

# A Study of Curative Interactions in *Cis*-1,4-Polyisoprene. VIII. Network Maturing Reactions in the *Cis*-1,4-Polyisoprene/Tetramethylthiuram Disulfide/ZnO System

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## SYNOPSIS

Several aspects concerning the network maturing reactions of the *cis*-1,4-polyisoprene (IR)/tetramethylthiuram disulfide (TMTD)/ZnO curing system, were evaluated with reference to previously published literature. The crosslink density increased progressively from  $1.42 \times 10^{-5}$  mol cm<sup>-3</sup> rubber at 140.0°C, to  $8.30 \times 10^{-5}$  mol cm<sup>-3</sup> at the higher temperature of 190.0°C, which tied in with the fact that natural rubber (NR) or IR/TMTD/ZnO systems show negligible reversion provided sufficient ZnO is present. The increase in the crosslink density value was accompanied by a systematic buildup of monosulfidic crosslinks, and a substantial decrease in the concentration of tetramethylthiuram monosulfide (TMTM). Calculations showed, in addition, that the increase in the concentration of zinc dimethyldithiocarbamate (ZDMC) and the decrease in the TMTM concentration, were interdependent. It is shown that TMTM, rather than ZDMC, was involved in the crosslink shortening reactions.

## INTRODUCTION

The network maturing reactions in the synthetic *cis*-1,4-polyisoprene (IR) or natural rubber (NR)/tetramethylthiuram disulfide (TMTD)/ZnO system, are concerned with the fate of the initial polysulfidic crosslinks on further heating.

The network efficiency calculations of Moore et al.<sup>1</sup> on the IR(100)/TMTD(4.0)/ZnO(4.0) vulcanizate cured at 140°C, were based on the assumptions that were outlined in an earlier publication.<sup>2</sup> The network formed in the initial stages of vulcanization was structurally complex ( $E = 15.7$  sulphur atoms combined in the network per chemical crosslink present, at 0.25 h), but became structurally more simple as crosslinking proceeded to the maximum crosslink density ( $E = 3.3$ , at 10 h). Treating the vulcanizate with sodium di-*n*-butyl phosphite,<sup>1</sup> indicated that the crosslinks were entirely di- and/or polysulfidic initially, but shortened on extended

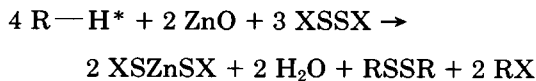
vulcanization, so that 80% of the crosslinks were monosulfidic on extended cure. Networks of IR/TMTD/ZnO vulcanizates were, in general, characterized by little *cis-trans* isomerization of the double bonds, and no appreciable scission of the main chain occurred during cure. Very low yields of conjugated species and cyclic monosulphides were formed.<sup>1,3</sup>

Morrison et al.<sup>4,5</sup> identified the competition between desulfuration and decomposition reactions as a major factor in determining the final vulcanizate network. The effective desulfuration of di- and polysulfidic crosslinks RS<sub>x</sub>SR (R = polyisoprenyl,  $x \geq 2$ ) would eventually result in thermally stable monosulfidic crosslinks. Likewise, di- and polysulfidic pendent groups RS<sub>x</sub>SX [ $x \geq 1$ , X = Me<sub>2</sub>NC(S)] may, apart from reacting to produce crosslinks, desulfurate to monosulfidic pendent groups RSX. The latter pendent groups were not regarded as precursors to crosslinks.<sup>6,7</sup>

Experiments with methylpentenyl di- or trisulfide/2-methyl-*pent*-2-ene/ZnO mixtures heated at 140°C, revealed that the crosslink desulfuration

process was enhanced by the zinc dimethyldithiocarbamate (ZDMC) complex [(XSZnSX) (L)] (L = pyridine) and that additional crosslinked sulfides were formed.<sup>7</sup> Substantial amounts of ZnS were also found. It was thus postulated that a high concentration of the soluble ZDMC complex [(XSZnSX) (L)] (L = nitrogen base, zinc carboxylate) would promote crosslink desulfuration relative to crosslink decomposition in the real vulcanizate; this, in turn, would result in a heat-resistant network with a higher degree of crosslinking characteristic of an efficient vulcanization system.<sup>4</sup>

Scheele et al.<sup>8,9</sup> found that ZDMC was formed in a limiting yield of 66 mol % in a fully-cured NR/TMTD/ZnO vulcanizate (calculated on the TMTD added), irrespective of variables such as the vulcanization temperature, the concentration of TMTD or the concentration of ZnO, ("provided the ZnO was sufficient to meet the necessary stoichiometric requirement"). Moore et al.<sup>10</sup> reported a limiting yield of 72 mol % ZDMC for the IR/TMTD/ZnO vulcanizate. Scheele et al.<sup>11</sup> postulated a stoichiometric relationship in an effort to explain this phenomenon:



\*R-H = polyisoprene.

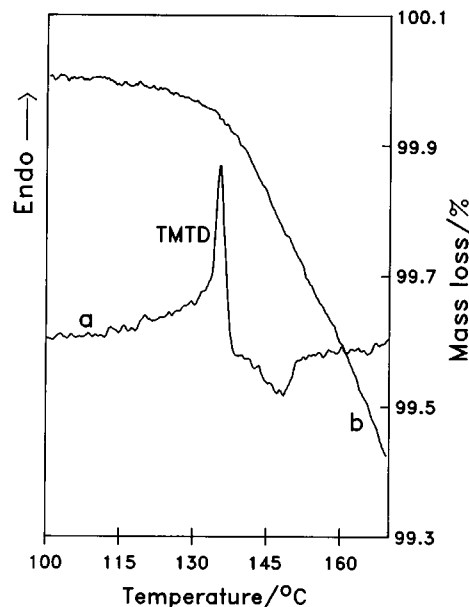
In the previous paper,<sup>14</sup> we reported on the formation of the initial polysulfidic crosslinks in the IR/TMTD/ZnO system. This paper is an extension of that work and deals with network maturing reactions in particular. To this end Figure 1 and Table I are reproduced.

## EXPERIMENTAL

The experimental details were given previous papers.<sup>12,13</sup> Samples were vulcanized in a DSC, and the network as well as extractables were analyzed.

## RESULTS AND DISCUSSION

The number of sulfur atoms per pendent group was calculated for the IR(100)/TMTD(8.86)/ZnO(3.00) system at the position 169.9°C along the DSC cure curve (Fig. 1). The calculation was justified since (i) the small mass loss of 0.59% at 169.9°C (Table I), implied that volatiles other than accelerator fragments were limited, and (ii) a neg-



**Figure 1** DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)/TMTD (8.86)/ZnO (3.00) (1.0/1.0 mole ratio). The vulcanizate quenched at 170°C appeared white and/or slightly transparent on swelling in benzene.  $M_i = 20.228$  mg.

ligible amount of cyclic sulfides are found in the vulcanizate network of IR/TMTD/ZnO systems.<sup>1,3</sup> The method of calculation was described earlier,<sup>14</sup> and the results are depicted in Table II. The calculation revealed that an excess of monosulfidic pendent groups were present at 169.9°C, but species such as RX may also have been present. The existence of the corresponding pendent group R'X (R' = 2-methylpent-2-enyl) was also inferred from model compound studies on the 2-methylpent-2-ene/TMTD/ZnO system.<sup>6,7</sup> Monosulfidic pendent groups RSX (R = polyisoprenyl) are not precursors to crosslinks<sup>6,7</sup> and thus survive as the most important main-chain modification in a fully-cured vulcanizate. These observations will explain the findings of Scheele et al.<sup>8,9</sup> and Moore et al.,<sup>10</sup> that the yield of ZDMC was limited in fully cured NR or IR/TMTD/ZnO vulcanizates; we are, however, not able to explain the fact that this limiting yield of ZDMC was, on average, always about 69 mol %.

A noticeable feature of the IR(100)/TMTD(8.86)/ZnO(3.00) system, was the progressive increase in the crosslink density at higher temperatures. This was in contrast to any of the other curing systems investigated in this study (viz. IR/TMTD, IR/sulphur/TMTD, IR/sulphur/ZDMC, IR/sulphur/ZDMC/ZnO, IR/sulphur/TMTD/ZnO), in

**Table I** Analysis of the Compound Shown, at Various Stages of Vulcanization

| Compound<br>(Parts Per<br>Hundred) | Temp.<br>(°C) | Compounds Extracted/mol % of Initial Reagent,<br>or TLC Observation |              |      |      |              | Mass<br>Loss<br>(%) | Degree of Cross-<br>Linking/mol cm <sup>-3</sup><br>Rubber Network × 10 <sup>5</sup> |                                |                                | Polysulfides<br>(%) |
|------------------------------------|---------------|---|--------------|------|------|--------------|---------------------|--|--------------------------------|--------------------------------|---------------------|
|                                    |               | S <sub>8</sub>  | TMTD         | TMTM | TMTU | ZDMC         |                     | 1/2M <sub>c</sub>  | 1/2M <sub>c</sub> <sup>a</sup> | 1/2M <sub>c</sub> <sup>b</sup> |                     |
| IR (100)                           | 140.0         |   | 15.2         | 48.9 | 0.0  | 19.2         | 0.11                | 1.42   | 0.67                           | 0.56                           | 52.8                |
| TMTD (8.86)                        | 146.9         | 0.0   | 9.7          | 33.1 | 0.0  | 34.5         | 0.22                | 3.16   | 2.33                           |                                | 26.3                |
| ZnO (3.00)                         | 169.9         |   | 3.2          | 14.2 | 0.0  | 52.7         | 0.59                | 5.27   | 5.10                           |                                | 3.2                 |
| (Fig. 1a)                          | 190.0         | 0   | <sup>c</sup> | 0    |      | <sup>d</sup> | 0.67                | 8.30   |                                |                                |                     |

<sup>a</sup> Crosslink density after 2 h propane-2-thiol/piperidine treatment.

<sup>b</sup> Crosslink density after 4 h propane-2-thiol/piperidine treatment.

<sup>c</sup> Compound barely detected with TLC.

<sup>d</sup> Compound easy to detect with TLC.

which reversion was prominent at higher temperatures. The increase in the crosslink density from  $1.42 \times 10^{-5}$  mol cm<sup>-3</sup> at 140.0°C, to  $8.30 \times 10^{-5}$  mol cm<sup>-3</sup> at the high temperature of 190.0°C (Table I), tied in with the well-known fact that NR or IR/TMTD/ZnO vulcanizates show negligible modulus reversion on extended cure, provided sufficient ZnO is present.<sup>3</sup>

Another characteristic feature of the IR/TMTD/ZnO system under discussion, was the steady decrease in the efficiency parameter *E* from 146.9°C (*E* = 3.5) to 169.9°C (*E* = 0.9), depicted in Figure 2. A similar trend in *E* was observed in the isother-

mal study by Moore et al.,<sup>1</sup> on the IR(100)/TMTD(4.0)/ZnO(4.0) system at 140°C. This behavior was, once again, in contrast to that of all the other vulcanization systems [cf. Fig. 2(a-e)], where *E* often increased drastically at higher temperatures. These experimental data are also in line with the

**Table II** Number of Sulfur Atoms per Pendent Group at 169.9°C<sup>a</sup>

| Quantity<br>Calculated                         | (mol cm <sup>-3</sup> Rubber Network) |
|--|---------------------------------------|
| Crosslink density                              | $5.27 \times 10^{-5}$                 |
| Number of pendent<br>groups                    | $15.1 \times 10^{-5}$                 |
| Network-bound<br>sulfur atoms <sup>b</sup>     | $4.8 \times 10^{-5}$                  |
| Sulfur atoms in<br>crosslinks <sup>c</sup>     | $5.6 \times 10^{-5}$                  |
| Sulfur atoms in<br>pendent groups <sup>d</sup> | ~ 0                                   |
| Sulfur atoms per<br>pendent group              | ~ 1 <sup>e</sup>                      |

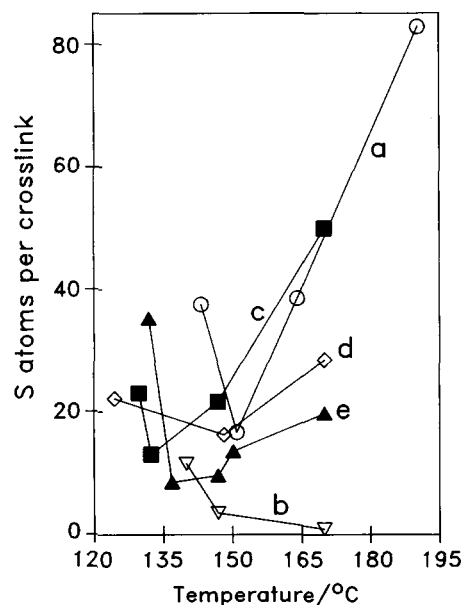
<sup>a</sup> Calculation from the DSC scan of the IR/TMTD/ZnO vulcanization compound from Table I.

<sup>b</sup> Refers to sulfur other than in the SX moieties of pendent groups.

<sup>c</sup> Assume trisulfidic and disulfidic crosslinks.

<sup>d</sup> Neglecting sulfur in the SX moieties of pendent groups.

<sup>e</sup> Refers to the indice *x* in RS<sub>x</sub>X (R = polyisoprenyl).



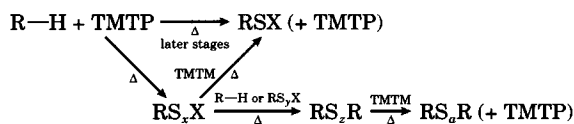
**Figure 2** The variation of the S atoms/crosslink ratio as the cure proceeded for the vulcanization systems below. The calculations did not take the sulfur atoms of the network-bound SX groups into account. The data points were connected merely to illustrate the general trends in *E*. (a) IR (100)/sulfur (9.46)/TMTD (8.86), (b) IR (100)/TMTD 8.86/ZnO (3.00), (c) IR (100)/sulfur (9.46)/ZDMC (11.27), (d) IR (100)/sulfur (9.46)/ZDMC (11.27)/ZnO (3.00), (e) IR (100)/sulfur (9.46)/TMTD (8.86)/ZnO (3.00).

observation that network destruction reactions were of little importance in NR or IR/TMTD/ZnO cures, and implied that the sulfur was utilized more efficiently at later stages of cure.

Porter<sup>4,7</sup> concluded from studies with model compounds that ZDMC played an important role in determining the vulcanizate structure. It was postulated that a high concentration of the ZDMC complex [(XSZnSX) (L)] (L = nitrogen base, zinc carboxylate), would enhance crosslink desulfuration over decomposition, which would eventually result in an efficient vulcanizate (EV) network. An alternate mechanism to account for the unusual resistance of NR or IR/TMTD/ZnO systems to reversion, will now be presented (Scheme 1).

It is significant that the decrease in the percentage of polysulfidic crosslinks of the IR/TMTD/ZnO compound (Table I), was accompanied by a systematic build up of monosulfidic crosslinks. The monosulfidic crosslinks increased from  $0.67 \times 10^{-5}$  mol cm<sup>-3</sup> at 140.0°C, to  $8.30 \times 10^{-5}$  mol cm<sup>-3</sup> at 190.0°C (Table III). Furthermore, the concentration of tetramethylthiuram monosulfide (TMTM) decreased substantially from 48.9 mol % to about 0% over this temperature range (Table I). We conclude that TMTM (rather than ZDMC) was involved in the desulfuration of polysulfidic crosslinks, and that additional crosslinks were introduced as a consequence thereof, in terms of the arguments given below.

Craig et al.<sup>15</sup> remarked that the decomposition of TMTM, at 140°C in the presence of NR, was negligible. It is also well-known that TMTM is not a vulcanizing agent. In the presence of sulfur, however, TMTM is regarded as an ultra-accelerator,<sup>16,17</sup> which, primarily due to its facile reaction with sulfur, yields TMTP as the active sulfurating agent.<sup>18</sup> A free sulfur analysis on the IR(100)/TMTD(8.86)/ZnO(3.00) system at 146.9°C on the DSC thermogramme, revealed that no free sulfur was present in the vulcanizate (Table I). Therefore, the only



**Scheme 1** Network maturing reactions proposed for the generation of monosulfidic crosslinks and pendent groups in the efficient NR or IR/TMTD/ZnO vulcanization systems ( $x$  and  $y \geq 2$ ,  $z < a$ ). The formation of DMDCA and its involvement with ZnO are omitted for the sake of brevity.

other source of sulfur, which could have contributed to the disappearance of TMTM at higher temperatures, was the network-bound sulfur. It is suggested that TMTM would extrude sulfur atoms from the initial polysulfidic crosslinks to yield shorter crosslinks. The extruded sulfur and TMTM would form tetramethylthiuram polysulfides (TMTP), which would react with the IR chain to form pendent groups (Scheme 1). Pendent groups of the type  $\text{RS}_x\text{X}$  ( $x \geq 2$ ) would generate more crosslinks. The latter reactions would be accompanied by the liberation of dimethyldithiocarbamic acid (DMDCA), in exactly the same manner as that described in a previous publication.<sup>14</sup> The DMDCA will react instantly with ZnO to form ZDMC and water. These findings are once again in accord with the literature<sup>10,19,20</sup> and those reported in this paper (Table I), viz. that the increase in the ZDMC concentration paralleled the curing curve.

TMTM should also be able to extrude sulfur from pendent groups such as  $\text{RS}_x\text{X}$  ( $x \geq 2$ ), in which case the relatively stable monosulfidic pendent groups would eventually form. However, this route appeared to be less important. Calculations on the IR/TMTD/ZnO system under discussion, revealed that 15.4 mol % and 22.5 mol % of the initial TMTD was network-bound at 140.0 and 169.9°C, respectively. Since this increase in the number of pendent groups was accompanied by a large increase of 270% in the crosslink density (Table I), it can readily be seen that there must have been a dynamic pendent group association with and dissociation from the IR chains as the cure proceeded. It was therefore more likely that the passive monosulfidic pendent groups would form in the advanced stages of cure, since the probability of forming TMTP molecules of a lower sulfur rank would increase (Scheme 1). In the limit, for example, a TMTM molecule would extrude one sulfur atom from a sulfidic crosslink to form TMTD. The TMTD molecule itself may then react with the isoprene chain to form DMDCA and a monosulfidic pendent group via reaction (2) in the previous publication.<sup>14</sup>

The arguments in the preceding two paragraphs were substantiated by the fact that the decrease in the TMTM concentration, and the increase in the ZDMC concentration, were related as the cure progressed in the IR/TMTD/ZnO compound (Table I). To illustrate, the sum of chemical species (other than TMTM) which could potentially have formed ZDMC at the later stages of cure, was (15.2 mol % TMTD + 15.4 mol % network-bound TMTD) = +30.6 mol % at the position 140.0°C. Thus, the

**Table III The Variation of the Polysulfidic, Mono- and/or Disulfidic Crosslinks at Various Temperatures Along the DSC Curve, for the IR/TMTD/ZnO System from Table I**

| Temperature/°C  | 140.0 | 146.9 | 169.9 | 190.0            |
|---|-------|-------|-------|------------------|
| Polysulfides<br>(mol cm <sup>-3</sup> rubber network × 10 <sup>5</sup> )            | 0.67  | 2.23  | 5.10  | 8.30             |
| Mono- and/or disulfides<br>(mol cm <sup>-3</sup> rubber network × 10 <sup>5</sup> ) | 0.75  | 0.83  | 0.17  | ~ 0 <sup>a</sup> |

<sup>a</sup> Assume negligible polysulfidic crosslinks were present.

maximum yield of ZDMC which was to be expected at full cure time was (19.2 mol % ZDMC + 30.6 mol % potential ZDMC) = 49.8 mol % ZDMC. This value was considerably less than the limiting yield of 72 mol % ZDMC reported<sup>10</sup> for the IR/TMTD/ZnO vulcanizate, implying that ZDMC must have originated partially from TMTM. However, since TMTM and ZnO *per se* do not react at vulcanization temperatures,<sup>12</sup> ZDMC was most probably formed from TMTM as a consequence of the network maturing reactions proposed in Scheme 1.

Scheele et al.<sup>21</sup> reported that no ZnS was formed in NR/TMTD/ZnO cures. Moore et al.<sup>1,10</sup> observed that ZnS was formed in the later stages of the efficient IR(100)/TMTD(4.0)/ZnO(4.0) vulcanization at 140°C, though the maximum yield was only 3.8 mol % ZnS (after 10 h), calculated on the initial amount of ZnO. The formation of ZnS was characteristic of ZDMC-accelerated sulfur vulcanization, particularly during the formation of pendent groups, as will be demonstrated in a forthcoming paper. Porter<sup>7</sup> showed convincingly that ZnS could also be formed on the desulfuration of methylpentenyl di- or trisulfides/2-methylpent-2-ene/ZnO mixtures, at 140°C in the presence of the ZDMC complex [(XSZnSX) (L)] (L = nitrogen base). The virtual absence of ZnS in the IR or NR/TMTD/ZnO vulcanization process, implied that a very small number of the ZDMC molecules that formed were associated with either desulfuration or decomposition reactions—the reaction of ZDMC with the network-bound sulfur atoms was thus merely a secondary network maturing reaction. The large percentage of TMTM, which was involved in the network desulfuration reactions of the IR(100)/TMTD(8.86)/ZnO(3.00) system (Table I), renders this a much more important reagent in the maturing reactions. It can be remarked that the desulfuration process with thiuram species would be more beneficial than desulfuration involving ZDMC, since sulfur was utilized more efficiently in IR/TMTD/ZnO vulcani-

zation systems, than in NR/sulfur/ZDMC/ZnO compounds (see future publication in this series).

## CONCLUSIONS

A new mechanism is proposed to account for the progressive shortening of polysulfidic crosslinks, on vulcanizing NR or IR/TMTD/ZnO compounds. TMTD decomposed rapidly to form TMTP and TMTM in the early stages of curing. TMTM was postulated to extrude sulfur from polysulfidic crosslinks, which would eventually lead to a heat resistant network with monosulfidic crosslinks. The very low percentage of ZnS which was found in the advanced cure stages of the IR/TMTD/ZnO compounds<sup>1,10</sup> argued against the contention that ZDMC was involved in the desulfuration of polysulfidic crosslinks<sup>4,7</sup> in NR or IR/TMTD/ZnO systems. The latter aspect will receive more attention in a later paper.

We wish to thank the Foundation for Research and Development and Gentyre Industries for financial assistance.

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Received January 24, 1991

Accepted April 11, 1991