# Study of Curative Interactions in cis-1,4-Polyisoprene. XII. The cis-1,4-Polyisoprene-Sulfur-Tetramethylthiuram Disulphide-ZnO-Stearic Acid Vulcanization System

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## SYNOPSIS

Several aspects on the mechanism of vulcanization in the synthetic cis-1,4-polyisoprene (IR)-sulfur-tetramethylthiuram disulphide (TMTD)-ZnO system were harmonized. The differential scanning calorimetry (DSC) thermograms showed that the vulcanization processes became better resolved on increasing the curative loading in the compound. Two major crosslinking reactions occurred consecutively in the IR (100)-sulfur (9.46)-TMTD (8.86)-ZnO (3.00) mixture, viz the IR-sulfur-TMTD-ZnO and IR-sulfur-zinc dimethyldithiocarbamate (ZDMC) (or IR-sulfur-ZDMC-ZnO) reactions. In the first process poly- and disulfidic pendent groups $RS_xSX$ ($R$ = polyisoprenyl, X = $Me_2NC$ (S), $x \geq 1$) formed via the $IR-XSS_xSX$ reaction, and in the second via the $IR-XSS_xZnSSX$ reaction. Thermogravimetric analysis (TGA) and high-pressure liquid chromatography (HPLC) data showed that dimethyldithiocarbamic acid liberated during the IR-sulfur-TMTD-ZnO reaction was trapped by ZnO to yield ZDMC. Hence ZDMC was a product, and not precursor, of this crosslinking process. A comparison of reactions in IR-sulfur-TMTD-ZnO and poly(ethylene-co-propylene)-sulfur-TMTD-ZnO mixtures showed that the participation of IR molecules was essential for ZDMC formation. The ZDMC concentration remained constant at $\sim$ 38.4 mol % during the later stages of cure, showing that it did not participate in the desulfuration reactions of polysulfidic links. In the presence of stearic acid the stearic acid-ZnO reaction occurred at 87°C as was manifested by an intense crystallization peak of zinc stearate. The vulcanization processes were the same both in the presence and absence of stearic acid.

## INTRODUCTION

Crosslinking in cis-1,4-polyisoprene (IR)-tetramethylthiuram disulfide (TMTD) and IR-sulfur-TMTD vulcanization systems occurred via the formation of polysulfidic pendent groups, resulting from the interaction of IR with tetramethylthiuram polysulphide (TMTP) molecules.[1,2] These vulcanizates were, however, inferior due to the detrimental reactions of the decomposition products of dimethyldithiocarbamic acid (DMDCA), forming as a by-product of the IR-thiuram sulfenyl radical reaction. DMDCA was rapidly trapped in the presence of ZnO

to yield zinc dimethyldithiocarbamate (ZDMC), whereby crosslink formation was considerably enhanced.[3] The IR-sulfur-ZDMC curing system was characterized by the formation of ZnS and during crosslinking also liberated DMDCA. Again ZnO (or zinc stearate) was needed to limit attack by the degradation products of DMDCA on sulfidic crosslinks.[4,5]

The addition of a fatty acid as a co-activator to a vulcanization recipe, generally increases the crosslinking yield at the expense of noncrosslinking species. The Moore-Trego efficiency parameter $E$ decreased, for example, from 13.5 to 3.2 at the advanced stages of cure in the cis-1,4-polyisoprene (IR) (100)-tetramethylthiuram disulfide (TMTD) (4)-ZnO (4) compound.[6] However, the $E$ value decreased from 7.9 to 2.1 when lauric acid (1.5 phr) was added to the formulation vulcanized at 140°C.

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This work reports on the vulcanization reactions occurring in the IR-sulfur-TMTD-ZnO and IR-sulfur-TMTD-ZnO-stearic acid systems and shows that the IR-sulfur-TMTD-ZnO reaction preceeds the crosslink reactions involving ZDMC and sulfur.

## EXPERIMENTAL

Experimental details were given in previous papers.[7,8] Samples were vulcanized in a differential scanning calorimeter (DSC) and the network as well as extractables were analyzed.

## RESULTS AND DISCUSSION

### DSC Curves

#### *The Effect of Curative Loadings*

A DSC thermogram of the IR (100)-sulfur (2.36)-TMTD (2.27)-ZnO (3.00) (0.25/0.25/1.00 mole ratio) compound displayed the curing curve as a single exotherm [Fig. 1(a)]. On progressively increasing the sulfur and TMTD loadings, but maintaining the sulfur-TMTD ratio constant in the compound, the different processes in the reaction sequence became more clearly resolved [Fig. 1(a)-(f)]. These curves were very reproducible under the experimental conditions that were employed.

#### *The Effect of Scan Rate*

In order to optimize the separation of the thermal events in the IR(100)-sulfur (9.46)-TMTD (8.86)-ZnO (3.00) (1.0/1.0/1.0 mole ratio) compound, the scan rate was varied. Some peaks merged at scan rates above 7.5°C/min [cf. Figs. 1(f) and 2] and an optimum resolution of the peak $G_1$ in Figure 1(f), was obtained when a scan rate of 4.0°C/min was employed. (A scan rate of 2.5°C/min was used in this study. As the resolution differed little from that at 4.0°C/min, it allowed the results to be compared with earlier work recorded at 2.5°C/min.) Except for the enthalpy changes that were connected with the dissolution of sulfur and TMTD, no other thermal events were observed on scanning the sulfur-TMTD-ZnO (1.0/1.0/1.0 mole ratio)[9] mixture at 20°C/min to 165°C. The curing curves of the IR-sulfur-TMTD-ZnO system immediately demonstrated the involvement of IR in the thermal events.

#### The IR-Sulfur-TMTD-ZnO Reaction

It was easy to discern the melting of sulfur at 109.9°C in the IR-sulfur-TMTD-ZnO vulcanization ther-
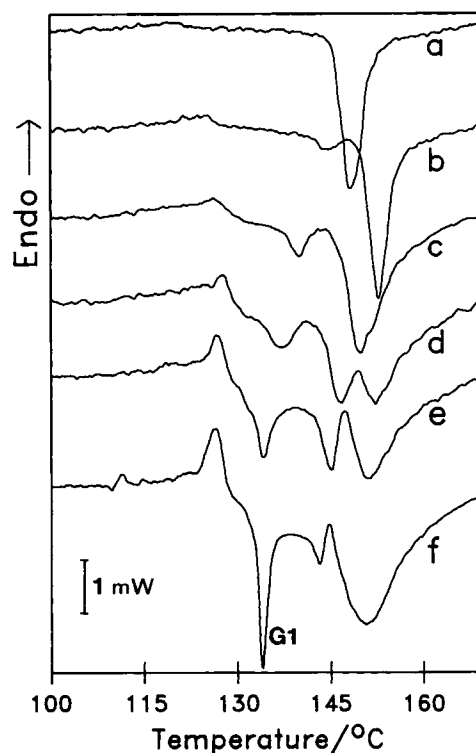


**Figure 1** DSC spectra. Scan rate 2.5°C/min. (a) IR (100)-sulfur (2.36)-TMTD (2.22)-ZnO (3.00) (0.25/0.25/1.00 mole ratio), $M_i$ = 18.079 mg. (b) IR (100)-sulfur (3.59)-TMTD (3.37)-ZnO (3.00) (0.38/0.38/1.00 mole ratio), $M_i$ = 17.925 mg. (c) IR (100)-sulfur (4.73)-TMTD (4.43)-ZnO (3.00) (0.50/0.50/1.00 mole ratio), $M_i$ = 17.911 mg. (d) IR (100)-sulfur (5.96)-TMTD (5.58)-ZnO (3.00) (0.63/0.63/1.00 mole ratio), $M_i$ = 17.961 mg. (e) IR (100)-sulfur (7.09)-TMTD (6.65)-ZnO (3.00) (0.75/0.75/1.00 mole ratio), $M_i$ = 17.991 mg. (f) IR (100)-sulfur (9.46)/TMTD (8.86)-ZnO (3.00) (1.0/1.0/1.0 mole ratio), $M_i$ = 16.909 mg.

mogram [Fig. 3(a)]. The dissolution of TMTD that started at 121.2°C was 6.8°C earlier than the liquefaction of TMTD in the IR-sulfur-TMTD system.[1] An illuminative result was that the exotherm $G_2$, was not due to a precursor reaction to crosslinking but was associated with the crosslinking reaction itself. The crosslink density was 1.46 × 10⁻⁵ mol/cm³ rubber at 131.9°C and increased drastically to 11.51 × 10⁻⁵ mol/cm³ rubber at 136.9°C (Table I). Previous experience with regard to the shape of DSC peaks led us to believe that the narrowish peak $G_2$ was due to the rapid formation and crystallization of ZDMC. High-pressure liquid chromatography (HPLC) analysis showed a rapid increase in ZDMC concentration from 7.54 × 10⁻²$M$ at 131.9°C to 1.88 × 10⁻¹$M$ at 136.9°C. It is known that ZDMC is sparingly soluble in many solvents,[10] and the isoprene rubbers are no exception.[11,12]
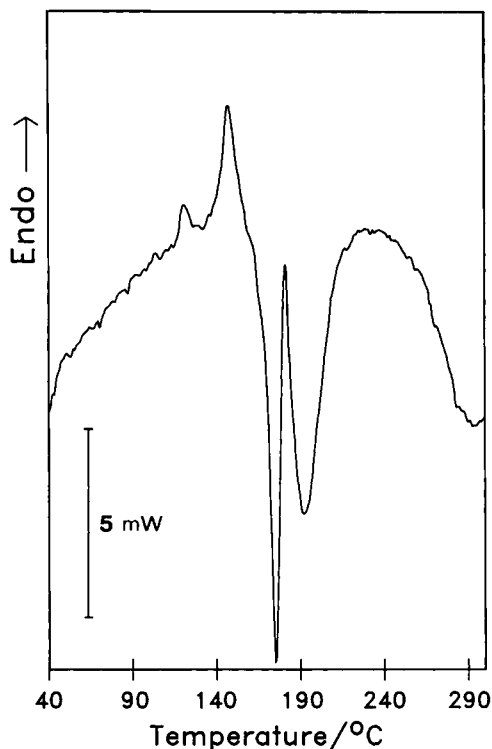
**Figure 2** DSC spectrum. Scan rate 20.0°C/min. IR (100)-sulfur (9.46)-TMTD (8.86)-ZnO (3.00) (1.0/1.0/1.0 mole ratio), $M_i$ = 17.006 mg.

It was significant that the concentration of ZDMC, expressed in terms of mol % TMTD originally present, increased from 22.5 mol % at 131.9°C to 56.0% at 136.9°C (Table I). Since a scan rate of 2.5°C/min was employed in these analysis, it implied that the ZDMC yield had increased by an additional 33.5 mol % within 2 min. This remarkable increase in the ZDMC concentration reemphasized the participation of the IR molecules in the formation of ZDMC. TMTD and ZnO were very reluctant to react per se in the absence of IR,[2,9] such that a yield of only 16.7 mol % ZDMC was obtained on refluxing a TMTD–ZnO (1.00/29.55 mole ratio) mixture, in *n*-decane–benzene, at 150°C for 3 h.

The preceding arguments were substantiated further by the spectacular difference in the DSC curves of IR and poly(ethylene-co-propylene) (EPM) compounded with sulfur, TMTD, and ZnO [Figs. 3(a), 4]. In the EPM compound the melting of sulfur at 109.5°C was followed by the dissolution of TMTD at 117.7°C and no other thermal events occurred up to 190°C, which implied that TMTD (or TMTP) and ZnO were very reluctant in reacting to form ZDMC. The solubility parameters[13] of EPM [$\delta$ = 16.1 $(MJ/m^3)^{1/2}$] and IR [$\delta$ = 16.5 $(MJ/m^3)^{1/2}$] are of similar magnitude. If ZDMC or zinc perthiomercaptides $XSS_xZnSX$ [X = $Me_2NC(S)$, $x$

$\geq$ 1] had formed in situ prior to vulcanization, as claimed,[14-16] one would have expected it to crystallize in EPM as it did in IR. These findings concurred with DSC, thin-layer chromatography (TLC), and Raman spectroscopic evidence; that is, sulfur, TMTD, and ZnO per se were extraordinary sluggish to form ZDMC.[9,17] A TLC analysis showed that the major components of the extracted EPM–sulfur–TMTD–ZnO sample were sulfur and TMTD, while the concentrations of TMTM and ZDMC were negligible (Table I).

### Evidence for the Active Sulfurating Agent

In interpreting DSC thermogrammes[9] and Raman spectra[17] of heated sulfur–TMTD and sulfur–TMTD–ZnO systems, we concluded[2] that the sulfur–TMTD reaction to yield TMTP proceeded independently of ZnO. A HPLC analysis on the sulfur–TMTD (1.0/1.0 mole ratio) system, heated isothermally for 5 min at 145.7°C, revealed that TMTD (70.8 mol %), TMTM (5.0%), and no tetramethyl thiourea (TMTU) were present.[9] These results led to the conclusion that TMTP was the active sulfurating agent in IR–sulfur–TMTD–ZnO vulcani-
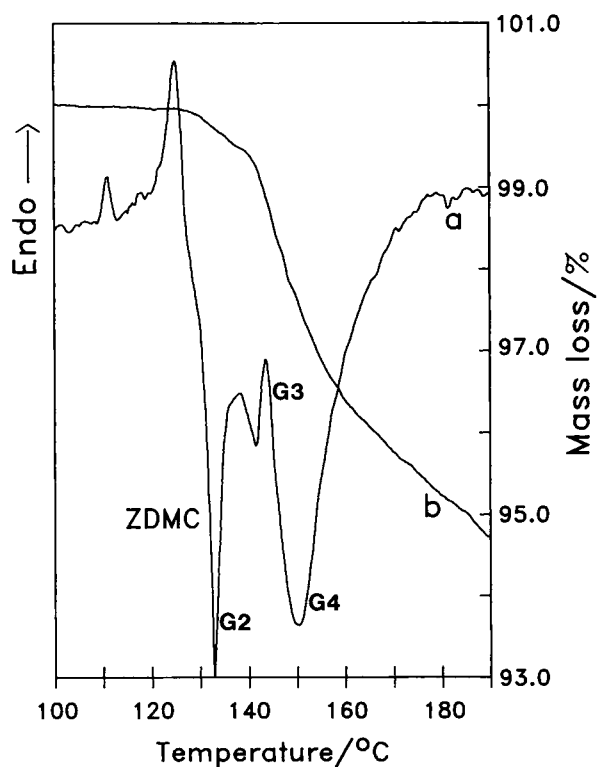


**Figure 3** DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)-sulfur (9.46)-TMTD (8.86)-ZnO (3.00) (1.0/1.0/1.0 mole ratio), $M_i$ = 17.005 mg. The same sample quenched at 170°C appeared yellow-brown/opaque on swelling in benzene. (b) TGA spectrum.

Table I   Analysis of the Compounds Shown, at Various Stages of Vulcanization

| Compound (parts per hundred) | Temp. (°C) | Compounds Extracted per mol % of Initial Reagent, or TLC Observation | | | | | Mass Loss (%) | Degree of Crosslinking per mol/cm³ Rubber Network × $10^5$ | | | Polysulfides (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $S_8$ | TMTD | TMTM | TMTU | ZDMC | | 1/2Mc | 1/2Mc[a] | 1/2Mc[b] | |
| IR (100) sulfur (9.46) TMTD (8.86) ZnO (3.00) [Fig. 3(a)] | 128.8 | | | | | | 0.12 | 0.00 | | | |
| | 131.9 | 80.8 | 31.2 | 9.1 | 0.0 | 22.5 | 0.25 | 1.46 | | 0.20 | 86.3 |
| | 136.9 | 63.6 | 8.0 | 10.8 | 0.0 | 56.0 | 0.46 | 11.51 | 2.81 | 2.72 | 76.4 |
| | 141.4 | | | | | | 0.74 | 16.44 | 3.71 | | 77.4 |
| | 146.9 | 15.2 | 5.7 | 0.0 | 0.0 | 64.9 | 1.88 | 23.77 | 4.60 | 4.76 | 80.0 |
| | 150.2 | 2.0 | 4.9 | 0.0 | 0.0 | 38.1 | 2.41 | 19.42 | 5.27 | 5.27 | 72.9 |
| | 170.0 | 0.0 | 4.0 | 0.0 | 0.0 | 38.7 | 4.15 | 13.62 | 6.30 | 6.34 | 53.5 |
| EPM (100) sulfur (9.46) TMTD (8.86) ZnO (3.00) (Fig. 4) | 190.0 | c | c | d | | d | 0.47 | ?e | | | |

a Crosslink density after 2 h propane-2-thiol–piperidine treatment.
b Crosslink density after 4 h propane-2-thiol–piperidine treatment.
c Compound easy to detect with TLC.
d Compound barely detected with TLC.
e Neither a control sample of pure EPM scanned at 2.5°C/min to 190°C, nor this sample dissolved in benzene. The sample was assumed not to have crosslinked.
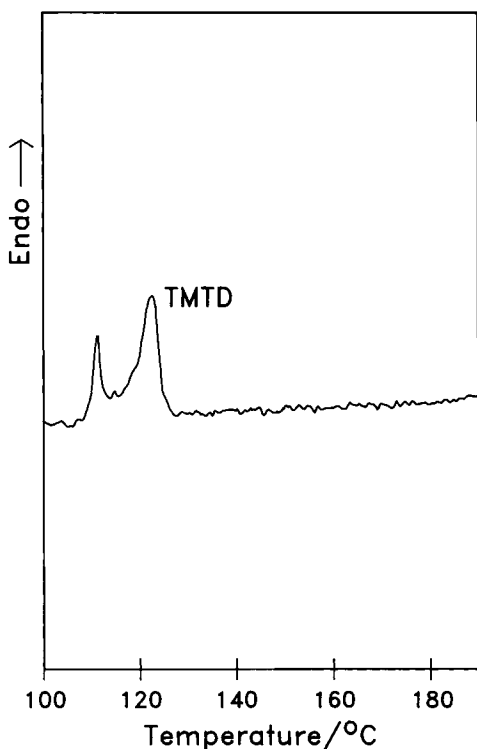
**Figure 4**  DSC spectrum. Scan rate 2.5°C/min. EMP (100)-sulfur (9.46)-TMTD (8.86)-ZnO (3.00) (1.0/1.0/1.0 mole ratio), $M_i$ = 14.175 mg. The sample appeared pinkish after the scan and whitish/opaque on swelling in benzene.

zation and was formed via the equilibrium reaction (1):

$$TMTM + \tfrac{1}{8}S_8 \underset{\Delta}{\rightleftarrows} TMTD + S_8 \underset{\Delta}{\leftrightarrows} TMTP \quad (1)$$

Previous studies[17] on a sulfur-TMTD (2.0/1.0 mole ratio) blend at 145°C revealed electron spin resonance (ESR) signals at $g$ = 2.02 and 2.006 [Fig. 5(a)]. These were assigned to thiuram persulfenyl radicals $XS_xS^\bullet$ and cyclic radicals of the type $Me_2NC^\bullet S_x$, respectively. Similar resonance lines $G_5$ were present on heating the IR-sulfur-TMTD-ZnO system at 120°C in this study [Fig. 5(b)]. Therefore, as in the case of IR-TMTD and IR-TMTD-ZnO systems,[2] where TMTP also formed, a rapid equilibrium of the kind shown below exists in the very early stages of the IR-sulfur-TMTD-ZnO vulcanization system.

$$XSS_xSX \quad \leftrightarrow \quad XS_xS^\bullet + XS^\bullet$$
$$\underset{\substack{\text{rapid}\\\text{equilibrium}}}{\Delta}$$
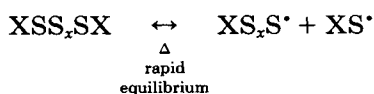
## The Existence and Nature of Pendent Groups

The HPLC analysis revealed that TMTD had reacted rapidly during the IR-sulfur-TMTD-ZnO vulcanization in that only 31.2 mol % was extracted at 131.9°C (Table I). The rate of ZDMC formation was (as for the IR-TMTD-ZnO compound)[2] much slower than the disappearance of TMTD, as only 22.5 mol % ZDMC had formed at that stage. The further increase in the ZDMC concentration on heating to 146.9°C was therefore, to some extent, related to the reaction of SX groups other than those of TMTD, such as pendent groups.

The exceedingly high $E$ value of 35.2 at 131.9°C (Fig. 6) was taken as evidence that an abundance of pendent groups had formed prior to crosslinking. The ratio decreased steeply to 8.5 Sc atoms/crosslink at 136.9°C, since the pendent groups had dissociated from the isoprene chain with the concomitant formation of crosslinks. The crosslink density increased from 1.46 × $10^{-5}$ mol/cm$^3$ rubber at 131.9°C to 11.51 × $10^{-5}$ mol/cm$^3$ at 136.9°C (Table I).
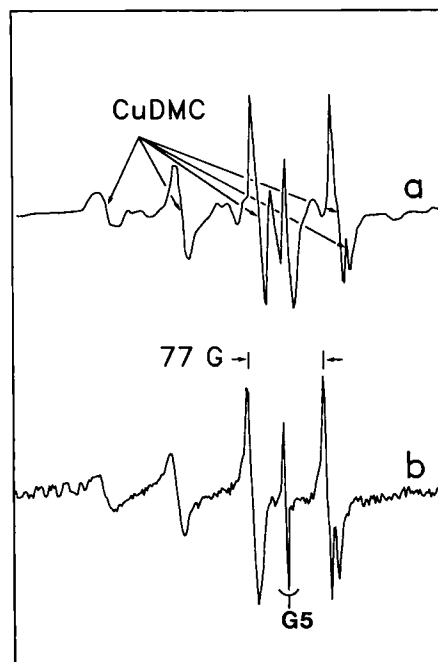


**Figure 5**  ESR spectra of various curative combinations in the absence or presence of IR. (a) Sulfur-TMTD (2.0/1.0 mole ratio) mixture heated at 145°C for 120 min, then quenched and spectrum recorded at −56°C.[16] The signals due to copper(II) dimethyldithiocarbamate (CuDMC) are marked. (b) The IR (100)-sulfur (9.46)-TMTD (8.86)-ZnO (3.00) mixture heated at 120°C, and spectrum recorded after ∼ 5 min.
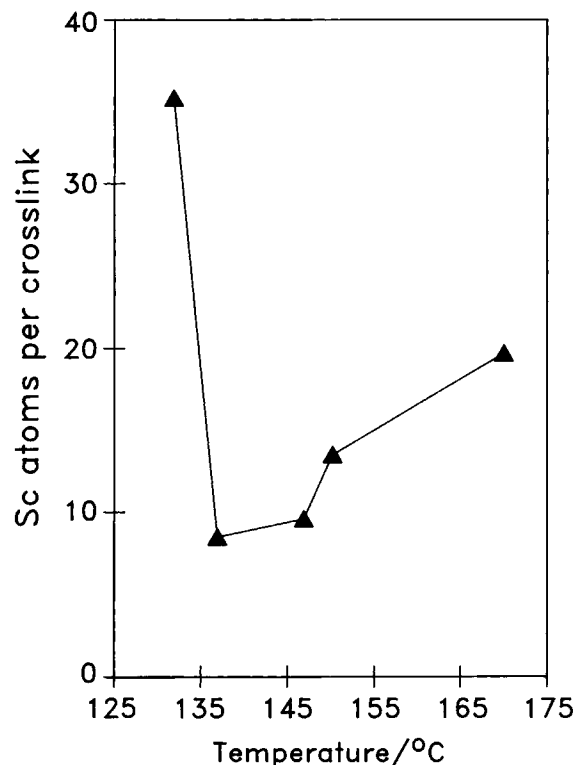
**Figure 6**   The variation of the Sc atoms–crosslink ratio as the cure proceeded for the IR (100)–sulphur (9.46)–TMTD (8.86)–ZnO (3.00) vulcanization system. The calculations did not take the sulfur atoms of the network-bound SX groups into account. The data points were connected merely to illustrate the general trends in $E$.

The low mass loss of 0.25% at 131.9°C (Table I) justified the calculation[1] of the number of sulfur atoms per pendent group for the IR–sulfur–TMTD–ZnO system at this point in the reaction. The sulfur

rank $x$ of 2.09 in $RS_xSX$ (R = polyisoprenyl) was, on average, higher for the IR–sulfur–TMTD–ZnO system at 131.9°C (Table II) than the rank $x$ of 1.24 previously found[2] for the IR (100)–TMTD (8.86)–ZnO (3.00) compound at 140.0°C. Since pendent groups of the type $RS_xSX$ ($x \geq 1$) are precursors to crosslinks, these figures could explain the observation that the percentage of polysulfidic crosslinks was in general much higher for the IR–sulfur–TMTD–ZnO vulcanizate than for the IR–TMTD–ZnO compound.[2]

### Mechanism for the Formation of Pendent Groups

The mechanism for the formation of pendent groups would be the same as that of the IR–TMTD–ZnO system,[2] viz

$$R - H + XS^{..}SS_xX \rightarrow RSS_xX + XSH \quad (2)$$
$$\underset{\text{fast}}{\overset{\text{very}}{\Delta}}$$
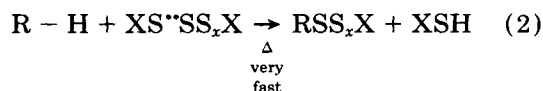
where H is $\alpha$-methylic or $\alpha$-methylenic hydrogen. Arguments used to substantiate the probability of reaction (2) hold here as well. For example, the formation of ZDMC initially proceeded at a much faster rate than the formation of crosslinks, as 5.2 ZDMC molecules/crosslink were present at the position 131.9°C (Table I). These ZDMC molecules were not formed directly from TMTD as the reluctancy of sulfur, TMTD, and ZnO to form ZDMC has been demonstrated previously.[9] It was also reasoned in an earlier paper,[2] that the reaction of pendent groups to form crosslinks was the rate-determining step in vulcanization. The extraordinary high initial concentration of ZDMC thus originated from the re-

**Table II   Calculation of Number of Sulfur Atoms per Pendent Group at 131.9°C in the DSC Scan of the IR–Sulfur–TMTD–ZnO Vulcanization Compound of Table I**

| Quantity Calculated | mol/cm$^{-3}$ Rubber Network |
|---|---|
| Crosslink density | $1.46 \times 10^{-5}$ |
| Number of pendent groups | $22.6 \times 10^{-5}$ |
| Network-bound sulfur atoms[a] | $51.5 \times 10^{-5}$ |
| Sulfur atoms in crosslinks[b] | $4.2 \times 10^{-5}$ |
| Sulfur atoms in pendent groups[c] | $47.3 \times 10^{-5}$ |
| Sulfur atoms per pendent group | $3.09$[d] |

[a] Refers to sulfur other than in the SX moieties of pendent groups.
[b] Assume trisulfidic and disulfidic crosslinks.
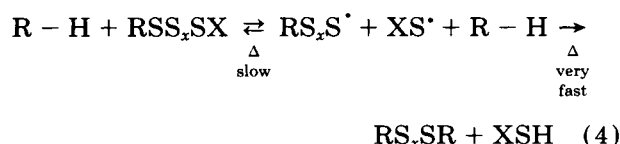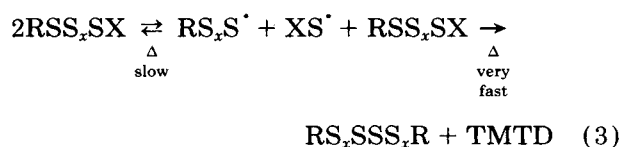[c] Neglecting sulfur in the SX moieties of pendent groups.
[d] Refers to the indice $x$ in $RS_xX$ (R = polyisoprenyl).

action of DMDCA, formed via reaction (2), and ZnO. These aspects, therefore, once again confirm the relative importance of reaction (2) as a route in the formation of pendent groups.

## Formation of the Initial Polysulfidic Crosslinks

Plausible mechanistic routes for the formation of the initial polysulfidic crosslinks were discussed in detail before.[2] Similar arguments would hold here, and the modes of crosslinking via reactions (3) and (4) would be the same.

$$2RSS_xSX \underset{\underset{\text{slow}}{\Delta}}{\rightleftarrows} RS_xS^{\bullet} + XS^{\bullet} + RSS_xSX \underset{\underset{\text{very fast}}{\Delta}}{\rightarrow}$$

$$RS_xSSS_xR + TMTD \quad (3)$$

$$R - H + RSS_xSX \underset{\underset{\text{slow}}{\Delta}}{\rightleftarrows} RS_xS^{\bullet} + XS^{\bullet} + R - H \underset{\underset{\text{very fast}}{\Delta}}{\rightarrow}$$

$$RS_xSR + XSH \quad (4)$$

where H is $\alpha$-methylic or $\alpha$-methylenic hydrogen.

## Generation of ZDMC Mechanistic Aspects

The effectiveness with which ZnO had trapped the DMDCA generated via reactions (2) and (4) in IR–sulfur–TMTD–ZnO vulcanization was revealed by the smallish peak G6 in the DTGA curve [Fig. 7(b)]. The maximum rate of evaporation was 0.17%/min between the temperatures 128.8 and 136.9°C. There was a mass loss of only 0.34% in this temperature range (Table I). The presence of ZnO thus largely reduced the formation of $Me_2NH$ and $CS_2$, due to the preferential reaction of DMDCA and ZnO to form ZDMC. The detrimental effects of $Me_2NH$ on the vulcanization ingredients and sulfidic entities bound to the network[3,5] were thereby inhibited.

Scheele et al.[18,19] and Moore et al.[20] found that ~ 69 mol % ZDMC was, on average, formed in fully cured polyisoprene–TMTD–ZnO vulcanizates. An explanation has already been presented to account for this phenomenon.[21] However, the maximum yield of ZDMC increased to a limiting value of ~ 90 mol % when a natural rubber–sulfur–TMTD–ZnO stock containing 4 g atoms of sulfur per mole of TMTD was vulcanized.[22] The authors hold that these differences could be related to the nature of the active sulfurating agent $XS_xSX$ ($x \geq 1$), especially toward the later stages of cure. The presence of elemental
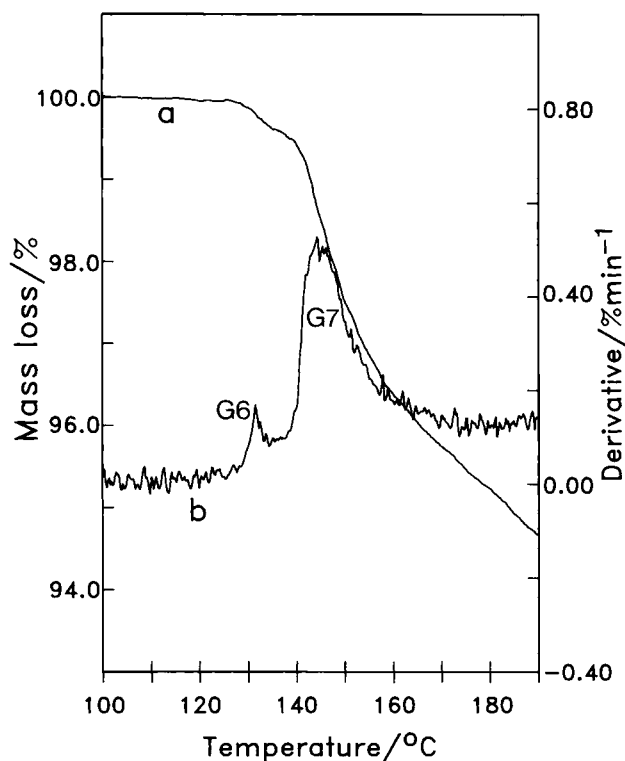


**Figure 7** TGA spectrum. Scan rate 2.5°C/min. (a) IR (100)–sulfur (9.46)–TMTD (8.86)–ZnO (3.00) (1.0/1.0/1.0 mole ratio). (b) DTGA spectrum.

sulfur in TMTD-based systems would increase the sulfur rank $x$ in the active sulfurating agent. This would further the continuous formation of pendent groups such as $RS_xSX$ ($x \geq 1$) and DMDCA via reaction (2). These pendent groups may crosslink via reactions (3) or (4), which would increase the yield of ZDMC by the ensuing reaction of DMDCA and ZnO. The probability of forming monosulfidic pendent groups, which tend to remain in the network,[11,14] would thereby be minimized. On the other hand, since ZDMC decomposes on vulcanization,[4] a too high concentration of elemental sulfur in the IR–sulfur–TMTD–ZnO compound would decrease the ultimate yield of ZDMC.

## The IR–Sulfur–ZDMC (or IR–Sulfur–ZDMC–ZnO) Reaction

Several arguments could be presented to show that the thermal events above 136°C in the IR–sulfur–TMTD–ZnO curing curve were inter alia due to the IR–sulfur–ZDMC (or IR–sulfur–ZDMC–ZnO) vulcanization [Fig. 3(a)]. It implied therefore that two

consecutive crosslink reactions had occurred in the IR–sulfur–TMTD–ZnO system, and it was particularly significant that these reactions became well separated in the DSC analysis. (See discussion on DSC Curves.) The thermal events of the IR–sulfur–ZDMC (or IR–sulfur–ZDMC–ZnO) crosslink reaction were thus superimposed onto that of the network maturing reactions related to the IR–sulfur–TMTD–ZnO reaction.

The general shape of the IR–sulfur–ZDMC curing curve (Fig. 1 of Ref. 4) was in agreement with the shape of the latter part of Figure 3(a), attributed to the IR–sulfur–ZDMC reaction. The relative positions of the curves did, however, differ to some extent. It was pointed out previously[4] that ZDMC had decomposed on vulcanization in IR–sulfur–ZDMC systems. The same applies to the IR–sulfur–ZDMC reaction in the IR–sulfur–TMTD–ZnO compound, as the peak $G_3$ resulted from the evaporation of gases (such as $Me_2NH$ and $CS_2$). The thermogravimetric analysis (TGA) curve [Fig. 3(b)] revealed that a second evaporation process had started concurrently with the endotherm $G_3$ in the DSC trace at 141°C. The DTGA curve of the IR–sulfur–TMTD–ZnO system [Fig. 7(b)] also showed that the second evaporation peak $G_7$ was much more intense than the peak $G_6$. The maximum rate of evaporation was 0.54%/min at 141.4°C. Since the net enthalpy in the DSC curve was exothermic at that stage [Fig. 3(a)], and the crosslink density increased sharply from $11.51 \times 10^{-5}$ mol/ $cm^3$ (at 136.9°C) to $23.77 \times 10^{-5}$ mol/$cm^3$ rubber (at 146.9°C), it implied once again that the enthalpy of vulcanization was strongly exothermic.[1,4] Note that the relatively inefficient manner whereby DMDCA was trapped above 141°C would not necessarily imply that all of the ZnO became depleted in the IR–sulfur–TMTD–ZnO reaction. It could also have been that the ZDMC, which was rapidly formed below 137°C due to the IR–sulfur–TMTD–ZnO reaction (see discussion on IR–sulfur–TMTD–ZnO Reaction), had encrusted part of the ZnO particles, which were therefore less readily available to trap DMDCA at later stages of cure.

Moreover, the endotherm $G_3$ and the exotherm $G_4$ resulted chiefly from the extra-network material sulfur and ZDMC, which were present at 136.9°C in the IR–sulfur–TMTD–ZnO vulcanizate (Table I). The assertion was confirmed by means of the experiments below. An IR (100)–sulfur (9.46)–TMTD (8.86)–ZnO (3.00) vulcanizate was quenched at 138.7°C, extracted with benzene, and the dried network was rescanned. A very weak exotherm was observed [Fig. 8(b)], which
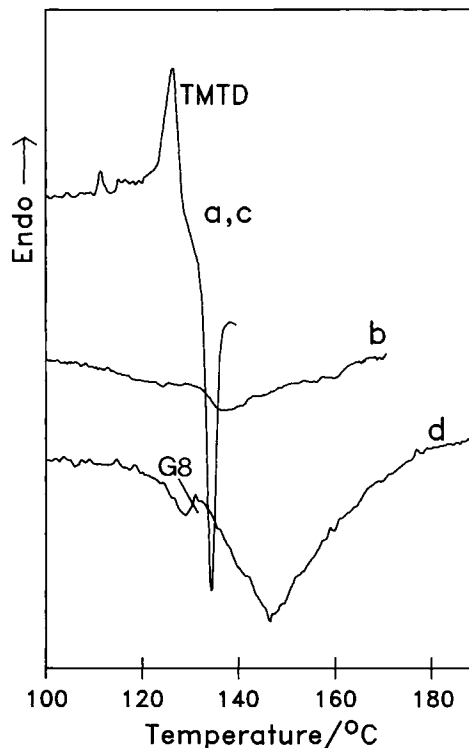


**Figure 8** DSC spectra. Scan rate 2.5°C/min. (a) IR (100)–sulfur (9.46)–TMTD (8.86)–ZnO (3.00) sample quenched at 138.7°C, $M_i$ = 16.925 mg. (b) Extracted sample rescanned to 170°C. (c) IR (100)–sulfur (9.46)– TMTD (8.86)–ZnO (3.00) sample quenched at 139.0°C, $M_i$ = 16.973 mg. (d) Sample rescanned directly to 190°C.

most likely originated from further reactions of the network-bound material, such as the initial polysulfidic crosslinks and pendent groups. A mass loss of only 0.55% was calculated by weighing the extracted dry sample before and after the rescan. As a control, an IR–sulfur–TMTD–ZnO sample was scanned to 139.0°C, quenched with liquid nitrogen, and was rescanned directly [Fig. 8(d)]. A mass loss of 3.65% was calculated by weighing the quenched sample before and after the rescan, implying that peak $G_8$ was most probably due to volatilization. It was evident that the rate of energy dissipation had increased in the DSC spectrum of the control sample relative to the proof sample [cf. Figs. 8(b) and 8(d)], and the general appearance of this curve resembled that of the IR–sulfur–ZDMC curing curve [cf. Fig. 1 of Ref. 4 and 8(d)]. Since elemental sulfur (63.6 mol %) and ZDMC (56.0 mol %) were the most abundant extra-network compounds in the IR–sulfur–TMTD–ZnO vulcanizate at 136.9°C, these experiments provided direct evidence that the enthalpy above 137°C in Figure 3(a) was due to IR–sulfur–ZDMC vulcanization.

The findings above were enriching with respect to mechanism of Bateman et al.[15] on TMTD-based vulcanization systems in which the in situ formation of ZDMC or zinc perthiomercaptides $XSS_xZnSX$ were postulated as an early step prior to vulcanization. The fact that the IR–sulfur–ZDMC (or IR–sulfur–ZDMC–ZnO) crosslinking route ensued as a consequence of the products formed in the IR–sulfur–TMTD–ZnO reaction was further evidence that $XSS_xZnSX$-type species are not formed as the first step in TMTD-based vulcanization compounds.

## Mechanistic Aspects on the IR–Sulfur–ZDMC (or IR–Sulfur–ZDMC–ZnO) Reaction

The mechanism of the IR–sulfur–ZDMC (or IR–sulfur–ZDMC–ZnO) vulcanization has been elaborated on previously.[4,5] These arguments would of course also hold in the present situation, and therefore only a few pertinent remarks will now be made.

As the free sulfur was essentially depleted at 150.2°C (Table I), the rest of the IR–sulfur–TMTD–ZnO curing enthalpy must have originated from network maturing reactions. The concentration of ZDMC, however, remained constant at ~ 38.4 mol % between 150.2 and 170.0°C, which implied (as before)[5] that ZDMC did not partake in the network maturing reactions. The concentration of polysulfidic crosslinks decreased sharply from $19.02 \times 10^{-5}$ mol/cm$^3$ at 146.9°C to $7.29 \times 10^{-5}$ mol/cm$^3$ at 170.0°C, mainly due to their destruction (Table III).

## Variation of the Crosslink Types in the IR–Sulfur–TMTD–ZnO Vulcanization System

An interesting phenomenon of the IR–sulfur–TMTD–ZnO vulcanization system was the variation in the percentage polysulfidic crosslinks compared to that already reported[1,2,4] for the compounds IR–sulfur–TMTD, IR–TMTD–ZnO, IR–sulfur–ZDMC, and IR–sulfur–ZDMC–ZnO. In all but the IR–sulfur–TMTD–ZnO system, there was a monotonic decrease in the percentage of polysulfidic crosslinks toward later stages of cure. The percentage of poly-

sulfidic crosslinks in the IR–sulfur–TMTD–ZnO system (Table I), however, decreased from 86.3% (at 131.9°C) to 76.4% (at 136.9°C), after which it increased to 80.0% at (146.9°C) and then dropped sharply to 53.5% (at 170.0°C). The reason for the increase in the percentage of polysulfidic crosslinks from 136.9 to 146.9°C was due to the IR–sulfur–ZDMC (or IR–sulfur–ZDMC–ZnO) reaction that occurred in this temperature region. There was, in actual fact, a dramatic increase of 116.4% in the number of polysulfidic crosslinks between 136.9 and 146.9°C (Table III).

## The Importance of the ZnO–Sulfur Ratio

It was self-evident from the preceding discussion that the physical properties of a vulcanizate could be controlled by the type of crosslink reaction that would dominate in the IR–sulfur–TMTD–ZnO system. For example, the IR–sulfur–TMTD–ZnO reaction occurred in the IR (100)–sulfur (4.73)–TMTD (8.86)–ZnO (3.00) (0.5/1.0/1.0 mole ratio) vulcanization system, but the IR–sulfur–ZDMC (or IR–sulfur–ZDMC–ZnO) reaction was limited due to the limiting amount of free elemental sulfur. This can be seen from the evaporation peak $G_3$, as it was concealed in the DSC thermogram of this compound [cf. Figs. 3(a) and 9(a)]. In the presence of less sulfur the amount of ZnO was, evidently, more than sufficient to limit evaporation.

As expected the reaction of ZnO and DMDCA was enhanced in the presence of more ZnO. The volatilization peak $G_3$ in the DSC curve of the IR (100)–sulfur (9.46)–TMTD (8.86)–ZnO (6.00) (1.0/1.0/2.0 mole ratio) compound appeared at a later stage than for the equimolar mixture [cf. Figs. 3(a) and 9(b)]. It was, however, clear that the amount of ZnO was still not enough to trap all of the DMDCA formed in the first vulcanization system.

## The IR–Sulfur–TMTD–ZnO–Stearic Acid System

It was relatively easy to interpret the complex DSC spectrum of the IR (100)–sulphur (9.46)–TMTD

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

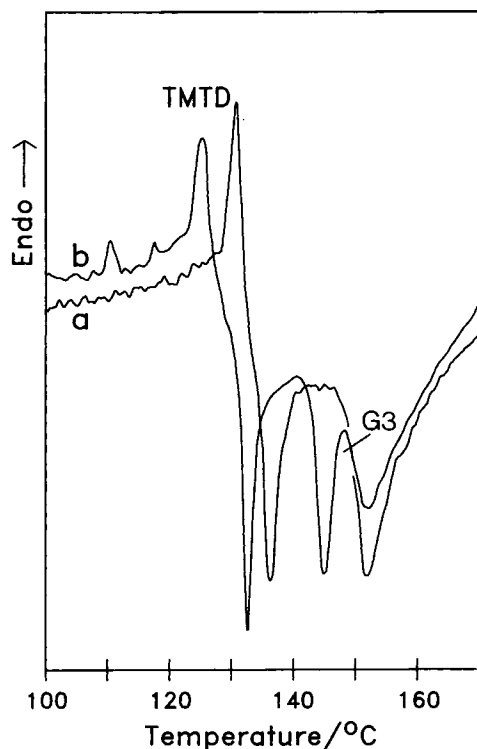| Temperature (°C) | 131.9 | 136.9 | 141.4 | 146.9 | 150.2 | 170.0 |
|---|---|---|---|---|---|---|
| Polysulfides (mol/cm$^{-3}$ rubber network $\times$ 10$^5$) | 1.26 | 8.79 | 12.73 | 19.02 | 14.16 | 7.29 |
| Mono- and/or disulfides (mol/cm$^{-3}$ rubber network $\times$ 10$^5$) | 0.20 | 2.72 | 3.71 | 4.75 | 5.26 | 6.33 |

**Figure 9**  DSC spectra. Scan rate 2.5°C/min. (a) IR (100)-sulphur (4.73)-TMTD (8.86)-ZnO (3.00) (0.5/1.0/1.0 mole ratio), $M_i$ = 19.856 mg. (b) IR (100)-sulfur (9.46)-TMTD (8.86)-ZnO (6.00) (1.0/1.0/2.0 mole ratio), $M_i$ = 17.064 mg.

(8.86)-stearic acid (10.49)-ZnO (3.00) (1.0/1.0/1.0/1.0 mole ratio) system depicted in Figure 10 by comparing it with that obtained in the absence of stearic acid (Fig. 1). The total spectrum [Fig. 10(a)] revealed the melting of stearic acid below 60°C, followed by an intense zinc stearate crystallization peak at 87.2°C. The corresponding exotherm appeared at 86.5°C in a duplicate run. Zinc stearate was formed at 165°C on scanning a stearic acid-ZnO (1.0/1.0 mole ratio) mixture at 20°C/min in the absence of IR.[23] The stearic acid-ZnO reaction was, however, catalyzed by the addition of $H_2O$ and, on heating a stearic acid-ZnO-$H_2O$ (1.0/1.0/1.0 mole ratio) mixture, occurred rapidly just after the stearic acid had melted. It is possible that $H_2O$ formed in the stearic acid-ZnO reaction of the vulcanization mixture was trapped in the rubber and catalyzed the reaction.

The endotherm $H_1$ in Figure 10(b) was due to the melting of zinc stearate that masked the melting of sulfur. Peak $H_2$ was ascribed to the liquefaction of TMTD (cf. Fig. 1). These interactions were the

same as those observed for the sulfur-TMTD-stearic acid-ZnO (1.0/1.0/1.0/1.0 mole ratio) mixture scanned at 5°C/min.[9] But, after the liquefaction of TMTD in the IR medium, there was, however, a strong interaction with the IR chains. The exotherm $H_3$ resulted from the crystallization of zinc dimethyldithiocarbamate (ZDMC), a product of the IR-sulfur-TMTD-ZnO[2] (or zinc stearate) vulcanization reaction. It was confirmed with TLC that ZDMC was formed in the reaction above. Free stearic acid was most likely also regenerated in the IR-sulfur-TMTD-zinc stearate reaction, as it has been reported[24] that lauric acid forms in the IR-TMTD-zinc laurate vulcanizate. The large volatilization peak $H_4$ was superimposed on the IR-sulfur-ZDMC (or IR-sulfur-ZDMC-zinc stearate) reaction exotherm $H_5$ [cf. Figs. 1 and 10(b)]. The exotherm $H_6$ above ~ 150°C was mainly due to network maturing reactions.

The melting peak of zinc stearate was very prominent in the DSC curve of the IR-sulfur-TMTD-zinc stearate vulcanization compound (Fig. 11), and the same explanations that were presented to elu-
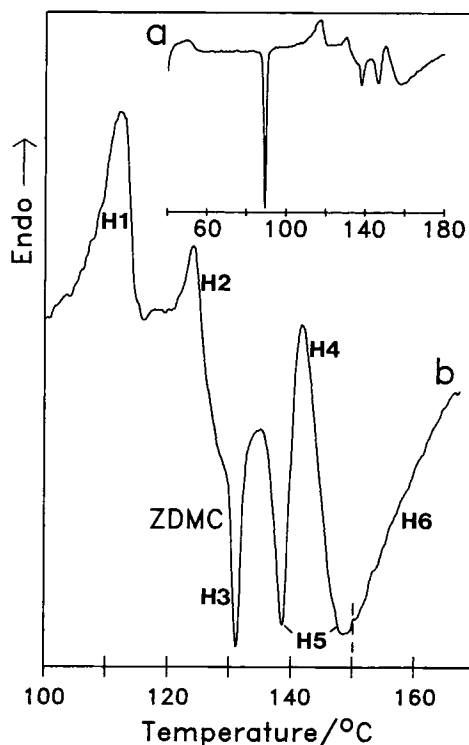


**Figure 10**  DSC spectrum. Scan rate 2.5°C/min. (a) IR (100)-sulfur (9.46)-TMTD (8.86)-stearic acid (10.49)-ZnO (3.00) (1.0/1.0/1.0/1.0 mole ratio), $M_i$ = 17.933 mg. (b) An expanded part of the spectrum.
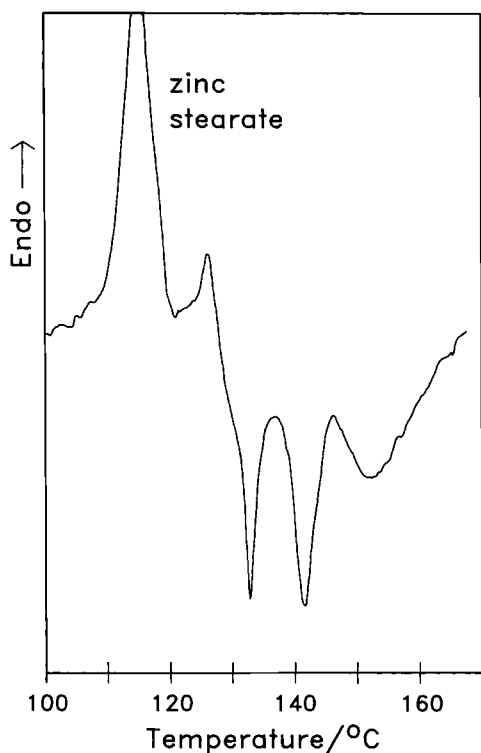
**Figure 11** DSC spectrum. Scan rate 2.5°C/min. IR (100)-sulfur (9.46)-TMTD (8.86)-zinc stearate (23.91) (1.0/1.0/1.0 mole ratio), $M_i$ = 17.994 mg.

cidate the DSC curve of the IR–sulfur–TMTD–stearic acid–ZnO system would also be valid in this case. It was thus noticeable that the vulcanization thermograms of the IR–sulfur–TMTD–ZnO, IR–sulfur–TMTD–stearic acid–ZnO and IR–sulfur–TMTD–zinc stearate compounds (Figs. 1, 10, and 11) were nearly identical. Therefore, although reactions of the kind TMTD–stearic acid, sulfur–TMTD–stearic acid and TMTD–stearic acid–ZnO were detected above 130°C in the absence of IR,[9] these reactions were of negligible importance in the TMTD-accelerated sulfur vulcanization of IR. The findings were in contrast with the proposal of Porter[10] that the in situ formation of ZDMC or $XS_xSZnSX$ [X = $Me_2NC$ (S)] would involve the reaction of ZnO, fatty acid, and accelerator, as the first step in TMTD-accelerated sulfur vulcanization.

## CONCLUSION

Two consecutive crosslinking reactions dominated in the IR–sulfur–TMTD–ZnO vulcanization compound, viz. the IR–sulfur–TMTD–ZnO and IR–sul-

fur–ZDMC (or IR–sulfur–ZDMC–ZnO) reactions. The same two crosslinking reactions were observed in the presence of stearic acid.

The spectacular difference in the DSC curves of the IR–sulfur–TMTD–ZnO and EPM–sulfur–TMTD–ZnO mixtures provided more evidence that ZDMC or zinc perthiomercaptides $XSS_xZnSX$ were not formed in situ prior to vulcanization as claimed.[14-16] The DTGA curve on the IR–sulfur–TMTD–ZnO compound emphasized that ZnO was extremely efficient in trapping DMDCA that was formed on crosslinking in the IR–sulfur–TMTD–ZnO reaction. The stoichiometric amount of ZnO was, however, not enough to inhibit the decomposition of DMDCA, which formed as a by-product in the IR–sulfur–ZDMC reaction.

In connection with the network maturing reactions in the IR–sulfur–TMTD–ZnO compound, it was once again found that ZDMC played no role in the shortening of polysulfidic crosslinks.[5,21] The free sulfur was essentially depleted at 150.2°C, after which the ZDMC concentration remained constant at ∼ 38.4 mol % between 150.2 and 170.0°C. Since ZDMC decompose on vulcanization, these results implied that ZDMC was not involved in the desulfuration of sulfidic crosslinks. The concentration of polysulfidic crosslinks decreased from 14.16 × 10⁻⁵ mol/cm³ to 7.29 × 10⁻⁵ mol/cm³ in this temperature range, mainly due to their destruction.

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