

**Structural Characterization of Vulcanizates.
Part VIII. The *N*-Cyclohexylbenzothiazole-2-
sulfenamide-Accelerated Sulfur Vulcanization of
Natural Rubber at 140–180°C. and of Synthetic
cis-1,4-Polyisoprene at 140°C.**

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Synopsis

Vulcanization of natural rubber at 140°C. with a CBS-accelerated sulfur system of conventional type gives rise to a structurally complex network in which the number of sulfur atoms combined per chemical crosslink present increases from 12 to 21 with increasing reaction time. The complexity of the network increases with increasing temperature of vulcanization. Crosslinking of a purified synthetic *cis*-1,4-polyisoprene proceeds more slowly and yields a slightly more complex network. Despite this overall similarity the natural rubber vulcanizates exhibit considerably higher tensile strengths.

INTRODUCTION

In the preceding paper¹ it was shown that in the sulfur vulcanization of natural rubber (NR) accelerated by *N*-cyclohexylbenzothiazole-2-sulfenamide (CBS) in the presence of zinc oxide and lauric acid the efficiency of utilization of sulfur for crosslinking the rubber is high if a moderately high ratio of accelerator to sulfur is used (1.5:1 by weight). Further, the efficiency is insensitive to changes in fatty acid concentration and to cure temperature in the range 100–140°C. when this high ratio is used. In this paper we describe the effect on crosslinking efficiency of reducing the ratio of accelerator to sulfur to the more conventional level of 0.24 to 1, as used in a natural rubber tire-tread mix, the influence of cure temperature in the range 140–180°C. on the efficiency of this system, and the structural characteristics of comparable synthetic *cis*-1,4-polyisoprene (IR) vulcanizates.

MATERIALS AND EXPERIMENTAL METHODS

Synthetic *cis*-1,4-polyisoprene (Shell Chemical Co., WP 300) was a sample of high molecular weight, $[\eta]_{\text{benzene}}$ 10.7, of the type produced for extension with oil. Infrared spectral analysis showed the absence of 1,2 and

trans-1,4 groups; the 3,4 groups were estimated at 6%. It was extracted for 4 days with hot acetone before use, to remove added antioxidant (found after extraction: ash 0.2%, S 0.01%). Other materials were those described in Part VII.¹

The general experimental methods of Parts VI¹ and VII² of this series were used with the following exceptions:

(1) The number-average molecular weight \bar{M}_n of the IR after mixing was derived from the limiting viscosity number in toluene by means of the relationship³

$$[\eta]_{\text{toluene}} = 9.00 \times 10^{-6} \bar{M}_n^{1.026}$$

(2) To facilitate the molding of sheets during curing at 180°C., the rubber mix was pressed out and cured between sheets of aluminum foil. Rapid cooling from 160 and 180°C. was effected by quenching the hot molds in cold water.

(3) Vulcanized sheets were stored at -26°C. to minimize any post-vulcanization crosslinking,¹ but were allowed to stand at room temperature for at least 1 hr. before measurements were made with them.

(4) Mooney-Rivlin plots of stress-strain measurements made on IR vulcanizates showed no unusual features, and values of the elastic parameters $C_{1,RV}$ and $C_{2,RV}$ were obtained from them in the usual way. The extension ratios λ^* , at which the experimental plots departed from linearity by 2.5% of C_1 , were measured on selected NR vulcanizates.

(5) Values of the degree of chemical crosslinking, $(2M_{c,\text{chem}}^{\text{RH}})^{-1}$, of the IR vulcanizates were obtained from values of $C_{1,RH}$ (the C_1 of the rubber hydrocarbon component of the network) by means of the relationship observed for natural rubber [Part VII,¹ eq. (3)]. It is assumed that this relationship will be applicable generally to polyisoprenes of close to 100% *cis*-1,4 structure, with the reservation that differences in primary molecular weight distribution may lead to small differences in the magnitude of the chain-end correction (see also Part IX⁴).

RESULTS AND DISCUSSION

Natural Rubber: Effect of Accelerator Concentration

Reduction of the weight ratio of sulfenamide to sulfur from the value of 1.5:1 used in the previous paper to the level 0.24:1 (see Table I) characteristic of commercial usage in NR tire-tread formulations has a marked effect on the degree of crosslinking obtainable from a given quantity of sulfur. Thus, whereas the lower ratio produces 0.54×10^{-4} "moles" of chemical crosslinks per gram of rubber hydrocarbon (RH) from 2.5 parts sulfur per 100 rubber (Fig. 1, mix A at 140°C.), the higher ratio gives 0.77×10^{-4} "moles" of chemical crosslinks from only 1.5 parts sulfur per 100 rubber (mix B, Fig. 1 of Part VII¹). The ratio of accelerator to sulfur also has an important influence on the reversion characteristics of the curing system. As Figure 1 shows, further heating beyond the point of maximum

TABLE I
Mix Formulations and Cure Temperatures Used in the Preparation
of CBS-Accelerated NR- and IR-Sulfur Vulcanizates

	Mix no.	
	A	B
Parts, wt.		
RSS1	100	—
Extracted IR	—	100
Sulfur	2.5	2.5
CBS	0.6	0.6
Zinc oxide	5.0	5.0
Lauric acid	0.7	1.45
Cure temp., °C.	140, 160, 180	140

crosslinking of the system with the lower ratio leads to a substantial loss of crosslinks (to the extent of 50% loss at 360 min.), but only a limited deterioration is observed with the system of high accelerator content (Fig. 1 of Part VII¹).

These features are reflected in changes in efficiency E (the number of sulfur atoms combined in the vulcanizate network per chemical crosslink formed), which affords a measure of the overall complexity of the network. In the technically important system of high sulfur content and low CBS-to-sulfur ratio the formation of one crosslink requires the combination of 12

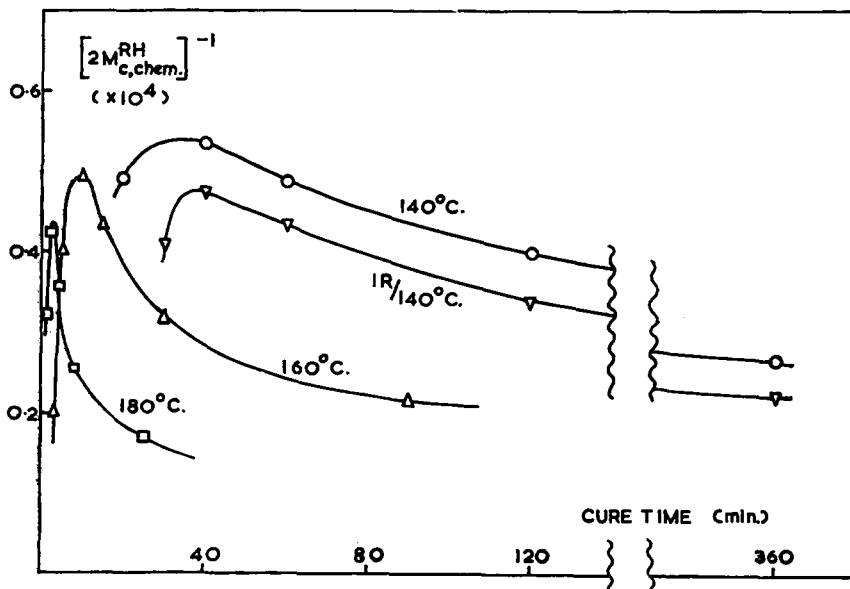


Fig. 1. Relation between degree of chemical crosslinking, $(2M_{c,chem}^{RH})^{-1}$, and vulcanization time as a function of vulcanization temperature and polymer type (mixes A and B, Table I).

TABLE II
Chemical Characterization of Vulcanizate Networks Derived from CBS-Accelerated NR-Sulfur System (Mix A, Table I)

Cure time, min.	Wt. loss on			[S ²⁻] of RV, wt.-%	[S _c] (× 10 ⁴) ^b	[S ²⁻] (× 10 ⁴) ^c	Deg. crosslink. (× 10 ⁴) ^d	E ^o	F ^t
	[S _c + S ²⁻] extr. vulc., wt.-%	[S _c + S ²⁻] of RV, ^a wt.-%	extrn. raw vulc., %						
At 140°C.									
20	1.92 ₃	1.84 ₃	2.54	0.228	5.68	0.80	0.49	11.6	1.6
40	2.40 ₃	2.30	3.11	0.383	6.73 ₅	1.36	0.54	12.5	2.5
60	2.41	2.30	3.20	0.426	6.58	1.50	0.49	13.4	3.1
120	2.44	2.33	3.10	0.501	6.42 ₅	1.76	0.40	16.0	4.4
360	2.38 ₃	2.28	3.15	0.641	5.76	2.25	0.27	21.4	8.3
At 160°C.									
3	0.77	0.69 ₅	5.75	0.03	2.34	0.11	0.20	11.6	0.52
5	1.45	1.35	5.04	0.068	4.49	0.24	0.40	11.1	0.59
10	2.39	2.27 ₅	3.34	0.321	6.86	1.13	0.50	13.9	2.3
15	2.45	2.33 ₅	3.49	0.393	6.81 ₅	1.38	0.44	15.7	3.2
30	2.46	2.34	3.63	0.505	6.45	1.77	0.32	20.1	5.5
90	2.43	2.31	3.70	0.634	5.88 ₅	2.23	0.22	26.8	10.1
At 180°C.									
1	0.97	0.89	5.03	0.049	2.95	0.17	0.32	9.2	0.53
2	2.11	2.00	3.76	0.254	6.13	0.89	0.42	14.5	2.1
4	2.47	2.36	3.29	0.390	6.91 ₅	1.37	0.36	19.4	3.8
8	2.41	2.30 ₅	3.08	0.562	6.12 ₅	1.97	0.26	24.0	7.7
25	2.43	2.31 ₅	3.44	0.616	5.97	2.16	0.17	35.8	12.6

^a Corrected for the sulfur content of the raw rubber; RV, raw vulcanizate.

^b Gram-atom of sulfur per gram of rubber hydrocarbon in the network.

^c Gram-ion of sulfide per gram of rubber hydrocarbon in the network.

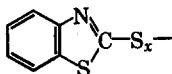
^d Gram-mole chemical crosslinks per gram of rubber hydrocarbon in the network.

^e Number of sulfur atoms combined in the network per chemical crosslink present.

^t Number of sulfide ions formed per chemical crosslink in the network.

sulfur atoms initially, but this increases to 21 as cure proceeds. This contrasts with the *reduction* in E with cure time from 8 to 4.4 in the system with high CBS-to-sulfur ratio. This improvement in efficiency and in resistance to reversion as the ratio of accelerator to sulfur is increased can be pursued still further, and technically valuable vulcanizates with E values as low as 3.5 have been obtained⁵ with a ratio of 15:1 of CBS to sulfur.

In the present system, since the sulfur combined in the network $[S_c]$ together with that present as zinc sulfide $[S^{2-}]$ never greatly exceeds 8.07×10^{-4} g.-atom per gram of RH in the network, or 2.5 g. of sulfur per 100 g. of NR (Table II), the presence of accelerator moieties terminating pendant sulfur groupings, as



can contribute little to the high E values observed. The latter are caused in part by the presence of a high proportion of polysulfidic (as opposed to di- and monosulfidic) crosslinks but principally by the presence of cyclic monosulfide groups distributed along the main rubber chains.⁶

In general network complexity, including extent of modification by these groups, this high-sulfur low-accelerator system resembles the "inefficient" MBT-accelerated system described in Part VI,² for which E values ranging from 14 to 19 with increasing cure time were observed. The similarity between these two systems is ascribed to their containing similar concentrations, relative to sulfur, of soluble zinc benzothiazol-2-yl mercaptide (ZMBT) complexes, which are believed to be the actual accelerators.⁷ In the present CBS system, although the accelerator-to-sulfur ratio is low, practically all the ZMBT formed from the CBS and zinc laurate (or zinc oxide) is likely to be in soluble form and, therefore, active in sulfuration, owing to complex formation by cyclohexylamine (and to a minor extent by zinc laurate); in the MBT system referred to above considerably more ZMBT will be formed (MBT/sulfur ratio, 1:1) but much of it will be in the free state and largely insoluble, since complex formation will be limited by the small amount of zinc laurate present and the essential absence of amine (although some of the nitrogenous bases present in the NR activate ZMBT in vulcanization, presumably by complex formation⁷).

The marked reversion of high-sulfur CBS-accelerated vulcanizates on long cure and the considerable degree of main-chain modification by cyclic monosulfide formation which they undergo are attributed to the low actual accelerator concentration. Polysulfide crosslinks are the primary products of the vulcanization process, and these are subsequently shortened to di- and monosulfide crosslinks by a desulfuration process catalyzed by a zinc accelerator mercaptide complex, the sulfur removed becoming available for further crosslinking.⁷ This leads to an improvement in crosslinking efficiency with reaction time, as in the low-sulfur systems. If the concentration of the complex is low, desulfuration proceeds slowly, and polysulfide cross-

TABLE III
Physical Characterization of Vulcanizate Networks Derived from CBS-Accelerated NR-Sulfur System (Mix A, Table I) and Estimates of Degree of Chemical Crosslinking of Rubber Hydrocarbon Component of Networks

Cure time, min.	[η] _{benz.} rubb. hydrocarb. mix at 25°C., dl./g.	\bar{M}_n rubb. hydrocarb. compound of mix $\times 10^{-6}$	Elastic parameters, dynes/cm. ² $\times 10^{-6}$			λ^*	Equil. ν_r of network in <i>n</i> -decane at 25°C.	χ	$C_{1,RH}$ at 25°C. ^a ($\times 10^4$) ^b	Deg. crosslink.
			$C_{1,RV}$ at 21°C.	$C_{2,RV}$ at 21°C.	$C_{1,BRM}$ at 25°C.					
At 140°C.										
20	3.12	2.30	1.62	1.15	—	—	—	—	1.70	0.49
40	3.07 ^c	2.28	1.50	1.12	1.51	—	0.2845	0.427	1.81	0.54
60	3.12	2.30	1.73	1.26	—	—	—	0.428	—	—
120	3.07	2.28	1.70	1.12	1.72	—	0.2997	—	1.69	0.49
360	3.12	2.30	1.62	1.22	—	—	0.2890	0.430	—	—
	3.07	2.28	1.54	1.20	1.55	—	—	—	1.48	0.40
	3.07	2.28	1.41	1.20	—	—	—	—	0.436	—
	3.12	2.30	1.36	1.12	1.37	—	0.2795	0.436	1.13	0.27
	3.07	2.28	1.03	1.16	—	—	—	—	—	—
	3.07	2.28	1.15	1.09	1.15	—	0.2658	0.445	—	—

At 160°C.										
3	2.96	2.23	0.88	0.94	0.88	—	0.218	0.411	0.92	0.20
5	2.96	2.23	1.41	1.12	1.42	2.57	0.267	0.410	1.47	0.40
10	2.96	2.23	1.62	1.13	1.63	2.43	0.297	0.434	1.69	0.50
15	2.96	2.23	1.48	1.13	1.50	2.50	0.293	0.437	1.55	0.44
30	2.96	2.23	1.21	1.09	1.22	2.59	0.274	0.448	1.26	0.32
90	2.96	2.23	0.94	0.99	0.95	2.86	0.249	0.451	0.98	0.22
At 180°C.										
1	2.76	2.12	1.20	1.10	1.21	—	0.255	0.420	1.25	0.32
2	2.76	2.12	1.44	1.21	1.45	2.67	0.282	0.428	1.51	0.42
4	2.76	2.12	1.28	1.06	1.29	2.67	0.274	0.438	1.34	0.36
8	2.76	2.12	1.02	0.97	1.03	2.82	0.249	0.438	1.07	0.26
25	2.76	2.12	0.76	0.91	0.76	3.07	0.220	0.440	0.79	0.17

^a Dynes/cm.² × 10⁻⁶.

^b Gram-mole chemical crosslinks per gram of rubber hydrocarbon in the network, $(2M_{c, \text{chem}})^{-1}$.

^c Repeat mix.

links have the opportunity to undergo thermal destruction, giving rise to conjugated diene and triene groupings and zinc sulfide, probably accompanied by cyclic monosulfides. Such is the case with the high-sulfur system, in which the predominance of polysulfide crosslinks at all stages of cure has been confirmed by the "chemical probe" technique.⁶

Natural Rubber: Effect of Temperature

Raising the temperature of vulcanization in conventional accelerated sulfur curing systems is known to lead to more pronounced modulus reversion and to deterioration in vulcanizate properties generally. This is illustrated for the high-sulfur CBS-accelerated system in Figure 1, which shows that the number of chemical crosslinks obtainable (at optimum cure) decreases with increasing temperature in the range 140–180°C. The changes in crosslinking efficiency which these results reflect are shown in Figure 2. Efficiencies do not vary greatly with temperature before maximum crosslinking is reached, but they then become increasingly disparate, high temperatures being associated with high E values. The latter may be due to increased thermal disruption of polysulfidic crosslinks with concomitant redistribution of sulfur into cyclic monosulfide groups on the main rubber

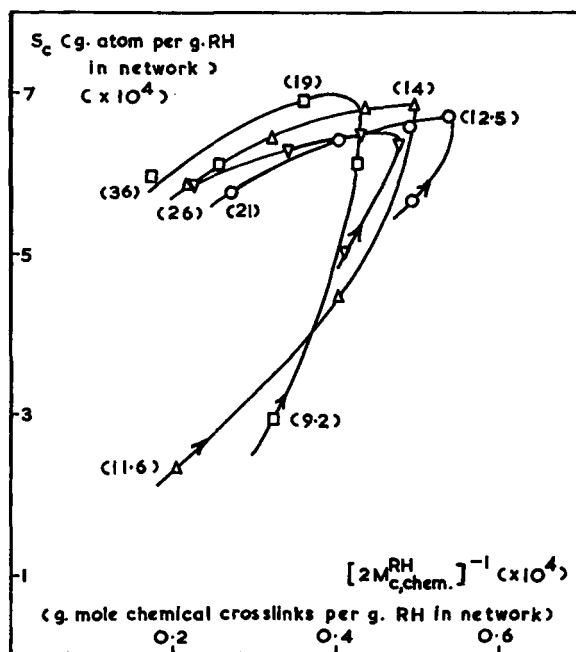


Fig. 2. Relation between sulfur combined in the network, $[S_c]$, and the degree of chemical crosslinking, $(2M_{c,chem}^{RH})^{-1}$, as a function of time and temperature of vulcanization and of polymer type. Curves correspond to those in Figure 1. Arrows on curves indicate direction of increasing vulcanization time. Values of the sulfur crosslinking efficiency E are given in parentheses on the curves.

TABLE IV
Physical Characterization of Vulcanizate Networks Derived from CBS-Accelerated IR-Sulfur System (Mix B, Table I) and Estimates of Degree of Chemical Crosslinking of Rubber Hydrocarbon Component of the Networks

Cure time at 140°C., min.	[η] _{benz.} rubb. hydrocarb. compound mix at 25°C., dl./g.	\bar{M}_n rubb. hydrocarb. compound of mix $\times 10^{-6}$	Elastic parameters, dynes/cm. ² $\times 10^{-4}$			Equil. ν , of network in <i>n</i> -decane at 25°C.	$C_{1,RH}$ at 25°C. ^a	χ	Deg. crosslink. ($\times 10^4$) ^b
			$C_{1,RV}$ at 21°C.	$C_{2,RV}$ at 21°C.	$C_{1,ERM}$ at 25°C.				
30	2.27	1.92	1.42	1.16	1.42	0.279	0.43	1.44 ₆	0.41
40	2.27	1.92	1.59	1.14	1.59	0.294	0.43	1.61 ₆	0.47 ₆
60	2.27	1.92	1.49	1.16	1.49	0.290	0.43 ₆	1.51 ₆	0.43 ₆
120	2.27	1.92	1.25	1.16	1.25	0.276	0.44 ₆	1.27	0.34
360	2.27	1.92	0.93	1.05	0.92 ₆	0.249	0.45	0.94	0.22 ₆

^a Dynes/cm.² $\times 10^{-6}$.

^b Gram-mole of chemical crosslinks per gram of rubber hydrocarbon in the network, $(2M_c^{RH})^{-1}$.

chains or to scission of the main chains during cure at the higher temperatures, which would lead to an apparent reduction in the degree of crosslinking. Evidence that the second factor does not contribute to the observed high E values is obtained from measurements of λ^* —which has been shown⁸ to depend on the degree of crosslinking but to be independent of the molecular weight of the main chains. Comparison of the values of λ^* and $(2M_{c, \text{chem}}^{\text{RH}})^{-1}$ for the vulcanizates prepared at 160 and 180°C. (Table III) with the empirical relationship between these two quantities established by Mullins⁸ indicates that no reduction in molecular weight of the main chains occurs during vulcanization, i.e., that no main-chain scission takes place.

Synthetic *cis*-1,4-Polyisoprene

In replacing NR by extracted IR (mix B, Table I) additional lauric acid was included in the mix to bring the total acid content up to that of the

TABLE V
Modulus (MR 100) and Tensile Strength Data for Vulcanizates Derived from the CBS-Accelerated NR- and IR-Sulfur Systems (Mixes A and B, Table I)*

Cure time, min.	MR 100, kg./cm. ²	Tensile strength, kg./cm. ²
Mix A		
At 140°C.		
20	8.4	394
40	8.65	345
60	8.3	312
120	7.5	276
360	6.3	262
At 160°C.		
3	5.1	179
5	7.9	302
10	8.3	259
15	7.8	259
30	7.6	204
90	5.6	201
At 180°C.		
1	6.4	295
2	7.7	310
4	7.1	249
8	5.9	183
25	5.0	103
Mix B		
At 140°C.		
30	7.55	258
40	8.3	229
60	7.9	212
120	7.0	221
360	5.65	193

* Figures for MR 100 are means of two results; those for tensile strength are medians of three results.

TABLE VI
Chemical Characterization of Vulcanizate Networks Derived from the CBS-Accelerated IR-Sulfur System (Mix B, Table I)

Cure time at 140°C., min.	[S _c + S ²⁻] extr. vulc. (wt.-%)	Wt. loss on extrn. raw vulc. (%)	[S _c + S ²⁻] of RV ^a (wt.-%)	[S ²⁻] of RV ^a (wt.-%)	[S _c] ^b (× 10 ⁴)	[S ²⁻] ^c (× 10 ⁴)	Deg. crosslink. ^d (× 10 ⁴)	E ^o	F ^f
30	1.72	3.39	1.66	0.190	5.03	0.65	0.41	12.3	1.59
40	2.22	2.62	2.16	0.306	6.34	1.05	0.47 ₅	13.4	2.21
60	2.32	2.38	2.27	0.366	6.49	1.25	0.43 ₅	15.0	2.87
120	2.34	2.32	2.29	0.450	6.27	1.54	0.34	18.4	4.53
360	2.28	2.16	2.23	0.519	5.85	1.77	0.22 ₅	26.0	7.85

^a RV, raw vulcanizate.

^b Gram-atom of sulfur per gram of rubber hydrocarbon in the network.

^c Gram-ion of sulfide per gram of rubber hydrocarbon in the network.

^d Gram-mole of chemical crosslinks per gram of rubber hydrocarbon in the network, $(2M_c^{RH})^{-1}$.

^e Number of sulfur atoms combined in the network per chemical crosslink present.

^f Number of sulfide ions formed per chemical crosslink present in the network.

NR mix (the NR, which was not extracted, contained acid equivalent to 0.75 wt.-% lauric acid).

Under these equivalent conditions of cure at 140°C. the IR took somewhat longer to reach its maximum crosslink density, which was 10% lower than that attained by NR (Fig. 1). In the loss of crosslinks on further curing, however, the two rubbers behaved identically. Since the amounts of sulfur combined by the two rubbers were similar, the lower crosslinking level reached by the IR afforded slightly higher E values (Fig. 2) throughout cure. However, less zinc sulfide is formed both absolutely and pro rata with crosslinking during vulcanization of the synthetic rubber (compare Table VI with Table II).

The near-equivalence in magnitude of values of χ and of the elastic parameter $C_{2,RV}$ for IR vulcanizates (Table IV) with the corresponding values for NR vulcanizates (Table III) is consistent with the overall similarity in their network complexity and with the similar stereoregularity of the two polymers (contrast the differences in these parameters observed⁴ when NR is compared with equilibrium-isomerized NR containing about 60% *trans*-1,4 groupings).

In marked contrast to these points of resemblance the tensile strengths of the IR vulcanizates (Table V) are very much lower than those of the corresponding NR vulcanizates. This may be due partly to the lower initial number-average molecular weight of the synthetic rubber (Table IV) but, despite the similarity referred to above, the small degree of steric inhomogeneity of the IR is almost certainly a contributing factor. As little as a few per cent of 1,2, 3,4, or *trans*-1,4 groups in a *cis*-1,4-polyene is known⁹⁻¹¹ to be sufficient to reduce tensile strength considerably by limiting the degree of crystallization on stretching. Steric inhomogeneity of this magnitude would probably not affect the parameters χ and $C_{2,RV}$ referred to above.

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Résumé

La vulcanisation du caoutchouc naturel à 140°C avec un système accéléré CBS du soufre du type conventionnel donne lieu à un réseau de structure complexe dans lequel le nombre d'atomes de soufre combinés par pont chimique présent croît de 12 à 21 en augmentant la durée de réaction. La complexité du réseau croît avec une température croissante de vulcanisation. Le pontage d'un polyisoprène purifié synthétique entièrement *cis*-1,4 est plus lent et fournit un réseau légèrement plus complexe. Malgré cette similitude générale, les vulcanisats de caoutchouc naturel manifestent nettement des forces de tension plus fortes.

Zusammenfassung

Die Vulkanisation von Naturkautschuk bei 140°C. mit einem CBS-beschleunigten Schwefelsystem von konventionellem Typ führt zu einem strukturell komplexen Netzwerk, in welchem die Zahl der pro vorhandener Vernetzung chemisch gebundenen Schwefelatome mit steigender Reaktionsdauer von 12 auf 21 zunimmt. Der komplexe Charakter des Netzwerkes nimmt mit steigender Vulkanisationstemperatur zu. Die Vernetzung eines gereinigten synthetischen *cis*-1,4-Polyisoprens verläuft langsamer und liefert ein etwas komplexeres Netzwerk. Trotz dieser äusseren Ähnlichkeit zeigt das Naturkautschukvulkanisat eine beträchtlich höhere Zugfestigkeit.

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