Structural Characterization of Vulcanizates. XI. Network-Bound Accelerator Residues

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Synopsis

Radiotracer techniques have been used to determine amounts of accelerator which become bound to the vulcanizate networks during the vulcanization of NR with sulfur and CBS. Three different vulcanization systems have been studied, having different proportions of accelerator to sulfur. The vulcanizates have also been characterized in terms of the numbers and types of chemical crosslinks present and the results of the bound accelerator analyses have been considered in relation to the crosslink levels and distribution.

INTRODUCTION

Several authors have obtained evidence for the formation of network-bound accelerator residues (referred to subsequently as pendent groups) during the accelerated sulfur vulcanization of natural rubber (NR) and synthetic cis-polyisoprene. Some of this work[1,2] has been carried out in the absence of activators (zinc oxide, fatty acid and nitrogenous bases) and, because of Watson's observation[3] that the level of pendent groups in vulcanization with tetramethylthiuram disulfide (TMTD) and zinc oxide is considerably reduced when activators are present, it is of questionable validity when trying to assess the importance of this type of network structural feature in commercially used vulcanization systems. However, a sufficient number of results has been published for activated vulcanization systems to suggest that under certain vulcanization conditions, pendent groups can represent an important structural feature of vulcanizates.

Skinner and Watson[4] found, on the basis of sulfur analysis figures, that substantial numbers of pendent groups are formed when NR is vulcanized with sulfur in the presence of zinc oxide, lauric acid, and a large excess of N-cyclohexylbenzothiazole-2-sulfenamide (CBS) as accelerator. Campbell and Wise[5] were able to demonstrate the presence of pendent groups in the vulcanization of NR using 2-mercaptobenzothiazole (MBT) and its derivatives as accelerators in the presence of zinc stearate. They found that accelerator residues bound to the rubber chains by di- or polysulfidic bonds were present in the vulcanizing system before the onset of crosslinking and apparently reach a maximum concentration during the early stages of crosslink formation. This suggests that di- and polysulfidic pendent

1409

groups act as intermediates in crosslink formation.   Moore and Watson[6] obtained convincing evidence for the presence of such network-bound intermediates in the vulcanization of synthetic *cis*-polyisoprene with TMTD and zinc oxide, and Bateman et al.[7] have presented a general mechanistic scheme for the accelerated vulcanization of NR in which di- and polysulfidic pendent groups are key intermediates between the sulfurating complexes formed from the accelerator, sulfur, zinc oxide, and activators and the initially formed polysulfidic crosslinks.

The purpose of the work reported here was to obtain quantitative information on the importance of pendent groups in relation to the numbers of chemical crosslinks in accelerated sulfur vulcanizates prepared with a sulfenamide accelerator (CBS) in the presence of zinc oxide and fatty acid, and to obtain some indication of the proportions of these groups which are attached to the rubber chains by monosulfide and by di- and polysulfide bonds.   Radiochemical techniques were employed, using CBS labelled with C^{14} in the aromatic ring.   Vulcanizates were prepared from mixes having three different proportions of CBS and sulfur, corresponding to conventional, semiefficient, and efficient vulcanizing conditions.

EXPERIMENTAL

Preparation of C^{14}-Labelled CBS

Freshly distilled aniline (0.93 g) was dissolved in a mixture of saturated brine (5 ml) and $2N$ sulfuric acid (9 ml) and the solution was added to a continuous-flow liquid–liquid extraction apparatus. C^{14}-Aniline hydrogen sulfate (0.5 mC, ca. 3 mg) was washed into the apparatus with $2N$ sulfuric acid (2 × 0.5 ml) and saturated brine (3 × 1 ml).   The solution was made alkaline with $4N$ sodium hydroxide (10 ml) and extracted continuously with ether for 5 hr.   Removal of ether from the dried extract gave free radioactive aniline (0.89 g).   Use of less rigorous procedures for dilution and extraction of C^{14}-aniline gave poorer recoveries. The aniline was heated in vacuo with carbon disulfide (0.73 g), elemental sulfur (0.31 g), and a trace of water (approx. 0.02 g) in a sealed tube at 220°C for 28 hr.[8] Satisfactory yields of MBT could not be obtained in the absence of water. The crude reaction product was extracted with 2% sodium hydroxide solution (5 × 5 ml) and the filtered extract was acidified to pH 4 with 10% sulfuric acid.   The precipitated MBT was collected, washed with water, and dried in vacuo (1.28 g, 80.5%).   The MBT was dissolved in water (32 ml) containing sodium hydroxide (0.62 g) and freshly distilled cyclohexylamine (2.26 g).   This solution was stirred vigorously at room temperature and a solution of iodine (1.98 g) and potassium iodide (2.13 g) in water (25.5 ml) was added over a period of 2 hr.   The mixture was stirred for a further hour and the precipitated CBS was collected, washed thoroughly with water, and dried in vacuo (1.77 g, 87%).   The total activity of the product was 0.294 mC (6154 d/s/mg), representing an overall radiochemical yield of

59%. The radiochemical purity as determined by isotope dilution analysis was 98%.

For use in vulcanization, the radioactive CBS was diluted to 5.39 g with pure, unlabelled CBS to give CBS of activity 2115 d/s/mg. This was sufficient to allow accurate detection of less than 5% of the added accelerator in vulcanizates having the lowest accelerator level.

Preparation of Benzothiazolyl Mono-, Di-, and Tetrasulfides

Cyclohex-2-enyl-2-benzothiazolyl monosulfide[9] and 1,3-dimethylbut-2-enyl-2-benzothiazolyl disulfide[10] were prepared by published procedures. Attempts to prepare bis-2-benzothiazolyl tetrasulfide by the method of Levi[11] using sulfur monochloride and the zinc salt of MBT (commercial sample) gave inseparable mixtures containing large amounts of bis-2-benzothiazolyl disulfide. The tetrasulfide was obtained by reaction of the anhydrous sodium salt of MBT[12] (2.6 g) with sulfur monochloride (1.3 ml) in sodium-dried ether at room temperature for 5 hr. The product was recrystallized from benzene/petroleum ether; mp 109°–10°, lit. 108°–10°. Access of moisture while the product was still contaminated with sulfur monochloride caused disproportionation. The purified material gave a theoretical yield of MBT on reduction with sodium borohydride and estimation of the liberated MBT by means of its ultraviolet absorption peak at 326 mμ.[2]

Preparation and Analysis of Vulcanization

Vulcanizates were prepared as 1-mm-thick sheets at 140°C by a slight variation of normal mixing procedures. Radioactive CBS and NR (RSS1, yellow circle; 10 g) were dissolved in benzene (200 ml) and the solution was freeze dried to constant weight. This mixture was blended with more rubber (10 g) containing zinc oxide (Gold Seal), lauric acid, and sulfur (sieved, 80 mesh). Details of the mix compositions for the vulcanization systems studied are given in Table I.

Chemical crosslink densities were obtained via stress–strain measurements on dry vulcanizate samples by previously described procedures[13,14] and analysis of the distribution of crosslink types was carried out using propane-2-thiol and n-hexanethiol chemical probe reagents.[13,15]

TABLE I
Mix Compositions for Vulcanization Systems Studied[a]

	A	B	C
Zinc oxide	5.0	5.0	5.0
Lauric acid	0.7	1.0	1.0
Sulfur	2.5	1.5	0.4
C[14]-CBS	0.6	2.37	6.0

[a] Parts per 100 parts RSS1 Yellow Circle.

Nonbound accelerator residues (including the zinc salt of MBT) were extracted from the vulcanizates by immersion for 24 hr in a solution of acetic acid (5%) in acetone/chloroform/methanol azeotrope at room temperature, followed by continuous extraction with hot azeotrope (approx. 50°C) for 48 hr under nitrogen. The complete extraction cycle was repeated three or four times, to constant radioactivity of the vulcanizates.

Vulcanizate activities were determined by combustion analysis on 40–50-mg samples using the Schoniger oxygen flask technique.[16] The carbon dioxide was absorbed by direct addition of a mixture of 1:8 ethanolamine/-methoxyethanol (10 ml) and toluene phosphor solution (10 ml; 12 g butyl PBD/ℓ.) to the cooled combustion flask after combustion. An aliquot (15 ml) of this solution was counted directly in a liquid scintillation counter (Tracerlab SC/532). The carbon dioxide absorbent caused substantial quenching, resulting in counting efficiencies of 35%–40% (determined using Cs^{137} external standard). Recovery of carbon dioxide from the combustion of C^{14}-hexadecane standard (10 mg) on filter paper (100 mg) by this procedure was 98%–99%.

RESULTS

Details are given in Table II of the observed total level of accelerator or accelerator fragments (benzothiazole groups) in the vulcanizates prior to extraction or chemical treatment, together with the levels calculated from the weights of C^{14}-CBS used in their preparation and the total weights of the mixes. Agreement is within the experimental variation for vulcanization system C, but is less satisfactory for systems A and B, where loss of accelerator before, but not during, vulcanization occurs. At least part of this loss was shown to occur during freeze drying of the benzene solution of rubber and accelerator. Because of these losses, the mix compositions in Table I

TABLE II
Total Accelerator Fragments in Unextracted Vulcanizates

	Moles of accelerator fragment/g RH, $\times 10^5$		
	A	B	C
Cure time, min			
20	2.01	8.36	24.7
30	2.04	8.56	25.8
40	2.02	—	24.9
45	—	8.52	—
60	2.05	—	26.2
75	—	9.07	—
120	2.07	8.52	24.8
240	—	8.19	—
360	2.01	—	25.7
Average value	2.03	8.54	24.9
Mix	2.05	8.78	—
Calculated value	2.50	9.98	24.8

must be regarded as nominal, the actual level of accelerator in series A (the worst case) being 17% below the stated level.

The reliable estimation of the total numbers of pendent groups was critically dependent upon the efficient extraction of all nonbound accelerator by-products from the network under conditions which, ideally, did not result in any cleavage of the pendent groups. The simple zinc salt of MBT is reported to be soluble in benzene[17] but disproportionates fairly readily to a basic salt in the presence of moisture. This basic salt is essentially insoluble in common organic solvents and would not be extracted from vulcanizates by normal extraction procedures (e.g., with acetone or acetone/chloroform/methanol azeotrope). Campbell and Wise[5] have reported the use of a dilute solution of acetic acid in benzene for extraction of zinc salts of MBT and a similar procedure was adopted in the present work. It was found that commercially available zinc salt of MBT (basic salt) was appreciably more soluble in a solution of acetic acid (5%) in acetone/-chloroform/methanol azeotrope than in the azeotrope alone. Vulcanizates were therefore immersed in the acetic acid solution for 24 hr and then extracted with hot azeotrope for 48 hr under nitrogen. It was necessary to repeat the entire extraction sequence three or four times to obtain constant levels of activity in the extracted vulcanizates, but in most cases at least 90% of the extraction occurred in the first cycle. This procedure was preferred to an alternative one of extracting the vulcanizates with amine, since labile polysulfidic features in the network were less likely to be attacked under mild acid conditions than in the presence of base.

The stability of disulfidic pendent groups of the type I ($x = 2$) toward the acetic acid/azeotrope solution was confirmed by recovery of I (R = 1,3-dimethylbut-2-enyl, $x = 2$) essentially unchanged, on the basis of TLC analysis, after five days at room temperature in the solvent mixture.

I
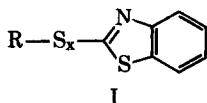
In contrast, 2,2'-tetrathiobis(benzothiazole) liberated free MBT slowly on standing at room temperature in a solution of acetic acid (5%) in 1:1 methanol/chloroform. MBT equivalent to approximately 10% of the initial tetrasulfide was identified by ultraviolet absorption measurement after 15 hr. This suggests that pendent groups attached to the rubber chains by three or more sulfur atoms (I, $x \geqslant 3$) would undergo some degradation during acetic acid/azeotrope extraction of vulcanizates. Results quoted for total pendent group levels in this paper therefore include all mono- and disulfidic pendent groups (I, $x = 1$ or 2) but may not include the true number of groups having three or more sulfur atoms between the benzothiazole residue and the hydrocarbon chain.

Watson[10] reported that the disulfide I (R = 1,3-dimethylbut-2-enyl, $x = 2$) reacted with propane-2-thiol ($0.4M$) and piperidine ($0.4M$) in heptane at room temperature to give the piperidinium salt of MBT, 1,3-dimethylbut-
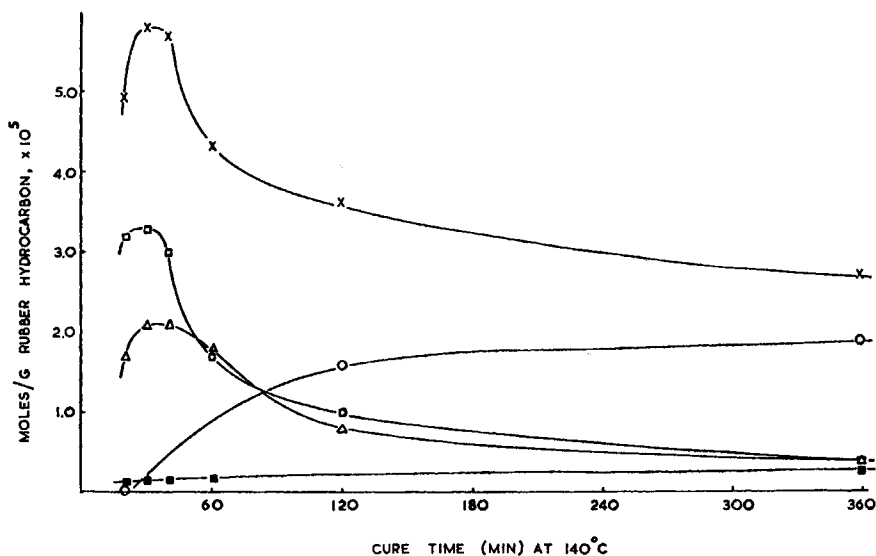
Fig. 1. Distribution of crosslink types and pendent accelerator groups as a function of cure time at 140°C for the vulcanization system RSS1 (100), S (2.5), CBS (0.6), ZnO (5.0), lauric acid (0.7): (x) total crosslinks; (O) monosulfide crosslinks: (△) disulfide crosslinks; (□) polysulfide crosslinks; (■) total pendent groups.

2-enyl isopropyl disulfide and a small amount of diisopropyl disulfide.   This reaction has now been shown to be quantitative within 5 min at room temperature, whereas the monosulfidic pendent group model (I, R = cyclohex-2-enyl, $x = 1$) was recovered unchanged after 15 hr under the same conditions.   Thus, treatment of vulcanizates with propane-2-thiol ($0.4M$) and piperidine ($0.4M$) under the conditions for quantitative cleavage of polysulfide crosslinks[13,15] would also result in complete removal of all disulfidic (and polysulfidic) pendent groups (I, $x \geqslant 2$) and the activities of the vulcanizates after such treatment and subsequent acetic acid/azeotrope extraction represent the levels of monosulfidic pendent groups (I, $x = 1$).

The results of analysis of the total number of pendent groups and of the number of monosulfidic pendent groups for the three vulcanization systems (A, B, and C, Table I) are shown in Figures 1, 2, and 3.   The figures also show the total crosslink levels and the levels of mono-, di-, and polysulfide crosslinks as a function of cure time.   The crosslink distributions are in reasonably good agreement with results previously reported for these vulcanization systems,[13] the differences in detail arising most probably from small differences in cure behavior between nominally identical mixes of rubber and vulcanization ingredients.   Such differences have previously been encountered[13] for the vulcanization system B in Table I.

For vulcanization system A (Fig. 1), the total level of pendent groups was very low compared with the total number of crosslinks at all cure times. At optimum crosslinking, the total number of pendent groups was 3% of the total number of crosslinks.   This percentage rose to 9 at very long cure
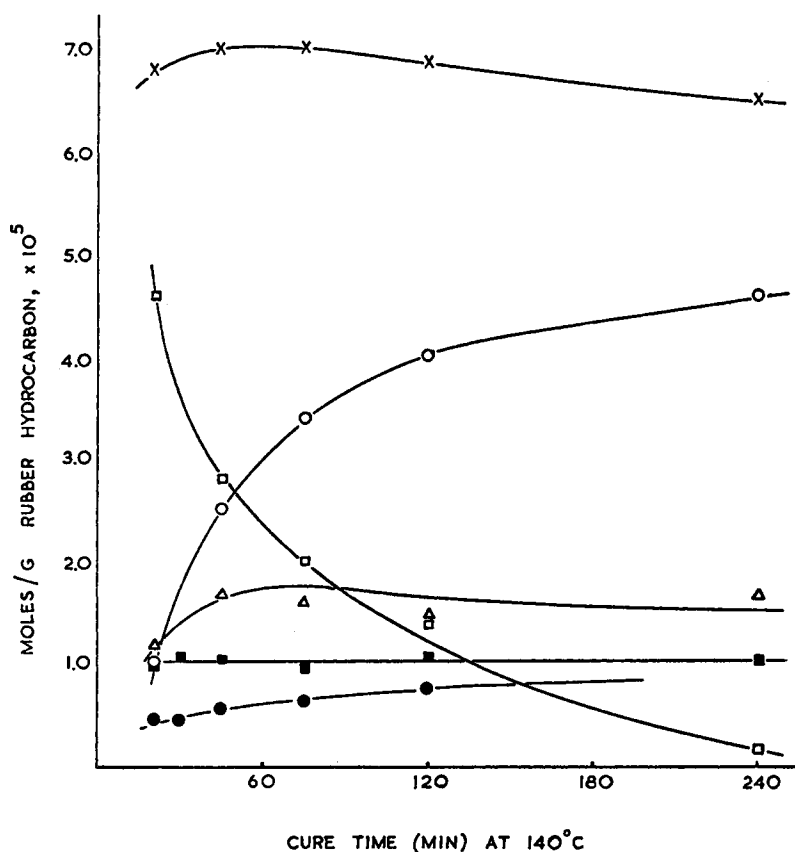
Fig. 2. Distribution of crosslink types and pendent accelerator groups as a function of cure time at 140°C for the vulcanization system RSS1 (100), S (1.5), CBS (2.37), ZnO (5.0), lauric acid (1.0): (x) total crosslinks; (O) monosulfide crosslinks; (△) disulfide crosslinks; (□) polysulfide crosslinks; (■) total pendent groups; (●) monosulfide pendent groups.

times, owing partly to a slight increase in the absolute amount of pendent groups but mainly to a considerable loss of crosslinks on overcure. At long cure times, the total amount of pendent groups was 12% of the amount of accelerator initially present in the mix. The radioactivities of these vulcanizates after propane-2-thiol treatment and extraction with acetic acid in azeotrope were slightly lower than for the extracted vulcanizates before treatment with thiol, but the differences were negligible on the crosslink density scale of Figure 1. The pendent groups in this system were therefore almost entirely monosulfidic at all cure times.

The total level of pendent groups in vulcanization system B remained essentially constant at 11% of the accelerator initially present in the mix throughout the cure range studied. At optimum cure, the level was 14% of the total number of crosslinks. At a cure time of 20 min, approximately
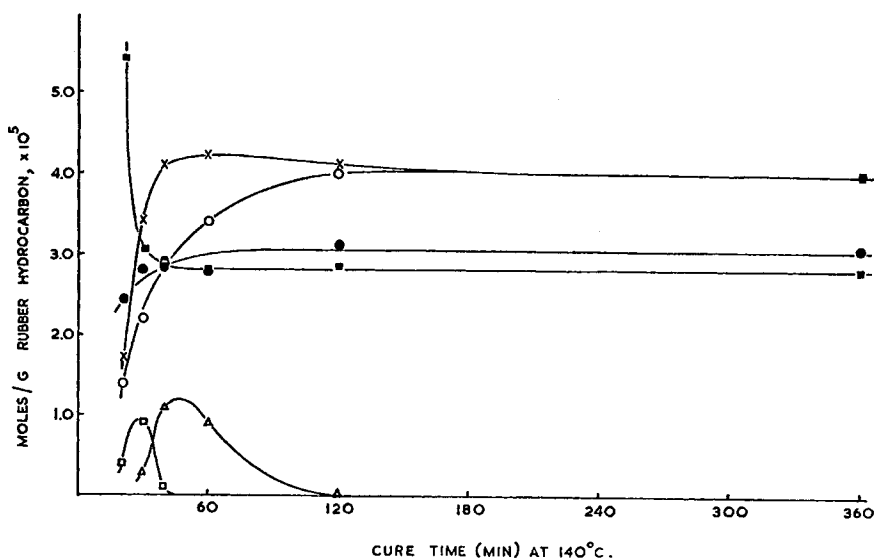
Fig. 3. Distribution of crosslink types and pendent accelerator groups as a function of cure time at 140°C for the vulcanization system RSS1 (100), S (0.4), CBS (6.0), ZnO (5.0), lauric acid (1.0): (x) total crosslinks; (O) monosulfide crosslinks; (△) disulfide crosslinks; (□) polysulfide crosslinks; (■) total pendent groups; (●) monosulfide pendent groups.

half of the pendent groups were poly- or disulfidic, whereas at long cure times they were almost entirely monosulfidic.

For vulcanization system C, the total pendent group level was three times higher than the total crosslink level at a cure time of 20 min. As vulcanization progressed, the number of pendent groups decreased very rapidly and the number of crosslinks simultaneously increased until the total pendent group level was 67% of the total crosslink level at a cure time of 60 min. Thereafter, the levels did not change significantly. The amount of accelerator bound in the network at a cure time of 60 min was 11% of the accelerator initially present in the mix. At a cure time of 20 min, more than half of the pendent groups were di- or polysulfidic and as vulcanization progressed these disappeared, leaving only monosulfidic groups at cure times greater than 40 min. There is a small discrepancy in the experimental results for monosulfidic pendent groups. These are slightly higher than the results for total pendent groups at the longer cure times.

DISCUSSION

For the conventional vulcanization system (system A), the pendent groups are unlikely to make a significant contribution to the physical properties of the vulcanizate unless they exert an influence considerably out of proportion to their concentration relative to the concentration of

crosslinks. Their significance decreases even further when considered in relation to the fact that at least six sulfur atoms are combined in the network as noncrosslinking modifications of the polymer chain for each crosslink present at optimum cure.[18]   As the efficiency of the crosslinking system is increased, by increasing the ratio of accelerator to sulfur in the mix, the numerical importance of pendent groups increases until they become a major structural feature of the vulcanizates.   Consideration of the level of pendent groups in the 60-min cure of vulcanization system C in conjunction with Moore's E' value of 3.6 for the same vulcanization system at this cure time[19] shows that cyclic sulfides and pendent groups make approximately equal contributions to the network structure.   Both are present in concentrations equivalent to 65%–70% of the chemical crosslinks.   Skinner and Watson[4] reached a similar conclusion for this vulcanization system on the basis of sulfur analysis figures.

The dipole moment of methyl-2-benzothiazolyl monosulfide (I, R = Me, $x = 1$) is $1.42D$[20] and the dipole moment of monosulfidic pendent groups would be expected to be close to this value.   This dipole is not large, but in the nonpolar hydrocarbon environment of a rubber vulcanizate it could be sufficient to provide a certain amount of secondary interaction between the polymer chains.   An alternative mode of contribution of the pendent groups to chain interactions could be via coordination with zinc compounds in the vulcanizate (cf. formation of complexes between zinc chloride and CBS, etc.[21]).   Both the dipolar and the coordination types of interaction would be weaker than covalent crosslinking.   They would probably be labile under stress or at elevated temperatures and could give rise to energy dissipation or heat buildup effects under dynamic stress conditions.   Some evidence for adverse effects of pendent groups on the physical properties of vulcanizates can be derived from a reconsideration of results of Bristow and Tiller[22] for resilience and fatigue resistance of a series of NR vulcanizates prepared under a variety of conditions designed to produce networks having different structures.   The results show that fatigue life is independent of crosslink length, but decreases progressively as the number of pendent groups increases through the series of vulcanizates represented by the following mix compositions (all containing zinc oxide, stearic acid, and antioxidant): CBS (0.54), S (2.7); CBS (0.5), S (2.5) overcured; CBS (6.3), S (0.44); and TMTD (4.0), S (0.0).

The results for resilience (on a different series of vulcanizates, but including some of those listed above) are adequately interpreted by the original proposal of Bristow and Tiller that shortening the length of the crosslink leads to poorer resilience, but they are also entirely consistent with an interpretation in which pendent groups exercise a predominant influence on the resilience.   This ambiguity cannot be resolved from the evidence at present available.

The sulfidic structure of the pendent groups at early cure times undergoes a pronounced change as the ratio of accelerator to sulfur in the mix is increased.   In the conventional vulcanization system (system A), no

evidence could be obtained for di- or polysulfidic pendent groups even at the earliest cure time, although the sensitivity of the measurements was adequate for their detection.   In contrast to this, there is clear evidence for a rapid accumulation of di- and polysulfidic pendent groups prior to or at the onset of crosslinking in the efficient system (system C).   System B shows intermediate behavior, where there is no indication of an early peak in the total pendent group level but considerable proportions of di- and polysulfidic pendent groups are present at early cure times.

If it is accepted that di- and polysulfidic pendent groups represent precursors to crosslinks,[7,19] the pendent group insertion reaction or some step prior to it must represent the overall rate-determining step in the vulcanization process under the conditions for system A.   Milligan[23] has suggested that the rate-determining step in the vulcanization of purified cis-polyisoprene with amine and zinc carboxylate complexes of the zinc salt of MBT is the reaction of the complex with elemental sulfur.   The ratio of accelerator to sulfur in this work was comparable to that of vulcanization system B.   However, the rapid accumulation of di- and polysulfide pendent groups prior to crosslink formation under efficient vulcanization conditions (system C) shows that conversion of pendent groups to cross links represents the rate-determining step under these conditions.   Two factors may be responsible for this difference from systems with lower accelerator-to-sulfur ratios.   In the first place, the rate of formation of the intermediate pendent groups can be expected to be faster on the basis of a mass action effect.   Secondly, it is probable that the average number of sulfur atoms in the initially formed pendent groups is lower than under conventional vulcanization conditions because increased competition of accelerator fragments for available free sulfur would lead to formation of sulfurating species containing fewer sulfur atoms.   The shorter poly-sulfidic pendent groups would be expected to be less reactive and lead to a lower rate of conversion of pendent groups to crosslinks.   This latter effect cannot be a predominant one since the overall rate of crosslink formation is known to increase with increasing ratio of accelerator to sulfur.[24]

The mode of formation of monosulfidic pendent groups is of some interest. At long cure times, when pendent accelerator groups are entirely mono-sulfidic in all three vulcanization systems, the pendent group level is a constant proportion ($11 \pm 1\%$) of the amount of accelerator initially present in the system.   This situation could arise if an independent addi-tion reaction leading directly to monosulfidic pendent groups was occurring in competition with the steps intermediate to crosslink formation.   Dogad-kin et al.[25] have shown that direct addition of MBT to rubber chains occurs during mastication at 120°C, and this most probably leads to monosul-fidic pendent groups (or terminal groups).   However, a similar observa-tion has not been reported for sulfenamide accelerators, and the method of preparation of vulcanizates in the present work (mixing of accelerator and rubber in solution and blending of this rubber, after drying, with a master batch of the other ingredients) represents much milder conditions than

those studied by Dogadkin and co-workers. Furthermore, the mono-sulfidic pendent groups in the present work cannot arise directly from the original accelerator since their formation continues after the onset of crosslinking, and Campbell and Wise[2,5] have shown that sulfenamide accelerator as such is completely consumed before the onset of crosslinking. The alternative explanation for formation of monosulfidic pendent groups is that di- and polysulfidic pendent groups undergo desulfuration in the same way as di- and polysulfidic crosslinks[23] as a competing reaction to crosslink formation. If this is the case, there is no obvious reason for the observed constancy of the proportion of accelerator finally present as monosulfidic pendent groups.

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