Benzothiazole-Accelerated Sulfur Vulcanization. I. 2-Mercaptobenzothiazole as Accelerator for 2,3-Dimethyl-2-butene

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ABSTRACT: 2,3-Dimethyl-2-butene (TME) was used as a model compound for polyisoprene in a study of 2-mercaptobenzothiazole (MBT)-accelerated sulfur vulcanization. Mixes that contained curatives only were heated in a DSC to various temperatures, while those that also contained TME were heated isothermally at 150°C in evacuated, sealed glass ampules. Heated mixtures were analyzed for residual curatives, intermediates, and reaction products by HPLC. It is proposed that MBT forms polysulfidic species (BtS_xH) in the presence of sulfur and that these react with TME via a concerted, substitutive reaction pathway to form polysulfidic hydrogen-terminated pendent groups of varying sulfur rank ($TME–S_xH$). MBT is released as a by-product of this reaction. Crosslinking occurs slowly as a result of the interaction of polythiol pendent groups, the rate being dependent on the pendent group concentration. H_2S is released on crosslinking. 2,3-Dimethyl-2-butene–1-thiol was synthesized and reacted in the presence of sulfur to confirm the formation of crosslinked products ($TME–S_x–TME$). Benzothiazole-terminated pendent groups ($TME–S_xBt$) were not observed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1377–1385, 2000

Key words: vulcanization; 2-mercaptobenzothiazole; 2,3-dimethyl-2-butene; model compound

INTRODUCTION

With many accelerators, crosslinking is initiated by accelerator polysulfides, formed by the interaction of sulfur with the accelerator.[1–3] Dogadkin et al.[4–7] proposed that 2-mercaptobenzothiazole (MBT) and sulfur react to produce 2-hydropersulfide benzothiazole (BtS_xH, $x > 1$). Gradwell and McGill[8] found no evidence of BtS_xH formation on HPLC analysis of MBT/sulfur mixes heated to various temperatures and concluded that if such species did form they were short-lived. However,

Gradwell et al.[9] did invoke the transient formation of BtS_xH to explain the influence of MBT on the formation of 2-bisbenzothiazole-2,2′-polysulfides (MBTP) when 2-bisbenzothiazole-2.2′-disulfide (MBTS) was heated with MBT. A number of routes have been proposed to account for crosslinking in MBT-accelerated sulfur vulcanization. Dogadkin et al.[6] proposed the formation of HS_x radicals, resulting from the interaction of MBT with sulfur:

$$BtSH + S_8 \leftrightarrows BtS^\bullet + {}^\bullet S_8H \leftrightarrows BtS_yH + {}^\bullet S_z^\bullet$$
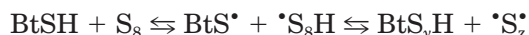
Reaction of the HS_x radicals with the polymer would produce polysulfidic mercaptans, which by reaction with other polymer chains could produce crosslinks. Tsurugi and Nakabayashi[10] suggested

that sulfur formed biradicals which reacted with MBT to produce benzothiazole radicals. The latter would open the sulfur ring, producing more sulfur biradicals. BtS radicals also removed hydrogen from the model compound, and crosslinked products resulted from the combination with sulfurated model compound radicals. Campbell and Wise[11] suggested crosslinking via benzothiazole-terminated pendent groups. Gradwell and McGill[8] proposed that HS^+ cations either interacted with double bonds in the rubber chain, setting up an autoaccelerating chain reaction similar to unaccelerated sulfur vulcanization, or did so after reaction with sulfur.

This article reexamines the MBT-accelerated vulcanization reaction, using 2,3-dimethyl-2-butene (TME) as model compound for polyisoprene. With model compounds, reaction intermediates and species containing accelerator pendent groups should more readily be observed.

EXPERIMENTAL

Materials

MBT (chemical purity 95%, Thiotax, Flexsys, Brussels, Belgium), sulfur (S_8; 98% soluble in CS_2, AECI, Modderfontein, South Africa), and 2,3-dimethyl-2-butene (chemical purity 99.9%, Aldrich Chemical Co., Milwaukee, WI) were used. Reaction between oxygen and unsaturated olefins results in the formation of hydroperoxides.[12] TME is expected to form 3-hydroperoxide-2,3-dimethyl-2-butene.

MBT was purified by recrystallization from hot benzene. The presence of hydroperoxides in TME was determined using a Merck Merchoquant 10011 peroxidase enzyme test kit, with detectable concentrations ranging between 1 and 25 mg/L. TME was introduced onto sticks tipped with peroxidase, exposed to water vapor, and peroxide concentrations determined by a color intensity comparison against a reference card.

It is well known that RSH compounds can be oxidized to their dimeric compounds, RSSR, and the conversion of MBT to MBTS by hydroperoxides has been demonstrated.[13] The addition of TME, containing trace amounts of hydroperoxides, to MBT led to its complete conversion to MBTS within 1 min at 150°C. Removal of peroxides from TME is essential if it is to be used as a model compound for polyisoprene in MBT-accelerated sulfur vulcanization studies.

Table I   Compositions of Mixtures Reacted

Composition	Mass (g)	Mol Ratio
(a) TME/MBT		
TME	0.355	33.9
MBT	0.024	1.1
(b) TME/MBT/sulfur		
TME	0.355	33.9
MBT	0.024	1.1
Sulfur	0.034	1
(c) TME/sulfur		
TME	0.355	33.9
Sulfur	0.037	1.1

TME is immiscible with water, and on shaking with an aqueous solution of ferrous sulfate, hydroperoxides are converted to the corresponding alcohols in a reaction at the interface. Testing of the solution after treatment confirmed the removal of hydroperoxides. The alcohol formed is insoluble in water and remains in the TME phase. MBT vulcanization is not affected by the presence of even large amounts of alcohol. This was established by comparing the MBT vulcanization systems using freshly opened (and purified) TME and the same systems using TME with a high 2,3-dimethyl-3-butene-2-ol content. To minimize oxidation of TME once a bottle had been opened, it was stored under nitrogen at $-10°C$.

Master batches of curatives were prepared by mixing appropriate ratios of the various curatives, using a mortar and pestle. Interaction between curatives in the absence of a model compound was studied by heating in a DSC or TG at 5°C/min, and residual curatives and products were analyzed by HPLC as described.[14–16] For model compound studies, individual samples were prepared by transferring the appropriate mass of the compounded mixture (Table I) and the volume of TME required into glass ampules (8 mL), which were sealed under a vacuum. TME/MBT/sulfur ratios of 33.9:1.1:1 were used. These ratios equate to the ratio of monomer units in polyisoprene (IR) to the accelerator used in numerous studies in these laboratories. Reactions were carried out by fully immersing sealed ampules in an oil bath at $150 \pm 0.5°C$. A mechanical shaker was used to agitate mixes during heating. The ampules were removed from the oil bath at preset times and the reaction quenched by immersion of the ampules in liquid nitrogen. The ampules were allowed to equilibrate to room tem-

perature before being opened. The reaction mixture was dissolved in dichloromethane (25 mL), quantitatively transferred to a 100-mL volumetric flask, and diluted to a volume with methanol. The HPLC procedure and identification and quantitative analysis of curatives and their derivatives have been described.[14,15,17] Curatives have limited solubility in TME and could be separated from TME on cooling of a solution containing curatives, when the latter crystallized out from the solution. This was achieved by placing the glass ampules containing the reaction mixtures in liquid nitrogen for a specific period of time. Freezing of TME (f.pt. $-74.28°C$) was avoided, and at the lower temperature, TME, TME-bound intermediates, and crosslinked products, which remained soluble in TME, were poured off the solid residue. The process was repeated until no more solids formed on cooling. It was impossible to remove sulfur completely and a small amount (<5 mol %) was always present in the liquid containing TME-bound curatives.

HPLC retention times of crosslinked products were assigned by comparison with HPLC and H-NMR spectra of the reaction products published by Versloot et al.[18] for tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization of TME. The crosslinked products produced by MBT and MBTS vulcanization of TME can be expected to be similar to those produced by TMTD. To confirm this, a TME/TMTD/sulfur (33.9:1.1:1) sample was heated at 150°C for 40 min, at which point the reaction products largely comprise monosulfidic and polysulfidic crosslinked products.[18,19] TME/MBTS/sulfur (33.9:1.1:1) and TME/MBT/sulfur (33.9:1.1:1) samples were heated likewise. For each sample, the reaction products were separated by thin-layer chromatography (TLC) and the different bands lifted and injected into the HPLC. Components that produced the same retention times were detected in all three systems and identified by H-NMR as bis(alkenyl) crosslinked products (TME–S_x–TME). These H-NMR spectra matched the published[18] TME/TMTD/sulfur H-NMR crosslinked product spectra. Crosslinked products could not be separated as single compounds (i.e., TME–S–TME, TME–S_2–TME, etc.) but only as similar compounds containing varying amounts of sulfur (i.e., TME–S_x–TME, $x > 0$) and, thus, all were assigned the same response factor, namely, that of a commercially pure crosslinked product, CH_3—S—CH_3; thus, the concentrations of crosslinked products do not indicate absolute val-

ues. Heating TME with only sulfur produced additional types of crosslinked products.[20] A TME/sulfur (33.9:1.1) mixture was heated at 150°C for 2 h and three bands were separated by TLC. H-NMR analysis confirmed these to represent three crosslinked product types, namely, bis(alkenyl), alkenyl alkyl, and bis(alkyl).[20]

Syntheses

2,3-Dimethyl-2-butene–1-thiol (TME–SH)

TME–SH, a starting material used in the synthesis of 2,3-dimethyl-2-butene-1-benzothiazole-disulfide (TME–S_2Bt) and a compound used in determining the MBT vulcanization mechanism, was synthesized from 1-bromo-2,3-dimethyl-2-butene. Thiourea (9.17 g) was added to 150 mL preboiled, cooled, and nitrogen-flushed ethanol in a 500-mL round-bottomed flask. To this, 17.26 g of synthesized 1-bromo-2,3-dimethyl-2-butene[20] was added dropwise and the solution refluxed for 48 h. The system was kept under nitrogen throughout the refluxing. The ethanol was evaporated under reduced pressure at 30°C. Sodium hydroxide (4.8 g) was added to 100 mL boiling water, and after it had cooled to room temperature, it was added to the crystalline residue that remained after the removal of the ethanol. The system was flushed with nitrogen and allowed to reflux for 1 h. After it had cooled to room temperature, the solution was acidified to pH 2 with concentrated hydrochloric acid and shaken for 10 min. TME–SH was extracted with five 10-mL aliquots of dichloromethane. TME–SH was distilled off once the dichloromethane had been removed by reduced pressure at 20°C. Distillation of the residue under a water vacuum between 40 and 80°C yielded TME–SH. Characteristic H-NMR ($CDCl_3$) spectral lines were observed at 1.37 ppm (triplet H), 1.65 ppm (singlet 3H), 1.69 ppm (singlet 3H), 1.71 ppm (singlet 3H), and 3.15 ppm (doublet 2H) in the recorded proton spectrum.

2,3-Dimethyl-2-butene–1-benzothiazole-disulfide (TME–S_2Bt)

TME–S_2Bt was synthesized from TME–SH and MBT by a procedure adapted from that used to synthesize 2,3-dimethyl-2-butene-1-dimethyldithiocarbamate-disulfide.[21] Characteristic H-NMR ($CDCl_3$) lines were observed at 1.69 ppm (singlet 3H), 1.77 ppm (singlet 3H), 1.83 ppm (singlet 3H), 3.74 ppm (singlet 2H), 7.30–7.50 ppm, and 7.80–7.90 ppm (multiplet 4H of benzothiazole frag-

ment) in the recorded proton spectrum. Sulfur analysis: 33.5%, calculated 34.2%.

2,3-Dimethyl-2-butene–1-benzothiazole-polysulfides (TME–S_xBt)

In article 3 in this series, it will be shown that TME–S_xBt pendent groups readily form on heating TME/MBTS/sulfur. To establish if TME–S_xBt formed in the TME/MBT/sulfur reaction, HPLC peaks attributable to such groups were identified by heating TME/MBTS/sulfur (33.9:1.1:1) at 150°C for 12 min. At this point, HPLC analysis showed the reaction products to comprise largely MBT, MBTS, MBTP, and seven other species. Curatives were separated from TME and TME-bound compounds by the freeze technique described. HPLC analysis of the solution gave seven peaks, the second of which coincided with that of synthesized TME–S_2Bt. H-NMR spectra (CDCl$_3$) of the liquid compounds were similar to that of synthetic TME–S_2Bt. All CH$_3$ peaks were coincident with those of TME–S_2Bt. However, several CH$_2$ peaks were evident, each resulting from the range of sulfurated compounds [from the monosulfidic benzothiazole-terminated pendent group (3.72 ppm) to the higher ranked sulfides (3.77 ppm)]. These HPLC peaks were used to identify TME benzothiazole-terminated pendent groups. The monosulfidic benzothiazole-terminated pendent group, which was the only benzothiazole-terminated pendent group detected in the MBT-accelerated sulfur vulcanization of TME, was allocated the response factor of TME–S_2Bt.

The concentrations of the reactants, intermediates, and products are expressed in terms of the initial concentration of the reactant. Crosslinked products are expressed as a mol % of added sulfur.

H$_2$S was detected with the lead acetate test. Filter paper that had been dipped into a saturated lead acetate solution (aqueous) until the surface was damp, but not wet, was held over the neck of the glass ampule to detect if any H$_2$S was released as the ampule was opened.

RESULTS AND DISCUSSION

MBT/Sulfur Interaction

As was reported,[8,22] MBT was found to be thermally stable and, on heating in a DSC at 5°C/min, produced only a melting endotherm, peaking at 178°C. On heating MBT/sulfur (1:1), the sulfur solid–solid transition and melting were followed by the endothermic melting/dissolution of MBT in the molten sulfur at 155°C.

Numerous authors[4–7] have suggested the interaction of MBT with sulfur to give active MBT polysulfides (BtS$_x$H). Gradwell and McGill[8] found no evidence for BtS$_x$H formation on HPLC analysis of MBT/sulfur mixes heated to 130, 160, and 170°C and concluded that if such species did form they were short-lived. Holding MBT/sulfur isothermally at 155°C for 20 min resulted in a slight decrease in the MBT concentration (4 mol %) and a greater decrease in the sulfur concentration (10 mol %). Minute amounts of MBTM, MBTS, and 2-bisbenzothiazole-2,2′-trisulfide (BtS$_3$Bt) as well as H$_2$S was formed, possibly by limited oxidation. (Fig. 1). However, there was no indication that BtS$_x$H was formed; HPLC analysis showed no additional peaks, even under gradient elution conditions. Failure to detect BtS$_x$H does not disprove their transient existence. It is also possible that dissolution for HPLC analysis may assist the decomposition of any BtS$_x$H formed. MBT reduces the induction period for the formation of MBTP from MBTS and this has been attributed to the interaction of MBT with MBTS to produce MBTM and BtSSH.[9]

TME/MBT (33.9:1.1)

In the absence of sulfur, MBT does not vulcanize polyisoprene (IR)[8] or natural rubber.[21] No crosslinking was observed on heating TME/MBT at 150°C, although trace amounts of monosulfidic benzothiazole-terminated pendent groups formed slowly (3 mol % after 40 min). The formation of such pendent groups has been proposed[6] in rubber, where they result from the interaction of MBT with chain-end radicals, formed during mastication. As noted in the Experimental section, hydroperoxides readily form in TME, and although removed from the system as far as possible, residual traces may generate TME radicals which could trap MBT, resulting in small amounts of benzothiazole-terminated pendent groups.

TME/Sulfur (33.9:1.1)

On heating at 150°C, the formation of small amounts of alkenyl alkyl and bis(alkenyl) crosslinked products were observed after 15 and 25 min, respectively (Fig. 2). Farmer and Ship-
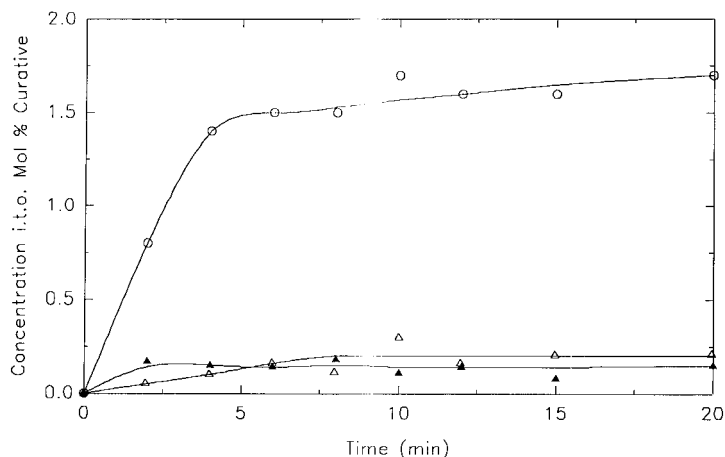
Figure 1 HPLC analysis of the benzothiazole reaction products formed when heating the MBT/sulfur (1:1) system isothermally at 155°C: (▲) MBTM; (△) MBTS; (○) BtS$_3$Bt.

ley[23] also suggested that alkenyl alkyl crosslinked products were predominant in natural rubber vulcanization and that a maximum of six sulfur atoms was detected in crosslinked products. Secondary crosslink products were proposed but none were detected in TME studies.

TME/MBT/Sulfur (33.9:1.1:1)

On adding sulfur to TME/MBT, slow crosslinking, accompanied by H$_2$S evolution, was observed after 6 min at 150°C (Fig. 3). The monosulfidic product was detected after 12 min and, like other sulfurated crosslinked products, continued to increase in concentration throughout the reaction.

H-NMR confirmed the formation of only bis(alkenyl) crosslinked products (TME–S$_x$–TME, x = 2–7) (Fig. 4). Decreasing the MBT concentration in the mixture from 1.1 to 0.25 mol delayed the onset of crosslinking from 6 to 10 min (cf. Figs. 3 and 5). H$_2$S was detected at this time and monosulfidic crosslinked products were detected after 20 min (Fig. 6). The MBT concentration remained essentially constant (Figs. 3 and 5) and only trace amounts of monosulfidic benzothiazole-terminated pendent groups were detected throughout the reaction. In rubber systems, also, MBT is not consumed during crosslinking.[6,8,11,22] Campbell and Wise[11] vulcanized natural rubber with
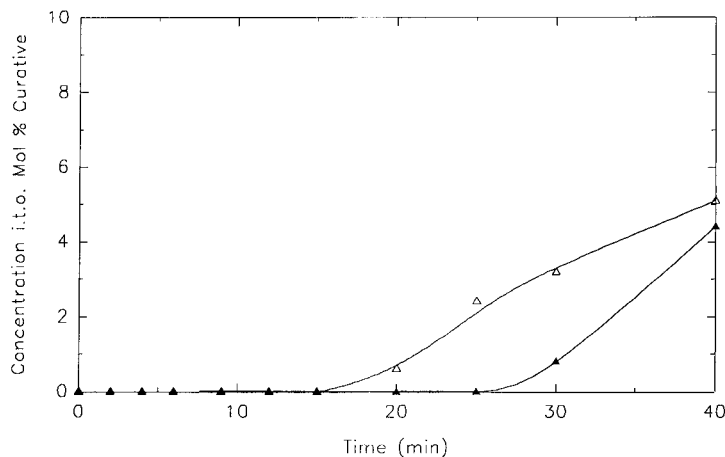

Figure 2 HPLC analysis of alkenyl alkyl and bis(alkenyl) crosslinked products formed when heating the TME/sulfur (33.9:1:1) system isothermally at 150°C: (△) sum of TME–S$_x$–R (x = 1–6; R = alkyl); (▲) sum of TME–S$_x$–TME (x = 1–6).
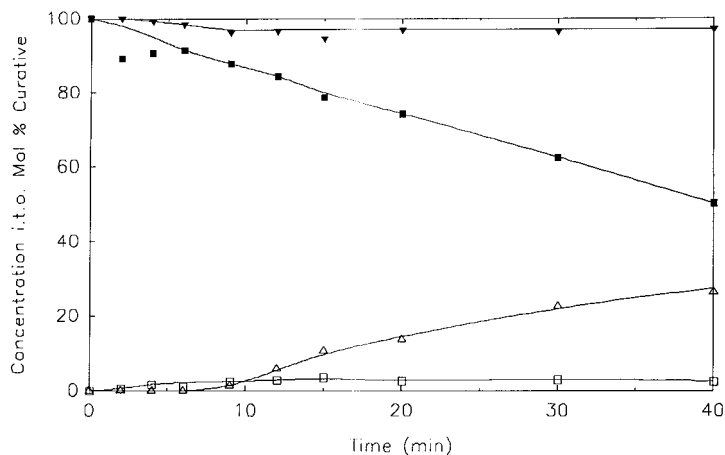
Figure 3 HPLC analysis of the TME/MBT/sulfur (33.9:1.1:1) system heated isothermally at 150°C: (▼) MBT; (□) TME–SBt; (■); sulfur; (△) sum of TME–S_x–TME (x = 1–7).

1.07% MBT and 2.47% sulfur. They noted that the MBT concentration decreased during the initial stages of the reaction and that MBTP and polysulfidic benzothiazole-terminated pendent groups formed. Neither MBTP nor benzothiazole-terminated pendent groups were detected with TME.

Crosslinking Reaction

A number of crosslinking routes have been suggested. Tsurugi and Nakabayashi[10] suggested that MBT-accelerated sulfur vulcanization of diphenylmethane proceeded via BtS_x and diphenylmethane radicals. The formation of some MBTP and benzothiazole-terminated pendent groups, which may be expected to result from radical combinations, were not observed with the TME systems. With natural rubber, Campbell and Wise[11] proposed reaction via benzothiazole-terminated pendent groups, but no such groups, which are readily observed with TME/MBTS/sulfur, were observed in TME/MBT/sulfur reactions. Gradwell and McGill[8] proposed reaction via HS^+ cations in a route that would require the formation of alkenyl alkyl crosslinked products. H-NMR showed that all crosslinked products (Fig. 4) were bis(alkenyl). It must be concluded that the crosslink
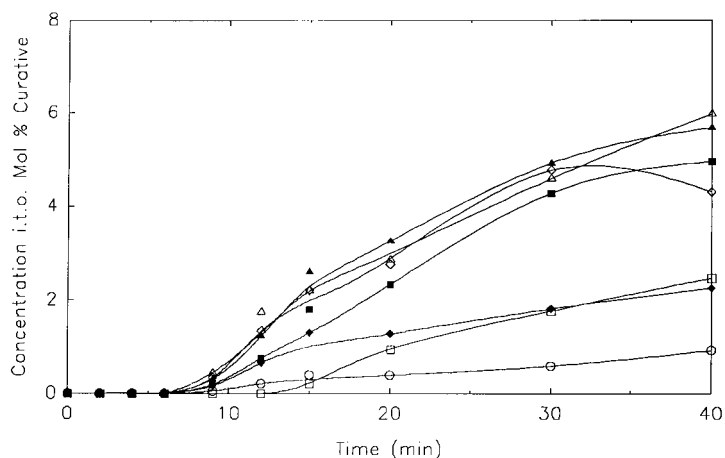

Figure 4 HPLC analysis of bis(alkenyl) crosslinked products formed when heating the TME/MBT/sulfur (33.9:1.1:1) system at 150°C: (□) TME–S–TME; (■) TME–S_2–TME; (△) TME–S_3–TME; (▲) TME–S_4–TME; (◇) TME–S_5–TME; (◆) TME–S_6–TME; (○) TME–S_7–TME.
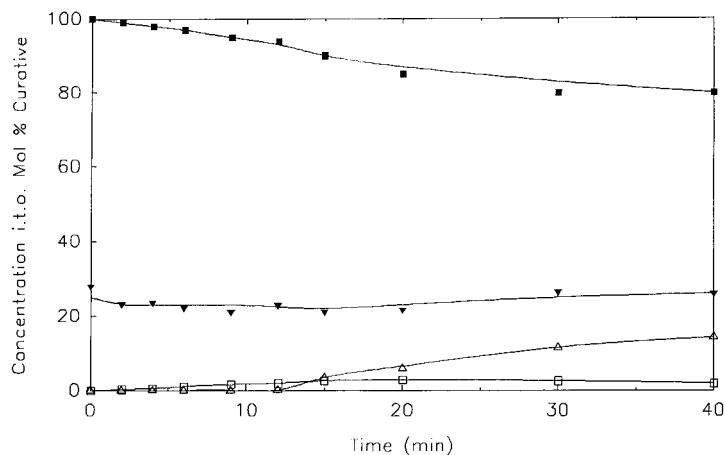
Figure 5 HPLC analysis of the TME/MBT/sulfur (33.9:0.25:1) system heated isothermally at 150°C: (▼) MBT; (□) TME–SBt; (■) sulfur; (△) sum of TME–S_x–TME ($x = 1$–6).

intermediate was short-lived, not UV active, or broke down in solution, thus escaping detection in the HPLC analysis. It is proposed that crosslinking involves the transient formation of BtS$_x$H of different sulfur rank. As noted, BtS$_x$H was not detected by HPLC, although Dogadkin et al.[4–7] proposed its formation on reaction of MBT with sulfur, and Gradwell et al.[9] invoked their transient formation to explain the influence of MBT on the formation of MBTP, when MBTS and sulfur were heated with MBT. Reaction of BtS$_x$H with TME in a concerted reaction will lead to 2,3-dimethyl-1-thiols of different sulfur rank and the regeneration of MBT, the concentration of which would remain constant, as observed:
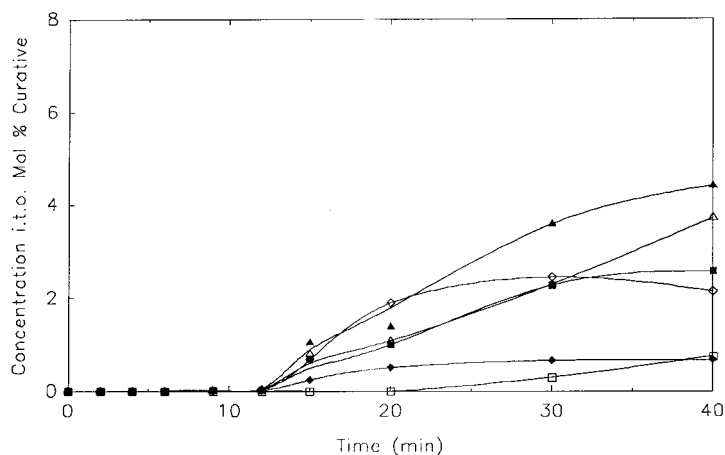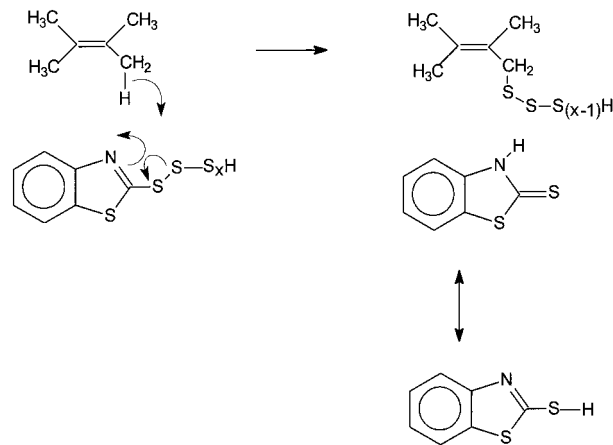

Figure 6 HPLC analysis of bis(alkenyl) crosslinked products formed when heating the TME/MBT/sulfur (33.9:0.25:1) system at 150°C: (□) TME–S–TME; (■) TME–S_2–TME; (△) TME–S_3–TME; (▲) TME–S_4–TME; (◇) TME–S_5–TME; (◆) TME–S_6–TME.
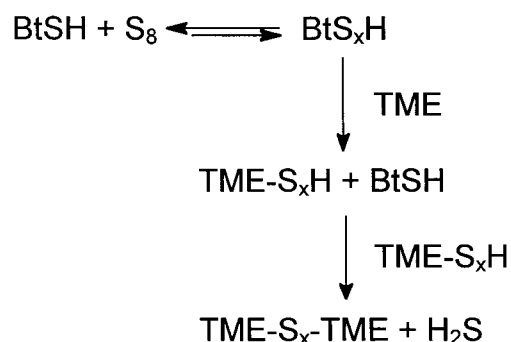
Hydrogen terminated-pendent groups exhibit weak UV absorption and would not be recorded by the UV detector of the HPLC. H-NMR proved unsuccessful in detecting TME–S_xH, possibly as they are too unstable and their concentration was too low.

Indirect proof of the existence of such pendent groups is provided by the following experiment: Mercaptans (RSH) can readily be oxidized to disulfides (RSSR) by the addition of peroxides or hydroperoxides.[13,24] By analogy, the hydrogen-terminated polysulfidic pendent groups, TME–S_xH, should form dimeric products. An ampule containing TME/MBT/sulfur (33.9:1.1:1) was heated at 150°C for 4 min and the reaction quenched. HPLC analysis showed no crosslinked products, as was to be expected, crosslinking only occurring after 6–9 min (Fig. 3). MBT and sulfur were removed from the liquid TME components (TME and TME–S_xH) by the freeze preparation process described in the Experimental section. Heating the TME–liquid for an additional minute produced no crosslinked products, while on heating after the addition of 3-hydroperoxide-2,3-dimethyl-1-butene, low concentrations of crosslinked products were detected, suggesting the presence of molecules with hydrogen-terminated polysulfidic pendent groups. It is proposed that crosslinking results from the interaction of thiols and is accompanied by the liberation of H_2S, detected by its smell and the lead acetate test:

$$2 \text{ TME—S}_x\text{H} \rightarrow \text{TME—S}_x\text{—TME} + \text{H}_2\text{S}$$

To demonstrate crosslinking between thiols, TME–SH was synthesized and 0.1 mol added to 33.9 mol TME. On heating at 150°C for 20 min, low concentrations of crosslinked products were obtained. On increasing the concentration of thiol in the reaction mixture, crosslinking occurred earlier and higher concentrations of crosslinked products formed. Heating TME–SH with sulfur in the absence of TME led to immediate crosslinking, with H_2S evolution. In the absence of sulfur, no reaction occurred, indicating the need for the formation of polysulfidic thiols. A recent article[25] also reported the crosslinking of TME–SH in the presence of sulfur, but H_2S formation was not detected and a metathesis reaction leading to polysulfanes, H_2S_n, was suggested.

It is proposed that crosslinking results from the reaction between thiols, rather than between thiols and TME. This would account for the long induction period prior to crosslinking, the second-order reaction between thiols occurring only once their concentration has been built up.

Scheme 1   MBT-accelerated sulfur vulcanization of TME.

CONCLUSIONS

Although there is no direct proof for the formation of MBT polysulfides, it is proposed that their transient formation from the interaction of MBT with sulfur, and their reaction with TME, results in the production of hydrogen-terminated polysulfidic pendent groups (TME–S_xH) and the regeneration of MBT. Poly(sulfidic benzothiazole)-terminated pendent groups (TME–S_xBt), commonly reported for MBT-accelerated sulfur vulcanization, were not detected. Crosslinking is proposed to result from the reaction between TME–S_xH pendent groups but is slow and initiates only after an induction period during which the concentration of these groups builds up to a point at which the rate of reaction becomes measurable. H_2S is liberated as a product of crosslinking. The overall MBT-accelerated sulfur vulcanization of TME is illustrated in Scheme 1.

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