

# Vulcanization of Chlorobutyl Rubber. II. A Revised Cationic Mechanism of ZnO/ZnCl<sub>2</sub> Initiated Crosslinking

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Received 5 October 1999; accepted 26 January 2000

**ABSTRACT:** Data relating to the ZnO/ZnCl<sub>2</sub>-accelerated vulcanization of chlorinated poly(isoprene-coisobutylene) (CIIR or chloro-butyl) is examined. ZnCl<sub>2</sub> and conjugated diene butyl units on the polymer chain are both precursors to crosslinking, and a revised cationic mechanism is proposed to account for crosslinking, taking into account the involvement of conjugated diene butyl in the process. It is demonstrated that Zn<sub>2</sub>OCl<sub>2</sub> will catalyze dehydrohalogenation, and the formation of catalytic amounts of Zn<sub>2</sub>OCl<sub>2</sub> by the reaction of ZnCl<sub>3</sub><sup>-</sup> with ZnO, followed by H<sup>+</sup> abstraction to give Zn<sub>2</sub>OCl<sub>2</sub> and HCl, is essential in the overall crosslinking reaction sequence. The HCl is trapped by ZnO as ZnCl<sub>2</sub>. It is proposed that the abstraction by Zn<sub>2</sub>OCl<sub>2</sub> of HCl in a concerted reaction leads to Zn(OH)Cl and ZnCl<sub>2</sub>. Zn(OH)Cl remains in the polymer as an unextractable salt, while 50% of the chlorine in the rubber is extracted as ZnCl<sub>2</sub> when compounds reach their equilibrium crosslink density. ZnCl<sub>2</sub> initiates crosslinking by the abstraction of chlorine from the chain, but a crosslink will only result when a carbocation on a dechlorinated isoprenoid unit is close to a conjugated diene butyl on an adjacent chain; if not, dehydrohalogenation will result in the formation of a further conjugated diene butyl unit at that point in the chain. The maximum crosslink density achieved is only 1/4 that theoretically possible, as crosslinking restricts chain movement and limits the number of chance meetings between carbocations on the polymer and conjugated diene butyl units. Zinc stearate promotes dehydrohalogenation, ZnCl<sub>2</sub> being the only chloro-zinc salt formed. Reversion occurs in compounds where there is insufficient ZnO to trap all of the chlorine present in the rubber. HCl per se does not attack the polymer, but promotes reversion only in the presence of carbocations on the chain, i.e., during the crosslinking process. Trapping of HCl by ZnO prevents reversion. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2302–2310, 2000

**Key words:** chloro-butyl; vulcanization; mechanism; ZnO; ZnCl<sub>2</sub>

## INTRODUCTION

It has been suggested<sup>1</sup> that crosslinks in ZnO accelerated vulcanization of chlorinated poly(isoprene-coisobutylene) (CIIR or chloro-butyl) comprised ether linkages, but Kuntz et al.<sup>2</sup> showed that there was no evidence for the formation of

ether crosslinks in the reaction of 3-chloro-2-methyl-1-pentene with ZnO.

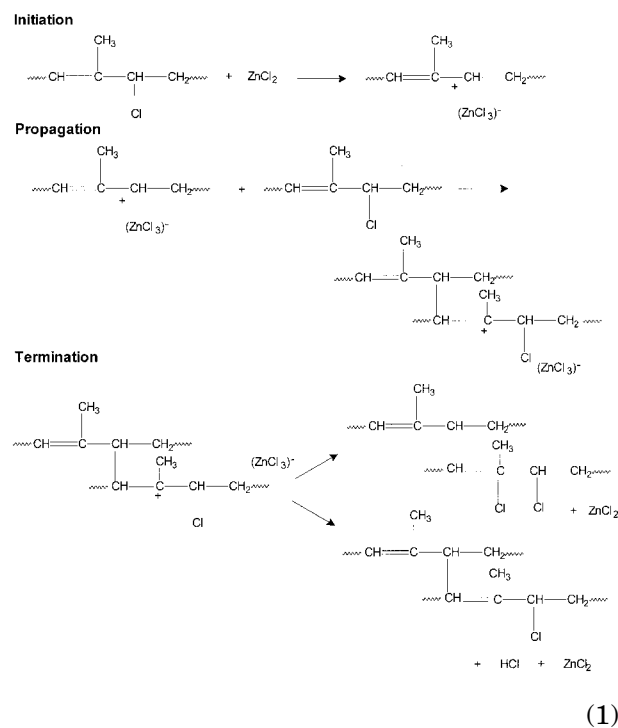
Upon heating CIIR with ZnO, the loss of HCl results in the formation of ZnCl<sub>2</sub> and a conjugated diene on the polymer.<sup>2–5</sup> All authors agree that ZnCl<sub>2</sub> formation precedes crosslinking. The presence of a conjugated diene and a dienophile before crosslinking has prompted consideration of a Diels-Alder type reaction.<sup>2,4</sup> Diels-Alder reactions of model compounds have been shown to occur readily.<sup>4</sup> At 110°C, the reaction with maleimide was essentially complete within 10 min, and with

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*Journal of Applied Polymer Science*, Vol. 78, 2302–2310 (2000)  
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naphthoquinone, 80% complete in 25 min.<sup>6</sup> CIIR can be linked to bis-maleimides via diene groups on the chain generated by reaction with ZnO.<sup>6-8</sup> However, these studies did not take into account the possible effect of ZnO added and ZnCl<sub>2</sub> formed *in situ*. Vukov<sup>4</sup> found that upon heating chlorinated or brominated model compound 2,2,4,8,8-pentamethyl-4-nonene with ZnO, more than 90% of the halogen was lost, but crosslinked species formed very slowly, and he concluded that a Diels-Alder reaction does not play a role in crosslinking in the presence of ZnO. Kuntz et al.<sup>2</sup> found an increase in cure time with a decrease in crosslink density on mixing a conjugated diene butyl with CIIR, and likewise concluded that the Diels-Alder reaction was not a key factor in the crosslinking process.

The most widely accepted theory, as postulated by Baldwin et al.,<sup>3</sup> eq. (1) and supported by Kuntz et al.<sup>2</sup> and Vukov,<sup>4</sup> postulates a cationic reaction in which ZnCl<sub>2</sub>, formed *in situ*, is responsible for crosslinking.



By implication, crosslinking will result immediately on heating CIIR with ZnCl<sub>2</sub>, as opposed to ZnO formulations where ZnCl<sub>2</sub> must first form. However, it was reported in an earlier article<sup>5</sup> that while ZnCl<sub>2</sub> reduced the induction period prior to crosslinking, it was not eliminated, even with 5 phr ZnCl<sub>2</sub>. Kuntz et al.<sup>2</sup> noted that conju-

gated dienes did form prior to crosslinking, but concluded that they played no role in crosslinking beyond enabling the formation of ZnCl<sub>2</sub>, the addition of a conjugated diene butyl to CIIR reducing the reaction rate and crosslink density. However, we found that the induction period prior to crosslinking in CIIR was eliminated only in the presence of ZnCl<sub>2</sub> and conjugated diene butyl, both being necessary precursors to crosslinking.<sup>5</sup>

This article examines data in this and the previous article,<sup>5</sup> and proposes a modification of the cationic crosslinking mechanism as put forward by Baldwin et al.,<sup>3</sup> the modified mechanism attributes roles to both ZnCl<sub>2</sub> and conjugated diene butyl. Secondly, the article examines the reversion process. Curing CIIR with ZnCl<sub>2</sub>, alone or with ZnO/ZnCl<sub>2</sub> mixtures, containing insufficient ZnO to trap all of the chlorine evolved during crosslinking, resulting in reversion.<sup>2,5</sup>

## EXPERIMENTAL

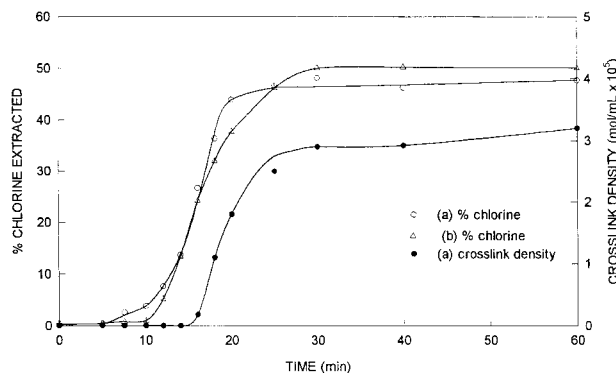
Materials and experimental procedures were described in the previous article in this series.<sup>5</sup> For total zinc analysis (ZnO and ZnCl<sub>2</sub>) samples were digested in sulfuric acid and heated over an open flame to volatilize excess sulfuric acid. The digested sample was heated at 950°C for 2 h and the residue dissolved in a small amount of HCl. The concentration of zinc was determined by Atomic Absorption (AA).

## RESULTS AND DISCUSSION

### Diels-Alder Reaction

If the Diels-Alder reaction applied, ZnO or ZnCl<sub>2</sub> would not be required once a conjugated diene was present. Because a number of studies<sup>2,4</sup> relating to the possibility of a Diels-Alder reaction did not mention the possible role of ZnO present in the system, it was decided to pursue investigation of the Diels-Alder reaction by heating CIIR with a conjugated diene in the absence of ZnO.

A CIIR(100)/ZnO(5) sample was heated to a point that would allow for the formation of conjugated diene butyl, but no crosslinking.<sup>5</sup> Dissolution of the sample and the extraction of 19% chlorine on heating for 13 min at 150°C confirmed that vulcanization had not occurred, yet some conjugation had formed. To ensure that crosslinking, if it did occur, was solely due to a Diels-Alder



**Figure 1** Crosslink density and extractable chlorine analysis of (a) CIIR(100)/ZnO(3)/Zn<sub>2</sub>OCl<sub>2</sub>(5), and extractable chlorine analysis of (b) CIIR(100)/ZnO(3), heated isothermally at 150°C.

reaction, it was necessary to remove any other compounds present, i.e., ZnO and ZnCl<sub>2</sub>. The heated sample was dissolved and centrifuged, thus allowing the rubber fraction to be separated from insoluble zinc. The rubber was precipitated by addition of methanol and dried under vacuum for 7 days. Zinc analysis by AA showed that this procedure successfully removed all the ZnO added and ZnCl<sub>2</sub> formed.

The dried rubber would contain the essential ingredients necessary for Diels-Alder reactions, viz. a dienophile and a conjugated diene, and should, therefore, crosslink when heated. However, when samples were heated for 60 min at 150°C, no crosslinking was observed. This supports the experiments of Kuntz et al.<sup>2</sup> and Vukov,<sup>4</sup> indicating that crosslinking of CIIR by ZnCl<sub>2</sub> does not occur via a Diels-Alder mechanism.

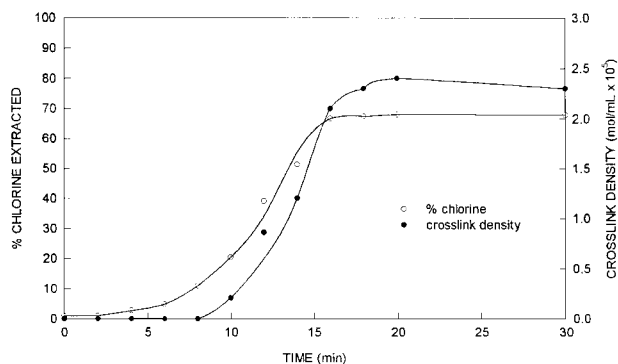
### Crosslinking Precursors

It was shown in the earlier article<sup>5</sup> that ZnCl<sub>2</sub>, formed prior to crosslinking, catalyzed dehydrohalogenation and shortened the induction period prior to crosslinking. Dehydrohalogenation results in the formation of ZnCl<sub>2</sub> and conjugated diene butyl, both of which are required to be present in the polymer before crosslinking will commence, i.e., both are precursors to crosslinking.<sup>5</sup> Although only 50% of the chlorine in the polymer is extractable as ZnCl<sub>2</sub>, compounds with insufficient ZnO to trap all of the chlorine present in the polymer show reversion.<sup>5</sup> This suggests that an insoluble zinc oxychloride (Zn<sub>2</sub>OCl<sub>2</sub>) or zinc hydroxychloride (Zn(OH)Cl) may form.

### Insoluble Zinc Compounds

The formation of insoluble zinc-oxychlorides results on mixing a concentrated syrupy ZnCl<sub>2</sub> solution and ZnO,<sup>9</sup> both reagents that are present upon heating CIIR and ZnO. To determine whether the formation of such an insoluble salt could promote dehydrohalogenation, Zn<sub>2</sub>OCl<sub>2</sub> was synthesized via this procedure and mixed with CIIR. Prior to its inclusion, the compound was crushed, and washed with water to remove unreacted ZnCl<sub>2</sub>. Total zinc analysis revealed the compound to be comprised of 59.81 mass % zinc (theoretical for Zn<sub>2</sub>OCl<sub>2</sub> = 60.08%). Upon heating CIIR samples mixed with 5 phr Zn<sub>2</sub>OCl<sub>2</sub> and 3 phr ZnO at 150°C, the formation of ZnCl<sub>2</sub> was detected after 7.5 min, and a maximum of 48% of the chlorine was extractable as ZnCl<sub>2</sub>, associated with a crosslink density of  $3.2 \times 10^{-5}$  mol/mL (Fig. 1). The slightly earlier formation of ZnCl<sub>2</sub> that occurred with CIIR(100)/ZnO(3)<sup>5</sup> and detection of approximately 50% of the chlorine as ZnCl<sub>2</sub> shows that, like ZnCl<sub>2</sub>, Zn<sub>2</sub>OCl<sub>2</sub> promotes dehydrohalogenation. ZnCl<sub>2</sub> is very hygroscopic, and can readily disperse in the rubber, but Zn<sub>2</sub>OCl<sub>2</sub> is a solid, and despite crushing the material, the product added to the rubber still comprised fairly large grains, much bigger than ZnO particles.

When CIIR was mixed with larger quantities of Zn<sub>2</sub>OCl<sub>2</sub> (20 phr) and heated, the formation of ZnCl<sub>2</sub> occurred more readily than when CIIR was heated with ZnO (Fig. 2). After heating the former system for only 8 min at 150°C, 11% of the chlorine was extractable as ZnCl<sub>2</sub>, compared with 1% when CIIR was heated with 5 phr ZnO,<sup>5</sup> confirming that Zn<sub>2</sub>OCl<sub>2</sub> indeed promotes dehydrohalogenation. However, its addition to compounds did not increase the amount of extractable chlorine,



**Figure 2** Crosslink density and extractable chlorine analysis of CIIR(100)/Zn<sub>2</sub>OCl<sub>2</sub>(20) heated isothermally at 150°C.

and it was clearly not decomposed in the reaction, its function being purely catalytic.

In all the isothermal experiments conducted with the incorporation of more than 1 phr ZnO, no more than 50% of the chlorine is extractable,<sup>5</sup> suggesting that the remaining chlorine either remained bound to the polymer or formed an insoluble zinc-chloro species. If 50% of the chlorine remained bound to the rubber it would imply that the crosslinking process per se, as distinct from reactions that lead to conjugated diene butyl formation, do not involve dehydrohalogenation, but merely a rearrangement of the Cl position during crosslinking to the neighboring diene. To trap 50% of the chlorine in the polymer as ZnCl<sub>2</sub> would require a ZnO loading of 0.63 g ZnO in 100 g of rubber. However, compounds with 1 phr ZnO showed reversion (CIIR(100)/ZnO(1) and CIIR(100)/ZnO(1)/ZnCl<sub>2</sub>(5)).<sup>5</sup> ZnO is a solid, and failure of 1 phr ZnO to prevent reversion may simply indicate that it is not readily available to react with HCl evolved at all locations within the polymer. Alternatively, part of the ZnO may have been consumed in the formation of an insoluble zinc chloride species, not detected in the analysis for ZnCl<sub>2</sub>.

A CIIR(100)/ZnO(4) compound was heated for 30 min at 150°C and the ZnCl<sub>2</sub> formed extracted. Similar to previous systems,<sup>5</sup> 50% of the chlorine was extractable as ZnCl<sub>2</sub>. The sample was then treated with a benzene/ethanol solution containing a known amount of 3 M HCl to convert residual ZnO and any insoluble zinc salts to ZnCl<sub>2</sub>. The extract was titrated with AgNO<sub>3</sub> and found to contain more chlorine than the amount in the added HCl. The excess chlorine amounted to 87% of the chlorine in the polymer not extracted as ZnCl<sub>2</sub> after heating (i.e., 43% of the total chlorine). Thus, it is evident that most of the chlorine is removed from the polymer on crosslinking, 50% being present as ZnCl<sub>2</sub>, and the remainder as an insoluble zinc salt, possibly Zn(OH)Cl and/or Zn<sub>2</sub>OCl<sub>2</sub>.

### Proposed Crosslinking Mechanism

The most widely accepted theory, as postulated by Baldwin et al.<sup>3</sup> and supported by Kuntz et al.<sup>2</sup> and Vukov,<sup>4</sup> postulates a cationic reaction in which ZnCl<sub>2</sub>, formed *in situ*, is responsible for crosslinking. Conjugated diene butyls were not attributed a role in the mechanism. Results obtained in this and the previous article<sup>5</sup> do not accord with the cationic mechanism as proposed by Baldwin et al.<sup>3</sup> Even with the inclusion of 5 phr

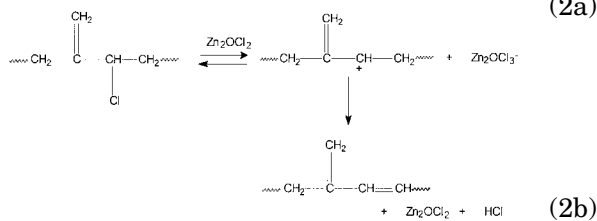
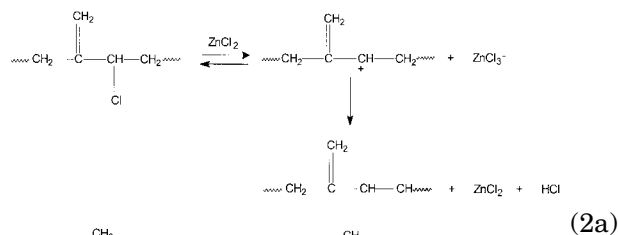
ZnCl<sub>2</sub>, an induction period before crosslinking was observed, albeit considerably shorter than that observed with CIIR(100)/ZnO(5). By implication, the mechanism suggests that the extent of vulcanization in both the CIIR/ZnO and CIIR/ZnCl<sub>2</sub> compounds will be the same. However, reversion reactions, evident in the CIIR/ZnCl<sub>2</sub> system, yet absent from CIIR/ZnO, prevent crosslinking from attaining similar magnitudes to that achieved in the presence of ZnO.<sup>5</sup>

Baldwin et al.<sup>3</sup> suggested that crosslinking via a cationic mechanism involves the abstraction of Cl<sup>-</sup> by ZnCl<sub>2</sub>, leading to a carbocation on the polymer chain. The carbocation interacts with a neighboring chain, resulting in a crosslink and a cation on the second chain. The reaction is terminated either by the transfer of Cl<sup>-</sup> from ZnCl<sub>3</sub><sup>-</sup> to the cation, or by the abstraction by ZnCl<sub>3</sub><sup>-</sup> of H<sup>+</sup> and the formation of a double bond in the chain. ZnCl<sub>2</sub> and HCl result. In the first case, no Cl is removed from the chain on crosslinking, while in the second case only half of the available Cl is abstracted. Baldwin et al.<sup>3</sup> reported that most of the available chlorine in the polymer could be abstracted as ZnCl<sub>2</sub> on crosslinking with ZnO. They suggested that it is unlikely that the propagation step proceeds very far, although the abstraction of most of the chlorine would indicate that reaction of the carbocation with a neighboring chain may be repeated, only the termination step being associated with chlorine retention by the polymer as shown in eq. (1). Kuntz et al.<sup>2</sup> extracted 87% of the available chlorine at 163°C.

Although the mechanism in eq. (1) identifies initiation, propagation, and termination reactions, the initiation step carries through to crosslink formation. The data presented in the previous article<sup>5</sup> suggests that the overall crosslinking process comprises two distinct processes. There was a change in the ratio of mol ZnCl<sub>2</sub> formed, to the mol of crosslinks (i.e., crosslink density), during the heating process.<sup>5</sup> As ZnCl<sub>2</sub> is formed before the onset of crosslinking, a high ratio applies in the initial stages of crosslinking; at 14 min, the ratio was 360 (3.6 × 10<sup>-5</sup> mol ZnCl<sub>2</sub>/mL rubber, 1/2Mc = 0.01 × 10<sup>-5</sup> mol/mL rubber), while after 40 min, when the maximum crosslink density and ZnCl<sub>2</sub> evolution had occurred, the ratio was approximately 2 (8.2 × 10<sup>-5</sup> mol ZnCl<sub>2</sub>/mL rubber, 1/2Mc = 3.9 × 10<sup>-5</sup> mol/mL rubber). The decrease in the ratio suggests that the formation of ZnCl<sub>2</sub> and crosslinking are two separate events, and that dehydrohalogenation does not automatically lead

through to crosslink formation. Upon heating the samples for longer than 40 min, the ratio remains constant. Furthermore, the induction period observed, even in the presence of 5 phr  $\text{ZnCl}_2$ , points to the formation of an intermediate to which crosslinking can occur. The mechanism proposed in eq. (1) would not require such an induction period. Only in blends with polybutadiene (BR) and polyisoprene (IR), where the diene rubber supplies a structure to which crosslinking can occur, is the induction period eliminated.<sup>5</sup> In the CIIR/BR blend,<sup>5</sup> only 16 mol % of the total chlorine was extractable as  $\text{ZnCl}_2$  at a crosslink density of  $5.7 \times 10^{-5}$  mol/mL. If it is assumed that a further 16 mol % chlorine was removed from the polymer in the form of an insoluble zinc salt, the chlorine loss would equate to  $5.0 \times 10^{-5}$  mol chlorine/mL compound. This approximates to the crosslink density found ( $5.7 \times 10^{-5}$  mol/mL) that shows that at essentially all of the sites on the polymer chain at which chlorine was removed, crosslinking resulted. Little conjugation occurred, the loss of chlorine adjacent to a double bond in BR preferentially leading to crosslink formation. This supports the contention that, the second step that results in crosslink formation, is quite distinct from that which leads to conjugation.

It is proposed that the first step is the formation of a conjugated diene butyl on the polymer chain, the dehydrohalogenation reaction being catalyzed by  $\text{ZnCl}_2$  or  $\text{Zn}_2\text{OCl}_2$ . The following reaction sequence may be considered.

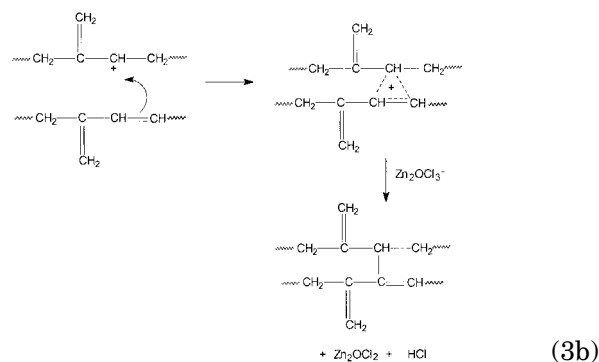
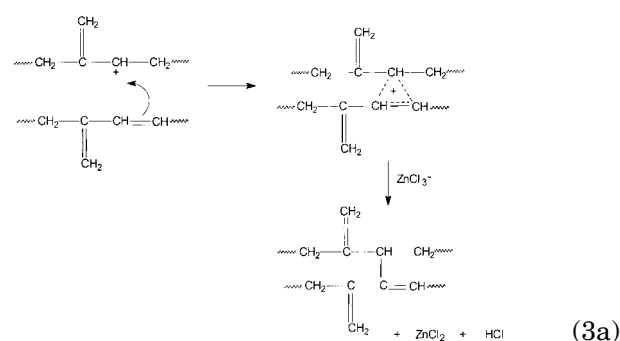


In the presence of  $\text{ZnO}$ , the  $\text{HCl}$  will be trapped as  $\text{ZnCl}_2$ , and the reaction would become autocatalytic.

An analogous reaction catalyzed by  $\text{Zn}_2\text{OCl}_2$  may be envisaged.

The second step involves crosslinking to the conjugated diene butyl. It is proposed that when a carbocation is formed on a polymer chain adjacent to a conjugated diene butyl, or in the blend adjacent to a diene unit in BR or IR, crosslinking results in preference to conjugated diene butyl formation. Most of the chlorine is removed from the polymer on crosslinking, which implies that in the second step, chlorine must also be abstracted. A  $\text{ZnCl}_2$  initiated reaction sequence, as shown in eq. (3a) may be considered.

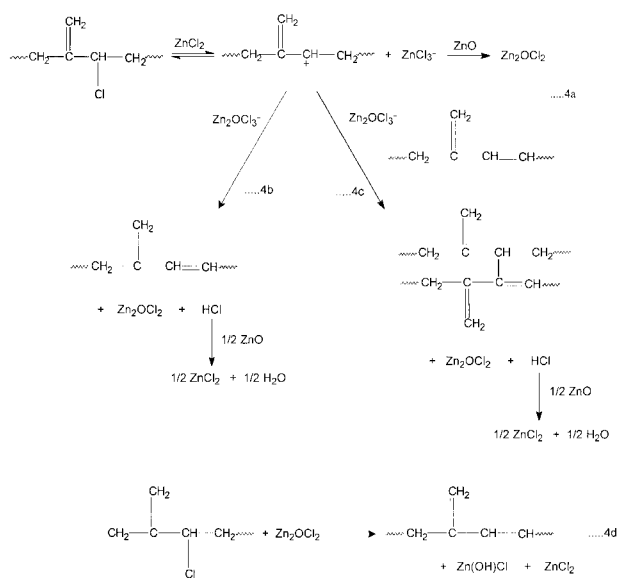
Again, an analogous reaction involving  $\text{Zn}_2\text{OCl}_2$  may be envisaged.



If all of the chlorine were abstracted from the polymer via eqs. (2) and (3), 100% should be extractable as  $\text{ZnCl}_2$ , which is not the case, and clearly the reaction sequence is more complex than suggested above. In the presence of moisture,  $\text{ZnO}$  and  $\text{ZnCl}_2$  may react to form  $\text{Zn}_2\text{OCl}_2$ .<sup>5,9</sup> However, in the polymer environment, this reaction is clearly limited, if it occurs at all; it would be impossible to explain why, in the presence of excess  $\text{ZnO}$ , the same amount of  $\text{ZnCl}_2$  always remained unreacted in all systems.

Thus, an insoluble zinc salt, other than  $\text{Zn}_2\text{OCl}_2$ , must form in the system. A reaction mechanism is required in which half of the chlorine present in the

polymer appears as  $\text{ZnCl}_2$  and half as an insoluble zinc salt. Because both the  $\text{ZnCl}_2$  and the  $\text{Zn}_2\text{OCl}_2$  initiated reactions lead to 50% of the chlorine in the polymer being trapped as  $\text{ZnCl}_2$ , a cyclic mechanism involving both species is indicated. The following reaction sequence is proposed.



The carbocation resulting from chlorine abstraction by  $\text{ZnCl}_2$  may either form a conjugated diene butyl or crosslink, if adjacent to a suitable conjugated diene butyl.

The reaction sequences 4a–b and 4a–c consume  $\text{ZnCl}_2$  and generate  $\text{Zn}_2\text{OCl}_2$  and another reaction, that generates  $\text{ZnCl}_2$  at the expense of  $\text{Zn}_2\text{OCl}_2$ , must clearly be involved. In the presence of  $\text{Zn}_2\text{OCl}_2$ ,  $\text{ZnCl}_2$  formation and crosslinking initiated earlier (Figs. 1 and 2), and it is proposed that dehydrohalogenation by  $\text{Zn}_2\text{OCl}_2$  (reaction 4d), possibly via a concerted mechanism, occurs.

$\text{Zn}_2\text{OCl}_2$  plays a catalytic role in the reaction, but the role of  $\text{ZnCl}_2$  is autocatalytic, the  $\text{ZnCl}_2$  concentration increasing by 2  $\text{ZnCl}_2$  in every reaction cycle [eqs. (4a), (4b), (4d), or (4a), (4c), (4d)]. Half of the chlorine abstracted appears as  $\text{Zn(OH)Cl}$ , and half as  $\text{ZnCl}_2$ . The involvement of both  $\text{ZnCl}_2$  and  $\text{Zn}_2\text{OCl}_2$  in the cycle is necessary to account for the quantitative product spectrum, i.e., 50% of the chlorine on the polymer being extractable as  $\text{ZnCl}_2$  and the remainder being present as an insoluble zinc salt. The product yield requires a reaction cycle that links the formation of soluble and insoluble zinc salts, and this implies that in the presence of  $\text{ZnO}$ ,  $\text{ZnCl}_3^-$

must readily be trapped as  $\text{Zn}_2\text{OCl}_3^-$  in preference to its reaction as in eq. (2a). Dehydrohalogenation via eq. (2b) must be discounted, because, as noted earlier, this would enable 100% of the chlorine abstracted to appear as  $\text{ZnCl}_2$ . Instead, dehydrohalogenation via the concerted reaction is proposed.

Because the amount of  $\text{ZnCl}_2$  extractable is always 50%, it is clear that in the polymer environment  $\text{Zn}_2\text{OCl}_2$  does not form as a result of the reaction between  $\text{ZnCl}_2$  and  $\text{ZnO}$ . Instead, its formation via  $\text{ZnCl}_3^-$  is proposed.

$\text{Zn}_2\text{OCl}_2$  plays a catalytic role, and its concentration in the rubber will be low at all times. In compounds where 5 phr  $\text{Zn}_2\text{OCl}_2$  was added to the formulation [CIIR(100)/ $\text{Zn}_2\text{OCl}_2$ (5)/ $\text{ZnO}$ (3)] (Fig. 1), a crosslink density of only  $3 \times 10^{-5}$  mol/mL was achieved, although 50% of the chlorine still appeared as  $\text{ZnCl}_2$ .  $\text{Zn}_2\text{OCl}_2$  comprised large grains, and the number of sites in the CIIR at which it could influence the reaction was limited. With 20 phr  $\text{Zn}_2\text{OCl}_2$  (Fig. 2) a lower crosslink density ( $2.3 \times 10^{-5}$  mol/mL) was achieved at equilibrium, but 68% of the chlorine was extracted as  $\text{ZnCl}_2$ . This accords with the proposed reaction mechanism. Dehydrohalogenation by  $\text{Zn}_2\text{OCl}_2$ , via eq. (4d), leads to conjugated diene butyl and the liberation of  $\text{ZnCl}_2$ , one molecule of  $\text{ZnCl}_2$  (2 chlorine atoms) being extractable for every chlorine atom removed from the polymer chain. With this high  $\text{Zn}_2\text{OCl}_2$  loading, abstraction of much of the chlorine results in conjugated diene butyl formation, and only when chlorine is abstracted by  $\text{ZnCl}_2$  via eq. (4a) does crosslinking become a possibility. Hence, the crosslink density is lower, and the amount of  $\text{ZnCl}_2$  formed higher than in  $\text{ZnO}/\text{ZnCl}_2$  formulations.

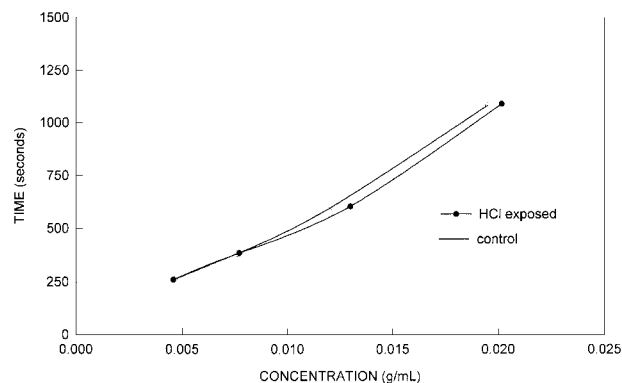
### Crosslinking vs. Dehydrohalogenation

The proposed preferential crosslinking reaction of a dehalogenated isoprenoid cation with a conjugated diene butyl, rather than its dehydrohalogenation, implies that the activation energy of crosslinking is lower than that of dehydrohalogenation. The DSC curve<sup>5</sup> of CIIR(100)/ $\text{ZnO}$ (5)/ $\text{ZnCl}_2$ (1) heated at  $5^\circ\text{C}/\text{min}$  showed the onset of the first exotherm, associated with the formation of  $\text{ZnCl}_2$  (a product of dehydrohalogenation), to occur at  $153^\circ\text{C}$ . The amount of extractable  $\text{ZnCl}_2$  increased rapidly only above  $153^\circ\text{C}$ . By comparison, when CIIR(50)/BR(50)/ $\text{ZnO}$ (5)/ $\text{ZnCl}_2$ (1) was heated at  $5^\circ\text{C}/\text{min}$ , a gel was detected at  $142^\circ\text{C}$ , thus confirming that when a diene is available,

crosslinking can occur more readily than dehydrohalogenation. Furthermore, as shown earlier, the crosslink density achieved in the CIIR(50)/BR(50)/ZnO(5)/ZnCl<sub>2</sub>(1) system equated to the amount of ZnCl<sub>2</sub> formed, i.e., dehydrohalogenation led to crosslinking in preference to conjugated diene butyl formation.

In isothermal systems, when sufficient ZnO was present to prevent reversion, 50% of the chlorine in the polymer was extractable as ZnCl<sub>2</sub> when the crosslink density reached  $4 \times 10^{-5}$  mol/mL. Upon prolonged heating, the system was stable, and the crosslink density remained constant. However, the number of crosslinks formed in the process was only about 1/4 that expected. As the polymer contains 1.21 mass % chlorine, and it is proposed that 2 mol of chlorine are evolved for every mol of crosslink formed, a crosslink density of  $15.7 \times 10^{-5}$  mol/mL can be calculated in terms of the proposed mechanism, compared to the observed equilibrium value of  $4 \times 10^{-5}$  mol/mL. Similarly, Baldwin et al.<sup>3</sup> reported only 10% of the reactive sites in the average CIIR chain to have permanently engaged in the crosslinking process. In terms of the proposed reaction mechanism, dehydrohalogenation leads to a conjugated diene butyl unit that will crosslink with an adjacent dehalogenated unit that contains a highly reactive carbocation. Thus, for crosslinking to occur, a conjugated diene butyl unit must be in close proximity with a cation on an adjacent polymer chain. However, the formation of crosslinks decreases the mobility of the polymer, thereby reducing the possibility of reactive units coming into contact with one another, and thus accounting for the low crosslink density recorded. When crosslinking is impossible, conjugated diene butyl formation occurs. The zinc-chloro by-products of the reaction are identical.

A maximum crosslink density of  $4.0 \times 10^{-5}$  mol/mL was recorded when samples, which contained sufficient ZnO to prevent reversion, were heated isothermally at 150°C. However, when these systems were heated in the DSC at 5°C/min, lower maximum crosslink densities were measured. Crosslinking requires conjugated diene butyl and unreacted chlorinated isoprenoid units in the polymer to assume adjacent positions. The rates of movement of chain segments and of dehydrohalogenation will increase with temperature. The lower crosslink densities achieved at programmed heating rates, as opposed to isothermal experiments, suggests that the rate of dehydrohalogenation, resulting in con-



**Figure 3** Flow times in Ubbelohde viscometer for solutions of CIIR heated at 150°C in the absence and presence of HCl.

jugated diene butyl formation, increases more rapidly with temperature than does the rate of movement of chain segments. Hence, less pairing of suitable reactive units results and conjugated diene butyl formation assumes greater importance than crosslinking. The by-product spectrum of eqs. (4b) and (4c) are similar.

### Reversion Reactions

Reversion has been shown to occur on heating various systems.<sup>5</sup> These include CIIR formulations with no curatives, ZnCl<sub>2</sub> only, and ZnO loadings less than that required to trap all of the chlorine. Dehydrohalogenation results in the formation of conjugated diene butyl and HCl. Because reversion occurs when there is no or insufficient ZnO to trap the HCl, the role of HCl in the reversion process was investigated.

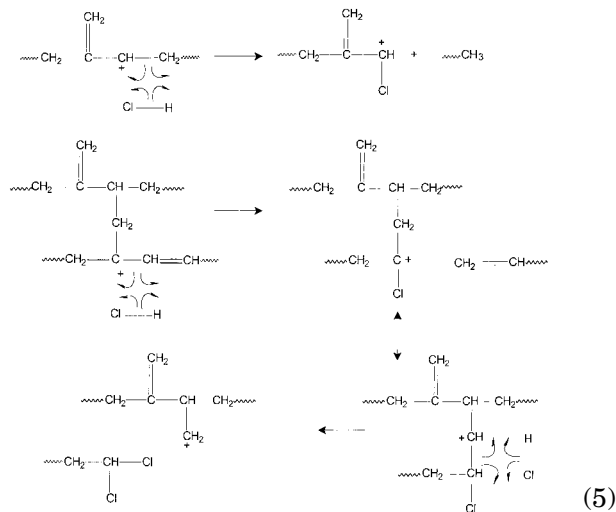
Thin films of CIIR, deposited from solution on the walls of a pill vial, were subjected to HCl(g) at 150°C for 30 min. The exposed samples were dissolved in benzene, and the flow times in a Ubbelohde viscometer determined for solutions of various concentrations. Figure 3 shows that the flow times for solutions of similar concentration were the same for samples that had and had not been exposed to HCl, thus proving that HCl did not initiate chain scission at 150°C.

In another experiment, CIIR(100)/ZnCl<sub>2</sub>(5) samples were heated for 10 min at 150°C and the crosslink density measured ( $0.95 \times 10^{-5}$  mol/mL). After extraction of the ZnCl<sub>2</sub>, samples were subjected to HCl(g) at 150°C for 6 min. Even after HCl treatment, the crosslink density of  $0.95 \times 10^{-5}$  mol/mL was unchanged.

In a third experiment, six CIIR(100)/ZnCl<sub>2</sub>(5) samples were heated for 10 min at 150°C, fol-

lowed by crosslink density measurements ( $1.0 \times 10^{-5}$  mol/mL). Half of the samples were heated for an additional 6 min at  $150^\circ\text{C}$  in the presence of  $\text{HCl}(\text{g})$ , while half were heated for the same duration in the absence of  $\text{HCl}$ . It was shown in article 1 of this series<sup>5</sup> that in the absence of  $\text{HCl}$ , reversion occurred on heating samples and accounted for a decrease of 36% in the crosslink density. However, in the presence of  $\text{HCl}$ , a decrease of 83% in the crosslink density is associated with additional heating.

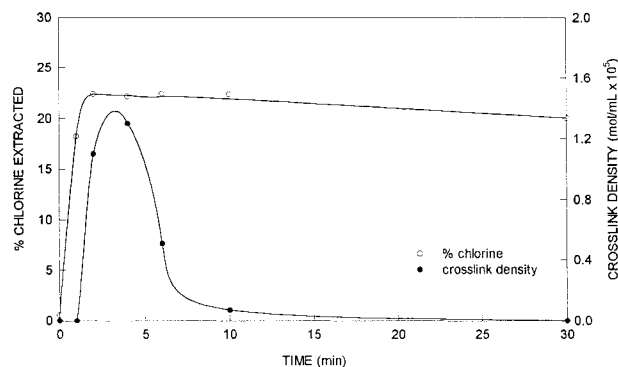
In the second experiment described above,  $\text{ZnCl}_2$  was extracted before reheating of the samples, preventing dehydrohalogenation, while in the third experiment  $\text{ZnCl}_2$  present would catalyze dehydrohalogenation. Dehydrohalogenation is accompanied by reversion, the chain scission process being accelerated by heating in a  $\text{HCl}$  atmosphere. Clearly,  $\text{HCl}$  facilitates chain scission only under conditions where dehydrohalogenation is occurring, i.e., where carbocations are present on the polymer chain. It is proposed that chain scission results from the attack of  $\text{HCl}$  on the carbocation as shown in eq. (5),



i.e., when  $\text{HCl}$  is not removed from the system by  $\text{ZnO}$ , chain scission competes with the crosslinking process. In accord with the proposed mechanism, addition of sufficient amounts of  $\text{ZnO}$  will trap  $\text{HCl}$  formed and prevent reversion; 50% of the chlorine liberated as  $\text{HCl}$  is trapped as  $\text{ZnCl}_2$ , and the remainder as an insoluble zinc salt, proposed to be  $\text{Zn}(\text{OH})\text{Cl}$ .

#### Effect of Zinc Stearate

The crosslink densities and extractable chlorine formed on heating samples of CIIR mixed with 5



**Figure 4** Crosslink density and extractable chlorine analysis of CIIR(100)/zinc stearate(5) heated isothermally at  $150^\circ\text{C}$ .

phr zinc stearate, for various times at  $150^\circ\text{C}$  are presented in Figure 4. Zinc analysis of the extract by AA, and chloride analysis with  $\text{AgNO}_3$  revealed the extractable zinc to be  $\text{ZnCl}_2$ . Extractable chlorine and crosslinks formed readily on heating CIIR mixed with zinc stearate. After only 1 min, 18% of the chlorine was extractable as  $\text{ZnCl}_2$ , and the very rapid formation of  $\text{ZnCl}_2$  shows that, unlike  $\text{ZnO}$ , zinc stearate actively promotes dehydrohalogenation.  $\text{ZnCl}_2$  formed prior to crosslinking, indicating the formation of a conjugated diene on the polymer chain and crosslinking via the mechanism proposed earlier.

A maximum of 22% of the chlorine was extractable as  $\text{ZnCl}_2$  after heating the sample for 4 min. This corresponds to the maximum amount of chlorine that could be abstracted as  $\text{ZnCl}_2$  by the quantity of zinc stearate added, which shows that no other zinc salt formed. Once all of the zinc stearate has been converted into  $\text{ZnCl}_2$ , further heating will result in the same reactions as occurred when CIIR/ $\text{ZnCl}_2$  was heated, i.e., dehydrohalogenation, crosslinking and reversion, with reversion dominating.

The inclusion of a suitable  $\text{HCl}$  trap, like  $\text{ZnO}$ , will prevent reversion. Indeed, it was found that the inclusion of 2 phr  $\text{ZnO}$  in a CIIR(100)/zinc stearate(5) formulation prevented crosslink destruction, and a maximum crosslink density of  $4.0 \times 10^{-5}$  mol/mL was recorded after 30 min at  $150^\circ\text{C}$ .

Formulations used by Baldwin et al.<sup>3</sup> included stearic acid, which readily forms zinc stearate on reaction with  $\text{ZnO}$ .  $\text{ZnCl}_2$  is the only zinc salt formed in zinc stearate initiated dehydrohalogenation of CIIR, and its presence in formulations would account for the abstraction of the consider-



ably larger amounts of  $\text{ZnCl}_2$  than the 50% reported in this and the previous article,<sup>5</sup> where no stearic acid was added.

## CONCLUSIONS

Dehydrohalogenation initiated by  $\text{ZnCl}_2$ ,  $\text{Zn}_2\text{OCl}_2$  or zinc stearate results in the formation of  $\text{ZnCl}_2$  and conjugated diene butyl units in the polymer chain.  $\text{ZnCl}_2$  and conjugated diene butyl are both precursors to crosslink formation. Crosslinking involves reaction between a conjugated diene butyl and a cation formed on a isoprenoid unit when chlorine is abstracted by  $\text{ZnCl}_2$ . The reaction comprised two distinct steps, viz. dehydrohalogenation, leading to the formation of crosslink precursors, and crosslinking per se. Both steps are accompanied by the loss of HCl. All the chlorine on the polymer is abstracted on vulcanization, but only half appears as  $\text{ZnCl}_2$ , the remainder of the chlorine being trapped as an insoluble zinc salt, possibly  $\text{Zn}(\text{OH})\text{Cl}$ . A modification of the crosslinking reaction mechanism proposed in the literature<sup>2-4</sup> is suggested in which conjugated diene butyls play an essential role. Literature mechanisms do not consider conjugated diene butyl to participate in crosslinking.

Although reaction between  $\text{ZnO}$  and  $\text{ZnCl}_2$  can lead to  $\text{Zn}_2\text{OCl}_2$ , little if any  $\text{Zn}_2\text{OCl}_2$  forms via this route in the polymer, and instead,  $\text{Zn}_2\text{OCl}_2$  forms on vulcanization as a result of the reaction of  $\text{ZnCl}_2$  with  $\text{ZnO}$ .

The crosslink efficiency is low, the equilibrium crosslink density being only 25% of that possible when considering the number of chlorinated isoprenoid units in the polymer. Crosslinking will only occur if, during dehydrohalogenation, the cation formed on the isoprenoid unit is adjacent to a conjugated diene butyl unit, if not, dehydrohalogenation will result in the formation of yet an-

other conjugated diene butyl in the polymer chain.

HCl does not attack the polymer, but where HCl, evolved during the crosslinking reaction is not trapped by  $\text{ZnO}$ , the polymer develops a yellow and later deep brown color, and chain scission reactions dominate over the crosslinking process, i.e., HCl attack occurs only when cations are present on the polymer chain.

Zinc stearate promotes dehydrohalogenation and crosslinking, all of the chlorine abstracted appearing as  $\text{ZnCl}_2$ . The conversion of zinc stearate to  $\text{ZnCl}_2$  explains the high yields of  $\text{ZnCl}_2$  reported in the literature with  $\text{ZnO}$ /stearic acid formulations, compared to the formation of 50%  $\text{ZnCl}_2$  found in this study where stearic acid was omitted.

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

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