

Thiuram-Accelerated Sulfur Vulcanization. II. The Formation of Crosslink Precursors

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SYNOPSIS

2,3-Dibutyl-2-butene (TME) was used as a model for polyisoprene in studying the formation of pendent groups that act as precursors to crosslink formation during tetramethylthiuram disulfide (TMTD)-accelerated sulfur vulcanization. TME was heated at 130°C with TMTD, TMTD/sulfur, and TMTD/sulfur/ZnO in sealed tubes for various times, after which the mixture was analyzed by HPLC. Tetramethylthiuram monosulfide (TMTM) and tetramethylthiuram polysulfides (TMTP) formed rapidly. The rate at which these bound to the network could not be accounted for in terms of a free-radical mechanism, and a concerted mechanism was proposed. Dimethyldithiocarbamic acid (Hdmtc), a product of pendent group formation, is stable at vulcanization temperatures and does not decompose to dimethylamine. Instead, it exchanges with thiuram pendent groups. The resultant thiol pendent groups are unreactive and their formation delays the onset of crosslinking. After a few minutes at 130°C, there appears to be no further increase in the number of pendent groups, but this is due to the thiol groups being undetectable in the HPLC analyzer. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Network-bound accelerator residues, also referred to as pendent groups, are believed to originate from the reaction of the active sulfurating agent with the unsaturated rubber chain. Pendent groups have been observed in polyisoprene (IR) and in natural rubber/tetramethylthiuram disulfide (TMTD)/ZnO vulcanizates, as well as in model compound studies on zinc-containing vulcanization systems. They are considered to be the immediate precursors to crosslinking.¹⁻³

Kruger and McGill^{2,3} could not account for all of the initial TMTD in HPLC and TG analyses of the early stages of cure in IR/TMTD/sulfur and IR/TMTD/ZnO vulcanizates, and concluded that the TMTD unaccounted for was network bound. Higher proportions of nitrogen and sulfur were network bound in the early stages of IR/TMTD/ZnO cures,⁴ and is in agreement with earlier reports.^{5,6} The proportions decreased at a rate commensurate with the

formation of crosslinks. Model compound studies have confirmed the existence of rubber-bound intermediate compounds.^{1,7,8} The concentration of these species went through a maximum and decreased at longer reaction times due to their conversion into crosslinks.

Although extensive research in this field has been undertaken, it is still not clear whether the formation of the rubber-bound accelerator involves radical or polar intermediates, or a combination of both. Dogadkin,⁵ Craig,⁹ Scheele,¹⁰ Bevilacqua,¹¹ Blokh,¹² Ferington,¹³ and their co-workers have advanced a free-radical mechanism for the accelerated sulfur vulcanization of elastomers, while Coleman,¹⁴ Wolfe,¹⁵ Shelton,¹⁶ Manik,¹⁷ and their co-workers suggested that both free-radical and polar reactions occur.

Tetramethylthiuram polysulfide (TMTP) would undergo homolytic cleavage to yield thiuram persulfenyl (XS_x) radicals. Monosulfenyl radicals are well established as abstractors of hydrogen atoms,¹⁸ and it would be reasonable to assume that thiuram persulfenyl radicals would also abstract hydrogen from the IR chain. These radicals would react reversibly with the rubber to form polyisoprenyl rad-

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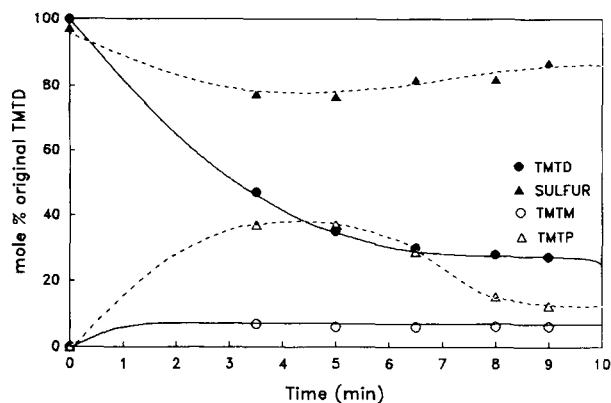


Figure 1 HPLC analyses of reactants and products in TME/TMTD/sulfur vulcanization.

the oil bath and cooling it in liquid nitrogen in order to quench any further reactions.

The reaction vessels were allowed to equilibrate to room temperature after liquid nitrogen cooling. The vessels were opened and the reaction mixture was dissolved in dichloromethane (approx. 15 mL). This solution was quantitatively transferred into a volumetric flask and diluted to 250 mL with methanol. The reaction products were analyzed by HPLC. The product analysis procedures have been described.²³

Retention times of peaks due to vulcanization intermediates (pendent groups) and crosslinked products in HPLC chromatograms of reaction mixtures were assigned by comparison with HPLC spectra of reaction products determined and published by Versloot et al.^{7,8}

Intermediates and reaction products that could not be isolated in sufficient purity, i.e., Hdmtc, pendent groups, and crosslinked products, were assigned the same extinction coefficients as the accelerator they were most closely related to. Changes in the concentration of these species as the reaction progresses are more important in the context of this study than the ability to quantify the formation of intermediates and products.

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.

RESULTS AND DISCUSSION

Vulcanization of TME with TMTD and sulfur in the presence and absence of ZnO was studied by

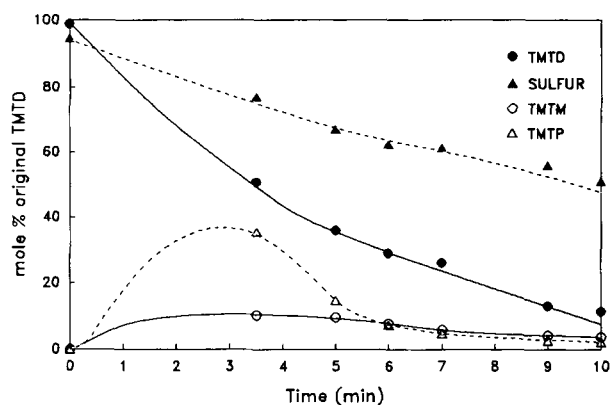


Figure 2 HPLC analyses of reactants and products in TME/TMTD/sulfur/ZnO vulcanization.

heating TME/TMTD/sulfur and TME/TMTD/sulfur/ZnO mixtures at 130°C for preset time periods. As in the absence of TME,^{23,24} TMTD and sulfur react rapidly to form TMTM and TMTP (Figs. 1 and 2). TMTP of sulfur rank 3–10 are detected, but most of the TMTP formed are trisulfidic and, to a lesser extent, tetrasulfidic. TMTP of higher sulfur rank are formed in much lower concentrations.

Formation of Crosslink Precursors

TMTP react with the model compound to form pendent groups and Hdmtc (Figs. 3 and 4). On the basis of ESR data¹⁴ it was postulated that the formation of pendent groups proceeds via a free-radical reaction, initiated by thiuram persulfenyl and thiuram sulfenyl radicals originating from thermal cleavage of S–S bonds in TMTP.

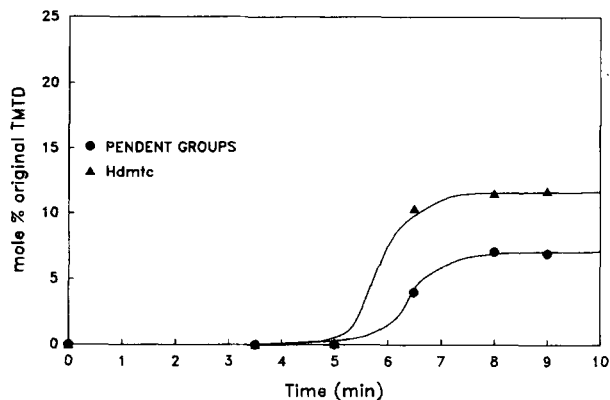
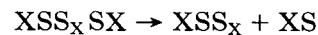


Figure 3 HPLC analyses of Hdmtc and pendent groups in TME/TMTD/sulfur vulcanization.

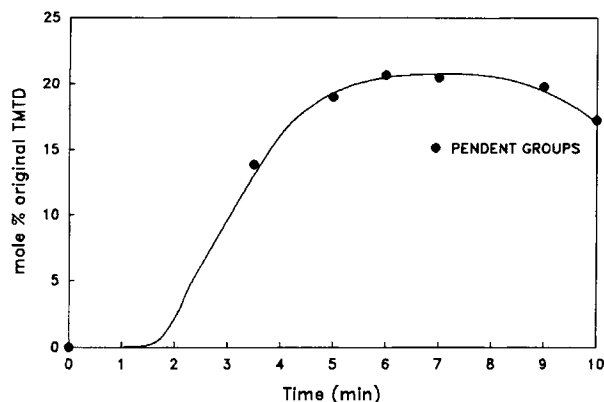
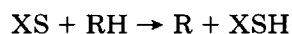


Figure 4 HPLC analyses of pendent groups in TME/TMTD/sulfur/ZnO vulcanization.

The sulfenyl radical is then said to abstract hydrogen from the chain to form Hdmtc and an isoprenyl radical, which recombines with the remaining persulfenyl radical to form a sulfurated pendent group.



The data in Figures 1 and 3 and Figures 2 and 4 clearly disprove this postulate.

Thiuram sulfenyl radicals are produced via the homolysis of TMTD at an early stage in the vulcanization reaction. Yet no early interaction between thiuram sulfenyl radicals and olefin molecules occurs, and this is confirmed by the absence of both Hdmtc and pendent groups in product mixtures at this stage. Thiuram radicals preferentially take part in sulfur extraction reactions and radical recombinations to form TMTP.²³ Pendent groups and Hdmtc are formed only once a high TMTP concentration is reached.

It is proposed that the formation of pendent groups proceeds via a concerted reaction involving TMTP and an allylic hydrogen of a model compound, with the resultant removal of the hydrogen atom as Hdmtc (reaction 1). Disulfidic pendent groups are formed first due to the presence of high concentrations of thiuram tri- relative to tetrasulfides, and especially the TMTP of higher sulfur rank. The rate of formation of the pendent groups of higher sulfur rank is much slower (Figures 5 and 6). The relatively high concentration of thiuram trisulfides also ensures that most of the pendent groups formed are disulfidic.

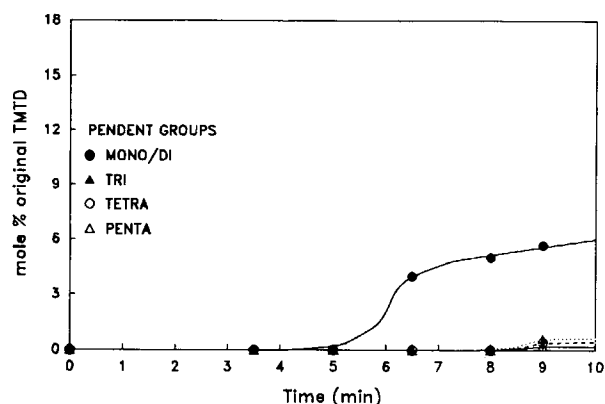
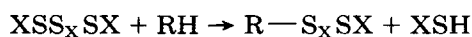


Figure 5 HPLC analyses of individual pendent groups in TME/TMTD/sulfur vulcanization.

It is suggested that the presence of thiuram persulfenyl and sulfenyl radicals in ESR spectra of TMTD-based vulcanizates can be ascribed to their generation during TMTP formation^{23,24} and not to their involvement in pendent group formation.

The onset of pendent group formation is earlier in the presence of zinc (cf. Figs. 3 and 4). The ZnO particle may facilitate interaction between TMTP and the olefin molecule by weakening the S-S bond in the TMTP molecule. Pendent group formation is a substitutive reaction (reaction 1), but Hdmtc is not observed in measurable quantities in the presence of ZnO.

Hdmtc Stability

Dogadkin et al.⁵ detected Me₂NH upon heating geraniol, isopropylbenzene, and NR with TMTD at 140°C, and ascribed its presence to the formation and subsequent decomposition of Hdmtc during vulcanization. The formation of TMTU in TMTD-

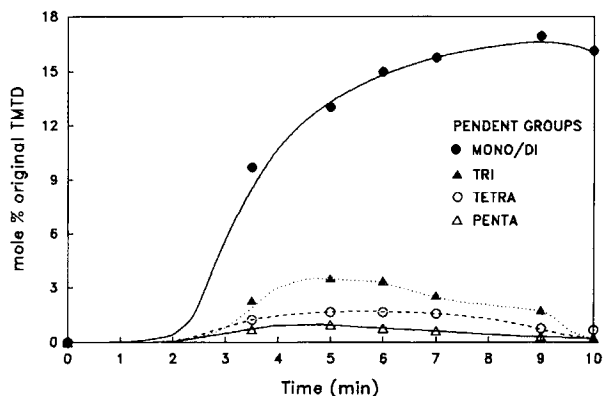


Figure 6 HPLC analyses of individual pendent groups in TME/TMTD/sulfur/ZnO vulcanization.

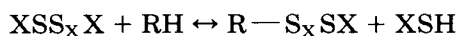
containing vulcanizates,^{25,27} as well as the induction period in TMTD-based cures,^{2,4,25} has been attributed to amine-catalyzed decomposition of thiuram curatives and crosslink precursors. The source of amine was reputed to be the decomposition of Hdmtc.

The reaction of Me₂NH with thiuram species was investigated by heating curative mixtures (approx. 1 g) with Me₂NH (approx. 0.5 mL) in evacuated sealed glass tubes at 150°C for 5 min. The results confirmed the findings of Delépine²⁶ in that TMTD and Me₂NH reacted to form TMTU and dimethylammonium dimethyldithiocarbamate (dma.dmtc) as the major products. Sulfur was detected in low concentrations. The same product spectrum was obtained with TMTM/Me₂NH, except that no sulfur was produced. The presence of sulfur did not affect the reaction of TMTD with Me₂NH (TMTD/sulfur 1 : 1 mol ratio), and TMTU and dma.dmtc were again the major reaction products.

Although there is a significant concentration of Hdmtc present after 12 min in the TME/TMTD/sulfur reaction, neither TMTU nor dma.dmtc was detected in the reaction mixture. This argues against the postulated decomposition (under the experimental conditions) of Hdmtc into Me₂NH and CS₂, since the reaction of Me₂NH with thiuram species would be very rapid.

Pendent Group-Hdmtc Interaction

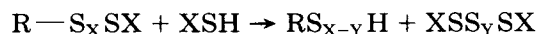
The high TMTP concentration in the early stages of the reaction ensures that pendent group formation proceeds at a fast rate. In the absence of ZnO, the rate of pendent group formation seemingly decreases with the decrease in TMTP concentration (after 5 min), and an apparent equilibrium situation is reached wherein the concentrations of TMTP, Hdmtc, and pendent groups remain essentially constant (Figs. 1 and 3). This would suggest a rapidly reversible reaction in the formation of pendent groups.



The formation of pendent groups proceeds via a concerted reaction in which S—S bonds are broken and new C—S bonds are formed with the removal of hydrogen. A reversible reaction would require breaking of the C—S bond between the thiuram persulfenyl fragment and the olefin. C—S bonds are much stronger than S—S bonds (dissociation energies: C—S = 698 kJ/mol, S—S = 425 kJ/mol),^{29,30}

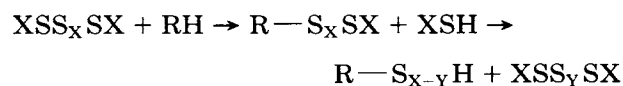
and it is, therefore, difficult to reconcile reverse substitution.

Instead, it is proposed that a rapid exchange between accelerator terminated pendent groups and Hdmtc occurs, involving the breaking of weaker S—S bonds rather than C—S bonds in pendent groups, and resulting in the reformation of TMTP (reaction 2).



TMTP are formed in high concentrations in the early stages of vulcanization. Upon pendent group formation the TMTP concentration decreases rapidly and the concentrations of Hdmtc and pendent groups increase correspondingly. With the increase in the Hdmtc concentration, exchange with pendent groups will accelerate. A dynamic situation is reached in which the rate of TMTP consumption to form pendent groups and Hdmtc equals the rate of reformation of TMTP due to Hdmtc exchange with pendent groups formed. Hence, the concentrations of both TMTP and Hdmtc will remain essentially constant.

The overall reaction can be represented as follows:



The continued decrease in TMTD concentration shows that new accelerator fragment terminated (thiuram) pendent groups are constantly produced. These subsequently undergo exchange with Hdmtc to produce hydrogen terminated (thiol) pendent groups. The UV response of thiol pendent groups, as opposed to thiuram pendent groups containing UV-active accelerator fragments, will be weak and the concentration of detectable pendent groups will remain essentially constant. (An HPLC peak, attributable to thiol pendent groups, was not detected in any of the reaction mixtures. However, it is also possible that these pendent groups coelute with thiuram pendent groups, thereby masking them in the HPLC chromatogram.)

This apparent equilibrium is not observed in the presence of ZnO. TMTD and TMTP are consumed at a much faster rate (cf. Figs. 1 and 2) and the concentration of detectable pendent groups increases rapidly (cf. Figs. 3 and 4). Pendent groups of high sulfur rank are detected in the early stages of vulcanization in the presence of ZnO. Exchange between thiuram pendent groups and Hdmtc will not occur because Hdmtc is removed by reaction

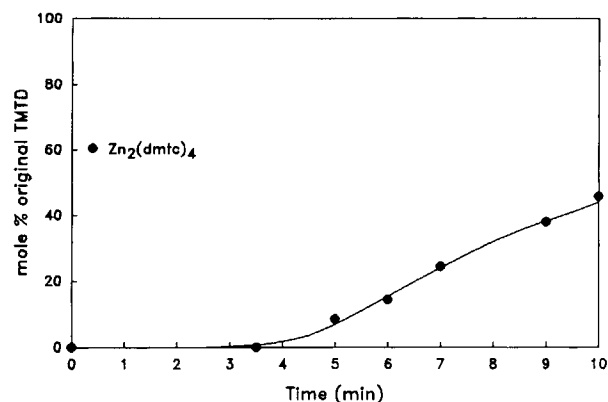


Figure 7 HPLC analyses of $Zn_2(dmtc)_4$ in TME/TMTD/sulfur/ZnO vulcanization.

with ZnO to form $Zn_2(dmtc)_4$ and H_2O (Fig. 7). Unreactive, undetectable thiol pendent groups are not produced in appreciable concentrations, and the detectable pendent group concentration will increase rapidly. The correspondingly rapid decrease in the TMTD and TMTP concentrations is attributed to their not being reformed. In the absence of ZnO, TMTD and TMTP are reformed in the exchange reaction that led to thiol pendent group formation.

The effect of Hdmtc removal, by ZnO, on the rate of pendent group formation and TMTP consumption is consistent with the above mechanism.

Formation of $Zn_2(dmtc)_4$

Thus, while $Zn_2(dmtc)_4$ is produced at an early stage in TME/TMTD/sulfur/ZnO vulcanization, zinc perthiomercaptides are not formed prior to the formation of pendent groups, but as a product of pendent group formation. $Zn_2(dmtc)_4$ does not result from direct interaction between TMTD and ZnO. TMTP are the active sulfurating species in thiuram-accelerated sulfur vulcanization in the presence of ZnO. This is consistent with our previous report.²⁴

Mixtures of TME/TMTD/sulfur/ZnS were vulcanized at 130°C. The reaction proceeds in an analogous manner to the TME/TMTD/sulfur/ZnO reaction. TMTD and sulfur react rapidly to form TMTM and TMTP (Fig. 8), and TMTD is consumed at a fast rate. No $Zn_2(dmtc)_4$ is produced at this stage of the reaction. The TMTP concentration passes through a maximum and then decreases as reaction with TME occurs. Pendent groups and Hdmtc are formed (Fig. 9).

Most of the Hdmtc is removed through reaction with ZnS to form $Zn_2(dmtc)_4$ and H_2S , and the curve of $Zn_2(dmtc)_4$ concentration parallels that of the

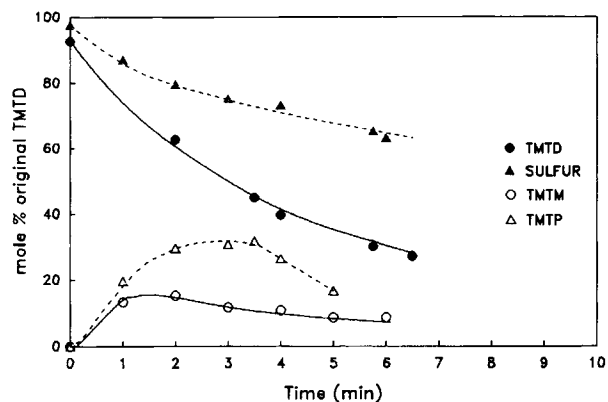


Figure 8 HPLC analyses of reactants and some products in TME/TMTD/sulfur/ZnS vulcanization.

pendent groups. ZnS is a less efficient acid trap than ZnO, and some Hdmtc is detected in the product spectrum (Fig. 9). $Zn_2(dmtc)_4$ is, again, a product of pendent group formation, and provides further evidence that TMTP, rather than zinc perthiomercaptides, are the active sulfurating species in thiuram-based vulcanization, even in the presence of ZnO.

The finding that ZnS can react with Hdmtc to form $Zn_2(dmtc)_4$ conflicts with the findings of DSC experiments performed by Kruger and McGill.³¹ However, it should be borne in mind that Hdmtc, which reacts less rapidly with ZnS, could escape from the DSC pans used by Kruger and McGill. No escape of volatiles is possible from the sealed glass tubes used in the present study.

CONCLUSIONS

TMTP are the initial active sulfurating agents in TMTD-accelerated sulfur vulcanization, both in the

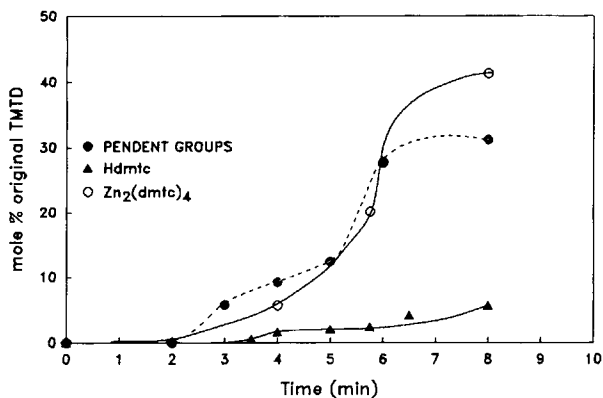


Figure 9 HPLC analyses of some products in TME/TMTD/sulfur/ZnS vulcanization.

presence and absence of ZnO. TMTP react with the model olefin via an irreversible, concerted mechanism to form thiuram pendent groups and Hdmtc, rather than by hydrogen abstraction by thiuram sulphenyl and persulphenyl radicals originating from the breakdown of TMTP. Zinc perthiomercaptides are not formed prior to pendent group formation and do not function as the active sulfurating agents as previously proposed.

Crosslink formation is delayed in thiuram-based cures in the absence of ZnO. Significant deactivation of pendent groups occurs and has been attributed to the destruction of crosslink precursors by Me₂NH, formed in the decomposition of Hdmtc. The present study indicates that Hdmtc is stable under vulcanization conditions. Instead, thiuram pendent groups and Hdmtc participate in an exchange reaction wherein TMTP are regenerated and unreactive thiol pendent groups are formed.

In the presence of ZnO, deactivation of pendent groups through thiuram pendent group-Hdmtc exchange is limited due to Hdmtc removal, and the onset of crosslinking is early compared to TMTD-based cures.

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