

# Benzothiazole-Accelerated Sulfur Vulcanization. V. 2-Bisbenzothiazole-2,2'-disulfide/ZnO and 2-Bisbenzothiazole-2,2'-disulfide/(2-mercaptobenzothiazole)Zinc(II) as Accelerators for 2,3-Dimethyl-2-butene

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**ABSTRACT:** 2-Bisbenzothiazole-2,2'-disulfide (MBTS)-accelerated sulfur vulcanization in the presence of ZnO and bis(2-mercaptobenzothiazole)zinc(II) [Zn(mbt)<sub>2</sub>] 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 residual curatives, intermediates, and products were analyzed by HPLC. ZnO enhances MBTS-accelerated sulfur vulcanization, possibly through its formation of Zn(mbt)<sub>2</sub> on reaction with 2-mercaptobenzothiazole (MBT) released on pendent group formation. Zn(mbt)<sub>2</sub> is an accelerator in its own right, but in conjunction with MBTS, a synergistic effect is observed. Interaction between Zn(mbt)<sub>2</sub> and sulfurated MBT and/or 2-bisbenzothiazole-2,2'-polysulfides (MBTP) is proposed to lead to the more rapid sulfuration of Zn(mbt)<sub>2</sub>, while Zn(mbt)<sub>2</sub> catalyzes the crosslinking of benzothiazole-terminated pendent groups formed by the interaction of MBTP with the model compound. When ZnO in the formulation is replaced by Zn(mbt)<sub>2</sub>, the induction period before the rapid onset of crosslinking is reduced as the release of MBT required for Zn(mbt)<sub>2</sub> formation is eliminated. MBTS-, Zn(mbt)<sub>2</sub>-, and MBTS/Zn(mbt)<sub>2</sub>-accelerator systems lead to similar crosslink densities; only the rate of the reaction is influenced by Zn(mbt)<sub>2</sub>. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1413–1422, 2000

**Key words:** vulcanization; 2-bisbenzothiazole-2,2'-disulfide; bis(2-mercaptobenzothiazole)zinc(II); sulfur; 2,3-dimethyl-2-butene

## INTRODUCTION

It is well known that 2-bisbenzothiazole-2,2'-disulfide (MBTS)-accelerated sulfur vulcanization is enhanced in the presence of activators such as ZnO.<sup>1–3</sup> The mechanism of activation is, however, unclear. Kapur et al.<sup>4</sup> suggested that MBTS and ZnO react within the first minute at 150°C, form-

ing bis(2-mercaptobenzothiazole)zinc(II) [Zn(mbt)<sub>2</sub>] and 2-bisbenzothiazole-2,2'-polysulfides (MBTP), although in an earlier article in this series,<sup>5</sup> no reaction was observed. Other authors<sup>1,6</sup> also found no Zn(mbt)<sub>2</sub> formation on heating MBTS/ZnO to 200°C. Zn(mbt)<sub>2</sub> will result from the reaction of ZnO with 2-mercaptobenzothiazole (MBT) released during vulcanization.<sup>7–9</sup> However, while reaction between ZnO and MBT occurs readily during compounding, with complete consumption of MBT, the reaction appears more limited and confined to the ZnO surface when MBT is released during the vulcanization process where

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shearing forces, necessary to expose fresh ZnO surfaces for reaction, do not operate.<sup>9</sup> On heating MBT/ZnO (1:1) at 150°C in the absence of a rubber or model compound, the reaction also does not go to completion, with about 15 mol % MBT remaining after 40 min.<sup>7,9</sup> Nevertheless, the formation of MBT will have a direct impact on vulcanization in the presence of ZnO as Zn(mbt)<sub>2</sub> is an accelerator in its own right.<sup>7-10</sup> Zn(mbt)<sub>2</sub>-accelerated sulfur vulcanization of 2,3-dimethyl-2-butene (TME) was discussed in article II<sup>7</sup> of this series. The literature differs on the stage in the reaction at which MBT is first detected. The release of MBT on pendent group formation in MBTS-accelerated sulfur vulcanization has been reported,<sup>11-13</sup> while other authors<sup>14,15</sup> suggested that it is formed only on crosslinking.

Furthermore, benzothiazole-terminated pendent groups crosslinked rapidly in the presence of Zn(mbt)<sub>2</sub>, the reactivity of Zn(mbt)<sub>2</sub> toward benzothiazole-terminated pendent groups being dependent on the number of sulfur atoms within the pendent group, the lower sulfur rank pendent groups being less reactive.<sup>7</sup> This was confirmed when, on heating TME-S<sub>2</sub>Bt with Zn(mbt)<sub>2</sub> at 150°C for 40 min, no reaction was observed. Morrison<sup>11</sup> also reported poor crosslinking of model compound 2-methyl-2-pentene in the absence of zinc, but the presence of Zn(mbt)<sub>2</sub> led to a greater crosslink density and this was suggested to result from Zn(mbt)<sub>2</sub> rapid crosslinking of polysulfidic benzothiazole-terminated pendent groups.<sup>11,16,17</sup>

The catalytic crosslinking by bis(dimethyldithiocarbamate)zinc(II) [Zn<sub>2</sub>(dmtc)<sub>4</sub>] of thiuram pendent groups in tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization was demonstrated both in TME systems<sup>18,19</sup> and in polyisoprene (IR) compounds.<sup>20</sup> It was suggested<sup>1</sup> that benzothiazole-terminated pendent groups in polyisoprene (IR) can crosslink by reaction with neighboring chains or form cyclic sulfides by reaction with the same chain. The observed increased crosslink density, and the increase in the ratio of MBT released to crosslinks formed on adding ZnO to IR/MBTS/sulfur compounds, was attributed to ZnO promoting crosslinking of benzothiazole-terminated pendent groups, thus leading to less cyclization. This article examined the role of ZnO and Zn(mbt)<sub>2</sub> in MBTS-accelerated sulfur vulcanization using model compound 2,3-dimethyl-2-butene.

## EXPERIMENTAL

### Materials

2-Bisbenzothiazole-2,2'-disulfide (MBTS, chemical purity 93%, Orchem, Sasolburg, South Africa), 2-mercaptobenzothiazole (MBT, chemical purity 95%, Thiotax, Flexsys, Brussels, Belgium), bis(2-mercaptobenzothiazole)zinc(II) [Zn(mbt)<sub>2</sub>, Bayer, Leverkusen, Germany], ZnO (Zinc Process, Cape Town, South Africa), sulfur (S<sub>8</sub>, 98% soluble in CS<sub>2</sub>, AECI, Modderfontein, South Africa), and 2,3-dimethyl-2-butene (TME, chemical purity 99.9%, Aldrich Chemical Co., Milwaukee, WI) were used. The synthesis of 2,3-dimethyl-2-butene-benzothiazole disulfide (TME-S<sub>2</sub>Bt) and the removal of hydroperoxides from TME were described.<sup>21</sup>

Curatives and TME were heated in evacuated sealed tubes for various times at 150°C and residual curatives, intermediates, and crosslinked products analyzed by HPLC.<sup>21</sup> Experimental procedures were described in detail in an earlier article<sup>21</sup> in this series. Curative loadings used in the reaction mixtures are indicated in parentheses as mol ratios. In the figures, the concentrations of 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.

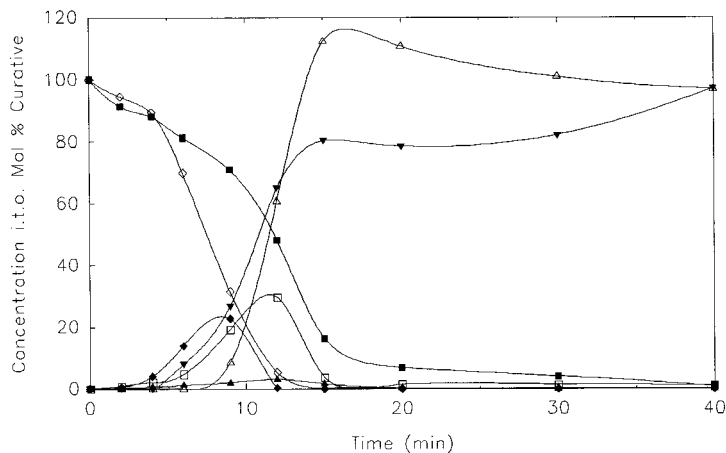
## RESULTS AND DISCUSSION

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

As was found on heating TME/MBTS,<sup>13</sup> TME/MBTS/ZnO did not vulcanize TME, and comparable, limited MBTS degradation occurred, while small amounts (<1 mol %) of MBTP (BtS<sub>3</sub>Bt and BtS<sub>4</sub>Bt) and even fewer pendent groups (TME-SBt and TME-S<sub>2</sub>Bt) formed. ZnO does not influence the formation of MBTM and MBTP in the absence of sulfur,<sup>5</sup> and the limited formation of MBTP was consistent with this. MBTP and benzothiazole-terminated pendent groups are intermediate products in the vulcanization reaction,<sup>3,12,22</sup> and their limited formation explains the lack of vulcanization.

### TME/MBTS/SULFUR/ZnO (33.9:1.1:1:1)

The addition of 1 mol ZnO to the TME/MBTS/sulfur system<sup>13</sup> changed the vulcanization reaction markedly (Fig. 1). Crosslinking no longer



**Figure 1** HPLC analysis of the TME/MBTS/sulfur/ZnO (33.9:1.1:1:1) system heated isothermally at 150°C: (▼) MBT; (◇) MBTS; (▲) MBTM; (■) sulfur; (◆) sum of BtS<sub>x</sub>Bt ( $x = 3-6$ ); (□) sum of TME-S<sub>x</sub>Bt ( $x = 1-6$ ); (△) sum of TME-S<sub>x</sub>-TME ( $x = 1-10$ ).

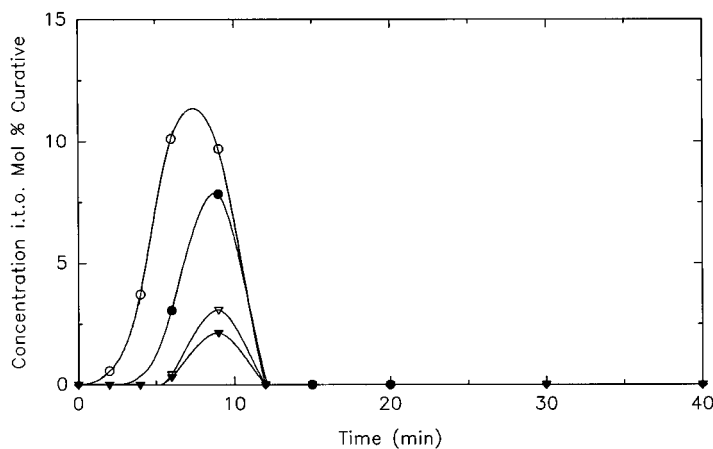
occurred after 15 min, as found in the absence of ZnO,<sup>13</sup> but started at 6 min and, once initiated, was extremely rapid, with the maximum crosslink product concentration being attained within 15 min. H<sub>2</sub>S was detected on crosslinking while it was not formed in the absence of ZnO.<sup>13</sup>

MBTS consumption was initially slow but accelerated after 4 min, with complete consumption occurring after 15 min (Fig. 1). Sulfur also was initially consumed slowly, but once crosslinking initiated, its consumption increased greatly, with only 0.8 mol % remaining after 40 min.

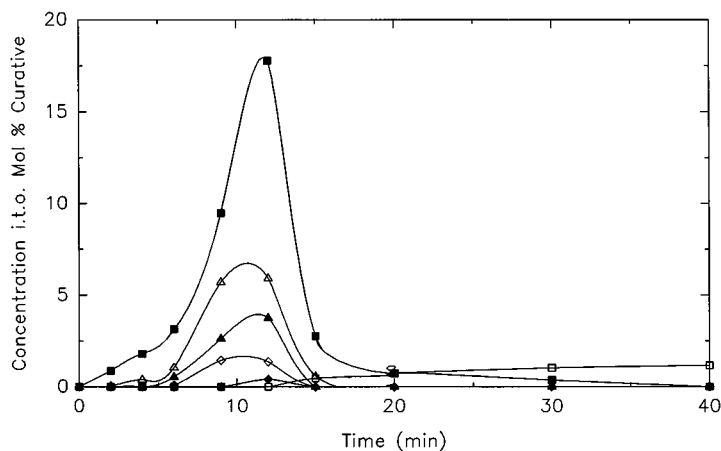
MBTS and ZnO do not interact at vulcanization temperatures<sup>1,5,6</sup> and initiation of the reaction is similar to that in the absence of ZnO.

MBTP were produced after a slight induction period (Fig. 2), with BtS<sub>3</sub>Bt being detected at 2 min, BtS<sub>4</sub>Bt at 4 min, and BtS<sub>5</sub>Bt and BtS<sub>6</sub>Bt at 6 min. Rapid consumption occurred after 9 min with MBTP being completely consumed by 12 min. The more rapid formation of MBTP than in the absence of ZnO is in line with earlier data where it was shown<sup>5</sup> that ZnO accelerates the formation of MBTP when heated in the presence of sulfur.

MBTP are highly reactive,<sup>1</sup> and in the absence of ZnO, their reaction with TME to form benzothiazole-terminated pendent groups was attributed to the highly electronegative nitrogen atom within the benzothiazole fragment.<sup>12</sup> Polysulfidic benzothiazole-terminated pendent groups were



**Figure 2** HPLC analysis of MBTP formed when heating the TME/MBTS/sulfur/ZnO (33.9:1.1:1:1) system isothermally at 150°C: (○) BtS<sub>3</sub>Bt; (●) BtS<sub>4</sub>Bt; (▽) BtS<sub>5</sub>Bt; (▼) BtS<sub>6</sub>Bt.



**Figure 3** HPLC analysis of pendent groups formed when heating the TME/MBTS/sulfur/ZnO (33.9:1.1:1:1) system isothermally at 150°C: (□) TME-SBt; (■) TME-S<sub>2</sub>Bt; (△) TME-S<sub>3</sub>Bt; (▲) TME-S<sub>4</sub>Bt; (◇) TME-S<sub>5</sub>Bt; (◆) TME-S<sub>6</sub>Bt.

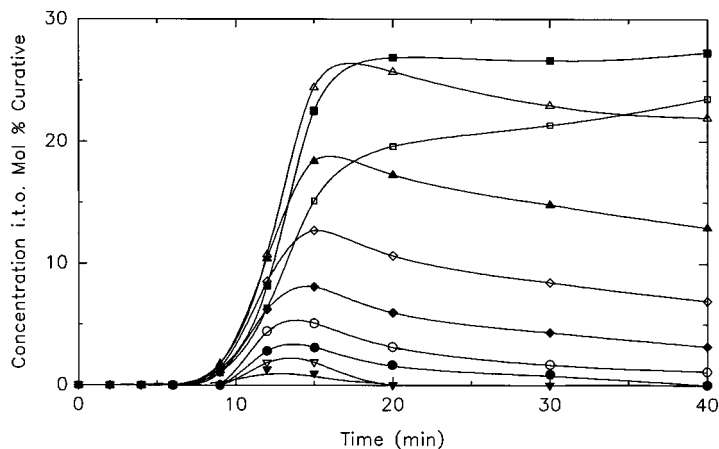
produced slowly during the initial stages of the reaction (Fig. 3), while the MBTP concentrations were low, and reaction accelerated as the MBTP concentration increased (Fig. 2). TME-S<sub>2</sub>Bt was formed before the higher sulfurated pendent groups as BtS<sub>3</sub>Bt was the most abundant MBTP (Fig. 2 and ref. 13) Polysulfidic benzothiazole-terminated pendent groups with a sulfur content of up to 5 were detected. Rapid consumption was evident after 12 min and no pendent groups were detected after 30 min, other than the monosulfidic benzothiazole-terminated pendent group, although it only formed in trace amounts and attained a concentration of 1.7 mol % after 40 min.

As in the absence of ZnO,<sup>13</sup> MBTP liberated MBT on forming benzothiazole-terminated pendent groups (Fig. 1). MBT was produced after 2 min and its formation initially followed that of pendent group formation. As ZnO is present, it may trap MBT as Zn(mbt)<sub>2</sub>, which can act as an accelerator in its own right as discussed earlier.<sup>7</sup> If all benzothiazole groups in MBTS were converted to MBT, this would equate to 100 mol % MBT in Figure 1. It can be seen that up to 80 mol % MBT remained extractable, which implies that no more than 20 mol % was trapped as Zn(mbt)<sub>2</sub>. This observation is in line with other articles<sup>1,7,9</sup> where an interfacial reaction, leading to a layer of insoluble Zn(mbt)<sub>2</sub> at the ZnO particle surface, was suggested.

Crosslinking initiated between 6 and 9 min and thereafter rapidly accelerated (Fig. 4). Crosslinking slowed dramatically after 15 min, at which time all the MBTS and most of the sulfur had been consumed. The concentration of all

crosslinked products consisting of more than two sulfur atoms decreased in concentration after 15 min. The monosulfide was the only crosslinked product that continued to increase in concentration throughout the reaction. <sup>1</sup>H-NMR showed all crosslinked products to be bis(alkenyl) in nature.

Crosslinking is commonly said to result from pendent group-pendent group and pendent group-chain reactions.<sup>22</sup> However, it was shown earlier<sup>13</sup> that these reactions are slow and that in MBTS-accelerated sulfur vulcanization crosslinking results from the combination of benzothiazole-terminated and hydrogen-terminated polysulfidic pendent groups. In the presence of ZnO, the crosslinking reaction, once initiated, is too fast (Fig. 4) to form via this route alone. Clearly, for such a rapid reaction, both benzothiazole- and hydrogen-terminated pendent groups would have to form very rapidly. It was proposed<sup>21</sup> that in MBT-accelerated sulfur vulcanization hydrogen-terminated pendent groups formed by BtS<sub>x</sub>H reacting with TME, but as BtS<sub>x</sub>H reacts rapidly with MBTS to form MBTP,<sup>23</sup> the reaction with TME to form hydrogen-terminated pendent groups will occur only once the MBTS concentration is low. The formation of hydrogen-terminated pendent groups in MBT-accelerated sulfur vulcanization is not very rapid,<sup>21</sup> and it can be questioned whether the MBT concentration (0.77 mol/33.9 mol TME) at 12 min, the point at which crosslinking is rapid, is sufficient to ensure the rapid reaction observed. Zn(mbt)<sub>2</sub> was shown to vulcanize TME rapidly after a 4-min induction period<sup>7</sup> and, thus, once formed, Zn(mbt)<sub>2</sub> will ensure the rapid formation of crosslinked products via zinc-con-



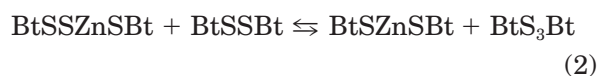
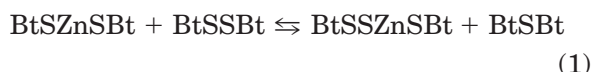
**Figure 4** HPLC analysis of crosslinked products formed when heating the TME/MBTS/sulfur/ZnO (33.9:1.1:1:1) system isothermally at 150°C: (□) TME-S-TME; (■) TME-S<sub>2</sub>-TME; (△) TME-S<sub>3</sub>-TME; (▲) TME-S<sub>4</sub>-TME; (◇) TME-S<sub>5</sub>-TME; (◆) TME-S<sub>6</sub>-TME; (○) TME-S<sub>7</sub>-TME; (●) TME-S<sub>8</sub>-TME; (▽) TME-S<sub>9</sub>-TME; (▼) TME-S<sub>10</sub>-TME.

taining pendent groups as discussed in the second article in this series.<sup>7</sup>

### Synergism

MBTS is consumed more rapidly than in the absence of ZnO, while sulfur consumption and crosslinked product formation occurred more rapidly than in either the MBTS-accelerated (ref. 13) or Zn(mbt)<sub>2</sub>-accelerated (ref. 7) reaction. The decrease of pendent groups to produce crosslinked products differed from the TME/MBTS/sulfur system<sup>13</sup> in that, in the absence of ZnO, the pendent group concentration only started to decrease after 15 min, at which stage they had attained an additive concentration of 26 mol %, while in the presence of ZnO, they were consumed rapidly after 6 min (Fig. 1). The difference can be ascribed to the formation of Zn(mbt)<sub>2</sub>. Thus, while MBTS affected the Zn(mbt)<sub>2</sub>-accelerated reaction, Zn(mbt)<sub>2</sub> also influenced the MBTS reaction, pointing to a synergistic effect between the accelerators.

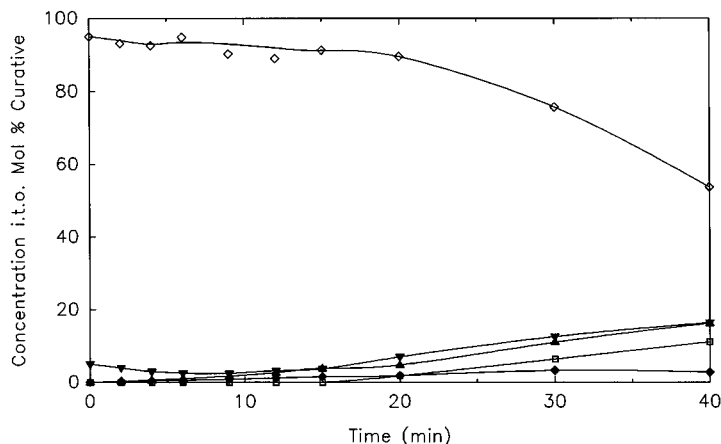
As proposed earlier,<sup>5</sup> ZnO facilitates MBTP formation by opening the cyclic sulfur ring, allowing more rapid sulfuration of MBTS. The liberation of MBT in pendent group formation will result in Zn(mbt)<sub>2</sub>, which can further promote MBTP formation by exchange reactions with MBTS [reactions (1) and (2)]<sup>5</sup>:



Acceleration of MBTP formation by Zn(mbt)<sub>2</sub> is much greater than is acceleration by ZnO, which increases MBTP formation by activating cyclic sulfur.<sup>5</sup> However, in the presence of sulfur, MBTP formation is rapid and, consequently, is less markedly influenced by Zn(mbt)<sub>2</sub> addition. Reaction (2) is reversible and it is equally likely that MBTP formation accelerates Zn(mbt)<sub>2</sub> sulfuration. Furthermore, MBT was found to accelerate Zn(mbt)<sub>2</sub> vulcanization<sup>7</sup> and this was attributed to sulfuration of Zn(mbt)<sub>2</sub> by BtS<sub>x</sub>H, formed by the interaction of MBT with cyclic sulfur. Exchange of MBTS with sulfurated Zn(mbt)<sub>2</sub> will further accelerate MBTP formation. BtS<sub>x</sub>H also exchanges with MBTS to accelerate MBTP formation.<sup>23</sup> The net result of these very rapid exchange reactions will be to facilitate the buildup of MBTP and the formation of sulfurated Zn(mbt)<sub>2</sub>, which has a transient existence only.

Apart from catalyzing the formation of the active sulfurating agent (MBTP) for MBTS-accelerated sulfur vulcanization (cf. Fig. 7 with Fig. 2 and Fig. 2 in ref. 13), Zn(mbt)<sub>2</sub> promotes the crosslinking of benzothiazole-terminated pendent groups resulting from the MBTP interaction with the model compound (cf. Fig. 8 with Fig. 3 and Fig. 3 in ref. 13 and Fig. 9 with Fig. 4 and Fig. 5 in ref. 13). It was shown in an earlier article<sup>7</sup> that Zn(mbt)<sub>2</sub> decreases the benzothiazole-terminated





**Figure 5** HPLC analysis of the TME/MBTS/Zn(mbt)<sub>2</sub> (33.9:1.1:1) system heated isothermally at 150°C: (▼) MBT; (◇) MBTS; (▲) MBTM; (■) sulfur; (◆) sum of BtS<sub>x</sub>Bt ( $x = 3-4$ ); (□) sum of TME-S<sub>x</sub>Bt ( $x = 1-5$ ).

pendent group concentration on heating TME-S<sub>2</sub>Bt with sulfur, while in the absence of Zn(mbt)<sub>2</sub>, little reaction occurs. Thus, Zn(mbt)<sub>2</sub> catalyzes two stages of the MBTS-accelerated reaction (MBTP formation and pendent group crosslinking), while the formation of Zn(mbt)<sub>2</sub> and its sulfuration are a direct consequence of pendent group formation initiated by the MBTS-accelerated reaction. The possibility of an interaction between Zn(mbt)<sub>2</sub> and pendent groups was reported by Morrison et al.<sup>11,16,17</sup> In tetramethylthiuram disulfide (TMTD)-accelerated systems also, zinc stearate, Zn<sub>2</sub>(dmtc)<sub>4</sub>, and ZnO were shown to facilitate crosslinking reactions,<sup>19</sup> the efficiency of the zinc complex decreasing in the order shown. Zinc stearate was also shown to accelerate the crosslinking of MBTS-accelerated sulfur systems, leading to much higher crosslink densities.<sup>20</sup> A concerted mechanism, involving the interaction of Zn<sup>2+</sup> with the electronegative nitrogen atom in the benzothiazole group or the C=S sulfur in the thiuram, and between similar atoms in the ligand on the zinc-accelerator complex and a hydrogen on a neighboring chain, was proposed.<sup>20</sup>

Gradwell and McGill<sup>1</sup> noted that in IR vulcanizates the ratio of crosslinks to MBT liberated was much higher on addition of ZnO to the compound. They suggested that a considerable amount of cyclization occurred in the absence of ZnO, and as the crosslink density was appreciably higher with ZnO, it was proposed that ZnO reduced these cyclization reactions, and instead of cyclizing, pendent groups crosslinked. In IR compounds, MBT was not detected on pendent group

formation and limited Zn(mbt)<sub>2</sub> formation occurred only on crosslinking when MBT was released.

### H<sub>2</sub>S Formation

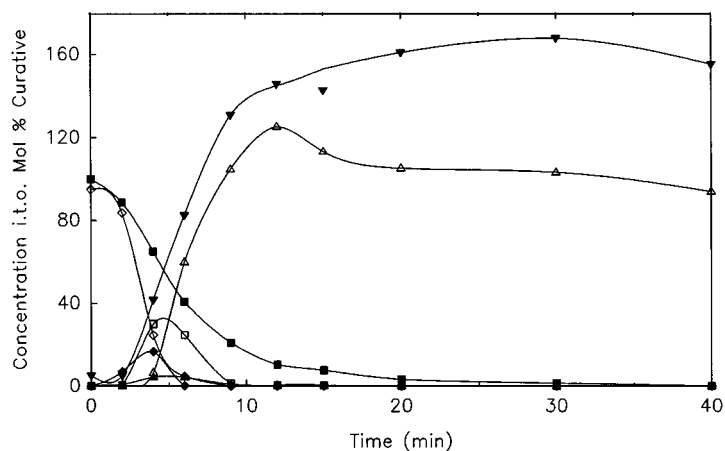
H<sub>2</sub>S does not form in MBTS-accelerated sulfur vulcanization<sup>13</sup> but does form in Zn(mbt)<sub>2</sub> vulcanization.<sup>7</sup> As Zn(mbt)<sub>2</sub>-accelerated sulfur vulcanization contributes to the crosslinking process in the TME/MBTS/sulfur/ZnO system, H<sub>2</sub>S formation can be ascribed to the latter reaction.

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

On heating at 150°C for 40 min, no crosslinked products were formed, although slightly larger concentrations of MBTP and pendent groups were observed when compared to the system containing ZnO. This is consistent with the increased formation of MBTP in ZnO-containing systems in the absence of TME<sup>5</sup> and can be ascribed to exchange reactions (1) and (2). Benzothiazole-terminated pendent groups were produced after 15 min and molecules with a sulfur rank of up to 5 were observed (Fig. 5). MBT was released on pendent group formation.

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

Both MBTS and Zn(mbt)<sub>2</sub> are accelerators for vulcanization in the presence of sulfur, although the reaction mechanisms are quite different, the MBTS reaction occurring via benzothiazole-terminated pendent groups,<sup>13</sup> and the Zn(mbt)<sub>2</sub> reaction, via zinc-containing pendent groups.<sup>7</sup> With



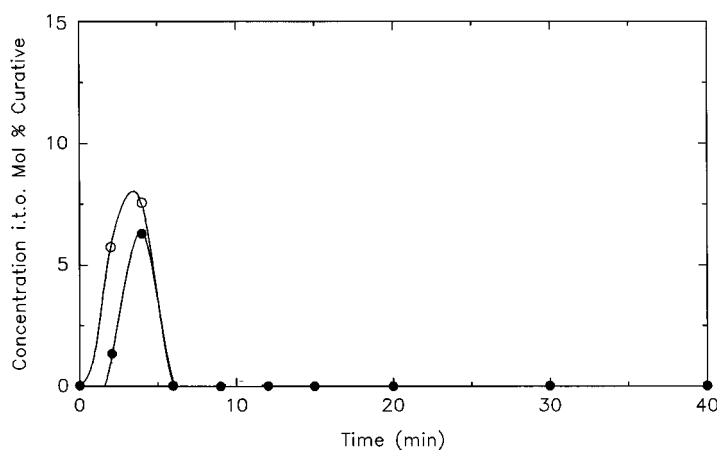
**Figure 6** HPLC analysis of the TME/MBTS/Zn(mbt)<sub>2</sub>/sulfur (33.9:1.1:1:1) system heated isothermally at 150°C: (▼) MBT; (◇) MBTS; (▲) MBTM; (■) sulfur; (◆) sum of BtS<sub>x</sub>Bt (x = 3–4); (□) sum of TME–S<sub>x</sub>Bt (x = 1–7); (△) sum of TME–S<sub>x</sub>–TME (x = 1–10).

both accelerators present at the outset, the reaction proceeded at a greater rate than with either single accelerator, confirming the synergistic effects discussed above. MBTS vulcanized TME after 15 min,<sup>13</sup> and Zn(mbt)<sub>2</sub>, after 4 min,<sup>7</sup> while in the above system, vulcanization occurred between 2 and 4 min (Fig 6).

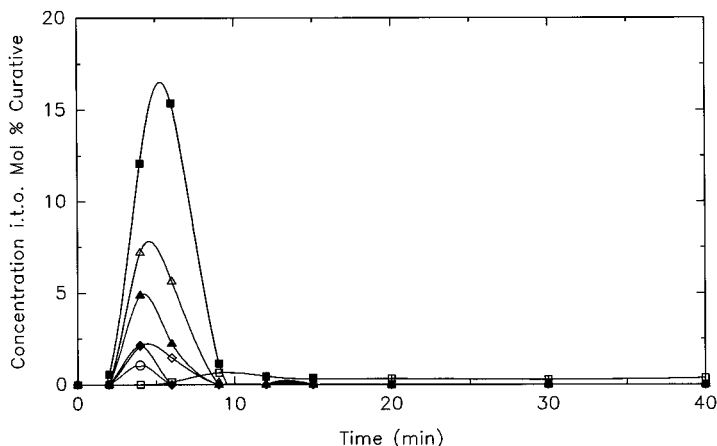
Both MBTS and sulfur were consumed extremely rapidly from the outset and resulted in the rapid production of MBTP, although only BtS<sub>3</sub>Bt and BtS<sub>4</sub>Bt were detected (Fig. 7). These rapidly reacted further, with complete consumption after 6 min. Rapid production of benzothiazole-terminated pendent groups was evident after 2 min. The lower sulfurated pendent groups were again in higher concentration (except for TME–

SBt) than the higher sulfur-ranked pendent groups, with TME–S<sub>2</sub>Bt being the most abundant (Fig. 8). Pendent groups with a sulfur rank of up to 8 were observed. MBT and H<sub>2</sub>S were released. [In terms of the method used to express the MBT concentration, the complete conversion of all benzothiazole groups in both MBTS and Zn(mbt)<sub>2</sub> would lead to 200 mol % MBT.] The formation of benzothiazole-terminated pendent groups is indicative of a contribution by the MBTS as an accelerator in the overall reaction, while the release of H<sub>2</sub>S shows that both MBTS- and the Zn(mbt)<sub>2</sub>-accelerated reactions contribute to cross-link formation.

The more rapid decrease in the concentration of benzothiazole-terminated pendent groups in



**Figure 7** HPLC analysis of MBTP formed when heating the TME/MBTS/Zn(mbt)<sub>2</sub>/sulfur (33.9:1.1:1:1) system isothermally at 150°C: (○) BtS<sub>3</sub>Bt; (●) BtS<sub>4</sub>Bt.

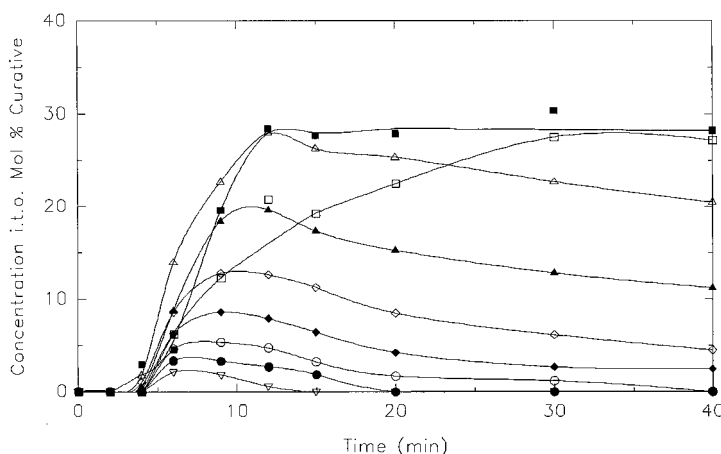


**Figure 8** HPLC analysis of pendent groups formed when heating the TME/MBTS/ $Zn(mbt)_2$ /sulfur (33.9:1.1:1:1) system isothermally at 150°C: (□) TME-SBt; (■) TME-S<sub>2</sub>Bt; (△) TME-S<sub>3</sub>Bt; (▲) TME-S<sub>4</sub>Bt; (◇) TME-S<sub>5</sub>Bt; (◆) TME-S<sub>6</sub>Bt; (○) TME-S<sub>7</sub>Bt.

this system compared to TME/MBTS/sulfur/ $ZnO$ , where  $Zn(mbt)_2$  first had to form in the reaction, suggests that  $Zn(mbt)_2$  is more reactive than is  $ZnO$ , which was present from the outset in the latter system, in catalyzing the crosslinking of pendent groups. This is in agreement with the greater efficiency of the zinc-accelerator complex versus  $ZnO$  in crosslinking pendent groups in tetramethylthiuram disulfide-accelerated systems.<sup>20</sup> The more rapid formation of MBTP and consumption of benzothiazole-terminated pendent groups shows the catalytic influence of  $Zn(mbt)_2$  in the

MBTS-accelerated reaction. Likewise, the shortening of the induction period of 5 min in the TME/ $Zn(mbt)_2$ /sulfur system to 4 min in the mixed accelerator system (Fig. 1) indicates the involvement of MBTS and its polysulfides in the sulfuration of  $Zn(mbt)_2$ . Synergism, as discussed earlier, applies.

A high concentration of crosslinked products developed (Fig. 9) and products with a maximum sulfuration of 10 were detected, although species with a lower sulfuration were the most abundant. Similar amounts of crosslinked products of differ-



**Figure 9** HPLC analysis of crosslinked products formed when heating the TME/MBTS/ $Zn(mbt)_2$ /sulfur (33.9:1.1:1:1) system isothermally 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; (▼) TME-S<sub>10</sub>-TME.



ent sulfur rank formed with MBTS,  $Zn(mbt)_2$ , and  $MBTS/Zn(mbt)_2$  as the accelerator, the main difference between the accelerator systems being in the rates of the crosslinking processes. Desulfuration was evident for all polysulfidic crosslinked products with a sulfur content greater than 2. Once again, the concentration of the monosulfidic crosslinked product continued to increase as the reaction progressed.

## CONCLUSIONS

MBT, released on pendent group formation by MBTP, reacts with ZnO to form  $Zn(mbt)_2$ . Interaction of MBT and MBTS with sulfur to form sulfurated species, and the exchange of ligands with  $Zn(mbt)_2$ , is proposed to facilitate sulfuration of the latter.  $Zn(mbt)_2$  acts as an accelerator in its own right, but also catalyzes the crosslinking of benzothiazole-terminated pendent groups formed in the MBTS-accelerated reaction. The crosslink density and relative amounts of crosslinked products of different sulfur rank obtained in MBTS-,  $Zn(mbt)_2$ -, and  $MBTS/Zn(mbt)_2$ -accelerated systems are similar.

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