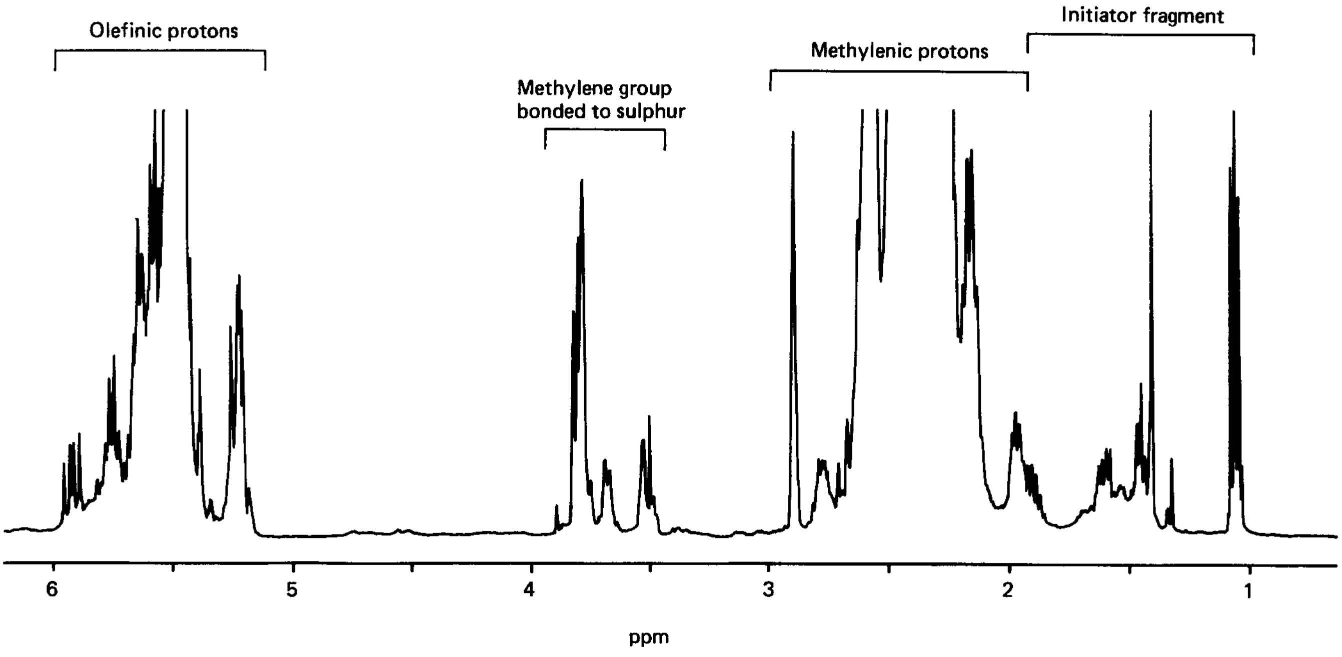


Figure 1 ^{1}H n.m.r. spectrum of chloroprene–sulphur copolymer (sample A), measured in $CDCl_3$

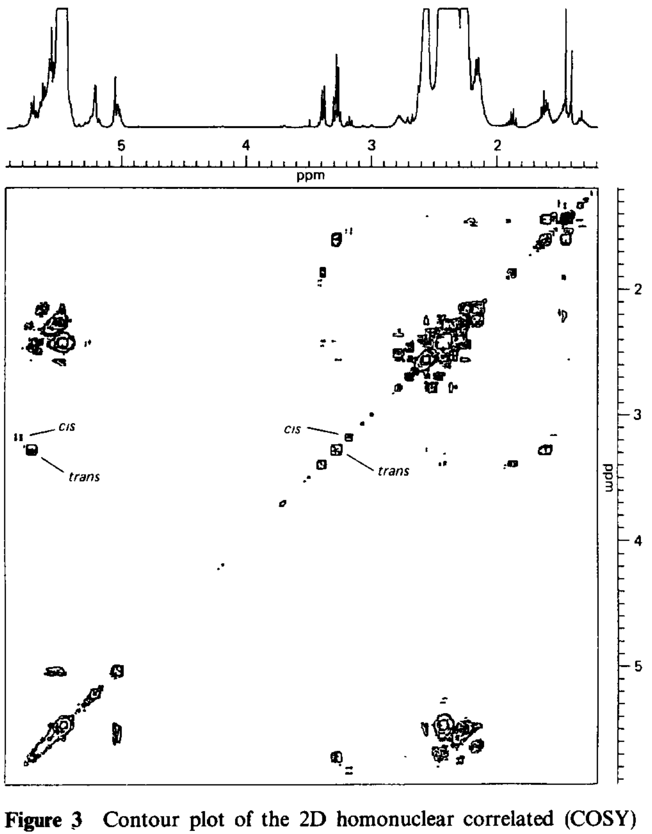
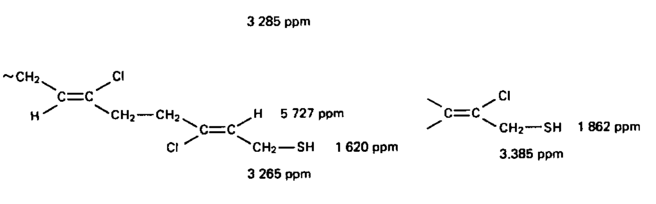


Figure 3 Contour plot of the 2D homonuclear correlated (COSY) spectrum of sample B. The normal spectrum is contained along the diagonal, and cross peaks connect protons which are J-coupled

than the *trans* one[15]. According to this rule, the 3.178 ppm centred triplet is assigned to the *cis* isomer while both the 3.285 ppm and the 3.265 ppm centred triplets are assigned to the *trans* isomers. These assignments are supported by the chemical shifts of the model compounds. Two kinds of methyl protons of *cis* 2-chloro-2-butene resonate in a higher field than those of *trans* 2-chloro-2-butene[16]. The appearance of two kinds of *trans* isomer peaks is explained by the effect of neighbouring units analogous to the case of polybutadiene[17]. Since *trans* isomer and tail-to-head linkages are predominant in polychloroprene, the major triplet is assigned to $-\underline{\mathrm{CH}}_2-\mathrm{SH}$ of the tail-to-head linkage and the minor one to that of the head-to-head linkage. Complete assignments are summarized below.



The intensity ratio of the head-isomer peaks to the tail-isomer peaks is 22:39 for sample B. If the sulphur units are incorporated into the polymer chain only by normal propagation mechanism, this ratio should become 1:1. This difference between the structures in the copolymer and in the homopolymer suggests the existence of the unique feature for the copolymerization of chloroprene and sulphur, which cannot be explained only by the usual copolymerization mechanism based on the Lewis–Mayo equation.

In order to investigate the effect of sulphur rank on the chemical shifts of methylenic protons, sample A was reduced by triphenylphosphine with various feed compositions (samples C–G) as shown in *Table* 1. Triphenylphosphine, a mild reductant, desulphurizes the polysulphide linkage of sulphur units to gradually yield shorter length linkages. We are able to assign the signals of $-\underline{\mathrm{CH}}_2-\mathrm{S}_x-$ to the methylene group bonded to a polysulphide of particular length by comparison of the ^{1}H n.m.r. spectra and the average sulphur rank of the samples which have polysulphides of differing length. *Table 2* indicates that sulphur content continuously decreases with increasing feed-composition of the reductant.

Figure 4 shows a comparison of the expanded spectra of samples A and C–G in the region of $-\underline{\mathrm{CH}}_2-\mathrm{S}-$ resonances. The signals on the whole shift upfield gradually with decreasing sulphur content. In particular, signals at lower field become less intense or disappear and new signals appear in the upper field. For instance, the signal at 3.821 ppm of sample A disappears in the spectrum of sample D while the new signal appears at 3.812 ppm in the latter. The longer polysulphide linkages are desulphurized more rapidly. In the spectra of samples F and G the signals for $-\underline{\mathrm{CH}}_2-\mathrm{SH}$ also appear.

Comparisons of the whole spectra of samples C–G with *Figure 1* indicate that the difference exists only in the region shown in *Figure 4*. Other portions of the copolymer, including the reactive 1,2-unit, remain unchanged after reduction with triphenylphosphine.

The molecular weights of the samples, as shown in *Table 2*, decrease according to the formation of thiol, i.e. cleavage of the polysulphide linkage, similar to the case of sample B.

In *Figure 4*, peaks in all the spectra are overlapped in a somewhat complicated manner. Signals in this region should be composed of doublet and singlet resonances except for the coupling with thiol protons. The 2D J-resolved spectra were used to distinguish the doublets and the singlets, and to measure their chemical shifts. For example, the 2D J-resolved spectrum of sample D is shown in *Figure 5* where the doublets and the singlets are clearly identified. The observed chemical shifts are summarized in *Table 3*.

We can calculate the average sulphur rank, R, using the relationship:

$$R = W/N \times 88.5/32$$

where W corresponds to the ratio of the weight of combined sulphur to that of chloroprene units and N corresponds to the ratio of the number of sulphur units to chloroprene units, that is the relative intensity of $-\underline{\mathrm{CH}}_2-\mathrm{S}-$. W is given by:

$$W = A/(1 - A - B)$$

In this equation A is the combined sulphur content, B is the correction term which includes the contents of contaminants and initiator fragment. Relative intensities and the average sulphur ranks are summarized in *Table 4*.

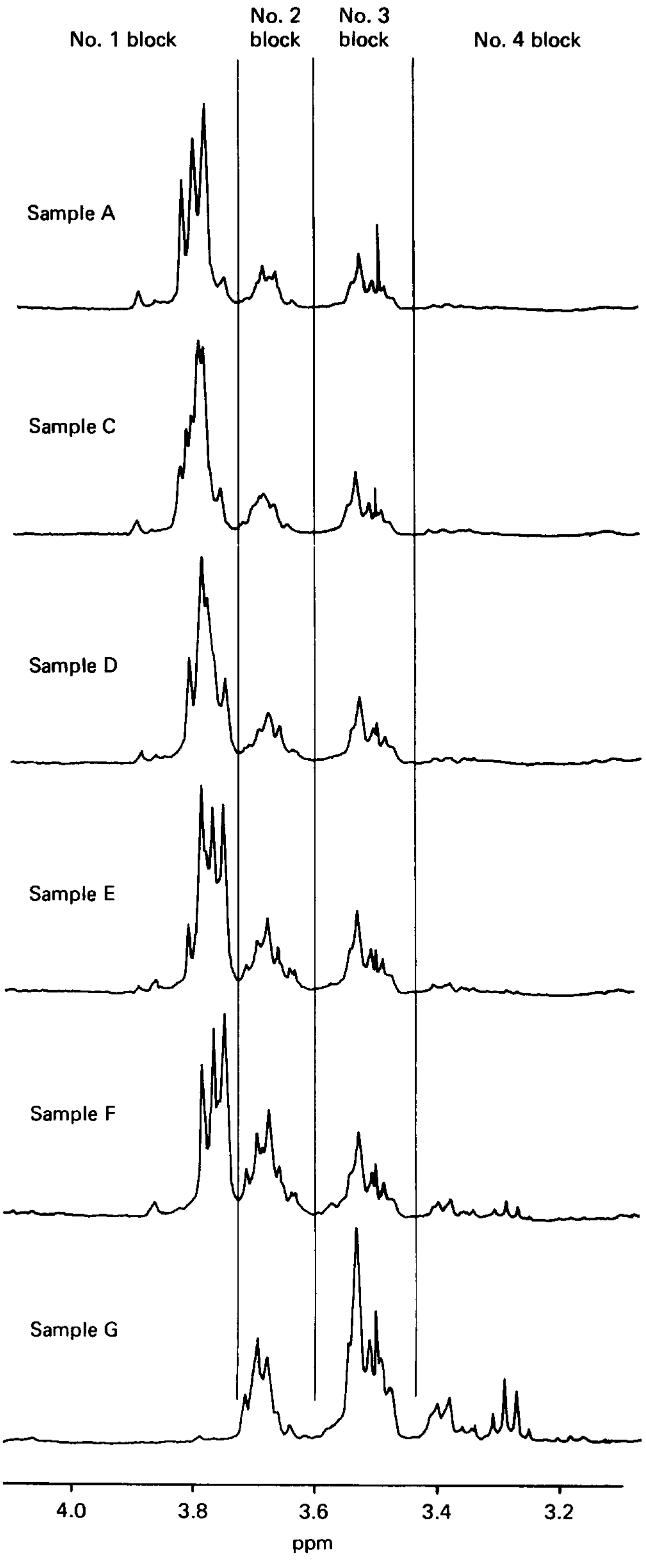


Figure 4 Comparison of the expanded ^1H n.m.r. spectra of samples A, C–G in the region of $-CH_2-S-$ resonances

The average sulphur rank decreases with desulphurization finally becoming 2.0 for sample G.

In all the spectra shown in *Figure 4*, the resonances can be divided into almost 4 blocks in spite of gradual spectral changes and a wide range of average sulphur rank. This indicates the possibility of assignment of resonances in each block to one of the particular sulphur ranks. No. 1 block is in the region 3.90–3.73 ppm, No. 2 in 3.73–3.60 ppm, No. 3 in 3.60–3.45 ppm and No. 4 in 3.45–3.15 ppm. For each spectrum, the relative intensities of each block are also summarized in *Table 4*. No. 1 and No. 2 blocks change both in relative intensities and resonance patterns. Block No. 4 begins to appear after formation of the thiol as seen in the spectra of samples F and G. On the contrary, No. 3 block changes in relative intensities only. The resonance patterns of No. 3 block remain unchanged from sample A to G.

It is important to know which is the final product, i.e. disulphide, monosulphide or thiol when desulphurization of the copolymer by triphenylphosphine proceeds. Generally, the reaction mechanism and the final product

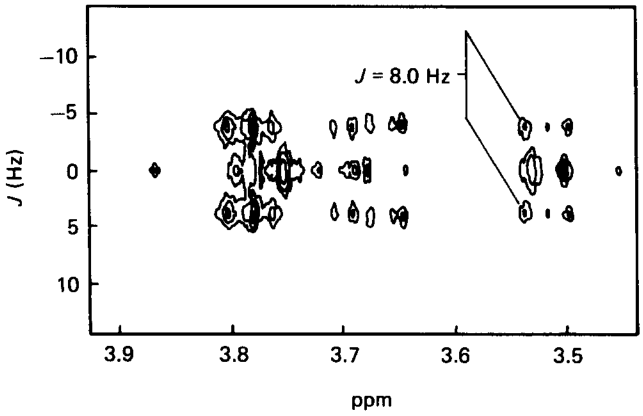


Figure 5 Contour plot of the 2D *J*-resolved spectrum of sample D

Table 3 Chemical shift data[a] in the region 3.45–3.83 ppm[b] obtained on 2D *J*-resolved spectra

A	C	D	E	F	G
3.822 3.804 d	3.822 3.804 d				
	3.812 3.792 d	3.812 3.793 d	3.812 3.792 d		
3.804 3.784 d	3.804 3.784 d				
	3.792 3.774 d	3.793 3.773 d	3.790 3.772 d	3.790 3.772 d	
3.784 s	3.784 s	3.784 s			
3.774 3.754 d	3.774 3.754 d	3.774 3.754 d	3.772 3.755 d	3.772 3.754 d	
3.754 s	3.754 s	3.754 s	3.755 s	3.754 s	
			3.716 3.699 d	3.716 3.699 d	3.716 3.695 d
			3.699 3.680 d	3.699 3.680 d	3.695 3.679 d
			3.685 s	3.689 s	3.689 s
3.690 3.670 d			3.680 s	3.680 s	
	3.681 3.663 d	3.683 3.665 d	3.680 3.663 d		
			3.663 3.643 d	3.663 3.643 d	
	3.642 s	3.643 s	3.643 s	3.643 s	3.643 s
3.552 3.532 d	3.550 3.530 d	3.552 3.532 d	3.551 3.531 d	3.551 3.531 d	3.550 3.530 d
3.532 s	3.530 s	3.532 s	3.531 s	3.531 s	3.530 s
3.510 3.490 d	3.509 3.490 d	3.510 3.490 d	3.509 3.490 d	3.508 3.490 d	3.509 3.490 d

[a] Given in ppm with respect to the shift for tetramethylsilane
[b] d and s represent doublet and singlet, respectively

of desulphurization, with tertiary phosphorus compounds, depend mainly on the solvent, type of polysulphide and type of phosphine, as shown in the next paragraph.

Dialkyl disulphide was resistant to triphenylphosphine in dry boiling benzene, with no monosulphide being formed. The reaction of allyldisulphide with triphenylphosphine in benzene at 80°C to 90°C for 6 h, produced diallylmonosulphide accompanying an allylic rearrangement. In the presence of water (protic solvent), the reaction products were the phosphine oxide and the thiol[18].

The processes of sulphur–sulphur bond cleavage have been examined in detail by Harpp and Smith who studied the desulphurization of trisulphides by several phosphines[19]. Desulphurization proceeds by two steps: the first is the nucleophilic attack by phosphine to form the intermediate (the phosphonium salt); the second is the SN2 displacement of RS^- at the S atom (central sulphur removal) or of RSS^- at the C atom (terminal sulphur removal). If the SN2 displacement at C atom proceeds, the monosulphide can be formed, and if not, the reaction halts forming the disulphide. The intermediate phosphonium salt is hydrolysed to the phosphine oxide and the thiol.

Although the copolymer (sample A) is also one of allylpolysulphides, the possibility of the formation of monosulphide and the rearrangement is assumed to be small because the desulphurization was done under mild conditions and the presence of a chlorine atom at the double bond diminishes the reactivity of the allyl site. In our case the thiol was probably formed from the disulphide with the proceeding of the reaction in the presence of methanol or a small amount of water.

In summary, the peak pattern of the No. 3 block is unchanged by the desulphurization, indicating that all the resonances appearing in No. 3 block are corresponding to the same sulphur rank. The peaks in the No. 3 block resonate at lower field than $-\underline{\mathrm{CH}}_2-\mathrm{SH}$. The average sulphur rank of sample G, in which the major block is No. 3, is 2.0. From these results, we can assign almost all peaks in the No. 3 block to $-\underline{\mathrm{CH}}_2-\mathrm{S}_2-$. From the spectrum of sample B, it becomes apparent that three doublets and one singlet should comprise the one set corresponding to the particular sulphur rank. Furthermore, an additive property of chemical shift should be set up between the contributions from the structural differences of sulphur units and from those of chloroprene units. The one set corresponding to the disulphide is composed of doublet (3.551, 3.531 ppm), singlet (3.531 ppm), doublet (3.510, 3.490 ppm) and doublet (3.410, 3.388 ppm, No. 4 block). We conclude that the signals of $-\underline{\mathrm{CH}}_2-\mathrm{S}_1-$ are not detectable in *Figure 4*.

In contrast to the case of No. 3 block, the peaks in each of No. 1 and No. 2 blocks cannot be assigned on the whole to one of the particular sulphur ranks. The chemical shift between $-\underline{\mathrm{CH}}_2-\mathrm{S}_x-$ and $-\underline{\mathrm{CH}}_2-\mathrm{S}_{x+1}-$ becomes smaller with increasing x, clearly evident from the example of dimethylpolysulphide as shown in *Table 5*[13]. The contribution to the chemical shift from the sulphur rank differences should be smaller than that from the structural differences of the chloroprene units in the region 3.6–3.9 ppm, corresponding to the sulphur rank 3–8.

In an effort to obtain further quantitative interpretation, the average sulphur rank of sulphur units other than disulphide and thiol, R_p, was calculated from that of all the sulphur units and the relative intensities of the 4 blocks as follows:

$$R_\mathrm{p}=(R-2C)/(1-C)$$

where C is the peak intensity ratio of No. 3 and No. 4 blocks to all blocks. The contribution of thiol to the average sulphur rank is 2, identical to that of the disulphide. The results are also summarized in *Table 4*.

It is concluded that the average sulphur rank of sample A is on the whole 6.2 and partly 7.2 (No. 1+No. 2 blocks). From this large average sulphur rank value we can assign almost all peaks in the No. 1 and No. 2 blocks of sample A to $-\underline{\mathrm{CH}}_2-\mathrm{S}_8-$. This finding is important, because there have been some ambiguities concerning the monomeric sulphur which participates in the copolymerization, i.e. cyclohexa-, cyclohepta- or cyclooctasulphide[20]. Our results clearly indicate that S_8 is the true monomer. The one set corresponding to the octasulphide is composed of doublets (3.822, 3.804 ppm) and (3.804, 3.784 ppm), a singlet (3.784 ppm) and the doublet (3.690, 3.670 ppm). From *Table 3* the presence of the singlet (3.754 ppm), the doublet (3.774, 3.754 ppm) and the singlet (3.690 ppm) corresponding to the shorter polysulphides, diminishes the average sulphur rank (No. 1+No. 2 blocks) of sample A to 7.2 from 8.0.

Table 4 Relative intensities and average sulphur rank

Sample	Relative[a] intensity	Intensity ratios[b] of 4 blocks	Average[c] sulphur rank	Average[d] sulphur rank
A	1.98%	65:15:20:0	6.2	7.2
C	2.05%	62:16:20:2	4.6	5.4
D	1.99%	59:19:22:0	4.2	4.8
E	1.88%	56:20:20:4	3.9	4.5
F	1.97%	42:28:22:8	3.3	3.9
G	2.03%	0:26:50:24	2.0	2.0

[a] Ratio of (resonance intensity of $\underline{\mathrm{CH}}_2$–S–)/(resonance intensity of all methylenic protons of chloroprene units)

[b] Intensity ratios of resonances appeared in the region 3.73–3.90 ppm:3.60–3.73 ppm:3.45–3.60 ppm:3.15–3.45 ppm

[c] Average length of all the polysulphide linkages including thiol calculated as disulphide, corresponding to the resonances in the region 3.15–3.90 ppm

[d] Average length of longer polysulphide linkages than disulphide, corresponding to the resonances in the region 3.6–3.9 ppm

Table 5 Chemical shifts of methyl protons in $\mathrm{CH_3S_xCH_3}$[a]

x	1	2	3	4	5	6	7	8
Shift	2.159	2.375	2.521	2.615	2.632	2.663	2.688	2.707

[a] Given in ppm with respect to the shift for tetramethylsilane cited from ref. 13

Table 6 Chemical shifts[a] and assignments[b] of methylene resonances of original and desulphurized copolymers

	$x=8$	$x=?^c$	$x=?^c$	$x=3$	$x=2$	–SH[d]
head	3.784	–	3.754	3.689	3.531	3.385
tail-	3.822	3.812	3.793	3.716	3.551	3.285
trans	3.804	3.793	3.773	3.699	3.531	
tail-	3.804	3.793	3.773	3.699	3.509	3.265
trans	3.784	3.773	3.754	3.680	3.490	
tail-	3.690	3.683	3.663	–	3.410	3.178
cis	3.670	3.665	3.643	–	3.388	

[a] Given in ppm with respect to the shift for tetramethylsilane
[b] x represents the length of the polysulphide linkage
[c] Not assigned
[d] Chemical shifts of centre signal in triplet

For sample G the peaks of No. 1 block disappear completely and the peaks of No. 2 block are assumed to be assigned to –$\underline{\mathrm{CH}}_2$–$\mathrm{S}_3$–. However, the average sulphur rank (No. 2 block) is 2.0, which is inconsistent with this assignment. The average sulphur rank (No. 2+No. 3+No. 4 blocks) can also be calculated from the relative intensities of each block and corresponding sulphur rank, i.e. 3 for No. 2 block and 2 for No. 3 and No. 4 blocks. The relative intensity of No. 2 block (26/100) affects this value a little, which is calculated to be 2.26. This inconsistency is probably attributable to the inaccuracy of the sulphur analysis and the presence of triphenylphosphine sulphide, while the average sulphur rank (No. 1+No. 2 blocks) of sample F is 3.9, supporting this assignment. For sample F, the ratio of resonance intensities of No. 1 to No. 2 blocks is 42:28. The resonances of No. 1 block correspond to a sulphur rank greater than 3. Thus, the average value of 3.9 must be derived from the rank value of 3 and that greater than 3. The doublets (3.716, 3.699 ppm) and (3.699, 3.680 ppm) and the singlet (3.689 ppm) are assigned to –$\underline{\mathrm{CH}}_2$–$\mathrm{S}_3$–. The shoulder peak of No. 3 block in the region 3.55–3.6 ppm is tentatively assigned to the tail-*cis* isomer corresponding to the trisulphide.

All the chemical shifts summarized in *Table 3* are rearranged using the rule that four pairs of peaks comprise the one set corresponding to the particular sulphur rank and that an additive property of chemical shift is set up between the contributions from the sulphur rank and from the structural differences of chloroprene units. Six sets of peaks are defined as shown in *Table 6*. To summarize, of the six sets four correspond to the octa-, tri-, disulphide and thiol, respectively. It is difficult to assign the remaining two sets to the remaining four sulphur ranks: 4, 5, 6 and 7, because of the lack of quantitative examination. Moreover, the other two sets may be missed because of the slight chemical shift difference which results from the sulphur rank difference and the complicated overlapping of spectra. Quantitative estimates of sulphur rank distribution can be clearly obtained for the disulphide and the thiol.

From these assignments, we re-examined the spectrum of the chloroprene–sulphur copolymer (*Figure 1*). The sulphur units in the copolymer are composed of polysulphide bridges longer than the monosulphide, the largest portion of which is composed of octasulphide. There is no monosulphide. The octasulphide should be formed simply by the radical attack on the elemental sulphur (the eight-membered unstrained ring form) and the following propagation of polysulphenyl radical (ring-opening form) to monomeric chloroprene.

The singlet at 3.892 ppm can probably be assigned to another head isomer, =CCl–$\underline{\mathrm{CH}}_2$–$\mathrm{S}_8$–. This signal cannot be assigned to the protons of the methylenic group bonded to longer polysulphides than octasulphide, because the appearance of the singlet peak alone is inconsistent with the pattern of signals corresponding to other polysulphides. This isomer is not detectable for sample B, the fully reduced copolymer, because of the small peak intensity. Making comparisons with the chemical shifts of model compounds[16], this isomer may be *trans* while the singlet at 3.784 ppm may be assigned to the *cis* isomer. Similarly, the singlet at 3.643 ppm may be assigned to the head-*trans* isomer corresponding to the disulphide. For a similar pattern, the singlet of small intensity at lower field and the singlet of large intensity at upper field are also observed in the spectrum of the polymer terminal of n-dodecylmercaptan-modified polychloroprene, =CCl–$\underline{\mathrm{CH}}_2$–SR[21]. However, the predominance of the *cis* isomer for –$\mathrm{CH_2}$–CH=CCl–$\mathrm{CH_2}$–S_x– and –$\mathrm{CH_2}$–CH=CCl–$\mathrm{CH_2}$–SR is inconsistent with the main chain structure of polychloroprene, in which the predominant isomer is *trans*.

The possibility of the presence of longer polysulphides than octasulphide in this copolymer is considered to be negligible. Below the floor temperature, polysulphenyl radicals cannot continue growth with elemental sulphur in analogy with the homopolymerization of sulphur. The recombination of polysulphenyl radicals is also assumed to be small, because of the smallness of sulphur feed ratio and the low reactivity of sulphur.

It is not yet known what type of reaction mechanism produces the clearly visible disulphide and other polysulphides concealed behind the octasulphide. In order to answer this question and to elucidate the copolymerization mechanism for chloroprene and sulphur, it should be effective to associate the sulphur rank distribution with the copolymerization conditions. These examinations are still under investigation in our laboratory.

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