Benzothiazole-Accelerated Sulfur Vulcanization. III. 2-Bisbenzothiazole-2,2′-disulfide as Accelerator for 2,3-Dimethyl-2-butene

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ABSTRACT: 2-Bisbenzothiazole-2,2′-disulfide (MBTS)-accelerated sulfur vulcanization, in the absence of ZnO, was studied using 2,3-dimethyl-2-butene (TME) as a model for polyisoprene. Reactions were carried out in sealed tubes at 150°C and the residual curatives, intermediates, and products were analyzed by HPLC at various stages of the reaction. The formation of accelerator-terminated polysulfidic pendent groups is accompanied by the liberation of 2-mercaptobenzothiazole (MBT) and more MBT is liberated on crosslinking. Bis(alkenyl)-crosslinked products with varying degrees of sulfuration result. It was shown that crosslinking by a reaction between pendent groups and the model compound, and by disproportionation of pendent groups, leads to limited crosslinking. H_2S was not evolved during crosslinking. 2,3-Dimethyl-2-butene–benzothiazole disulfide (TME–S_2Bt) and 2,3-dimethyl-2-butene–1-thiol (TME–SH) were synthesized and it was shown that rapid crosslinking occurs between TME–S_xBt and TME–S_xH (where $x > 1$), the reaction liberating MBT. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1395–1404, 2000

Key words: vulcanization; 2-bisbenzothiazole-2,2′-disulfide; 2,3-dimethyl-2-butene; model compound

INTRODUCTION

2-Bisbenzothiazole-2,2′-disulfide (MBTS)-accelerated sulfur vulcanization has been extensively studied,[1–9] although debate still exists as to the formation of 2-mercaptobenzothiazole (MBT) during pendent group formation and the nature of the crosslinking reaction. On vulcanizing polyisoprene with MBTS and MBTS/sulfur in a DSC at a programmed heating rate, Gradwell and McGill[5] found the amount of extractable MBTS to decrease, and this was interpreted as an indication of pendent group formation, although MBT was not detected prior to the onset of crosslinking. The

data suggested that pendent group formation was an additive rather than a substitutive process, but how this occurred was unclear. Campbell and Wise[3] also noted that, in natural rubber/MBTS/sulfur vulcanizates, the MBT concentration remained small during the induction period prior to crosslinking, whereafter it increased in parallel with the crosslink density. Numerous authors[2,4,8,9] found that MBT was released when 2-bisbenzothiazole-2,2′-polysulfides (MBTP) reacted with rubber to form pendent groups and suggested a substitution reaction.

Morrison,[1] who studied MBTS/sulfur vulcanization at 140°C using 2-methyl-2-pentene as a model for polyisoprene, suggested that pendent groups formed exclusively at the methylene sites, releasing MBT as a by-product. Although the formation of pendent groups is open to debate, it is agreed that MBT is released upon crosslink-
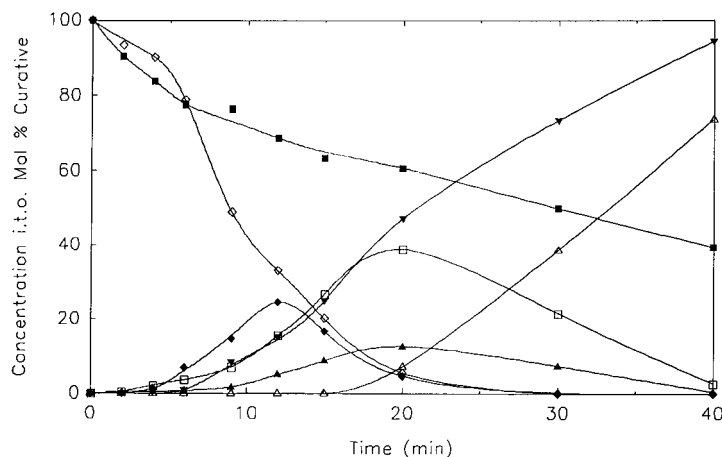
Figure 1   HPLC analysis of the TME/MBTS/sulfur (33.9:1.1:1) system heated isothermally at 150°C: (▼) MBT; (◇) MBTS; (▲) MBTM; (■) sulfur; (◆) sum of BtS_xBt ($x = 3-8$); (□) sum of TME–S_xBt ($x = 1-7$); (△) sum of TME–S_x–TME ($x = 1-10$).

ing.[1,3,5,8] Gradwell and McGill[5] proposed a pendent–chain crosslinking reaction in which the more electronegative nitrogen atom, contained within the benzothiazole fragment of the pendent group, removed a hydrogen atom from a neighboring rubber chain, resulting in the formation of MBT and a crosslink. The number of crosslinks produced was fewer than the amount of MBT released, and the difference was attributed to cyclization reactions where a nitrogen atom could abstract a hydrogen atom on the same chain as the pendent group, thereby producing MBT and a cyclic sulfide. Other authors[2,4,10] proposed reaction via radicals, with the production of carbon–carbon crosslinks. However, the use of chemical probes failed to produce evidence of carbon–carbon crosslinks in MBTS-accelerated sulfur vulcanization of polyisoprene.[5] This article reexamined MBTS-accelerated sulfur vulcanization with respect to pendent group and crosslink formation, using the model compound 2,3-dimethyl-2-butene (TME).

EXPERIMENTAL

MBTS (chemical purity 93%, Orchem, Sasolburg, South Africa), sulfur (S_8; 98% soluble in CS_2, AECI, Modderfontein, South Africa), and TME (chemical purity 99.9%, Aldrich Chemical Co., Milwaukee, WI) were used. The synthesis of 2,3-dimethyl-2-butene–benzothiazole disulfide (TME–S_2Bt) and 2,3-dimethyl-2-butene–1-thiol (TME–SH) and the removal of hydroperoxides from TME have been described.[11]

Experimental procedures have been described in detail.[11] Solutions of curatives in TME were heated in evacuated sealed tubes for various times at 150°C and residual curatives, intermediates, and crosslinked products were analyzed by HPLC.[11] Curative loadings used in the reaction mixtures are indicated in parentheses as mol ratios. In the figures, 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.

RESULTS AND DISCUSSION

TME/MBTS (33.9:1.1)

Heating TME/MBTS (33.9:1.1) isothermally at 150°C did not lead to vulcanization within 40 min and 2-bisbenzothiazole-2,2'-trisulfide (BtS_3Bt) was the only MBTP formed in measurable quantities. MBT was detected after 9 min and attained a concentration of 2 mol % after 40 min. Mono- and disulfidic benzothiazole-terminated pendent groups were detected after 9 min and, additively, their concentrations attained 0.19 mol % after 40 min. No other benzothiazole-terminated pendent groups were detected. The lack of vulcanization was not unexpected as few MBTP and pendent groups formed. On heating for longer periods and at higher temperatures, some vulcanization was observed with polyisoprene.[5]
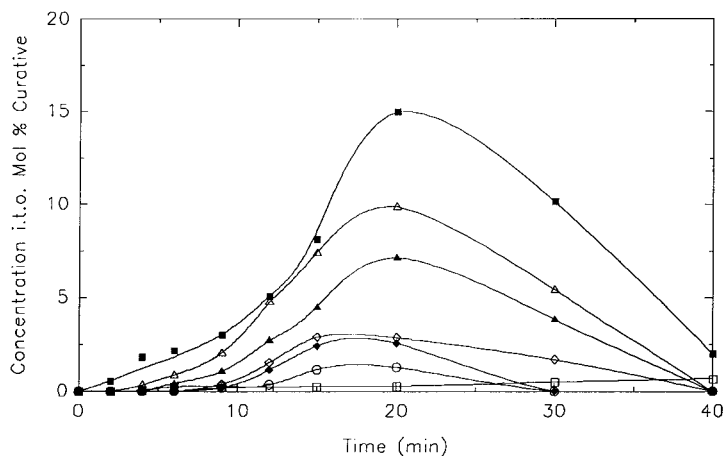
TME/MBTS/Sulfur (33.9:1.1:1)

The rate of the MBTS reaction in TME is greatly enhanced by the presence of sulfur (Fig. 1). The
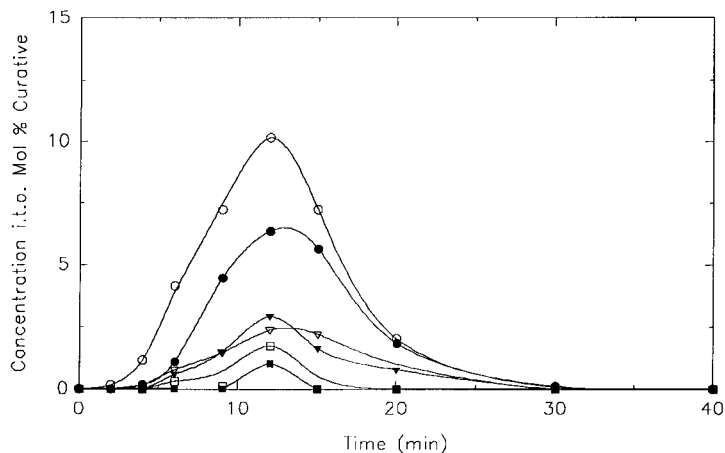
Figure 2 HPLC analysis of MBTP formed when heating the TME/MBTS/sulfur (33.9:1.1:1) system isothermally at 150°C: (○) BtS_3Bt; (●) BtS_4Bt; (▽) BtS_5Bt; (▼) BtS_6Bt; (□) BtS_7Bt; (■) BtS_8Bt.

initially slow MBTS reaction accelerated after 4 min, with the MBTS being completely consumed within 30 min. MBTP up to BtS_6Bt were detected (Fig. 2). BtS_3Bt was the most abundant MBTP and attained a maximum concentration of 10.1 mol % at 12 min. Lower sulfur rank MBTP were higher in concentration and were detected before the higher sulfur rank MBTP. The relative concentrations of MBTP are similar to those found in the absence of TME.[12] The formation of MBTP has been discussed.[12] Sulfur was consumed from the outset and 39.5 mol % remained after 40 min. MBT production was coincident with pendent group formation and attained a concentration of 94.4 mol % after 40 min (Fig. 1).

MBTP are highly reactive[5] and their reaction with TME resulted in total MBTP consumption between 20 and 30 min. Pendent groups with a sulfur rank of up to 7 were produced, with the disulfidic being the most abundant at 14.9 mol % after 20 min (Fig. 3). As lower sulfur rank MBTP are formed first and in higher concentrations than are higher sulfur rank MBTP (Fig. 2), pendent groups of lower sulfur rank should be the most abundant, as is reflected in Figure 3 where BtS_3Bt is the most abundant MBTP, and $TME–S_2Bt$, the most abundant pendent group. The lower sulfur rank pendent groups were detected before the higher sulfur rank groups.

Figure 3 HPLC analysis of pendent groups formed when heating the TME/MBTS/ sulfur (33.9:1.1:1) system isothermally at 150°C: (□) $TME–SBt$; (■) $TME–S_2Bt$; (△) $TME–S_3Bt$; (▲) $TME–S_4Bt$; (◇) $TME–S_5Bt$; (◆) $TME–S_6Bt$; (○) $TME–S_7Bt$.
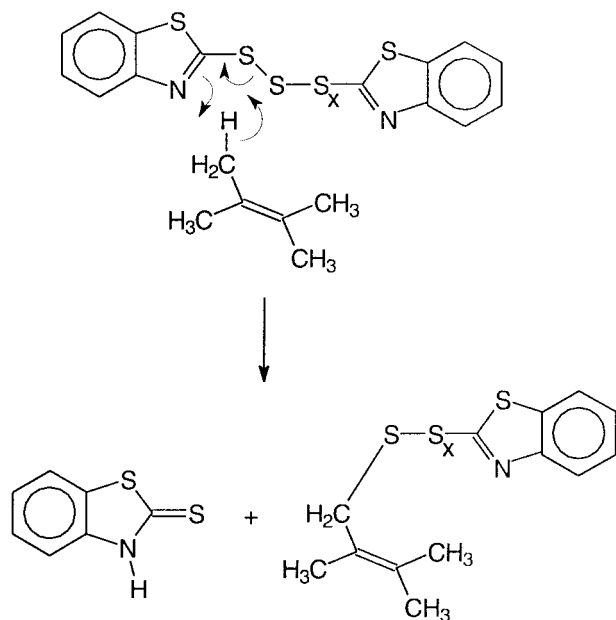
Figure 4 Proposed MBTP reaction with TME to produce pendent groups and MBT.

The proposal of Coran[8] that pendent group formation occurs by the highly electronegative nitrogen atom within the benzothiazole groups abstracting an α-methylenic hydrogen atom from TME via a concerted reaction to produce MBT and TME–S_xBt is supported (Fig. 4). TME vulcanization occurred between 15 and 20 min, where a series of polysulfidic crosslinked products (TMT–S_x–TME, $x = 1$–10) were detected (Fig. 5). The lower sulfur rank crosslinked products were the most abundant, except for TME–S–TME, which
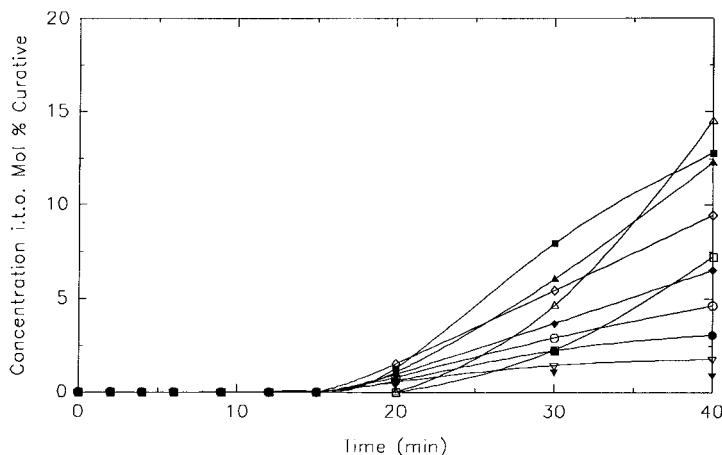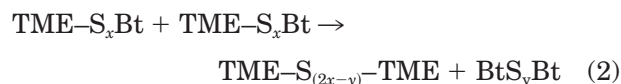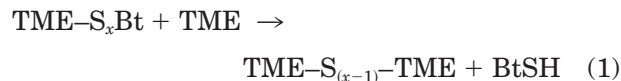
formed in lower amounts. Crosslinked products were confirmed as bis(alkenyl) by H-NMR. The MBT concentration continued to increase throughout the crosslinking reaction and its production paralleled that of the total crosslinked product concentration (Fig. 1). No H_2S was detected.

Role of MBT

In the presence of sulfur, MBT is an accelerator in its own right.[11,13–16] The release of MBT will result in the accelerated formation of MBTP as a result of the exchange between polysulfides of MBT (BtS_xH) and MBTS.[12] The reaction between BtS_xH and MBTS is extremely fast and it is suggested that only when the MBTS concentration decreases will the slower reaction between BtSH and TME produce hydrogen-terminated pendent groups (TME–S_xH).[11]

Induction Period

It has been proposed that crosslinked products form as a result of pendent group interaction with the chain[5,17] or by disproportionation with other pendent groups.[17] The former reaction would result in MBT formation, while the latter would give MBTS or MBTP [reactions (1) and (2)]:

$$TME\text{–}S_x Bt + TME \rightarrow$$
$$TME\text{–}S_{(x-1)}\text{–}TME + BtSH \quad (1)$$

$$TME\text{–}S_x Bt + TME\text{–}S_x Bt \rightarrow$$
$$TME\text{–}S_{(2x-y)}\text{–}TME + BtS_y Bt \quad (2)$$

Figure 5 HPLC analysis of crosslinked products formed when heating the TME/MBTS/sulfur (33.9:1.1:1) system isothermally 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; (●) TME–S_8–TME; (▽) TME–S_9–TME; (▼) TME–S_{10}–TME.
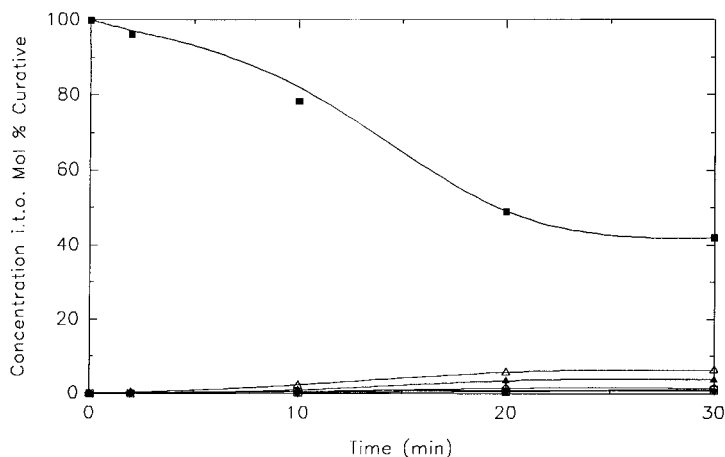
Figure 6 HPLC analysis of pendent groups formed when heating the n-hexane/TME–S_2Bt/sulfur (33.9:0.3:0.6) system isothermally at 150°C: ($\square$) TME–SBt; ($\blacksquare$) TME–S_2Bt; ($\triangle$) TME–S_3Bt; ($\blacktriangle$) TME–S_4Bt; ($\diamond$) TME–S_5Bt; ($\blacklozenge$) TME–S_6Bt.

However, the delay period prior to crosslinking (cf. Figs. 1 and 5) is puzzling if either of the above crosslinking reactions were to apply. Crosslinked products were detected after 15 min, at which time a total pendent group concentration of 26 mol % existed. If a pendent–chain reaction were to apply, crosslinking should have commenced, albeit slowly, as soon as pendent groups had formed. For crosslinking to occur via pendent group–pendent group interaction, the pendent group concentration would have to build up for a reaction at a measurable rate, yet crosslinking continued even when, in the latter stages of a reaction, the pendent group concentration dropped to well below the concentration of 26 mol % at which it commenced (Fig. 1). MBT formed at the same time as crosslinked products, and not MBTS or MBTP, as would be expected for a reaction between pendent groups. It is true that any MBTP formed will be consumed in further reactions, but, as will be shown below, crosslinking from pendent group–pendent group interaction contributes little to the overall reaction.

n-Hexane/TME–S_2Bt (33.9:0.3)

TME–S_2Bt was synthesized as described[11] and 0.3 mol, the maximum concentration detected in the TME/MBTS/sulfur system (Fig. 3), was heated in n-hexane (33.9 mol) for 40 min. No crosslinked products were detected. Neither had MBT or MBTP formed and only a small amount of TME–S_2Bt (less than 0.1 mol %) had disproportionated into TME–SBt and TME–S_3Bt. If crosslinking occurred via pendent group–pendent group interaction, crosslinked products should

have been detected. Thiuram disulfidic pendent groups are likewise unreactive. On heating TME–$S_2C(S)NMe_2$ in n-hexane at 140°C for 3 h, only 0.52% disproportionated to give a trisulfidic crosslinked product.[18] Bis(dimethyldithiocarbamate)zinc(II) catalyzed the reaction, and on heating for 3 h, a conversion of 3% was found.

TME/TME–S_2Bt (33.9:0.3)

The above experiment was repeated with TME in place of n-hexane to establish the feasibility of pendent–chain reactions. Again, no crosslinked products were detected. Neither MBT nor MBTP formed and only a small amount of disproportionation occurred. Thus, TME–S_2Bt is stable (when heated at 150°C for 40 min) and the consumption of TME–S_2Bt during TME/MBTS/sulfur vulcanization (Fig. 3) must be due to an additional factor. It may be that TME–S_2Bt is too unreactive, and the reaction of higher sulfurated pendent groups was investigated. Reaction between thiuram disulfidic pendent groups on TME and TME was likewise limited: Conversions of just over 1% occurred in 3 h at 140°C with conversions to the bis(alkenyl)trisulfide of 3–3.5% in the presence of the zinc-accelerator catalyst.[18]

n-Hexane/TME–S_2Bt/Sulfur (33.9:0.3:0.6)

Sulfuration of TME–S_2Bt produced pendent groups of higher sulfur rank and up to TME–S_6Bt were detected (Fig. 6). Their reactivity was, however, low as evidenced by TME–S_6Bt still being present at 30 min. The crosslinking reaction was slow and few crosslinked products were produced at 20 min
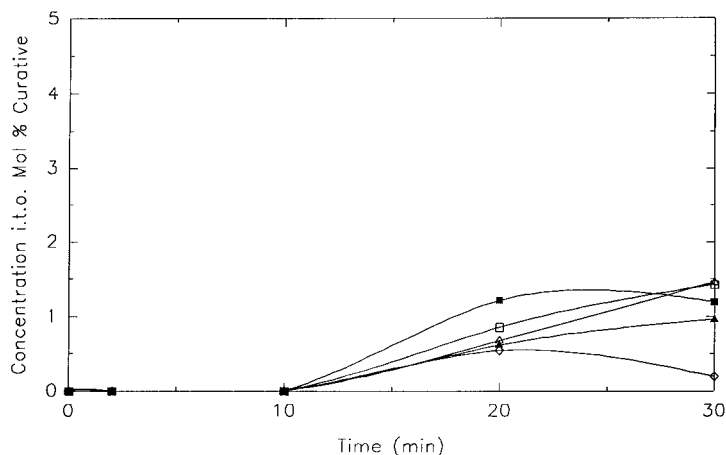
Figure 7 HPLC analysis of crosslinked products formed when heating the n-hexane/ TME–S_2Bt/sulfur (33.9:0.3:0.6) system isothermally at 150°C: (□) TME–S–TME; (■) TME–S_2–TME; (△) TME–S_3–TME; (▲) TME–S_4–TME; (◇) TME–S_5–TME.

(Fig. 7). Products with a maximum sulfur rank of 5 were detected. MBT formation was coincident with crosslink product formation. BtS_3Bt and BtS_4Bt were detected after 2 min, and as they are inert toward n-hexane, their concentrations continued to increase (Fig. 8). No H_2S was detected. On heating the thiuram disulfidic pendent group with sulfur in hexane conversions to crosslinked products increased from 0.52 to 5%.[18]

The production of some MBT (Fig. 9) and trace amounts of MBTP (Fig. 8) point to limited vulcanization occurring via both routes, that is, via pendent–chain (MBT production) and pendent group–pendent group (MBTP production) interactions. n-Hexane is saturated and unreactive toward MBTP, and the MBT produced must result

from interaction with methyl groups on TME–S_2Bt. Both reactions are clearly extremely slow.

TME/TME–S_2Bt/Sulfur (33.9:0.3:0.6)

Heating TME–S_2Bt (0.3 mol) in the presence of TME/sulfur (33.9:0.6) resulted in the onset of vulcanization within 10 min (cf. Figs. 9 and 10). The vulcanization process was initially slow and accelerated as the reaction continued. A total crosslink product concentration of 29 mol % was produced after 30 min. Crosslinked products with a sulfur rank of up to 4 were detected before 10 min (Fig. 11), while those with a sulfur rank 5–10 were only detected after 10 min. MBT was detected after 10 min and continued to form
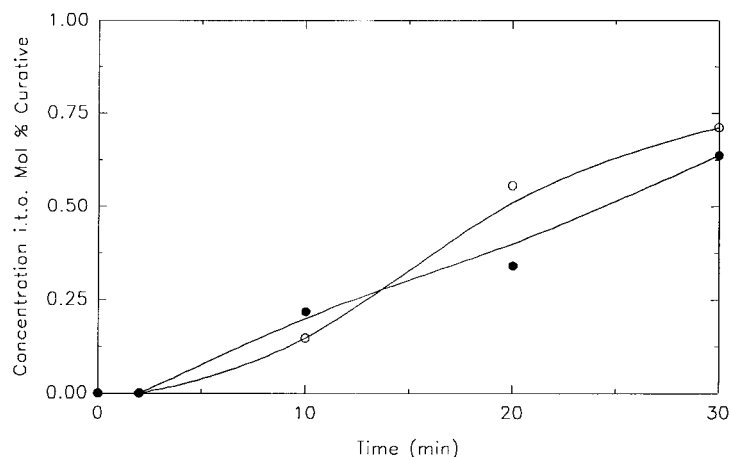
Figure 8 HPLC analysis of MBTP formed when heating the n-hexane/TME–S_2Bt/ sulfur (33.9:0.3:0.6) system isothermally at 150°C: (○) BtS_3Bt; (●) BtS_4Bt.
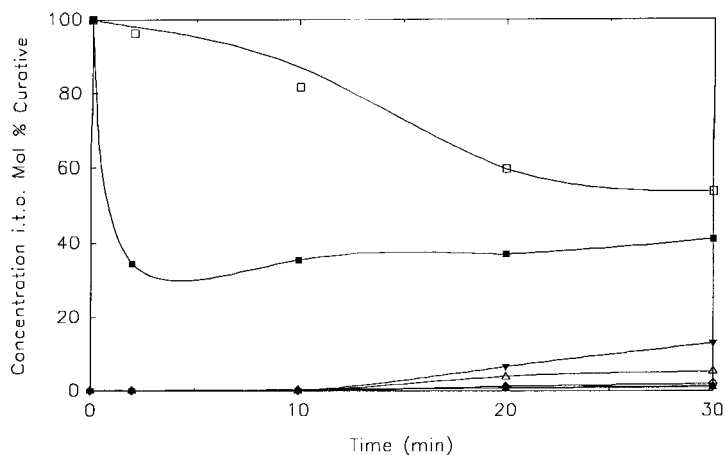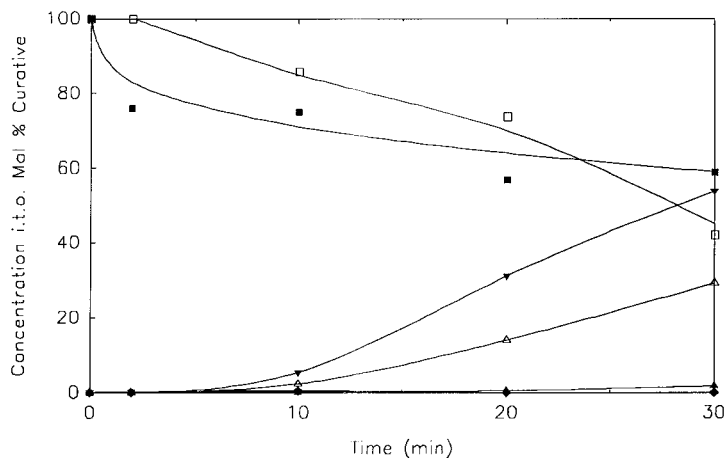
Figure 9 HPLC analysis of the n-hexane/TME–S$_2$Bt/sulfur (33.9:0.3:0.6) system iso-thermally at 150°C: (▼) MBT; (■) sulfur; (♦) sum of BtS$_x$Bt (x = 3,4); (□) sum of TME–S$_x$Bt (x = 1–6); (△) sum of TME–S$_x$–TME (x = 1–5).

throughout the reaction. Trace amounts of MBTP were detected in the initial stages of the reaction, but were totally consumed within 20 min (Fig. 12). A small amount of higher sulfur rank pendent groups, with a maximum sulfur rank of 6, were detected, but only the TME–S$_3$Bt concentration was significant. Pendent groups with a sulfur rank greater than 3 were totally consumed after 30 min (Fig. 13). No H$_2$S was detected.

Sulfur is capable of vulcanizing TME but the reaction is very slow, only initiating after 15 min[11] and the crosslinked product concentration is too low to account for the concentrations observed when TME–S$_2$Bt is present. Furthermore, sulfur vulcanization produces additional cross-linked product types,[11] while only bis(alkenyl)

crosslinked products were detected in TME/TME–S$_2$Bt/sulfur (33.9:0.3:0.6). The contribution of unaccelerated sulfur crosslinking of TME in this system can therefore be ignored.

The TME/TME–S$_2$Bt/sulfur (33.9:0.3:0.6) vul-canization reaction is similar to that of TME/MBTS/sulfur (33.9:1.1:1) in that the reaction produced MBT (Figs. 1 and 10) and crosslinked products with different degrees of sulfuration (Figs. 5 and 11). If the reaction were predominantly pendent group–pendent group in nature, the same crosslink concentrations should have been attained in both hydrocarbons, that is, in n-hexane/TME–S$_2$Bt/sulfur and in TME/TME–S$_2$Bt/sulfur. The formation of trace amounts of MBTP in both cases (Figs. 8 and 12) shows that pendent group–

Figure 10 HPLC analysis of the TME/TME–S$_2$Bt/sulfur (33.9:0.3:0.6) system isother-mally at 150°C: (▼) MBT; (■) sulfur; (♦) sum of BtS$_x$Bt (x = 3,4); (□) sum of TME–S$_x$Bt (x = 1–6); (△) sum of TME–S$_x$–TME (x = 1–10).
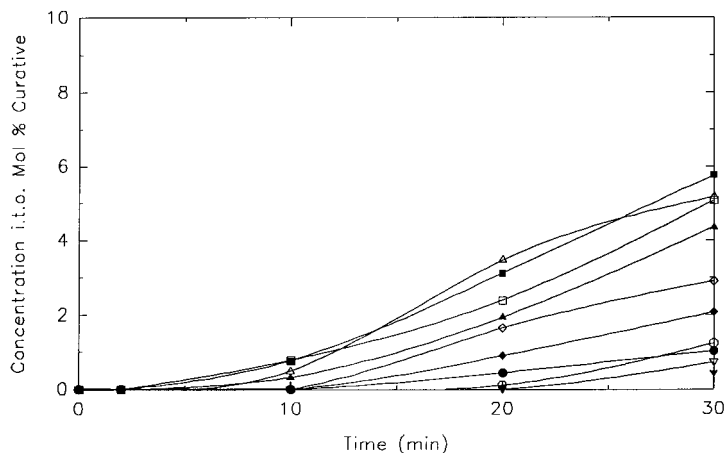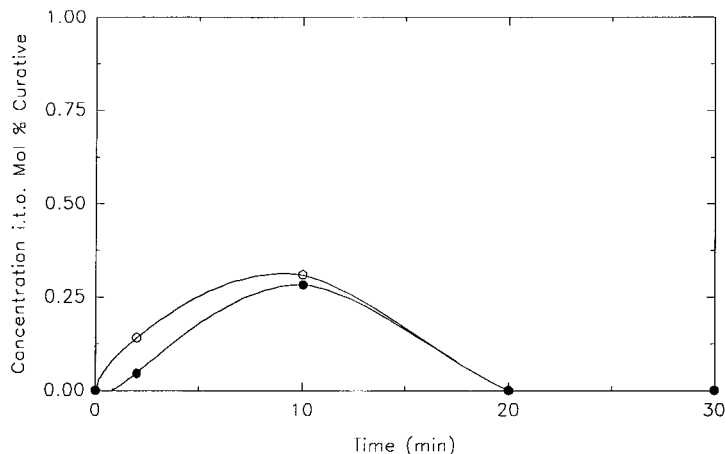
Figure 11 HPLC analysis of crosslinked products formed when heating the TME/TME–S_2Bt/sulfur (33.9:0.3:0.6) system isothermally at 150°C: (□) TME–S–TME; (■) TME–S_2–TME; (△) TME–S_3–TME; (▲) TME–S_4–TME; (◇) TME–S_5–TME; (♦) TME–S_6–TME; (○) TME–S_7–TME; (●) TME–S_8–TME; (▽) TME–S_9–TME; (▼) TME–S_{10}–TME.

pendent group crosslinking constitutes a minor reaction. The crosslinked product concentration is much higher in TME than in *n*-hexane (cf. Figs. 9 and 10), showing that TME participates in the crosslinking reaction. However, if TME alone were responsible for the reaction with TME–S_2Bt, crosslinking should have been initiated much earlier in the TME/MBTS/sulfur (33.9:1.1:1) system where reasonable quantities of TME–S_xBt (up to TME–S_7Bt) were detected from 10 min onward (Fig. 3), yet crosslinking only occurred at 15 min (Fig. 5). Furthermore, as the pendent group concentration decreased in TME/MBTS/sulfur (33.9:1.1:1) (Fig. 1), the crosslinking reaction should have slowed. Figure 1 shows that although the

pendent group concentration after 30 min was below that at 15 min crosslinked products continued to form readily. Thus, TME must participate in the formation of an intermediate that cannot be formed in *n*-hexane. This intermediate must either react as soon as it is formed or be non-UV active as no additional product peaks were detected by HPLC.
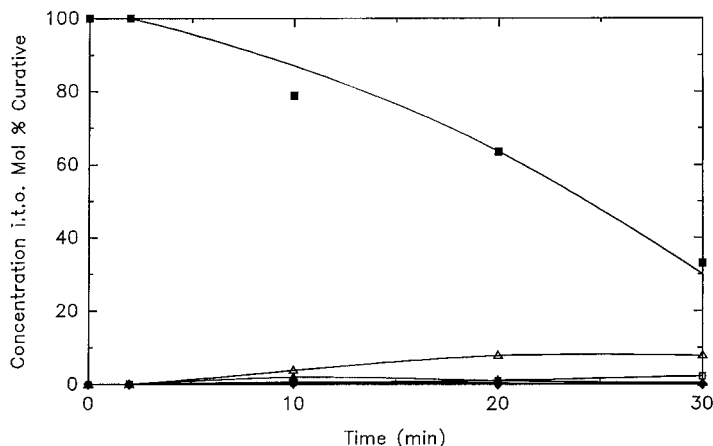
Crosslinking Reaction

It has been proposed[2,10,14,15,19,20] that MBT and sulfur react to produce BtS_xH. These are highly reactive toward MBTS[12] and result in the rapid formation of MBTP. However, after 20 min, very

Figure 12 HPLC analysis of MBTP formed when heating the TME/TME–S_2Bt/sulfur (33.9:0.3:0.6) system isothermally at 150°C: (○) BtS_3Bt; (●) BtS_4Bt.

Figure 13 HPLC analysis of pendent groups formed when heating the TME/TME–S_2Bt/sulfur (33.9:0.3:0.6) system isothermally at 150°C: (□) TME–SBt; (■) TME–S_2Bt; (△) TME–S_3Bt; (▲) TME–S_4Bt; (◇) TME–S_5Bt; (◆) TME–S_6Bt.
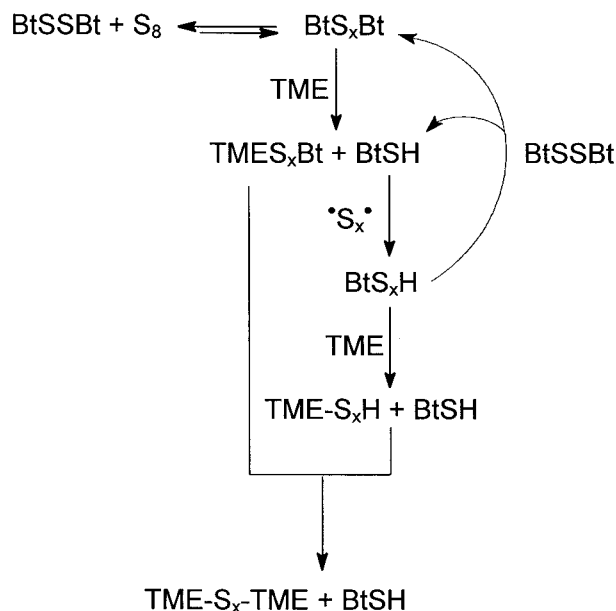
little MBTS and MBTP remain in the TME/MBTS/sulfur (33.9:1.1:1) system, at which point BtS_xH becomes available to react with TME to produce $TME–S_xH$ as proposed earlier.[11] The latter can produce crosslinked products with the evolution of H_2S, but as H_2S was not detected in the TME/MBTS/sulfur (33.9:1.1:1) system, and high concentrations of crosslinked products formed, an alternative, more rapid crosslinking route must exist. It is argued below that the interaction of $TME–S_xH$ and $TME–S_xBt$ is responsible for the formation of crosslinked products and the release of MBT as a by-product.

TME–S_2Bt and TME–SH were synthesized[11] and an equimolar mixture heated at 150°C. This resulted in the rapid disappearance of both components and the formation of MBT (98 mol %) and a small amount of crosslinked products (3 mol %). No other product was detected by HPLC but a product, other than the expected $TME–S_2–TME$, must clearly have formed. The two TME–S fragments may disproportionate to form cyclic sulfides, but the reactions were not pursued. Instead, the participation of $TME–S_xH$, as opposed to the monosulfidic thiol, was investigated.

$TME–S_xH$ could not be synthesized, but the addition of sulfur to TME–SH has been shown[11,20] to lead to crosslinking. The reaction time required for the formation of crosslinked products is dependent on the thiol concentration.[11] As shown earlier (Fig. 7), TME–S_2Bt reacts slowly with sulfur in n-hexane to produce small amounts of higher-rank pendent groups and crosslinked products. Heating n-hexane/TME–S_2Bt/TME–SH/sulfur (33.9:0.1:0.1:0.2) for 5 min produced a large amount of crosslinked products and 95 mol %

MBT. No H_2S was liberated. During a similar 5-min period, neither TME–S_2Bt (Fig. 7) nor TME–SH[11] produced crosslinked products when heated in the others' absence with sulfur in n-hexane. This indicates that crosslinked products resulted from the interaction of TME–S_2Bt with $TME–S_xH$.

The following experiment also emphasizes the role of thiols in crosslinking $TME–S_xBt$ groups. A TME/MBTS/sulfur (33.9:1.1:1) system was heated for 12 min. At this stage, a large number of pendent groups were present but no crosslinks were detected (Fig. 1). Residual curatives (including MBT and sulfur) were removed as described,[11] and on reheating for a further 28 min, the formation of a small amount of crosslinked products was observed. TME–S_2Bt, TME–S_3Bt, and TME–S_4Bt were still detected in appreciable quantities. In a TME/MBTS/sulfur (33.9:1.1:1) system, heated for 40 min (12 plus 28 min) without the removal of curatives, only trace amounts of TME–S_2Bt were present (Fig. 3). The reason for the difference is due to the absence of $TME–S_xH$ in the former system. These could not be produced due to the removal of sulfur (and MBT). A small amount of MBT was produced on crosslinking between $TME–S_xBt$ and the few $TME–S_xH$ present in the system at that time, but few additional $TME–S_xH$ formed due to the low concentrations of MBT and sulfur. The lack of $TME–S_xH$ limited the crosslinking reaction and left residual $TME–S_xBt$ groups. The crosslinked products ($TME–S_x–TME$) retained their original unsaturation on both TME fragments, and a purely substitutive reaction is proposed for both the formation of pendent groups and crosslinked products.

BtSSBt + S$_8$ ⇌ BtS$_x$Bt

TME ↓

TMES$_x$Bt + BtSH   BtSSBt

•S$_x$• ↓

BtS$_x$H

TME ↓

TME-S$_x$H + BtSH

↓

TME-S$_x$-TME + BtSH

Scheme 1 MBTS-accelerated sulfur vulcanization of TME.

CONCLUSIONS

MBTP react with TME to form benzothiazole-terminated polysulfidic pendent groups and MBT. Although it is commonly accepted that benzothiazole-terminated pendent groups lead to crosslinking either by disproportionation or by reaction with a neighboring chain, it is shown that these reactions contribute little to crosslink formation in TME. Instead, crosslinking is seen to result from interaction between polysulfidic benzothiazole-terminated pendent groups and hydrogen-terminated polysulfidic pendent groups formed from the reaction of BtS$_x$H with TME. The interaction of BtS$_x$H with TME is proposed to occur only once most of the MBTS has been consumed, and the rapid exchange of BtS$_x$H with MBTS to form MBTP and MBT is no longer dominant. This explains the long induction period observed prior to crosslinking. MBT is a by-product of benzothiazole-terminated pendent group formation and of crosslinking; thus, MBTS-accelerated sulfur vulcanization of TME occurs via a purely substitu-

tive pathway. H-NMR shows crosslinked products to be entirely bis(alkenyl). The overall MBTS-accelerated vulcanization reaction of TME is shown in Scheme 1.

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