Sulfur Group Analysis in Unaccelerated Vulcanization of Natural Rubber

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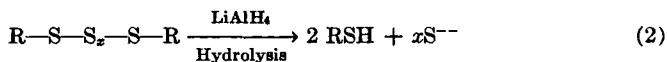
Synopsis

The reaction of lithium aluminum hydride forming mercaptan with disulfides and mercaptan as well as hydrogen sulfide with polysulfides has been applied in order to characterize the structure of the crosslinks in the case of unaccelerated vulcanization of natural rubber with sulfur. The mercaptans formed were determined amperometrically, and the hydrogen sulfide was determined as cadmium sulfide. These measurements, coupled with the estimation of total crosslinks as measured by swelling, provide valuable information as to the distribution of different crosslinks (monosulfide, polysulfide, cyclic structures, etc.) in the vulcanizate. When extended to compounds of different sulfur concentrations (2.92–33.9%) these studies show how the distribution of different linkages changes with sulfur concentration from compositions corresponding to soft rubber to those corresponding to hard rubber. The present study provides conclusive evidence that the long polysulfidic crosslinks first formed during vulcanization decrease in chain length as vulcanization progresses. Polysulfides also increase with the increasing sulfur content in the stock except in the range 6–10%. Monosulfidic crosslinks increase with increasing sulfur in the stock. In contrast to accelerated vulcanization, a high proportion of combined sulfur was found to be present in cyclic structures, and this increases with temperature of curing. These findings tally with the results of the earlier workers and have been explained with the present day ideas of the vulcanization reaction. Inaccuracies in the measurements and inherent limitations of the method were discussed.

In recent years chemical probes like lithium aluminum hydride,[1–3] triphenylphosphine,[4] sulfite ions,[5,6] and radioactive sulfur (S[35]),[7] which react with specific groups have been increasingly used for the structural characterization of vulcanizate networks. Such studies, which have mainly been advanced by Studebaker and Nabors[1,2] and Moore and Porter,[8] have provided considerable insight into the chemical nature of crosslinks in vulcanized rubber which was not heretofore possible by the application of physical methods. These studies, however, relate mostly to accelerated systems which are technically useful and do not deal with the technically unsound unaccelerated systems. The information about the structural characteristics of these simple rubber–sulfur systems is, however, of no less importance, since the complete understanding of the vulcanization process requires knowledge of the accelerated as well as that of the unac-

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celerated process.   Moreover, conventional vulcanizates are far too complex to be studied directly, as the large number of components greatly magnify the reaction possibilities.   Also, on increasing the proportion of sulfur in the simple rubber–sulfur system, one will, on vulcanization of the compound, encounter a complete range of products of different rigidity and will ultimately get what is technically known as ebonite or hard rubber.[9] As the rubber–sulfur ratio changes from the range corresponding to soft rubber to that corresponding to hard rubber the type of linkage is known to change from predominantly intermolecular crosslinking in soft rubber to predominantly intramolecular linking in hard rubber.[10]   It would be of interest to study the number of crosslinks, their nature, and the proportion of sulfur utilized in forming intermolecular and intramolecular links in this complete range as one goes from soft rubber to hard rubber stage by gradual manipulation of the proportion of sulfur.   This has not previously been done and has, therefore, been attempted in the present study, lithium aluminum hydride being used as a chemical probe.

Lithium aluminum hydride has been well characterized as a powerful reducing agent for many types of organic compounds, and its reaction with organic disulfides and polysulfides has been discussed by Arnold, Lien, and Alm[11] and also by Studebaker.[1]   The latter author is also mainly responsible for the application of this technique in the vulcanized system.[1-3]   In essence, a disulfide molecule is converted by this reducing agent to two molecules of mercaptan [eq. (1)]; a polysulfide molecule, R—S—S$_x$—S—R is converted to two molecules of mercaptan and x sulfide ions [eq. (2)], while most of the monosulfides are not attacked under the conditions employed.

$$R—S—S—R \xrightarrow[\text{Hydrolysis}]{\text{LiAlH}_4} 2RSH \tag{1}$$

$$R—S—S_x—S—R \xrightarrow[\text{Hydrolysis}]{\text{LiAlH}_4} 2\ RSH + xS^{--} \tag{2}$$

If the total crosslinks are determined by the swelling method according to the Flory-Rehner equation,[12] then the monosulfide crosslinks (or more specifically the sum of the crosslinks not attacked by LiAlH$_4$) can be obtained by the difference.   Again, from a knowledge of the proportion of sulfur in all these intermolecular processes, that involved in intramolecular processes or cyclic structures can be calculated as difference.

EXPERIMENTAL

Experimental procedures are almost the same as reported by Studebaker and Nabors[1] with necessary modifications.   The only major difference is in the different techniques employed for titration of the mercaptans formed. Whereas Studebaker employed the potentiometric method, an amperometric method[13,14] was used in the present investigation.   The former method, as mentioned by these authors involves many difficulties, as in

some cases very poor breaks were found while in some others no definite mercaptan breaks could be located. Also the amperometric method is likely to be more sensitive and less susceptible to extraneous influences than the potentiometric method.

Preparation of the Vulcanizates

Smoked sheets (RSS-1) having the analysis 1.75% acetone extract, 96.20% rubber hydrocarbon,[15] 2.60% protein, and 0.35% ash were mixed with sulfur (E. Merck) of required quantity in a 8 × 4 in. Berstoff laboratory mixing mill at about 70°C., care being taken to ensure uniform dispersion and to limit breakdown to just sufficient for uniform dispersion. An adequate amount of the mix was put in a 10 × 7 in. mold with six circular 1.5 × 0.1 in. cavities and was vulcanized in Wabash hydraulic press fitted with temperature control at a total pressure of 2000 lb. at different times and temperatures as necessary. The vulcanization time was counted from the instant the press was closed and full pressure applied the instant the press was released. The sample was immediately put under cold water in order to stop the reaction.

Extraction and Swelling of the Sample

The vulcanized sample was crushed to powder or made into thin sheet, depending on the flexibility of the sample, by being passed two or three times through the cold, close nip of the mixing mill. The resultant mass was then subjected to cold extraction for seven days with an alcohol–benzene mixture (1:2), the solvent being changed each day. Hot extraction was avoided in order to exclude the possibility of scission of polysulfide bonds. The sample was then dried at room temperature, subjected to further milling (two or three passes) and dried in vacuum for 24 hr. at room temperature. A weighed amount (0.5 g.) of the extracted and dried sample was then taken in the reaction flask and allowed to swell completely in n-hexane. The presence of n-hexane in the tetrahydrofuran (THF) used as solvent for LiAlH₄ did not interfere with the reduction or titration in the subsequent steps.

Apparatus for Reduction

A 250-ml. round-bottomed flask, fitted with condenser and two side arms for introducing dry nitrogen and for the addition of reagents respectively, was used. The top of the condenser was connected through a stopcock to the inlet of a conical flask containing cadmium acetate solution. The reaction flask was placed in a water bath at 24°C., and the whole assembly was then placed on a magnetic stirrer.

Reduction of Rubber Sample

The reaction flask was cooled by ice, and air was removed by passing through a slow stream of nitrogen. A 20-ml. portion of treated THF (with

enough dissolved $LiAlH_4$, prepared by the method described by Studebaker and Nabors[1]) was added through the side arm.   To this was added dropwise from a pipet 5 ml. of the $LiAlH_4$ solution in THF (10 g. of $LiAlH_4$ in 100 ml. of THF, distilled from completely treated THF).   Then the ice in the bath was replaced with water and the temperature brought to 24°C.   The mixture was then stirred for about 3 hr. with the magnetic stirrer.   When the reaction was complete, the bath was again adjusted to ice temperature and the excess $LiAlH_4$ destroyed by carefully adding drops of distilled water until the evolution of hydrogen ceased.   The flask was then again brought to 24°C., the outlet of the condenser connected to an Erlenmeyer conical flask containing 50 ml. of 2.5% cadmium acetate solution acidified with 5 ml. of concentrated glacial acetic acid.   Then 25 ml. of 15% sulfuric acid was added to the mixture for hydrolysis and the side arm closed at once. The flask was then flushed with a slow stream of nitrogen for about half an hour, to sweep all H_2S formed on hydrolysis to the Erlenmeyer flask containing cadmium acetate.

Estimation of Sulfur as Mercaptan and Sulfide

The contents of the reaction flask were washed into a 250-ml. beaker with dry ethanol, filtered, and the solution brought to 250 ml. with ethanol in a volumetric flask.   A known volume of this solution was then estimated with silver nitrate ($0.005N$) by the method of amperometric titration developed by Kolthoff and Harries[14] and adapted in this laboratory for various analysis of rubber chemicals.[13,16−18]

Cadmium sulfide formed by the passage of H_2S was estimated iodometrically, and the sulfur so obtained is termed polysulfide sulfur in the discussion.

Crosslinking Measurement

Vulcanized rectangular samples weighing approximately 0.7 g. were allowed to swell for six days at 20°C. in dry benzene containing 0.2% phenyl-β-napthylamine as antioxidant.   The swelled sample was lightly blotted with a filter paper in order to remove any adhering solvent, then immediately weighed in a stoppered weighing bottle, dried in vacuum at 80°C., and weighed again.   The total crosslinks were then calculated from the equation,[12]

$$M_c = -\rho V_1 v_2^{1/3}/[(kv_2^2/2) + \ln(1 - v_2) + v_2]$$

which takes the approximate form,

$$M_c \cong 2\rho V_1/v_2^{5/3}(1 - k)$$

when higher terms in the expansion of $\ln(1 - v_2)$ are neglected.

In this equation V_1 represents the molar volume of the solvent, ρ is the density of the polymer, M_c is the molecular weight of the chain between crosslinks, v_2 is the volume fraction of the polymer in the swollen gel, and k is the interaction parameter which has been shown by Adams and

Johnson[19] to remain substantially constant at 0.437.   The reciprocal of the M_c values gives the number of effective network chains (ν), which when halved gives the number of crosslinks.

Combined and Total Sulfur

Combined and total sulfur were determined by the standard Zn–HNO_3 process.[15]

RESULTS AND DISCUSSION

Polysulfide Sulfur

Table I shows the sulfur balance and the distribution of sulfur in the formation of different types of linkages in the total range 2.92–33.9% of sulfur on the weight of the total stock, i.e., covering the whole range of soft
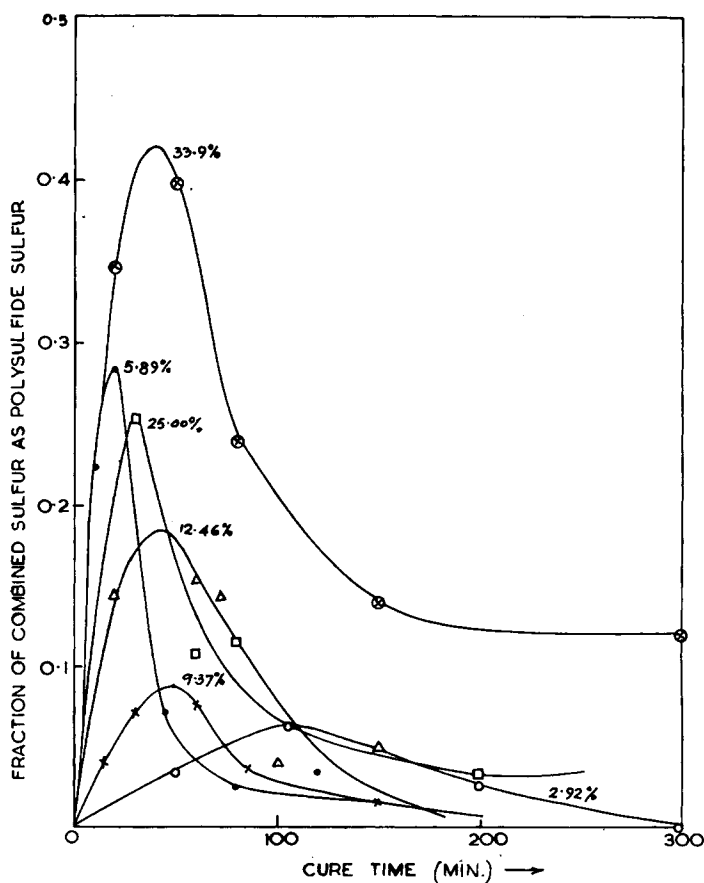

Fig. 1. Variations of fraction of polysulfide sulfur with sulfur concentration: (O) 2.92%; (●) 5.89%; (×) 9.37%; (Δ) 12.46%; (□) 25.0%; (⊗) 33.9%. Cure temperature 160°C.

TABLE I. Data for Sulfur Group Analysis (Cure Temperature 160°C.)

| g./g. stock	Total S %	Total S atoms/g. × 10³	Vulcanization time, min.	Combined S, atoms/g. × 10³	Mercaptan S (after reduction), atoms/g. × 10³	Polysulfide S, atoms/g. × 10³	Thiol S, atoms/g. × 10³	Monosulfide S, atoms/g. × 10³ (calc.)	S in cyclic structures, atoms/g. × 10³ (calc.)	Fraction polysulfide S, (calc.)	S as monosulfide, %	S as cyclic structures, %
0.0301	2.92	0.9380	50	0.7988	0.3082	0.0277	0.0241	—	—	0.0346	—	—
			106	0.8627	0.1720	0.0541	0.0415	—	—	0.0622	—	—
			200	0.8723	0.1561	0.0246	0.0251	—	—	0.0265	—	—
			300	0.9266	0.0935	Trace	0.0277	0.0050	0.8004	0.0000	0.54	86.38
0.0626	5.89	1.9563	10	0.7160	0.1367	0.1599	0.0275	—	—	0.2234	—	—
			20	0.8435	0.1870	0.2395	0.0824	0.0120	0.3226	0.2839	1.42	38.24
			45	1.5274	0.3803	0.1091	0.1051	0.0370	0.8959	0.0715	2.42	58.66
			80	1.5939	0.1867	0.0387	0.1195	0.0320	1.2170	0.0243	2.01	76.35
			120	1.4943	0.1883	0.0525	0.1228	0.0170	1.1137	0.0351	1.14	67.22
0.1034	9.37	3.2313	15	0.9069	0.1342	0.0364	0.0393	0.0130	0.6840	0.0402	1.43	75.44
			30	1.1138	0.1531	0.0786	0.0940	0.0430	0.7487	0.0706	3.86	67.20
			60	2.0688	0.2947	0.1566	0.0989	0.0380	1.4806	0.0757	1.84	71.53
			85	2.3447	0.3269	0.0862	0.1421	0.0450	1.7445	0.0368	1.92	74.40
			150	2.3101	0.1359	0.0340	0.1817	0.0980	1.8605	0.0148	4.22	80.52
0.1423	12.46	4.4468	20	1.2750	0.0227	0.1841	0.0442	0.1280	0.8960	0.1444	10.04	69.81
			60	2.9857	0.1307	0.4548	0.0642	0.1980	2.1380	0.1524	6.63	71.60
			70	2.9760	0.1967	0.4264	0.0749	0.1800	2.0980	0.1432	6.04	70.49
			100	3.1435	0.1338	0.1261	0.0447	0.1840	2.6549	0.0401	5.86	84.47
			150	2.9755	0.1303	0.1524	0.0228	0.1480	2.5220	0.0512	4.98	84.76
0.3333	25.0	10.4156	30	4.2749	0.2248	1.0791	0.0875	0.1780	2.7055	0.2524	4.16	63.28
			60	8.0541	0.3139	0.8773	0.0958	0.4390	6.3281	0.1089	5.45	78.56
			80	7.2875	0.5477	0.8453	0.1041	0.4010	5.3894	0.1161	5.50	73.96
			200	5.8083	0.4957	0.1884	0.1000	0.4580	4.5662	0.0324	7.88	78.63
0.5129	33.9	16.0281	20	12.8194	0.5495	4.4576	0.1608	—	—	0.3477	—	—
			50	14.1641	0.2514	5.6662	0.0614	0.7080	7.4771	0.4001	5.01	52.91
			80	11.9516	0.1726	2.8596	0.0142	1.0760	7.8292	0.2393	9.02	65.67
			150	11.3700	0.2647	1.5873	0.0047	1.0300	8.4833	0.1393	9.06	74.61
			300	11.1951	0.1172	1.3569	0.0189	1.1040	8.5961	0.1213	9.87	76.85
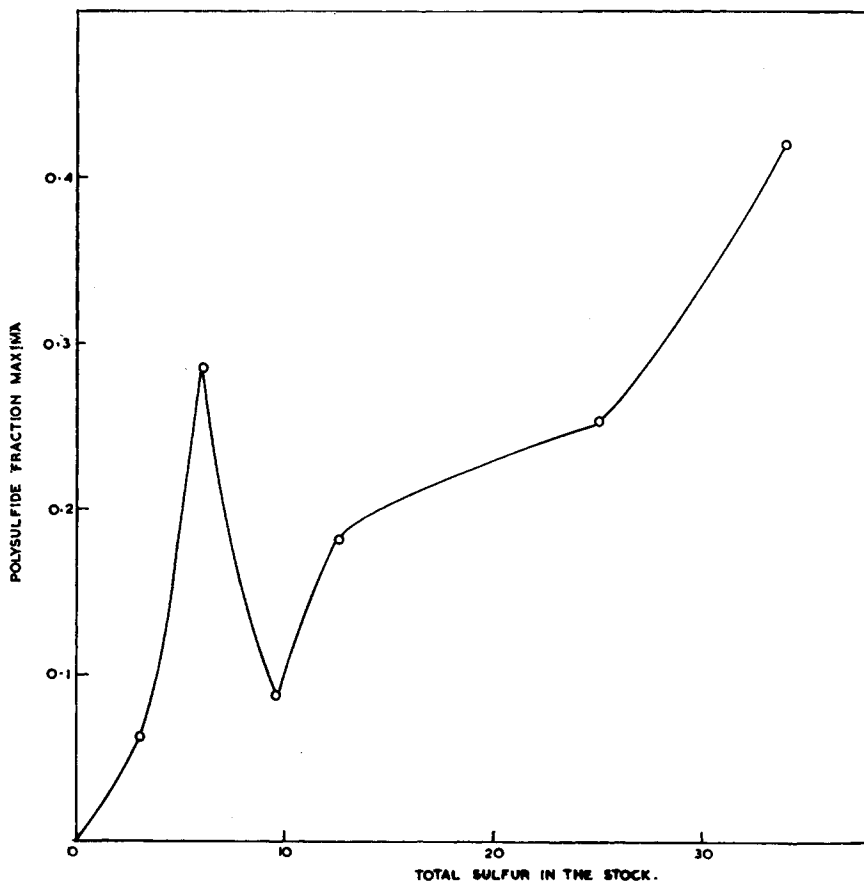
Fig. 2. Variation of the maximum polysulfide concentration with rubber–sulfur ratio in the stock at 160°C.

rubber to that of hard rubber. It will be seen from this table and also from Figure 1 that polysulfide sulfur in every case goes through a maximum with reaction time and that the fraction of sulfur combined as polysulfide (S_x in R—S—S_x—S—R) goes on increasing as the sulfur composition in the stock increases, except in the range 6–10%. This is amply demonstrated in Figure 2, which plots fraction of polysulfide sulfur at the maximum points in curves in Figure 1 against total sulfur in the stock. The maximum portion of sulfur as polysulfide in this series is as high as 40% of total combined sulfur. Figure 2 gives a composite picture of the processes taking place as the proportion of sulfur in the stock is increased. At first, the crosslinking reaction (intermolecular) increases with sulfur up to about 6% sulfur stock. On further increase of sulfur the degradation reactions gain prominence and crosslinks are broken. At more than about 10% sulfur another type of building reaction (probably intramolecular) sets in which becomes S-shaped on further increase of sulfur, indicating an auto catalytic type of reaction,
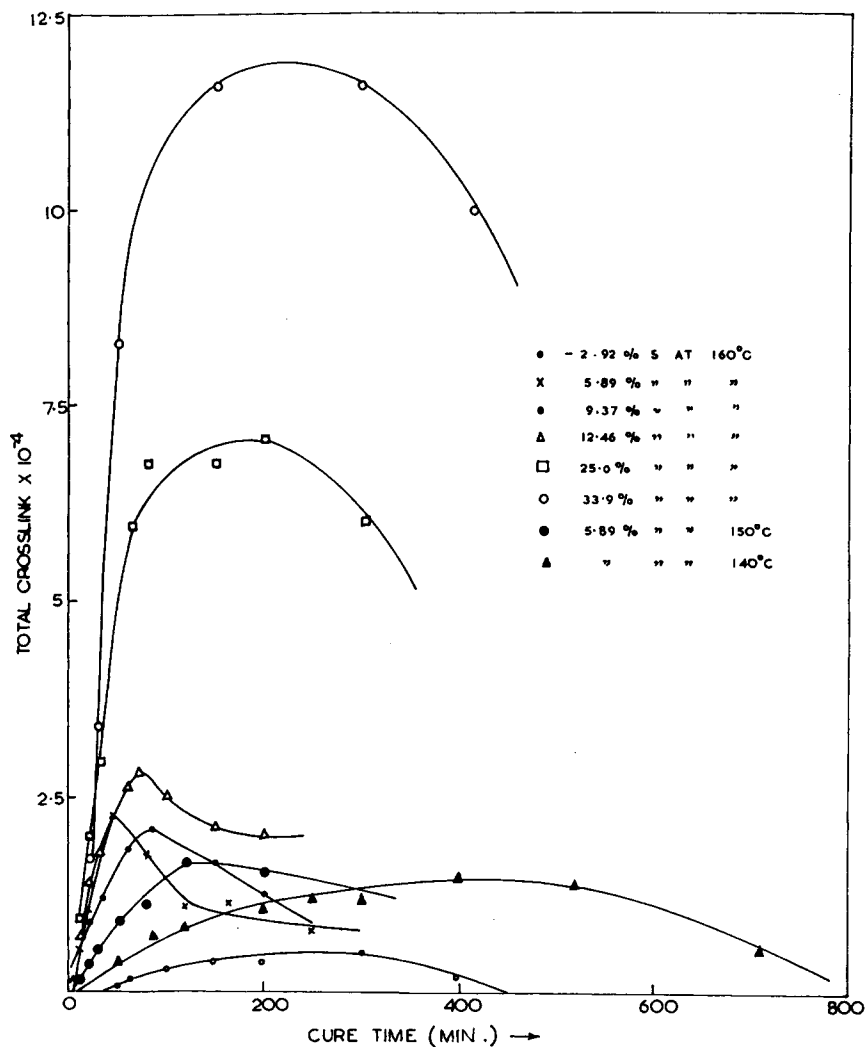
Fig. 3. Variation of total crosslinks with cure time and temperature.

probably because of the activating influence of the links already formed. The range 6–10% is well within the range of "rotten rubber stage" which is very much prone to the oxidative degradation reactions.[20]   Prominence of these degradative reactions is not likely to allow crosslinkages to be formed in sufficient number, and polysulfide linkages, being particularly susceptible to oxidative degradation reactions, are likely to decrease in this range.

The competing nature of the two opposite reactions is also evident from the shape of the curve in Figure 1 which follow along normal curves, i.e., along concave curves with respect to the time axis for increase and along convex curves for decrease.   The results are complicated but may be

explained qualitatively by the assumption that two opposing factors determine the course of the polysulfide content.

The nature of the curves also supports the prevalent concept that in the vulcanization reaction polysulfide linkages are first formed which later on are regrouped to more stable structures containing fewer sulfur atoms.[4,21-23] A comparison of Figure 1 with Figure 3 which shows the total crosslinks as a function of time justifies this contention, where it will be seen that the maximum polysulfide formation is attained much earlier than the maximum crosslinking. In other words, degradation of polysulfide links is followed by the formation of other types of linkages. Whether there is any quantitative correspondence is difficult to state at the present because of the interplay of various other factors. At least the relation is not likely to be the same for all the compositions studied because of the sharp contrast in the structures that are ultimately obtained by variation of the sulfur composition. Whereas the structures in the soft rubber stage are predominantly intermolecular, those in the hard rubber stage are mostly intramolecular.

It may also be observed in Figure 1 that the reactions in 2.92% sulfur stock are much slower than stock containing 5.89% sulfur. This is likely to be so because of the mass effect, but that is not the whole picture. The increase in polysulfide content in the latter stock may take place in two ways. Firstly, there may be an increase in the number of such linkages; secondly, there may be an increase in the polysulfide chain length. Again, a comparison of the corresponding curves of these stocks in Figures 1 and 3 will roughly show that whereas the crosslinking maximum increases by 2.5-fold, a 5-fold increase of polysulfide maximum is observed. This can only be explained by saying that in the latter stock comparatively more sulfur atoms enter into the linkages already formed. This has been explained by Bresler et al.[24] by assuming that after an initial formation of polysulfide linkages, the corresponding points itself would take on the properties of a very active free radical, and be capable of an activating influence on the saturated sulfur molecule S_8. The S_8 ring then opens to form a biradical which is able to unite the small sulfur chain atoms with two fragments of hydrocarbon which have been activated by the primary sulfur combination. Consequently, the polysulfide chain length increases. A simple calculation would show that whereas the average number of sulfur atoms in the polysulfide chain at the peak (Fig. 1) at 2.92% sulfur is 2.63, the average number in the 5.89% sulfur stock is 4.58. The greater number of sulfur atoms per chain in the higher sulfur stock makes the chain more unstable to heat, and the steeper depression of the higher sulfur curves in Figure 1 may be attributed to this.

Another interesting point in Table I and Figure 1 is the high yield of polysulfide sulfur in the two high sulfur stocks (25% and 33.9%). These compositions are well within the range of hard rubber.[25] The high yield of polysulfide in these stocks shows that as is the case with soft rubber, hard rubber formation is also preceded by polysulfide formation which on decomposition goes to form the intramolecular links in hard rubber. This is in

TABLE II

Data for Sulfur Group Analysis (Total Sulfur in Stock = 5.89%)

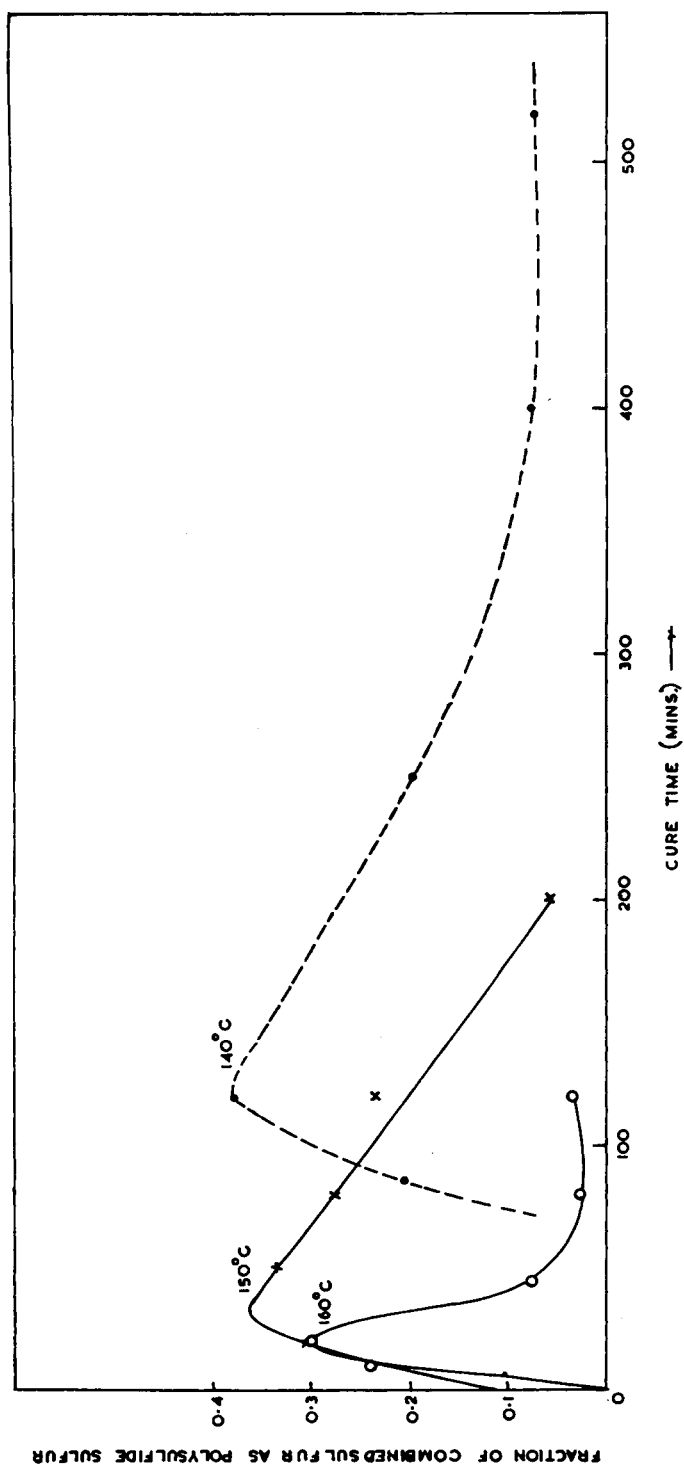| Temp., °C.	Vulcanization time, min.	Combined atoms/g. × 10³	Mercaptan S, after reduction, atoms/g. × 10³	Polysulfide atoms/g. × 10³	Thiol S, atoms/g. × 10³	Monosulfide S, atoms/g. × 10³ (calc.)	Sin cyclic structures, atoms/g. × 10³	Fraction of polysulfide S (calc.)
160	10	0.7160	0.1376	0.1599	0.0275	—	—	0.2234
	20	0.8435	0.1870	0.2395	0.0823	0.0120	0.3226	0.2839
	45	1.5274	0.3803	0.1091	0.1051	0.0370	0.8959	0.7145
	80	1.5939	0.1876	0.0387	0.1195	0.0320	1.2170	0.2428
	120	1.4943	0.1883	0.0525	0.1228	0.0170	1.1137	0.0351
150	20	0.7836	0.1096	0.2258	0.0083	—	—	0.2881
	50	0.6674	0.1065	0.2092	0.0581	0.0440	0.2496	0.3126
	80	1.0693	0.1641	0.2759	0.0833	0.0340	0.5120	0.2581
	120	1.1623	0.2338	0.2600	0.0697	0.0490	0.5498	0.2238
	200	1.4943	0.1694	0.0800	0.0617	0.0440	1.1392	0.0536
140	86	0.4782	0.0857	0.0930	0.0123	0.0260	0.2612	0.1945
	120	0.6010	0.0797	0.2125	0.0458	0.0390	0.2240	0.3535
	250	0.9696	0.0770	0.1792	0.0591	0.0810	0.5733	0.1848
	400	1.3547	0.2184	0.0963	0.0800	0.0380	0.9220	0.0711
	520	1.5872	0.1510	0.1066	0.0737	0.0640	1.1919	0.0672

Fig. 4. Variation of polysulfide sulfur fraction with temperature. Sulfur in stock = 5.89%.

accord with the findings of Bateman, Moore, and Porter[26,27] with low molecular weight dienes, where they state that "cyclic monosulfides formed from the 1:5 diene are essentially secondary products resulting from the first formed polysulfides which engage in proton transfer processes to give sulfurated carbonium ion species: these effect intramolecular heterolysis of adjacent polysulfide linkages." Kuzminskiĭ and Borkova[23] state that the activation energy in the process of hard rubber vulcanization, calculated from the relation of temperature to loss in unsaturation, is 23 kcal./mole, while the activation energy of the vulcanization of soft rubber reaches 30 kcal./mole. The lowering of the energy barrier was attributed to the large specific reaction rates of the secondary reactions of the combination of sulfur with the sulfur links already formed. These reactions take place much more easily than the primary combination of sulfur with rubber. The presence of polysulfides with as many as 25 sulfur atoms per chain has also been inferred by these authors from their experiments with radioactive sulfur. It may, however, be noted in Figure 1 that in these stocks, the yield of polysulfides does not come down to the low values obtained for the lower sulfur stocks, although the internal temperatures of these stocks are probably much higher during cure due to the high exothermicity of the hard rubber reactions. These residual polysulfides may be located in the cyclic structures themselves which are supposed to be more stable. These observations are in contradiction with those of Kuzminskiĭ and Borkova,[23] who state that the polysulfide bonds are not observed in a hard rubber at optimum vulcanization.

Table II and Figure 4 show the variation of polysulfide yield of 5.89% sulfur stock with change of temperature. It will be seen that as the temperature is raised the maxima for polysulfide formation move to shorter reaction times and that they also become more and more sharply defined. This is in agreement with Scheele.[28] No conclusion can, however, be drawn from these curves as to whether the maximum polysulfide content is dependent on temperature. However, a slight decrease of the maximum yield with increase of temperature is noticeable; this may be attributed to the greater instability of the polysulfide bonds at higher temperatures.

Monosulfide Sulfur

Table I and Figure 5 show the values of monosulfide sulfur calculated from the monosulfide crosslinks as given in Table III. It may be seen that the yield of monosulfide sulfur goes on increasing with increasing percentage of sulfur in the stocks. The nature of the curves is more or less the same in all cases, and they do not show maxima due to reversion at longer cure times as in the case of polysulfide linkages; this points to the inherent stability of the monosulfide linkages once they are formed. The slight reversion in the case of two lowest sulfur compositions may be correlated with the reversion of polysulfide links and to the fact that monosulfide linkages are calculated as a difference. The values at the smaller cure times in Table I in the case of 2.92% sulfur show negative monosulfide sulfur which will be discussed

TABLE III. Distribution of Crosslinks in Different Stocks (Cure Temperature = 160°C.)

Total S Atoms/g. × 10³	%	Vulcanization time, min.	Total crosslinks, mole/g. × 10³ (calc.)	R—S—S_z—SR crosslinks, mole/g. × 10⁴ (calc.)	R—S—R crosslinks, mole/g. × 10⁴ (calc.)	x in R—S—S_z—S—R	Avg. no. of S atoms per crosslink[a]
0.9380	2.92	50	0.1321	1.54	(−1.41)	0.18	60.4
		106	0.2937	0.86	(−0.57)	0.63	30.0
		200	0.4139	0.78	(−0.37)	0.32	21.0
		300	0.5135	0.46	0.05	0.00	18.0
1.9563	5.89	10	0.55	0.68	(−0.13)	2.35	11.0
		20	1.05	0.93	0.12	2.58	8.0
		45	2.27	1.90	0.37	0.57	6.6
		80	1.25	0.93	0.32	0.42	12.6
		120	1.11	0.94	0.17	0.56	13.4
3.2313	9.37	15	0.80	0.67	0.13	0.54	11.2
		30	1.19	0.76	0.43	1.03	9.2
		60	1.85	1.47	0.38	1.07	11.0
		85	2.08	1.63	0.45	0.53	11.2
		150	1.66	0.68	0.98	0.50	13.7
4.4463	12.46	20	1.39	0.11	1.28	16.70	9.2
		60	2.63	0.65	1.98	7.00	11.4
		70	2.78	0.98	1.80	4.35	10.7
		100	2.50	0.66	1.84	1.91	12.5
		150	2.13	0.65	1.48	2.34	14.0
10.4156	25.0	30	2.90	1.12	1.78	9.63	14.7
		60	5.95	1.56	4.39	5.62	13.5
		80	6.75	2.74	4.01	3.09	10.8
		200	7.05	2.47	4.58	0.76	8.2
16.0281	33.9	20	1.72	2.75	(−1.03)	16.21	74.5
		50	8.33	1.25	7.08	45.33	17.0
		80	11.62	0.86	10.76	33.25	10.3
		150	11.62	1.32	10.30	12.02	9.8
		300	11.62	0.58	11.04	23.40	9.6

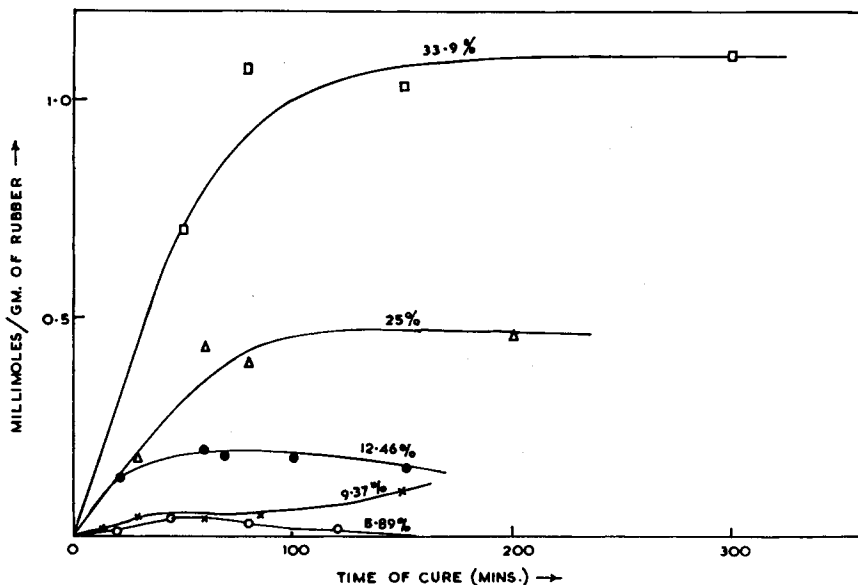[a] Calculated from the ratio total combined sulfur/total crosslinks.

Fig. 5. Variation of monosulfide sulfur with cure time at 160°C.

later.   The fraction of monosulfide sulfur in the different stocks ranges from about 5 to 20% of the total stock (Table I).   The high yield of monosulfides particularly evident in the two highest sulfur stocks may be correlated with the presence in these of intramolecular cyclic structures which behave virtually as crosslinks when situated opposite to one another, due to the high polarity of the sulfur atoms.[10]

Sulfur in Cyclic Structures

The fact that about 40–55 sulfur atoms must be combined[29] in the natural rubber network to produce one physically effective chemical crosslink unit, gives a quantitative expression to the known marked inefficiency of sulfur as a crosslinking agent in unaccelerated rubber–sulfur systems and indicates the considerable structural complexity of the resultant network.   The low crosslinking efficiency of sulfur as revealed in this work and elsewhere[29] is consistent with the results obtained from the reaction of sulfur with mono-olefins and 1,5-dienes.[26]   This is explained as due to the formation of (a) crosslinked units containing long polysulfide chains as outlined above; (b) the vicinal sulfidic crosslinks which act physically as a single crosslink; and (c) cyclic sulfides which constitute important modifications of the main polyisoprene chains.

In unaccelerated natural rubber (NR)–sulfur systems, the formation of cyclic sulfides constitutes the main network defect.   In fact, Moore et al.[4,8] have shown that in a NR–sulfur system containing 10% sulfur, about 76–95% of sulfur is in the cyclic structures, depending on the time of heating. In the present investigation the maximum of each series shows that about

76–86% of sulfur is present in cyclic structures. The slight difference may be attributed partly to the higher temperature (160°C.) used in the present investigation and partly to the difference in the composition and a shorter time of cure. It was observed by Bloomfield[30] that nature of the structures formed by the action of rubber and sulfur is time-dependent, and that there occurs an increase of cyclic structures at the expense of crosslinked units concurrent with change of structures in the intramolecular units themselves, as the reaction is continued for longer times. A consideration of Table II also shows that the amount of sulfur in cyclic structures increases with temperature. Also, the sulfur present in cyclic structures in the present work has been calculated as a difference after considering the sulfur present in all the intermolecular processes. This is not valid, at least for the compositions (25% and 33.9%) in the region of hard rubber, which is known to consist predominantly of intramolecular linkages. Assuming the monosulfide linkages in hard rubber are probably intramolecular in character (which is not unjustified in the light of our present knowledge of the structure of hard rubber), if the percentages of sulfur as monosulfide and cyclic structure (Table I) are added together, the total so obtained shows that sulfur in cyclic structures amounts to 85–96% of the total combined sulfur, which more or less agrees with the data of Moore et al. It is possible that a portion of the mercaptan sulfur in Table I arises from reduction of disulfide bonds[10] in intramolecular structures, at least in the higher sulfur stocks which would otherwise have further increased the sulfur in cyclic structures. However, it is not possible to come to any unequivocal conclusion regarding the above points without actual determination of the cyclic structures as was done in numerous investigations by Moore, Bateman, et al.[26,27,29] but is outside the scope of the present investigations.

Distribution of Crosslinks

The distribution of the different types of crosslinks in various sulfur compositions is presented in Table III and Figures 6 and 7.

It may be seen in Figure 6a that the number of polysulfide crosslinks at shorter cure times is greater than the total crosslinks, which sounds absurd. This observation is, however, in agreement with that of Studebaker,[2] who remarked that polysulfides present in a vulcanizate may exceed the total crosslinks, particularly with rubber stocks in which little or no soluble zinc is present. He explained that this is probably associated with the presence of polysulfides with only one end attached to the rubber molecule, the other end presumably terminated by an accelerator moiety (or hydrogen). A contribution to this excess of polysulfides to total crosslinks as determined from swelling measurements would also be made by scission of the polymer backbone during the earliest stages of cure as described by Craig.[31] There may also be present few ineffective crosslinks (vicinal crosslinks) which virtually do not affect swelling and thus contribute to the lower value of the total crosslinks. These factors are also responsible for the negative values of monosulfide crosslinks in Figure 6a which are calculated as a difference.
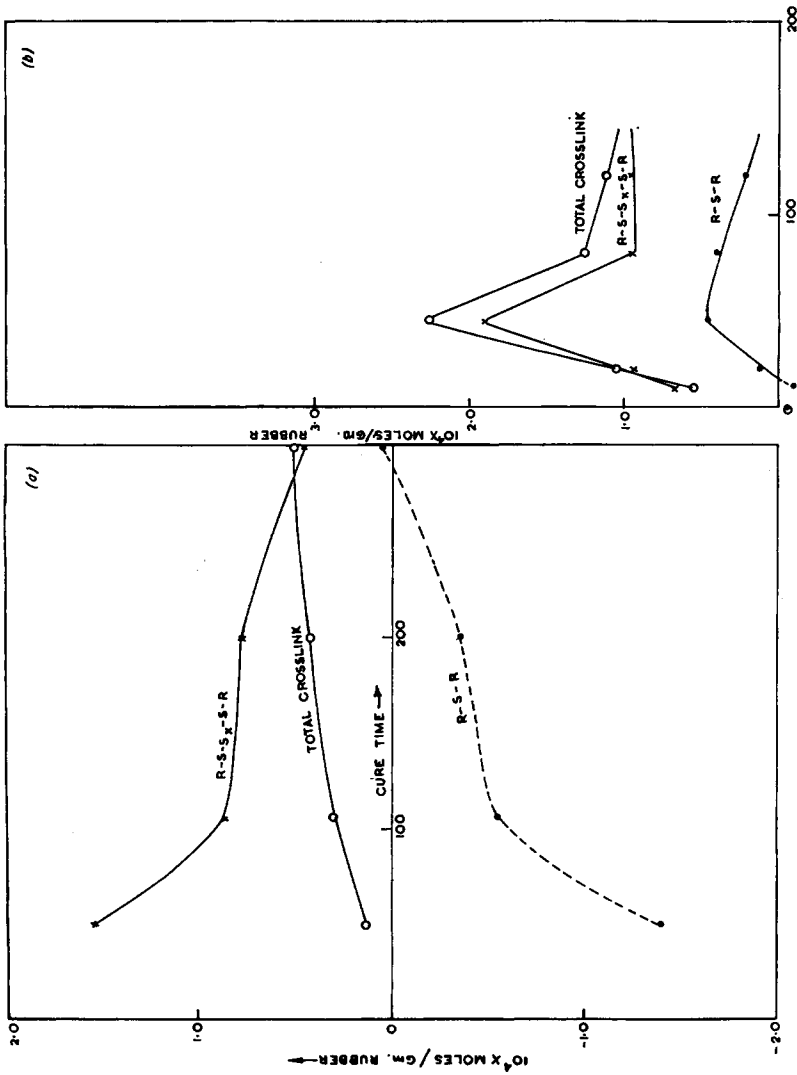
Fig. 6. Distribution of different crosslinks with changes in rubber-sulfur ratio of the stock and cure at 160°C.: (a) 2.92% sulfur in stock; (b) 5.89% sulfur in stock.
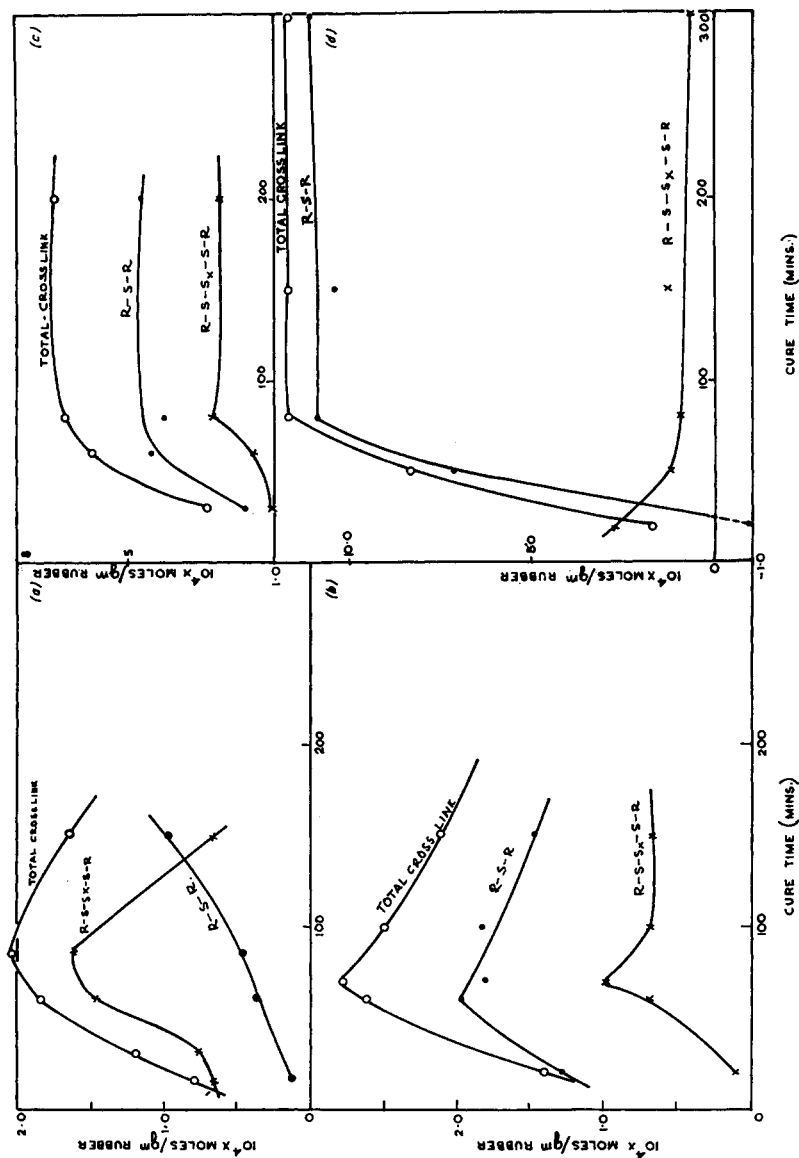
Fig. 7. Distribution of different crosslinks with change in rubber–sulfur ratio of the stocks and cure at 160°C.: (a) 9.37% sulfur in stock; (b) 12.46% sulfur in stock; (c) 25.0% sulfur in stock; (d) 33.9% sulfur in stock.
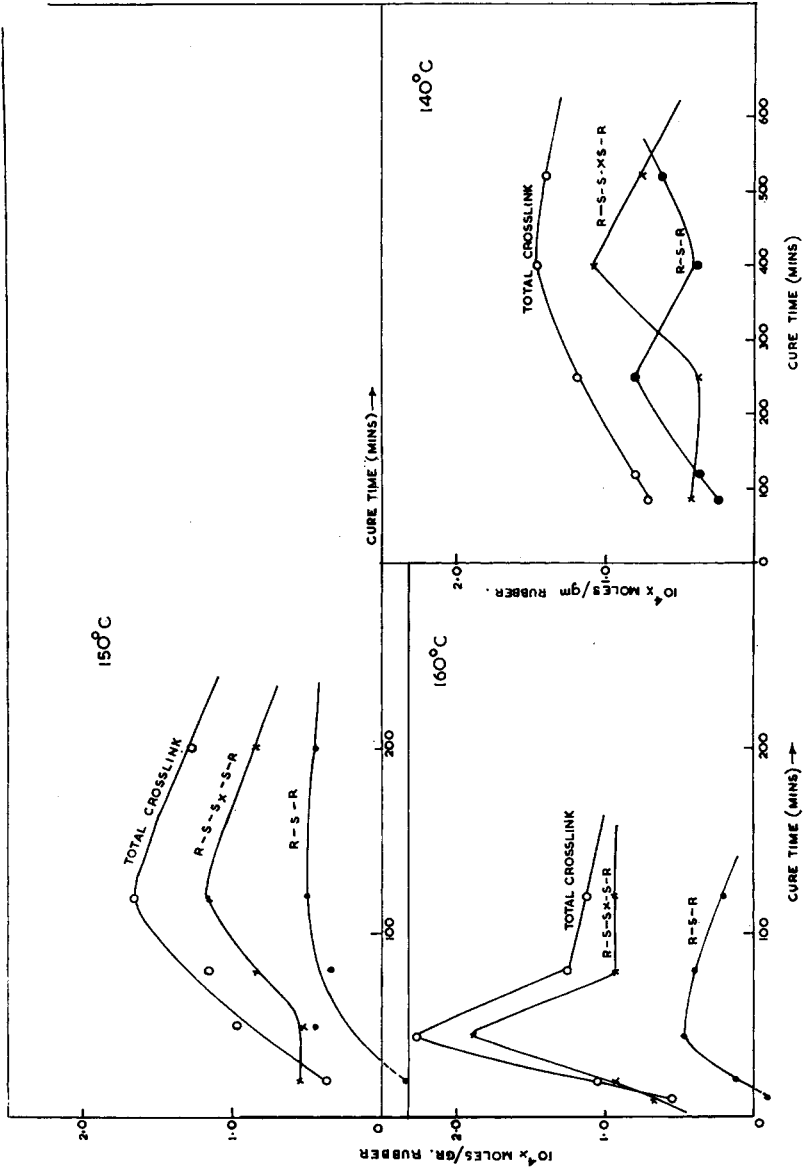
Fig. 8. Distribution of different crosslinks in 5.89% sulfur stock with various cure temperatures.

This is an inherent inaccuracy in the analysis which cannot be avoided until an accurate, direct method for the analysis of monosulfides is developed.

Figure 6b shows the distribution of crosslinks in 5.89% sulfur stocks. The comparative instability of crosslinks at longer cure times of this stock which corresponds to the composition of the "rotten rubber stage" is evident here also by the steep decrease of the number of crosslinks. Measurements at different temperatures (Table IV and Fig. 8) show that the number of crosslinks decreases with decreasing temperatures, and the reversion is less prominent the lower the temperature.

TABLE IV

Crosslink Distribution at Different Temperatures (Total Sulfur in Stock = 5.89%)

Temp., °C.	Vulcani- zation, time, min.	Total mole/g. $\times 10^4$	R—S—S_x —S—R crosslinks, mole/g. $\times 10^4$ (calc.)	R—S—R crosslinks, mole/g. $\times 10^4$ (calc.)	x in R—S—S_x —S—R
160	10	0.55	0.68	(—0.13)	2.35
	20	1.05	0.93	0.12	2.58
	45	2.27	1.90	0.37	0.57
	80	1.25	0.93	0.32	0.42
	120	1.11	0.94	0.17	0.56
150	20	0.37	0.55	(—0.18)	4.10
	50	0.97	0.53	0.44	3.95
	80	1.16	0.82	0.34	3.36
	120	1.66	1.17	0.49	2.22
	200	1.28	0.84	0.44	0.95
140	86	0.69	0.43	0.26	2.16
	120	0.79	0.40	0.39	5.31
	250	1.19	0.38	0.81	4.72
	400	1.47	1.09	0.38	0.88
	520	1.39	0.75	0.64	1.42

The interesting points in Figure 7 are an increase of the total crosslinks with increasing sulfur concentration, a decrease of the R—S—S_x—S—R crosslinks, and an increase of the R—S—R crosslinks which comes as a difference. The higher total and monosulfide crosslinks may presumably be due to increasing formation of intramolecular structures with lower number of sulfur atoms which act as effective crosslinks due to van der Waal's forces between polar sulfur atoms situated opposite to one another, as shown in Figure 9.

This is particularly true in high sulfur stocks (Fig. 7c, 7d). It might be said on the basis of the statistical theory of rubber elasticity that intramolecular structures would not affect the number of crosslinks as determined by equilibrium swelling. This would, however, hold good for low sulfur systems where swelling is high and where the statistical theory is strictly applicable. In the hard rubber systems, as in the two highest sul-
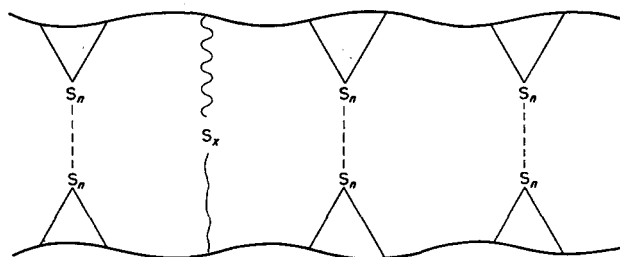
Figure 9.

fur stocks in the present study, swelling is not high and so intermolecular interactions arising out of intramolecular structures would not probably be negligible. The lower polysulfide links may be explained as due to (a) decomposition of the polysulfides supposed to be formed as an intermediate, [26] as a result of high exothermicity of the reaction as the proportion of the sulfur in the stock increases,[32] (b) possible incomplete reaction with LiAlH₄ as the vulcanizate becomes more and more hard, and (c) an abrupt increase in the velocity of the hard rubber reaction, with formation of mainly monosulfide and disulfide intramolecular bonds as was reported by Bhaumik, Banerjee, and Sircar;[32] this is also evident from Figures 7c and 7d.

CONCLUSIONS

The present investigation is an attempt to follow the distribution of sulfur in the various linkages as the reaction changes from a predominantly intermolecular to intramolecular one. The results are explained in the light of the current theories of vulcanization reactions and knowledge of the structure of the vulcanizates as the sulfur composition changes.

There are, however, some inherent inadequacies in this study. These are (1) doubtful applicability of the Flory-Rehner equation for hard rubber vulcanizates which was applied here in absence of any better known method; (2) doubt as to the complete reaction of all the R-S-S$_x$-S-R links with LiAlH₄; (3) inability of LiAlH₄ to differentiate between intermolecular and intramolecular links; (4) absence of any known method to determine R-S-R links (which were calculated as differences); (5) inability of LiAlH₄ to distinguish between R-S-S-R and R-S-S$_x$-S-R links; (6) the inclusion of C-C crosslinks, if any, in R-S-R links; (7) the assumption that dangling ends, short-circuited or double crosslinks, and network entanglements are nonexistent.

However, in the absence of any better known method, the present study gives, at least a qualitative picture as to how the linkages change with sulfur content and is likely to be of value until a better method, free from the above limitations are available. Incidentally investigations are being taken up in this laboratory with triphenyl phosphine as a chemical probe. This compound can distinguish between intermolecular and intramolecular

polysulfide links[3] but is not, however, free from the other limitations mentioned above. Most of the uncertainties mentioned above also apply to similar studies so far published in the literature.[1-4,8,28] The additional limitations in the present study are applicability of the Flory-Rehner equation and the limitation inherent in a simple rubber–sulfur system where the structure of the vulcanizate is more complicated due to the simultaneous presence of considerable proportions of intermolecular and cyclic structures. The detailed structures of the crosslinked sulfides are still in doubt, but substantial advances have been made in recent years towards their characterization. Thus, they are not considered, as originally visualized,[25,33] to contain solely open-chain diisoprene units linked in an alkylalkenyl polysulfide structure, but cyclic structures of the types as put forward by Bateman et al.[27] are also believed to be incorporated at points adjacent to sulfur crosslinks. It is not overly optimistic to assume that complete structural elucidation of the vulcanizate will be possible in the very near future with the help of the powerful analytical tools developed in recent years. The rubber chemist will then be in a much better position to design his compound with an eye to the specific types of structures rather than to physical properties which give only a composite picture.

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Résumé

On a caractérisé les structures, pontées du caoutchouc naturel lors d'une vulcanisation non-accélérée au soufre par une réaction à l'hydrure de lithium aluminium formant des mercaptans au départ des disulfures ainsi que du sulfure d'hydrogène au départ des polysulfures. Les mercaptans formés ont été dosés par ampérométrie et le sulfure d'hydrogène sous forme de sulfure de cadmium. Ces mesures ainsi que la détermination du nombre total de ponts mesuré par gonflement, donnent des informations valables sur la distribution des différents ponts dans le vulcanisat (monosulfures, polysulfures, structure cyclique). Lorsqu'on étend l'étude aux substances à concentrations différentes en soufre (2.92–33.9%), on trouve une variation dans la distribution des différents ponts en fonction des concentrations variables en soufre depuis celle correspondant au caoutchouc mou jusqu'à celle du caoutchouc dur. Cette étude montre d'une manière concluante que le pontage par de long polysulfures apparaît en premier lieu au cours de la vulcanisation et diminue en longueur lors du processus de vulcanisation. Les polysulfures augmentent aussi avec le pourcentage de soufre dans l'échantillon excepté dans le domaine de 6 à 10%. Les pontages par monosulfures augmentent avec la quantité de soufre. Par contre, lors de la vulcanization rapide, on trouve une grande proportion de soufre combiné sous forme de structures cycliques qui augmentent avec la température du traitement. Ces observations concordent avec les résultats antérieurs et sont expliquées suivant les idées actuelles concernant la vulcanisation. On discute les erreurs de mesure et les limitations inhérentes à la méthode.

Zusammenfassung

Die Reaktion von Lithium-aluminiumhydrid mit Disulfiden unter Bildung von Mercaptan sowie mit Polysulfiden unter Bildung von Mercaptan und Schwefelwasserstoff wurde zur Charakterisierung der Struktur der Vernetzungsstellen im Fall der unbeschleunigten Vulkanisation von Naturkautschuk mit Schwefel angewendet. Das gebildete Mercaptan wurde amperometrisch und der Schwefelwasserstoff als Kadmiumsulfid

bestimmt. Diese Messungen liefern zusammen mit der Bestimmung des totalen Vernetzungsgehaltes durch Quellungsmessungen wertvolle Angaben über die Verteilung verschiedener Vernetzungsstellen. (Monosulfid, Polysulfid, cyklische Struktur etc.) im Vulkanisat. Bei Ausdehnung auf Mischungen mit verschiedener Schwefelkonzentration (2.92–33.9%) zeigen diese Untersuchungen, wie sich die Verteilung der verschiedenen Bindungen bei einer Änderung der Schwefelkonzentration von derjenigen in Weichgummi zu derjenigen in Hartgummi ändert. Die vorliegende Untersuchung liefert schlüssige Beweise dafür, dass während der Vernetzung zuerst lange Polysulfidvernetzungen gebildet werden, welche bei fortschreitender Vulkanisation an Kettenlänge abnehmen. Die Polysulfide nehmen auch mit steigendem Prozentgehalt an Schwefel zu, mit Ausnahme des Bereichs von 6–10%. Monosulfidische Vernetzungen nehmen mit steigendem Schwefelgehalt zu. Im Gegensatz zur beschleunigten Vulkanisation wurde bei zunehmender Vulkanisationstemperatur ein hoher Anteil von gebundenem Schwefel in cyklischer Struktur gefunden. Diese Befunde stimmen mit den Ergebnissen früherer Autoren überein und wurden auf Grundlage der heutigen Vorstellungen über die Vulkanisationsreaktion erklärt. Die Messgenauigkeit und die spezifischen Grenzen der Methode wurden diskutiert.