Sulfur Vulcanization of Polyisoprene Accelerated by Benzothiazole Derivatives. I. Comparison of Sulfur and 2-Mercaptobenzothiazole Accelerated Reactions

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SYNOPSIS

Polyisoprene compounds with sulfur and with sulfur and 2-mercaptobenzothiazole (MBT) were vulcanized by heating in a differential scanning calorimeter (DSC) at a programmed rate. The reaction was stopped at various temperatures along the thermogram and the product analyzed by determining the crosslink density and crosslink type, and by determining the amount of extractable curatives and soluble reaction products by high-performance liquid chromatography. DSC cure curves and plots of crosslink density and extractable sulfur vs. temperature for the unaccelerated and MBT accelerated compounds can be made to coincide by shifting them along the temperature axis. It is suggested that MBT accelerated sulfur vulcanization occurs by the same mechanism as unaccelerated sulfur vulcanization, with SH$^+$ ions from MBT adding across the carbon–carbon double bond, thus increasing the rate at which the reaction is initiated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Various reviews[1,2] suggest that in unaccelerated sulfur vulcanization crosslink formation occurs via a cationic reaction mechanism. In a limited study of the polyisoprene (IR)/sulfur system, Kruger and McGill[3] heated compounds at a programmed rate in a differential scanning calorimeter (DSC) and measured the crosslink density at the vulcanization exotherm maximum, at which point all of the sulfur had been consumed. Other studies involving the use of DSC were by Brazier and Nickel[4] and Brazier[5] who reported mainly on enthalpy changes that occur on vulcanizing natural rubber with sulfur.

In many instances of accelerated sulfur vulcanization the accelerator and sulfur interact to form a polysulfidic accelerator complex that then reacts with the polymer chain to form accelerator terminated polysulfidic pendent groups.[6-8] Crosslinking results from the reaction of these groups with rubber molecules[7] or with pendent groups.[8] 2-Mercaptobenzothiazole (MBT), a well-known accelerator for

the sulfur vulcanization of rubber, does not on its own lead to crosslinking,[9] even after 2 h at 140°C.

A reaction between MBT and sulfur has been proposed by many authors.[10-14] Gordon[15] assumed that the MBT was activated by sulfur according to the following reaction where Bt represents the benzothiazole group:

$$BtSH + S_8 \rightarrow BtSS_xH$$
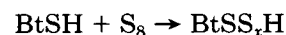
Dogadkin[11] claimed to have isolated 2-hydropersulfide benzothiazole (BtSS$_x$H) from a melt of sulfur and MBT after heating in a tube to 140°C as well as from natural rubber vulcanized in a press. Their identification was based on a characteristic absorption maximum for polysulfides in the region of 330 μm. It should be noted that Huke and Kendall[16] and Campbell and Wise[10] show MBT to have an absorption maximum at 326 μm.

Dogadkin et al.[13] proposed that because the reaction of MBT with the rubber proceeds with appreciable velocity only in the presence of sulfur, the following reaction was likely to occur:

$$BtSH + S_8 \leftrightarrow BtS + HS_8 \leftrightarrow BtSS_xH + S_{8-x}$$
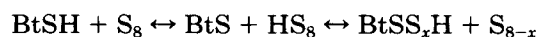
The $HS_n^{\cdot}$ radical then unites with rubber forming a polymeric mercaptan as the first step in the cross-linking process. Taneja and Banerjee[17] also suggested that sulfur disappears by a free radical mechanism similar to the chain mechanism proposed by Farmer and Shipley[18] for unaccelerated sulfur vulcanization. The free radicals would derive from a sulfur–accelerator complex.

Campbell and Wise[10] vulcanized natural rubber with 1.07% MBT and 2.47% sulfur. They found a significant drop in the MBT concentration accompanied by an increase in RS_xSBt (the natural rubber–polythiobenzothiazole intermediate) or the $BtSS_xSBt$ derivatives. The formation of these derivatives did not account for all the MBT, 27% of which could not be defined. All the MBT was recovered at the completion of reaction.[10]

On heating MBT with ^{35}S in a sealed ampule at 140°C for 6 h, sulfur exchange occurs. However, the active sulfur atom now present in MBT does not interchange with sulfur during the vulcanization process.[13,19]

This article looks at the interaction of MBT with sulfur and compares the results of a DSC study of unaccelerated sulfur vulcanization of IR with the MBT accelerated process.

EXPERIMENTAL

Materials: IR, Karbochem (South Africa); MBT, Monsanto (Belgium); sulfur (99.5% purity), AECI (South Africa).

The single components were ground fine, weighed on the microbalance, and sealed in aluminum DSC pans. When studying combinations of curatives, master batches were prepared by weighing out components to give mixtures of 1 : 1 mole ratios. These were then ground with a pestle and mortar to obtain an intimate contact between the curatives before weighing and sealing in aluminum DSC pans.

Compounds were mixed in a Brabender Plasticoder fitted with a W30 type head of 30-mL capacity using a fill factor of 0.8. The rubber was added to the head and masticated for 6 min at 40 rpm. Curatives were then added while the mixer rotated at 30 rpm. Use of a refrigerated thermostat ensured that the temperature of the head did not exceed 40°C during the mixing process.

The amount of curative in parts per hundred rubber added to the rubber is in the form IR (100)/ MBT (6.2)/S (9.5). The curatives were used in the ratio of 1 mol : 1 mol unless stated otherwise. All of the curatives were added as 33.5×10^{-5} mol/mL rubber.

Studies of curative interaction and the vulcanization process were conducted with a Du Pont 910 DSC and mass loss determinations were conducted on a Du Pont 951 Thermogravimetric Analyzer, as described earlier.[20] The reaction was stopped at points along the DSC thermogram and the system analyzed as described.[20,21] M_i and M_f represent the initial and final sample masses, respectively. Crosslink densities were determined by swelling in benzene[22] and the percentage polysulfidic crosslinks by treatment with propane-2-thiolpiperidine.[23] Extractable curatives and the residue of mixes (without rubber) heated to various temperatures were analyzed by high performance liquid chromatography (HPLC).[20,22] Peak identification has been described.[20] The flowsheet summarizes the vulcanization and analysis procedure.

Encapsulate weighed rubber in DSC pan.
Vulcanize in the DSC to preselected temperature.
Remove from DSC pan and place in benzene (48 h).

If sample swells:
Remove and weigh swollen rubber.
Place in fume cupboard to deswell.

Analysis of extractable curatives.
Evaporate benzene and inject residue in HPLC
    after dissolution in dichloromethane/methanol.

Place rubber under vacuum (48 h).

Remove from vacuum and reweigh.
Calculate crosslink density.
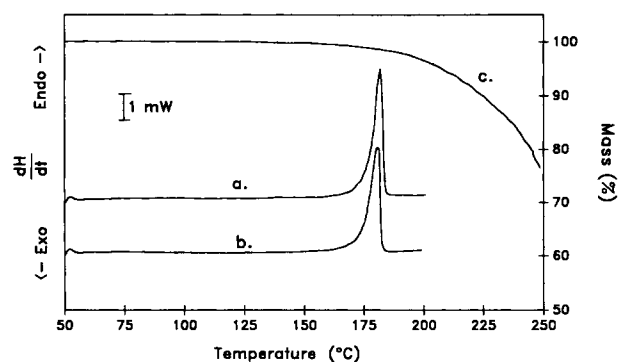**Calculate sulfur atoms/crosslink.**

If sample dissolves:
Evaporate benzene in fume cupboard.

Add acetone to extract curatives (48 h).

Analysis of extractable curatives.
Combine acetone extracts and evaporate.
Inject residue in HPLC after dissolution in
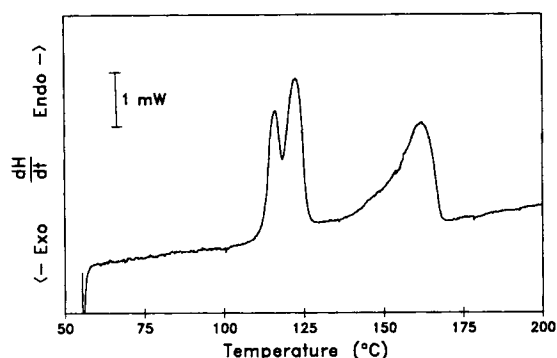   dichloromethane/methanol.

RESULTS

MBT/Sulfur Interaction

The DSC thermogram of MBT (Fig. 1) shows a melting endotherm at 182°C (onset 176°C) when heated to 200°C at 5°C/min. The thermogravimetric (TG) curve (Fig. 1) shows a gradual mass loss on heating with a total mass loss of 23% on heating to 250°C and 87% on further heating to 300°C at 5°C/min. A sample of MBT that was heated to 200°C did not show any change when analyzed with the HPLC; while a MBT sample that was heated to 300°C also showed only MBT remaining. The mass loss may be ascribed to the evaporation of MBT and not to any decomposition reactions of MBT. Luyt et al.[24] also found MBT to be thermally stable when heated to 190°C, but did not record that the sample volatilized fairly readily at these temperatures. Raman spectra[25] of MBT showed no changes on heating at 150°C for periods up to 90 min.

A DSC analysis (Fig. 2) of the MBT/sulfur (1 : 1 mole ratio) combination showed the sulfur solid–solid transition and melting endotherms[22] followed by an endotherm attributed to the dissolution of the MBT in the sulfur. This is consistent with the thermograms reported by Luyt et al.,[24] who noted the dissolution of MBT in sulfur on a hot-stage microscope. The crystallization of MBT from solution was observed on cooling in the DSC.[24] HPLC analysis of the products was carried out on heating MBT/sulfur (1 : 1 mole ratio) to 130, 160, and 170°C in different experiments in the DSC. Even when analyzed by HPLC immediately after heating, no products were found apart from the original MBT and sulfur. There was no evidence for the formation of 2-hydropersulfidebenzothiazole accelerator com-

Figure 2 DSC thermogram: heating rate 5°C/min. MBT/sulfur (1 : 1 mole ratio), M_i = 9.261 mg.

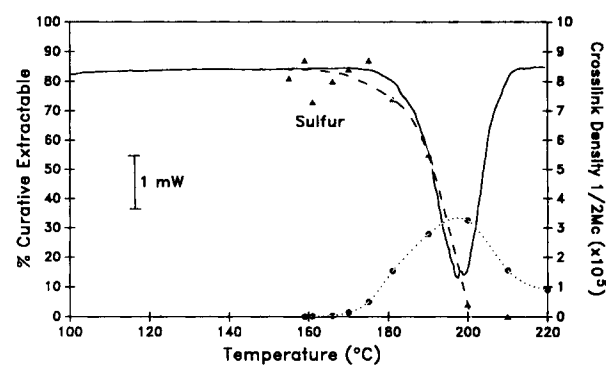plexes ($BtSS_xH$); if such complexes do form they are short lived.

A mass loss of less than 1% occurred on heating to 200°C and this could be due to the evaporation of some of the components. It is noticeable that MBT volatilized more slowly from the sulfur solution than on its own.

IR/Sulfur

The DSC thermogram of an IR/sulfur compound was similar to that reported by Kruger and McGill[3] and shows a single large vulcanization exotherm starting at 171°C and peaking at about 199°C (Fig. 3). To allow comparison of the DSC vulcanization of accelerated systems with the unaccelerated sulfur reaction, the DSC vulcanization process was followed in more detail than was reported earlier.[3]

Crosslinking starts at 160°C, well before the onset of the exotherm, the maximum crosslink density coinciding with the peak, at which point all of the sul-

Figure 1 DSC thermograms: heating rate 5°C/min. (a) MBT, M_i = 7.4103 mg, M_f = 5.994 mg; (b) rescan after cooling to 25°C. TG thermogram: heating rate 5°C/min. (c) MBT, M_i = 12.8570 mg.

Figure 3 Analysis of the IR/sulfur vulcanization system. DSC thermogram, heating rate 2.5°C/min, M = 19.3326 mg. (· · ·) Crosslink density $\frac{1}{2}M_c$ (×10^{5}). (---) % Curative extractable.

fur has been consumed (Fig. 3). After the peak, reversion reactions dominate. Note that 40% of the energy evolution occurs after all of the sulfur has been consumed. The Moore–Trego[26] efficiency (E), defined as the number of sulfur atoms for each crosslink formed, improves until 190°C when it is at 39. At the peak of the DSC exotherm E has a value of 72 S atoms/crosslink (Table I).

IR/MBT/Sulfur

On its own MBT does not lead to vulcanization of IR. MBT was mixed into the rubber and was heated in the DSC at 2.5°C/min. Table II shows that at elevated temperatures a small amount of MBT binds to the polymer. All samples remained soluble in benzene indicating that no crosslinks had formed. This is consistent with a report by Lorenz and Echte[9] who found that no vulcanization of nitrile rubber (NR) occurred with MBT. They recovered 97.8% of the original MBT after heating an NR/MBT compound at 140°C for 2 h. MBT does, however, appear to attach to the chain during mixing, up to 16% of the MBT being unextractable after a mixing time of 18 min. This is consistent with a study by Dogadkin et al.[13]

The DSC scan of an IR (100)/MBT (6.2)/sulfur (9.5) mix shows a very broad exotherm starting at 145–150°C and peaking at 187°C (Fig. 4). Crosslinking can first be detected at 155°C $(1/2M_c = 1.56 \times 10^{-7}$ mol/mL), essentially at the start of the exotherm. Sulfur is consumed as the reaction progresses, with all of the sulfur having reacted at the peak of the DSC exotherm. This coincides with the maximum crosslink density, after which reversion reactions dominate. Initially all crosslinks are polysulfidic, the percentage decreasing progressively as the reaction progresses. Only a small percentage of the MBT is bound to the network, the extractable fraction decreasing from 0.95 to 0.85 during the course of the reaction (Fig. 4). This contrasts with a study by Luyt[14] that reports a sharp decline re-

sulting in the loss of most of the extractable MBT on vulcanization of an identical compound, but is consistent with NMR studies by Krejsa and Koenig[27] and MBT extraction data of others.[19,25] Small amounts (<4 mol %) of MBTs are detected above 140°C.

The vulcanization behavior of the system is very similar to that obtained with sulfur only. Thus, if plots of extractable sulfur and plots of crosslink density vs. vulcanization temperature are shifted by 12°C, they coincide with similar curves for the vulcanization of IR/sulfur compounds (cf. Figs. 3, 4). The maximum crosslink density obtained is somewhat higher in the presence of MBT. While the DSC exotherm is broader, the peak coincides with that for sulfur vulcanization if the 12°C shift is applied.

In compounds containing less MBT the fate of the MBT during reaction is more clearly illustrated than in the above case where the decrease in MBT during vulcanization appears to be limited. When 1.2 phr MBT [IR (100)/MBT (1.2)/sulfur (9.5)] is employed, a rapid decrease in MBT concentration accompanies crosslinking, the rate of decrease exceeding the rate of sulfur consumption (Fig. 5). Little MBT remains once all of the sulfur has been consumed. In a compound with 3.1 phr MBT [IR (100)/MBT (3.1)/sulfur (9.5)], about 60% of the MBT remains when all of the sulfur has been consumed and no further decrease in extractable MBT occurs (Fig. 6).

As in the case of compounds with 6.2 phr MBT [IR (100)/MBT (6.2)/sulfur (9.5)], plots of crosslink density and sulfur consumption vs. temperature can be made to coincide with similar plots for the IR/sulfur system by shifting the curves by 3°C (1.2 phr MBT) and 6°C (3.1 phr MBT), respectively. In all cases the addition of MBT leads to a broadening of the DSC exotherm, the extent of the broadening increasing with increased MBT loading. With 6.2 phr MBT the onset of the exotherm occurs some 20–25°C earlier, although the peak position is shifted by only 12°C, which is equivalent to the amount by

Table I   Moore–Trego Efficiency for Different Curative Systems

Temp. (°C)	IR/Sulfur (100/9.5)	IR/MBT/Sulfur (100/6.2/9.5)	IR/MBT/Sulfur (100/3.1/9.5)	IR/MBT/Sulfur (100/1.2/9.5)
170	276	53	175	251
175	64			
181	42	44	47	56
190	39	54	67	53
200	72	86	87	91

Table II   Percentage MBT Extractable from IR/(100)/MBT/(6.2) Compound

Temp. (°C)	MBT (%)
170	88
183	87
200	85
215	83

Compound heated at 2.5°C/min to different temperatures.

which the various graphs must be shifted to make them coincident with those for the IR/sulfur system. With 3.1 phr MBT, the onset temperature is shifted by 15°C and the peak position by 6°C; and with 1.2 phr MBT, the onset is shifted by 8°C and the peak by 3°C.
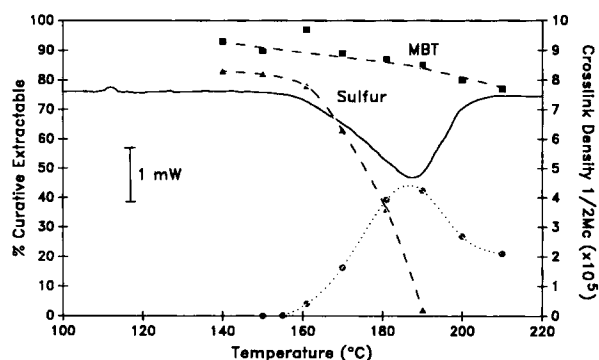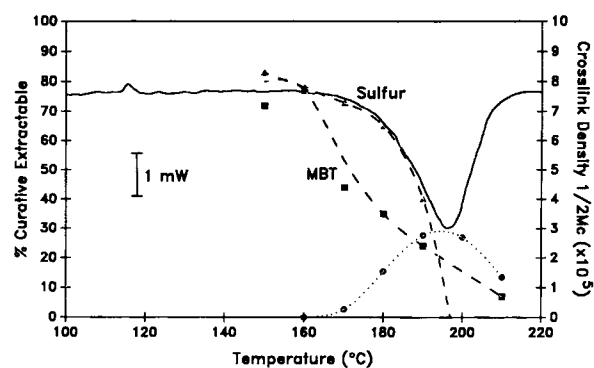
DISCUSSION

MBT/Sulfur Interaction

The formation of MBT polysulfides is commonly invoked as the first step in MBT accelerated sulfur vulcanization.[10–14,17] However, no evidence for the formation of BtS_xH, resulting from a reaction between MBT and sulfur, could be obtained; and it must be concluded that, should such a species form, it has limited stability. The accelerating effect of MBT must be explained by a mechanism not involving MBT polysulfides.

IR/MBT/Sulfur

The addition of MBT to an IR/sulfur compound leads to the earlier initiation of crosslinking: the
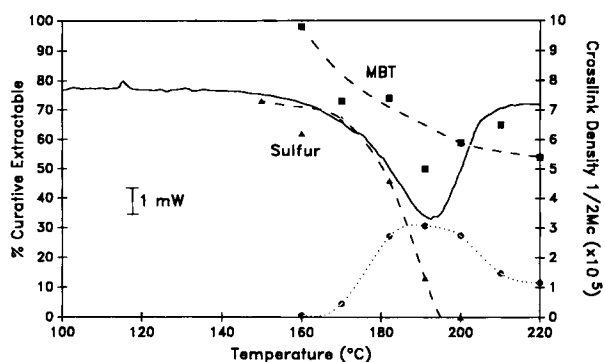

Figure 5   Analysis of the IR/(1.2) MBT/sulfur vulcanization system. DSC thermogram heating rate 2.5°C/min, M_i = 18.9457 mg, M_f = 18.9453 mg. (· · ·) Crosslink density $\frac{1}{2}M_c$ (×10⁵). (---) % curative extractable.

larger the MBT loading, the more readily is crosslinking initiated (Figs. 4–6). A low MBT loading does not noticeably affect the curve of crosslink density vs. temperature. The coincidence of the various plots for the sulfur and MBT/sulfur systems, when shifted along the temperature axis, suggests that the crosslinking mechanism is the same as applies to unaccelerated sulfur vulcanization, the difference lying in the availability of the species that initiate the autocatalytic chain reaction applicable to unaccelerated sulfur vulcanization.[1,2] The Moore–Trego efficiency of sulfur utilization also is not greatly affected by the addition of MBT (Table I).

Although thiols such as MBT readily ionize in the presence of bases,[28,29]

$$BtSH + OH^- \rightleftharpoons BtS^- + H_2O,$$
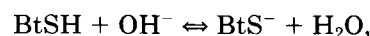
the sulfenyl or persulfenyl anions (resulting from interaction with S_8) cannot play an important role

Figure 4   Analysis of the IR/(6.2) MBT/sulfur vulcanization system. DSC thermogram heating rate 2.5°C/min, M_i = 21.3316 mg, M_f = 21.2889 mg. (· · ·) Crosslink density $\frac{1}{2}M_c$ (×10⁵). (---) % curative extractable.


Figure 6   Analysis of the IR/(3.1) MBT/sulfur vulcanization system. DSC thermogram heating rate 2.5°C/min, M_i = 20.7207 mg, M_f = 20.7148 mg. (· · ·) Crosslink density $\frac{1}{2}M_c$ (×10⁵). (---) % curative extractable.

in vulcanization as they are unlikely to react with carbon–carbon double bonds. The carbon–sulfur bond in thiols is generally weaker than the sulfur-hydrogen bond; that is in CH_3SH and C_2H_5SH the S—H bond strengths are 89 and 87 kJ/mol, respectively, and the C—S bond strengths are 67 and 63.5 kJ/mol, respectively.[2,30,31] Mayer[30] notes that, compared to the saturated carbon atom, the sulfur atom has a low electronegativity and a considerable tendency to become polarized or ionized and the formation of a sulfur cation is conceivable in principle, viz.,

$$R_3CSH \rightarrow R_3C^- + SH^+$$
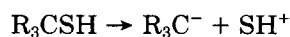
or in the case of MBT

$$BtSH \rightarrow Bt^- + SH^+$$
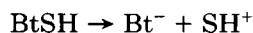
It is suggested that the SH^+ cation either interacts with the double bond in the rubber chain, setting up an autoaccelerating chain reaction similar to that found in unaccelerated sulfur vulcanization, or does so after interaction with elemental sulfur.
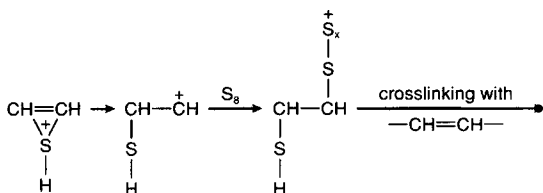
Thus MBT acts as an initiator for crosslinking but does not otherwise alter the course of the reaction. Increased MBT loadings increases the availability of SH^+ ions and leads to the earlier onset of vulcanization (Figs. 4–6).

As MBT is not consumed in the absence of sulfur, addition of the MBT anion (Bt^-) to the cyclic carbon cation in the above equation appears unlikely. (The tertiary hydrogen resulting from such addition would ensure instability of the product and would encourage the reverse reaction.) When an IR/MBT compound is heated to 200°C only 15% of the MBT is rendered unextractable, indicating that MBT addition across the double bond is very limited. With the sulfur loadings employed, approximately 0.2 mol of MBT is bound to the chain, irrespective of the initial MBT loading (1.0, 0.5, or 0.2 mol MBT/mol sulfur) and no further decrease in the extractable MBT occurred once all of the sulfur had been consumed. Lorenz and Echte[9] also showed that the MBT consumption was independent of the amount of MBT in the compound and that once all of the

sulfur had been utilized, no further consumption of MBT occurred. MBT may be consumed by the addition of the accelerator anion to the persulfuryl cation, thus *inter alia* terminating the reaction. By analogy to the reaction of pendent groups in tetramethylthiuram disulfide accelerated vulcanization,[7,8] such accelerator terminated polysulfidic pendent groups may crosslink, accounting for the presence of a small amount of MBTS found in the compounds once crosslinking has commenced. (This would be a minor crosslinking reaction.) Most of the MBTS formed in such reactions will react further and lead to more crosslinking. Lorenz and Echte[9] found that the amount of MBT bound to the chain increased with increased temperature; this would suggest that the termination reaction assumes increased importance at elevated temperatures. However, at all temperatures, once all of the sulfur has been consumed, no further addition of MBT to the chain occurs. The higher maximum crosslink densities obtained with higher MBT loadings (Figs. 4–6) would be consistent with more chain initiating steps giving a more efficient sulfur usage at the point where all the sulfur has been consumed ($E = 54, 87, 91$, respectively).

CONCLUSIONS

Similarities between the DSC cure curves and plots of crosslink density and extractable sulfur vs. temperature, for unaccelerated and MBT accelerated sulfur vulcanization, point to the accelerated and unaccelerated reactions occurring by a similar mechanism. It is suggested that SH^+ ions, formed from MBT, add across the double bond on the rubber chain, initiating a cationic chain reaction similar to that observed with sulfur alone. The accelerator merely serves as a source of cationic chain initiators, thus ensuring the earlier onset of crosslinking. The proposed mechanism obviates the need to postulate the formation of polysulfides of MBT, the formation of which could not be verified.

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