Copolymerization of chloroprene with elemental sulphur. 1H n.m.r. study on the sequence length of polysulphide linkages in the copolymer

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Free radical copolymerization of chloroprene (Cp) with elemental sulphur (S_8) was studied in a range of temperatures from 20 to 100°C as a function of total monomer concentration. The sulphur rank distribution for the sulphur unit $-S_x-$, where $2 \leqslant x \leqslant 8$, has been examined by observing proton nuclear magnetic resonance spectra of the methylene group directly bonded to sulphur. The effect of total monomer concentration and polymerization temperature on the copolymer structure is explained by the depropagation process involving both carbon–sulphur and sulphur–sulphur bond scissions. It was found that the population of polysulphide linkages shorter than octasulphide, such as $-S_2-$ and $-S_3-$, increases with dilution or with increasing polymerization temperature. Disulphide linkages were favourably formed at rather low temperatures with dilution; other polysulphide linkages such as $-S_3-$ became more favourable at higher temperatures. The back-biting mechanism, in which a propagating radical of a terminal Cp unit attacks a penultimate sulphur unit, is proposed for the depropagation process to explain the sulphur rank distribution.

INTRODUCTION

Very few studies have been made on the direct copolymerization of organic monomers with elemental sulphur (S_8). At relatively high temperatures near the floor temperature of S_8 (159°C), copolymerization has been reported to occur for some olefins with S_8 by thermal initiation[1,2]. Penczek et al.[3] have reported the copolymerization of propylene sulphide with S_8 at 80°C by an anionic initiator, and obtained high molecular weight copolymers. Matsuda et al.[4] have recently prepared copolymers of phenylacetylene with S_8 in a range of temperatures from 30 to 100°C by a radical initiator, but the molecular weight of the copolymers is low.

It is well known that most radical polymerizations, at relatively low temperatures, are inhibited or strongly retarded by the presence of S_8[5-8], while chloroprene (Cp) and S_8 are copolymerized readily by a free-radical mechanism at lower temperatures[9,10]. Although this copolymer is one of the well known synthetic rubbers, very little is known about its copolymerization mechanism. There still remain some unresolved problems. How is the sulphur incorporated into the polychloroprene chain? Is the sulphur incorporated as linear S_8 or smaller sulphur fragments?

In a previous paper[11], we suggested from 1H nuclear magnetic resonance (n.m.r.) spectra that the major sulphur unit in the copolymer is octasulphide, the next is disulphide and the least common units are the other polysulphides composed of 3–7 sulphur atoms. It was also shown that the stereochemistry of the Cp unit adjacent to the sulphur unit is different from that in the homosequence. The formation of shorter polysulphide linkages and the difference in stereochemistry cannot be

explained only by the Mayo–Lewis type copolymerization mechanism. In the present paper, the copolymer structure is characterized with copolymerization conditions to clarify what kind of reaction explains the formation of shorter polysulphide linkages. The distribution of the sulphur rank, i.e. the sequence length of sulphur monomeric units in the chain, will be investigated by observing 1H n.m.r. spectra of the methylene group directly bonded to sulphur.

EXPERIMENTAL

Chloroprene was supplied by Denki Kagaku Kogyo Co. Ltd. Other compounds and solvents were commercial reagents. Chloroprene and diluents were distilled in a nitrogen atmosphere under reduced pressure just before use. The purity of chloroprene was confirmed to be 99.8% by gas chromatography.

Copolymerization

Polymerizations proceeded homogeneously in spherical flasks. Carbon disulphide and toluene were used as diluents for copolymerizations at low and high temperatures, respectively. A typical procedure was as follows. Chloroprene (100 g, 1.13 mol) and sulphur (20 g, 7.82×10^{-2} mol) were radically polymerized with an initiator, 2,2'-azobis-2,4-dimethyl valeronitrile (1.25 g, 5.0×10^{-3} mol) at 40 ± 0.1°C in carbon disulphide (100 g, 1.32 mol). After 7.5 h the reaction mixture was poured into a large amount of methanol containing a trace of antioxidant, 2,6-di-tertbutyl-4-methylphenol. The conversion of chloroprene was confirmed to be 21% by gas chromatography. To a solution (about 10 wt%) of the copolymer in 200 cm³ of benzene, 40 cm³ of methanol

was added and then left overnight in the dark at 5°C. Precipitated sulphur was removed by decantation. The copolymer was reprecipitated from benzene solution by an addition of methanol and then freeze-dried from benzene solution. The copolymer was stored at −60°C.

Characterization

[1]H n.m.r. spectra were observed in deuteriochloroform (CDCl$_3$) at 27°C using a JEOL GX-400 spectrometer operated at 400 MHz. Polymer concentrations were about 0.20 g cm^{-3} for all samples. Tetramethylsilane (TMS) was used as an internal standard for chemical shifts. Thirty-two transients were accumulated by using a 45° pulse and a pulse interval of 7 s. Peak intensities of well separated signals in the spectra were determined by the standard software package for integration attached to the spectrometer.

The proton two-dimensional (2D) J-resolved experiment was performed with the $90°-t_1/2-180°-t_1/2-t_2$ pulse sequence. A total of eight 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 of 8192 data points each.

The methods of determining the amounts of total sulphur and free sulphur and calculating average sulphur ranks of samples have been described elsewhere[11].

RESULTS AND DISCUSSION

In a previous paper[11], we have demonstrated that [1]H n.m.r. spectroscopy is a powerful tool for characterizing the structure of Cp–S$_8$ copolymer, which has, in part, the following structure:
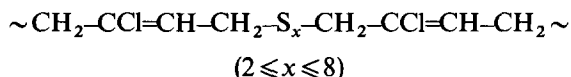
$$\sim CH_2-CCl=CH-CH_2-S_x-CH_2-CCl=CH-CH_2 \sim$$

$$(2 \leqslant x \leqslant 8)$$

Figure 1 shows the [1]H n.m.r. spectrum of the copolymer
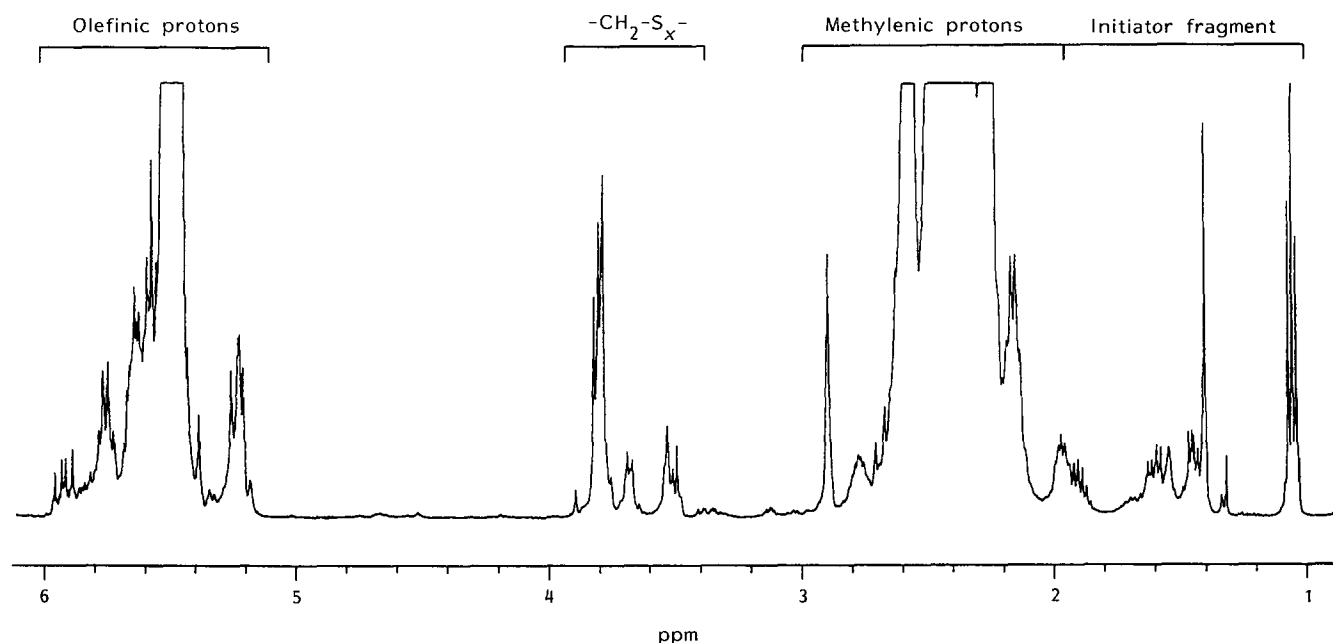
with assignments. The resonances of $-CH_2-S_x-$, observed in the region 3.37–3.90 ppm, are very sensitive to the sulphur rank, x, and the stereochemistry of the Cp unit. The peak assignments have been determined for $-CH_2-S_2-$, $-CH_2-S_3-$ and $-CH_2-S_8-$. From the spectrum of this region, we can obtain information on the sulphur unit content and the sulphur rank distribution.

Copolymerization details are given in *Table 1*. The effect of polymerization conditions, i.e. total monomer concentration (samples A, B, C, D and E) and polymerization temperature (samples F, C, G, H and I), on the copolymer structure was investigated. Polymerization conditions were restricted by the solubility of S$_8$ in chloroprene–diluent mixture. To eliminate the effect of Cp conversion, Cp conversions were controlled to become almost constant (about 20%) for all copolymerizations.

Remarkable spectral changes are induced by the change of polymerization conditions. *Figure 2* shows the expansions of the $-CH_2-S_x-$ resonances for samples A, E and I. Resonances 1, 2, 3 and 4 were assigned to $-CH_2-S_8-$, and resonances 5, 6, 7 and 8 were assigned to $-CH_2-S_2-^{11}$. One singlet and three doublets which were assigned to four stereochemical isomers of the Cp unit comprise the one set corresponding to the particular sulphur rank. Although the resonances of $-CH_2-S_x-$, where $3 \leqslant x \leqslant 7$, are not clearly visible in *Figure 2*, they must be present between the resonances of $-CH_2-S_2-$ and $-CH_2-S_8-$. In all spectra shown in *Figure 2* the resonances can be divided into three blocks, in spite of significant changes of resonance patterns. Block 1 is in the region 3.73–3.90 ppm. Block 2 in the region 3.60–3.73 ppm and Block 3 in the region 3.37–3.60 ppm. Block 3 contains all the resonances of $-CH_2-S_2-$ and one doublet corresponding to $-CH_2-S_3-^{11}$. This doublet corresponds to the same stereochemical isomer of the Cp unit as resonances 4 and 8. As this doublet should be small, the relative intensity of Block 3 is regarded as that of $-CH_2-S_2-$ to simplify the quantitative interpretation.

The sulphur unit content and the relative intensities of

Olefinic protons $-CH_2-S_x-$ Methylenic protons   Initiator fragment

Figure 1   400 MHz [1]H n.m.r. spectrum of 2p–S$_8$ copolymer (sample G), measured in CDCl$_3$ at 27°C

Table 1 Polymerization data for $Cp-S_8$ copolymers[a]

Sample	Monomer conc. in feed, [Cp] (mol l^{-1})	Polymerization temp. (°C)	Initiator conc. (mol l^{-1})	Polymerization time (h)	Cp conversion (%)	M_w[b] ($\times 10^{-4}$)
A	5.7	40	0.025	7.5	21	6.4
B	4.1	40	0.018	7.5	22	5.2
C	3.1	40	0.014	10.0	20	4.7
D	2.2	40	0.010	13.0	19	4.4
E	1.2	40	0.005	16.0	18	2.6
F	3.1	20	0.220	15.0	15	3.2
G	3.1	60	0.006	3.0	20	3.8
H	3.1	80	0.008	1.3	28	2.7
I	3.1	100	0.007	0.7	18	3.7

[a] $[S_8]/[Cp]$ molar ratio in feed is 0.069 for all copolymerizations.
  Initiator: A–G, 2,2′-azobis(2,4-dimethylvaleronitrile); H, 2,2′-azobisisobutyronitrile; I, 1,1′-azobis(cyclohexane-1-carbonitrile). Diluent: A–G, carbon disulphide; H, I, toluene
[b] Weight-average molecular weight. Data obtained by g.p.c. and calibrated by polystyrene standard samples
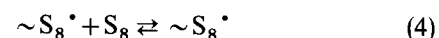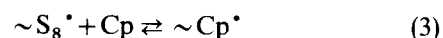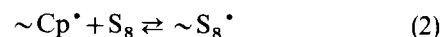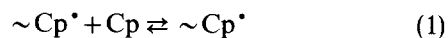
each block derived from the corresponding resonance areas are summarized in *Table 2*. From *Figure 2* and *Table 2* it is possible to extract some interesting tendencies. With decreasing total monomer concentration, in the order of samples A, B, C, D, E, the sulphur unit content decreases and the population of disulphide linkages significantly increases. With increasing population of disulphide linkages, the average sulphur rank, of course, diminishes. The average length of polysulphide linkages longer than disulphide, corresponding to the resonances in Blocks 1 and 2, can be calculated from the average sulphur rank and the relative intensities of each block. This value also diminishes with dilution, indicating the enhancement of other polysulphide linkages composed of 3–7 sulphur atoms.

The enhancement of polysulphides composed of 3–7 sulphur atoms is consistent with the difference in the resonance patterns of Block 2 for sample E and sample A. Resonance 4, corresponding to $-CH_2-S_8-$, occupies a large portion of Block 2 of sample A. On the contrary, other resonances overlap on resonance 4 in Block 2 of sample E. The 2D J-resolved spectrum was used to distinguish these resonances. *Figure 3* shows the expanded 2D J-resolved spectrum of sample E. *Figure 3* clearly shows that the doublet at 3.708 ppm, the doublet at 3.690 ppm and the singlet at 3.689 ppm, which were assigned to $-CH_2-S_3-^{11}$, are concealed in Block 2 of sample E.

With increasing polymerization temperature, in the order of samples F, C, G, H, I, the sulphur unit content increases and the population of disulphide linkages also increases. Moreover, the relative intensity of Block 2 increases. The resonance pattern of Block 1 for sample I is much broader than that for sample E, as shown in *Figure 2*. The broader resonance pattern results from a large number of closely spaced, unresolved chemical shifts corresponding to different sulphur ranks. These observations indicate that the population of polysulphides composed of 3–7 sulphur atoms becomes larger than that of disulphide with increasing polymerization temperature. Therefore, disulphide linkages are favourably formed at rather low temperatures with dilution. The formation of other polysulphides, such as $-S_3-$ units, becomes more favourable at higher temperatures.

The decrease of the sulphur unit content with decreasing total monomer concentration strongly

suggests that the copolymerization proceeds via a mechanism including a depropagation step of growing polysulphenyl radicals (equation (2)). For the copolymerization of Cp with S_8, primarily, the following propagation and depropagation steps can be assumed to be taking place:

$$\sim Cp^{\bullet} + Cp \rightleftarrows \sim Cp^{\bullet} \qquad (1)$$

$$\sim Cp^{\bullet} + S_8 \rightleftarrows \sim S_8^{\bullet} \qquad (2)$$

$$\sim S_8^{\bullet} + Cp \rightleftarrows \sim Cp^{\bullet} \qquad (3)$$

$$\sim S_8^{\bullet} + S_8 \rightleftarrows \sim S_8^{\bullet} \qquad (4)$$

The depropagation of equation (1) can be negligible under the conditions considered here. The reaction of equation (4) does not need to be taken into account because below the floor temperature polysulphenyl radicals cannot continue growth with S_8. Since depropagation and propagation are first- and second-order reactions, respectively, with the decrease of total monomer concentration, the propagation process is much more subject to dilution effect than the depropagation process, and it gives rise to the observed variability of copolymer composition. Thus the decrease of the sulphur unit content with dilution can be interpreted as a result of the increase in the depropagation rate relative to the propagation rate (equation (2)).

On the contrary, the increase of the sulphur unit content with increasing polymerization temperature should be interpreted as a result of the increase in the propagation rate relative to the depropagation rate (equation (2)). This tendency is inconsistent with usual reversible copolymerizations such as Cp–sulphur dioxide (SO_2) copolymerization[12], where the content of the SO_2 units in the copolymer decreases with increasing polymerization temperature. This inconsistency can be rationalized by the thermodynamic feature of S_8 polymerization. Polymerizations of common monomers, including SO_2, are exothermic and exoentropic[13]. On the contrary, polymerization of S_8 is endothermic and endoentropic[14]. Propagation–depropagation equilibrium in the former is established by increasing temperature to the ceiling temperature and that in the latter is established by lowering temperature to the floor temperature. Therefore, the temperature dependence of the copolymer composition in $Cp-S_8$ copolymerization is opposite to that in the usual reversible copolymerizations. The same
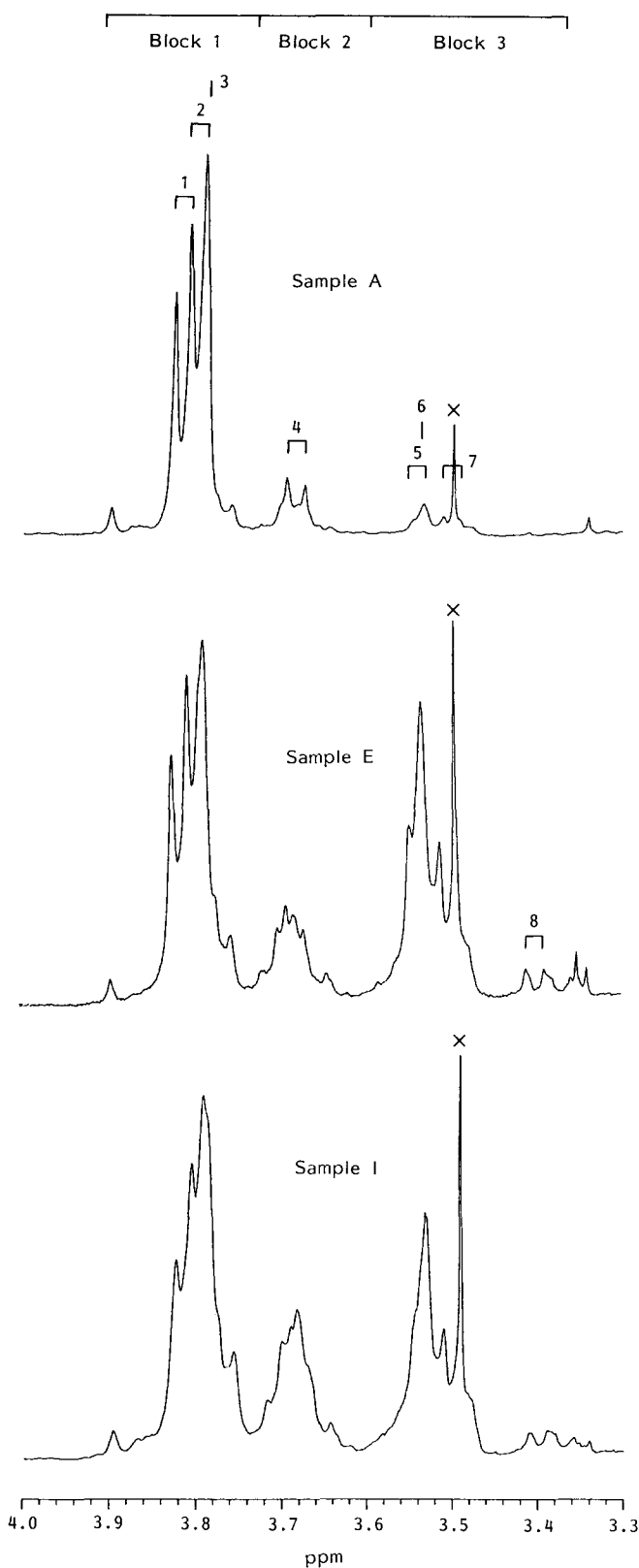
Figure 2 Comparison of the expanded ^{1}H n.m.r. spectra of samples A, E and I in the region of $-CH_2-S_x-$ resonances. Peak x (variable position and intensity) is due to methanol. Peak area of x is estimated from the integration curve

tendency has been reported for an anionic copolymerization of S_8 with propylene sulphide, which was also explained by the mechanism including the depropagation process[15].

The sulphur rank distribution is strongly influenced by

the total monomer concentration and polymerization temperature, indicating that the depropagation process is the key step in controlling the sulphur rank distribution. The population of shorter polysulphide linkages such as $-S_2-$ and $-S_3-$ units increases with dilution or with increasing polymerization temperature. Since $-S_8-$ units become in the great majority with increasing total monomer concentration and lowering polymerization temperature, it can be concluded that S_8 truly participates in the copolymerization (equation (2)). The polysulphide linkages shorter than $-S_8-$ should be formed by the secondary reaction where sulphur species other than S_8 probably depropagate. The temperature dependence of the sulphur rank distribution seems to be inconsistent with that of the copolymer composition. However, the opposite temperature dependence of the propagation–depropagation equilibrium is limited to S_8 polymerization. For example, it has been suggested that polymerization of S_6 is exothermic and exoentropic[14]. In conclusion, the enhancement of shorter polysulphide linkages such as $-S_2-$ and $-S_3-$ by the depropagation process and the absence of $-S_1-$ units in the copolymer are the remarkable features of $Cp-S_8$ copolymerization.

It is interesting to discuss what kind of reaction is controlling the length of polysulphide linkages. The depropagation process involving homolytic scission of the sulphur–sulphur bond is obviously the key step in controlling it. Conceivably, the linear polysulphenyl radical, $\sim S_8{}^\bullet$, would decompose to shorter poly-sulphenyl radicals and smaller sulphur species:

$$\sim S_8{}^\bullet \rightarrow \sim S_{8-y}{}^\bullet + S_y \qquad (5)$$
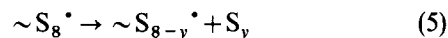
It is important to consider the stability of resulting radicals and products when the depropagation proceeds. In equation (5), the formation of smaller sulphur species S_y, where $1 \leqslant y \leqslant 5$, seems to be thermodynamically unfavourable under present conditions. These high energy sulphur species have been found at much higher temperatures, e.g. in sulphur vapour[16], while homocyclic sulphur allotropes S_6 and S_7 are well known to be formed in liquid sulphur[17] or by dissolution of S_8 in polar solvents at ambient temperature[18]. S_6 and S_7 have been isolated in crystalline form and well characterized[19]. On the other hand, considering the stability of resulting radicals, it is assumed that conditions are unfavourable for the thiyl radical, $\sim S_1{}^\bullet$, to be formed in equation (5). The polysulphenyl radicals, $\sim S_x{}^\bullet$, are more stable than the thiyl radical because the unpaired electron of sulphur participates in a π-bond as long as at least one sulphur–sulphur bond is present. Absence of $-S_1-$ units in the $Cp-S_8$ copolymer supports the above discussion.

It has been suggested that S_6 has a much greater reactivity than S_8 because of bond distortion. S_6 has been found to react 10^4 times faster than S_8 with nucleophilic agents[19]. There may be the possibility for additional participation of resulting S_6 in the radical copolymerization even though its concentration is much lower than that of free sulphur (S_8 form) in the system. Therefore, the presence of $-S_2-$ and $-S_6-$ units can be rationalized by equation (5). However, equation (5) is insufficient to explain the presence of other polysulphide linkages, e.g. $-S_3-$ units, since homocyclic sulphur allotropes with smaller ring size than S_6 have not yet been isolated or characterized[19].

There may be another possibility for the reaction

Table 2 Sulphur rank distribution and average sulphur rank of the copolymer

Sample	Sulphur unit content[a] (%)	Relative intensity[b]			Average sulphur rank[c]	Average sulphur rank[d]
		Block 1	Block 2	Block 3		
A	2.40	0.78	0.13	0.09	6.7	7.2
B	2.29	0.71	0.14	0.15	6.5	7.3
C	2.13	0.67	0.14	0.19	6.1	7.1
D	1.92	0.60	0.14	0.26	5.4	6.6
E	1.79	0.46	0.14	0.40	4.4	6.0
F	1.68	0.75	0.14	0.11	6.9	7.5
G	2.52	0.60	0.15	0.25	5.2	6.3
H	4.74	0.54	0.18	0.28	4.8	5.9
I	5.06	0.47	0.20	0.33	4.6	5.9

[a] Resonance intensity of $-CH_2-S_x-$ relative to all methylenic protons of the Cp unit
[b] Block 1 corresponds to signals in the region 3.73–3.90 ppm, Block 2 to 3.60–3.73 ppm and Block 3 to 3.37–3.60 ppm
[c] Average length of polysulphide linkages calculated from the sulphur unit content and the results of sulphur analysis
[d] Average length of polysulphide linkages longer than disulphide, corresponding to resonances in the region 3.60–3.90 ppm
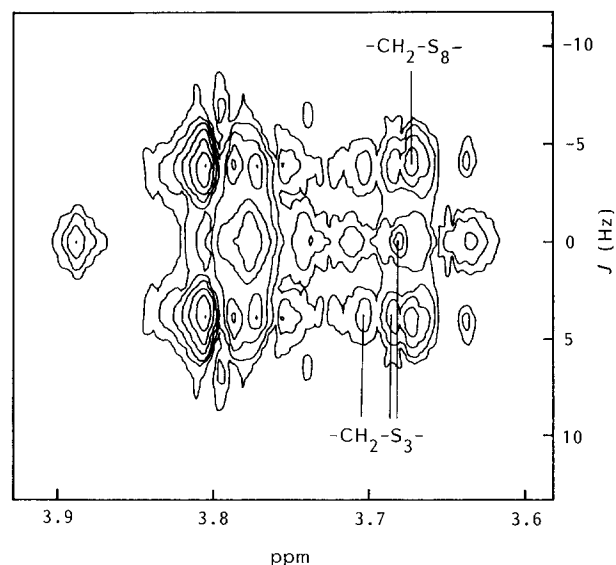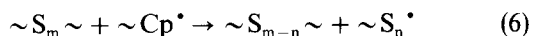

Figure 3 Contour plot of the 2D J-resolved spectrum of sample E, showing Blocks 1 and 2 of the $-CH_2-S_x-$ region

controlling the sulphur rank distribution, which includes the radical attack on the polysulphide linkages in the copolymer already formed:

$$\sim S_m \sim + \sim Cp^\bullet \rightarrow \sim S_{m-n} \sim + \sim S_n^\bullet \qquad (6)$$

However, this intermolecular reaction is, of course, second-order and inconsistent with the control by the depropagation process. The concentration of $-S_m-$ is much lower than that of free sulphur because of the low reactivity of S_8 and the low conversion. For instance, the concentration ratio, $-S_m-/S_8$, is about 0.07 for sample C when Cp conversion is 20%. Therefore, the contribution from the reaction of equation (6) to the sulphur rank distribution can be ignored, unless there is a great difference between the reactivity of $-S_m-$ and that of S_8.

To explain the enhancement of both $-S_2-$ and $-S_3-$ units with dilution, the following back-biting mechanism is proposed.

$$\sim S_8-Cp^\bullet \rightarrow \sim S_{8-z}{}^\bullet + Cp{\supset}S_z \qquad (7)$$
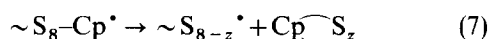
In this equation, the resulting polysulphenyl radical, $\sim S_{8-z}{}^\bullet$, continues growth with chloroprene and $-S_{8-z}-$

units are formed in the copolymer. A similar mechanism has been proposed for an anionic copolymerization of S_8 with 2,2-dimethylthiiran[20]. On the basis of the temperature dependence of sulphur rank distribution, $Cp{\supset}S_6$ is supposed to be mainly formed at rather low temperatures with dilution. With increasing polymerization temperature, the cyclic polysulphides of smaller ring size may become favourable.

It is difficult to predict which reaction is more probable to explain the formation of $-S_2-$ units, equation (5) or equation (7). We cannot compare the stability of S_6 in equation (5) with that of cyclic polysulphides in equation (7). The stability of these homo- and heterocyclic compounds may depend on their ring size and bond distortion. It has been suggested for homocyclic sulphur allotropes that the larger the ring size, the greater is the probability that some of the configurations allow strain-free rings. However, the stability of the rings does not depend on their size[19]. Although the diversity of chemical reactions concerning cumulated sulphur–sulphur bonds complicates the interpretation of sulphur rank distribution, it can be concluded that equation (7) is suitable for the unifying explanation of the experimental evidence. Further evidence should be obtained by direct detection of cyclic polysulphides formed in the copolymerization.

ACKNOWLEDGEMENTS

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