

# Benzothiazole-Accelerated Sulfur Vulcanization. II. 2-Mercaptobenzothiazole/Zinc Oxide and Bis(2-mercaptobenzothiazole)Zinc(II) as Accelerators 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 in the presence of ZnO. Mixes of curatives and TME were heated isothermally in evacuated sealed glass ampules at 150°C for various times and the reaction intermediates and products analyzed by HPLC. In the absence of sulfur, even though MBT and ZnO react to form bis(2-mercaptobenzothiazole)zinc(II) [Zn(mbt)<sub>2</sub>], no crosslinking resulted. On addition of sulfur, the (incomplete) conversion of MBT and ZnO to Zn(mbt)<sub>2</sub> permitted vulcanization from the outset. Benzothiazole-terminated pendent groups were not detected, and crosslinking is proposed to occur via pendent groups that incorporate zinc. It is proposed that polysulfidic Zn(mbt)<sub>2</sub> reacts with TME to form zinc-containing pendent groups and MBT. These zinc-containing pendent groups are highly reactive and react with TME to form crosslinked products and MBT. The reaction was more rapid and the induction period prior to crosslinking was removed on increasing the MBT concentration in the system. This is ascribed to an exchange reaction between Zn(mbt)<sub>2</sub> and MBT polysulfides, formed by the interaction of MBT with sulfur, leading more rapidly to high concentrations of polysulfidic Zn(mbt)<sub>2</sub> and, hence, to zinc-containing pendent groups. MBT released during Zn(mbt)<sub>2</sub>-initiated crosslinking would, in part, contribute to crosslinking via TME-S<sub>x</sub>H. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1386–1394, 2000

**Key words:** vulcanization; 2-mercaptobenzothiazole; bis(2-mercaptobenzothiazole)zinc(II); 2,3-dimethyl-2-butene; model

## INTRODUCTION

2-Mercaptobenzothiazole (MBT) and ZnO readily react<sup>1–5</sup> to form the zinc-accelerator complex bis(2-mercaptobenzothiazole)zinc(II) [Zn(mbt)<sub>2</sub>]. Kapur et al.<sup>4</sup> observed the formation of Zn(mbt)<sub>2</sub>, zinc oxybenzothiazole (ZnOBt<sup>+</sup>), and 2-bisbenzothiazole-2,2'-polysulfides (MBTP) by Raman spectroscopy in MBT/ZnO mixes heated at 150°C.

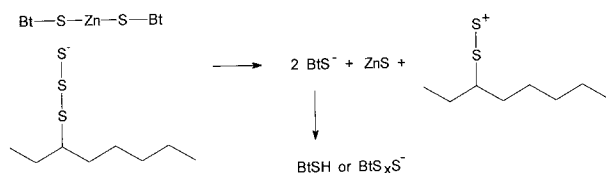
Echte and Lorenz<sup>1</sup> showed that, in natural rubber formulations containing MBT/sulfur/ZnO, sulfur decreased according to the first-order rate law. As the same acceleration was attained when MBT/ZnO was substituted with Zn(mbt)<sub>2</sub>, they concluded that the initial step in the MBT/sulfur/ZnO vulcanization reaction was the formation of Zn(mbt)<sub>2</sub> and that it should be regarded as the actual accelerator. Auerbach,<sup>3</sup> too, suggested that Zn(mbt)<sub>2</sub> was formed on heating MBT and ZnO. However, Zn(mbt)<sub>2</sub> was found to react with rubber in the presence of sulfur, and only when the

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sulfur concentration became very low did  $\text{Zn}(\text{mbt})_2$  accumulate to any measurable extent.

Gradwell and McGill<sup>5</sup> reported that MBT/ZnO-accelerated sulfur vulcanization was equivalent to  $\text{Zn}(\text{mbt})_2$ -accelerated sulfur vulcanization as MBT was rapidly converted to  $\text{Zn}(\text{mbt})_2$  during the mixing process. They suggested that sulfur initiated the vulcanization reaction via the formation of persulfenyl cations. From DSC and rheometer cure curves, they concluded that the few polysulfidic crosslinks initially formed via unaccelerated sulfur vulcanization<sup>6-8</sup> gave rise to polysulfidic anion fragments still bound to the polymer chain and that these decomposed  $\text{Zn}(\text{mbt})_2$  to  $\text{BtS}^-$  anions and  $\text{ZnS}$ .  $\text{BtS}^-$  anions accelerated the vulcanization reaction by abstracting hydrogen from the polymer chain or by reaction with sulfur, thereby increasing its activity toward the chain. MBT was detected at the same time as the crosslinking:



$\text{Zn}(\text{mbt})_2$  reacted sparingly with the model compound diphenylmethane, and Tsurugi and Fukuda<sup>9</sup> suggested that the initial step of the vulcanization reaction involved reaction between  $\text{Zn}(\text{mbt})_2$  and sulfur.  $\text{BtS}$  radicals were proposed to form and the process was described as similar to that of MBT-accelerated sulfur vulcanization.<sup>10</sup>

The literature is in agreement that MBT and ZnO readily form  $\text{Zn}(\text{mbt})_2$ , but controversy surrounds the mechanism of the crosslinking reaction and the involvement of polysulfidic accelerator-terminated pendent groups. This article examined the mechanism of  $\text{Zn}(\text{mbt})_2$ -accelerated sulfur vulcanization using 2,3-dimethyl-2-butene (TME) as a model for polyisoprene. The reactions of MBT/sulfur/ZnO and  $\text{Zn}(\text{mbt})_2$ /sulfur with TME were compared and the effect of MBT on the  $\text{Zn}(\text{mbt})_2$ /sulfur vulcanization process was examined.

## EXPERIMENTAL

### Materials

2,3-Dimethyl-2-butene (TME; chemical purity 99.9 %, Aldrich Chemical Co., Milwaukee, WI), 2-mercaptobenzothiazole (MBT; chemical purity

**Table I** Analyses of TME-SZnS-TME

Element	% Calculated	% Experimental
C	48.7	47.1
H	7.5	7.5
N	0.0	0.0
S	21.6	21.1
Zn	22.1	25.8

95 %, Thiotax, Flexsys, Brussels, Belgium), bis(2-mercaptobenzothiazole)zinc(II) [ $\text{Zn}(\text{mbt})_2$ ]; Bayer, Leverkusen, Germany), zinc oxide (ZnO; Zinc Process, Cape Town, South Africa), and sulfur ( $\text{S}_8$ ; 98% soluble in  $\text{CS}_2$ , AECI, Modderfontein, South Africa) were used.

The experimental procedures have been described.<sup>11,12</sup> Solutions of the curatives in TME were heated in evacuated sealed tubes for various times at 150°C and the residual curatives, intermediates, and crosslinked products analyzed by HPLC.<sup>11</sup> The crosslinked products were characterized by H-NMR.<sup>11,13</sup> The curative loadings used in the reaction mixtures are indicated in parentheses as mole 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.

Commercially available  $\text{Zn}(\text{mbt})_2$  contains approximately 20% MBT and, if not removed, alters the  $\text{Zn}(\text{mbt})_2$ -accelerated sulfur vulcanization pathway. MBT removal from  $\text{Zn}(\text{mbt})_2$  was described,<sup>5</sup> but benzene was substituted for methanol during the dissolution process.

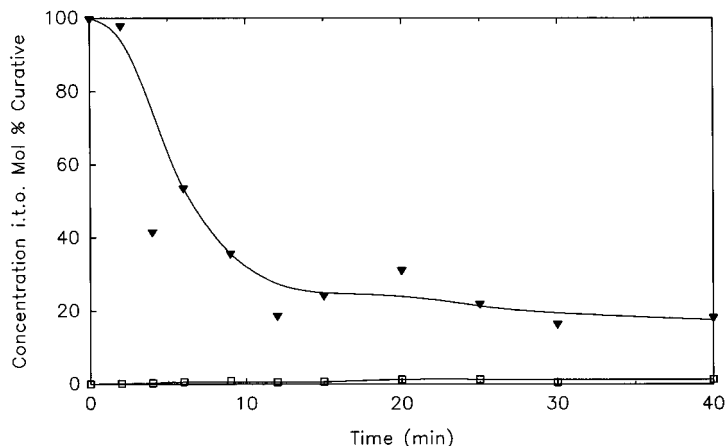
### Synthesis of Bis(2,3-dimethyl-2-butene-1-thiol)zinc(II) (TME-SZnS-TME)

Mol ratios of 2:1 for 2,3-dimethyl-2-butene-1-thiol (TME-SH)<sup>11</sup> and ZnO were used in the preparation of bis(2,3-dimethyl-2-butene-1-thiol)zinc(II) (TME-SZnS-TME). The reaction was conducted isothermally in a sealed glass ampule at 150°C for 10 min. The solid residue was washed with three 5-mL aliquots of dichloromethane and dried under a vacuum. CHN, sulfur,<sup>14</sup> and zinc (atomic absorption spectroscopy) analyses are presented in Table I.

## RESULTS AND DISCUSSION

### TME/MBT/ZnO (33.9:1.1:1)

Heating TME/MBT/ZnO in TME did not lead to vulcanization, but  $\text{Zn}(\text{mbt})_2$  was formed from the



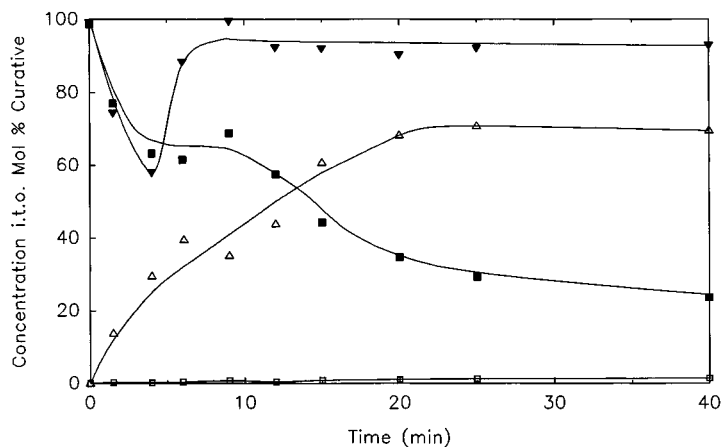
**Figure 1** HPLC analysis of the TME/MBT/ZnO (33.9:1.1:1) system heated isothermally at 150°C: (▼) MBT; (□) TME-SBt.

reaction between MBT and ZnO. The lack of vulcanization was not unexpected as neither MBT nor  $\text{Zn}(\text{mbt})_2$  are sulfur-donor accelerators, that is, accelerators that do not require elemental sulfur to crosslink. The formation of  $\text{Zn}(\text{mbt})_2$  from MBT/ZnO mixes has been discussed.<sup>1-5</sup> MBT consumption was rapid from the outset but slowed after 10 min (Fig. 1), and 18 mol % MBT remained after 40 min. Gradwell and McGill<sup>5</sup> found that 12 mol % MBT remained when heating an MBT/ZnO (1:1) mixture in a DSC to 200°C and ascribed the failure of a complete reaction to the coating of ZnO particles by  $\text{Zn}(\text{mbt})_2$ . Besides minor amounts (1.5 mol % after 20 min) of monosulfidic benzothiazole-terminated pendent groups detected on heating TME with MBT/ZnO, no other

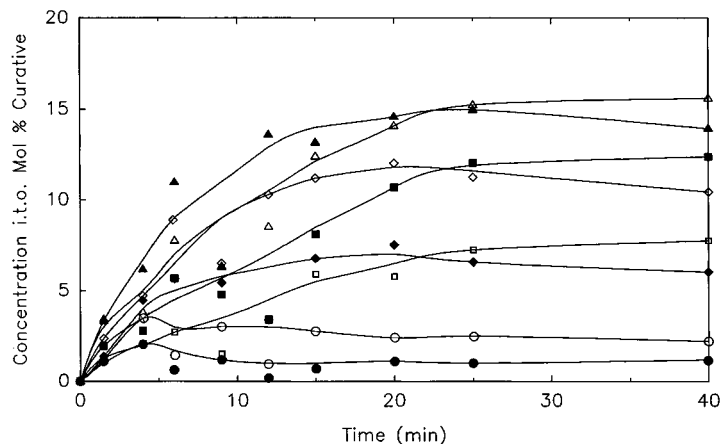
benzothiazole-terminated pendent groups were detected.

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

In the presence of sulfur, MBT and ZnO not only reacted rapidly to form  $\text{Zn}(\text{mbt})_2$ , but crosslinked products and  $\text{H}_2\text{S}$  were detected after heating for 2 min at 150°C (Figs. 2 and 3). Gradwell and McGill<sup>5</sup> found that by mixing MBT and ZnO with polyisoprene they could only extract 5% MBT from the compound and concluded that MBT and ZnO reacted during compounding to form  $\text{Zn}(\text{mbt})_2$ . The initial decrease in MBT concentration (Fig. 2) is attributed to  $\text{Zn}(\text{mbt})_2$  formation but MBT was liberated again during the vulcani-



**Figure 2** HPLC analysis of the TME/MBT/sulfur/ZnO (33.9:1.1:1:1) system heated isothermally at 150°C: (▼) MBT; (□) TME-SBt; (■) sulfur; (△) sum of TME-S<sub>x</sub>-TME ( $x = 1-8$ ).



**Figure 3** HPLC analysis of crosslinked products formed when heating the TME/MBT/sulfur/ZnO (33.9:1.1:1:1) system at 150°C: (□) TME-S-TME; (■) TME-S<sub>2</sub>-TME; (△) TME-S<sub>3</sub>-TME; (▲) TME-S<sub>4</sub>-TME; (◇) TME-S<sub>5</sub>-TME; (◆) TME-S<sub>6</sub>-TME; (○) TME-S<sub>7</sub>-TME; (●) TME-S<sub>8</sub>-TME.

zation reaction and 90% of the benzothiazole fragments of Zn(mbt)<sub>2</sub> could be accounted for as MBT.

MBT is capable of vulcanizing TME in the presence of sulfur,<sup>11</sup> but, clearly, in the presence of ZnO, the reaction is markedly faster with crosslinked products detected after 2 min. This vulcanization system was found to be very similar to the TME/Zn(mbt)<sub>2</sub>/MBT/sulfur system that will be discussed below.

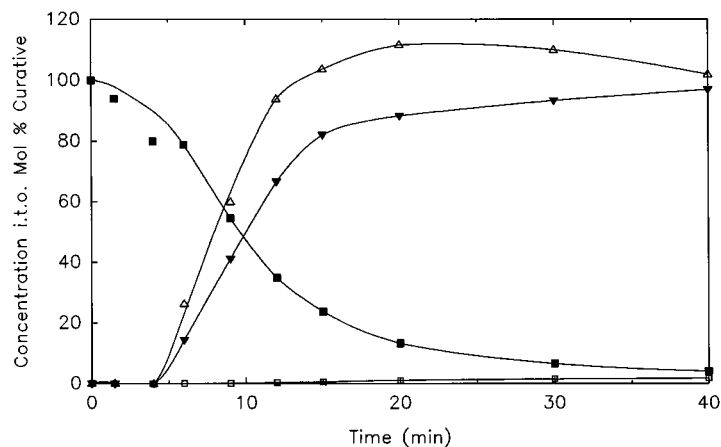
#### TME/Zn(mbt)<sub>2</sub> (33.9:1.1)

Heating TME with Zn(mbt)<sub>2</sub> did not lead to TME vulcanization, and even after 40 min, no extractable compounds were detected by HPLC. This is

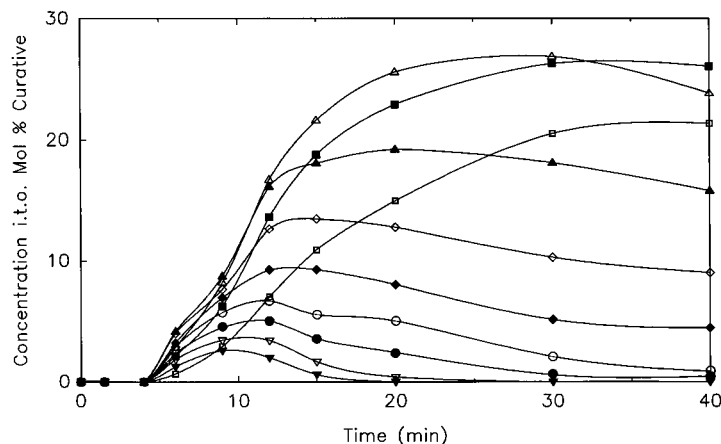
consistent with the findings of Echte and Lorenz<sup>1</sup> and of Gradwell and McGill.<sup>5</sup>

#### TME/Zn(mbt)<sub>2</sub>/Sulfur (33.9:1.1:1)

In the presence of sulfur, Zn(mbt)<sub>2</sub>-accelerated TME vulcanization initiated after 4 min with MBT, bis(alkenyl) crosslinked products (Figs. 4 and 5), and H<sub>2</sub>S were detected. No benzothiazole-terminated pendent groups, other than trace amounts of monosulfidic benzothiazole-terminated pendent groups, were detected throughout the TME vulcanization reaction. This differs from some studies<sup>2,15</sup> which reported the formation of polysulfidic benzothia-



**Figure 4** HPLC analysis of the TME/Zn(mbt)<sub>2</sub>/sulfur (33.9:1.1:1) system heated isothermally at 150°C: (▼) MBT; (□) TME-SBt; (■) sulfur; (△) sum of TME-S<sub>x</sub>-TME ( $x = 1-10$ ).



**Figure 5** HPLC analysis of crosslinked products formed when heating the TME/ $\text{Zn}(\text{mbt})_2$ /sulfur (33.9:1.1:1) system at  $150^\circ\text{C}$ : ( $\square$ ) TME-S-TME; ( $\blacksquare$ ) TME-S<sub>2</sub>-TME; ( $\triangle$ ) TME-S<sub>3</sub>-TME; ( $\blacktriangle$ ) TME-S<sub>4</sub>-TME; ( $\diamond$ ) TME-S<sub>5</sub>-TME; ( $\blacklozenge$ ) TME-S<sub>6</sub>-TME; ( $\circ$ ) TME-S<sub>7</sub>-TME; ( $\bullet$ ) TME-S<sub>8</sub>-TME; ( $\nabla$ ) TME-S<sub>9</sub>-TME; ( $\blacktriangledown$ ) TME-S<sub>10</sub>-TME.

zole-terminated pendent groups. It must be questioned whether polysulfidic benzothiazole-terminated pendent groups are produced at all in the present model system or whether their reaction is such that rapid consumption precludes detection.

#### Crosslinking Reactions

To answer the above questions, polysulfidic benzothiazole-terminated pendent groups (TME-S<sub>x</sub>Bt;  $x = 1-7$ ) were prepared<sup>11</sup> by heating TME/MBTS/sulfur (33.9:1.1:1) for 12 min and separating these from the other curatives using the described<sup>11</sup> freeze-separation technique. The resultant solution was analyzed by HPLC, and besides polysulfidic benzothiazole-terminated pendent groups, only a small amount (<5 mol %) of sulfur was detected. Unreacted TME remains in the liquid phase. The solution was heated in a vacuum-sealed ampule for 4 min and analyzed by HPLC. No crosslinked products were detected. Another sample, prepared in the same way, was heated for 4 min with  $\text{Zn}(\text{mbt})_2$ . Crosslinking occurred with the release of MBT and  $\text{H}_2\text{S}$ . All pendent groups with a sulfur rank greater than 5 were totally consumed, but those of a lower sulfur rank were still detected. A  $\text{Zn}(\text{mbt})_2$ /sulfur (1:1) mixture was added to another sample and heated for 4 min. A similar crosslinking reaction occurred and benzothiazole-terminated pendent groups with a sulfur rank of up to 4 were still detected.

2,3-Dimethyl-2-butene-1-benzothiazole-disulfide (TME-S<sub>2</sub>Bt) (0.3 mol) was synthesized using

a recently described<sup>16</sup> method for the synthesis of 2,3-dimethyl-2-butene-1-dimethyldithiocarbamate disulfide and heated in the presence of TME for 4 min. No crosslinking was evident. The experiment was repeated with the addition of  $\text{Zn}(\text{mbt})_2$ . Once again, no crosslinking was evident. Thus,  $\text{Zn}(\text{mbt})_2$  is unable to crosslink TME-S<sub>2</sub>Bt within the 4-min heating period, although pendent groups of higher sulfur rank were readily crosslinked. These reactions suggest that had polysulfidic benzothiazole-terminated pendent groups formed in the  $\text{Zn}(\text{mbt})_2$ -accelerated sulfur vulcanization<sup>17</sup> at least those of lower sulfur rank should have been detected.

As no polysulfidic benzothiazole-terminated pendent groups were formed, another intermediate that could lead to crosslinking, but that could not be detected by HPLC, must have been formed. It is proposed that the pendent groups that form incorporate zinc are insoluble in TME at room temperature, and, hence, remain undetected in the HPLC analysis. Attempts to prove the existence of these zinc-TME compounds were unsuccessful when analyzing the TME/ $\text{Zn}(\text{mbt})_2$ /sulfur (33.9:1.1:1) system directly. Instead, the monosulfidic zinc-TME compound TME-SZnS-TME was synthesized. This can be regarded as a model compound with a zinc-containing sulfidic pendent group. The terminal group is TME and not benzothiazole, as would be the case in  $\text{Zn}(\text{mbt})_2$ -accelerated sulfur vulcanization. The crosslinking reactions of the compound were studied.

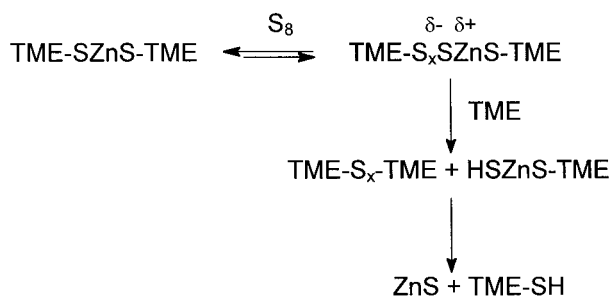
The TME/ $\text{Zn}(\text{mbt})_2$ /sulfur (33.9:1.1:1) system produced crosslinked products rapidly once

crosslinking began. Thus, if TME–SZnS–TME were analogous to the proposed zinc-containing pendent groups in the Zn(mbt)<sub>2</sub>-accelerated reaction, it should lead to rapid crosslinking in the presence of sulfur. The compound is monosulfidic and no reaction occurred when it was heated with TME in the absence of sulfur. Polysulfidic zinc-accelerator species have not been isolated and, if formed, must have a transient existence. TME–S<sub>x</sub>ZnS<sub>x</sub>–TME would likewise be highly reactive.

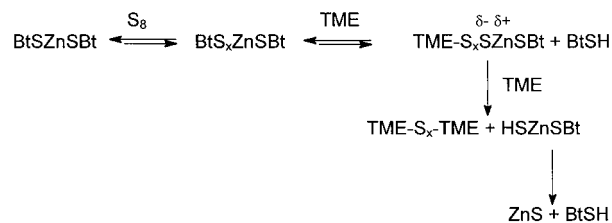
TME/TME–SZnS–TME/sulfur (33.9:1.1:1) was heated for 2 min and HPLC confirmed the formation of crosslinked products. H<sub>2</sub>S was evolved. This was taken as proof that sulfuration of the zinc compound and its subsequent reaction was rapid. The crosslinked product spectrum resembled that formed on heating TME/Zn(mbt)<sub>2</sub>/sulfur (33.9:1.1:1) (Fig. 5). In both systems, the di-, tri-, tetra-, and pentasulfidic crosslinked products were the most abundant, with H<sub>2</sub>S and crosslinked products up to TME–S<sub>9</sub>–TME detected.

TME–SZnS–TME was found to be soluble in TME at 150°C, but sparingly soluble at room temperature and, hence, remained behind as a precipitate during the sample preparation for HPLC. Small amounts of TME–SZnS–Bt, formed in the TME/Zn(mbt)<sub>2</sub>/sulfur system, would likewise go undetected.

The proposed TME/TME–SZnS–TME/sulfur (33.9:1.1:1) vulcanization mechanism is summarized in Scheme 1. In the presence of sulfur, TME–SH crosslinks with H<sub>2</sub>S evolution<sup>11</sup> and this reaction may, in part, account for crosslinking and for H<sub>2</sub>S formation. In Scheme 2, the crosslinking mechanism for TME–SZnS–TME is extended to a mechanism for Zn(mbt)<sub>2</sub>-accelerated sulfur vulcanization. The zinc-containing pendent groups form in the second step. Comparison of Schemes 1 and 2 show that TME–SZnS–



**Scheme 1** Proposed TME/TME–SZnS–TME/sulfur reactions.



**Scheme 2** Proposed TME/Zn(mbt)<sub>2</sub>/sulfur reactions.

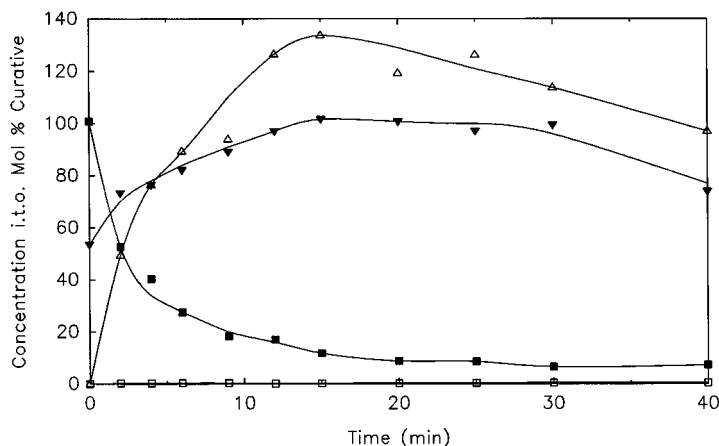
TME can be regarded as a symmetric intermediate in the Zn(mbt)<sub>2</sub> reaction. As the nitrogen atom in the benzothiazole group is highly electronegative, it, rather than the sulfur atom attached to zinc, will abstract hydrogen from TME. Hence, a zinc-containing benzothiazole pendent group and BtSH will form, rather than a benzothiazole-terminated pendent group and HSZnSBt. Although this would require the formation of MBT prior to crosslinking, the extremely rapid reaction of sulfurated zinc species would make it difficult to detect MBT before crosslinking. Thus, crosslinking via TME–S<sub>x</sub>H, formed in an MBT-initiated reaction,<sup>11</sup> could contribute to crosslink formation.

Gradwell and McGill<sup>5</sup> also suggested that no benzothiazole-terminated groups formed. They observed the coincident formation of MBT and crosslinking as was also observed in the TME studies reported here (Fig. 4).

### Induction Period

In the TME/Zn(mbt)<sub>2</sub>/sulfur (33.9:1.1:1) system, a 4-min induction period prior to the crosslinked product formation is evident (Fig. 4). This can be explained in terms of the limited contact between Zn(mbt)<sub>2</sub> and activated sulfur. Sulfur is extremely soluble in TME, and when the samples were heated, sulfur dissolved into the TME phase. The gentle, mechanical shaking of the ampule helped this process. Thus, sulfur was effectively separated from the Zn(mbt)<sub>2</sub> that is insoluble in TME and remained at the bottom of the ampule.

On heating TME/Zn(mbt)<sub>2</sub> with a commercial insoluble polymeric sulfur for 4 min, H<sub>2</sub>S, MBT (7 mol %), and the crosslinked products (5 mol %) were detected, while with soluble octacyclic sulfur, neither MBT nor the crosslinked products were evident at 4 min (Fig. 4). By adding excess soluble sulfur (3 mol) and heating without shaking of the ampule, 3 mol % MBT and 4 mol % of the crosslinked products were detected after 4



**Figure 6** HPLC analysis of the TME/Zn(mbt)<sub>2</sub>/MBT/sulfur (33.9:1.1:1:1) system heated isothermally at 150°C: (▼) MBT; (□) TME-SBt; (■) sulfur; (△) sum of TME-S<sub>x</sub>-TME ( $x = 1-9$ ).

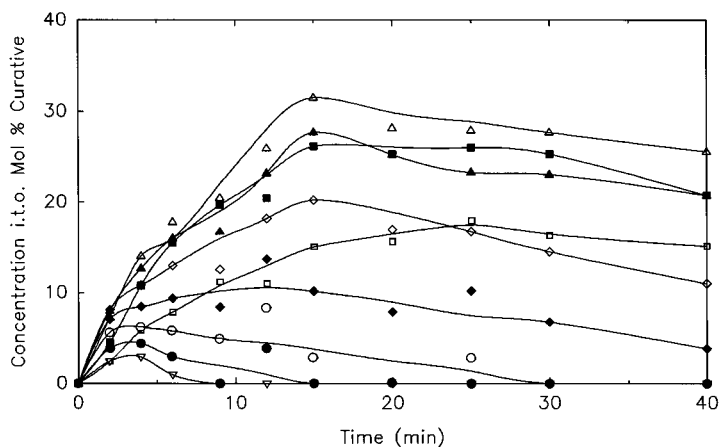
min, that is, the system crosslinked earlier as some sulfur remained as an undissolved residue. H<sub>2</sub>S was again liberated.

From these experiments, it is evident that crosslinking resulted earlier if the system was manipulated to allow for a greater contact between Zn(mbt)<sub>2</sub> and sulfur. However, the induction period could not be completely eliminated. It is suggested that, to react, sulfur must be activated and that this activation involves opening of the sulfur ring. Activated sulfur reacts with Zn(mbt)<sub>2</sub> to produce polysulfidic Zn(mbt)<sub>2</sub>. The induction period was therefore interpreted as a delay in the formation of polysulfidic Zn(mbt)<sub>2</sub>.

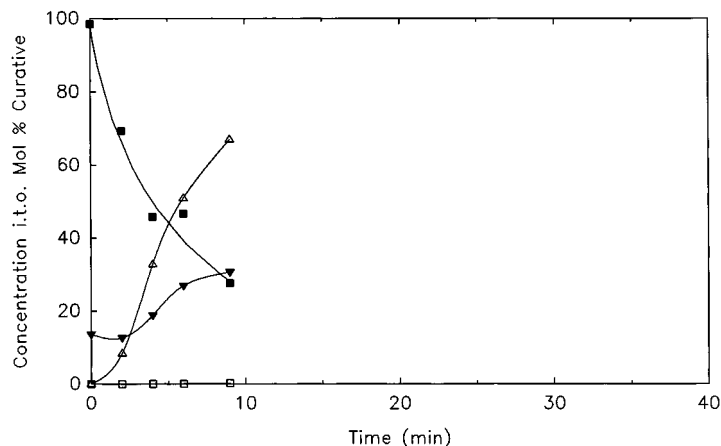
#### Effect of MBT

Adding 1 mol MBT to TME/Zn(mbt)<sub>2</sub>/sulfur (33.9:1.1:1) resulted in TME vulcanization after 2 min (Figs. 6 and 7). H<sub>2</sub>S and the liberation of additional MBT were also detected at this time. This behavior of the system is similar to that of the TME/MBT/sulfur/ZnO system (cf. Figs. 2 and 6). Gradwell and McGill<sup>5</sup> also noted an earlier onset of crosslinking when adding MBT to a polyisoprene/Zn(mbt)<sub>2</sub>/sulfur compound.

MBT is proposed<sup>2,18-22</sup> to form BtS<sub>x</sub>H when heated with sulfur. Reaction of the latter with TME is slow<sup>11</sup> and cannot account for the rapid



**Figure 7** HPLC analysis of crosslinked products formed when heating the TME/Zn(mbt)<sub>2</sub>/MBT/sulfur (33.9:1.1:1:1) system at 150°C: (□) TME-S-TME; (■) TME-S<sub>2</sub>-TME; (△) TME-S<sub>3</sub>-TME; (▲) TME-S<sub>4</sub>-TME; (◇) TME-S<sub>5</sub>-TME; (◆) TME-S<sub>6</sub>-TME; (○) TME-S<sub>7</sub>-TME; (●) TME-S<sub>8</sub>-TME; (▽) TME-S<sub>9</sub>-TME.



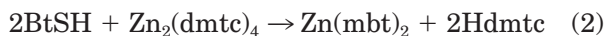
**Figure 8** HPLC analysis of the TME/Zn(mbt)<sub>2</sub>/MBT/sulfur (33.9:1.1:0.25:1) system heated isothermally at 150°C: (▼) MBT; (□) TME-SBt; (■) sulfur; (△) sum of TME-S<sub>x</sub>-TME (*x* = 1–9).

formation of crosslinked products observed in the presence of Zn(mbt)<sub>2</sub>. It is therefore more likely that BtS<sub>x</sub>H exchanges<sup>23</sup> with Zn(mbt)<sub>2</sub> to produce polysulfidic zinc species and MBT (reaction 1):



According to the mechanism proposed in Scheme 2, polysulfidic Zn(mbt)<sub>2</sub> reacts rapidly with TME and its formation from the outset would result in the formation of crosslinked products from the outset (Fig. 6).

The ready exchange of accelerator fragments with ligands on accelerator compounds has been demonstrated.<sup>23</sup> Analysis by HPLC showed a decrease in the MBT and bis(dimethyldithiocarbamate)zinc(II) [Zn<sub>2</sub>(dmtc)<sub>4</sub>] concentrations on heating Zn<sub>2</sub>(dmtc)<sub>4</sub>/MBT (1:2) at 150°C for 5 min in an open system. Mass loss calculations confirmed that the amount of dimethyldithiocarbamic acid (Hdmtc) lost by evaporation equaled the amount of MBT consumed (reaction 2):



The reaction was not taken to completion and the zinc residue may comprise a mixed zinc-accelerator complex [Zn(mbt)<sub>x</sub>(dmtc)<sub>y</sub>].

On decreasing the MBT concentration from 1 to 0.25 mol in the TME/Zn(mbt)<sub>2</sub>/sulfur mix, a short induction period was evident (as opposed to none) and the initial reaction rate was slower (cf. Figs. 6 and 8). However, as more MBT formed on crosslinking, the reaction accelerated. The reac-

tion between MBT and sulfur results in the formation of sulfur biradicals,<sup>18–21</sup> and as these may react more readily with Zn(mbt)<sub>2</sub> than with octacyclic sulfur in forming polysulfidic Zn(mbt)<sub>2</sub>, this may also contribute to the shortened induction period when MBT is added to the formulation.

## CONCLUSIONS

Zn(mbt)<sub>2</sub> forms from the reaction of MBT with ZnO, but does not crosslink TME in the absence of sulfur. In the presence of sulfur, Zn(mbt)<sub>2</sub> leads to rapid crosslinking. The formation of polysulfidic benzothiazole-terminated pendent groups was not observed. It was shown that the reactivity of benzothiazole-terminated pendent groups is sufficiently slow, even in the presence of Zn(mbt)<sub>2</sub>, for their detection, if formed. It is proposed that crosslinking occurs via pendent groups containing zinc. Sulfuration of Zn(mbt)<sub>2</sub> allows reaction with TME, leading to the formation of zinc-TME compounds (TME-S<sub>x</sub>ZnSBt) and the liberation of MBT. Further rapid reaction of the zinc-containing pendent group with a second TME molecule leads to the formation of sulfurated crosslinked species and a zinc compound that decomposes to ZnS and MBT. MBT liberated in the reaction can contribute to crosslinking via TME-S<sub>x</sub>H.

In the presence of MBT and sulfur, the formation of BtS<sub>x</sub>H and their exchange with Zn(mbt)<sub>2</sub> results in the rapid sulfuration of Zn(mbt)<sub>2</sub> via an exchange reaction that re-releases MBT into the



system. TME-S<sub>x</sub>ZnSBt compounds are thus formed more rapidly and their rapid reaction with TME ensures the rapid formation of crosslinked products. As sulfuration of Zn(mbt)<sub>2</sub> is the rate-limiting step and the BtS<sub>x</sub>H concentration is dependent on the MBT concentration, high initial concentrations of MBT ensure an initially more rapid reaction. Both accelerator systems [MBT and Zn(mbt)<sub>2</sub>] produced unsaturated crosslinked products [bis(alkenyl)], which indicates a substitutive rather than additive vulcanization reaction pathway.

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