

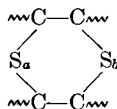
## Structural Characterization of Vulcanizates. Part II. Use of Triphenylphosphine to Determine the Structures of Sulfur Linkages in Unaccelerated Natural Rubber-Sulfur Vulcanizate Networks

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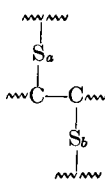
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### I. INTRODUCTION

In Part I of this series<sup>1</sup> it was shown that about 40 to 55 sulfur atoms are required to react to produce one chemical crosslink in networks obtained from unaccelerated natural rubber (NR)-sulfur systems at 140°C. The low crosslinking efficiency of sulfur in these systems is ascribed on the basis of the products derived from model olefin sulfurations at 140°C.<sup>2-4</sup> to the sulfur being wastefully combined in: (a), polysulfidic crosslinks, rubber—S<sub>x</sub>—rubber, where  $x > 1$ ; (b), cyclic monosulfides situated along the polyisoprene chains at sites distant from the crosslinks; and (c), nonrandom crosslinks as in structures (I) and (II) where sulfur attachments are on vicinal carbon atoms of the polyisoprene chain. The crosslinking efficiency data given in Part I<sup>1</sup> necessarily



(I)



(II)

give only a general qualitative indication of the presence of these sulfurated linkages in the network. The further quantitative structural characterization of the network requires knowledge of: (1) the average length of the polysulfidic crosslink, i.e., the value of  $x$  in rubber—S<sub>x</sub>—rubber; (2) the change in  $x$  with time of cure; and (3) the proportion of the combined sulfur which is present in isolated cyclic monosulfide structures. We now report semiquantitative descriptions of the structural features (1)–(3) for vulcanizate networks derived from the system: NR(100)-sulfur(10) cured at

140°C. for 2–24 hours. The data have been obtained by treating the extracted networks, of known degrees of crosslinking  $1/2M_{c, \text{chem}}^*$  and combined sulfur contents S<sub>c</sub>, with triphenylphosphine in benzene at 80°C. and subsequent determination of the limiting values of the combined sulfur not removable by the reagent as triphenylphosphine sulfide.

### II. MATERIALS, EXPERIMENTAL METHODS, AND RESULTS

#### Materials

Triphenylphosphine, recrystallized from absolute ethanol, had a melting point of 80.0°C. AnalaR benzene was dried over sodium. The NR-sulfur vulcanizate networks were prepared, freed from uncombined sulfur, and characterized with respect to combined sulfur content S<sub>c</sub> and degree of chemical crosslinking  $1/2M_{c, \text{chem}}^*$  as described in Part I.<sup>1</sup> The values of  $1/2M_{c, \text{chem}}^*$  used here are those obtained by correcting for main chain scission by means of the  $\lambda^*$  technique of Mullins<sup>5</sup> in addition to correcting for chainend effects and network entanglements.<sup>6</sup>

#### Treatment of Networks with Triphenylphosphine

Weighed amounts of the extracted vulcanizates (ca. 0.5 g.) and triphenylphosphine (ca. 1 g.-mole/g.-atom of S<sub>c</sub> in vulcanizate) were evacuated in glass tubes for 2 hr. at 10<sup>-6</sup> mm. Hg pressure. Once-degassed benzene (ca. 10 ml.) was then introduced into the tubes *in vacuo* by the evaporative distillation technique of Moore and Watson,<sup>7</sup> and the tubes were then sealed *in vacuo*. The vulcanizates were allowed to imbibe the triphenylphosphine and benzene and then the reactants

TABLE I  
Treatment of NR-Sulfur Vulcanizate Networks with Triphenylphosphine for 96 Hr. at 80°C. in Benzene

Expt. no.	Cure time at 140°C., hr.	Description of sample and treatment	S <sub>c</sub> in network, %	Sample insoluble in benzene after treatment, wt.-% of original	<i>n</i> -Decane swelling of network at 25°C. for 48 hr.	
					Gel, %	Swelling ratio (w/w)
—	2.0	Untreated original network	1.68	—	98.5	4.05
1	2.0	Control	1.69	98	99.4	4.40
2	2.0	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P-treated	1.34	98	99.0	4.30
—	4.0	Untreated original network	3.46	—	99.5	3.04
3	4.0	Control	3.44	100	99.8	3.24
4	4.0	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P-treated	2.90	99	98.8	3.00
5	4.0	Unextracted vulcanizate, (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P-treated	2.80	91	—	—
—	7.0	Untreated original network	5.93	—	99.0	2.42
6	7.0	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P-treated	5.12	99	96.2	2.61
7	7.0	Unextracted vulcanizate, (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P-treated	5.07	92	97.0	2.56
—	24.0	Untreated original network	9.03	—	97.0	1.70
8	24.0	Control	9.03	98	98.4	1.60
9	24.0	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P-treated	8.63	97	100	1.80
—	24.0	Untreated original network	8.89	—	97.0	1.70
10	24.0	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P-treated	8.67	100	96.0	1.81

were heated for 96 hr. at 80.0°C. The treated vulcanizates were freed from triphenylphosphine and triphenylphosphine sulfide by continuous extraction with cold benzene for 24 hr. in nitrogen in the dark and the extracted vulcanizates then dried to constant weight and their sulfur contents determined. Control experiments were carried out in which the extracted vulcanizates were treated as above but in the absence of triphenylphosphine. To check that the original 24 hr. hot acetone extraction to remove uncombined sulfur (cf. 1) did not cause redistribution of the polysulfidic sulfur in the network, experiments similar to the above were carried out on unextracted vulcanizates with the use of 1 g.-mole of triphenylphosphine per g.-atom of sulfur (uncombined and combined) in the vulcanizate. The gel contents and equilibrium gel swelling ratios (weight of swollen rubber/weight of deswollen gel rubber) of the original and treated vulcanizates were determined at 25°C. in *n*-decane as described previously.<sup>7</sup> The results are given in Table I.

### III. DISCUSSION OF RESULTS

Treatment of the vulcanizate networks with triphenylphosphine under the conditions specified above effects the removal of part of the combined

sulfur without any appreciable degradation of the network (Table I). The proportion of combined sulfur so removed decreases with increasing cure time (Table II). The results from the control experiments (Expts. 1, 3, 8 of Table I) indicate that treatment of the networks in the absence of triphenylphosphine does not alter the combined sulfur content. That the experimental conditions used are sufficient to remove all of the potentially removable sulfur was checked by retreatment of the sample obtained from Expt. 4; there was no decrease in the combined sulfur content. Comparison of the results obtained for the extracted and unextracted vulcanizates treated with triphenylphosphine (cf. Expts. 4 and 5, 6, and 7) suggest that there is only slight redistribution of polysulfidic sulfur during the hot acetone extraction procedure.

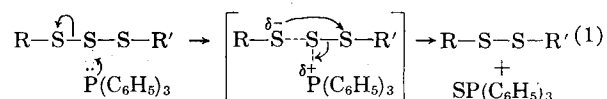
Complementary studies<sup>8,9</sup> of the reaction of triphenylphosphine at 80°C. with simple mono-, di-, and polysulfides indicate firstly, that sulfur in organic monosulfides (including the cyclic monosulfides obtained from the sulfuration of 2,6-dimethylocta-2,6-diene<sup>3</sup>) cannot be removed by the reagent, and, secondly, that the limiting number of sulfur atoms removed from organic polysulfides (R—S<sub>x</sub>—R'; where R, R' are alkyl, aralkyl, or

TABLE II  
 Structural Features of Networks Obtained from NR(100)-Sulfur(10) at 140°C.

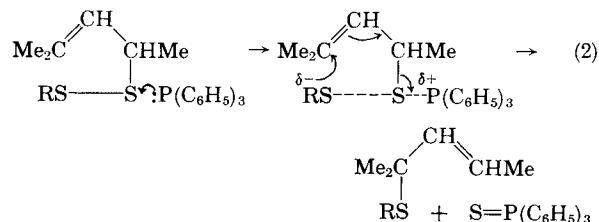
Cure time, hr.	$1/2M_{c,chem}^*$ g.-moles chemical crosslinks/g. rubber hydrocarbon $\times 10^5$ (based on $\lambda^*$ values) <sup>a</sup>	Combined sulfur in network $S_c$ , % <sup>a</sup>	Crosslinking efficiency, sulfur atoms combined in network per chemical crosslink formed <sup>a</sup>	% $S_c$ removed by treatment with $P(C_6H_5)_3$	(1)		(3) % $S_c$ present in cyclic monosulfide structures
					Average no. of sulfur atoms in each crosslink	(2) Change in $x$	
2	1.0	1.68	53	20	12-13	—	76-77
4	2.1	3.46	53	16	10-11	~2	79-81
7	4.2	5.93	47	13.5	7-8	~5	83-85
24	7.1	8.89	43	2.5	2-3	~10	93-95
24	7.1	9.03	44	4.5	3-4	~9	91-93

<sup>a</sup> Data of Part I.<sup>1</sup>

alkenyl and  $x \geq 2$ ) depends on the nature of the R and R' groups. When R and R' are both alkyl or benzyl,  $x$  is reduced to 2, but when R and R' are both alkenyl (e.g.,  $R = R' = CH_2=CH-CH_2-$ ;  $MeCH=CH-CH_2-$ ;  $Me_2C=CH-CH_2-$ ;  $Me_2C=CH-CHMe-$ ) then  $x$  is reduced to 1. For the only alkyl alkenyl disulfide so far examined ( $RS_2R'$ , where  $R = Et-$  and  $R' = Me_2C=CH-CHMe-$ ),  $x$  is reduced to 1. By analogy with the nucleophilic displacement mechanism proposed for the reaction of triphenylphosphine with elemental sulfur in benzene,<sup>10</sup> the desulfurization process for the dialkyl and dibenzyl polysulfides is represented as in reaction (1):



In the case of the dialkenyl disulfides and the alkyl alkenyl disulfide the desulfurization proceeds by an  $S_N2'$  mechanism with allylic rearrangement of one of the alkenyl groups,<sup>8,9</sup> e.g.:



Here,  $R = Et-$  or  $Me_2C=CH-CHMe-$ .

The above data suggest that the partial desulfurization of the NR-sulfur networks by triphenylphosphine results from the conversion of all polysulfidic links into either mono- or disulfide

links. If it is assumed that all polysulfidic links in the original networks are intermolecular and elastically effective (i.e., intramolecular polysulfidic links and vicinal sulfurated crosslinks as in (I) and (II) are absent) then a preliminary indication can be given (Table II) of the structural features (1)-(3) discussed above. Because of our ignorance regarding the validity or otherwise of the assumptions made above, the results given under (1), (2), and (3) in Table II must be regarded as having only semiquantitative significance. They do, however, confirm and amplify the conclusions from the model sulfuration experiments<sup>2-4</sup> that in the early stages of cure long polysulfidic crosslinks are formed which on further cure decrease in length to give eventually very short sulfurated crosslinks, and that a high proportion of the sulfur combined in the network is present in cyclic monosulfides. The extent which this type of main chain modification can assume is emphasized by the data for the 24 hr. vulcanizate network which shows that in the formation of this network approximately 40% of the diene units of the original NR molecules are converted into cyclic monosulfide units.

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### Synopsis

Treatment of unaccelerated natural rubber-sulfur vulcanizate networks with triphenylphosphine in benzene at 80°C. effects the removal of part of the combined sulfur, the proportion removed decreasing with increasing cure time. This partial desulfurization of the network is attributed, on the basis of the mode of interaction of simple organic di- and polysulfides with triphenylphosphine, to the conversion of polysulfide linkages in the network into either mono- or disulfide groups. Knowledge of the amount of sulfur removed by the reagent, and of the chemical degree of cross-linking and combined sulfur content of the untreated networks permits the following semiquantitative conclusions to be reached concerning the structures of the sulfur linkages in the networks: (1) long polysulfidic crosslinks ( $-S_{11}-$  to  $-S_{12}-$ ) are initially formed, which on continued cure progressively decrease in length to a limiting value of  $-S_2-$  to  $-S_4-$ ; and (2) a very high proportion of the combined sulfur (ca. 77% for short cure times, increasing to ca. 95% on extended cure) is present in cyclic monosulfide groups situated along the polyisoprene chains.

### Résumé

Let traitement de réseaux non accélérés de caoutchouc naturel vulcanisé au soufre, avec de la triphénylphosphine dans du benzène à 30° produit l'élimination d'une partie du soufre combiné, la proportion enlevée diminuant en fonction de la durée du traitement. Sur la base du mode d'action de

simples di- et polysulfures organiques avec la triphénylphosphine, on attribue cette désulfuration partielle du réseau à la transformation des liaisons polysulfurées dans le réseau en groupes soit monosoit disulfures. La connaissance de la quantité de soufre enlevé par le réactif, du degré chimique de pontage et de la teneur en soufre combiné dans les réseaux non traités permet de tirer des conclusions semi-quantitatives en ce qui concerne la structure des liaisons de soufre dans le réseau (1). On forme au début de longues soudures polysulfurées croisées ( $-S_{11}-$  à  $-S_{12}-$ ) qui, en continuant l'opération, diminuent progressivement en longueur jusqu'à une valeur limite de  $-S_2-$  à  $-S_4-$ ; et (2) une proportion très élevée du soufre combiné (ca 77% pour des traitements de courte durée, augmentant à ca 95% après un traitement prolongé) est présente dans des groupes cycliques monosulfurés, situés le long des chaînes polyisopréniques.

### Zusammenfassung

Behandlung von beschleunigerfreien, vernetzten Naturkautschuk-Schwefelvulkanisaten mit Triphenylphosphin in Benzol bei 80°C führt zur Entfernung eines Teils des gebundenen Schwefels, wobei der entfernte Anteil mit steigender Vulkanisationsdauer abnimmt. Diese teilweise Entschwefelung des Netzwerks wird, auf Grundlage der Reaktionsweise einfacher organischer Di- und Polysulfide mit Triphenylphosphin, auf die Umwandlung von Polysulfidbrücken im Netzwerk in Mono- oder Disulfidgruppen zurückgeführt. Kenntnis der durch das Reagens entfernten Schwefelmenge und des chemischen Vernetzungsgrades sowie des Gehalts des unbehandelten Netzwerks an gebundenem Schwefel erlaubt es folgende halbquantitative Schlüsse bezüglich der Struktur der Schwefelbrücken im Netzwerk zu ziehen: (1) anfänglich werden lange Polysulfidvernetzungen ( $-S_{11}-$  bis  $-S_{12}-$ ) gebildet, welche bei fortgesetzter Vulkanisation eine schrittweise Längenabnahme bis zum Grenzwert  $-S_2-$  bis  $-S_4-$  erfahren; (2) ein sehr hoher Bruchteil des gebundenen Schwefels (ca. 77% bei kurzer Vulkanisationsdauer, bei längerer Vulkanisation auf ca 95% ansteigend) liegt in Form von zyklischen, an der Polysoprenkette befindlichen Monosulfidgruppen vor.

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