

# Vulcanization of Polychloroprene Rubber. I. A Revised Cationic Mechanism for ZnO Crosslinking

H. Desai, K. G. Hendrikse,\* C. D. Woolard

Physical and Polymer Chemistry Research Group, Nelson Mandela Metropolitan University, P.O. Box 77000, Port Elizabeth, 6031, South Africa

Received 3 February 2005; accepted 20 November 2005

DOI 10.1002/app.23904

Published online 6 April 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Data relating to the vulcanization of mercaptan-grade polychloroprene (CR) by ZnO and MgO (alone or in combination) are examined. Compounds were vulcanized through the isothermal heating of samples at 140°C in a laboratory press and at programmed rates in a differential scanning calorimeter. The reaction was stopped at various points during the heating process. The crosslink densities were determined via swelling. Extractable ZnCl<sub>2</sub> and MgCl<sub>2</sub> were analyzed by atomic absorption spectrometry. Three different crosslinking processes were identified. The first crosslinking process involved the activation of the highly reactive tertiary allylic 1,2-units along the polymer chain, whereas the second and third crosslinking processes were attributed to the activation toward crosslinking of 3,4- and 1,4-units, respectively. The crosslinking

reactions of the 1,2-units comprised three distinct steps: isomerization (promoted by ZnO), dechlorination, and crosslinking. ZnCl<sub>2</sub> (which formed during compounding and upon crosslinking) promoted crosslinking, and its addition to formulations decreased but did not eliminate the induction period before crosslinking. MgO retarded the crosslinking process by limiting the formation of ZnCl<sub>2</sub> during mixing. The results of the CR/ZnO system are discussed, and a modified cationic mechanism for crosslinking is proposed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 865–876, 2007

**Key words:** rubber; vulcanization; polychloroprene; ZnO; MgO

## INTRODUCTION

Polychloroprene (CR) is an important specialty elastomer that is widely used in many varied technological applications because it has good resistance to aging, favorable flame-retardant behavior, and good low-temperature flexibility.<sup>1,2</sup> The individual monomeric repeating units can take up to five basic configurations,<sup>1–4</sup> as illustrated in Figure 1.

CR can be crosslinked upon heating,<sup>5,6</sup> the reaction being facilitated by the addition of ZnO or ZnCl<sub>2</sub>.<sup>7</sup> Miyata and Atsumi<sup>8</sup> and Kuntz et al.<sup>9</sup> disproved early suggestions that crosslinking in the presence of ZnO involved an ether linkage, although such a mechanism has recently been resuscitated.<sup>10</sup> It has also been suggested by various authors<sup>9–12</sup> that a Diels–Alder reaction does not play a role in crosslinking in the presence of ZnO. It is widely agreed that an important step in the vulcanization of CR involves the allylic rearrangement of 1,2-polymerized units in CR.<sup>5,9,13</sup>

Kuntz et al.<sup>9</sup> suggested the involvement of an allylic carbocation. Vukov,<sup>11</sup> on heating the model compound 2,2,4,8,8-pentamethyl-4-nonene, proposed a mechanism in which two competing reactions occurred: the formation of a conjugated diene and actual crosslinking. Diene formation, the dominant reaction, was thought to precede crosslinking as it resulted in the formation of a zinc oxychloride or zinc chloride, which was proposed as a catalyst for the crosslinking reaction. Crosslinking was thought to proceed cationically.

Mallon et al.,<sup>14</sup> on the basis of differential scanning calorimetry (DSC) studies, suggested a radically different hypothesis for the crosslinking of CR by ZnO. They proposed that crosslinking for CR comprised two competing reactions involving the isomerized and unisomerized species of the 1,2-units, which provided the sites for crosslinking in the CR polymer chain. The first reaction was fairly rapid and was proposed to involve the crosslinking of unisomerized 1,2-units. The second reaction occurred much more slowly and was said to involve the crosslinking of isomerized 1,2-units. It was proposed that ZnCl<sub>2</sub> catalyzed the first reaction, whereas ZnO promoted the allylic rearrangement of the 1,2-units.

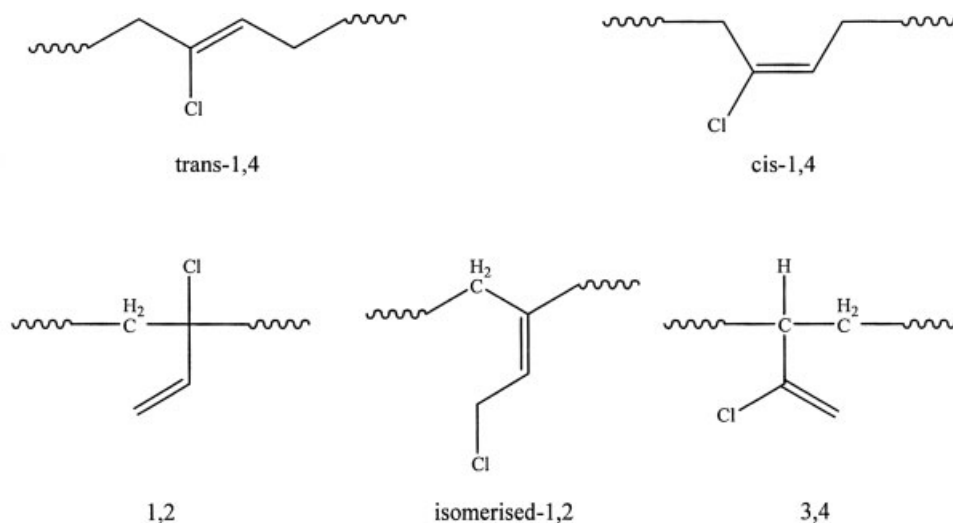
It is possible that the mechanism applicable to CR resembles that at work in other chlorine containing rubbers such as chlorobutyl rubber (CIIR). Baldwin et al.<sup>15</sup> proposed a cationic mechanism in which ZnCl<sub>2</sub>, formed *in situ*, is responsible for crosslinking CIIR. This is illustrated in Scheme 1. It involves initiation by the

\*Present address: Sugar Milling Research Institute (University of Natal).

Correspondence to: C. D. Woolard (christopher.woolard@nmmu.ac.za).

Contract grant sponsor: South African National Research Foundation; contract grant number: GUN 2046777.

Contract grant sponsor: Nelson Mandela Metropolitan University Research Committee.



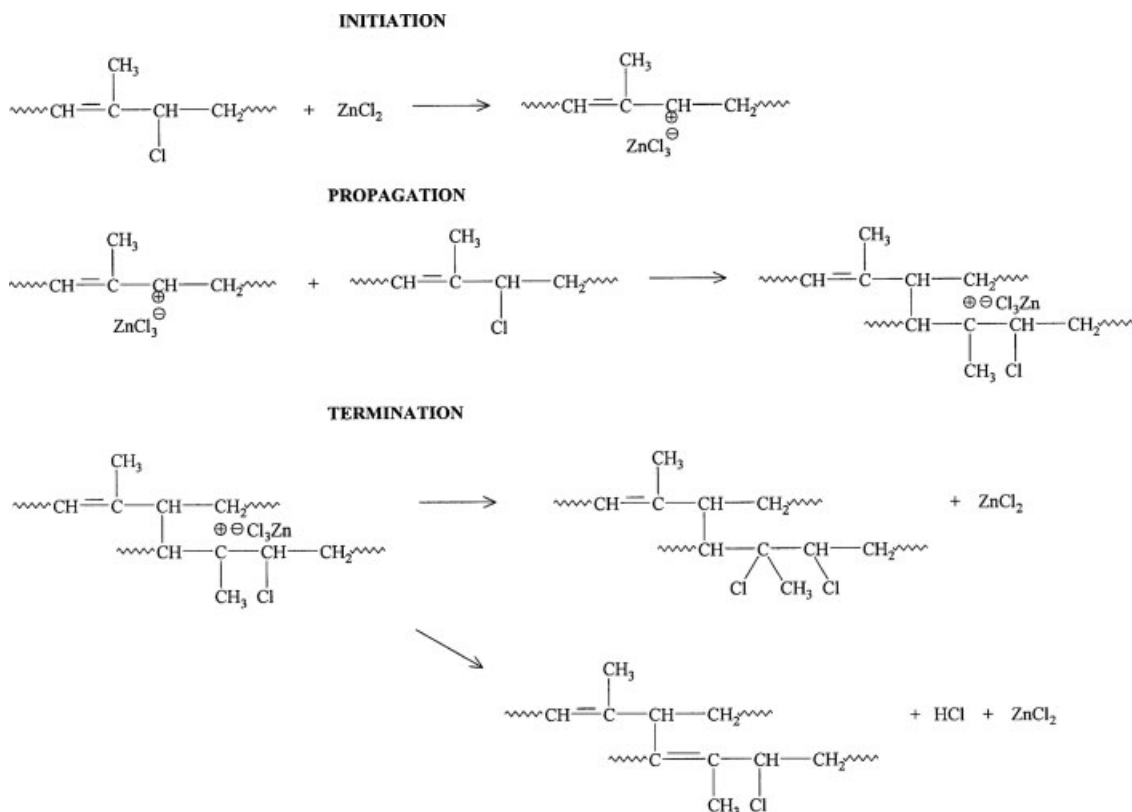
**Figure 1** Isomeric structures typically found in CR.

abstraction of a chlorine atom by  $\text{ZnCl}_2$  to form a carbo-cation.

$\text{MgO}$  is commonly used with  $\text{ZnO}$ .<sup>2,13</sup> This causes the cure rate to be decreased and extends the scorch time before vulcanization. Cure systems containing  $\text{MgO}$  generally lead to vulcanizates with better physical properties. The role of  $\text{MgO}$  in vulcanization is thought to be that of a mop<sup>13,16</sup> as it scavenges the chloride ions

resulting from crosslinking. It was also suggested by Kuntz et al.<sup>9</sup> that the retarding effect of  $\text{MgO}$  (which is a Lewis base) is brought about by magnesium coordinating to the Lewis acid, thereby deactivating  $\text{ZnCl}_2$ , the crosslinking catalyst.

This article reports the crosslinking of CR compounds with  $\text{ZnO}$  and  $\text{MgO}$ , identifies the roles of  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{ZnCl}_2$ , and conjugated dienes in the vul-



**Scheme 1** Cationic mechanism proposed by Baldwin et al.<sup>15</sup> for the vulcanization of CIIR by  $\text{ZnO}$ .

canization process, and proposes a modification of the cationic crosslinking mechanism as put forward by Baldwin et al.<sup>15</sup>

## EXPERIMENTAL

The materials used in this article were mercaptan-grade CR (Baypren 210, Bayer, Leverkusen, Germany), rubber-grade ZnO (Zinc Process, Springs, South Africa), CR-grade MgO (Premier Chemicals, Pensacola, FL), and granular ZnCl<sub>2</sub> (Saarchem, Krugersdorp, South Africa).

The compounds were mixed in a Brabender plastimeter (Duisburg, Germany) as described by Mallon et al.,<sup>14</sup> with the exception that an N50H mixing head with an 80-mL capacity was also employed. Formulations quoted in parentheses in the text are parts per hundred parts of rubber. The compounds were vulcanized at a programmed rate (1°C/min) in sealed aluminum pans in a TA Instruments Q100 differential scanning calorimeter (N<sub>2</sub> purge gas, flow rate = 50 mL/min) (New Castle, DE) and isothermally in a vulcanization press at 140°C.

The reaction was stopped at various temperatures (DSC) or times (press), and soluble zinc (ZnCl<sub>2</sub>) and magnesium (MgCl<sub>2</sub>) were extracted with procedures previously described by Mallon et al.,<sup>14</sup> the exception being that a 50/50 (v/v) ethanol/toluene solution was used instead of ethanol/benzene because benzene is a known carcinogen. It was found with control samples containing known amounts of ZnCl<sub>2</sub> and MgCl<sub>2</sub> that averages of 86% ( $\pm$  3%) ZnCl<sub>2</sub> and 81% ( $\pm$  2%) MgCl<sub>2</sub> were extracted from unvulcanized samples. For vulcanized samples, averages of 100% ( $\pm$  0.5%) ZnCl<sub>2</sub> and 90% ( $\pm$  0.5%) MgCl<sub>2</sub> were extracted. A PerkinElmer 603 atomic absorption (AA) spectrophotometer with a PerkinElmer 10-cm burner control (Waltham, MA) was used for zinc ( $\lambda$  = 213.9 nm) and magnesium ( $\lambda$  = 285.2 nm) analysis. An acetylene–air mixture at an acetylene pressure of 85 kPa and an air pressure of 220 kPa was used for the flame. The percentage of extractable chlorine quoted in the figures and text refers to the mass percentage of the total chlorine originally present in CR. The percentage of Cl in the original CR was determined to be 36.2% by the combustion of small samples in O<sub>2</sub>, the dissolution of the evolved gases in KOH/H<sub>2</sub>O<sub>2</sub> (aqueous),<sup>17</sup> and the analysis of chlorine by inductively coupled plasma/mass spectrometry with a PerkinElmer Elan 6000 inductively coupled plasma/mass spectrometry instrument.

The crosslink densities were determined with the Flory–Rehner<sup>18</sup> equation via the swelling of samples in toluene. A polymer–solvent interaction parameter ( $\chi$ ) of 0.386 for the CR–toluene system was calculated from literature data.<sup>19</sup> The percentage of carbon–carbon crosslinks was determined with a methyl iodide chemical probe,<sup>20</sup> which cleaved all sulfur crosslinks.

Structural characterization and monitoring of isomerization were performed with nuclear magnetic resonance (NMR) spectroscopy. Spectra were obtained on a Bruker Spectrospin 300 NMR instrument at 300 MHz (Fallanden, Switzerland). CDCl<sub>3</sub> was used as the solvent. Further monitoring of the reaction progress was performed with Fourier transform infrared (FTIR) spectroscopy, which was obtained with a Digilab Excalibur HE FTIR spectrophotometer (Carton, MA). Spectra were recorded from 4000 to 600 cm<sup>-1</sup> with a Miracle attenuated total reflectance accessory (Pike Technologies, Madison, WI) against an air background. The number of scans was 200, and the resolution was 1 cm<sup>-1</sup>.

By courtesy of Continental Tyre S.A., rheometer-cure curves were obtained on an Alpha Technologies 2000E moving die rheometer (Swindon, UK). All rheometry was performed at 140 and 150°C.

## RESULTS

### Structural characterization of CR

Coleman and coworkers<sup>21–23</sup> suggested the use of <sup>13</sup>C-NMR to estimate the percentage of structural isomers in CR. A sample of Baypren 210 was dissolved in CDCl<sub>3</sub> and subjected to the <sup>13</sup>C-NMR pulse sequence detailed by Coleman et al.<sup>21</sup> With corrections for the nuclear Overhauser effect in Coleman and Brame,<sup>22</sup> it was estimated that the percentage of trans-1,4-units was 76.2%, the percentage of cis-1,4-units was 16.0%, the percentage of 1,2-units was 1.45%, and the percentage of 3,4-units was 1.75%. Coleman et al.<sup>21</sup> suggested that the resonance at 130.1 ppm was due to isomerized 1,2-units. Miyata and Atsumi,<sup>5</sup> however, disputed this identification. We found further resonances at 147.9, 148.9, and 149.5 not identified by Coleman et al. Integrating across all resonances in the region of 117.7–130.3 ppm accounted for 4.5% of the sample. We prefer not to assign these peaks (including the peak at 130.1 ppm) but would suggest that they are more likely resonances of cis- and trans-olefinic carbons in the center of a triad in which at least one of the outer isomeric units in the triad is a 1,2- or 3,4-unit.

The percentages of the various isomers were also estimated with <sup>1</sup>H-NMR spectra according to the method of Miyata and Atsumi.<sup>5</sup> On the basis of the methylene region of the spectrum (1.8–3 ppm), the concentration of 1,4-units was estimated to be 96.7%, that of 1,2-units was estimated to be 1.30%, and that of 1,4-units was estimated to be 1.96%. With the olefinic region of the spectrum (5–6 ppm), the presence of 1,4-units was estimated to be 97.0%, that of 1,2-units was estimated to be 1.15%, and that of 3,4-units was estimated to be 1.85%. Like Miyata and Atsumi, we interpreted the absence of a doublet at 4.14 ppm and the singlets at 3.05 and 3.13 ppm as indicative of the absence of isomerized 1,2-units. This can be observed in

the NMR spectrum of the original CR shown later in Figure 3(a).

In the rest of this article, we use an average percentage of 1.30% (standard deviation = 0.15%) for 1,2-units and 1.86% (standard deviation = 0.10%) for 3,4-units.

### CR alone

Industrially, the vulcanization of CR in the presence of ZnO and curatives typically occurs above 150°C. Isothermal studies at 140°C provide a slower reaction, making the elucidation of the vulcanization mechanism easier.

The presence of a chlorinated isoprenoid unit in the CR backbone allows crosslinking to take place when this rubber is heated in the absence of curatives.<sup>5,6</sup> CR samples were heated at 140°C for various times, and the crosslink density was measured as a function of the heating time. No crosslinking was observed in the first 3 h. After 24 h, the extent of crosslinking was still low when a crosslink density of  $2.30 \times 10^{-6}$  mol/mL was recorded. The crosslink density at this point corresponded to 1.4% of the tertiary allylic Cl being involved in crosslink formation, assuming crosslinking to involve the reaction between a rearranged 1,2-unit and a 1,4-unit in the chain, as suggested by Miyata and Atsumi.<sup>5</sup>

Unlike the dynamic calorimetry study conducted by Mallon et al.<sup>14</sup> (40–260°C), no thermal events were apparent in the isothermal DSC curve, as CR is relatively stable at 140°C.

### CR/ZnO(5)

It was demonstrated by Mallon et al.<sup>14</sup> that both the crosslink density and the rate of the crosslinking reaction are not significantly unaffected by the ZnO loading. A 5 phr ZnO loading is typically used in industry and hence was used in this study.

A CR/ZnO(5) compound was heated isothermally for various time intervals at 140°C. The extractable chlorine in the form of ZnCl<sub>2</sub> that was produced by the reaction was determined by AA, and the crosslink density was measured (Fig. 2). The obtained curve was significantly different from that observed in the absence of the metal oxide. Figure 2 is a typical isothermal curve obtained for CR/ZnO mixes. The trends (increases in the extractable chlorine and crosslink density) obtained isothermally at 140°C were similar to those obtained in the dynamic calorimetry study conducted by Mallon et al.<sup>14</sup> Unlike the dynamic calorimetry system,<sup>14</sup> the isothermal DSC curve at 140°C showed no exothermic events, and the rate of chlorine formation was much slower than during heating to higher temperatures in the dynamic calorimetry study.<sup>14</sup>

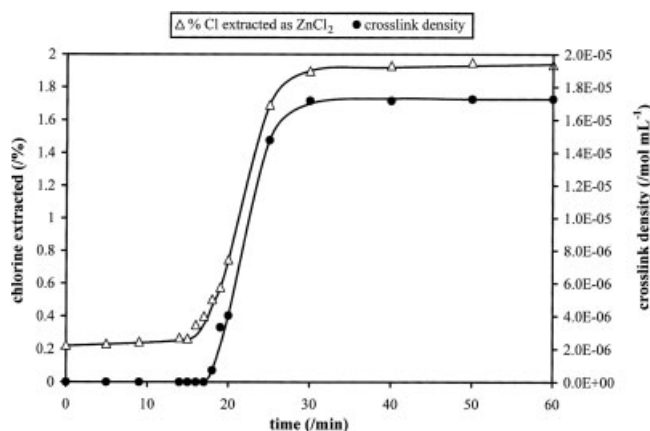
The extraction and analysis of soluble zinc gave an indication of the quantity of HCl evolved in the vulcan-

ization reaction. Extractable chlorine was present at the onset of the reaction (0.2%) and remained constant until 14 min (Fig. 2). This corresponded to less than 1.9% of the original zinc added to the system. On further heating, the extractable chlorine increased gradually. Between 20 and 25 min, there was a substantial increase in extractable chlorine that reached a maximum after 40 min and corresponded to approximately 16% of the original zinc added to the formulation. Crosslinking commenced after 18 min when the extractable chlorine increased to 0.5%. After 40 min, 1.9% chlorine was extracted, at which point a crosslink density of  $1.72 \times 10^{-5}$  mol/mL was recorded. This corresponds to 10.4% of the tertiary allylic Cl atoms in the CR rubber being involved in crosslink formation if one assumes that each tertiary allylic Cl gives rise to one crosslink. On the other hand, if two tertiary allylic Cl sites are necessary for each crosslink, the efficiency with respect to such chlorines is 20.8%. Further heating did not result in the formation of more ZnCl<sub>2</sub> or significant crosslinking. If all the tertiary allylic Cl atoms were involved in the crosslinking reaction and we assume that the crosslinking involved the reaction of a rearranged 1,2-unit and a 1,4-unit, as suggested by Miyata and Atsumi,<sup>5</sup> a maximum crosslink density of  $1.65 \times 10^{-4}$  mol/mL should be expected.

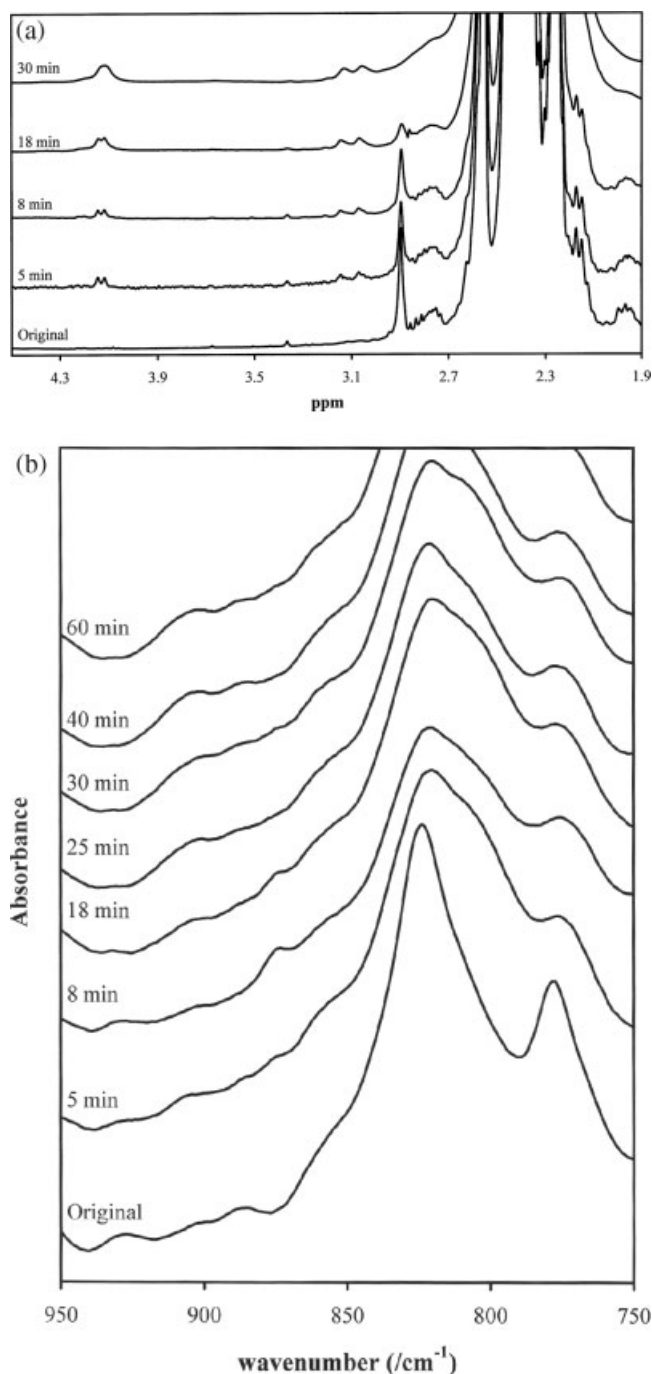
The increase in the amount of extractable chlorine preceded the increase in the crosslink density slightly by about 2 min. Figure 2 shows that the shape of the curve for extractable zinc versus the reaction time resembled that for the change in the crosslink density with time.

With a methyl iodide probe solution, which cleaved all sulfur crosslinks, the crosslink type was determined. As expected for a system in which ZnO was the sole vulcanizing agent, all the crosslinks were entirely C—C in nature.

Figure 3(a) shows the NMR spectra recorded for CR/ZnO(5) samples vulcanized for different times at



**Figure 2** Crosslink density and extractable chlorine analysis of CR/ZnO(5) heated isothermally at 140°C.



**Figure 3** (a)  $^1\text{H-NMR}$  and (b) FTIR spectra of CR/ZnO(5) heated isothermally at  $140^\circ\text{C}$ .

$140^\circ\text{C}$ . Because crosslinked CR does not dissolve in  $\text{CDCl}_3$  but swells instead, the spectra in Figure 3(a) have been normalized so that the peak areas due to methylene hydrogens (4.2–1.85) are the same. Noticeable is the formation of a doublet at 4.11 and 4.14 and two singlets at 3.05 and 3.13. These are attributed to the formation of isomerized 1,2-units.<sup>5</sup> Simultaneously, the singlet at 2.89 and the peaks near 1.97 decreased in intensity. These peaks are assigned to unisomerized 1,2-units. This clearly indicates that isomerization occurs

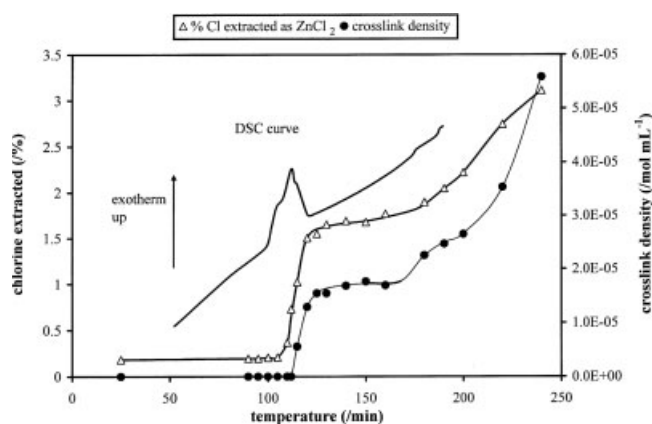
early on (as early as 5 min) and precedes crosslinking (which starts at 17 min; Fig. 2). Upon crosslinking, noticeable broadening of the various peaks can be observed. There also appears to be a decrease in the area of the peaks near 2.75 (assigned to 3,4-units), although the disappearance is slower than for the 1,2-units. Table I contains data for the percentage of chlorine-containing units as a function of time. The fact that the sum of the percentage of 1,2-units (isomerized and unisomerized) is less than the initial percentage indicates that these units are involved in crosslinking. The data also suggest that 3,4-units are also crosslinked. A similar decrease in the olefinic protons assigned to 1,2- and 3,4-units was observed.<sup>5</sup> The isomerization and loss of unisomerized 1,2-units on crosslinking are corroborated by FTIR spectra reported in Figure 3(b). The spectra detail the  $=\text{CH}$  out-of-plane vibrations. That for the 1,2-units at  $925\text{ cm}^{-1}$  decreases from the outset and is completely absent by the onset of crosslinking (18 min). Simultaneously, a peak at  $900\text{ cm}^{-1}$  forms. This band is ascribed to  $=\text{CH}$  out-of-plane stretches in which a Cl is not attached to the double bond, that is, isomerized 1,2-units and the products of dehydrohalogenation. The peak due to 3,4-units at  $880\text{ cm}^{-1}$  appears to decrease slightly. No significant change in the shape of the cis-1,4-peak (shoulder at  $850\text{--}870\text{ cm}^{-1}$ ) and the trans-1,4-peak at  $825\text{ cm}^{-1}$  could be observed.

Similar trends were observed upon the dynamic heating of CR/ZnO(5) at  $1^\circ\text{C}/\text{min}$  (Fig. 4). The DSC curve showed at least two (possibly three) closely situated thermal events. The onset of the first exothermic event was at  $105^\circ\text{C}$ . A further exothermic event, centered at  $114^\circ\text{C}$  with a shoulder at  $117^\circ\text{C}$ , was observed. A small amount of extractable chlorine was present at the onset of the reaction at  $25^\circ\text{C}$ . The extracted chlorine remained fairly constant when heated to  $110^\circ\text{C}$ , at which temperature the amount of extractable chlorine rapidly increased. By  $114^\circ\text{C}$ , 0.7% of the chlorine present in CR was extractable, yet no crosslinking had taken place. It is evident from Figure 4 that crosslinking initially increased rapidly (the crosslink density of 5.6

**TABLE I**  
Presence of Various Isomeric Structures During the Vulcanization of CR/ZnO(5) at  $140^\circ\text{C}$  as Determined by  $^1\text{H-NMR}$  Spectroscopy

Time (min)	Unisomerized 1,2-units (%)	Isomerized 1,2-units (%)	3,4-units (%)
0	1.3	0.0	1.9
2	1.0	0.1	1.8
5	0.9	0.2	1.7
8	0.9	0.3	1.6
17	0.4	0.6	1.4
30	0.0	0.8	1.3

The percentages are those of chlorine-containing units.



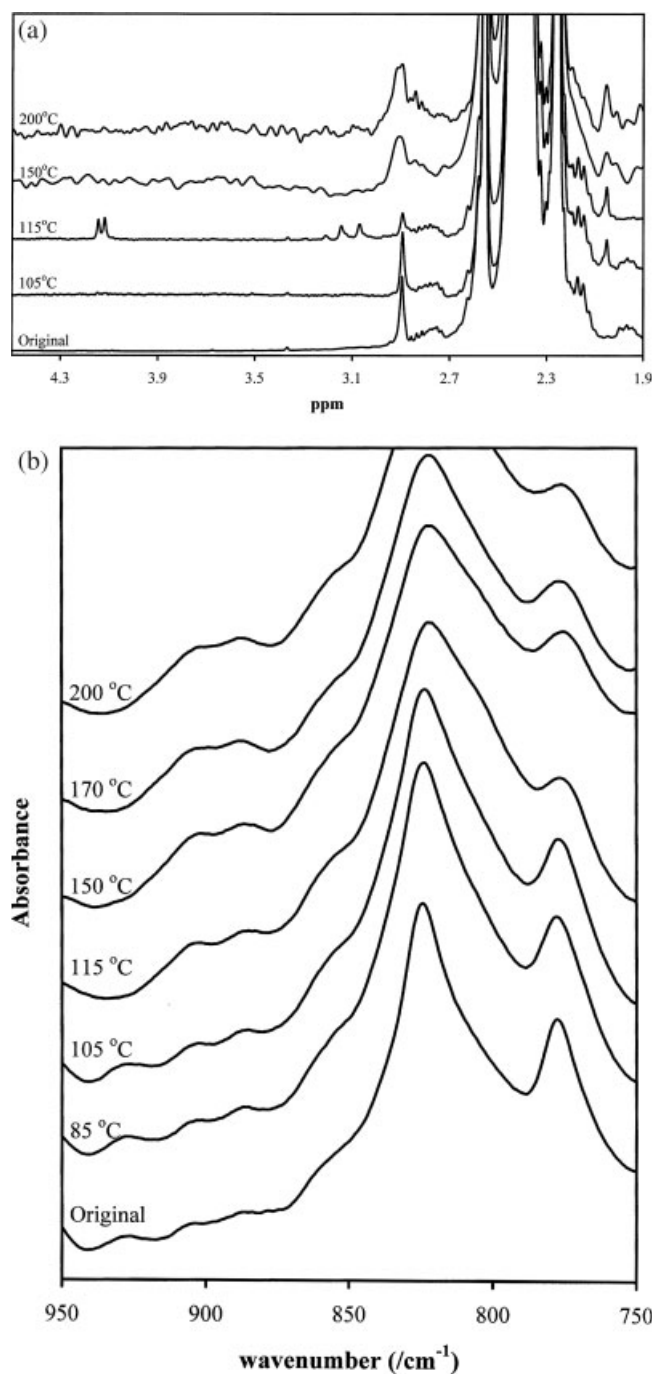
**Figure 4** DSC curve (exotherm up), crosslink density, and extractable chlorine analysis of CR/ZnO(5) heated at 1°C/min.

$\times 10^{-6}$  mol/mL at 115°C increased to  $1.6 \times 10^{-5}$  mol/mL at 145°C), and then it remained constant up to 160°C when 1.8% chlorine was extractable. A more gradual increase in the extent of crosslinking was then observed till 220°C, at which temperature a crosslink density of  $3.5 \times 10^{-5}$  mol/mL corresponding to 2.7% extractable chlorine was recorded. At still higher temperatures, the crosslink density increased further. This last increase can likely be associated with the thermovulcanization of CR.<sup>14</sup>

The exact nature of the reaction for the first DSC exotherm (onset at 105°C) could not be ascertained (Fig. 4). The second DSC exotherm coincides with the rapid formation of ZnCl<sub>2</sub> and is therefore possibly associated with the trapping of HCl by ZnO, whereas the rapid increase in the crosslink density of the sample coincides with the shoulder at 117°C. From 175°C upward, there is a slight exothermic deviation in the DSC curve. This may partially be due to the thermovulcanization of CR.

Figure 5(a) shows how the <sup>1</sup>H-NMR spectrum of the CR/ZnO(5) compound varies as it is heated. At 105°C, there are no significant differences between the compound and unvulcanized CR. By 115°C, noticeable isomerization of the 1,2-units has occurred, as evidenced by the appearance of the doublet at 4.11 and 4.14 and two singlets at 3.05 and 3.13. By 150°C, these peaks have disappeared, and this indicates the complete crosslinking and/or dehydrohalogenation of these isomerized 1,2-units. As the temperature rises still further, a large peak can be observed to form at 2.90. This peak can be ascribed to bisallylic methylene hydrogens, which arise from the dehydrohalogenation of 1,4-units. The 150 and 190°C spectra are less well resolved because these spectra were obtained from swollen rather than dissolved compounds. Table II contains data for the presence of isomeric units at different temperatures. Isomerization occurs at a low temperature. The percentage of 3,4-units at higher temperatures is uncertain because of overlapping with the bisallylic

methylenes. The percentage of bisallylic methylene units may thus contain a contribution from 3,4-units. The percentage of 3,4-units is likely to be higher at 150°C. Importantly, the percentage of bisallylic units formed at higher temperatures exceeds the percentage of 1,2- and 3,4-units in the original sample, indicating at these temperatures that 1,4-units must be dehydrohalogenated and thus activated toward crosslinking. Like Miyata and Atsumi,<sup>8</sup> we observed no resonances characteristic of ether crosslinks.



**Figure 5** (a) <sup>1</sup>H-NMR and (b) FTIR spectra of CR/ZnO(5) heated at 1°C/min.

TABLE II  
Presence of Various Isomeric Structures During the Heating of CR/ZnO(5)  
at 1°C/min as Determined by <sup>1</sup>H-NMR Spectroscopy

Temperature (°C)	Unisomerized 1,2-units (%)	Isomerized 1,2-units (%)	3,4-units (%)	Bisallylic methylene units (%)
Original	1.3	0.0	1.9	0.0
105	1.2	0.0	1.8	0.0
115	0.5	0.7	1.8	0.0
150	0.0	0.0	Uncertain	4.2
190	0.0	0.0	Uncertain	6.5

The percentages are those of chlorine-containing units. The percentage of 3,4-units at higher temperatures is uncertain because of overlapping with bisallylic methylene structures.

Figure 5(b) illustrates the changes in the FTIR spectra brought about by heating. The =CH<sub>2</sub> out-of-plane vibration of the 1,2-units at 925 cm<sup>-1</sup> disappeared by 115°C. Simultaneously, a peak at 900 cm<sup>-1</sup> can be observed to form. This peak continues to grow at higher temperatures when all isomerized units have disappeared, and this indicates that it is at least in part due to the products of dehydrohalogenation.

#### CR/ZnO(5)/ZnCl<sub>2</sub>(2)

Figure 6 presents a typical curve associated with a CR/ZnO/ZnCl<sub>2</sub> mix. The percentage of chlorine reported in the figures and text is only for ZnCl<sub>2</sub> formed in the reaction, the ZnCl<sub>2</sub> added having been subtracted from the total ZnCl<sub>2</sub> extracted.

The addition of ZnCl<sub>2</sub> to the CR/ZnO compound altered the onset time of the crosslinking reaction (i.e., the induction period was shorter), and this supported the proposal suggested by various authors<sup>9,11,14,15</sup> that ZnCl<sub>2</sub> is a crosslinking catalyst. However, the induction period was not completely eliminated. The equilibrium crosslink density that was achieved was similar to that obtained in the CR/ZnO system (cf. Figs. 2 and 6). The increase in the extractable chlorine was accompanied by an increase in the crosslink density. In the isothermal study at 140°C, ZnCl<sub>2</sub> formed rapidly after 5 min. By 10 min, 0.4% extraction of chlorine had been obtained. This corresponded to a crosslink density of 5.0 × 10<sup>-6</sup> mol/mL. The percentage of extractable chlorine and the crosslink density reached values of 1.7% and 1.7 × 10<sup>-5</sup> mol/mL, respectively, after 40 min. Interestingly the rate of crosslinking was slightly decreased with the addition of ZnCl<sub>2</sub> (cf. Figs. 2 and 6), and this suggested that although ZnCl<sub>2</sub> may be necessary for crosslinking, it may also promote side reactions. Like the system without ZnCl<sub>2</sub> added, the increase in ZnCl<sub>2</sub> preceded the crosslinking slightly.

It appeared that only 9.2% of the tertiary allylic Cl atoms were involved in crosslink formation in the CR/ZnO(5)/ZnCl<sub>2</sub>(2) system, assuming the reaction of 1,2-units with other structural isomers. The crosslink effi-

ciency was very low as only 0.28% of Cl in the CR rubber was used in the crosslinking reaction, assuming the involvement of two chlorines per crosslink.

When ZnCl<sub>2</sub> (5 phr) was mixed into the rubber without any ZnO, rapid crosslinking was noted that was similar to what was observed by Mallon et al.<sup>14</sup> As observed by Mallon et al., no exotherm was seen in the DSC thermogram for this system in the region of 105–145°C as was the case with ZnO inclusion. No peaks (assigned to isomerized 1,2-units, i.e., the doublet at 4.11 and 4.14 and the singlets at 3.05 and 3.13) were observed in the NMR spectra. This indicated that ZnCl<sub>2</sub> did not promote isomerization. The FTIR spectra, however, revealed the disappearance of the 1,2-band at 925 cm<sup>-1</sup> and the appearance of a band at 900 cm<sup>-1</sup>. This suggested that ZnCl<sub>2</sub> promoted crosslinking and dehydrohalogenation.

#### CR/MgO(4)

The percentage of chlorine consumed and the crosslink density of CR/MgO(4) heated at 140°C are shown in Figure 7. No exothermic events were discernable in the isothermal DSC curve. After mixing, 1.5% of MgO was

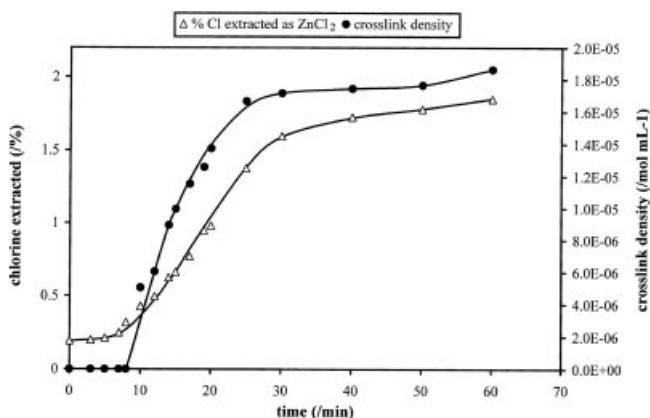
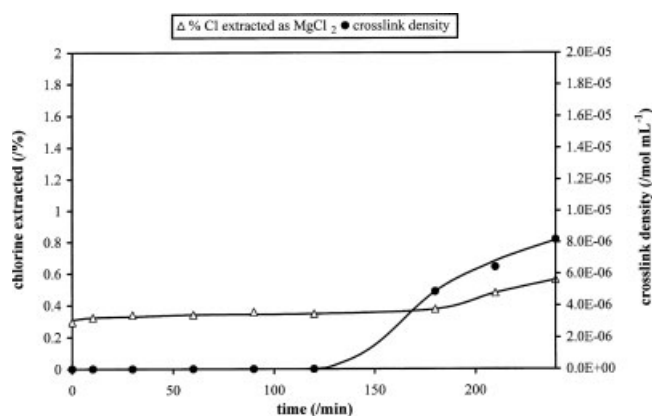


Figure 6 Crosslink density and extractable chlorine analysis of CR/ZnO(5)/ZnCl<sub>2</sub>(2) heated isothermally at 140°C.



**Figure 7** Crosslink density and extractable chlorine analysis of CR/MgO(4) heated isothermally at 140°C.

extracted as MgCl<sub>2</sub>. The MgCl<sub>2</sub> concentration remained constant until 140 min. Crosslinking commenced between 140 and 180 min (vs 18 min in the CR/ZnO system; cf. Figs. 2 and 7) when the extractable chlorine increased to 0.4%. A crosslink density of  $8.2 \times 10^{-6}$  mol/mL was recorded at 240 min, at which stage 0.56% of chlorine was extracted. This crosslink density corresponded to 5.0% of the tertiary allylic Cl atoms being involved in crosslink formation. This was clearly lower than when ZnO was used. Figures 2 and 7 are plotted on the same scale. As with ZnCl<sub>2</sub>, the increase in the crosslink density was accompanied by an increase in MgCl<sub>2</sub> extracted. C—C crosslinks, as determined with the aid of the methyl iodide probe solution, dominated in this system.

#### CR/ZnO(5)/MgO(4)

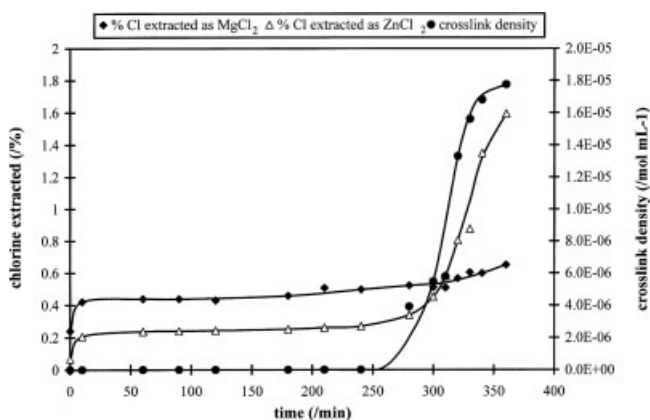
After compounding, 1.2% of MgO was extracted as soluble MgCl<sub>2</sub>, whereas only 0.6% zinc was extracted in comparison with 1.9% in the CR/ZnO system (cf. Figs. 2 and 8). In the isothermal study, the percentage of extractable chlorine in the form of ZnCl<sub>2</sub> and MgCl<sub>2</sub> remained fairly constant until 240 min. The formation of ZnCl<sub>2</sub> rather than MgCl<sub>2</sub> was more pronounced upon crosslinking. After 360 min, 1.6% chlorine was extracted as ZnCl<sub>2</sub> as opposed to 0.65% extracted as MgCl<sub>2</sub>. Collectively, this corresponded to 2.2% of the chlorine in the CR being involved in the formation of ZnCl<sub>2</sub> and MgCl<sub>2</sub>. MgO had the effect of delaying the crosslinking reaction (cf. Figs. 2 and 8). The retarding effect of MgO on crosslinking is well documented.<sup>1,13,14</sup> After 360 min, the crosslink density increased to  $1.8 \times 10^{-5}$  mol/mL. This implied that 10.8% of the tertiary allylic Cl atoms and at most 0.3% of all chlorine atoms in the CR rubber were involved in the crosslinking reaction. The increase in the crosslink density for the CR/ZnO/MgO system was accompanied by a rapid increase in the amount of extractable zinc, whereas the increase in the amount of extractable magnesium was

small in comparison. It was determined with the methyl iodide probe solution that the crosslinks were entirely C—C in nature.

#### Summary of the results

The results obtained for the various ZnO formulations exhibited similar trends, the more important features of which can be summarized as follows:

1. An induction period occurred before the onset of crosslinking in all the systems that were studied. The inclusion of ZnCl<sub>2</sub> in the formulation shortened, but did not eliminate, the induction period.
2. The slower reaction rates that were achieved by the performance of isothermal studies at 140°C showed that dehydrochlorination, as evidenced by the formation of ZnCl<sub>2</sub>, always preceded crosslinking. Dehydrochlorination, therefore, appeared to be a prerequisite for crosslinking.
3. NMR results showed that the isomerization of 1,2-units preceded crosslinking. Upon crosslinking, the concentrations of total 1,2- and 3,4-units decreased.
4. All systems in which ZnO was included generated ZnCl<sub>2</sub> during compounding, which increased in concentration before and during the crosslinking process.
5. ZnCl<sub>2</sub> was shown to be capable of crosslinking CR on its own. ZnCl<sub>2</sub> did not produce isomerization.
6. The crosslinking reaction was very inefficient. Less than 0.3% of all chlorine in the CR rubber was involved in crosslink formation.
7. The relationship between the crosslink density and the amount of HCl that evolved (detected as ZnCl<sub>2</sub> or MgCl<sub>2</sub>) for different compounds was not simple, although low extractable chlorine values corresponded to low crosslink den-



**Figure 8** Crosslink density and extractable chlorine analysis of CR/ZnO(5)/MgO(4) heated isothermally at 140°C.



sity values, and high percentages of extractable chlorine corresponded to high crosslink densities. The moles of HCl that evolved, however, exceeded the moles of crosslinks that formed.

## DISCUSSION

### Role of MgO

For compounds containing MgO, MgCl<sub>2</sub> is formed during mixing and also during vulcanization in the absence of ZnO. Where ZnO is added, MgO acts as a trap for HCl that evolves during vulcanization. Mallon et al.<sup>14</sup> showed that when ZnCl<sub>2</sub> and MgO are mixed into CR, an exchange reaction occurs, which indicates that the MgCl<sub>2</sub>/ZnO system is more stable than the ZnCl<sub>2</sub>/MgO system.

It is proposed that MgO scavenges chloride ions produced during mixing, thereby limiting the amount of ZnCl<sub>2</sub> that is formed. Starkweather and Walker<sup>16</sup> and Stevenson<sup>13</sup> also reported on this scavenging effect of MgO.

In addition, it is still possible, as suggested by Kuntz et al.,<sup>9</sup> that the retarding effect of MgO is brought about by the coordination of magnesium (MgO is a Lewis base) to the Lewis acid, thereby deactivating the crosslinking catalyst ZnCl<sub>2</sub>.

### Effect of ZnCl<sub>2</sub> and ZnO

It is apparent in CR/ZnO compounds (cf. Figs. 2 and 6) that the rate of dehydrochlorination increases upon ZnCl<sub>2</sub> formation, and this shows that ZnCl<sub>2</sub> rather than ZnO promotes dehydrochlorination. The facilitation of dehydrochlorination by ZnCl<sub>2</sub> is emphasized by the earlier formation of ZnCl<sub>2</sub> in the CR/ZnO(5)/ZnCl<sub>2</sub>(2) system in comparison with the CR/ZnO(5) system.

Upon the heating of CR and 5 phr ZnO for 17 min (Fig. 2), no crosslinking occurred, the reaction only proceeding rapidly once ZnCl<sub>2</sub> had formed; this suggests that ZnO itself is not involved in the dehydrochlorination process. Small amounts of ZnCl<sub>2</sub> are formed during chain scission and dehydrochlorination and during thermal dehydrochlorination in the early stages of heating. All of these lead to a buildup of ZnCl<sub>2</sub> that allows dehydrochlorination and crosslinking to proceed autocatalytically.

### Role of ZnCl<sub>2</sub> and dienes

The differentiation of the roles of ZnCl<sub>2</sub> and conjugated dienes in the system is difficult as both are products of dehydrochlorination and are not mutually exclusive. Hendrikse et al.,<sup>12</sup> in contrast to Kuntz et al.<sup>9</sup> and Baldwin et al.,<sup>15</sup> proposed that the formation of conjugated diene butyl, or a more reactive equivalent unit, is essential for the vulcanization of CIIR by ZnCl<sub>2</sub>. The importance of such a unit for the vulcanization of CR, how-

ever, is difficult to ascertain. It is our suspicion that such a unit is not necessary for crosslinking, although the formation of a conjugated diene via dehydrochlorination is probably responsible, as discussed further on, for the low efficiency of crosslinking in the CR/ZnO system.

In all the systems, the compounds that were produced became progressively more yellow until some were in fact brown. We suspect this was because of increased conjugation with time. Similar observations were made by Iván et al.<sup>3</sup>

From the data presented, it is clear that dehydrochlorination and the formation of ZnCl<sub>2</sub> are necessary for the vulcanization of CR by ZnO.

### Crosslinking reactions

In conventionally cured formulations, it is generally accepted that pendant groups are the precursors to the crosslinking reaction. It is also well known that halogenated rubbers can undergo vulcanization in the absence of any curing agents.<sup>5</sup>

The rheometer-cure curve for CR/ZnO(5) at 150°C showed marching cure behavior. An induction period was present before crosslinking. Isothermal vulcanization at 140°C in a press showed that a steady increase in the crosslink density occurred as the reaction progressed. Neither of these results is novel.

The dynamic DSC program (heated at 1°C/min) used in this study allowed crosslinking to be separated into a number of processes (Fig. 4). This distinction could not be made with isothermal studies as the crosslinking processes merge. The extent of the first crosslinking reaction increased rapidly after 115°C as the temperature was increased and reached a plateau value, at which it remained constant, before the onset of a less rapid increase in the crosslink density around 175°C. Upon further heating, a still greater increase in the crosslink density was observed (> 200°C).

The fact that the crosslink density reached limiting (plateau) values as the temperature was increased indicated that the species responsible for crosslinking was consumed. The evolution of HCl (detected as ZnCl<sub>2</sub>) showed that the plateau value for the CR/ZnO(5) compound corresponded to approximately 1.5% chlorine extracted. The 1,2-unit concentration of CR was estimated at 1.3%. Because the 1,2-units (tertiary allylic position) have the most reactive sites along the polymer chain, it is proposed that the first crosslinking processes involves the crosslinking of 1,2-units. Given the fact, however, that the percentage of chlorine extracted exceeds the number of moles of crosslinks, it is likely that the initial stage of crosslinking involves the activation of 1,2-units (not all of which go on to form crosslinks). We suggest that this activation involves the isomerization of 1,2-units.

The significant increase in crosslinking above 170°C indicates that less reactive species are likely involved in crosslink formation. It is suggested that as the temperature is raised, first 3,4-units and then 1,4-units in the main chain are activated by ZnCl<sub>2</sub>.

The discussion that follows argues that the crosslinking events observed in dynamic DSC studies conducted at 1°C/min (Fig. 4) are due to the crosslinking of 1,2-units, 3,4-units, and 1,4-units, respectively.

The marching cure obtained for rheometer-cured samples heated isothermally at 150°C can probably be ascribed, as suggested by the dynamic calorimetry studies at 1°C/min, to the slow crosslinking reaction of the less active 1,4-units.

### Isomerization

It was proposed by Mallon et al.<sup>14</sup> that crosslinking for CR comprises two competing reactions involving the isomerized and unisomerized species of the 1,2-units, which provide the sites for crosslinking in the CR polymer chain. They suggested that the first reaction, the crosslinking of unisomerized 1,2-units, is fairly rapid, whereas the second reaction, the crosslinking of isomerized 1,2-units, occurs more slowly and gives rise to a marching cure. ZnCl<sub>2</sub> catalyzes the first reaction by slowing the isomerization process, whereas ZnO promotes the allylic rearrangement of the 1,2-units into isomerized species.

Mallon et al.,<sup>14</sup> however, did not account for the fact that the percentage of polymeric chlorine consumed in their reactions was greater than 1.5% (the concentration of tertiary allylic 1,2-units in CR). It is our opinion then that the crosslinking processes cannot only be ascribed to the crosslinking of 1,2 isomerized and unisomerized units along the CR polymer chain.

It is proposed, as suggested by various authors<sup>5,23</sup> and in contrast to Mallon et al.,<sup>14</sup> that isomerization of the 1,2-units must take place before crosslinking of these units can occur. The isomerization of 1,2-units could probably explain the appearance of the induction period observed for various ZnO formulations.

### Proposed reaction mechanism

For halobutyl rubbers, the most widely accepted theory, as postulated by Baldwin et al.<sup>15</sup> and supported by Vukov<sup>11</sup> and Kuntz et al.,<sup>9</sup> proposes a cationic reaction in which ZnCl<sub>2</sub> (formed *in situ*) effects crosslinking. This implies that immediate crosslinking will occur when CR is heated with ZnCl<sub>2</sub>.

The results obtained in this study did not accord with the aforementioned cationic mechanism as, in all systems investigated, an induction period, attributed to the full allylic rearrangement of 1,2-units (discussed previously), was observed before crosslinking even

when 2 phr ZnCl<sub>2</sub> was included in the CR/ZnO(5) system (Fig. 6).

It is proposed that the first step in the crosslinking reaction at 140°C is the isomerization of 1,2-units by ZnO (Scheme 2). Thereafter, it is proposed that the second step in the crosslinking reaction of isomerized 1,2-units is the formation of a carbocation on the polymer chain, the dehydrochlorination reaction being catalyzed by ZnCl<sub>2</sub>. The dehydrochlorination reaction of the tertiary allylic positions will occur first, and once the tertiary allylic chlorines (1,2-units) are consumed, the less reactive 3,4- and 1,4-units will undergo dehydrochlorination. Although Scheme 2 involves the reaction of a primary carbocation, it is quite possible that before crosslinking can occur, this primary carbocation will rearrange to form a more stable tertiary carbocation. Unfortunately, current kinetic analyses do not allow us to predict how rapidly crosslinking will occur after carbocation formation, that is, whether cationic rearrangement will occur. It is thus quite possible that crosslinking results from the reaction of primary carbocations and tertiary carbocations with reactive double bonds.

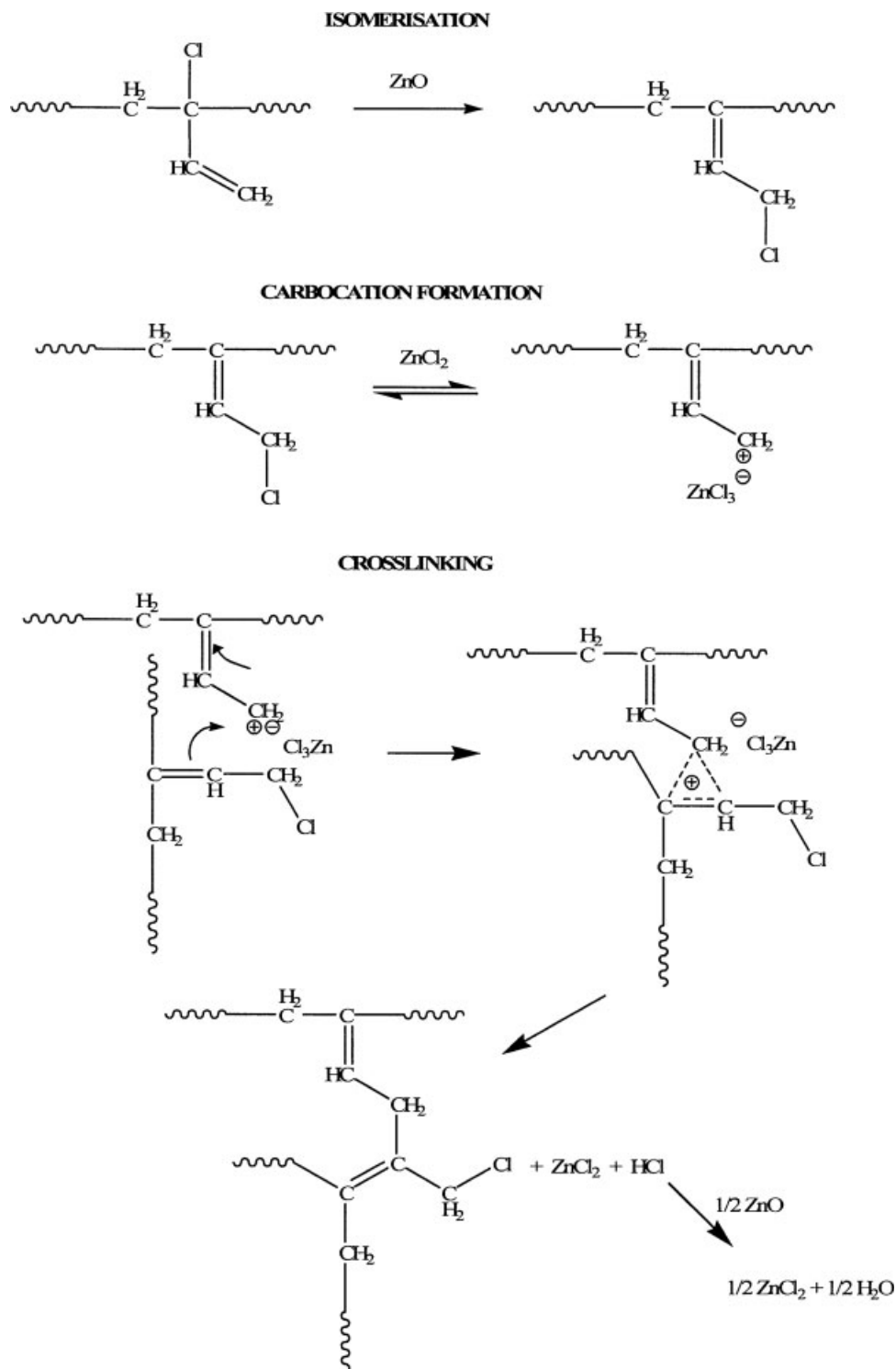
It is proposed that crosslinking, initiated by the formation of carbocation catalyzed by ZnCl<sub>2</sub>, involves the reaction between the carbocation on the CR polymer chain and a reactive double bond in the CR polymer chain. At low temperatures, it is likely that the only reactive bond is one in which Cl is not bonded to the double bond, that is, that of the isomerized 1,2-units.

It is suggested that crosslinking may result in a preference for dehydrochlorination only when a carbocation is formed on a polymer chain adjacent to the double bond of the reactive unit. In the presence of ZnO, HCl produced by these units will be trapped as ZnCl<sub>2</sub>, and this will result in an autocatalytic reaction.

As discussed previously, the 3,4- and 1,4-units are relatively stable. The crosslinking reaction for these units is not clear, and it is suggested that the reaction may proceed via an analogous ionic route (shown in Scheme 2 for the isomerized 1,2-unit).

As the polymer contains 1.3% (by mass) tertiary allylic chlorine (1,2-units) and it is proposed that 1 mol of allylic chlorine is consumed for every mole of crosslink formed, a maximum crosslink density of  $1.65 \times 10^{-4}$  mol/mL for the allylic chlorines can be calculated for the proposed mechanism. The number of crosslinks obtained in the CR/ZnO(5) compound (Fig. 2) is only about a tenth of that expected. Baldwin et al.<sup>15</sup> also reported that 10% of the reactive sites in the average CIIR chain engaged permanently in the crosslinking process.

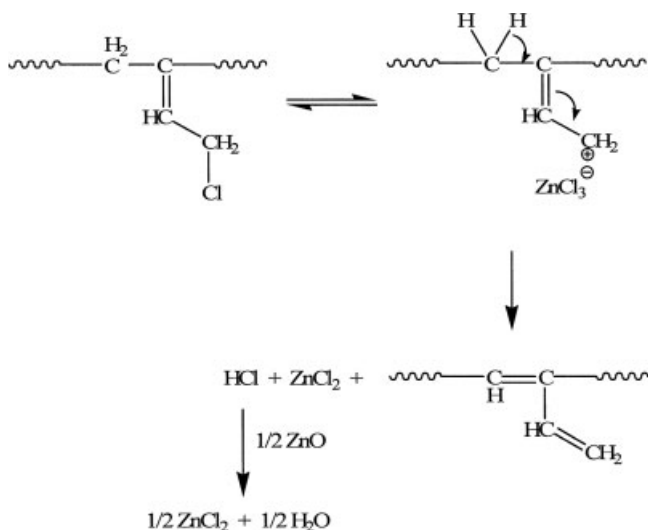
In terms of the proposed reaction mechanism, this low efficiency can be attributed to the formation of conjugated dienes via dehydrochlorination, as shown for the isomerized 1,2-units in Scheme 3. It is proposed that for crosslinking to occur, a reactive 1,2-unit that has not undergone dehydrochlorination must be in



**Scheme 2** Revised cationic mechanism proposed for the vulcanization of 1,2-units in CR by ZnO.

close proximity to a dechlorinated unit. When crosslinking is not viable, a conjugated diene will form instead. The formation of these dienes is catalyzed by  $\text{ZnCl}_2$ . As the  $\text{ZnCl}_2$  concentration increases, this reaction is more likely, and this explains why in the presence of added  $\text{ZnCl}_2$  the rate of crosslinking is slower than when  $\text{ZnCl}_2$  is not added.

Furthermore, the mobility of the CR polymer chain decreases with crosslink formation, and this further reduces the possibility of reactive units coming into contact with one another. This is supported by the dynamic calorimetry results conducted at  $1^\circ\text{C}/\text{min}$  (Fig. 4). Higher crosslink densities were obtained at increased temperatures. As more energy is available,



**Scheme 3** Formation of conjugated dienes from isomerized 1,2-units.

the mobility of the CR polymer chain increases. This could partially explain the higher crosslink densities obtained in the dynamic calorimetry studies because there is a greater probability of reactive units coming into contact with one another (cf. Figs. 2 and 4).

However, by 160°C, the complete reaction of isomerized 1,2-units had occurred. Thus, by this temperature there are no more reactive double bonds available. It is likely that 1,4-units undergo complete dehydrochlorination to form conjugated dienes at elevated temperatures in a mechanism analogous to that shown in Scheme 3. These dienes then provide the necessary reactive double bonds that can react with the appropriate carbocations to produce crosslinks. The temperature at which 3,4-units become crosslinkable is more difficult to ascertain, although a decrease in 3,4-units was observed in isothermal studies at 140°C. In line with their vinylic structure, it is expected that these will be more reactive toward dehydrochlorination than 1,4-units, whereas isomerized 1,2-units will be most reactive.

### CONCLUSIONS

The data presented here can best be explained in terms of a number of crosslinking processes that occur in CR and CR/ZnO systems. The first, fairly rapid process involves highly reactive tertiary allylic 1,2-units of the CR polymer chain. The isomerization of these 1,2-units occurs before crosslinking. The crosslinking of 1,2-units ceases once all the 1,2-units have been dechlorinated. The crosslinking of 3,4-units is thought to be slower. At elevated temperatures, the crosslinking of 1,4-units

occurs together with conjugated diene formation. This is much slower and is of little practical importance in vulcanization below 160°C. Reactions occurring during the marching phase of rheometer-cure curves can be ascribed to the crosslinking of these 1,4-units.

Upon the isothermal heating of CR at 140°C, crosslinking was observed after 24 h. CR, compounded with ZnO, crosslinked more rapidly, and crosslinking was preceded by the formation of ZnCl<sub>2</sub>, which promoted dechlorination and catalyzed crosslinking. Crosslinking involves the reaction between a cation formed on an isoprenoid unit and an alkene (which must be in close proximity to the cation) on the CR polymer chain. The addition of MgO to CR/ZnO systems retards the crosslinking reaction by trapping HCl and delaying the buildup of ZnCl<sub>2</sub> during the mixing process.

The authors thank Continental Tyre S.A. for the use of its rheometers.

### References

- Brydson, J. A. *Rubber Chemistry*; Applied Science: London, 1979.
- Forman, D. B. In *Rubber Technology*; Morton, M., Ed.; Van Nostrand Reinhold: New York, 1973.
- Iván, B.; Kennedy, J. P.; Plathottam, S. S. *J Polym Sci Polym Chem Ed* 1980, 18, 1685.
- Ferguson, R. C. *Anal Chem* 1964, 36, 2204.
- Miyata, Y.; Atsumi, M. *J Polym Sci Part A: Polym Chem* 1988, 26, 2561.
- Behal, M. *J Polym Sci* 1988, 35, 507.
- Troitskii, B. B. *Chem Technol Macromol Compd* 1974, 5, 172.
- Miyata, Y.; Atsumi, M. *Rubber Chem Technol* 1989, 62, 1.
- Kuntz, I.; Zapp, R. L.; Pancirov, R. J. *Rubber Chem Technol* 1984, 57, 813.
- Tripathy, A. R.; Patra, P. K.; Sinha, J. K.; Banerji, M. S. *J Appl Polym Sci* 2002, 83, 937.
- Vukov, R. *Rubber Chem Technol* 1984, 57, 284.
- Hendrikse, K. G.; McGill, W. J.; Reedijk, J.; Niewenhuizen, P. J. *J Appl Polym Sci* 2000, 78, 2290.
- Stevenson, A. C. In *Vulcanization of Elastomers*; Alliger, G.; Sjöthun, J., Eds.; Krieger: New York, 1978.
- Mallon, P. E.; McGill, W. J.; Shillington, D. P. *J Appl Polym Sci* 1995, 55, 705.
- Baldwin, F. P.; Buckley, D. J.; Kuntz, I.; Robinson, S. B. *Rubber Plast Age* 1961, 42, 500.
- Starkweather, H. W.; Walker, H. W. *Ind Eng Chem* 1937, 29, 872.
- Loadman, M. J. R. *Analysis of Rubber and Rubber-Like Polymers*; Kluwer: Dordrecht, 1998.
- Flory, P. J. *J Chem Phys* 1950, 18, 108.
- Polymer Handbook*, 4th ed.; Brandup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999.
- Naylor, R. F. *J Chem Soc* 1949, 4, 2749.
- Coleman, M. M.; Tabb, D. L.; Brame, E. G. *Rubber Chem Technol* 1977, 50, 49.
- Coleman, M. M.; Brame, E. G. *Rubber Chem Technol* 1978, 51, 668.
- Hepburn, C.; Hatam, E. A. *Plast Rubber Proc Appl* 1986, 6, 309.