

# Thiuram-Accelerated Sulfur Vulcanization. III. The Formation of Crosslinks

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## SYNOPSIS

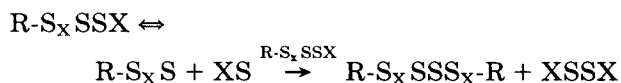
2,3-Dimethyl-2-butene (TME) was used as a model for polyisoprene in studying the formation of crosslinks in tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization. Mixtures of TME with TMTD, sulfur, and ZnO were heated in sealed tubes at 130°C for various times and the contents analyzed by HPLC. In the absence of ZnO crosslinking is delayed until most of the TMTD has been consumed. Crosslinking results from the interaction of thiuram and dimethylammonium pendent groups, tetramethylthiourea being formed as a byproduct. In the presence of ZnO two crosslinking reactions occur, viz (1) disproportionation between thiuram pendent groups, which gives TMTD as a byproduct; and (2) a zinc dimethyldithiocarbamate-catalyzed reaction between pendent groups and the olefin. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

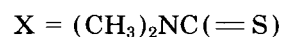
There are essentially two routes by which crosslinks can be formed in tetramethylthiuram (TMTD)-accelerated sulfur vulcanization.<sup>1-3</sup> The first route involves the disproportionation of two pendent groups on neighboring rubber chains to form a crosslink and a tetramethylthiuram monosulfide (TMTM), TMTD, or tetramethylthiuram polysulfide (TMTP) molecule, while crosslinking in the second route would proceed via an interaction between a pendent group and a neighboring chain.

It is generally accepted that TMTD-accelerated vulcanization in the absence of zinc is a free radical process. The first step requires the homolysis of S—S bonds in pendent groups to form thiuram persulfenyl (XS<sub>x</sub>) or thiuram sulfenyl (XS) radicals.<sup>4</sup> The disproportionation of pendent groups is the rate-determining step in thiuram-accelerated vulcanization.<sup>4-6</sup> These radicals could interact with another pendent group to form a polysulfidic crosslink and TMTD or TMTP. The disproportionation reaction would be consistent with the di-substitutive sulfur-ation pattern found in TMTD/ZnO vulcanization.<sup>7</sup>

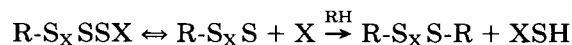
Crosslinking via this reaction would also account for the small quantities of TMTD that were always found in TMTD-based<sup>4</sup> cures.



where



Another route for crosslinking involves the abstraction of an allylic hydrogen atom from the IR chain by a sulfenyl radical, followed by the combination of the remaining thiuram persulfenyl and polyisoprenyl radicals to regenerate a pendent group. This would be extremely fast and can be viewed as an irreversible, concerted reaction without the formation of a true alkenyl radical intermediate.<sup>4</sup>



where

RH = rubber chain

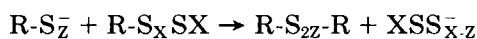
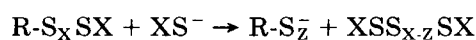
XSH = dimethyldithiocarbamic acid (Hdmtc)

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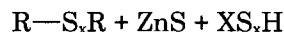
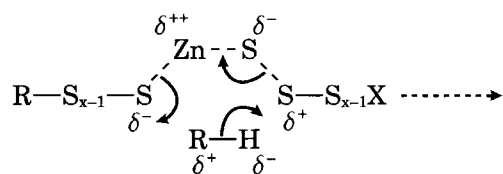
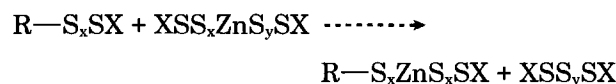
**Table I** Compositions of Mixtures Reacted

Composition	Mass (g)	Mol Ratio
a) TME/TMTD/Sulfur		
TME	0.710	34.0
TMTD	0.07	1.1
Sulfur	0.06	1.0
b) TME/TMTD/Sulfur/ZnO		
TME	0.710	34.0
TMTD	0.070	1.1
Sulfur	0.060	1.0
ZnO	0.213	10.5

In the presence of ZnO two reactions, both involving zinc dimethyldithiocarbamate ( $Zn_2(dmtc)_4$ ), have been proposed. In the first, the disproportionation of two rubber-bound intermediate compounds is catalyzed by thiuram sulfenyl or thiuram persulfenyl anions derived from  $Zn_2(dmtc)_4$ .<sup>3,7</sup>



Crosslinking in the second reaction is preceded by an interchange between the pendent group and the zinc perthiomercaptide to facilitate further sulfuration of the olefin, followed by reaction with the rubber chain.<sup>3,7</sup>



Zinc perthiomercaptides are a key intermediate in the NR/PRA reaction scheme for thiuram- and zinc dithiocarbamate-related vulcanization.<sup>3</sup> Their presence is largely based on circumstantial evidence though. We have reported<sup>8,9</sup> that there was no indication of zinc perthiomercaptides performing the role of active sulfurating agents in thiuram-accelerated sulfur vulcanization. Studies by Moore et al.<sup>10</sup> and Scheele et al.<sup>11</sup> indicated that the rate of  $Zn_2(dmtc)_4$  formation paralleled the rate of crosslinking in IR/TMTD/ZnO and NR/TMTD/ZnO vulcanization. This implies that  $Zn_2(dmtc)_4$  is

formed as a direct consequence of crosslink formation rather than as a precursor for crosslinks. Koenig et al.<sup>12</sup> and Kruger and McGill<sup>13</sup> also expressed the opinion that  $Zn_2(dmtc)_4$  or zinc perthiomercaptides were not formed prior to vulcanization.

This article reports on the reactions that lead to crosslinks both in the absence and presence of ZnO.

## EXPERIMENTAL

### Materials

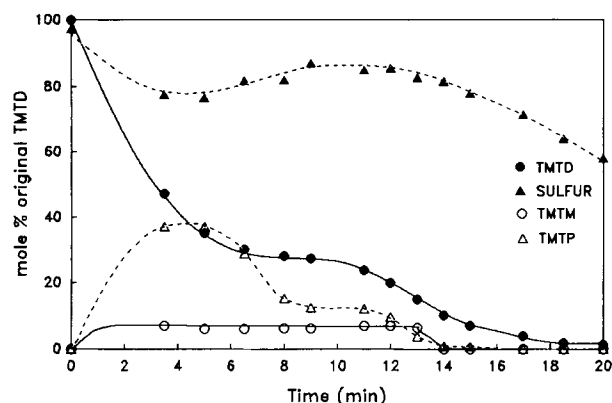
TMTD (Orac TMTD, chemical purity 97%, Orchem, SA), TMTM (vulkacit Thiuram MS, chemical purity 97.9%, Bayer, Germany), tetramethylthiourea (TMTU) (chemical purity 98%, Aldrich Chemical Co., Milwaukee, WI),  $Zn_2(dmtc)_4$  (vulkacit L, active ingredient 95%, Bayer, Germany) and 2,3-dimethyl-2-butene (TME) (chemical purity 99+%, Aldrich Chemical Co.).

The compositions of mixes used in model compound vulcanization are shown in Table I (1 mL TME = 0.709 g). The reactions were conducted in sealed tubes at 130°C and the mixture analyzed by HPLC as described earlier.<sup>9,14</sup>

To clarify aspects of the reaction a series of experiments were conducted in which the reaction was interrupted and certain reagents added to the reaction mixture. Thus, the appropriate mass of the compounded curative mixture (i) (Table II) and the required volume of TME were transferred into glass tubes, which were subsequently evacuated and sealed. The reaction mixture was maintained at 130°C for 13 min in an oil bath. The reaction vessel was removed after this time period, cooled in liquid nitrogen to quench the reaction, and opened. The appropriate curatives (ii) (Table II) were added to the reaction mixture in the vessel after it had reached room temperature. The reaction vessel was

**Table II** Compositions of Mixtures in Interrupted Reactions

Composition	Mass (g)	Mol Ratio
i) TME/TMTD/Sulfur		
TME	0.71	34.0
TMTD	0.07	1.1
Sulfur	0.06	1.0
ii) Added Curatives		
Control		
$Zn_2(dmtc)_4$	0.04	0.5
Me <sub>2</sub> NH	see text	

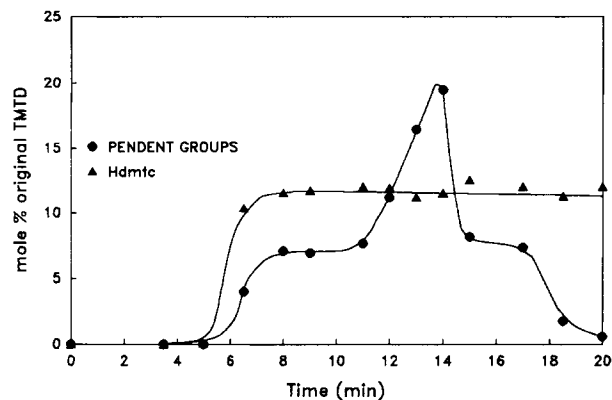


**Figure 1** HPLC analysis of reactants and products in TME/TMTD/sulfur vulcanization.

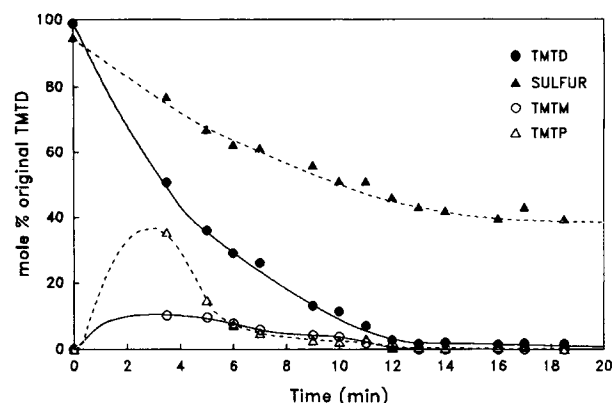
subsequently resealed under vacuum and subjected to further heating for preset time periods. Anhydrous dimethylamine ( $\text{Me}_2\text{NH}$ ) (approx. 0.5 mL) was added while the reaction vessel was in an ice bath. Due to the volatility of the amine (bp  $8^\circ\text{C}$ ), accurate and reproducible amounts could not be added. Exactly the same procedure was followed in the case of the control experiment, except that no further curatives were added after the reaction vessel was opened.

The concentrations of reactants, intermediates, and products are expressed in terms of the initial mol concentration of reactant, i.e., as the mol % reactant remaining, or mol % intermediate/product formed from that reactant.

In a preceding article<sup>9</sup> we reported on the formation of crosslink precursors (pendent groups) in thiuram-accelerated sulfur vulcanization and we now consider their reaction to form crosslinks between molecules.



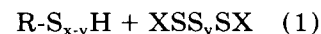
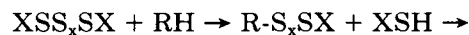
**Figure 2** HPLC analyses of pendent groups and Hdmtc in TME/TMTD/sulfur vulcanization.



**Figure 3** HPLC analyses of reactants and products in TME/TMTD/sulfur/ZnO vulcanization.

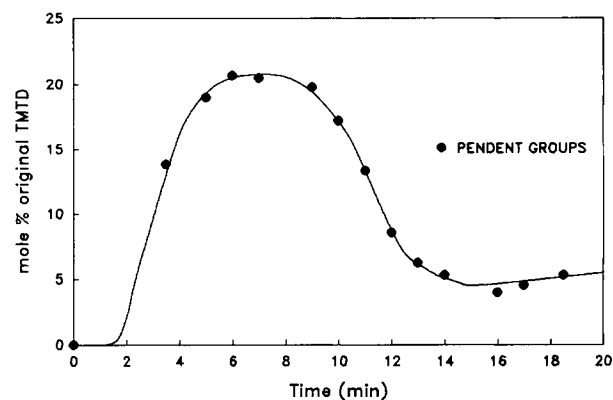
## RESULTS AND DISCUSSION

TMTD, which are the active sulfurating agents in TMTD-based cures,<sup>9</sup> both in the presence and absence of ZnO, react with TME to form thiuram pendent groups (Figs. 1 and 2 and Figs. 3 and 4). In the absence of ZnO these exchange with Hdmtc, liberated on pendent groups formation, to yield thiol pendent groups and TMTD.<sup>9</sup>

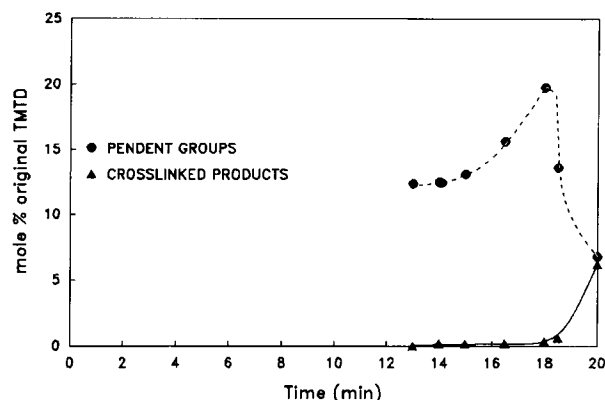


In the presence of ZnO, Hdmtc is trapped as  $\text{Zn}_2(\text{dmtc})_4$ , limiting the formation of thiol pendent groups.

The continued decrease in the TMTD concentration shows that the new thiuram pendent groups are constantly produced. These subsequently undergo Hdmtc exchange to form thiol pendent groups.

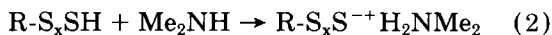


**Figure 4** HPLC analyses of pendent groups in TME/TMTD/sulfur/ZnO vulcanization.



**Figure 5** HPLC analyses of pendent groups and crosslinked products after interruption of the reaction in TME/TMTD/sulfur vulcanization.

The UV response of the latter would be weak compared to thiuram groups containing UV-active accelerator fragments, and the detectable pendent group concentration, as determined by HPLC, will, therefore, remain essentially constant. It was suggested<sup>9</sup> that towards the end of the plateau region in TMTD concentration (Fig. 1), the concentrations of thiuram sulfenyl and persulfenyl radicals decreases to the point where more and more radicals would decompose to dimethylamino radicals ( $\text{Me}_2\text{N}$ ), recombination of radicals being less favorable. The highly electronegative nitrogen on the  $\text{Me}_2\text{N}$  radical may abstract hydrogen from alkenes to form  $\text{Me}_2\text{NH}$  that reacts with thiol pendent groups to form amine-terminated thiol pendent groups (dimethylammonium pendent groups).



where  $^{+}\text{H}_2\text{NMe}_2$  = dimethylammonium.

Charge transfer complexes have a high UV extinction coefficient. The apparent increase in the pendent group concentration as the reaction progresses (Fig. 2) can largely be ascribed to the change in the nature of existing pendent groups, rather than the formation of new pendent groups.

### The reaction of $\text{Me}_2\text{NH}$

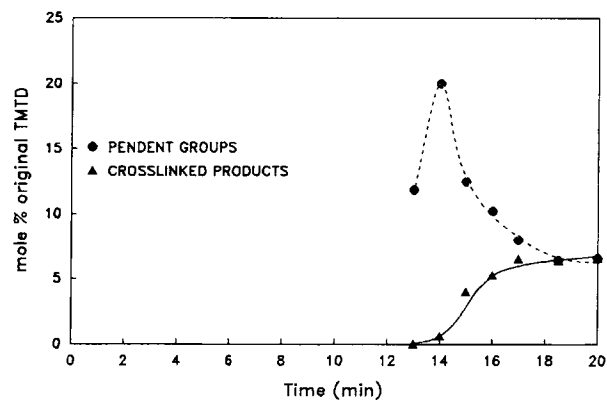
A study of the reaction of intermediate products provides further support for the proposed pendent group- $\text{Me}_2\text{NH}$  interaction. TME/TMTD/sulfur mixtures were heated at  $130^\circ\text{C}$  for 13 min. A high concentration of pendent groups exists in the system at this stage of the reaction. Based on our postulate, most of the detectable pendent groups (Fig. 2) will be dimethylammonium terminated. The concentra-

tion of thiuram pendent groups will be low due to pendent group exchange with Hdmtc and a high concentration of thiol pendent groups is expected, but they are not detectable.

$\text{Me}_2\text{NH}$  was added to the cooled product mixture in the reaction vessel after 13 min at  $130^\circ\text{C}$ . The vessel was resealed under vacuum and subjected to further heating. In the control experiment the reaction vessels were opened and then resealed under vacuum without the addition of further curatives. The procedure was followed to ensure an accurate and comparable control. The same time scale was used in graphical representations of the TME/TMTD/sulfur, control, and amine additive reactions. The graph data points at 13 min in the latter (e.g., Fig. 5), therefore, represents the time at which the reaction was restarted, i.e., 0 min.

As noted, reaction vessels were evacuated during the resealing process.  $\text{Me}_2\text{NH}$  is extremely volatile (b.p.  $8^\circ\text{C}$ ) and the decrease in pressure will result in the evaporation of some amine. Some of the dimethylammonium pendent groups will be decomposed as a consequence and will be reconverted into thiol pendent groups. The UV response of these groups is low in comparison with dimethylammonium pendent groups. The concentration of detectable pendent groups reached a maximum at 13 min (Fig. 2). On opening and resealing the system the concentration of these groups in both the control sample and in that to which  $\text{Me}_2\text{NH}$  was added, was lower (Figs. 5 and 6).

There is a delay in crosslinking in the control system. As suggested above,  $\text{Me}_2\text{NH}$  will be produced upon sulfenyl radical decomposition, and interaction of  $\text{Me}_2\text{NH}$  with thiol pendent groups will yield dimethylammonium pendent groups. The concentration of detectable pendent groups is seen to increase



**Figure 6** HPLC analyses of pendent groups and crosslinked products after the addition of  $\text{Me}_2\text{NH}$  in TME/TMTD/sulfur vulcanization.

gradually (Fig. 5) and crosslinks are eventually formed.

In comparison, addition of  $\text{Me}_2\text{NH}$  to the system leads to a rapid reaction (Fig. 6). The detectable pendent group concentration increases rapidly on heating due to the added  $\text{Me}_2\text{NH}$ , which will react rapidly with thiol pendent groups and form dimethylammonium groups. Due to the high concentrations of reactive groups, crosslinking occurs almost immediately.

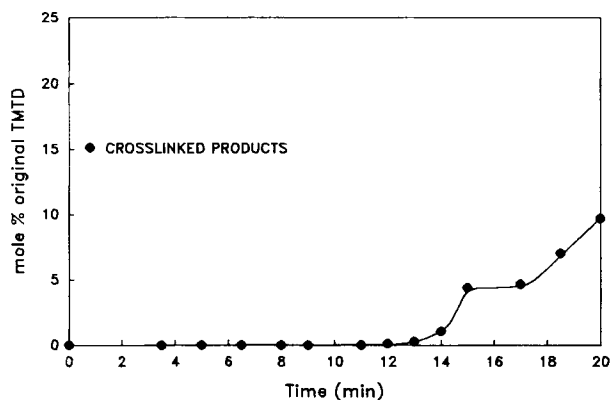
The above data suggests that thiol pendent groups are very unreactive compared to dimethylammonium pendent groups, crosslinking occurring as soon as there is a buildup of the latter.

### Formation of Crosslinks in the Absence of ZnO

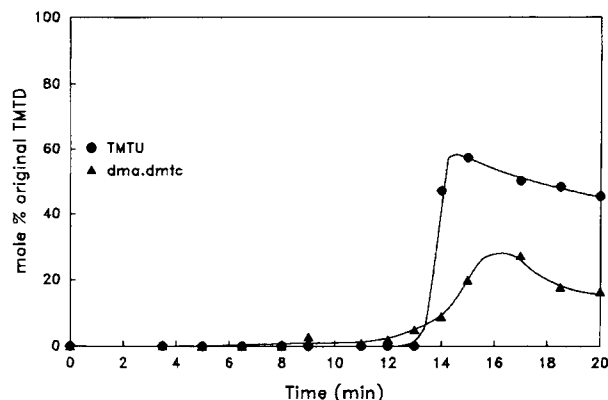
In order to form a crosslink, two model compound molecules or rubber chains must be in close proximity to each other. In rubber, certain measure of alignment of the chains must also occur to ensure the correct configuration of reactive pendent groups on the molecules.

Two facts are very noticeable regarding the crosslinking process. First, there is a delay in the onset of crosslinking (Fig. 7) until the further buildup of detectable pendent groups at 13 min, this buildup being attributed to the formation of dimethylammonium pendent groups (Fig. 2). This implies that thiol pendent groups are considerably less reactive. Second, TMTU is produced during the crosslinking reaction, specifically during the rapid consumption of pendent groups (cf. Figs. 2, 7, and 8).

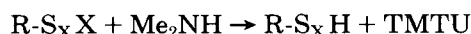
TMTU formation has been attributed to the attack of  $\text{Me}_2\text{NH}$  (originating from the decomposition of Hdmtc) on TMTD<sup>15-17</sup> and thiuram pendent groups.<sup>18</sup>



**Figure 7** HPLC analyses crosslinked products in TME/TMTD/sulfur vulcanization.



**Figure 8** HPLC analyses of TMTU and dma.dmtc in TME/TMTD/sulfur vulcanization.



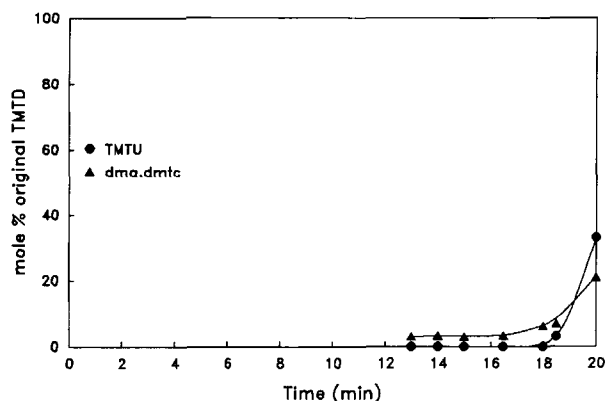
The coincidence of TMTU and crosslink formation is striking though. It was suggested earlier that  $\text{Me}_2\text{NH}$  starts forming, but via XS and not XSH decomposition as previously proposed.<sup>15-17</sup> The absence of TMTU prior to crosslinking (before 13 min) indicates that  $\text{Me}_2\text{NH}$  adds preferentially to thiol pendent groups rather than attacks TMTD.

It is proposed that crosslinks are formed via a rapid reaction between dimethylammonium and newly formed thiuram pendent groups, before the latter can exchange with Hdmtc. TMTU will be liberated in such a reaction.



Comparison of the control experiment, and that to which  $\text{Me}_2\text{NH}$  was added after 13 min at 130°C (cf. Figs. 5 and 6), indicates a rapid increase in the pendent group concentration upon the addition of  $\text{Me}_2\text{NH}$ . Crosslink formation is consequently accelerated. TMTU is formed as a product of the crosslinking reaction (Figs. 9 and 10). The addition of  $\text{Me}_2\text{NH}$  does not lead to the immediate formation of TMTU;  $\text{Me}_2\text{NH}$  preferentially adds to the thiol pendent groups.

Crosslink formation is delayed in TMTD-based cures relative to ZnO-containing vulcanizates, and the extent of crosslinking (crosslink density) is substantially lower in the absence of ZnO.<sup>18</sup> This was attributed to the destruction of crosslink precursors by  $\text{Me}_2\text{NH}$  originating from the decompo-



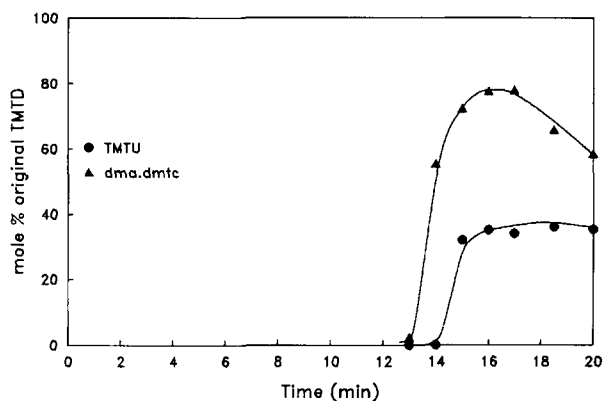
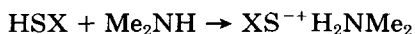
**Figure 9** HPLC analyses of TMTU and dma.dmtc after interruption of the reaction in TME/TMTD/sulfur vulcanization.

sition of Hdmtc in the absence of ZnO.<sup>18</sup> A delay in crosslink formation is also observed in TMTD-accelerated vulcanization of TME (Fig. 7) and we, too, propose the deactivation of pendent groups, but via a different route (reaction 2). Model compound data clearly show that TMTU does not form prior to crosslinking. Comparison of the crosslinked product concentrations in TME/TMTD/sulfur and TME/TMTD/sulfur/ZnO cures (Figs. 7 and 11) indicates though that similar crosslink densities are achieved in the final vulcanizates.

The difference between studies on model compounds and DSC studies conducted on rubber vulcanizates should be stressed. Model compound studies are conducted in closed systems and there is no possible escape of volatiles. This is not the case with curing in a DSC where significant mass losses<sup>19</sup> are detected in TMTD-based rubber vulcanization. Most of the pendent groups formed in TMTD vulcanization are deactivated by their exchange with Hdmtc<sup>9</sup> and in rubber cures (open system) Me<sub>2</sub>NH and CS<sub>2</sub>, produced during breakdown of sulfenyl radicals, will evaporate and reactivation of unreactive thiol pendent groups will not occur. The concentration of reactive pendent groups will be lower and will result in lower crosslink densities in the final vulcanizates.

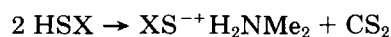
#### Dma.dmtc Formation

Certain other data also support the contention that thiol pendent groups trap Me<sub>2</sub>NH. Dimethylammonium dimethyldithiocarbamate (dma.dmtc) is formed in the reaction between Me<sub>2</sub>NH and Hdmtc

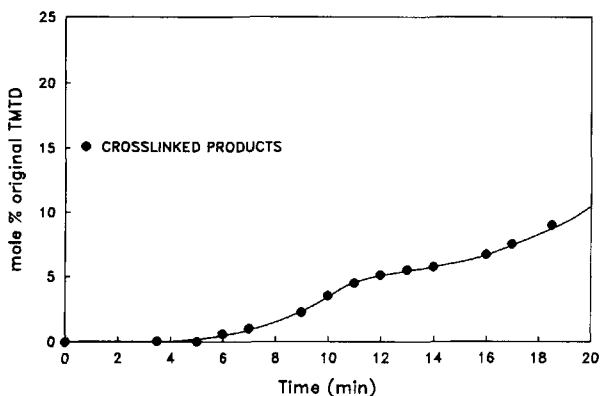


**Figure 10** HPLC analyses of TMTU and dma.dmtc after the addition of Me<sub>2</sub>NH in TME/TMTD/sulfur vulcanization.

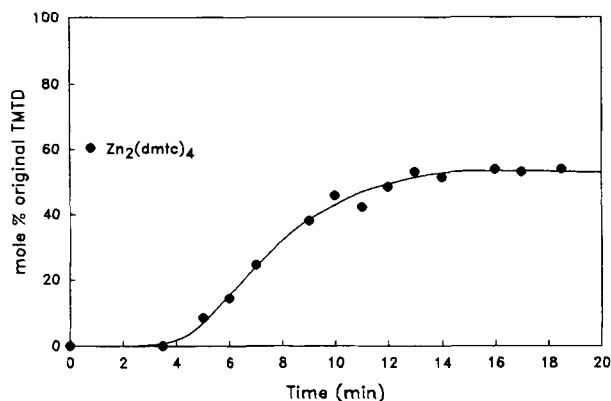
and from the reaction of two Hdmtc molecules<sup>20</sup>



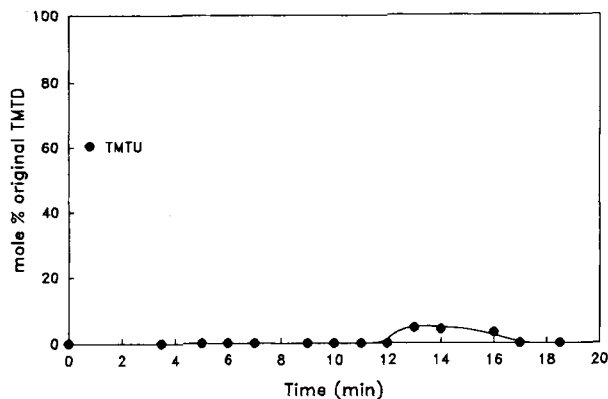
Dma.dmtc is formed in TMTD-accelerated vulcanization but no dma.dmtc is produced (via the second reaction) in the early stages of vulcanization; Hdmtc preferentially participates in exchange reactions with thiuram pendent groups to form thiols. The rate of formation of dma.dmtc is slow compared to the formation of dimethylammonium pendent groups (cf. Figs. 2 and 8), but increases during crosslinking when dimethylammonium pendent groups, and by implication thiol pendent groups, are rapidly consumed. Reaction between Me<sub>2</sub>NH and Hdmtc now occurs more readily. Higher concentrations of dma.dmtc are formed in the presence of added amine, compared to the TME/TMTD/sulfur system where amine is produced upon thiuram radical decomposition.



**Figure 11** HPLC analyses of crosslinked products in TME/TMTD/sulfur/ZnO vulcanization.



**Figure 12** HPLC analyses of  $Zn_2(dmtc)_4$  in TME/TMTD/sulfur/ZnO vulcanization.



**Figure 13** HPLC analyses of TMTU in TME/TMTD/sulfur/ZnO vulcanization.

### The Formation of Crosslinks in the Presence of ZnO

The onset of crosslinking in thiuram-based cures in the presence of ZnO is early compared to vulcanization in the absence of ZnO, but the rate of crosslink formation is more gradual (cf. Figs. 7 and 11).

Pendent groups are present in high concentrations in thiuram-based vulcanization with ZnO (Fig. 4). However, most of the Hdmtc produced during pendent group formation in TME/TMTD/sulfur/ZnO vulcanization is trapped in the form of  $Zn_2(dmtc)_4$  (Fig. 12) and limited pendent group-Hdmtc exchange occurs. This will allow crosslinking via pendent group disproportionation to occur at an earlier stage.

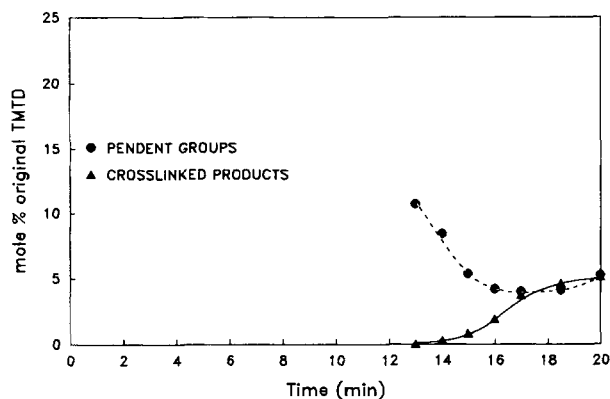
Thiuram radicals are present here, unlike in the TME/ $Zn_2(dmtc)_4$ /sulfur system,<sup>21</sup> and thiol pendent groups that do form are converted into dimethylammonium pendent groups later in the reaction. Though most of the crosslinks are formed via reaction between thiuram pendent groups, a small amount of TMTU is formed towards the end of the crosslinking reaction (Fig. 13).

In a series of experiments, mixtures of TME/TMTD/sulfur were heated at 130°C. The reactions were stopped after 13 min, at which point the dimethylammonium pendent group concentration would be high (Fig. 2).  $Zn_2(dmtc)_4$  was added to the mixtures in the reaction vessels. The vessels were subsequently resealed under vacuum and subjected to further heating. Earlier experiments, in which amine was added to the mixture (Figs. 5 and 6), showed that the concentration of detectable pendent groups increases until pendent group-pendent group crosslinking occurs. However, addition of  $Zn_2(dmtc)_4$  results in an immediate decrease in the detectable pendent group concentration (Fig. 14).

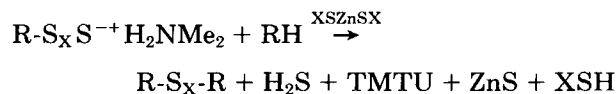
Pendent groups react immediately to form crosslinks in the presence of  $Zn_2(dmtc)_4$ , which acts as a catalyst.

No TMTU is formed in TME/ $Zn_2(dmtc)_4$ /sulfur vulcanization due to the absence of dimethylammonium pendent groups,<sup>21</sup> but TMTU is formed in the  $Zn_2(dmtc)_4$  additive reaction (Fig. 15). In the latter case, pendent groups were formed in the TME/TMTD/sulfur system and a high concentration of dimethylammonium pendent groups is present after 13 min.

Dimethylammonium pendent groups are formed in the reaction prior to  $Zn_2(dmtc)_4$  addition. The rapid decomposition, during crosslinking, of  $Zn_2(dmtc)_4$  which was added to the system, suggests rapid pendent group-chain rather than pendent group-pendent group crosslinking. The latter reaction<sup>9</sup> does not consume  $Zn_2(dmtc)_4$ . The overall reaction can be represented as follows:



**Figure 14** HPLC analyses of pendent groups and crosslinked products after the addition of  $Zn_2(dmtc)_4$  in TME/TMTD/sulfur vulcanization.



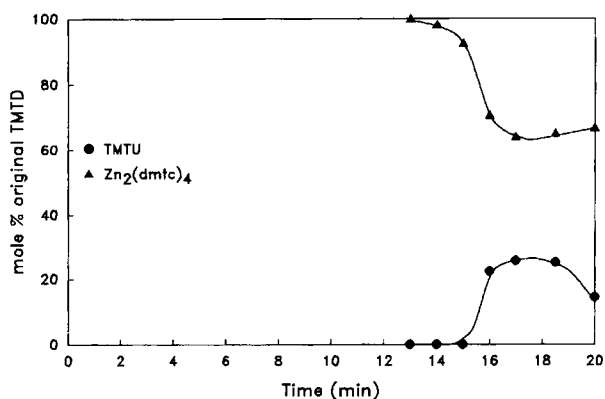
The role of  $\text{Zn}_2(\text{dmtc})_4$  produced during pendent group formation will be dealt with fully in Part 4.<sup>21</sup>

The reactivity of pendent groups is determined by the sulfur rank of the pendent group. The concentrations of the pendent groups decrease gradually as they are consumed (Fig. 16). Pentasulfidic pendent groups are the most reactive and participate first in crosslinking reactions, followed by tetra- and trisulfidic pendent groups.

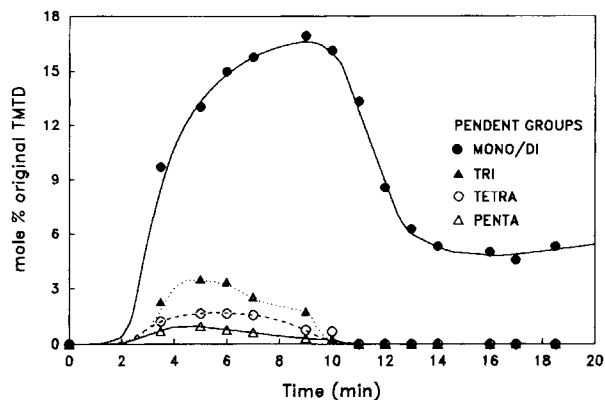
## CONCLUSIONS

Crosslink formation is delayed in thiuram-based cures in the absence of ZnO. Significant deactivation of pendent groups occurs and in the literature has been attributed to the destruction of crosslink precursors by  $\text{Me}_2\text{NH}$ , formed in the decomposition of Hdmtc. However, Hdmtc is stable under vulcanization conditions and participates in an exchange reaction with thiuram pendent groups to regenerate TMTD and to form unreactive thiol pendent groups, thus delaying crosslinking.

Initially thiuram sulfenyl and persulfenyl radicals are consumed, as TMTP, in the formation of pendent groups and Hdmtc. Once most of the TMTD has been consumed, the decrease in the concentration of thiuram radicals, originating from the homolysis of TMTD and scission of TMTP, leads to a lower probability of their recombining with XS or  $\text{XS}_x$  radicals and an increased likelihood of their decomposition into  $\text{Me}_2\text{N}$  radicals and  $\text{CS}_2$ . The highly electronegative  $\text{Me}_2\text{N}$  radicals abstract hy-



**Figure 15** HPLC analyses of TMTU and  $\text{Zn}_2(\text{dmtc})_4$  after the addition of  $\text{Zn}_2(\text{dmtc})_4$  in TME/TMTD/sulfur vulcanization.



**Figure 16** HPLC analyses of pendent groups in TME/TMTD/sulfur/ZnO vulcanization.

drogen from the model olefin to form  $\text{Me}_2\text{NH}$ .  $\text{Me}_2\text{NH}$  adds preferentially to thiol pendent groups to form reactive dimethylammonium pendent groups. Crosslinks are now formed via reaction between thiuram and dimethylammonium pendent groups, with the resultant formation of TMTU.

Deactivation of pendent groups through thiuram pendent group-Hdmtc exchange is limited in the presence of ZnO, which rapidly reacts with Hdmtc to form  $\text{Zn}_2(\text{dmtc})_4$  and  $\text{H}_2\text{O}$ . The onset of crosslinking is early compared to that in the absence of ZnO. Crosslinks are formed via two distinct processes. The first reaction involves the disproportionation of two pendent groups on neighboring olefin molecules (or rubber chains) to form a crosslink and TMTP. Crosslinks in the second reaction are formed via a  $\text{Zn}_2(\text{dmtc})_4$ -catalyzed reaction between pendent groups and free olefin.

Very little TMTU is produced upon crosslinking. Although reactivation of thiol pendent groups can take place, thiol group formation is limited because ZnO is an extremely efficient chemical trap for Hdmtc.

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