

## Structural Characterization of Vulcanizates. Part I. Crosslinking Efficiency of Sulfur in Unaccelerated Natural Rubber-Sulfur Systems

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### I. INTRODUCTION TO THE SERIES

This series of papers deals with the structural characterization of vulcanizates derived from natural rubber (NR) and related synthetic olefinic elastomers by various vulcanization procedures, especial emphasis being given to unaccelerated and accelerated sulfur vulcanization and to vulcanization by tetraalkylthiuram disulfide-zinc oxide systems. The ultimate aim of the work is to determine the relationship between the structures of vulcanizates and their physical properties and aging characteristics.

The primary structural requirement for obtaining a vulcanizate is the crosslinking of the elastomer chains to produce a three-dimensional network. The crosslinks may consist of covalent bonds as present in polysulfides ( $-\text{C}-\text{S}_x-\text{C}-$ ) or electrovalent bonds or quasi-electrovalent bonds as present in zinc salts (e.g.,  $-\text{C}-\overset{\delta-}{\text{S}}\cdots\cdots\overset{\delta+}{\text{S}}\cdots\cdots\text{Zn}\cdots\cdots$   $\text{S}-\text{C}-$ ). Complete definition of the crosslink requires knowledge of the actual structural unit interlinking the elastomer chains together with the detailed structures of those portions of the elastomer chains in the immediate vicinity of the crosslink. Other structural modifications of the elastomer chains can occur during the vulcanization process at sites distant from the crosslinks, examples of these main-chain modifications being: (1) the formation of cyclic monosulfides; (2) changes in the olefinic pattern of the parent elastomer; and (3) the scission of the main elastomer chains. In addition to the above components which comprise the vulcanizate network, there will also be present in most vulcanizates extra-network material such as filler or reinforcing agent, zinc oxide, or uncombined sulfur present in the original mix, or zinc soaps, zinc sulfide, and zinc salts of accelerators resulting from the vulcanization reaction. The complete structural characterization of a vulcanizate

thus requires a detailed quantitative description of all the above features which are simply represented in Figure 1.

Three main experimental approaches are available for determining the structures of vulcanizate networks. These approaches are essentially complementary and may be illustrated by reference to vulcanizates derived from unaccelerated and accelerated NR-sulfur systems.

(1) Determination of the crosslinking efficiency  $E$ , which is defined as the number of sulfur atoms combined in the network for each chemical crosslink formed. This quantity, which gives a composite picture of the degree of structural complexity of the network, is obtained directly from the amount of combined sulfur and the number of chemical crosslinks in the network. For NR-vulcanizates the latter quantity is determinable from values of the physically effective degree of crosslinking, obtained from either stress-strain or swelling measurements, and use of the calibration between the physically effective degree of crosslinking and the actual degree of chemical crosslinking as originally obtained by Moore and Watson<sup>1</sup> for a NR-di-*tert*-butyl peroxide system, and subsequently revised by Mullins.<sup>2</sup>

(2) Structural resolution of the products derived from the sulfuration of low molecular weight olefinic analogs of NR by means of elemental sulfur in the absence or presence of accelerators and auxiliary vulcanizing ingredients. This model-olefin approach has been particularly useful in elucidating the structures of NR-sulfur vulcanizates and is primarily responsible for our present understanding of the chemistry of sulfur vulcanization.<sup>3,4</sup>

(3) Treatment of vulcanizate networks with chemical reagents (chemical probes) which react with specific functional groups in the network and thus allow these groups to be detected and estimated. The method is exemplified by the use of

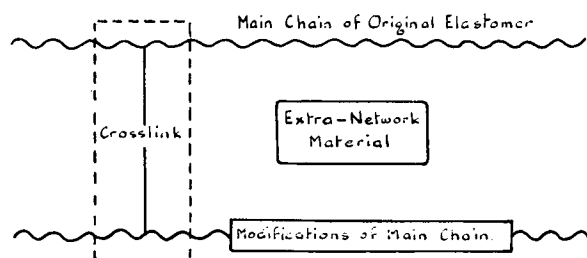


Fig. 1. Simple representation of structural features of a vulcanizate.

sulfite ions,<sup>5,6</sup> radioactive sulfur [<sup>35</sup>S],<sup>7</sup> lithium aluminum hydride,<sup>8,9</sup> and triphenylphosphine<sup>10</sup> to establish the nature of the sulfidic crosslinks in vulcanizates.

A number of other, physicochemical, methods have also been used in this context, including thermal stress-relaxation of vulcanizates in an inert atmosphere,<sup>6</sup> infrared spectroscopy,<sup>11,12</sup> and proton magnetic resonance spectroscopy.<sup>13,14</sup> These methods have not as yet yielded much critical information on network structures, though they and related techniques (e.g., ultraviolet spectroscopy<sup>12</sup>) may well prove valuable in the future in light of the information gained from methods (1)–(3).

## II. INTRODUCTION TO PART I

This paper deals with the determination of crosslinking efficiencies of sulfur in a series of unaccelerated NR-sulfur vulcanizates produced at 140°C. The method used is that described under (1) above, values of the degree of chemical crosslinking being derived from stress-strain measurements on the unextracted vulcanizates.

## III. MATERIALS AND EXPERIMENTAL METHODS

### Materials

Sieved flowers of sulfur (85-mesh sieve) was used throughout. Natural rubber smoked sheets (RSS1, yellow circle) from a large batch were lightly blended on a two-roll mill, and portions of this blend were used throughout the work described below.

### Preparation of Vulcanizates

In order to obtain uniformly crosslinked sheets of the vulcanizates the following method of compounding and curing was devised which ensured the solution of all the sulfur in the rubber throughout the mixing and curing operations. A master-

batch of sulfur (1 part) and NR (2 parts) was made on a mill at a roll temperature of 65–70°C.; then the required quantity of this masterbatch was added to rubber already banded on a two-roll mill at 100–110°C., and mixing was completed at this temperature by cutting back and rolling. Portions of the transparent mixed stock, containing either 6 or 10 parts of sulfur per hundred parts rubber, were then transferred to hot molds and immediately cured for the appropriate times at 140 ± 0.25°C. (for cure times up to 8 hr.) and at 140 ± 0.5°C. (for longer cure times). The molds were rapidly cooled by passing cold water through the platens before opening the presses. Stocks prepared as above could be used over a period of two days if, immediately prior to curing, they were warmed up by passing them five times through a mill at 100–110°C. at a nip opening of 0.01 in. followed by passage four times at 0.05 in. The degree of uniformity of crosslinking of the central 10 in. × 10 in. portions of 12 in. × 12 in. × 1/16 in. sheets of vulcanizates prepared as above is indicated by the following data: 44 type D dumbbells cut from two of these sheets, prepared from a NR(100)-sulfur (10) mix cured for 6 hr. at 140°C. in the top and bottom platens of the press had a mean relaxed modulus at 100% extension (mean MR<sub>100</sub>)<sup>15</sup> of 7.33 kg./cm.<sup>2</sup> with a standard deviation of 0.20 kg./cm.<sup>2</sup>. Preliminary experiments showed that much less uniformly crosslinked sheets than those described above were obtained when more conventional compounding and curing procedures were used.

### Determination of Number-Average Molecular Weights ( $\bar{M}_n$ ) of NR Prior to Crosslinking

These were derived from the limiting viscosity numbers,  $[\eta]$ , of the rubber hydrocarbon component of the mixes, the viscosity measurements being done as quickly as possible after the mixes had been compounded. Viscosities were determined on centrifuged benzene solutions at 25°C. and corrections were applied for the sulfur present in the solutions. There was no gel rubber in any of the mixes examined. Values of  $\bar{M}_n$  were derived from values of  $[\eta]$  (g./100 ml.)<sup>-1</sup> by use of the equation:  $[\eta] = 2.29 \times 10^{-7} \bar{M}_n^{1.33}$ , established by Mullins and Watson<sup>16</sup> for masticated NR.

### Stress-Strain Measurements on Vulcanizates

The equilibrium stress-strain properties of strips cut from the center of the vulcanized sheets were determined at 25°C. as described in detail else-

where.<sup>17</sup> The results were analyzed by plotting  $1/2fA_0^{-1}(\lambda - \lambda^{-2})^{-1}$  against  $\lambda^{-1}$ , where  $\lambda$  is the extension ratio produced by a load  $f$  in a sample having an original cross-sectional area  $A_0$ . At low and moderate extensions the stress-strain properties follow a linear behavior given by the equation:

$$1/2fA_0^{-1}(\lambda - \lambda^{-2})^{-1} = C_1 + \lambda^{-1}C_2 \quad (1)$$

where  $C_1$  and  $C_2$  are constants characterizing the vulcanizate. At higher extensions, departures from linearity occur, and the value of  $1/2fA_0^{-1}(\lambda - \lambda^{-2})^{-1}$  increases rapidly with decrease in  $\lambda^{-1}$ . Values of  $C_1$  and  $\lambda^*$ , the extension ratio at which the experimental stress-strain curve departs from the linear portion by 2.5% of  $C_1$ , were determined and used independently to determine the degree of chemical crosslinking ( $1/2M_{c, \text{chem}}^*$ ), where  $M_{c, \text{chem}}^*$  is the number-average molecular weight of the actual polyisoprene fraction of the chain segments in the network.

#### Determination of $M_{c, \text{chem}}^*$ from Values of $C_1$

In interpreting measured values of  $C_1$  in terms of  $M_{c, \text{chem}}^*$  corrections have to be applied to  $C_{1, \text{measured}}$  to allow for: (a) the effect of uncombined sulfur on the stress-strain properties of the vulcanizate network; and (b) the contribution of combined sulfur, present either in the crosslink or in the main polyisoprene chain, to the molecular weight of the chain segment. In correcting for (a) it was assumed that uncombined sulfur acted as a filler and thus the actual  $C_1$  for the network,  $C_1^N$ , is derivable from eq. (2):

$$C_{1, \text{measured}} = C_1^N(1 + 2.5c + 14.1c^2) \quad (2)$$

where  $c$  is the volume fraction of uncombined sulfur in the vulcanizate. Values of  $C_1^N$  reflect both the physically effective degree of crosslinking and the presence of network flaws due to chain ends.<sup>2,18</sup> Values of the number-average molecular weight of the chain segments in the network,  $M_{c, \text{chem}}^N$ , are then derived from the  $C_1^N$  values by means of eq. (3):<sup>2</sup>

$$C_1^N = (1/2\rho RTM_{c, \text{chem}}^{N-1} + 0.78 \times 10^6) \\ (1 - 2.3M_{c, \text{chem}}^N \cdot \bar{M}_n^{-1}) \text{ dynes/cm.}^2 \quad (3)$$

where  $\rho$  is the density of the vulcanizate network,  $R$  is the gas constant,  $T$  the temperature, and  $\bar{M}_n$  the number-average molecular weight of the primary polyisoprene chains—it being assumed that no chain scission occurs during cure. Equation (3) is a revised and improved form of the original rela-

tionship<sup>1</sup> between the physically effective degree of crosslinking ( $1/2M_{c, \text{phys}}^*$ ) and the actual chemical degree of crosslinking ( $1/2M_{c, \text{chem}}^*$ ) as obtained for a NR-di-*tert*-butyl peroxide vulcanization system.

Finally, to allow for the effect (b) above, values of  $M_{c, \text{chem}}^N$  are converted into values of  $M_{c, \text{chem}}^*$  by means of eq. (4):

$$M_{c, \text{chem}}^N = M_{c, \text{chem}}^*(1 - x)^{-1} \quad (4)$$

where  $x$  is the weight fraction of combined sulfur in the network.

#### Determination of $M_{c, \text{chem}}^*$ from $\lambda^*$

Mullins<sup>18</sup> has shown that values of  $\lambda^*$  depend on the degree of crosslinking of the network but are independent of the initial molecular weight of the NR chains, and has established an empirical relationship between  $\lambda^*$  and  $M_{c, \text{chem}}^*$  for peroxide-NR and sulfur-NR vulcanizates. This relationship has been used here to determine values of  $M_{c, \text{chem}}^*$  which will be independent of any scission of the polyisoprene chains which may occur during the vulcanization process. Any divergence between  $M_{c, \text{chem}}^*$  values obtained from  $C_1^N$  and  $\lambda^*$  reflects main-chain scission, and the extent of the divergence permits an estimate to be made of the amount of chain scission which occurs concurrently with the crosslinking process.

#### Determination of Combined Sulfur, $S_c$ , in the Vulcanizate Network

Portions of the vulcanizate strips on which stress-strain measurements had been performed were extracted with hot acetone in nitrogen in the dark for 24 hr. and then dried to constant weight *in vacuo* at room temperature. The combined sulfur contents of the networks were then determined by microcombustion of 20–25 mg. samples and the use of the following volumetric methods. Sulfur oxides were absorbed in 5% hydrogen peroxide and titrated with 0.02*N* sodium hydroxide. Sulfur contents thus obtained were corrected for the nitrogen and sulfur content of the original NR, this correction being equivalent to 0.05%  $S_c$ . After the alkalimetric titration, sulfate ion was determined complexometrically by a modification of the procedure of Tettweiler and Pilz,<sup>19</sup> the barium sulfate being precipitated from cold 30% ethanolic solution, and excess barium being titrated as recommended by Schwarzenbach and Irving.<sup>20</sup> There was no significant difference between the results obtained by the two titration procedures.

TABLE I  
Structural Characteristics of Unaccelerated Natural Rubber—Sulfur Vulcanizates (Cure Temp.: 140°C.)

Expt. no.	[ $\eta$ ] of NR in mix, 100 ml./g.	Cure time, hr.	$C_1$ , measured dynes/cm. <sup>2</sup> $\times 10^{-6}$ at 25°C.,	$\lambda^*$	Density of vulcanizate network $\rho$ , g./ml.	Combined sulfur $S_c$ , g. atoms S <sub>c</sub> /g. rubber hydrocarbon $\times 10^4$	$1/2M^*_{c, chem} \times 10^5$ , g.-moles chemical crosslinks/g. rubber hydrocarbon		Crosslinking efficiency $E$ , no. of sulfur atoms combined in network per chemical crosslink present	
							Based on $C_1$	Based on $\lambda^*$	Based on $C_1$	Based on $\lambda^*$
Mix 1: NR (100 parts)—Sulfur (10 parts)										
1	3.34	2.0	0.46	3.12	0.92	5.0	0.86	1.0	58	50
2	3.34	2.0	0.49	3.10	0.92	5.3	0.91	1.0	58	53
3	3.34	4.0	0.90	2.70	0.94	11.2	1.6	2.1	70	53
4	3.34	4.0	0.92	2.68	0.94	11.6	1.7	2.2	68	53
5	4.06	6.0	1.33	2.35	0.95	16.6	3.1	3.5	54	47
6	4.06	7.0	1.61	2.25	0.96	19.7	4.1 <sub>s</sub>	4.2	48	47
7	3.34	8.0	1.89	2.06	0.97	24.0	5.4	5.9	44	41
8	3.34	8.0	1.94	2.10	0.97	24.4	5.6 <sub>s</sub>	5.5	43	44
9	3.34	24.0	1.68	2.00	0.985	31.0	4.7 <sub>s</sub>	7.1	65	44
10	3.34	24.0	1.83	1.95	0.985	31.0	5.4	7.6	57	41
11	4.06	48.0	1.69	—	0.985	32.2	4.7 <sub>s</sub>	—	68	—
Mix 2: NR (100 parts)—Sulfur (6 parts)										
12	4.02	2.0	0.37	3.45	0.92	3.4	0.7	0.7	49	49
13	4.02	4.0	0.59	3.10	0.93	6.8	1.0	1.0	68	68
14	4.02	6.0	0.85	2.80	0.94	10.0	1.5	1.8	67	56
15	4.02	8.0	1.04	2.55	0.945	13.0	2.2	2.6	59	50
16	4.02	24.0	1.00	2.25	0.96	19.0	2.1	4.2	90	45
17	4.02	48.0	0.66	2.20	0.96	19.0	1.4	1.6	136	41

#### IV. EXPERIMENTAL RESULTS

Table I records the limiting viscosity numbers, [ $\eta$ ], of the rubber hydrocarbon component of the mixes, together with values of  $C_1$  and  $\lambda^*$  for the unextracted vulcanizates, and the densities, combined sulfur contents,  $S_c$ , and values of  $1/2M^*_{c, chem}$  for the vulcanizate networks. The last two quantities give values of the crosslinking efficiencies,  $E$ , which are recorded in Table I and presented, in parentheses, in Figure 2.

#### V. DISCUSSION

The observed divergence between values of  $1/2M^*_{c, chem}$  obtained from  $C_1$  and  $\lambda^*$  data (Table I and Fig. 2) is consistent with the occurrence of scission of the NR main chains during the vulcanization process.<sup>18</sup> The above divergence permits the extent of such scission to be estimated (Table II), and the data indicate that while scission is only slight at low cure times it becomes very important at long cure times and appears to be mainly responsible for the observed network degradation

(reversion) on extended cure. The mechanism of the scission process is obscure.

When allowance is made for main chain scission during cure, the data of Table I and Figure 2 indicate that about 40 to 55 sulfur atoms must be combined in the NR network to produce one physically effective chemical crosslink unit. These values give quantitative expression to the known marked inefficiency of sulfur as a crosslinking agent in unaccelerated NR—sulfur systems and indicate the considerable structural complexity of the resultant network. The low crosslinking efficiency of sulfur revealed here is consistent with results obtained from the reaction of sulfur with monoolefins and 1,5-dienes at 140°C.<sup>3</sup> which show that a considerable proportion of the reacted sulfur is wasted as far as crosslinking is concerned by the formation of: (a), crosslinked units containing long polysulfide chains; (b), cyclic monosulfides which constitute important modifications of the main polyisoprene chains; and (c) vicinal sulfidic crosslinks which act physically as a single crosslink.

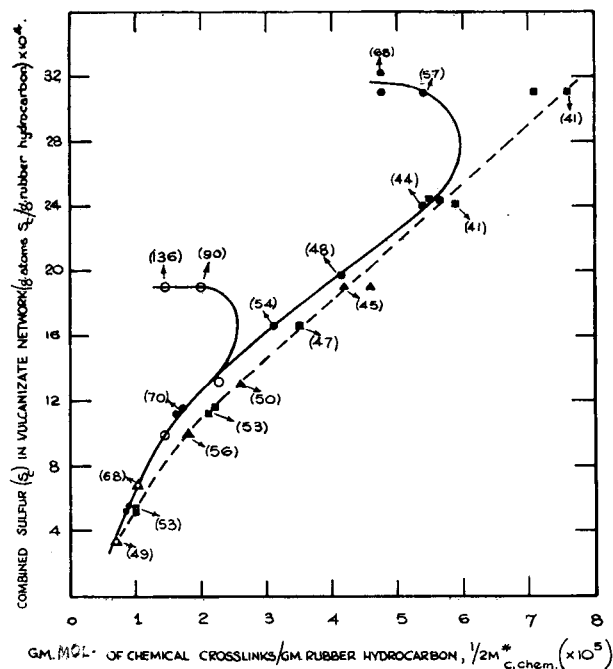


Fig. 2. Relationship between combined sulfur  $S_c$  and degree of chemical crosslinking  $1/2M^*_{c, chem.}$  for unaccelerated NR-sulfur vulcanizates cured at  $140^\circ\text{C}$ .: (●) NR (100 parts)-sulfur (10 parts),  $1/2M^*_{c, chem.}$  based on  $C_1$  data; (■) NR (100 parts)-sulfur (10 parts),  $1/2M^*_{c, chem.}$  based on  $\lambda^*$  data; (○) NR(100 parts)-sulfur (6 parts),  $1/2M^*_{c, chem.}$  based on  $C_1$  data; (▲) NR(100 parts)-sulfur (6 parts),  $1/2M^*_{c, chem.}$  based on  $\lambda^*$  data. Values in parentheses on the curves are the number of sulfur atoms combined in the network per chemical crosslink present.

TABLE II

Estimates of the Molecular Weights ( $\bar{M}_n$ ) of the NR Main Chains Before and After Cure

Expt. no.	Cure time, hr.	$\bar{M}_n \times 10^{-5}$	
		Before cure	After cure
Mix 1: NR (100 parts)-Sulfur (10 parts)			
1	2	2.4	2.0
2	2	2.4	2.1
3	4	2.4	1.6
4	4	2.4	1.6
5	6	2.8	1.9
6	7	2.8	(2.6)
7	8	2.4	1.5
8	8	2.4	(2.9)
9	24	2.4	0.63
10	24	2.4	0.67
Mix 2: NR (100 parts)-Sulfur (6 parts)			
12	2	2.7	2.7
13	4	2.7	2.7
14	6	2.7	2.1
15	8	2.7	1.5
16	24	2.7	0.67
17	48	2.7	0.36

The increase in crosslinking efficiency of sulfur with increasing cure time, apparent from the data based on  $\lambda^*$  values (Table I and Fig. 2), may be explained by initially formed polysulfide crosslinks reacting with polyisoprene chains in analogous manner to sulfur and thus supplementing the latter as a crosslinking agent. This is consistent with the extensive sulfuration of simple olefins by organic polysulfides at  $140^\circ\text{C}$ . or above.<sup>21,22</sup>

Part II of this series<sup>10</sup> describes the further structural resolution of unaccelerated NR-sulfur vulcanizate networks by use of triphenylphosphine as a chemical probe to determine the amount of the total combined sulfur which is present in crosslinked units and in cyclic monosulfide structures respectively.

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### Synopsis

The sulfur contents  $S_c$  and degrees of chemical crosslinking  $1/2M^*_{c,chem}$  have been determined for a series of vulcanizate networks obtained by curing unaccelerated natural rubber-sulfur mixes for various times at 140°C. The independent estimates of  $1/2M^*_{c,chem}$  were obtained for each vulcanizate from stress-strain measurements ( $C_1$  and  $\lambda^*$ ) on the unswollen vulcanizate and use of the methods described by Mullins. The disparity in the values of  $1/2M^*_{c,chem}$  obtained by the two methods reflects the scission of natural rubber main chains during the vulcanization process, the extent of such scission being found to increase with increasing cure time. When allowance is made for chain scission the  $S_c$  and  $1/2M^*_{c,chem}$  data yield values of the efficiency of sulfur as a crosslinking agent. It is found that between about 40 and 55 sulfur atoms must be combined in the network to produce one chemical crosslink, values which reflect the marked structural complexity of the network as is also inferred from the structures of the products derived from sulfur-olefin interaction at 140°C.

### Résumé

La teneur en soufre ( $S_c$ ) et le degré de pontage ( $1/2M^*_{c,chem}$ ) ont été déterminés pour une série de réseaux vulcanisés obtenus par vulcanisation non accélérée du caoutchouc naturel-soufre est mélangé à 140° durant divers temps de réaction. Deux estimations indépendantes de  $1/2M^*_{c,chem}$  chem., sont obtenues pour chaque vulcanisation par mesure de la force de tension ( $C_1$  et  $\lambda^*$ ) sur le réseau non gonflé et la description de ces méthodes sont donnés par Mullins. La

diversité dans les valeurs de  $1/2M^*_{c,chem}$ , obtenues par les deux méthodes reflète la scission de chaînes principales du caoutchouc naturel durant la vulcanisation, l'importance de cette scission augmentant avec le temps de vulcanisation. Quand on tient compte de la scission de la chaîne,  $S_c$  et  $1/2M^*_{c,chem}$  donnent la valeur de l'efficacité du soufre comme agent de pontage. On a trouvé qu'à peu près 40 à 55 atomes de soufre doivent être combinés dans le réseau pour produire un pontage chimique, valeurs qui reflètent la complexité marquée de la structure du réseau comme il découle aussi de la structure de produits dérivés par interaction soufre-oléfine à 140°C.

### Zusammenfassung

Schwefelgehalt ( $S_c$ ) und chemischer Vernetzungsgrad ( $1/2M^*_{c,chem}$ ) wurden für eine Reihe, durch Vulkanisation beschleunigerfreier Naturkautschuk-Schwefelmischungen während verschiedener Zeiten bei 140°C erhaltener, vernetzter Vulkanisate bestimmt. Zwei unabhängige Werte von  $1/2M^*_{c,chem}$  wurden für jedes Vulkanisat aus Spannung-Dehnungsmessungen ( $C_1$  und  $\lambda^*$ ) am nichtgequollenen Vulkanisat und durch die von Mullins beschriebenen Methoden erhalten. Die Widersprüche in den nach den beiden Methoden erhaltenen Werten von  $1/2M^*_{c,chem}$  sprechen für eine Spaltung der Ketten des Naturkautschuks während der Vulkanisation, wobei das Ausmass der Spaltung eine Zunahme mit zunehmender Vulkanisationsdauer zeigt. Unter Berücksichtigung der Kettenspaltung liefern die  $S_c$ - und  $1/2M^*_{c,chem}$ -Daten Werte für die Wirksamkeit von Schwefel als Vernetzer. Es ergibt sich, dass etwa 40 bis 55 Schwefelatome in Netzwerk gebunden werden müssen, um eine chemische Vernetzung zu erzeugen; diese Werte sprechen für die stark komplexe Struktur des Netzwerkes, auf welche auch aus der Struktur der Reaktionsprodukte der Einwirkung von Schwefel auf Olefine bei 140°C geschlossen werden kann.

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