Vulcanization of Chlorobutyl Rubber. III. Reaction Mechanisms in Compounds Containing Combinations of Zinc Dimethyldithiocarbamate, Tetramethylthiuram Disulfide, Sulfur, and ZnO

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ABSTRACT: Poly(isoprene-*co*-isobutylene) (IIR or butyl) and chlorinated poly(isoprene-*co*-isobutylene) (CIIR or chlorobutyl) compounds containing combinations of zinc dimethyldithiocarbamate [$Zn_2(dmtc)_4$], tetramethylthiuram disulfide (TMTD), sulfur, and ZnO were vulcanized at 150°C, the reaction was stopped at various points, crosslink densities were determined by swelling, and the concentrations of residual curatives and extractable reaction intermediates and products were determined by high-performance liquid chromatography and atomic absorption ($ZnCl_2$). In compounds that did not contain zinc, CIIR crosslinked more slowly than IIR and crosslinking could be explained by the same mechanism as applies to the vulcanization to highly unsaturated rubbers like polyisoprene. In zinc containing compounds, CIIR crosslinked faster because of dehydrohalogenation reactions that led to carbon–carbon crosslinks. As found with $ZnO/ZnCl_2$ formulations, both $ZnCl_2$ and conjugated diene butyl are essential precursors to crosslink formation. $Zn_2(dmtc)_4$ can trap HCl, thus preventing reversion and may also initiate dehydrohalogenation. When the equilibrium crosslink density is reached, 50% of the chlorine originally present in the rubber is extractable as $ZnCl_2$ and the remainder as dimethylthiocarbamic acid chloride. A mechanism to account for dehydrochlorination and crosslinking in the presence of $Zn_2(dmtc)_4$ is presented. In compounds with sulfur, crosslinking occurs via accelerated sulfur vulcanization and chlorine abstraction, leading to higher crosslink densities than is achieved with either curative system on its own. Carbon–carbon crosslinks predominate, the slower, accelerated sulfur reaction, making a lesser contribution to the overall reaction. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1309–1316, 2001

Key words: chlorobutyl; vulcanization; zinc dimethyldithiocarbamate; tetramethylthiuram disulfide; sulfur

INTRODUCTION

In a comprehensive review of poly(isoprene-*co*-isobutylene) (IIR or butyl rubber) Buckley[1] dealt with the properties of IIR and with the amounts of sulfur combined in the network for different crosslink densities and accelerator systems, including thiuram accelerators. IIR relies on the functionality of allylic hydrogen for crosslinking, whereas chlorinated poly(isoprene-*co*-isobutylene) (CIIR or chlorobutyl) contains the functionality of chlorine and can be crosslinked with ZnO alone. CIIR may be expected to vulcanize in the
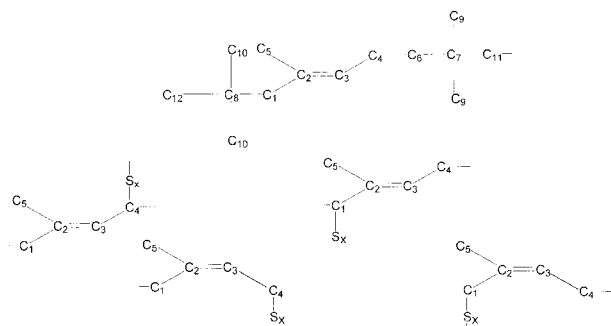
Figure 1   Structures resulting from accelerated sulfur vulcanization of IIR.[4]

normal way with tetramethylthiuram disulfide (TMTD)/sulfur, whereas increased rates of vulcanization are observed if ZnO is included and crosslinking is also more rapid than with ZnO alone. Hepburn and Hatam[2] studied the heat aging resistance of CIIR crosslinked with ZnO and TMTD/ZnO. CIIR is known to contain a small amount of *cis*-1,4-polyisoprene (IR) which could be utilized in crosslinking with TMTD, whereas ZnO would lead to crosslinking via the active chlorine. Baldwin et al.[3] noted that attainment of the full crosslink potential of CIIR by ZnO is slow, though the situation can be remedied by the inclusion of thiocarbamic acid derivatives. ZnO need not be included at all, and zinc dimethyldithiocarbamate [$Zn_2(dmtc)_4$] may be used on its own. The authors are not aware of a proposed mechanism for the $Zn_2(dmtc)_4$ reaction. Krejsa and Koenig[4] studied chemical microstructural changes in the accelerated sulfur cure of IIR with TMTD/sulfur/ZnO using solid state nuclear magnetic resonance and Fourier transform infrared. Isomerization occurred in the initial stages of vulcanization, the predominantly *trans*-isoprene units (9:1) changing to a 1:4 *trans/cis* ratio at equilibrium. Initially sulfuration resulted in polysulfidic links on C4 of both the *trans* and *cis* structures (Fig. 1), with desulfuration leading to the development of mono- and polysulfides on C1. No migration of the double bond, saturation or internal cyclization occurred, nor did any reaction occur at the isobutylene units. Thus, whereas accelerated sulfur vulcanization of IIR, not surprisingly, appears to follow mechanisms applicable to IR, the faster reaction that occurs in the accelerated sulfur vulcanization of CIIR must be attributed to $Zn_2(dmtc)_4$, formed during reactions initiated by interaction of accelerator polysulfides with the rubber chain because ZnO and TMTD do not react rapidly at vulcanization temperatures.[5,6]

This article first reports on a comparative study of the TMTD accelerated sulfur vulcanization of CIIR and IIR in the absence of ZnO, and by analyzing extractable reaction by-products present at different stages of the reaction; second, it identifies changes that occur in the vulcanization process when CIIR is vulcanized with $Zn_2(dmtc)_4$ and TMTD/sulfur/ZnO formulations. A mechanism for the $Zn_2(dmtc)_4$ crosslinking is proposed and the relative contribution of the accelerated sulfur and chlorine abstraction reactions to the overall crosslinking process is established.

EXPERIMENTAL

The materials used were the following: rubbers, ZnO, and $ZnCl_2$, which have been described.[7] TMTD (Flexsys, Brussels, Belgium), sulfur (AEC, Modderfontein, South Africa), and $Zn_2(dmtc)_4$ (Bayer, Leverkusen, Germany).

Compounding and vulcanization procedures were described in the first report in this series.[7] Formulations quoted in brackets in the text are parts per hundred rubber. Compounds were vulcanized at a programmed heating rate in a differential scanning calorimeter (DSC) or isothermally in a press at 150°C. Residual curatives, soluble reaction intermediates, and reaction by-products were extracted as described previously[8] and were analyzed by high-performance liquid chromatography (HPLC).[9,10] Products were separated on a Waters μ-Bondpak C18 Reverse Phase Radial-Pack column with 15:85 (v/v) water/methanol as mobile phase. To obtain separation of dimethylthiocarbamic acid chloride, a 20% water/80% methanol mobile phase was used. The identification and quantitative analysis of TMTD derivatives has been described previously.[10] Dimethylthiocarbamic acid chloride was identified by comparison of its HPLC retention time with that of a commercial compound. $ZnCl_2$, extracted from vulcanizates, was analyzed by atomic absorption spectroscopy.[7] In the Figures, the concentrations of reactants, intermediates, and products are expressed in terms of the initial mol concentrations of reactants, i.e., as the mol % of reactant remaining, or mol % intermediate/product formed from that reactant.
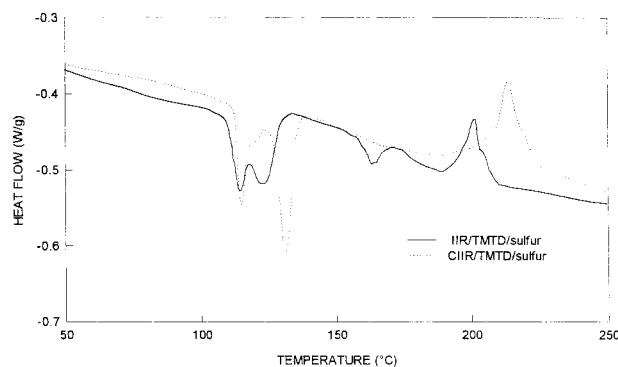
Figure 2 DSC curves of IIR and CIIR/TMTD(8.9)/sulfur(9.5) heated at 5°C/min.

Figure 4 Crosslink density and HPLC analysis of CIIR/TMTD(8.9)/sulfur(9.5) heated isothermally at 150°C.

RESULTS AND DISCUSSION

TMTD(8.9)/Sulfur(9.5) Formulations

The DSC cure curves (Fig. 2) showed the same thermal events as found with similar IR formulations,[11] viz., the melting of sulfur at 115°C and the melting/dissolution endotherm for TMTD in the rubber at a slightly higher temperature. The lower reactivity of CIIR, compared with that of IIR, is reflected in the later initiation of the crosslinking exotherm and the absence of the endotherm at 160°C in CIIR, attributed to the volatilization of Hdmtc that accompanies pendent group formation.[12–15]

On isothermal vulcanization at 150°C, HPLC analysis showed a decrease in extractable sulfur and TMTD and the formation of tetramethylthiuram polysulfides (TMTP) that gave rise to pendent group formation (Figs. 3 and 4). The formation of pendent groups was demonstrated by heating an IIR/TMTD/sulfur compound at 150°C
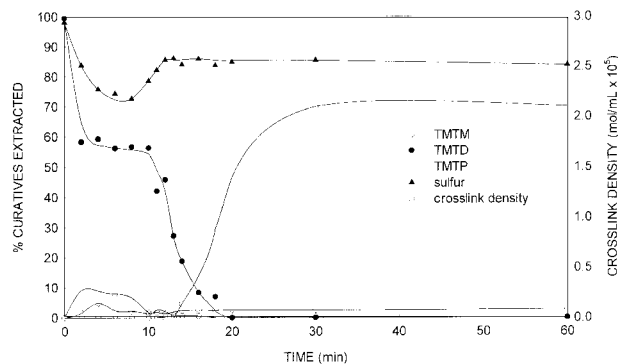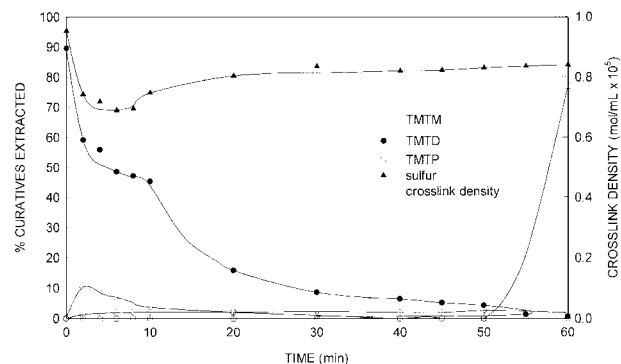

Figure 3 Crosslink density and HPLC analysis of IIR/TMTD(8.9)/sulfur(9.5) heated isothermally at 150°C.

under vacuum [to remove dimethyldithiocarbamic acid (Hdmtc)][15] for 10 min, followed by the extraction of residual curatives. On reheating for 10 min at 150°C, after the addition of zinc stearate that promotes the crosslinking of pendent groups,[16] a crosslink density of 2.4×10^{-5} mol/mL was measured, compared with essentially no crosslinking that occurred on reheating part of the extracted sample without zinc stearate addition. On reheating, an extracted sample with ZnO for 10 min at 150°C, $Zn_2(dmtc)_4$ was detected by HPLC, further proving the existence of thiuram pendent groups in the compound ($1/2Mc = 1 \times 10^{-5}$ mol/mL).

The limited regeneration of sulfur (Figs. 3 and 4) may, in part, be ascribed to desulfuration of polysulfidic thiuram terminated pendent groups as demonstrated by Krejsa and Koenig.[4] In highly unsaturated rubbers, such as IR, Hdmtc evolved in thiuram pendent group formation will itself participate in pendent group formation,[15] leading to rapid consumption of sulfur, but in IIR and CIIR, its role in desulfuration of pendent groups will be more noticeable. Hdmtc is unstable when dried and the procedure developed by Shelver et al.[15] to investigate the role of Hdmtc in the reaction was followed. An IIR(100)/TMTD(8.9)/sulfur(9.5) compound was heated for 10 min at 150°C, permitting the formation of pendent groups but not crosslinking. The rubber was dissolved and reprecipitated as a thin film on the sides and bottom of a pill vial and residual curatives were extracted with isopropyl alcohol for 48 h, the alcohol being replaced after 24 h, leaving behind only pendent groups. The extracted sample (A) was dissolved in benzene and cast as a thin film on an aluminium sheet. A film (B) of an
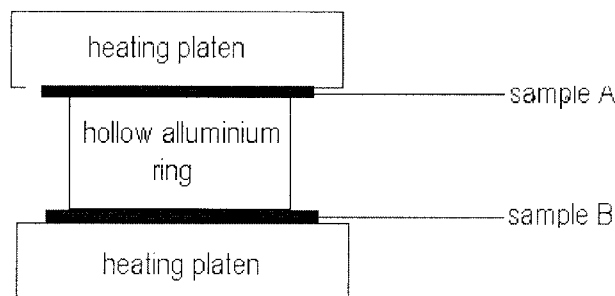
Figure 5 Apparatus used for the study of the effect of volatiles on pendent groups.

unheated IIR/TMTD/sulfur compound was cast on a similar sheet. After removal of the solvent by vacuum drying the sheets, with their adhering films, they were heated in a press, and the films were separated by an aluminium ring, as shown in Figure 5. On heating, Hdmtc, evolved from the lower film during pendent group formation, diffused into the upper film. Analysis of the upper film, after heating at 150°C for 10 min, revealed that 50% of the sulfur incorporated into the film on heating the initial compound, was now extractable as free sulfur. In a control experiment, in which film (A) was heated without exposure to Hdmtc, no sulfur was released.

The plateau or slow down in the rate of TMTD consumption (Figs. 3 and 4) shows that sulfur regeneration may also, in part, be attributed to an exchange between Hdmtc and TMTP as demonstrated by Shelver et al. (Reaction scheme i).[15]
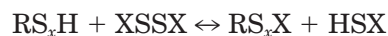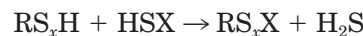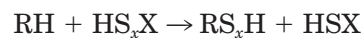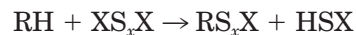
$$XS_xX + HSX \Leftrightarrow XSSX + HS_xX \rightarrow HSX + S \quad (i)$$
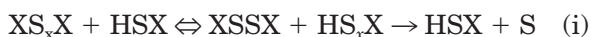
where $X = (CH_3)_2NC(S)-$

Regeneration of sulfur as well as accelerator was also reported for the IR/pentamethylenethiuram disulfide/sulfur system.[17]

Low crosslink densities developed despite the consumption of all of the accelerator, which further points to pendent groups being essentially monosulfidic and therefore unreactive.[13] According to the TMTD accelerated reaction mechanism, half of the accelerator could be volatilized as Hdmtc.[13,15,18,19]

The data is consistent with the vulcanization mechanism demonstrated to apply in IR compounds (Reaction scheme ii).[15]

$$XSSX + S_8 \leftrightarrow XS_xX$$

$$RH + XS_xX \rightarrow RS_xX + HSX$$

$$HSX + S_8 \rightarrow HS_xX$$

$$RH + HS_xX \rightarrow RS_xH + HSX$$

$$RS_xH + HSX \rightarrow RS_xX + H_2S$$

$$RS_xH + XSSX \leftrightarrow RS_xX + HSX$$

$$RS_xX + RS_xH \rightarrow RS_yR + HSX \quad (ii)$$

In the IIR compound, crosslinking did not initiate until the TMTD concentration had decreased to below 20 mol % (Fig. 3) when, as in IR systems,[15] the exchange between TMTD and thiol pendent groups becomes sufficiently slow for crosslinking between thiuram and thiol groups to occur. CIIR is less reactive than IIR and crosslinking was even further delayed (Fig. 4).

$Zn_2(dmtc)_4(11.3)$ and $Zn_2(dmtc)_4(11.3)/Sulfur(9.5)$ Formulations

$Zn_2(dmtc)_4$ is not a sulfur donor and will not vulcanize IIR. As in IR compounds, $Zn_2(dmtc)_4$ accelerated sulfur vulcanization of IIR occurred more rapidly than the TMTD/sulfur reaction (cf. Figs. 3 and 6). The mechanism of the $Zn_2(dmtc)_4$ accelerated sulfur reaction remains unclear. The possible involvement of polysulfidic $Zn_2(dmtc)_4$ complexes, that could lead to thiuram pendent groups similar to those participating in TMTD accelerated sulfur vulcanization, has been noted by various authors.[6,13,20] Such sulfur-rich zinc (II) com-
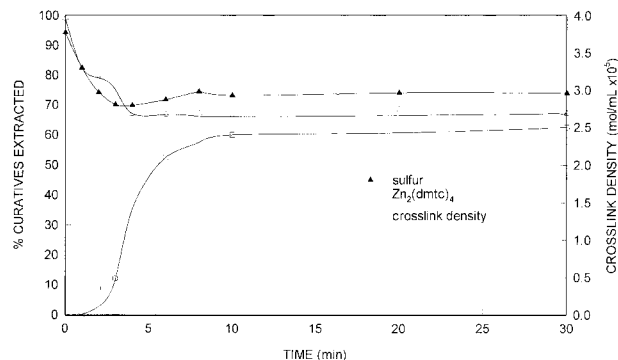

Figure 6 Crosslink density and HPLC analysis of IIR/$Zn_2(dmtc)_4(11.3)$/sulfur(9.5) heated isothermally at 150°C.

plexes have not been isolated though evidence for sulfur-rich zinc (II) complexes has been demonstrated in theoretical Density Functional calculations and mass spectroscopic analysis of $Zn_2(dmtc)_4$/sulfur.[21] Thiuram pendent groups that are proposed to result from the reaction of sulfur-rich zinc (II) complexes with the polymer have not been detected in model compound studies of $Zn_2(dmtc)_4$ accelerated systems.[13,22,23] Geyser and McGill[23] proposed that polysulfidic thiuram pendent groups did form, but crosslinked immediately in the presence of $Zn_2(dmtc)_4$ that catalyzed their crosslinking. Nieuwenhuizen et al.[24] proposed that sulfurated $Zn_2(dmtc)_4$ inserted sulfur into the allylic C—H bond and that crosslinking of the polysulfidic thiols was catalyzed by $Zn_2(dmtc)_4$.

Shelver and McGill[16] demonstrated that zinc stearate was more efficient than $Zn_2(dmtc)_4$ in crosslinking of thiuram pendent groups in IR. Zinc stearate was added from solution to a IIR/$Zn_2(dmtc)_4$(11.3)/sulfur(9.5) sample that had been heated at 150°C for 5 min. On reheating for 5 min, the crosslink density increased from 1.6×10^{-5} to 3.4×10^{-5} mol/mL, whereas reheating a similar sample in the absence of zinc stearate gave a crosslink density of only 2.3×10^{-5} mol/mL. The higher crosslink density achieved on addition of zinc stearate suggests the involvement of thiuram pendent groups in the crosslinking reaction.

The DSC cure curve for CIIR(100)/$Zn_2(dmtc)_4$(11.3) was analogous to that obtained with CIIR(100)/ZnO(5) and CIIR(100)/ZnO(5)/$ZnCl_2$(1) compounds.[7] It showed the endothermic melting of the calcium stearate stabilizer and an irregular, double peaked exotherm, starting at 138°C, earlier than in either of the above-mentioned ZnO/$ZnCl_2$ systems. As in ZnO/$ZnCl_2$ systems,[7,25] the shape of the exotherm is determined by the superimposition of an endotherm resulting from evaporation of volatiles (H_2S and HSX) formed in the reactions discussed below. Vulcanization at 150°C showed that $ZnCl_2$ formation preceded crosslinking (Fig. 7) and, as in ZnO compounds,[7] the maximum $ZnCl_2$ formed equated to 50% of the chlorine present in the polymer. There was a delay between the formation of $ZnCl_2$ and crosslinking, which indicates the necessity for conjugated diene butyl units in the chain to which crosslinking can occur, i.e., a crosslinking step similar to that in ZnO/$ZnCl_2$ compounds is indicated. Because formulations did not contain ZnO, the by-products formed must be different. HPLC analysis did not show the formation of products
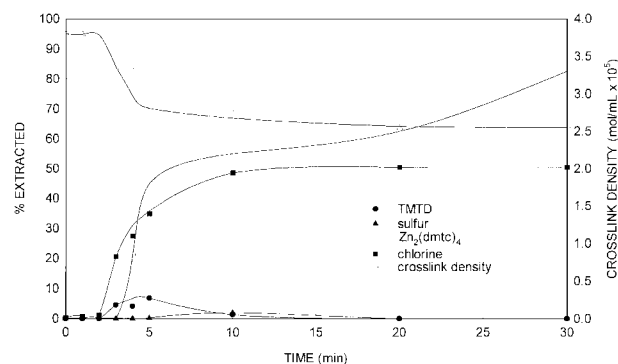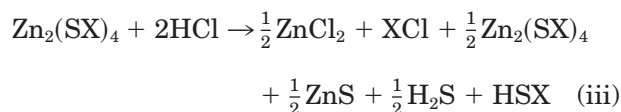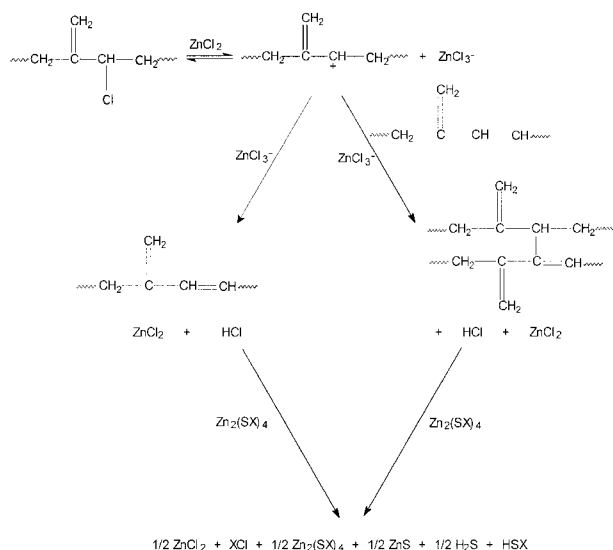

Figure 7 Crosslink density, HPLC, and extractable chlorine analysis of CIIR/$Zn_2(dmtc)_4$(11.3) heated isothermally at 150°C.

not found in IIR or IR vulcanizates. However, on using a mobile phase with a higher water content (20:80 water/methanol), HPLC analysis of the extract from a CIIR/$Zn_2(dmtc)_4$ compound, vulcanized at 150°C in a sealed tube, showed a peak at a shorter retention time than that of any of the other products. The peak corresponded to the elution time for dimethylthiocarbamic acid chloride. In another experiment, a CIIR/$Zn_2(dmtc)_4$ sample was vulcanized in a closed tube for 20 min at 150°C and extracted with benzene for 48 h. Comparison of the infrared spectrum of the extract with that of dimethylthiocarbamic acid chloride showed the characteristic C—Cl peak at $670 cm^{-1}$ and thus supported the identification of the compound formed on vulcanization as dimethylthiocarbamic acid chloride. The acid chloride boils at 98°C[26] and would readily be lost on vulcanization in a press. Exposure of $Zn_2(dmtc)_4$ to HCl gas at 150°C yielded $ZnCl_2$ and HPLC showed the formation of dimethylthiocarbamic acid chloride, i.e., the trapping of HCl by $Zn_2(dmtc)_4$ will yield the observed products. The amount of $Zn_2(dmtc)_4$ consumed was greater than could be accounted for by the amount of $ZnCl_2$ formed, i.e., the formation of some additional zinc compound (possibly ZnS) was indicated. On vulcanization, 50% of the chlorine present in the rubber is trapped as $ZnCl_2$ and it is suggested that the remainder is liberated as dimethylthiocarbamic acid chloride. The following reaction mechanism is proposed (Reaction scheme iii).

$$Zn_2(SX)_4 + 2HCl \rightarrow \tfrac{1}{2}ZnCl_2 + XCl + \tfrac{1}{2}Zn_2(SX)_4$$

$$+ \tfrac{1}{2}ZnS + \tfrac{1}{2}H_2S + HSX \quad \text{(iii)}$$

Scheme 4

Figure 8   Crosslink density, HPLC, and extractable chlorine analysis of CIIR/$Zn_2(dmtc)_4$(11.3)/sulfur(9.5) heated isothermally at 150°C.

As in ZnO/$ZnCl_2$ compounds,[25] crosslinking will occur if, during the abstraction of HCl, a carbocation on the polymer chain is adjacent to a conjugated diene butyl unit in the chain; if not, dehydrohalogenation will lead to the formation of further conjugated diene butyl (Reaction scheme iv).

The by-products of crosslinking and conjugated diene butyl formation are identical. Treatment of the vulcanizate with methyl iodide[27] showed that crosslinks were entirely carbon–carbon. The rapid formation of $ZnCl_2$ is detected after 2 min (Fig. 7) as opposed to 8 min in ZnO compounds,[7] suggesting that unlike ZnO that only acts as a HCl trap, $Zn_2(dmtc)_4$ may promote dehydrohalogenation. Lower crosslink densities result than with ZnO/$ZnCl_2$ formulations,[7] which may imply that dehydrohalogenation, initiated by $Zn_2(dmtc)_4$, does not lead to crosslinking, and that carbocations are formed only when $ZnCl_2$ abstracts chlorine from the chain, thus permitting crosslinking to adjacent conjugated diene butyl units. Reversion is prevented by the ability of $Zn_2(dmtc)_4$ to trap HCl. HCl initiated reversion was discussed in an earlier report in this series.[25]

The reason for the slow increase in crosslink density on prolonged heating as shown in Figure 7 is not known; no more $ZnCl_2$ is formed at this stage.

In CIIR(100)/$Zn_2(dmtc)_4$(11.3)/sulfur(9.5) compounds, the presence of sulfur would allow crosslinking via both accelerated sulfur and chlorine abstraction processes. Crossl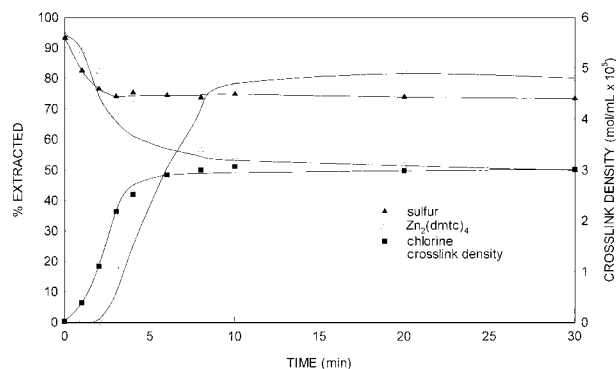inking was rapid and a higher crosslink density was achieved than in the absence of sulfur (cf. Figs. 7 and 8). The formation of $ZnCl_2$ preceded crosslinking and no induction period for $ZnCl_2$ formation (Fig. 8), seen in the absence of sulfur (Fig. 7), was observed. The immediate very rapid formation of $ZnCl_2$, implies that $Zn_2(dmtc)_4$ also could initiate dehydrohalogenation, and that it did not merely act as a HCl trap, as did ZnO.[7] The greater reactivity of $Zn_2(dmtc)_4$, when sulfur was present, may suggest that its interaction with sulfur and the transient formation of $Zn_2(dmtc)_4$ polysulfides facilitated its dissolution in the rubber, thereby rendering the $Zn_2(dmtc)_4$ more accessible for reaction than would be the case with insoluble $Zn_2(dmtc)_4$. Again, there was a delay between $ZnCl_2$ formation and crosslinking, indicating that the formation of conjugated diene butyl on dehydrohalogenation is a necessary precursor to crosslinking.[7,25]

Table I   Percentage of C—C and S—S Crosslinks of CIIR/$Zn_2(dmtc)_4$(11.3)/Sulfur(9.5) Heated Isothermally at 150°C

Time (min)	Percentage Crosslink	
	C—C	S—S
2	0	0
3	86	14
4	78	22
6	82	18
8	91	9
10	74	26
20	63	37
30	62	38

Treatment of the vulcanizate with methyl iodide[27] showed that the majority of the crosslinks were carbon–carbon (Table I). After 30 min, a crosslink density of 3.3×10^{-5} mol/mL was attributable to carbon–carbon crosslinks (62% of total), similar to the carbon–carbon crosslinks formed in the absence of sulfur (3.3×10^{-5} mol/mL).

TMTD(8.9)/Sulfur(9.5)/ZnO(5) Formulations

In CIIR compounds, TMTP led to pendent group formation with the release of Hdmtc that was trapped by ZnO as $Zn_2(dmtc)_4$ (Fig. 9). $ZnCl_2$ formation, initiated by $Zn_2(dmtc)_4$, was thus delayed compared with $Zn_2(dmtc)_4$ containing formulations, but occurred earlier than in CIIR/ZnO compounds, where ZnO did not catalyze dehydrohalogenation.[7] Crosslinking commenced at much the same time as in analogous IIR compounds but was much faster, most of the initially formed crosslinks being carbon–carbon because of the $Zn_2(dmtc)_4$ initiated dehydrohalogenation and $ZnCl_2$ promoted crosslinking reactions, with the slower sulfur vulcanization reactions contributing more to crosslink formation in the latter stages of the reaction (Table II). Both systems attain their maximum crosslink density after about 20 min, though a higher crosslink density prevailed in the chlorinated rubber. After 30 min, a crosslink density of 4.0×10^{-5} mol/mL was attributable to carbon–carbon crosslinks (69% of total), similar to the number of carbon–carbon crosslinks formed in the absence of sulfur (4.0×10^{-5} mol/mL).

CONCLUSIONS

TMTD accelerated sulfur crosslinking in IIR is slow because of the low degree of unsaturation in
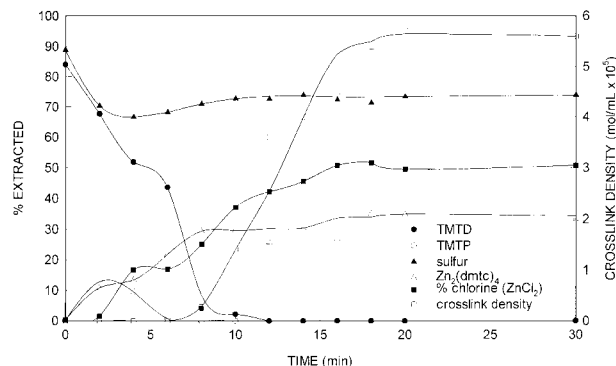
Figure 9 Crosslink density, HPLC, and extractable chlorine analysis of CIIR/TMTD(8.9)/sulfur(9.5)/ZnO(5) heated isothermally at 150°C.

Table II   Percentage of C—C and S—S Crosslinks of CIIR/TMTD(8.9)/Sulfur(9.5)/ZnO(5) Heated Isothermally at 150°C

	Percentage Crosslink	
	C—C	Time (min)
6	0	0
8	84	16
10	85	15
12	86	14
14	85	15
16	80	20
18	77	23
20	71	29
30	69	31

the polymer and even slower in CIIR where the chlorine atom α to the double bond deactivates the bond. $Zn_2(dmtc)_4$ catalyzes dehydrohalogenation, forming conjugated diene butyl and $ZnCl_2$, the precursors to crosslink formation. At equilibrium, 50% of the chlorine in the polymer is extractable as $ZnCl_2$ and the remainder is removed as dimethylthiocarbamic acid chloride. A reaction mechanism is proposed. $Zn_2(dmtc)_4$ promotes dehydrohalogenation but not crosslinking and lower crosslink densities develop than in $ZnO/ZnCl_2$ formulations. There is no reversion. On addition of sulfur, crosslinking via both accelerated sulfur and chlorine abstraction lead to higher crosslink densities than obtained with either system on its own, the bulk of the crosslinks being carbon–carbon. In CIIR/TMTD/sulfur/ZnO compounds, $Zn_2(dmtc)_4$ must form before crosslinking by chlorine abstraction can occur, and the induction period before the formation of $ZnCl_2$ and crosslinks is slightly longer than in $Zn_2(dmtc)_4$ formulations. High crosslink densities apply, most of the crosslinks being carbon–carbon, the slower accelerated sulfur reaction contributing less that 30% to the overall crosslink density.

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