

# *N,N'*-Pentamethylenethiuram Disulfide and *N,N'*-Pentamethylenethiuram Hexasulfide Accelerated Sulfur Vulcanization. III. Vulcanization of Polyisoprene and 2,3-Dimethyl-2-butene in the Absence of ZnO

C. P. REYNEKE-BARNARD, M. H. S. GRADWELL, W. J. MCGILL

Polymer Chemistry, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, 6000, South Africa

Received 25 August 1999; accepted 16 October 1999

**ABSTRACT:** Polyisoprene and model compound, 2,3-dimethyl-2-butene, were vulcanized with *N,N'*-dipentamethylenethiuram disulfide (CPTD), CPTD/sulfur and *N,N'*-dipentamethylenethiuram hexasulfide (CPTP6) in the absence of ZnO and residual extractable curatives and reaction intermediates analyzed by HPLC at various stages of the reaction. Accelerator polysulfides, required for the formation of accelerator-terminated polysulfidic pendent groups, form rapidly, or are present from the outset in the case of CPTP6. Model compounds confirm the formation of thiuram-terminated polysulfidic pendent groups as intermediates in the vulcanization process. Removal of pentamethylenedithiocarbamic acid (Hpmtc) from the system during heating delays the onset of vulcanization and leads to very low crosslink densities. Rubbers heated under vacuum can subsequently be crosslinked by the addition of zinc stearate, pointing to the presence in the compound of thiuram-terminated pendent groups. However, such pendent groups do not readily crosslink on their own, and hydrogen-terminated polysulfidic pendent groups, formed by the reaction of sulfurated Hpmtc with the polymer, are suggested to be involved in the crosslink formation. *N,N'*-Pentamethylenethiurea forms in the vulcanizate, but is not as product of crosslinking reactions, rather of CPTD degradation. The data are discussed with respect to mechanisms proposed in the literature for crosslinking, and it is concluded that the data support recently formulated mechanisms in which crosslinking involves reaction between thiuram and thiol-terminated pendent groups, with Hpmtc playing an essential role in the overall process. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1100–1111, 2000

**Key words:** vulcanization; *N,N'*-dipentamethylenethiuram sulfides; alkyldithiocarbamic acids; mechanism

## INTRODUCTION

Accelerator polysulfides are generally acknowledged to act as sulfurating agents for accelerated sulfur vulcanization in the absence of ZnO.<sup>1,2</sup> In tetramethylthiuram disulfide (TMTD)-acceler-

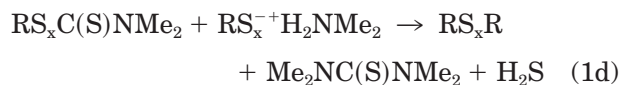
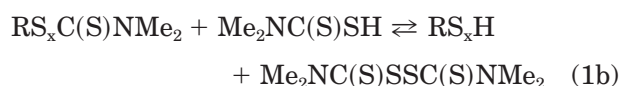
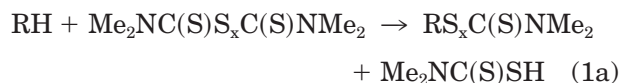
ated sulfur vulcanization, interaction of tetramethylthiuram polysulfides (TMTP) with the polymer chain via a concerted reaction<sup>1–4</sup> leads to the formation of thiuram-terminated pendent groups and dimethyldithiocarbamic acid (Hdmtc).<sup>1–6</sup> The formation of such pendent groups have been confirmed in model compound studies.<sup>4,6,7</sup> Crosslinking is said to result from the interaction between pendent groups or from a reaction between a pendent group and a neighboring polymer chain.<sup>7–9</sup>

Correspondence to: W. J. McGill.

Contract grant sponsor: Karbochem.

*Journal of Applied Polymer Science*, Vol. 78, 1100–1111 (2000)  
© 2000 John Wiley & Sons, Inc.

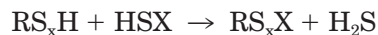
However, more recently it has been shown that pendent group chain reactions do not occur,<sup>10</sup> and that disproportionation reactions between pendent groups are slow,<sup>10-12</sup> and alternative crosslinking mechanisms have been suggested. Geysler and McGill<sup>13</sup> suggested that thiuram pendent groups exchanged with Hdmtc to form polysulfidic hydrogen-terminated pendent groups on the chain, and that these reacted further with dimethylamine, formed in the vulcanizate, to give dimethylammonium pendent groups. Tetramethylthiourea (TMTU) was detected coincident with the onset of crosslinking, and it was proposed that TMTU was a product of the crosslinking reaction between thiuram and dimethylammonium pendent groups.



Although the decomposition of TMTD to TMTU at vulcanization temperatures has been reported,<sup>1,14,15</sup> other authors<sup>16-18</sup> claim that it is stable at vulcanization temperatures, and TMTU is only formed in vulcanizates, i.e., it results from reactions associated with crosslinking. However, *N,N'*-dipentamethylenethiuram disulfide (CPTD) degrades to *N,N'*-pentamethylenethiourea (CPTU) at vulcanization temperatures<sup>16,19</sup> and, should it also form as a result of the crosslinking process, accelerated CPTU formation can be expected when CPTD and CPTD/sulfur are added to rubber.

More recently, it has been demonstrated that when Hdmtc is removed from the system during vulcanization, crosslinking is slow.<sup>11</sup> Shelver et al.<sup>12</sup> proposed reaction between Hdmtc and sulfur to form the more highly sulfurated acid, which reacted with the polymer to form polysulfidic hydrogen-terminated pendent groups. Rapid exchange of thiols with Hdmtc and TMTD led to thiuram-terminated pendent groups. Crosslinking is observed only once the TMTD concentration decreased to below 20 mol % of the original TMTD

loading, and this is attributed to the exchange reaction now being sufficiently slow to permit thiol and thiuram pendent groups to crosslink.



where X = (CH<sub>3</sub>)<sub>2</sub>NC(S)S—

As in the first reaction sequence, the formation of both thiuram and thiol pendent groups was proposed, but crosslinking was suggested to result from the interaction of thiuram and thiol pendent groups without the involvement of dialkylammonium crosslink pendent group intermediaries.

*N,N'*-dipentamethylenethiuram sulfides are available as di- and hexasulfides. The formation of accelerated polysulfides are a prerequisite for the formation of polysulfidic thiuram terminated pendent groups, and it has been suggested<sup>20</sup> that a delay in polysulfide formation will delay the onset of crosslinking. In the CPTD/sulfur system *N,N'*-dipentamethylenethiuram polysulfides (CPTP) form within a minute at 140°C,<sup>19</sup> and the replacement of CPTD/sulfur with *N,N'*-dipentamethylenethiuram hexasulfide (CPTP6) would have no beneficial effect in this regard.

This article examines the vulcanization of polyisoprene (IR) and of model compound 2,3-dimethyl-2-butene (TME) with *N,N'*-dipentamethylenethiuram sulfides and sulfur in the absence of ZnO, and discusses data obtained with respect to the earlier and more recently proposed crosslinking mechanisms.

## EXPERIMENTAL

### Materials

Polyisoprene (Afpren IR80, Karbochem South Africa), TME (Aldrich Chemical Co., 99.9%), CPTD (Robac P.T.D), and CPTD6 (Robac P.25) (Robinson Brothers Ltd, technical purity), sulfur (Holpro Analyticals, 99.94%). Hydroperoxides,

**Table I Acronyms Used**

Acronym	Name
CPTD	<i>N,N'</i> -dipentamethylenethiuram disulfide
CPTM	<i>N,N'</i> -dipentamethylenethiuram monosulfide
CPTP	<i>N,N'</i> -dipentamethylenethiuram polysulfide
CPTP6	<i>N,N'</i> -dipentamethylenethiuram hexasulfide
CPTU	<i>N,N'</i> -dipentamethylenethiourea
dma.dmtc	Dimethylammonium dimethyldithiocarbamate
Hdmtc	Dimethyldithiocarbamic acid
Hpmtc	Pentamethylenedithiocarbamic acid
IR	Polyisoprene
pip.pmtc	Pentamethyleneammonium pentamethylenedithiocarbamate
TME	2,3-Dimethyl-2-butene
TMTD	Tetramethylthiuram disulfide
TMTP	Tetramethylthiuram polysulfide
TMTU	Tetramethylthiourea
X in equations	alkyldithiocarbamyl

which may interfere with the crosslinking process, were removed from TME by shaking with aqueous ferrous sulfate.<sup>21</sup> Acronyms used are listed in Table I.

Compounds were mixed on a Brabender Plasticorder and vulcanized in a DSC at a programmed heating rate to various temperatures, or isothermally in a small mold at 150°C. Formulations are indicated in brackets in the text as parts per 100 rubber. Residual curatives and extractable reaction intermediates were analyzed by HPLC. Compounding, extraction, and HPLC procedures have been detailed.<sup>22,23</sup> Extractions were 80–95% efficient. CPTP6 contains 12 mol % sulfur as an impurity, and analyses of CPTP6 compounds prior to heating therefore show about 80 mol % CPTP6 and 12 mol % sulfur. The synthesis of compounds needed for HPLC identification and analyses have been described in an earlier articles in this series.<sup>19</sup> Crosslink densities were determined by swelling.<sup>23</sup> TME formulations were reacted in evacuated sealed tubes fully immersed in an oil bath at 150°C for various times, and analyzed by HPLC. A total of nine peaks in the HPLC chromatogram were found to increase and then decrease as the reaction progressed, and these were attributed to thiuram-terminated polysulfidic pendent groups (TME-S<sub>x</sub>X). The disulfidic pendent group, (2,3-dimethyl-2-butene-1-yl)(dimethyldithiocarbamate)disulfide (TME-S<sub>2</sub>X), was synthesized<sup>10</sup> by the dropwise addition of iodine (1.0 g) in pyridine (20 mL) to a solution of 2,3-dimethyl-2-butenethiol (0.55 g) and sodium pentamethyldithiocarbamate (0.50

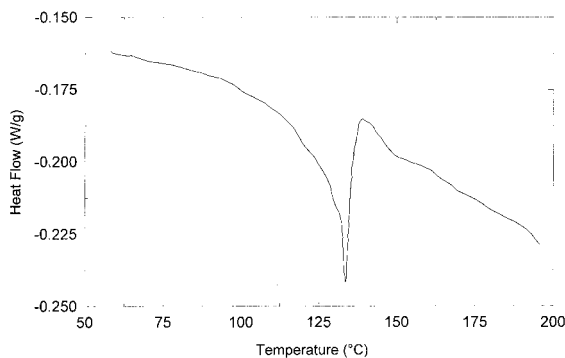
g). After removal of pyridine, the residue was extracted with diethylether and filtered. Using TLC, with dichloromethane as mobile phase, RS<sub>x</sub>X was isolated. Analysis for C<sub>12</sub>H<sub>21</sub>NS<sub>3</sub> (275.49): C 52.32, H 7.68, N 5.08%: found, C 52.31, H 7.71, N 4.80%. <sup>1</sup>H-NMR: δ = 1.62 (s, 9H), 1.75 (s, 3H), 1.78 (s, 3H), 3.52 (s, 2H), 3.90 (s, 2H), 4.27 ppm (s, 2H). <sup>13</sup>C-NMR: δ = 18.75, 21.31, 21.34, 24.60, 43.76, 76.99, 77.42, 77.84, 122.48, 132.79, 197.00 ppm. Upon injection into the HPLC the compound was found to elute coincident with the second of the series of peaks attributed to thiuram terminated polysulfidic pendent groups. Peaks in the HPLC attributed to crosslinked products were identified by comparing elution times with those of crosslinked product peaks characterized in these laboratories for the TME/2-bisbenzothiazole-2,2'-disulfide/sulfur system.<sup>21</sup>

In the figures and tables the concentrations of reactants, intermediates, and products are expressed in terms of the initial concentration of the reactant.

## RESULTS

### IR(100/CPTD(11.82))

To enable changes in the concentrations of reactant and extractable intermediates to be followed, higher curative concentrations were used than are commonly encountered with commercial vulcanizates where the properties of the product are



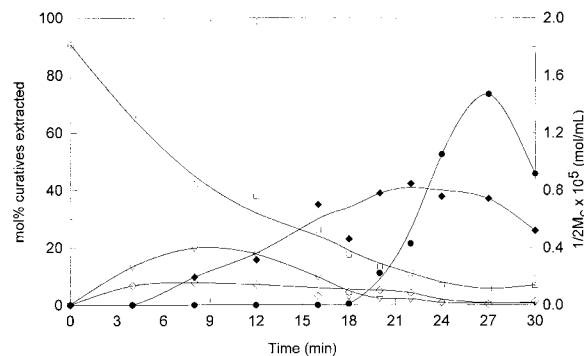
**Figure 1** DSC scan of IR(100)/CPTD(11.82) at 5°C/min.

important. The solubility of curatives in rubbers are highly dependent on temperature, increasing rapidly at or below vulcanization temperatures<sup>24</sup> and, with the high curative loadings used, curatives precipitated in compounds at room temperature. Consequently, the melting and dissolution of curatives in the rubber were observed as endothermic events on heating samples in the DSC. Thus, a DSC scan of IR/CPTD at 5°C/min revealed a small endotherm with a maximum at 133°C (Fig. 1) attributed to melting of CPTD (m.p. 132°C).<sup>19</sup> Above 145°C, the concentration of extractable CPTD decreased progressively, and approximately 5 mol % *N,N'*-dipentamethylenethiuram monosulfide (CPTM) and CPTP were detected. CPTU formation, accompanied by a mass loss (CS<sub>2</sub>), occurred above 160°C, and a lightly crosslinked network developed above 170°C (1/2Mc = 0.86 × 10<sup>-5</sup> mol/mL rubber at 180°C), at which point only 14 mol % CPTD remained extractable.

On isothermal vulcanization of IR/CPTD at 140°C the CPTD concentration decreased (Fig. 2), as expected. CPTM formed rapidly, as in the absence of rubber,<sup>19</sup> although its conversion to CPTU soon led to a decrease in concentration. CPTP formed, but remained at a low concentration, its rate of formation being matched by its rate of addition to the polymer chain as polysulfidic pendent groups. The CPTP concentration decreased after 24 min when the CPTD concentration became very low. Limited crosslinking initiated after 18 min when the CPTD concentration had dropped to about 20 mol %.

#### IR(100)CPTD(11.82)/Sulfur(9.46)

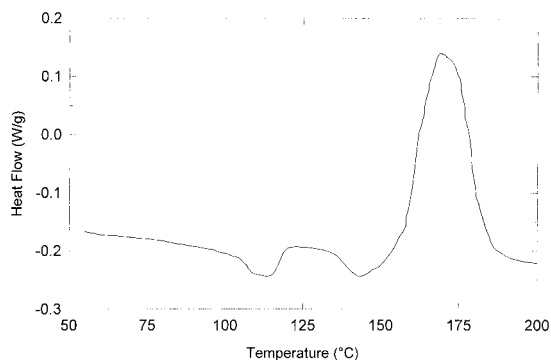
The first endotherm in the DSC scan of IR/CPTD/sulfur at 5°C/min was attributed to sulfur phase



**Figure 2** Crosslink density and HPLC analysis of reaction products extracted from IR(100)/CPTD(11.82) heated at 140°C. (◆) CPTU; (▽) CPTM; (■) CPTD; (◇) CPTP; (△) Sulfur; (●) 1/2Mc.

transitions. The second endotherm, associated with the escape of volatile by-products of the vulcanization process, overlapped with the vulcanization exotherm commencing at 150°C (Fig. 3). Similar thermal events were reported for TMTD accelerated sulfur vulcanization.<sup>5</sup>

Prior to heating of an IR/CPTD/sulfur sample, 87 mol % CPTD and 71 mol % sulfur were extractable from rubber films (Table II). Upon heating, the amount of extractable CPTD decreased and then increased again at 137°C, before decreasing to a very low value at the onset of crosslinking (150°C). The concentrations of extractable sulfur showed parallel variations, although its concentration decreased less rapidly than that of CPTD, and approximately 60 mol % remained extractable when crosslinking commenced. CPTP formed, its concentration remaining fairly constant until crosslinking after which little CPTP could be detected. Small amounts of CPTM were found above 137°C. CPTU formation commenced at 147°C.

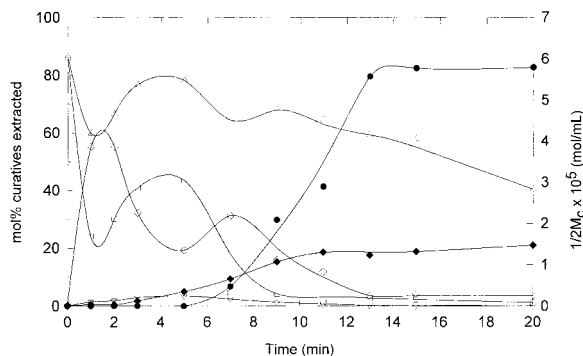


**Figure 3** DSC scan of IR(100)/CPTD(11.82)/sulfur(9.46) at 5°C/min.

**Table II** Crosslink Density and HPLC Analysis of Reaction Products Extracted from IR(100)/CPTD(11.82)/Sulfur(9.46) Heated at 5°C/min

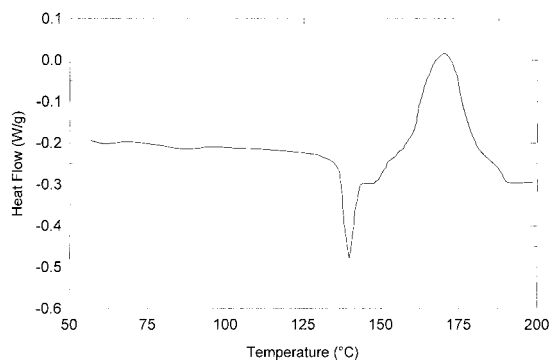
Temp (°C)	Mass Loss (%)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	CPTP (mol %)	Sulfur (mol %)	$1/2M_c$ (mol/mL $\times 10^5$ )
25	0	0	0	87	0	71	0
110	0	0	1	60	18	78	0
125	0.04	0	4	15	34	56	0
137	0.05	1	3	24	35	66	0
147	0.2	5	3	11	33	58	0.02
150	0.13	13	2	2	30	61	0.61
158	0.34	18	0	2	2	60	3.92
163	2.03	18	0	2	3	35	3.49
187	1.83	10	0	4	2	0	5.03

On isothermal vulcanization of IR/CPTD/sulfur at 140°C, the concentration of CPTD also decreased rapidly, with a concomitant increase in the concentration of CPTP (CPTP3–CPTP8 were detected, but only the total concentration of CPTP is reported). CPTD then increased again while CPTP decreased (Fig. 4). The concentration of extractable sulfur followed a similar trend to the concentration of CPTD, decreasing initially as CPTP increased, before increasing at 5 min when CPTP decreased. With the onset of crosslinking, the concentrations of CPTD, CPTP, and sulfur decreased, although the concentration of sulfur decreased less rapidly. CPTU formation followed a similar trend to its formation during the decomposition of CPTD/sulfur in the absence of rubber,<sup>19</sup> although CPTU ultimately formed in lower concentrations in vulcanizate. Crosslinking commenced after 7 min, and increased to  $5.57 \times 10^{-5}$  mol/mL at 15 min, where after a slow increase to  $5.79 \times 10^{-5}$  mol/mL was measured.

**Figure 4** Crosslink density and HPLC analysis of reaction products extracted from IR(100)/CPTD(11.82)/sulfur(9.46) heated at 140°C. (◆ CPTU; ▽ CPTM; □ CPTD; ◇ CPTP; △ Sulfur; ●  $1/2M_c$ ).**IR(100)/CPTP6(16.57)**

The DSC scan of IR/CPTP6 at 5°C/min revealed the melting of crystalline CPTP6 at 139°C and a partly hidden endotherm, commencing immediately after the melting of CPTP6, attributed to the escape of a volatile by-product (Fig. 5). Crosslinking reactions are reflected by the broad exotherm commencing at 155°C. Similar endothermic and exothermic events were observed during the heating of IR/CPTD/sulfur at 5°C/min (Fig. 3). Upon heating, the amount of extractable CPTD and sulfur increased with a concomitant decrease in the amounts of CPTP (Table III). CPTU formed, and crosslinking commenced at 150°C.

Upon isothermal vulcanization at 140°C, the concentration of CPTP decreased rapidly as the concentration of CPTD and sulfur increased (Fig. 6). The CPTP concentration then increased, while CPTD and sulfur decreased. Similar changes were observed during the isothermal vulcanization of IR/CPTD/sulfur (Fig. 4), but not during the

**Figure 5** DSC scan of IR(100)/CPTP6(16.57) at 5°C/min.

**Table III** Crosslink Density and HPLC Analysis of Reaction Products Extracted from IR(100)/CPTP6(16.57) Heated at 5°C/min

Temp (°C)	Mass Loss (%)	CPTU (mol %)	CPTM (mol %)	CPTD (mol %)	CPTP (mol %)	Sulfur (mol %)	1/2M <sub>c</sub> (mol/mL × 10 <sup>5</sup> )
25	0	0	0	0	79	12	0
135	0.01	0	0	22	28	30	0
140	0.03	0	2	30	30	45	0
145	0.05	1	2	45	14	62	0
150	0.1	9	2	13	24	38	0.1
155	3.12	14	1	5	14	34	2.17
163	2.52	16	0	2	4	22	4.36
170	1.8	17	0	5	7	27	3.21
180	2.04	16	0	15	0	31	1.7

isothermal heating of CPTD/sulfur or CPTP6 in the absence of rubber.<sup>19</sup> CPTU was detected after 5 min, but its rate of formation was slower than in the absence of rubber. Crosslinking commenced after 7.5 min and a maximum crosslink density of  $5.36 \times 10^{-5}$  mol/mL was measured at 16 min, where after a minimal decrease to  $5.29 \times 10^{-5}$  mol/mL was measured at 20 min.

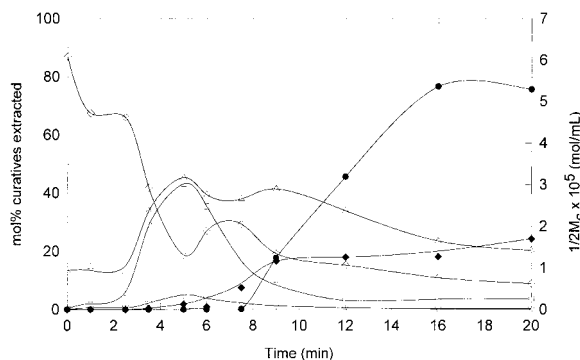
#### TME/CPTP6 (34.0 : 1.0 mol ratio)

HPLC analysis of TME/CPTP6, heated at 140°C, showed that a decrease in the concentration of CPTP coincided with an increase in the concentrations of CPTD and sulfur (Fig. 7), and therefore, followed an analogous trend to vulcanization of IR/CPTP6 (Fig. 6). After the initial decrease, the concentration of CPTP increased slightly, but this increase was much less than observed with IR/CPTP6. The concentration of sulfur remained constant on further heating, before decreasing at

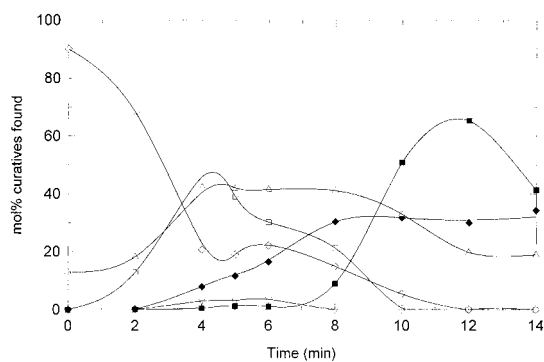
8 min, whereas the concentration of CPTD decreased rapidly during crosslink precursor formation. CPTU formation commenced earlier, and it formed in higher concentrations when compared to CPTU formation during vulcanization of IR/CPTP6.

Pendent groups consist of a TME molecule with a dithiocarbamyl moiety.<sup>6,25</sup> Pendent groups of varying sulfur rank were identified, and appeared to form in two stages (Fig. 8): an initial stage (0–6 min), involving the formation of pendent groups of various sulfur rank, followed by a second stage (6–10 min) during which predominantly tri- and tetrasulfide pendent groups were added.

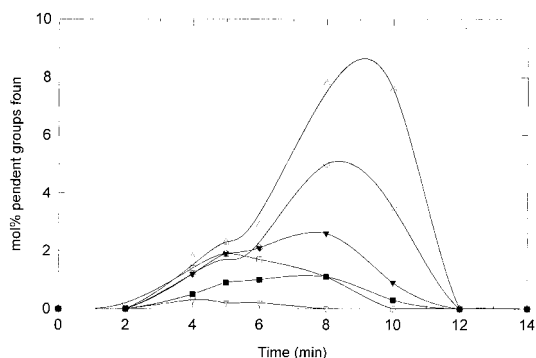
Crosslinked model compound was detected once the CPTD concentration decreased to approximately 20 mol % (Figs. 7 and 9). Di- and trisulfidic crosslink products were preferentially formed, with lesser amounts of other crosslink products. The formation of pentamethyleneam-



**Figure 6** Crosslink density and HPLC analysis of reaction products extracted from IR(100)/CPTP6(16.57) vulcanized at 140°C. (◆ CPTU; ▽ CPTM; □ CPTD; ◇ UCPTP; △ Sulfur; ● 1/2M<sub>c</sub>).



**Figure 7** HPLC analysis of reaction products found in TME/CPTP6 (34.0 : 1.0 mol ratio) heated at 140°C. (◆ CPTU; ▽ CPTM; □ CPTD; ◇ CPTP; △ Sulfur; ■ pip-pmtc).

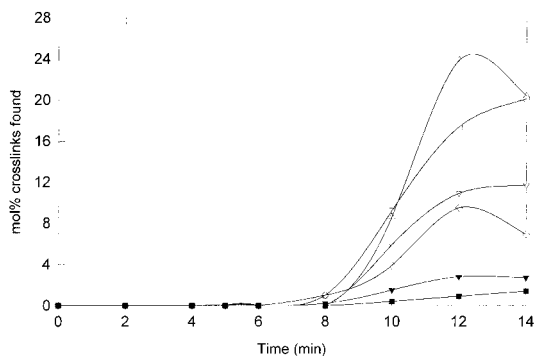


**Figure 8** HPLC analysis of thiuram crosslink precursors found in TME/CPTP6 (34.0 : 1.0 mol ratio) heated at 140°C. ( $\nabla$  R-S<sub>1</sub>-X;  $\square$  R-S<sub>2</sub>-X;  $\triangle$  R-S<sub>3</sub>-X;  $\diamond$  R-S<sub>4</sub>-X;  $\nabla$  R-S<sub>5</sub>-X;  $\blacksquare$  R-S<sub>6</sub>-X).

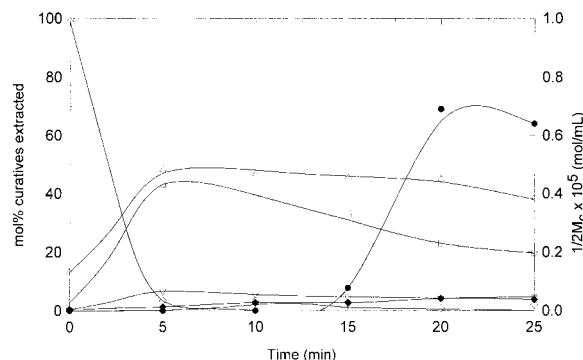
monium pentamethylenedithiocarbamate (pip · pmtc) was found to coincide with crosslink formation (Fig. 7 and 9). The model compound system was the only one in which pip · pmtc was detected on crosslinking.

#### IR(100)/CPTP6(16.57) Vulcanization under Vacuum

IR/CPTP6, deposited as a thin film inside glass sample tubes, was vulcanized at 140°C under vacuum to encourage the escape of volatile reaction products, particularly Hpmtc, which, by analogy to vulcanization of the TMTD/sulfur system, would be liberated during pendent group formation. The concentration of CPTP decreased rapidly, and resulted in the formation of 43 mol % CPTD and 48 mol % sulfur after 5 min vulcanization (Fig. 10); an analogous trend was observed during the vulcanization of IR/CPTP6 (Fig. 6).



**Figure 9** HPLC analysis of crosslinked model compound found in TME/CPTP6 (34.0 : 1.0 mol ratio) heated at 140°C. ( $\nabla$  R-S<sub>1</sub>-R;  $\square$  R-S<sub>2</sub>-R;  $\triangle$  R-S<sub>3</sub>-R;  $\diamond$  R-S<sub>4</sub>-R;  $\nabla$  R-S<sub>5</sub>-R;  $\blacksquare$  R-S<sub>6</sub>-R).



**Figure 10** Crosslink density and HPLC analysis of reaction products extracted from IR(100)/CPTP6(16.57) vulcanized at 140°C under vacuum. ( $\blacklozenge$  CPTU;  $\nabla$  CPTM;  $\square$  CPTD;  $\diamond$  CPTP;  $\triangle$  Sulfur;  $\bullet$  1/2Mc).

Increasing the vulcanization time, however, resulted in a slow decrease in the concentration of CPTD and sulfur, compared to the faster rate of decrease during vulcanization without vacuum (Fig. 6). In a vacuum, crosslinking only commenced after 15 min, while crosslinking took place after 8 min on vulcanization in a press. A maximum crosslink density of only  $0.69 \times 10^{-5}$  mol/mL was measured, compared to a maximum crosslink density of  $5.36 \times 10^{-5}$  mol/mL measured during vulcanization in a press. No CPTU was detected during the vulcanization under vacuum.

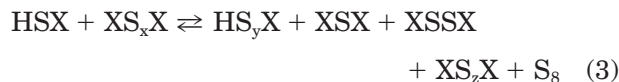
## DISCUSSION

### CPTP Formation

Lower amounts of CPTP formed on vulcanization of IR/CPTD and IR/CPTD/sulfur compared to CPTP formation in the absence of IR,<sup>19</sup> and can be attributed to interaction between CPTP and rubber to form thiuram-terminated polysulfidic pendent groups in a reaction analogous to that for other accelerator polysulfides.<sup>4,5,20</sup> Accelerator polysulfides are the active sulfurating agents for vulcanization, and the small amounts of CPTP formed in IR/CPTD (Fig. 2) would result in few pendent groups and the low degree of crosslinking observed.

Exchange reactions between dialkyldisulfides are well known,<sup>26</sup> and the ready exchange between TMTD and 2-bisbenzothiazole-2,2'-disulfide and between TMTD and 2-mercaptobenzothiazole has been demonstrated.<sup>27</sup> An exchange between Hdmtc and TMTP was suggested to be responsible in part for decrease in TMTP concen-

trations during TMTD accelerated vulcanization,<sup>12</sup> while partial degradation of Hdmtc to dimethylamine may also result in the formation of some TMTU via the amine catalyzed degradation of TMTD.



The observed increase in concentrations of CPTD and sulfur during the early stages of vulcanization in IR/CPTD/sulfur, IR/CPTP6 and TME/CPTP6 (Figs. 4, 6, and 7) point to a similar exchange between CPTP6 and Hpmtc.

### CPTU Formation

CPTU forms after an induction period and at a fairly constant although slightly slower rate than in the absence of rubber.<sup>16,19</sup> Its formation is clearly independent of the vulcanization process, and is catalyzed by amines formed in the system, as discussed in an earlier articles.<sup>16</sup> The slower formation of CPTU can be attributed to competition between amine attack on CPTP and the reaction of CPTP with the polymer chain to form thiuram-terminated pendent groups. During vulcanization, large amounts of Hpmtc are released when pendent groups form, yet this did not accelerate CPTU formation, indicating that Hpmtc must be consumed rapidly during the vulcanization process. During model compound vulcanization, CPTU formation commenced slightly earlier, and higher concentrations were detected than in IR vulcanization (cf. Figs. 6 and 7). Model compounds were studied in sealed sample tubes that would be more effective in preventing the escape of piperidene than a vulcanization press, and this may account for the more ready formation of CPTU in the former case.

### Thiuram-Terminated Pendent Group Formation

The formation and reaction of thiuram-terminated pendent groups in TME compounds (Fig. 8) shows that CPTD accelerated sulfur vulcanization occurs by an analogous mechanism to the TMTD-accelerated reaction.<sup>4,5</sup> Furthermore, IR/CPTP6, heated to 7.5 min at 140°C (Fig. 6), i.e., to a point prior to crosslink formation, and extracted with isopropyl alcohol to remove residual curatives, crosslinked upon further heating. This, too, points to the formation in the rubber of pendent groups that give rise to crosslinking. Such thiuram-

terminated pendent group formation is widely regarded to occur via a concerted mechanism, involving an accelerator polysulfide and the rubber chain or a model compound molecule,<sup>1,7-9</sup> with elimination of alkylthiocarbamic acid as a by-product. However, no Hpmtc was detected at any stage during the vulcanization of IR or TME, although Geyser and McGill<sup>4</sup> detected small amounts of Hdmtc, released in TMTD-accelerated formulations. Hpmtc must clearly be consumed rapidly in further reactions, possibly in the formation of polysulfidic hydrogen-terminated pendent groups as proposed by Shelver et al.<sup>12</sup> [eqs. (2a) and (2b)].

In a study of the TMTD-accelerated sulfur vulcanization of TME, Geyser and McGill<sup>4</sup> found thiuram pendent group formation to occur in a two stage process similar to that demonstrated in Figure 8. The increase in the concentrations of tri- and tetrasulfidic thiuram pendent groups detected coincides with a decrease in CPTD (Fig. 7). This more rapid increase in pendent groups is reproducible in duplicate experiments. Geyser and McGill<sup>4</sup> suggested that some thiuram pendent groups were converted to thiol pendent groups, and that the further increase in the concentrations of pendent groups observed by them at 12 min could be attributed to the interaction of the thiols with dimethylamine to form dimethylammonium pendent groups that eluted at the same HPLC retention time as thiuram pendent groups, but with a larger UV response. The formation and decomposition of thiol pendent groups could not be followed by HPLC, as thiols do not exhibit strong UV absorption.

In the second article in this series<sup>16</sup> it was shown that amines are responsible for decomposition of CPTD to thiourea, and the presence of thiourea in the vulcanizate would imply the availability of amines that can complex with thiol pendent groups as required by eq. (1c). The increase in HPLC peak areas, attributed to tri- and tetrasulfidic thiuram pendent groups, could therefore, be taken as support for the proposals of Geyser and McGill.<sup>4</sup> However, the conversion of thiol pendent groups, formed via polysulfidic Hpmtc [or Hdmtc, eq. (2b)], to thiuram pendent groups, would likewise give rise to an increase in the HPLC peak areas, i.e., the increased HPLC peak areas do not prove the formation of cyclopenteneammonium groups proposed by Geyser and McGill.<sup>4</sup>

It is argued below that eq. (2c) provides a more likely explanation for the accelerated formation of



thiuram pendent groups in Figure 8. In IR/CPTP6 systems, dissociation of CPTP6 and recombination of radicals to give CPTP of different sulfur rank, as evident in the absence of IR,<sup>19</sup> would occur, although the reaction rate would be lower due to IR acting as a diluent. Furthermore, accelerator polysulfides are available from the onset, and can add to the polymer chain as thiuram pendent groups. Hpmtc, liberated in the process, would participate in exchange reactions with CPTP and with thiuram pendent groups, and would affect the concentration of CPTP of different sulfur rank in the system at any particular time. Thus, exchange of polysulfidic Hpmtc with CPTD could account for the increase in CPTP between 5 and 7 min (Fig. 6). In contrast, isothermal vulcanization under vacuum led to the complete consumption of CPTP at 5 min (Fig. 10). Hpmtc would be removed from this system, preventing exchange with CPTD to reform CPTP of higher sulfur rank. Accelerator disulfides are unreactive towards the rubber chain, and have to be sulfurated before addition can occur. Though 40 mol % of sulfur was available for its sulfuration, the CPTD concentration decreased slowly. This may suggest that the diluting effect of IR noticeably influenced the reaction (Fig. 7). However, when Hpmtc was not removed by vacuum, and the same IR diluting effect would apply, CPTD decreased much more rapidly (cf. Figs. 6 and 10). This points to the importance of the alkyldithiocarbamic acid, both in forming thiol pendent groups, which can exchange with CPTD, and in forming CPTP via exchange between CPTD and polysulfidic Hpmtc.

No CPTU was detected during vulcanization of IR/CPTP6 under vacuum. Because the presence of Hpmtc was found to promote the formation of CPTU,<sup>16</sup> the absence of CPTU in IR/CPTP6 vulcanized under vacuum confirms the absence of Hpmtc in the rubber film. The net effect of the removal of Hpmtc, by vulcanizing in a vacuum, was to lower the crosslink density ( $5.36 \times 10^{-5}$  vs.  $0.69 \times 10^{-5}$  mol/mL), and thereby confirming the important role Hpmtc and other alkyldithiocarbamic acids play in the vulcanization process.<sup>12</sup>

### Crosslink Formation

Crosslinking is generally regarded to result from the disproportionation of accelerated pendent groups and/or from the interaction of such pendent groups with the polymer chain.<sup>1,7-9</sup> How-

ever, model compound studies have shown that neither thiuram<sup>10</sup> nor benzothiazole<sup>28</sup> pendent groups readily crosslink. McGill and Shelver<sup>11</sup> showed that thiuram pendent groups in IR crosslink rapidly upon addition of zinc stearate, while Nieuwenhuizen et al.<sup>10</sup> demonstrated the catalytic effect of ZDMC on the crosslinking of thiuram pendent groups in TME.

Geysler and McGill<sup>13</sup> contended that in TMTD systems crosslinking involved reaction between thiuram and dimethylammonium pendent groups, thiourea being liberated in the process. In the absence of rubber, TMTD does not decompose to TMTU at vulcanization temperatures,<sup>17,18</sup> and TMTU formation in vulcanizates was interpreted<sup>13</sup> as evidence for the crosslinking reaction sequence in eq. (1). CPTD decomposes to CPTU at vulcanization temperatures,<sup>19</sup> and CPTU is detected in vulcanizates well before the onset of crosslinking (Table III and Fig. 6 and 7). Geysler's mechanism would suggest that crosslinking should occur at much the same time as CPTU formation as both reactions rely on the presence of amine. Furthermore, the rate of CPTU formation on crosslinking should increase as CPTU is a product of the proposed crosslinking reaction, while Figures 6 and 7 show a decrease in the rate of CPTU formation once crosslinking starts. This mitigates against interaction between thiuram and cyclopenteneammonium pendent groups, i.e., the mechanism of Geysler and McGill,<sup>4,13</sup> playing an important role in crosslinking.

Data in this article support the mechanism proposed by Shelver et al.,<sup>12</sup> in which crosslinking results from the interaction of thiuram and thiol pendent groups; vulcanization under vacuum, that removed Hpmtc, delayed the onset of crosslinking by 7 min (cf. Figs. 6 and 10), and very low crosslink densities were achieved ( $0.69 \times 10^{-5}$  vs.  $5.36 \times 10^{-5}$  mol/mL). CPTD or CPTP are not reformed on crosslinking as would be expected if disproportionation contributed significantly to crosslink formation. Furthermore, upon heating the disulfidic thiuram pendent group of TME with sulfur at 140°C for 3 h, a conversion of only 5% was recorded,<sup>10</sup> while in the TME/CPTP6 system, all CPTP formed had reacted after 12 min (Fig. 8), suggesting that crosslinking involved more than the slow disproportionation of pendent groups. Versloot et al.,<sup>6</sup> found that thiuram pendent groups are unreactive in the absence of ZnO, while Geysler and McGill<sup>13</sup> reported rapid crosslinking in TME/TMTD/sulfur systems. The

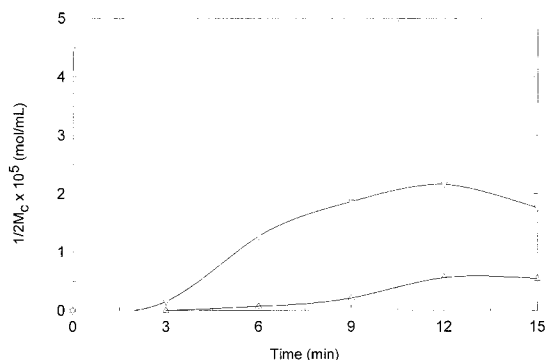
difference between the studies appears to be that in the former case Hdmtc condensed as dimethylammonium dimethyldithiocarbamic acid (dma · dmtc) in the upper section of the reaction tube that was not fully immersed in the oil bath at 150°C. Thus, while crosslinking by disproportionation between thiuram pendent groups does occur,<sup>10</sup> and is accelerated by zinc stearate<sup>11</sup> and zinc accelerator complexes,<sup>10,11</sup> it is suggested that, in the absence of zinc, crosslinking results largely from reaction between thiuram and thiol pendent groups.

Note that Hpmtc, liberated in the crosslinking reaction, could trap piperidine, giving rise to pip · pmtc observed in model compounds studies (Fig. 7). This would reduce the amount of amine available to convert CPTD to CPTU, accounting for the decreased rate of CPTU formation once crosslinking started (Figs. 6 and 7).

IR/CPTP6 was heated to a point prior to crosslinking, and residual curatives extracted. Upon reheating the compound, limited crosslinking occurred slowly (cf. Figs. 11 and 6), yet more rapidly and to a far greater extent than when a similar compound was heated under vacuum (cf. Figs. 10 and 11), when thiuram pendent groups could form, but not thiols, as Hpmtc was removed as fast as it formed. This indicates the presence in the compound of pendent groups that can react. The total amount of CPTM, CPTD, and CPTP formed on reheating was 1 mol %, together with 2 mol % sulfur.

### Induction Period

It will be noted that, irrespective of the curing system (CPTD, CPTD/sulfur, and CPTP6), the onset of crosslinking in isothermal reactions is delayed until the concentration of CPTD in the system falls to about 20 mol %. This occurs after 18 min in IR/CPTD (Fig. 2), 5 min in IR/CPTD/sulfur (Fig. 4), 7.5 min in IR/CPTP6 (Fig. 6), and 8 min in TME/CPTP6 (Fig. 7). In studies at programmed heating rates slightly lower CPTD concentrations prevail at the onset of crosslinking, IR/CPTD 14 mol % at 170°C, IR/CPTD/sulfur 11 mol % at 147°C (Table II), and IR/CPTP6 13 mol % at 150°C (Table III). Geyser and McGill<sup>13</sup> and McGill and Shelver<sup>28</sup> also noted that crosslinking in TMTD systems was delayed until the TMTD concentration decreased to about 20 mol %. Geyser suggested that only at low TMTD concentrations could thiuram radicals decompose rather



**Figure 11** Crosslink densities measured on reheating IR containing crosslink precursors formed on heating IR/CPTP6 at 140°C for 7.5 min, followed by extraction of residual curatives. (▽) 1/2Mc (overall); (△) 1/2Mc (mono- and disulfidic).

than recombine. At this point dimethyl ammonium pendent groups, necessary for the proposed crosslinking mechanism, could form and react with thiuram pendent groups.<sup>13</sup>

Shelver et al.<sup>12</sup> suggested that the rapid exchange of thiol pendent groups delayed crosslinking as pendent groups were predominantly thiuram terminated, and on their own do not crosslink rapidly.<sup>6,10</sup> Only at low TMTD concentrations did sufficient thiol pendent groups escape the exchange reaction to crosslink with thiuram pendent groups. Data detailed above support the proposals of Shelver et al.<sup>12</sup>

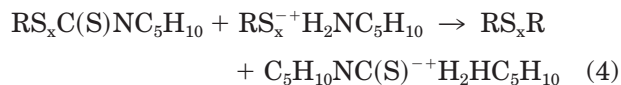
Furthermore, comparison of data on CPTD consumption in Figures 6 and 10 allow us to extend our understanding of crosslink precursor formation. In the IR/CPTP6 system (Fig. 6) the CPTD concentration drops from its maximum value to a very low value in 4 to 5 min while, when the same system is heated under vacuum (Fig. 10), the CPTD concentration changes slowly and by very much less over a period of 20 min. The latter system contains 40 mol % sulfur that could lead to CPTP and thiuram pendent groups, yet the reaction is slow, as evidence by the slow decrease in CPTD. It is proposed that in the presence of Hpmtc, thiol pendent groups form rapidly via sulfurated Hpmtc, and that these exchange with CPTD regenerating Hpmtc for further reaction, i.e., thiuram pendent groups form more rapidly via an exchange of CPTD with thiol pendent groups than directly from CPTP. As noted earlier, the increased formation of thiuram pendent groups found in TME systems between 6 and 8 min (Fig. 8), supports their rapid formation as

being due to an exchange between CPTD and the rapidly formed thiol pendent groups. The alkylthiocarbamic acid, not the thiuram accelerator, is the main source of pendent groups.

### Pip · pmtc Formation

In model compounds pip · pmtc was formed at the same time as crosslinked products, while Geysers and McGill<sup>13</sup> also detected dma · dmtc on crosslinking of TME/TMTD/sulfur formulations. In both CPTD and TMTD formulations the amine salt (pip · pmtc and dma · dmtc) was detected only in model compounds studies<sup>6,13</sup> and not in IR compounds.<sup>5,28</sup> A current project in these laboratories revealed that it is extremely difficult to extract dma · dmtc from IR due to its low solubility in the solvents used to swell the rubber during the extraction of residual curatives and reactions by-products. Thus, its formation in rubber may have been overlooked.

There are a number of routes to dma · dmtc or pip · pmtc formation. Hdmtc, condensing on the cold walls of a reaction tube, decomposes to dma · dmtc, while interaction between CS<sub>2</sub> and dimethylamine will also yield dma · dmtc.<sup>29</sup> Cyclopentaneammonium pendent groups proposed in the mechanism of Geysers and McGill<sup>11</sup> would release pip · pmtc on crosslinking according to eq. (4).



However, the ready formation of piperidine in CPTD systems<sup>16</sup> would not require the CPTD concentration to decrease to a given level before crosslinking via Geysers' mechanism, and this mitigates against pip · pmtc being a product of crosslinking.

### CONCLUSIONS

Data in this article support the contention of Shelver et al.<sup>12</sup> that alkylthiocarbamic acids play an essential role in the crosslinking process. Crosslinking of thiuram-terminated polysulfidic pendent groups by disproportionation is slow, and it is proposed that, as in TMTD systems, crosslinking results largely from reaction between thiuram-terminated pendent groups and thiols. Crosslinking liberates alkylthiocarbamic acids that can continue the process. Alkylthio-

carbamic acids are themselves good accelerators for such vulcanization and, indeed, it is suggested they are the main agents leading to pendent groups. The ready exchange between thiols and alkylthiocarbamic acids leads to pendent groups being predominantly thiuram terminated, and this delays the onset of crosslinking. Only once the alkylthiocarbamic acid concentration decreases, and newly formed thiols are not rapidly converted to thiuram pendent groups, does crosslinking between thiuram pendent groups and thiols occur.

We wish to thank the South African Foundation for Research and Development and Karbochem for financial assistance.

### REFERENCES

1. Nieuwenhuizen, P. J.; Van Duin, M.; McGill, W. J.; Reedijk, J. *Rubber Chem Technol* 1997, 70, 368.
2. Coran, A. Y. *Science and Technology of Rubber*; Eirich, F. R., Ed.; Academic Press Inc.: New York, 1978.
3. Bateman, L.; Moore, C. G.; Porter, M.; Saville, B. *The Chemistry and Physics of Rubber-Like Substances*; Maclaren & Sons Ltd.: London, 1963.
4. Geysers, M.; McGill, W. J. *J Appl Polym Sci* 1996, 60, 431.
5. Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1992, 45, 563.
6. Versloot, P.; Haasnoot, J. G.; Reedijk, J.; Van Duin, M.; Duynstee, E. F. J.; Put, J. *Rubber Chem Technol* 1994, 67, 252.
7. Porter, M. *In Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1977.
8. Moore, C. G.; Watson, A. A. *J Appl Polym Sci* 1964, 8, 581.
9. Morrison, N. J. *Rubber Chem Technol* 1984, 57, 86.
10. Nieuwenhuizen, P. J.; Timal, S.; Haasnoot, J. G.; Spek, A. L.; Reedijk, J. *Chem Eur J* 1997, 3, 1846.
11. McGill, W. J.; Shelver, S. R. *J Appl Polym Sci* 1999, 72, 1021.
12. Shelver, S. R.; Shumane, M.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 1999, 74, 1371.
13. Geysers, M.; McGill, W. J. *J Appl Polym Sci* 1996, 60, 439.
14. Coleman, M. M.; Shelton, J. R.; Koenig, J. L. *Rubber Chem Technol* 1973, 46, 957.
15. Dogadkin, B. A.; Shershnev, V. A. *Rubber Chem Technol* 1960, 33, 401.
16. Reyneke-Barnard, C. P.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 2000, 77, 2732.
17. Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1991, 42, 2669.

18. Geysler, M.; McGill, W. J. *J Appl Polym Sci* 1995, 55, 215.
19. Reyneke-Barnard, C. P.; Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 2000, 77, 2718.
20. Cambell, R. H.; Wise, R. W. *Rubber Chem Technol* 1964, 37, 635.
21. Morgan, B.; McGill, W. J. *J Appl Polym Sci* 2000, 76, 1377.
22. Gradwell, M. H. S.; McGill, W. J. *J Appl Polym Sci* 1995, 58, 2185.
23. Kruger, F. W. H.; McGill, W. J. *J Appl Polym Sci* 1992, 44, 581.
24. Gardiner, J. B. *Rubber Chem Technol* 1968, 41, 1313.
25. Versloot, P.; Haasnoot, J. G.; Reedijk, J.; Van Duin, M.; Duynstee, E. F. J.; Put, J. *Rubber Chem Technol* 1991, 65, 343.
26. Nelander, N.; Sunner, S. J. *Am Chem Soc* 1972, 94, 3576.
27. Giuliani, B. V. M. K.; McGill, W. J. *J Appl Polym Sci* 1995, 57, 1391.
28. McGill, W. J.; Shelver, S. R. *J Appl Polym Sci* 1999, 72, 1007.
29. Coleman, M. M.; Shelton, J. R.; Koenig, J. L. *Rubber Chem Technol* 1973, 46, 938.