

## Structural Characterization of Vulcanizates Part X. Thiol-Disulfide Interchange for Cleaving Disulfide Crosslinks in Natural Rubber Vulcanizates

D. S. CAMPBELL, *The Natural Rubber Producers' Research Association,  
Welwyn Garden City, Herts, England*

### Synopsis

The thiol-disulfide exchange reaction is shown to be applicable to cleavage of disulfide crosslinks in accelerated sulfur vulcanizates of natural rubber. The reaction, in conjunction with the previously reported selective cleavage of polysulfide crosslinks, is used to determine the distribution of crosslink types for several accelerated sulfur vulcanization systems as a function of cure time. Discrepancies between the results and published results obtained using the reagent sodium di-*n*-butyl phosphite for disulfide crosslink cleavage are discussed.

### INTRODUCTION

An essential part of the structural characterization of sulfur-vulcanized rubber networks is the determination of the amounts and types of chemical crosslinks present. This can be achieved by measuring chemical crosslink density before and after treatment with chemical reagents which specifically break particular types of crosslinks. Saville and Watson<sup>1</sup> have recently discussed this approach and have stressed the need for critical assessment of experimental procedures if even semiquantitative conclusions are to be drawn from the results. In particular, they stress the errors which can arise (a) through use of equilibrium volume swelling techniques for measuring crosslink density without adequate knowledge of the appropriate value of the solvent-polymer interaction coefficient,  $\chi$ , of the Flory-Rehner equation relating equilibrium volume swelling to physical crosslink density, and (b) through failure to distinguish between chemical crosslinks and the total number of physically effective crosslinks, which includes network entanglements.

The work of Mullins,<sup>2,3</sup> and Moore and Watson<sup>4</sup> has provided a route to estimation of the total chemical crosslink density in unfilled vulcanizates of natural rubber (*NR*).<sup>5</sup> This is based on the Mooney-Rivlin treatment<sup>1</sup> of stress-strain data in simple extension for dry vulcanizates and provides semiempirical corrections for the effects of chain ends and physical entanglements (eq. 1, where  $M_{c,chem}^{RH}$  and  $\bar{M}_n$  are, respectively, the number-average molecular weight of the rubber hydrocarbon chain segments be-

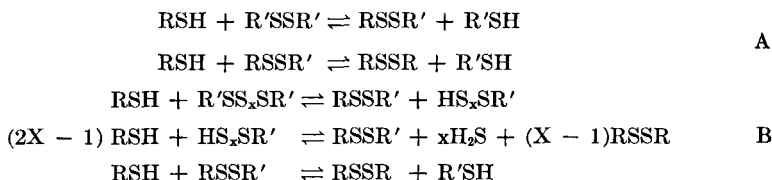
tween chemical crosslinks and the number average molecular weight of the polymer chains after mixing and before vulcanization).

$$C_{1,RH} = [RT(2M_{c,chem}^{RH})^{-1} + 0.78 \times 10^6] \times (1 - 2.3M_{c,chem}^{RH} \bar{M}_n^{-1}) \text{dyne cm}^{-2} \quad (1)$$

Use of this procedure for estimation of chemical crosslink density in conjunction with specific cleavage of particular crosslink types provides unambiguous information on chemical crosslink structure. In this respect the approach differs from that of Studebaker and Nabors,<sup>6</sup> which is based on chemical estimation of hydrogen sulfide and rubber-bound thiol groups after treatment of networks with lithium aluminium hydride, and does not distinguish between crosslinks and other sulfurated network features, e.g., pendent accelerator residues and cyclic structures. The existence of such network features has been adequately demonstrated by work on the sulfuration of model olefins<sup>7</sup> and by measuring the numbers of sulfur atoms combined in the networks per chemical crosslink present before and after treatment with triphenylphosphine.<sup>1,8,9</sup>

The requirements of a satisfactory chemical reagent for selective crosslink cleavage in vulcanizates have been described by Saville and Watson.<sup>1</sup> In addition to adequate characterization of the chemistry of the cleavage reaction using relevant model compounds, the reagent must be capable of homogeneous distribution in the rubber network and the excess must be easily removed after treatment. A reaction system which conforms to these requirements is the rapid cleavage of polysulfides at room temperature with a solution of propane-2-thiol (0.4*M*) and piperidine (0.4*M*) in *n*-heptane.<sup>1,10</sup> Under these reaction conditions disulfides react one thousand times as slowly and are essentially unaffected in the time required for complete cleavage of polysulfides.

The present paper describes the use of a more reactive thiol reagent system (hexane-1-thiol in piperidine solution) for combined cleavage of disulfides and polysulfides according to reaction Schemes A and B. From the known



relative reactivities of polysulfides and disulfides towards propane-2-thiol and piperidine in heptane solution, it can be concluded that reaction conditions which cause cleavage of disulfides at an experimentally useful rate will also result in extremely rapid cleavage of polysulfides.

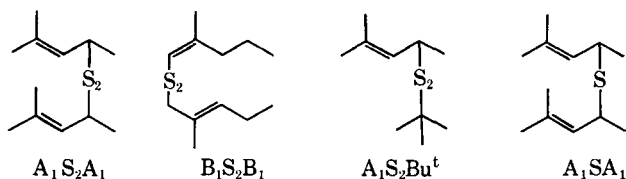
The reaction system studied represents an alternative to the existing method of combined di- and polysulfide cleavage using a solution of sodium

di-*n*-butyl phosphite (0.13*M* or 0.4*M*) in dry benzene,<sup>11</sup> and has been developed in an attempt to circumvent difficulties encountered with the latter reagent. Sodium di-*n*-butyl phosphite is hydrolyzed readily to sodium hydroxide, necessitating rigorous drying of the benzene solvent *and of the rubber sample* before treatment, to prevent formation of sodium hydroxide within the rubber network. In spite of precautions taken to dry rubber samples (storage *in vacuo*) this formation of sodium hydroxide may be the partial cause of the net increase in weight (approx. 5%) generally observed as a result of treatment of vulcanizates with the phosphite reagent.<sup>11</sup> Furthermore, dry vulcanizates after treatment with the phosphite reagent can give Mooney-Rivlin stress-strain curves with no well defined linear portion from which reliable values of the elastic constant,  $C_1$ , can be obtained. When satisfactory plots are obtained the corresponding values of the constant  $C_2$  are generally unusually high. Although stress-strain measurements on partially swollen samples avoid these difficulties, they are experimentally inconvenient and provide results which are not strictly applicable to calculation of crosslink density. This is because the Moore-Mullins-Watson calibration and the corrections for chain ends and physical entanglements are based on  $C_1$  values obtained from stress-strain measurements on dry samples, and Mullins<sup>2</sup> has pointed out that these are not identical with  $C_1$  values obtained from swollen samples.<sup>8</sup> The phosphite reagent causes a certain amount of degradation in carbon-carbon crosslinked vulcanizates<sup>11</sup> and this has been ascribed to cleavage of peroxidic linkages, even in unaged networks. The extent to which this sort of degradation contributes to the over-all degradation observed on treating sulfur vulcanizates with the phosphite reagent is uncertain and there is therefore some ambiguity in quantitative interpretation of the experimental results.

The results presented in this paper for the distribution of mono-, di-, and polysulfide crosslinks as a function of cure time for three accelerated sulfur vulcanization systems of *NR* were obtained by use of the hexanethiol reagent for combined cleavage of di-, and polysulfide crosslinks, and the propane-2-thiol reagent for selective cleavage of polysulfide crosslinks only.

## EXPERIMENTAL

Bis-(1,3-dimethylbut-2-enyl) disulfide ( $A_1S_2A_1$ ), and di-(2-methylpent-2-enyl) disulfide ( $B_1S_2B_1$ ) were prepared by published procedures.<sup>12,13</sup> *t*-Butyl 1,3-dimethylbut-2-enyl disulfide ( $A_1S_2Bu^t$ ) b.p. 79.5–80.5°/0.7 mm was prepared from *S*-(1,3-dimethylbut-2-enyl) thiuronium bromide<sup>12</sup> by conversion to the Bunte salt using sodium thiosulphate<sup>13</sup> and subsequent reaction with 2-methylpropane-2-thiol in aqueous-ethanolic sodium hydroxide. Di-(2-methylpent-2-enyl) monosulfide ( $A_1SA_1$ ) was prepared by a published procedure.<sup>13</sup> All other thiols, disulfides, and amines, were commercial products purified by fractional distillation. Benzyltrimethylammonium methoxide was a commercial product obtained as a 40% solution in methanol.



Vulcanizates were prepared as 1 mm thick sheets by normal mixing and vulcanization procedures from *NR* (RSS1 Yellow Circle), zinc oxide (Gold Seal), lauric acid, *N*-cyclohexylbenzothiazole-2-sulfenamide (*CBS*, recrystallized, m.p. 101–3°, sieved, 80 mesh) and sulfur (sieved, 80 mesh) or from *NR* (RSS1 Yellow Circle) and dicumyl peroxide (Table I).

Thiol and disulfide purities were assessed by gas-liquid chromatographic (glc) analysis. Saturated compounds had a purity not less than 97%. Alkenyl disulfides contained up to 7% of isoalkenyl isomers [1,3-dimethylbut-2-enyl 1,1-dimethylbut-2-enyl disulfide ( $A_1S_2A_2$ ), 2-methylpent-2-enyl 1-ethyl-2-methylallyl disulfide ( $B_1S_2B_2$ ), and 1,1-dimethylbut-2-enyl *t*-butyl disulfide ( $A_2S_2Bu^t$ )] but not more than 4% of other impurities.

Rates of exchange of butane-1-thiol with model disulfide compounds were measured by quantitative glc analysis. Response factors of reactant disulfides relative to appropriate internal standards were determined under the column conditions used for analysis of the corresponding reaction mixtures. Structurally isomeric disulfides were assumed to have the same response factors relative to a given internal standard. Response factors for mixed disulfides were estimated by graphical interpolation from the values for the appropriate pair of symmetrical disulfides. For each rate measurement, two standard solutions were prepared in piperidine, one containing reactant disulfide and internal standard for glc analysis and the other containing butanethiol. Reaction mixtures were prepared from equal aliquots of each solution and were analysed at appropriate time intervals, after quenching by pouring into *n*-heptane and extracting the piperidine with dilute hydrochloric acid. For reactions at 80°C, the reaction solutions were sealed *in vacuo* but for reactions at 25°C they were kept in stoppered

TABLE I  
Mix Compositions<sup>a</sup> and Curing Conditions for Vulcanization Systems

	<i>A</i>	<i>B</i>	<i>C</i> <sup>b</sup>	<i>D</i>	<i>E</i>	<i>F</i>
Zinc oxide	5.0	5.0	5.0	5.0	—	—
Lauric acid	0.7	1.0	1.0	1.0	—	—
Sulfur	2.5	1.5	1.5	0.4	—	—
<i>CBS</i>	0.6	2.37	2.37	6.0	—	—
Cumyl peroxide	—	—	—	—	0.5	1.0
Cure temperature (°C)	140	140	140	140	150	150
Cure time (hr)	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	1	1

<sup>a</sup> Parts per 100 parts RSS1 Yellow Circle.

<sup>b</sup> Nominally identical to *B* but prepared separately.

<sup>c</sup> Variable.

tubes under nitrogen. Reaction of  $A_1SA_1$  (0.1M) with butane-1-thiol (1.0M) in piperidine at 25°C *in vacuo* was followed in the same way.

Linear swelling measurements on rubber samples were carried out *in vacuo*. The rubber sample and reagent solution (or pure solvent) were placed in separate limbs of an apparatus consisting of two glass tubes connected near their upper ends by a short transverse tube. The solution was degassed in one limb, the apparatus sealed *in vacuo* and the solution then poured on to the sample through the transverse tube. The whole apparatus was immersed, with the sample horizontal, in a thermostat bath at  $25 \pm 0.2^\circ\text{C}$  and the change in length of the sample followed using a travelling microscope.

The standardized procedure for combined cleavage of di- and polysulfide crosslinks in vulcanizate samples was as follows. Unextracted vulcanizate samples were sealed *in vacuo* with a solution of hexane-1-thiol (1.0M) in piperidine (50 ml of reagent solution per g of rubber) by the procedure described above for linear swelling measurements. After a standard reaction time of 48 hrs at 25°C, the samples were removed from the reagent solution, surface-dried on filter paper as quickly as possible and dried to constant weight *in vacuo* (0.005 mm Hg) at room temperature.

Treatment in a stoppered tube under a blanket of nitrogen gave rise to more network degradation than did treatment *in vacuo* (Table VI) due to a small amount of oxidative degradation. This could be counteracted by addition of phenyl- $\beta$ -naphthylamine (1% w/v) to the system but subsequent extraction of the antioxidant with cold petroleum ether (b.p. 40–60°C) was necessary in order to obtain good Mooney-Rivlin stress-strain curves for the dry samples.

The procedure for cleavage of polysulfide crosslinks in thin (0.2 mm) vulcanizate samples with propane-2-thiol (0.4M) and piperidine (0.4M) in heptane solution has been described elsewhere.<sup>1</sup> Results presented in this paper were obtained by a modified procedure developed by R. M. Russell of these laboratories. Rubber samples (1 mm thick) were allowed to swell in heptane overnight at room temperature under an atmosphere of nitrogen. Sufficient propane-2-thiol and piperidine were then added to give concentrations of 0.4M for each reagent in the final solution. The samples were left in this solution for two hours at room temperature under nitrogen and then continuously extracted with petroleum ether (b.p. 40–60°C) overnight and dried to constant weight *in vacuo*.

At all stages of handling rubber samples considerable care was taken to avoid mechanical distortion. This was particularly important during chemical treatment and subsequent extraction and/or solvent removal. Strips of vulcanizate were extracted lying flat in a horizontal continuous extraction apparatus and were supported in aluminium foil during removal of solvent *in vacuo*. The strips were frequently eased free from the foil surface to prevent adhesion. Failure to observe these precautions often resulted in permanent deformation of the strips, rendering them unsuitable for stress-strain measurements.

The stress-strain measurements were made at room temperature using dry samples  $120 \times 30 \times 1$  mm in size on a precision, manual apparatus.<sup>5</sup> For untreated vulcanizates, the derived  $C_1$  parameter ( $C_{1,RV}$ ) was used to obtain  $C_{1,RH}$  the  $C_1$  parameter pertaining to the rubber hydrocarbon component of the network, by the procedure described by Bristow and Porter.<sup>14</sup> For vulcanizates which had been chemically treated, the  $C_1$  parameter derived from the stress-strain data was assumed to be  $C_{1,ERV}$ , i.e., the  $C_1$  parameter pertaining to the extracted rubber vulcanizate, and was used to calculate  $C_{1,RH}$ .<sup>14</sup> The magnitude of the corrections applied to  $C_{1,RV}$  and  $C_{1,ERV}$  did not exceed 5% for any of the vulcanization systems studied. Values of  $C_{1,RH}$  were used to determine concentrations of chemical crosslinks using equation 1. Concentrations of monosulfide crosslinks were obtained directly from  $C_{1,RH}$  after hexanethiol treatment, on the assumption that no carbon-carbon crosslinks were present.<sup>7</sup> Concentrations of polysulfide crosslinks were obtained by difference from total chemical crosslink density and chemical crosslink density after treatment with propane-2-thiol reagent, and concentrations of disulfide crosslinks were obtained by difference from chemical crosslink densities after treatment with propane-2-thiol and hexanethiol reagents.

## RESULTS AND DISCUSSION

### Rate of Thiol-disulfide Interchange

On the basis of preliminary results for the rate of the interchange reaction between the disulfide  $A_1S_2A_1$ , (0.10*M*) and butane-1-thiol (1.0*M*) under a number of different reaction conditions (Table II), reaction in piperidine solution at 25°C was chosen for further study. This amine swells *NR* vulcanizates to approximately the same extent as does benzene, and is therefore a suitable solvent for allowing easy access of thiol to the crosslinks, as well as being sufficiently basic to sustain a reasonably rapid rate of cleavage of the sulfur-sulfur bonds. The rates of reaction of several relevant model disulfides (0.10*M*) with butanethiol (1.0*M*) in piperidine solution at 25°C are shown in Fig. 1. Formation of product disulfides was followed in addition to the disappearance of reactant di-

TABLE II  
Reaction of bis-(1,3-dimethylbut-2-enyl) Disulfide ( $A_1S_2A_1$ , 0.10*M*)  
with butane-1-thiol (1.0*M*) under Various Conditions

Solvent	Temp. (°C)	Reaction time (hr)	% unchanged $A_1S_2A_1$
Heptane + 8% w/v piperidine	80	4.5	90
Piperidine	80	3.0	4
Piperidine	25	4.0	8
Pyridine	25	22	100
Di- <i>n</i> -butylamine	25	96.5	72

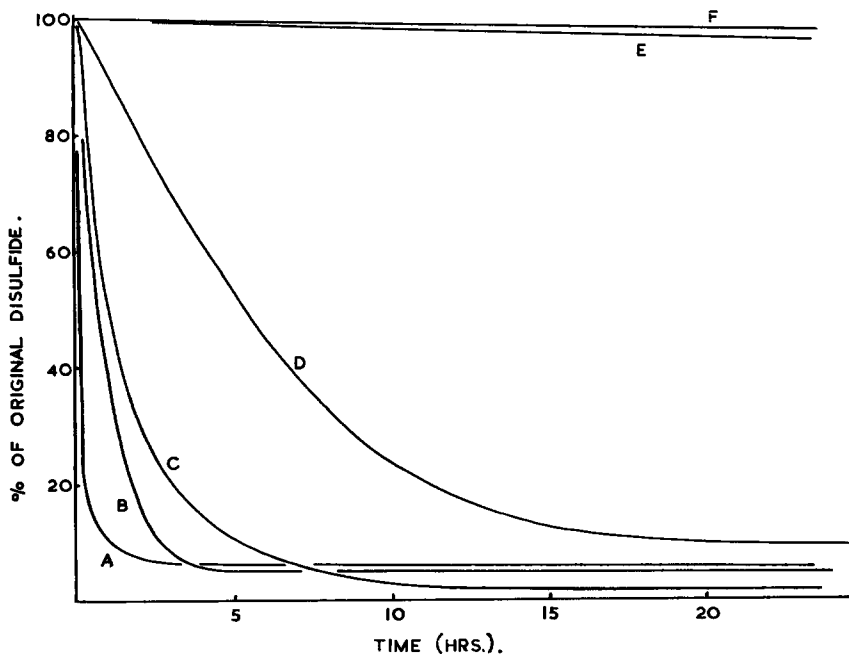


Fig. 1. Rates of reaction of disulfides (0.10M) with butane-1-thiol (1.0M) in piperidine solution at 25°C. A = di-(2-methylpent-2-enyl) disulfide, B = bis-(1,3-dimethylbut-2-enyl) disulfide, C = di-isopropyl disulfide, D = *t*-butyl 1,3-dimethylbut-2-enyl, E = di-*t*-butyl disulfide, and F = di-(1,3-dimethylbut-2-enyl) monosulfide.

sulfide and in each case good agreement with expected reaction stoichiometry was obtained, indicating clean thiol-disulfide interchange (Reaction Scheme A). Dialkenyl monosulfide ( $A_1S_2A_1$ ) was recovered almost quantitatively (95%) after 48 hrs under these conditions. The relative rates of reaction of the disulfides were in the order of steric accessibility of the sulfur-sulfur bonds, with the possible exception of the relative rates for  $A_1S_2A_1$  and di-isopropyl disulfide. The latter is somewhat less sterically hindered but reacts more slowly than  $A_1S_2A_1$ . Since di-*t*-butyl disulfide reacted extremely slowly, disulfide crosslinks having *t*-alkyl structures at both termini will remain essentially unbroken on treatment of vulcanizates with alkane-1-thiol in piperidine solution. This type of disulfide has not been detected in products of reaction of model olefins with various sulfur vulcanization systems,<sup>1,7</sup> and it is therefore considered to be of very minor importance in vulcanizates.

The thiol-disulfide interchange reactions attained equilibria in which small amounts of the reactant disulfides were still present.\* The positions of these equilibria in treatment of rubber networks is clearly of critical im-

\* A recent paper by Gorin, Doughty, and Gideon<sup>15</sup> discusses the general relationships between initial concentrations, equilibrium concentrations and equilibrium constants for the thiol-disulfide interchange system.

portance in determining the validity of the reaction system as a means of breaking disulfide (and polysulfide) crosslinks. Under the experimental conditions, where reagent thiol was initially in ten-fold excess over the reactant disulfide, 2, 5, 6 and 10% of the reactant disulfide remained in the reactions of di-isopropyl disulfide,  $A_1S_2A_1$ ,  $B_1S_2B_1$ , and  $A_1S_2Bu^t$ , respectively. In a rubber network having a high chemical crosslink density, the concentration of chemical crosslinks is of the order of  $1 \times 10^{-4}$  moles/g of rubber hydrocarbon, i.e., approximately  $9 \times 10^{-2}$  moles/l. When such a network is swollen to equilibrium in a piperidine solution of alkanethiol the volume fraction of rubber in the swollen gel ( $v_r$ ) is approximately 0.3 and the effective concentration of chemical crosslinks within the swollen gel is approximately  $2.7 \times 10^{-2}$  moles/l. The effective concentration of reagent thiol within the swollen gel is 0.7 moles/l, and therefore the ratio of reagent thiol concentration to concentration of chemical crosslinks *within the swollen gel* is at least 25:1 i.e., 2.5 fold greater than the ratio of thiol to reactant disulfide in the model experiments. In addition to this, dialkyl disulfide formed during reaction with the network equilibrates with the bulk of the reagent solution, thus reducing its effective concentration within the swollen gel (by a factor of 19, using 50 ml of reagent solution per g of rubber) and displacing the crosslink cleavage equilibrium further towards complete cleavage. On the basis of the above arguments there will be an experimentally insignificant number of disulfide crosslinks remaining at equilibrium on treatment of vulcanizates containing primary or secondary alkenyl or secondary alkyl disulfide crosslinks, but the situation may be slightly less satisfactory if tertiary alkyl structures make a major contribution to the total number of crosslinks. The latter situation is expected to arise only in unaccelerated sulfur vulcanization.<sup>7</sup>

### Reaction in Vulcanizates

Rates of reaction of disulfide crosslinks within a rubber network may differ from the rates of reaction of the model compounds in homogeneous solution. For this reason, an independent assessment of reaction rate in rubber systems was obtained by measurement of linear swelling of vulcanizates in a solution of hexane-1-thiol (1.0M) in piperidine as a function of time (Fig. 2). Hexanethiol was used in treatment of vulcanizates in preference to butanethiol because its lower volatility offered somewhat greater experimental convenience. The difference in reactivity of the two thiols was assumed to be insignificant. The results show that, for samples 1 mm thick, a standard reaction time of 48 hrs at 25°C is sufficient to ensure complete reaction even when the extent of degradation is large (compare Fig. 2 and crosslink density measurements in Table V). The shapes of the curves are complex functions of reaction rate and swelling rate and are strictly reproducible only for samples of the same size and geometry. Samples appreciably thicker than 1 mm may require longer treatment, because of the longer time required for equilibration with the reagent solution.



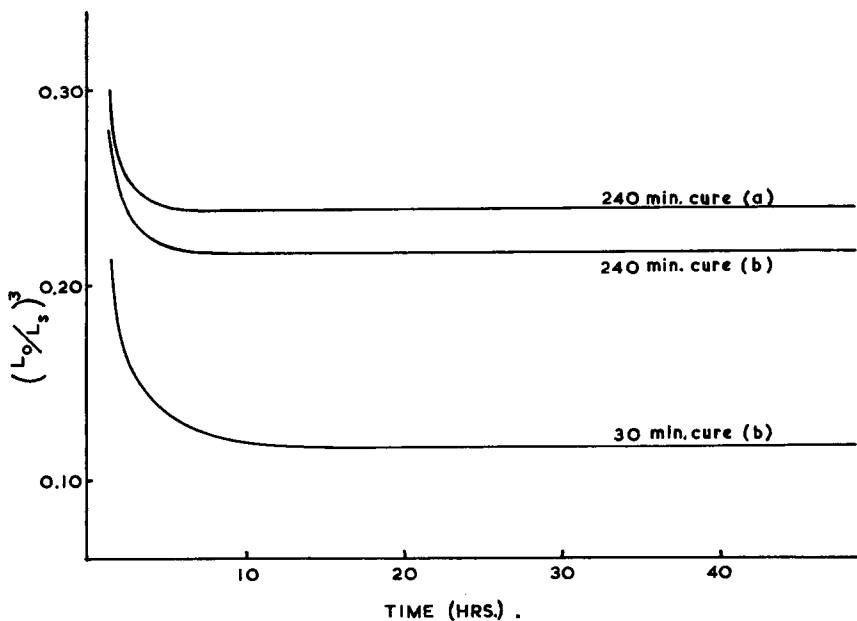


Fig. 2. Linear swelling measurements in (a) piperidine and (b) hexane-1-thiol (1.0M) in piperidine solution *in vacuo* at 25°C for samples from vulcanization system B, having the cure times shown.  $L_0$  is the initial length of the dry sample;  $L_s$  is the swollen length at a given time.

Treatment of carbon-carbon crosslinked vulcanizates with the hexanethiol reagent resulted in no network degradation (Table III, vulcanizates E and F), showing that network chains are not broken by the treatment. The slight increases in  $C_{1,RH}$  after treatment may reflect inaccuracies in the

TABLE III  
Control Experiments for Hexanethiol Treatment of Vulcanizates

Vulcanizate and cure time	$C_{1,RH}$ at 25°C, dynes/cm <sup>2</sup> ( $\times 10^{-6}$ ) <sup>a</sup>			Sulfur combined in network, % w/w	
	Unextracted vulcanizate	After hexane- thiol treat- ment	After equilibrium swelling in piperidine at 25°C	Unextracted vulcanizate	After hexane- thiol treat- ment
E	0.51	0.54	—	0.04	0.05
F	0.97	1.03	—	0.03	0.04
B, 240 min	2.10	—	2.17	—	—
B, 30 min	2.18	—	1.7 <sup>b</sup>	—	—

<sup>a</sup> Measured on dry samples. Also applies for Tables IV-VII.

<sup>b</sup> Estimated from measured  $v_r$  in piperidine and  $\chi = 0.400$ , the value of  $\chi$  found for B, 240 min cure, from  $v_r$  and  $C_{1,ERM}$  for the untreated dry vulcanizate.

corrections applied to the measured values of  $C_1$ ,<sup>14</sup> or may arise from some physical effect of the swelling-deswelling cycle. Similar increases were observed after vulcanizates had been swollen to equilibrium in benzene and dried *in vacuo*. Treatment of sulfur vulcanizates with piperidine at 25°C, in the absence of thiol caused no degradation when the polysulfide content of the network was low (Table III, vulcanizate *B*, 240 min) but a highly polysulfidic network (vulcanizate *B*, 30 min) suffered appreciable degradation, due, possibly, to direct cleavage of long-chain polysulfides by piperidine (c.f. reactions of elemental sulfur with amines<sup>16</sup>). For this reason control experiments in which vulcanizates are subjected to the experimental procedure for hexanethiol probe treatment in the absence of thiol are of no value.

### Comparison with Other Systems for Disulfide Cleavage in Vulcanizates

An attempt was made to use disulfide interchange as an alternative to thiol-disulfide exchange for cleavage of disulfides. The system investigated was the interaction of vulcanizate samples with a solution of di-*n*-hexyl disulfide (1.0*M*) in piperidine at 25°C in the presence of a low concentration of *n*-hexanethiol (0.01*M*) as catalyst. Network degradation occurred but the reaction was much too slow to be of practical value.

Treatment of a sample of vulcanizate *C*, 120 min cure, with a solution of thiophenol (2 ml) and benzyltrimethylammonium methoxide (0.57 ml) in a mixture of methanol and tetrahydrofuran (1:4, 40 ml) *in vacuo* at 25°C gave a result ( $C_{1,RH} = 1.67 \times 10^6$  dyne cm<sup>-2</sup> at 25°C) in good agreement with that obtained by treatment with the hexanethiol reagent (Table VI). This reagent system is similar to the one used by Frensdorff<sup>17</sup> and described by Cluff and Gladding,<sup>18</sup> but addition of methanol was found to be necessary to prevent precipitation of the substituted ammonium salt of thiophenol. Omission of the methanol led to significantly less degradation.

Some difficulties were encountered in obtaining a direct comparison of the results of treatment of vulcanizates with the hexanethiol reagent and with the sodium di-*n*-butyl phosphite reagent of Moore and Trego.<sup>11</sup> Samples of the 30, 45 and 120 min cures of vulcanizate *B* were treated with the phosphite reagent, but after treatment only the sample of the 120 min cure gave a Mooney-Rivlin plot (for the dry sample) from which a reliable value of the elastic constant,  $C_{1,RH}$ , could be obtained ( $C_{1,RH} = 0.95 \times 10^6$  dyne cm<sup>-2</sup> at 25°C, c.f.  $C_{1,RH} = 1.51 \times 10^6$  dyne cm<sup>-2</sup> at 25°C after hexanethiol treatment, Table V). For this one direct comparison, the phosphite reagent caused more network degradation than did the hexanethiol reagent. The difference between the results obtained using these two reagents tends to be confirmed by comparison of published results for monosulfide crosslink levels in different vulcanization systems<sup>11</sup> with the results in Tables IV to VII obtained using the hexanethiol reagent. However, these comparisons must be made with some caution because of the possi-

TABLE IV  
Distribution of Crosslink Types as a Function of Cure  
Time for Vulcanization System A<sup>a</sup>

Cure time (min)	$C_{1,RH}$ at 25°C dynes/cm <sup>2</sup> ( $\times 10^{-6}$ )			$(2M_{c,chem}^{RH})^{-1}$ g moles/g rubber hydrocarbon ( $\times 10^5$ )			
	Untreated	Hexane- thiol treated	Propane- 2-thiol treated	Total,	mono-,	di-,	poly-
	20	1.55	0	0.63	4.3	0.0	1.3
40	1.75	—	0.92	5.1	0.3 <sup>b</sup>	1.7 <sup>c</sup>	3.1
60	1.59	—	1.05	4.5	0.5 <sup>b</sup>	1.9 <sup>c</sup>	2.1
120	1.40	0.70	1.14	3.7	1.4	1.4	0.9
360	1.18	0.83	1.09	2.9	1.7	0.9	0.3

<sup>a</sup>  $M_n$  for rubber hydrocarbon in mix =  $2.28 \times 10^5$ , based on  $[\eta]_{\text{toluene}}$  measurement.

<sup>b</sup> Approximate values, estimated from degree of swelling in the hexanethiol reagent.

<sup>c</sup> Values dependent upon estimated monosulfide figures.

TABLE V  
Distribution of Crosslink Types as a Function  
of Cure Time for Vulcanization System B<sup>a</sup>

Cure time (min)	$C_{1,RH}$ at 25°C dynes/cm <sup>2</sup> ( $\times 10^{-6}$ )			$(2M_{c,chem}^{RH})^{-1}$ g moles/g rubber hydrocarbon ( $\times 10^5$ )			
	Untreated	Hexane- thiol treated	Propane- 2-thiol treated	Total,	mono-,	di-,	poly-
	30	2.18	0.80	1.66	7.0	1.7	3.1
45	2.28	0.87	1.77	7.4	1.9	3.4	2.1
120	2.20	1.51	2.09	7.1	4.2	2.4	0.5
240	2.10	1.71	2.04	6.7	5.1	1.3	0.3

<sup>a</sup>  $M_n$  for rubber hydrocarbon in mix =  $2.16 \times 10^5$  based on  $[\eta]_{\text{toluene}}$  measurement.

bility of nominally identical vulcanizates differing from one another in detailed network structure. Such differences can be seen in comparison of the results in Tables V and VI for two sets of vulcanizates prepared from separate mixes of the system RSS1 (100) S (1.5) CBS (2.37) ZnO (5.0) lauric acid (1.0). They do not arise from lack of reproducibility of the thiol treatment (c.f. values of  $C_{1,RH}$  after hexanethiol treatment in Table VI).

The discrepancies which exist between results of network characterization using the phosphite and the hexanethiol reagent systems are not such as to drastically alter the general picture of vulcanizate structure as a function of cure time or vulcanization recipe, but they are sufficient to warrant some further consideration.

As discussed earlier, the existence of an equilibrium involving unbroken disulfide crosslinks within the rubber network during treatment with hexanethiol reagent is not expected to be of experimental significance, but

TABLE VI  
Distribution of Crosslink Types as a Function of Cure  
Time for Vulcanization System C<sup>a</sup>

Cure time (min)	$C_{1,RH}$ at 25°C dynes/cm <sup>2</sup> ( $\times 10^{-6}$ )			$(2M_{c,chem}^{RH})^{-1}$ g moles/g rubber hydrocarbon ( $\times 10^5$ )			
	Un- treated	Hexane- thiol treated	Propane- 2-thiol treated	Total	mono-	di-	poly-
20	1.99	0.00 <sup>b</sup>	0.72	6.2	0.0	1.5	4.7
30	2.23	0.63 $\pm$ 0.02 <sup>c</sup> 0.75 <sup>e</sup>	1.24	7.2	1.3	1.9	4.0
45	2.38	1.07 $\pm$ 0.01 <sup>c</sup>	1.62	7.8	2.5	2.2	3.1
120	2.32	1.64 $\pm$ 0.00 <sup>d</sup> 1.73 <sup>e</sup> 1.63 <sup>f</sup> 1.56 $\pm$ 0.02 <sup>g</sup>	2.02	7.6	4.7	1.6	1.3
240	2.20	1.63 $\pm$ 0.01 <sup>e</sup>	2.04	7.1	4.8	1.6	0.7

<sup>a</sup>  $M_n$  for rubber hydrocarbon in mix =  $2.21 \times 10^5$  based on  $[\eta]_{\text{toluene}}$  measurement.

<sup>b</sup> Vulcanizate did not dissolve in reagent but was extremely highly swollen.

<sup>c</sup> Average of two separate measurements.

<sup>d</sup> Average of five separate measurements.

<sup>e</sup> Redetermined after storage of sample for several months at room temperature under an atmosphere of nitrogen.

<sup>f</sup> Treatment carried out under nitrogen in a stoppered tube in the presence of phenyl- $\beta$ -naphthylamine antioxidant.

<sup>g</sup> Treatment carried out under nitrogen in a stoppered tube in the absence of antioxidant. Average of five measurements.

TABLE VII  
Distribution of Crosslink Types as a Function of  
Cure Time for Vulcanization System D<sup>a</sup>

Cure time (min)	$C_{1,RH}$ at 25°C dynes/cm <sup>2</sup> ( $\times 10^{-6}$ )		$(2M_{c,chem}^{RH})^{-1}$ g moles/g rubber hydrocarbon ( $\times 10^5$ )	
	Untreated	Hexanethiol treated <sup>b</sup>	Total	mono-
40	0.97	0.67	2.2	1.4
60	1.38	1.00	3.7	2.3
120	1.63	1.38	4.7	3.7
360	1.47	1.43	4.0	3.9

<sup>a</sup> Based on an assumed value of  $2.20 \times 10^5$  for  $M_n$  of rubber hydrocarbon in the mix.

<sup>b</sup> Treatments carried out in stoppered tubes under nitrogen, in the absence of anti-oxidants.

rubber-bound thiol groups formed during the treatment could lead to reformation of crosslinks by addition to double bonds of adjacent rubber chains or by oxidation back to disulfide crosslinks. Cunneen<sup>19</sup> has shown that addition of alkanethiols to *NR* is slow, even in the presence of peroxide catalyst or uv light, and isomerisation of *NR* by alkanethiols does not occur in the absence of free radical catalysts and elevated temperatures.<sup>19</sup> This is in marked contrast to the effects of thiolacids.<sup>20</sup> The results of sulfur

analysis of peroxide cured vulcanizates before and after treatment with the thiol reagent (Table III) confirm that reagent thiol does not add to the double bonds in the network chains under the conditions of treatment, and by analogy, addition of rubber-bound thiol is unlikely to occur. Furthermore, any addition of rubber bound thiol occurring during treatment would introduce crosslinks into the network while the latter was in a highly swollen state. Such crosslinks would be elastically ineffective, and hence undetectable, during a large part of any stress-strain measurement on the unswollen sample. Addition of rubber-bound thiol in the dry vulcanizate after treatment would give elastically effective crosslinks, but such addition is shown to be unimportant by the results of redetermination of the elastic constant,  $C_{1,RR}$ , for two thiol-treated sulfur vulcanizates after several months storage at room temperature in an atmosphere of nitrogen. (Vulcanizate C, 30 and 120 min cures, Table VI). Stress-strain measurements were normally made within five days of the hexanethiol treatment. Oxidation of rubber-bound thiol groups by atmospheric oxygen to re-form disulfide crosslinks has been observed in the case of degraded polyurethane elastomers by Cluff and Gladding.<sup>18</sup> In the present work such a possibility was avoided by storing the thiol-treated samples in vacuo until immediately before stress-strain measurements were made. Any rapid oxidation to disulfide crosslinks during the stress-strain measurements would be expected to result in distorted Mooney-Rivlin curves due to continual increase in crosslink density as the measurement proceeded. The curves for thiol-treated vulcanizates were in fact free from distortion.

We conclude that the hexanethiol reagent provides a reliable means of cleaving all di- and polysulfide crosslinks in a network within an experimental accuracy of about 5%. By comparison with results obtained using the phosphite reagent we must conclude that the latter causes network degradation in excess of complete cleavage of these crosslinks.

The results in Tables IV-VII distinctly show two important features of accelerated sulphur vulcanization of *NR*. For any given ratio of accelerator to sulfur in the vulcanization recipe there is a steady increase in the number of monosulfide crosslinks as the cure time increases. Polysulfide crosslinks, formed at early cure times, are lost. As the ratio of accelerator to sulfur is increased monosulfide crosslinks are formed in the network much more rapidly and poly- and disulfide crosslinks make less significant contributions to the network structure.

## CONCLUSIONS

The moderately fast exchange reaction between alkanethiol and disulfides in piperidine solution has been shown to be applicable to cleavage of disulfide (and polysulfide) crosslinks in accelerated sulfur vulcanizates of *NR*. In conjunction with the previously reported reagent system for selective cleavage of polysulfide crosslinks only, the reaction has been used to determine the proportions of mono-, di-, and polysulfide crosslinks

in several such vulcanizates, on the assumption that there is no direct carbon-carbon crosslinking in the networks. There are quantitative discrepancies between the present results and data in the literature for the same vulcanization systems, obtained using the reagent sodium di-*n*-butyl phosphite for cleavage of di- and polysulfide crosslinks. The evidence presented in support of the quantitative reliability of the hexanethiol reagent is reasonably satisfactory but final confirmation of this reliability will require independent direct estimation of the numbers of mono-sulfide crosslinks in vulcanizates.

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