

# Modification of Rubber by Iodoform

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**ABSTRACT:** The activity of iodoform ( $\text{CHI}_3$ ) toward unsaturated rubbers was examined. Special attention was devoted to *cis*-1,4-(poly)isoprene (IR). The thermal decomposition of  $\text{CHI}_3$  was studied by ion mass spectroscopy, and the obtained data were used for the identification of pyrolysis products of  $\text{CHI}_3$  vulcanizates by pyrolytic gas chromatography. The kinetics of the chemical crosslinking of rubber were studied with a cure meter. The changes observed in the chemical structure of rubber were explained on the basis of  $^{13}\text{C}$ NMR and Fourier transform infrared spectroscopy, differential scanning calorimetry, equilibrium swelling, and chemical microanalysis data. Apart from crosslinking, a simultaneous modification of the rubber macromolecules took place, specifically the *cis*-

trans isomerization of IR. This resulted in a significant increase in the rubber hardness, especially after a postheat treatment accompanied by oxidation.  $\text{CHI}_3$ -IR vulcanizates behaved like thermoplastics because of the presence of a trans-1,4 phase, as confirmed by dynamic mechanical thermal analysis. The structure of the macromolecules treated with  $\text{CHI}_3$  and its effect on the physical properties of the material were compared with those of peroxide-IR vulcanizates. The influence of the modification on the surface energy, bacteriostaticity, and mechanical properties of the vulcanizates was examined. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 177–189, 2007

**Key words:** modification; rubber; structure

## INTRODUCTION

Halogenation as a method for polymer modification has been applied for many years. However, the choice of the halogen is usually limited to chlorine or fluorine atoms.<sup>1,2</sup> The introduction of halogen atoms to macromolecules, because of their electro-negative effect toward  $\pi$ -electrons of double bonds (chloroprene rubber), high polarization of C—Cl or C—F bonds [(poly)vinyl chloride and polytetrafluoroethylene (PTFE)], and some sterical hindrance, usually causes an increase in the chemical resistance and thermal stability of a modified polymer and influences its adhesion properties. Bromination<sup>3</sup> is applied rather seldom because of the chemical toxicity of bromine; however, bromobutyl rubber is an exception. In macromolecules of bromobutyl rubber or chlorobutyl rubber, a halogen atom is placed in the  $\alpha$  position to double bonds of isoprene units. Its presence, apart from an improvement in the adhesion, enabling covulcanization with other elastomers, enhances the rate of vulcanization. The introduction of fluorine into macromolecules, in comparison with chlorine or bromine, improves even to a higher extent their chemical resistance and thermal stability.

The energy of C—F bonds is 485 kJ/mol, which is of 140 kJ/mol higher than that of C—C bonds in aliphatic structures.<sup>4</sup> PTFE distinguishes itself by a very low surface energy, which in turn results in its low wettability and coefficient of friction. Special properties, being a result of its unique chemical structure with a surface layer composed of tightly packed fluorine atoms, makes PTFE the most popular example of fluoropolymers. Properties similar to those of PTFE, exhibited by fluorine rubber, justify its recent increasing applicability. Some disadvantages of fluoropolymers, discouraging their broader application, are undoubtedly the cost of the materials, almost 10 times higher than that of commonly used thermoplastics,<sup>5</sup> and ecological restrictions of the products of their decomposition. Almost no attention, according to the subject literature, has been devoted to iodination of polymers.<sup>6</sup> Taking into consideration the special properties of iodine-containing species, such as antisepticity,<sup>7</sup> polarity, and electrical conductivity, we find the low popularity of iodinated polymers to be unreasonable.

Because of the drawbacks of conventional vulcanization,<sup>8</sup> better alternatives have been sought for many years. The modification of macromolecules by the incorporation of iodine atoms could lead to a change in their configuration, enabling unconventional curing, which could create a chance to produce vulcanizates of unusual properties for special applications. Barson et al.,<sup>9</sup> taking into consideration the bond strength of various iodine compounds, came to a conclusion on their effectiveness as chain-

This article is dedicated to the memory of Professor Marian Kryszewski.

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TABLE I  
Compositions of the Studied Mixes

No.	Component	Composition (phr)								
		I	II	III	IV-VI	VII-XII	XIII	XIV	XV	XVI
1	Cariflex IR 305 (IR)	100						100	100	100
2	Nipol BR 1221 (BR)		100							
3	Nipol N41 (NBR)			100						
4	Ker 1500 (SBR)				100					
5	Buna EPG 3440 (EPDM)					100				
6	Dutral CO 054 (EPM)						100			
7	DCP	2						2	—	—
8	CHI <sub>3</sub>	—	5	5	1/3/5	1/3/5/10/15	5	5	1.25/2.5/5	—
9	Cl <sub>4</sub>	—						—	—	2.50

The rubber samples were vulcanized in a stainless steel mold at 160°C during  $\tau_{0.9}$  determined rheometrically according to ISO 3417.

transfer agents in radical polymerization. They are more effective than their bromine or chlorine analogues. The authors suggested an application of iodoform (CHI<sub>3</sub>) in the radical polymerization of styrene or methyl methacrylate because it is possible to synthesize telomers with end groups containing reactive iodine atoms. Not long ago, Thakur<sup>10</sup> proved that by the iodination of natural rubber one could increase its electrical conductivity by an order of magnitude; this was ascribed to the formation of sequences of conjugated double bonds in a polymer backbone. This discovery provoked more intensive studies of the possibility of obtaining a semiconductive (poly)butadiene by iodination.<sup>11,12</sup>

In this work, the modification of typical unsaturated elastomers by means of CHI<sub>3</sub> was studied. CHI<sub>3</sub> seemed particularly suitable for this purpose because of its relatively high molecular weight and low volatility, as well as its high reactivity toward double bonds and the possibility of its use as a free-radical transfer agent. The application of CHI<sub>3</sub> for the modification of elastomers has not been thoroughly investigated previously. Special attention was devoted to the possibility of crosslinking byproducts of the thermal decomposition of CHI<sub>3</sub>. Their reactivity was found highest for *cis*-1,4-(poly)isoprene (IR) in comparison with the other elastomers studied, and this determined that special attention should be paid to IR. The mechanisms of its modification are presented and discussed from the point of view of some physical characteristics of the rubber (surface energy and mechanical properties) in comparison with dicumyl peroxide (DCP) vulcanizates.

## EXPERIMENTAL

### Materials

IR (Cariflex IR 305, Kraton, Houston, TX), *cis*-1,4-(poly)butadiene (BR; Nipol BR 1221, Nippon Zeon, Tokyo, Japan), acrylonitrile-butadiene rubber (NBR; Nipol

N41, Nippon Zeon), styrene-butadiene rubber (SBR; Ker 1500, Z. Chem., Dwory, Oświęcim, Poland), ethylene-propylene-diene rubber (EPDM; Buna EPG 3440, Bayer, Leverkusen, Germany), or ethylene-propylene rubber (EPM; Dutral CO 054, DSM, Galeen, Netherlands) was mixed with CHI<sub>3</sub> (catalog no. 10,945-2, Sigma-Aldrich, Gillingham, UK) in a laboratory two-roll mill (David Bridge, Salford, UK). The compositions of the mixes are given in Table I. DCP (95% pure; Merck Shuchardt, Hohenbrunn, Germany) was used as a crosslinking agent, additionally enhancing the reaction of CHI<sub>3</sub> with isoprene rubber. To study the mechanisms of rubber modification with iodine species, a mix of IR with tetraiodomethane (Cl<sub>4</sub>; catalog no. 26,922-0, Aldrich), admixed instead of CHI<sub>3</sub>, was also prepared and examined.

### Techniques

#### Ion mass spectroscopy

The thermal decomposition of CHI<sub>3</sub> was run with an SDT 2960 apparatus (TA Instruments, New Castle, DE) coupled with a Thermo Star QMS 300 quadrupole mass spectrometer (Balzers, Liechtenstein) by a heated quartz capillary. The analysis was carried out at 160°C (temperature of vulcanization) in the range of  $m/z = 100-300$ . The obtained spectra were compared to the internet database of the National Institute of Standards and Technology (Gaithersburg, MD).

#### Kinetics of vulcanization

The kinetics of vulcanization were studied most often at 160°C (some experiments were run at higher temperatures of 170–190°C) with a WG-05 cure meter (Industrial Research Institute "Metalchem," Torun, Poland). Besides the determination of the time parameters of vulcanization (ISO 3417), the shearing modulus and the character of its evolution were also analyzed. Vulcmetric curves were used for calculations of the CHI<sub>3</sub> activity toward the elastomers studied.

The crosslinking rate constant ( $k$ ) and activation energy ( $E_a$ ) were calculated with a procedure described elsewhere.<sup>13</sup>

Assuming that an increase in the vulcanometric torque is related to progress of the reaction, the vulcanization can be described by eq. (1):

$$\frac{dM}{dt} = k \cdot (M_{\max} - M(t))^n \quad (1)$$

where  $M_{\max}$  is the maximum torque,  $n$  is the order of reaction, and  $M$  is the vulcanometric torque.

For a reaction of the first order, after a separation of variables and an integration, one can obtain the following form of eq. (1), which describes the course of crosslinking:

$$\text{Ln} \left[ \frac{M_{\max} - M_{\min}}{M_{\max} - M(t)} \right] = k \cdot t \quad (2)$$

where  $M_{\min}$  is the minimum torque.

For a reaction of the order of  $n$  (but different from  $n = 1$ ), a solution of eq. (1) takes the following form:

$$\left[ \frac{1}{(M_{\max} - M_{\min})^{(n-1)}} - \frac{1}{(M_{\max} - M(t))^{(n-1)}} \right] \cdot (n-1) = k \cdot t \quad (3)$$

To determine the order of crosslinking, the values of  $k$  and the coefficient of correlation ( $R$ ) were calculated, starting from  $n = 0.01$  with a step of 0.01 and finishing at  $n = 5$ . From the graphic relation between  $R$  and an assumed order of the crosslinking reaction, the latter was taken as the closest integer for which  $R$  showed a maximum.

$E_a$  was calculated from the well-known Arrhenius equation:<sup>14</sup>

$$\ln k = \ln A - \frac{E_a}{R \cdot T} \quad (4)$$

where  $A$  is a constant and  $R$  is the universal gas constant.

$E_a$  was obtained from the slope of the following dependence

$$\ln k = f \left( \frac{1}{T} \right) \quad (5)$$

for the kinetics of vulcanization determined for at least three different temperatures.

#### Pyrolytic gas chromatography

CHI<sub>3</sub>-rubber vulcanizates and CHI<sub>3</sub> samples were pyrolyzed for 5 s at 610 or 770°C, and the products were analyzed with a CPSil 5 column 0.53 mm in diameter and 30 m long, with helium flow of 30 mL/

min as a gas carrier. The column temperature was set to 40°C. The products of pyrolysis were identified on the basis of the available literature and our own experience.

#### Equilibrium swelling

The crosslink density of the IR vulcanizates was estimated from values of their equilibrium swelling in toluene<sup>15</sup> at various stages of vulcanization, which were assigned according to vulcanometric curves. The equilibrium swelling of the rubber in a solvent was determined according to the standard procedure described elsewhere.<sup>16</sup> CHI<sub>3</sub> vulcanizates of IR were additionally subjected to swelling experiments at 110°C in diphenyl ether.

#### Chemical microanalysis

Rubber samples were analyzed for the iodine content before and after 48 h of extraction with boiling methanol, which is a good solvent for both CHI<sub>3</sub> and Cl<sub>4</sub>, to estimate the amount of the halogen chemically bonded to IR.

#### <sup>13</sup>C-NMR

Products of the reaction of CHI<sub>3</sub> with a model substance, dodecene or squalene, as well as IR samples before and after modification by CHI<sub>3</sub>, dissolved in deuterated chloroform, were run with a Bruker (Billerica, MA) 500-Hz NMR spectrometer. The spectra were evaluated according to the positions of the carbon atoms, with reference to the work of Tanaka.<sup>17</sup>

#### Fourier transform infrared (FTIR) spectroscopy

Spectra of the reaction products of CHI<sub>3</sub> with model substances as well as fresh cross-sectioned IR vulcanizates were collected with a Bio-Rad 175C FTIR spectrometer (Krefeld, Germany) equipped with an internal reflection spectroscopy attachment (Split Pea, Harrick Scientific, Pleasantville, NY) operating with a Si crystal. Samples were run over a wavelength range of 400–4000 cm<sup>-1</sup> under experimental conditions of 32 scans/4 cm<sup>-1</sup> (resolution). Infrared spectra were analyzed with respect to the absorption bands originating from iodine species at 1260 and 755 cm<sup>-1</sup>.<sup>18</sup> Additionally, for IR samples, the ratio of the band absorptions ( $A_{960}/A_{840}$ ), following changes in a cis-trans configuration,<sup>19</sup> was calculated.

#### Differential scanning calorimetry (DSC)

IR vulcanizates were studied with a DSC 204 instrument (Netzsch, Selb, Germany) calibrated

with an indium standard. Samples of 5–6 mg were heated at a rate of 10°/min from –100 to +100°C, held at 100°C for 5 min, and cooled to the room temperature. Changes in the glass-transition temperature of IR and a melting peak, originating from a crystalline phase formed because of the modification of the macromolecular structure of isoprene rubber, were examined.

#### Dynamic mechanical thermal analysis (DMTA)

Measurements were performed with a Rheometrics (Piscataway, NJ) V instrument applying three-point bending over the temperature range of –100 to 100°C, the temperature changing at a rate of 2°/min. Samples of 40.0 mm × 4.0 mm were oscillated with the deformation amplitude of 1% and simultaneously the frequencies of 0.1, 1.0, and 10.0 Hz. DMTA spectra of IR modified with CHI<sub>3</sub> were run to obtain complementary data on the macromolecular relaxation of the modified rubber.

#### Mechanical properties

A significant deterioration of the elasticity made impossible a determination of the full characteristics of the modified isoprene rubber according to ISO 37. That is why microscale spherical indentation (with a stainless steel spherical indenter of  $R = 5 \mu\text{m}$ ) had to be carried out with a NanoTest 600 instrument (Micromaterials, Wrexham, UK)<sup>20</sup> to evaluate the extent of stiffening and ability of IR for stress relaxation.

#### Surface energy

The contact angles for distilled water and diiodomethane on the surface of IR vulcanizates were determined with a home-made goniometer containing a picture acquisition system and Multiscan 8.0 (Computer Scanning System, Warsaw, Poland) software for their analysis. Their values were then used for the calculation of the surface energy and its polar and dispersive components with the procedure proposed earlier.<sup>21</sup>

#### Bacteriostaticity

A freshly modified surface was covered with a suspension of *Escherichia coli* bacteria (100- $\mu\text{L}$  bacterial suspension with absorbance  $A_{620}$  equal to 1, which gave ca. 100–120 bacteria in the observation area under a microscope). After 24 h of incubation at 37°C, the bacteria were colored with a 5- $\mu\text{L}$  solution of bisbenzidine (100  $\mu\text{g}/\text{mL}$ ) in a 0.1M phosphorane buffer of pH = 7.4. In the next step, the surface of

the vulcanizate was treated with a 2- $\mu\text{L}$  solution of propidine iodide in 70% ethanol (500  $\mu\text{g}/\text{mL}$ ), and it was subjected to further incubation for another 15 min and placed under a microscope. Observations were made with a Olympus (Tokyo, Japan) GX71 fluorescent microscope equipped with a DP70 CCD camera. Pictures were acquired and analyzed with the analysis software. The experimental procedure allowed differentiation between living (colored white/blue with bisbenzidine) and dead (colored pink with propidine iodide) cells.

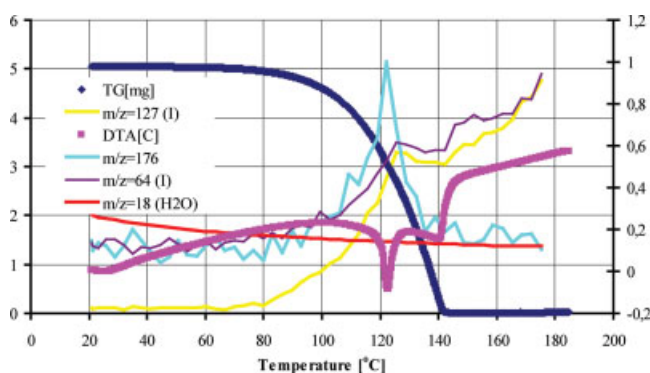
## RESULTS AND DISCUSSION

### Decomposition of CHI<sub>3</sub>

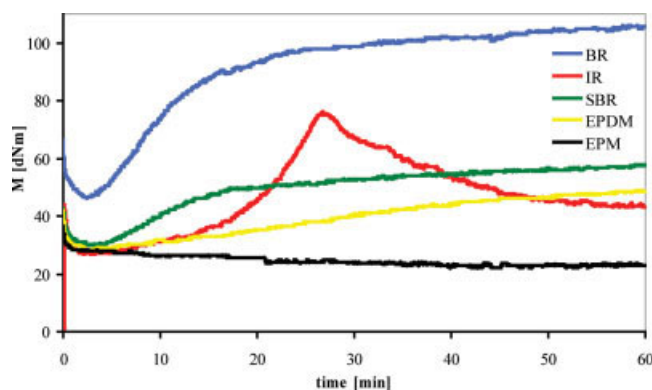
The thermogravimetric analysis of CHI<sub>3</sub> revealed that the sample started losing weight already at 80°C; together with our knowledge of its melting temperature of about 120°C, this can be interpreted as a sublimation process. Under further heating, a sample of CHI<sub>3</sub> changed color because of decomposition, the products of which started boiling at about 160°C. This means that at the vulcanization temperature they could either modify/crosslink macromolecules of an elastomer or escape in a gas form. The analysis of the thermal decomposition products of CHI<sub>3</sub> at 160°C is presented in Figure 1.

On the basis of a reference spectrum from the National Institute of Standards and Technology database, the following dominant peaks were ascribed to  $m/z$ : 64 for double-ionized iodine, 127 for an iodine radical (changes in a similar way to  $m/z = 64$ ), and 176, probably coming from the oxidation of CHI<sub>3</sub> or iodine (e.g., HIO<sub>3</sub>).

Apart from these, some minor peaks were also present in a spectrum. They could be associated with  $m/z$ : 128 for HI, 140 for  $\bullet\text{CHI}^+$ , 254 for I<sub>2</sub>, 267 for  $\bullet\text{CHI}_2$  or CHI<sub>2</sub><sup>+</sup>, and 394 for CHI<sub>3</sub>.

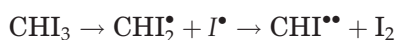


**Figure 1** Ion mass spectroscopy analysis of the thermal decomposition of CHI<sub>3</sub>. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

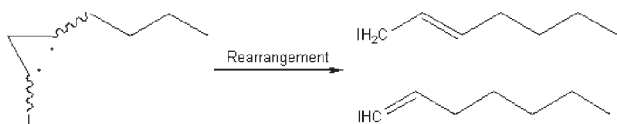


**Figure 2** Vulcanization kinetics of elastomers by  $\text{CHI}_3$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

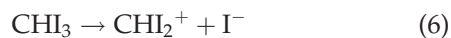
The analysis confirmed the radical character of the thermal decomposition of  $\text{CHI}_3$  proposed by Yang and Marolewski.<sup>22</sup>



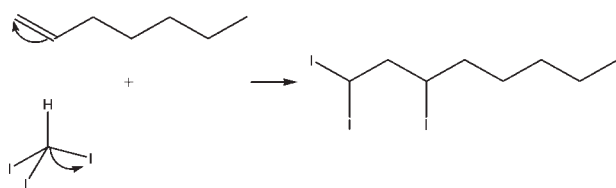
The created carbene is subjected to an addition to double bonds of an olefin (1-hexene), producing a three-member ring, which in turn is accommodated by polyolefin macromolecules<sup>23</sup> and after a rearrangement produces double bonds:<sup>24</sup>



Nevertheless, some minor contribution could also take place from heterolytic decomposition:<sup>25,26</sup>



According to Dostovalova et al.,<sup>26</sup> a high dipole momentum of  $\text{CHI}_3$  can produce the polarization of double bonds of polyolefins, facilitating the addition of iodine species and the steric matching



or, as suggested by other authors, disproportionation:<sup>27</sup>



Figure 1 probably presents two processes. The first one is associated with the decomposition of  $\text{CHI}_3$

with the release of iodine: a fast initial increase of lines for  $m/z = 64$  to  $m/z = 127$ . The second one, most likely a result of  $\text{I}^\bullet$  recombination, explains the further reduction of the above signals after a maximum is reached.

### Modification and crosslinking

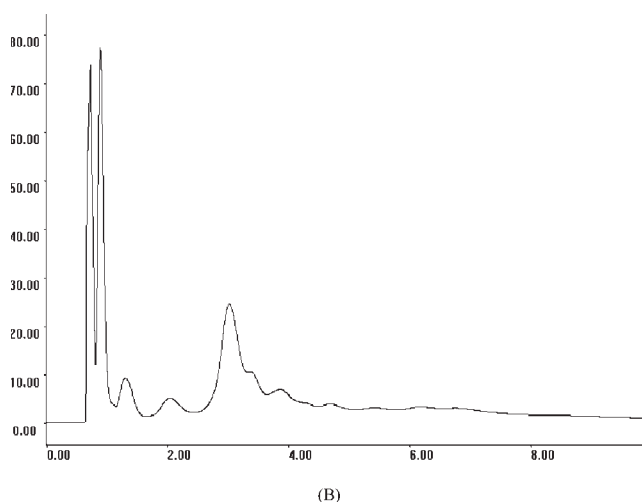
Vulcetric studies revealed that all the elastomers studied, apart from EPM, could be crosslinked by  $\text{CHI}_3$  (Fig. 2).

A activity similar to that of  $\text{CHI}_3$  toward elastomers is also exhibited by  $\text{Cl}_4$ , and this can be interpreted as evidence for the radical character of vulcanization. An admixing of an equimolar amount of hydroquinone, which is known as a very effective scavenger of free radicals,<sup>28</sup> to rubber mixes containing the iodine agents resulted in a lack of their vulcanization. Such an effect was expected first of all for  $\text{Cl}_4$ , which is able rather for nonpolar dissociation. The probability of an ionic addition of  $\text{CHI}_3$  to double bonds of isoprene monomer units was assumed on the basis of our previous work concerning studies of interactions between chloroform and diene rubbers.<sup>25</sup> Another reference<sup>26</sup> provides very valuable evidence for the radical character of dissociation taking place also in the case of  $\text{CHI}_3$ , which is likely to form ionic species, especially in polar media.

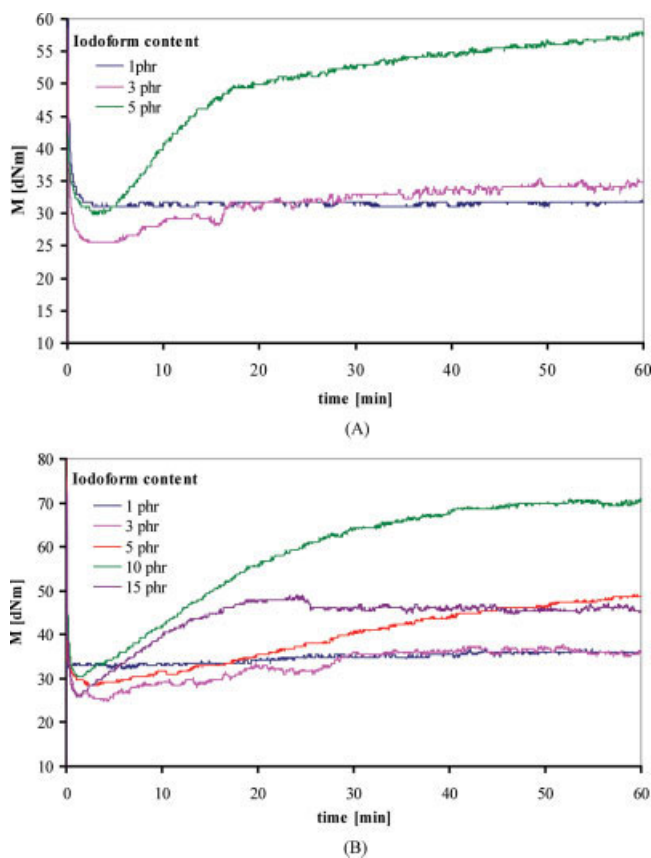
Taking into consideration a radical mechanism for the thermal decomposition of  $\text{CHI}_3$ , we can ascribe the peaks present in the chromatograph of pyrolyzed  $\text{CHI}_3$  (Fig. 3) to the following products: time of

$\text{CHI}_3$

(A)



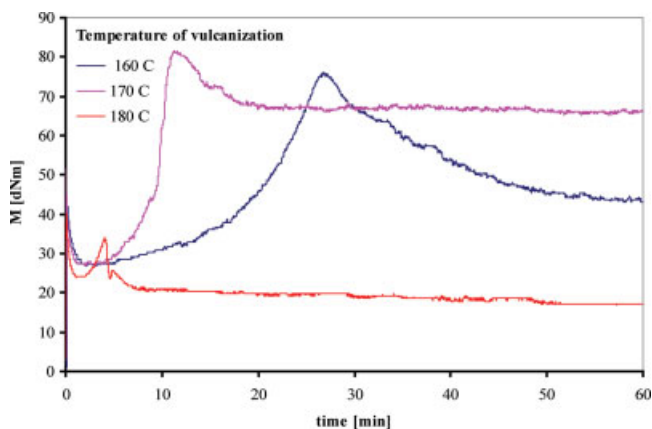
**Figure 3** Gas chromatography spectra of pyrolyzed  $\text{CHI}_3$  and  $\text{CHI}_3$  vulcanizates: (A) IR and (B) EPDM.



**Figure 4** Influence of the  $\text{CHI}_3$  content on the vulcanometric characteristics of elastomers: (A) SBR and (B) EPDM. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

retention ( $t_r$ ) (min) is 0.7 for  $\text{HI}$ , 1.1 for  $\text{I}_2$ , 3.1 for  $\text{CH}_2\text{I}_2$ , 4.0 for  $\text{CHI}_3$ , and 6.5 for  $\text{Cl}_4$ .

$\text{Cl}_4$  could not be detected with an ion mass spectroscopy method because of the mass limit of



**Figure 5** Influence of the temperature on the vulcanometric characteristics of IR crosslinked with 5 phr  $\text{CHI}_3$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the detector used. The analysis will be used afterwards to explain the roles of particular products in the modification/crosslinking of elastomers on the basis of chromatographs of their  $\text{CHI}_3$  vulcanizates.

To determine the possibility of crosslinking diene rubbers with  $\text{CHI}_3$ , some vulcanometric experiments were performed at  $160^\circ\text{C}$  on SBR and EPDM modified with 1–15 phr  $\text{CHI}_3$  (Fig. 4). Apart from this, the influence of the temperature (ranging from  $160$  to  $180^\circ\text{C}$ ) on the kinetics of IR vulcanization is demonstrated in Figure 5.

The lowering of the vulcanometric torque (the so-called reversion) is probably the result of the destruction of rubber macromolecules, which is suggested by the high reactivity of  $\text{CHI}_3$  toward IR (Table II), which is significantly higher in comparison with that toward BR. Apart from IR, a linear relationship between the double-bond concentration in rubber and  $k$  was found. IR also differs from other elastomers by a high  $E_a$  value of  $\text{CHI}_3$  crosslinking. The observed features, the parameters of which have been collected in Table II, led us to devote the next chapter to this particular system.

**TABLE II**  
Chemical Reactivity of  $\text{CHI}_3$  Toward the Studied Elastomers

Sample	Temperature ( $^\circ\text{C}$ )	$k$ (1/s)	$E_a$ (J/mol)
BR/5 phr $\text{CHI}_3$	160	0.001870	$97.6 \pm 9.6$
	170	0.003240	
	180	0.005360	
	190	0.010780	
IR/5 phr $\text{CHI}_3$	160	0.007650	169.4
	170	0.025430	
	180		
SBR/3 phr $\text{CHI}_3$	160	0.000951	$22.5 \pm 2.0$
	170	0.001108	
	180	0.001208	
	190	0.001425	
SBR/5 phr $\text{CHI}_3$	160	0.001592	$49.0 \pm 8.0$
	170	0.001807	
	180	0.002519	
	190	0.004073	
EPDM/3 phr of $\text{CHI}_3$	160	0.000459	$93.6 \pm 9.2$
	170	0.000699	
	180	0.001140	
EPDM/5 phr $\text{CHI}_3$	160	0.000758	$97.2 \pm 9.4$
	170	0.001382	
	180	0.002873	
	190	0.004421	
EPDM/10 phr $\text{CHI}_3$	160	0.001090	$117.4 \pm 15.1$
	170	0.001560	
	180	0.004520	
	190	0.007280	
EPDM/15 phr $\text{CHI}_3$	160	0.002100	$12.4 \pm 4.7$
	170	0.004100	
	180	0.008530	
	190	0.01540	

**TABLE III**  
Chemical Microanalysis of the Iodine Content in IR Vulcanizates

Sample	Iodine content (wt %)
Before extraction	
IR + 2.5 phr CHI <sub>3</sub>	0.88
IR + 2.5 phr CHI <sub>4</sub>	1.70
IR + 5 phr CHI <sub>3</sub> /t = 8 min	3.24
IR + 5 phr CHI <sub>3</sub> /t = 25 min	3.22
IR + 5 phr CHI <sub>3</sub> /t = 40 min	3.40
IR + 5 phr CHI <sub>3</sub> /dynamic aging <sup>b</sup>	2.37
IR + 5 phr CHI <sub>3</sub> /static aging <sup>c</sup>	1.28
After extraction <sup>a</sup>	
IR + 2.5 phr CHI <sub>3</sub>	0.79
IR + 2.5 phr CHI <sub>4</sub>	1.22
IR + 5 phr CHI <sub>3</sub> /t = 8 min	1.21
IR + 5 phr CHI <sub>3</sub> /t = 25 min	1.94
IR + 5 phr CHI <sub>3</sub> /t = 40 min	2.18

<sup>a</sup> Extraction with boiling methanol for 48 h.

<sup>b</sup> Twelve cycles at 120°C for 30 min and at 25°C for 5 min.

<sup>c</sup> For 20 h at 120°C.

### Modification/crosslinking of IR with CHI<sub>3</sub>

The crosslinking of IR by means of CHI<sub>3</sub> is a chemical reaction of the second order, whereas a peroxide reaction is of the first order. The calculated rate of the chemical reaction with CHI<sub>3</sub> ( $R > 0.999$ ) is higher for the former than for DCP used in the molar equivalent. An application of CHI<sub>3</sub> in an amount exceeding 2.5 phr leads to very high modification of rubber macromolecules, resulting finally in a significant brittleness of the material. In the light of the mixed character of CHI<sub>3</sub> decomposition, it cannot be excluded that iodine species modify IR macromolecules. Only some of the halogen could be extracted from the rubber (Table III); however, the amount left can hardly justify a significant change in the mechanical appearance of the material (Table IV).

The presence of iodine, associated with carbon species, is only slightly visible in the FTIR spectra (Fig. 6).

Also, the degree of swelling of IR modified with CHI<sub>3</sub> is surprisingly high in comparison with the significant stiffening of the rubber (Table V).

**TABLE IV**  
Micromechanical Properties of IR Modified with CHI<sub>3</sub>

Sample	Hardness (MPa)	Modulus (MPa)	Elastic recovery
IR + 2 phr DCP	1.92	3.03	0.850
IR + 2 phr DCP + 5 phr CHI <sub>3</sub>	13.53	86.51	0.330
IR + 5 phr CHI <sub>3</sub> /t = 8 min	5.61	118.25	0.146
IR + 5 phr CHI <sub>3</sub> /t = 25 min	18.52	851.43	0.107
IR + 5 phr CHI <sub>3</sub> /t = 40 min	3.15	22.41	0.281
IR + 5 phr CHI <sub>3</sub> /dynamic aging <sup>a</sup>	7.17	1659.29	0.017
IR + 5 phr CHI <sub>3</sub> /static aging <sup>b</sup>	36.04	1866.37	0.128

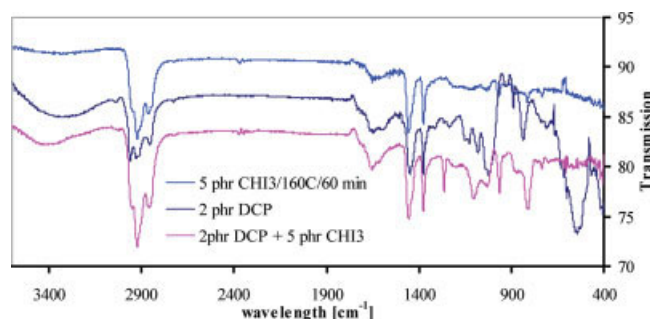
<sup>a</sup> Twelve cycles at 120°C for 30 min and at 25°C for 5 min.

<sup>b</sup> For 20 h at 120°C.

An explanation of the above observations was provided by <sup>13</sup>C-NMR spectra (Fig. 7), which revealed a splitting of the signals from A1 and A2 carbon atoms in *cis*-1,4-polyisoprene at about 135 and 125 ppm, respectively,<sup>17</sup> that can be ascribed to a partial *cis*-*trans* isomerization of the rubber due to its modification with iodine species. The same, as might be expected, concerns some of the A4 carbon atoms at about 26 ppm. Finally, the spectrum in Figure 7 also contains well-separated signals of A3 carbon atoms in *trans*-1,4 and *cis*-1,4 configurations at about 32 and 39 ppm, respectively.<sup>17</sup> Even though the spectrum of modified IR does not contain signals supporting a saturation of double bonds in macromolecules, as clearly visible in a conventionally halogenated (chlorinated) polyisoprene,<sup>29</sup> there are some new peaks appearing at about 37 and 48 ppm. They can be associated by analogy with A3 and A4 carbon atoms, their positions altered by the neighborhood of iodine species. New resonance peaks, originating from CHI<sub>3</sub> carbon modifying the IR molecule, appear at 138, 20, and 21 ppm.

A *cis*-*trans* isomerization of polyisoprene as well as its chemical modification due to an action of CHI<sub>3</sub> also seems apparent from an analysis of FTIR spectra<sup>30</sup> (Fig. 6). An absorption peak at 960 cm<sup>-1</sup>, originating from a *trans*-1,4 configuration of polyisoprene, significantly increases, whereas an indication of a *cis*-1,4 absorption at 840 cm<sup>-1</sup> is less evident; this can be ascribed to a lower extinction of the latter. FTIR spectra of the rubber after 8, 25, and 40 min of CHI<sub>3</sub> vulcanization (Fig. 8), followed by microchemical analysis for iodine (Table III), confirm the mechanism of the *cis*-*trans* isomerization of IR initiated with iodine species. Apart from this, iodine saturates double bonds in a *cis* phase. A crystalline *trans* phase, which is likely to be formed, can hardly be justified by DSC spectra (Fig. 9).

One can see a slight shift in the glass-transition temperature from -73°C for IR to -65°C; this goes in the direction of the literature data on the glass-transition temperature for a *trans*-1,4 form.<sup>31</sup> Other



**Figure 6** FTIR spectra of IR vulcanizates modified with CHI<sub>3</sub>: (a) 2 phr DCP, (b) 5 phr CHI<sub>3</sub>, and (c) 2 phr DCP plus 5 phr CHI<sub>3</sub>. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE V  
Equilibrium Swelling of IR Vulcanizates in Toluene

Sample	Time of vulcanization (min)	$m_0$ (mg)	$m_{sw}$ (mg)	$m_e$ (mg)	$1/Q_w$	$1/Q_v$
IR + 5 phr $\text{CHI}_3$ + 2 phr DCP	8	37.25	510.50	29.50	0.06	0.06
	25	35.50	538.75	26.25	0.05	0.05
	40	35.75	62.15	31.00	0.99	0.95
IR + 5 phr $\text{CHI}_3$	8	32.50	96.00	1.75	0.02	0.02
	25	33.50	169.75	31.00	0.22	0.21
	40	34.50	63.50	32.28	1.00	0.99
IR + 2 phr DCP	40	33.75	140.50	29.00	0.26	0.25

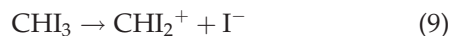
$m_0$  = initial mass of the sample,  $m_{sw}$  = mass of the swelled sample,  $m_e$  = mass of the extracted sample (dried to the constant mass),  $Q_w$  = mass equilibrium swelling,  $Q_v$  = volume equilibrium swelling,  $t_r$  = time of retention.

evidence is provided by a broad melting peak, centered at  $65^\circ\text{C}$ , which can be ascribed to the melting of a crystalline phase of *trans*-1,4-(poly)isoprene.<sup>31</sup> Its broadness is probably the result of a high distortion of supermolecular structures. Swelling experiments carried out in diphenyl ether at  $110^\circ\text{C}$  [well above the melting temperature of a crystalline phase of *trans*-1,4-(poly)isoprene] revealed only a small increase in the sample volume, which apart from crosslinking can be even to a higher extent associated with the polarization of C—I bonds.  $\text{CHI}_3$  vulcanizates of IR behave like thermoplastics, and this has been confirmed by repeated dynamic thermal experiments. DMTA spectra of the material reveal, apart from the characteristic loss tangent peak for IR at about  $25\text{--}30^\circ\text{C}$ , an extra one at about  $60\text{--}70^\circ\text{C}$ ,

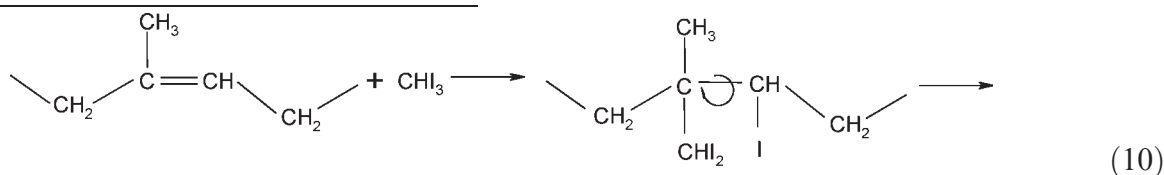
which can be ascribed to a *trans*-1,4 phase (Fig. 10). Its contribution to the total area under the loss tangent curves is significant, and this confirms the micromechanical data.

The vulcanization of IR with  $\text{CHI}_3$  differs from that made with DCP (Fig. 11). The former reaction can, however, be enhanced by an application of DCP.

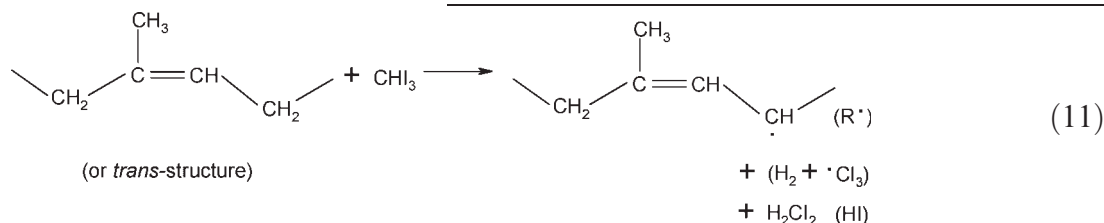
On the basis of the obtained results, the following mechanisms of IR modification/crosslinking with  $\text{CHI}_3$  are postulated:



Isomerization (free radical or ionic) is shown by



The abstraction of H atoms is shown by



Consecutive reactions include crosslinking

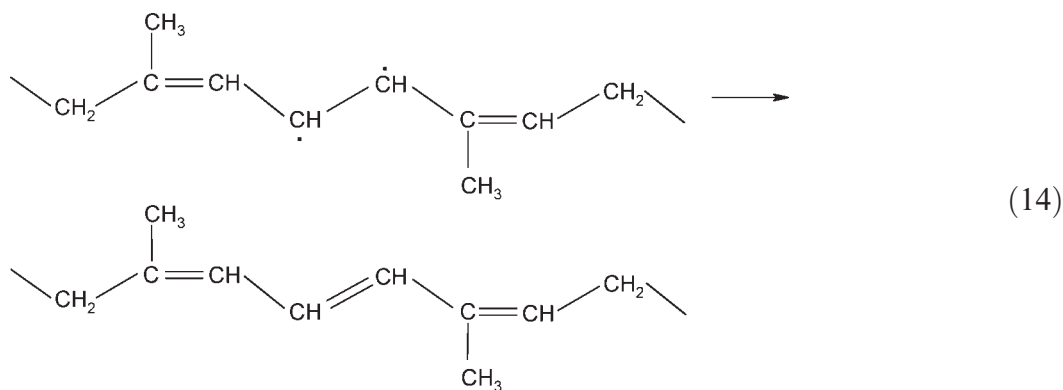


modification





and the formation of conjugated double bonds:<sup>32</sup>



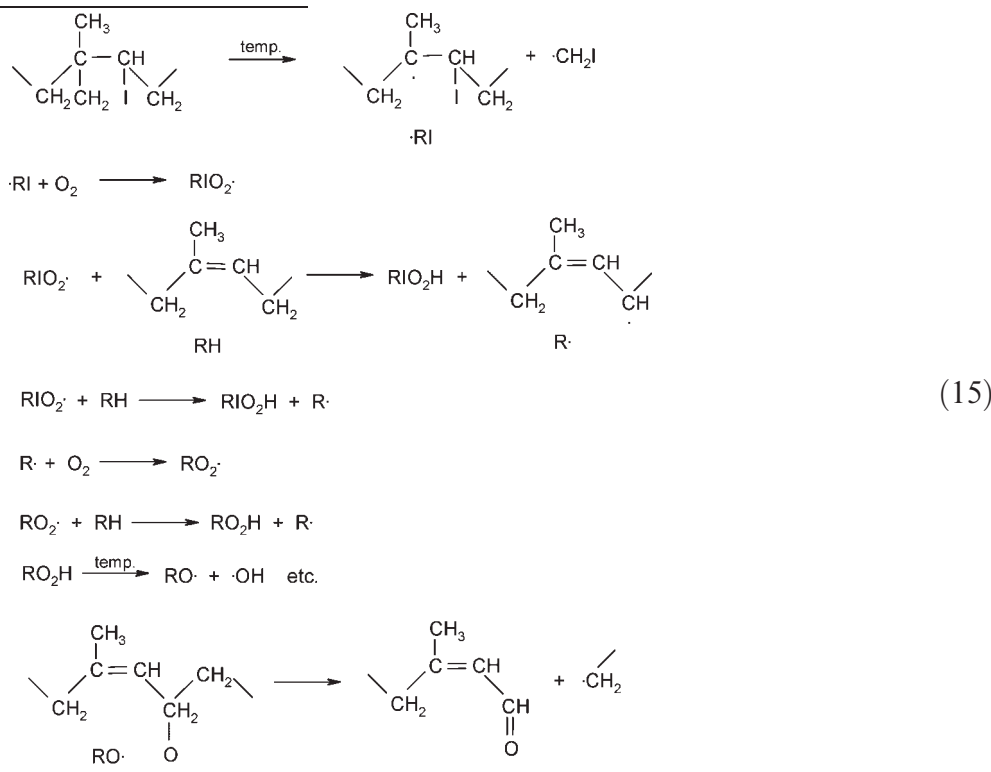
**Properties of the vulcanizates**

In light of the postulated structure of modified/crosslinked IR vulcanizates, the exploitation properties of the rubber can be interpreted as follows.

**Mechanical properties**

The hardness of IR modified with CHI<sub>3</sub> increases, as confirmed by a spherical microindentation. Nevertheless, the values determined for vulcanizates after a shorter time (following characteristic points from a vulcammetric curve; Table IV) confirm a reversion demonstrated by the kinetics of vulcanization (Fig. 11). A significant increase in the hardness and mechanical

modulus, registered for samples subjected to postheat aging, is probably the result of rubber crosslinking taking place with an involvement of oxygen species, being absent in a closed vulcanization mold. The most likely, a trans form of isoprene, produced by the modification is involved in the reaction, as can be deduced by a comparison of the material to the response of butadiene rubber to thermal aging. The modified material becomes harder and stiffer, resembling an ebonite (hardness = 175.20 MPa, modulus = 4711.44 MPa, elastic recovery = 0.304, as determined by a spherical indentation). The only difference concerns the value of the elastic recovery. The ebonite is a more elastic material. The following mechanism for preliminary oxidation of IR macromolecules is proposed:



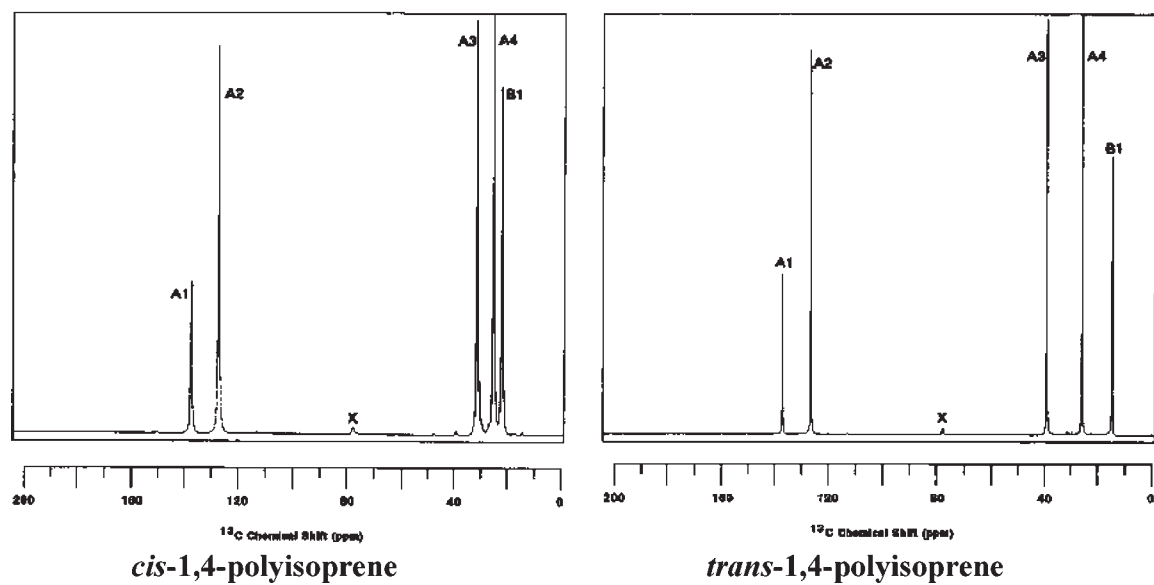
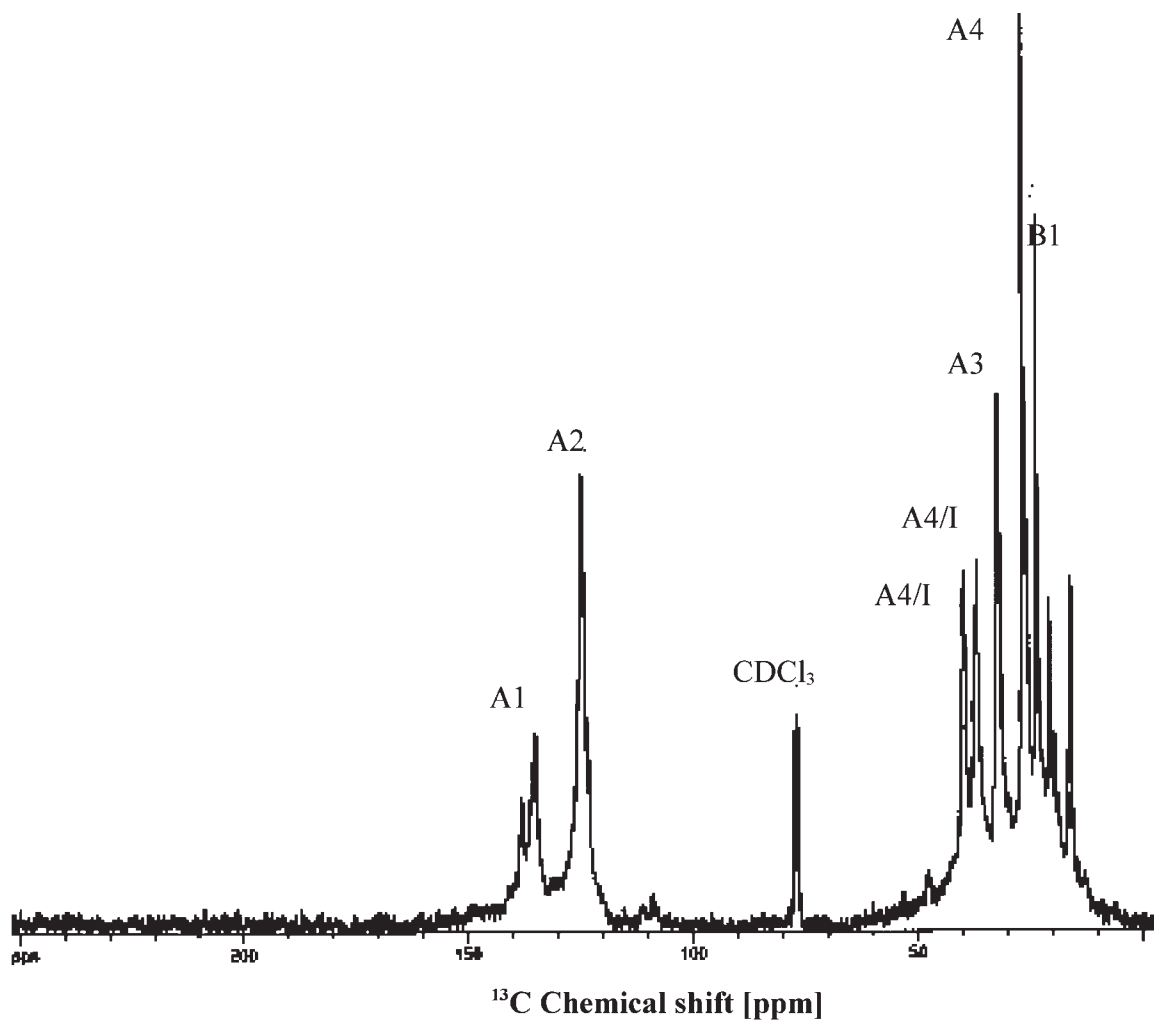
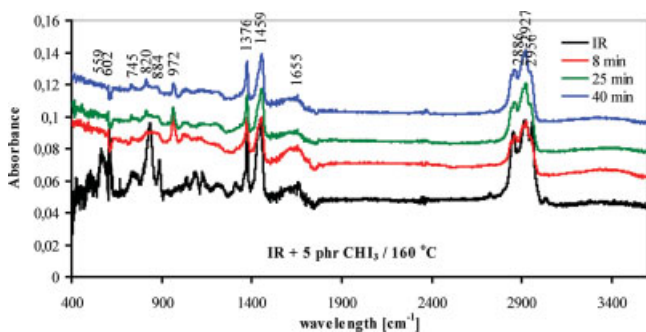


Figure 7  $^{13}\text{C}$ -NMR spectra of *cis*-1,4-polyisoprene modified with  $\text{CHI}_3$ .

In the light of the high values of the equilibrium swelling for the vulcanizates at maximum values of the vulcanometric modulus, it seems likely that the

main mechanism of modification, responsible for the data obtained, is *cis*-*trans* isomerization, with considerable participation of the crosslinking of a *cis*



**Figure 8** IR-CHI<sub>3</sub> vulcanization studied with FTIR: (a)  $t = 0$  min, (b)  $t = 8$  min, (c)  $t = 25$  min, and (d)  $t = 40$  min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

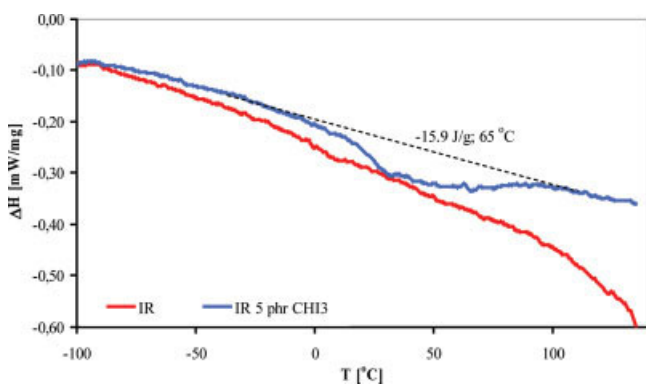
phase left. *trans*-1,4-(Poly)isoprene, contrary to a highly elastic *cis*-1,4 form, resembles a plastic. Thermal oxidation applied to samples after vulcanization is likely to crosslink a *trans* phase, making the material brittle. The modified rubber exhibits thermoplastic behavior.

Some oxidation of IR, resulting from the posttreatment, is limited mainly to the surface layer. A thin, highly oxidized, and crosslinked layer could be responsible for higher microhardness, as a measured with a NanoTest 600 instrument. Bulk FTIR spectra do not contain any significant absorption peaks associated with carbonyl, carboxyl, or hydroxy groups.

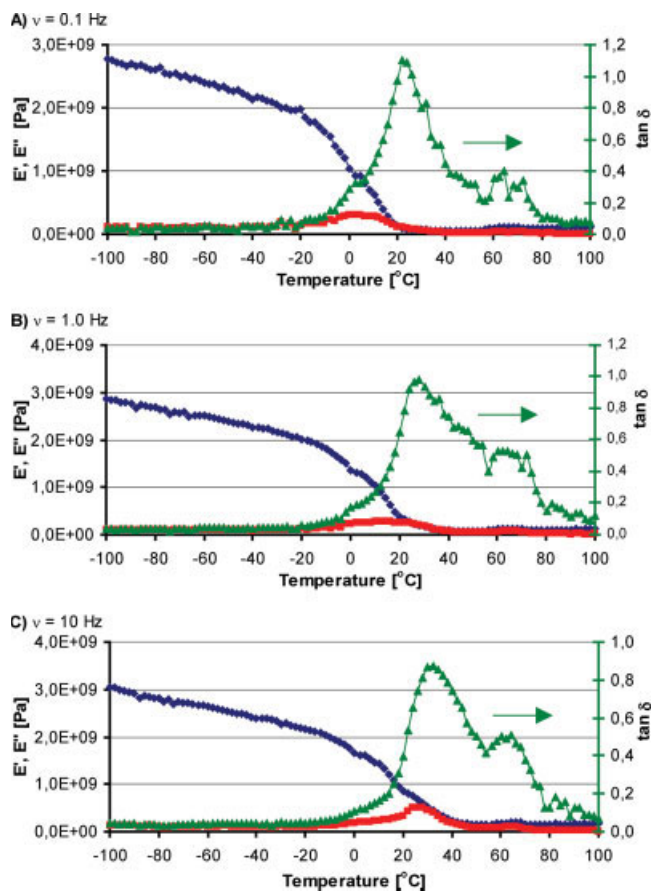
Surface energy and dielectric properties

The surface energy of IR samples changed slightly, especially because of an increase in their polar component (Fig. 12).

The crosslinking and isomerization, resulting in enhanced supermolecular organization, can both change the dispersive component also. A small

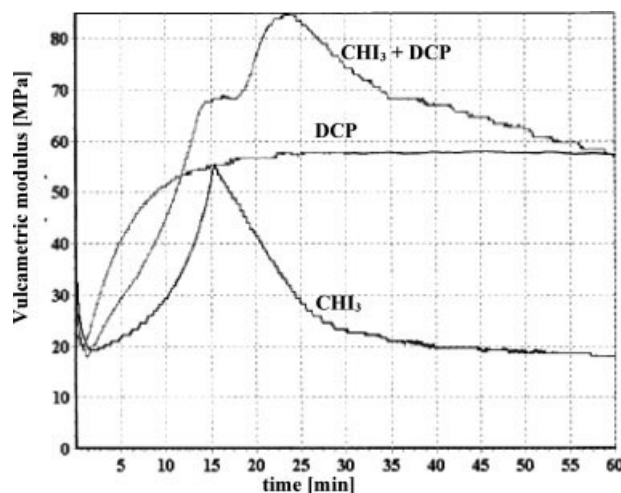


**Figure 9** Influence of CHI<sub>3</sub> vulcanization on the structure of IR as studied by DSC. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

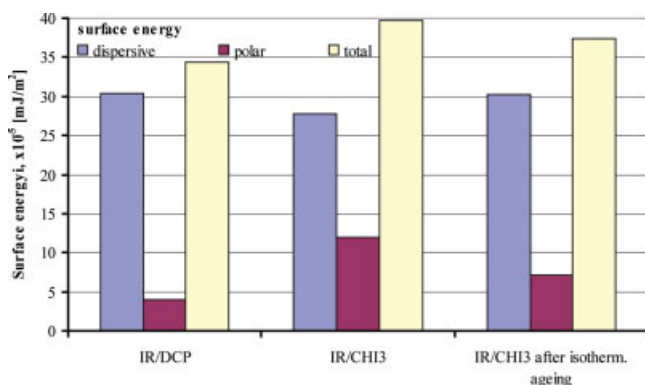


**Figure 10** DMTA spectra of CHI<sub>3</sub> vulcanizates of IR: (A)  $\nu = 0.1$  Hz, (B)  $\nu = 1.0$  Hz, and (C)  $\nu = 10.0$  Hz. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

amount of iodine, detected by chemical microanalysis, is not able to dramatically alter the polar component of the surface energy; however oxidation, accompanying the modification, is likely to be a reason.



**Figure 11** Vulcanization kinetics of IR.

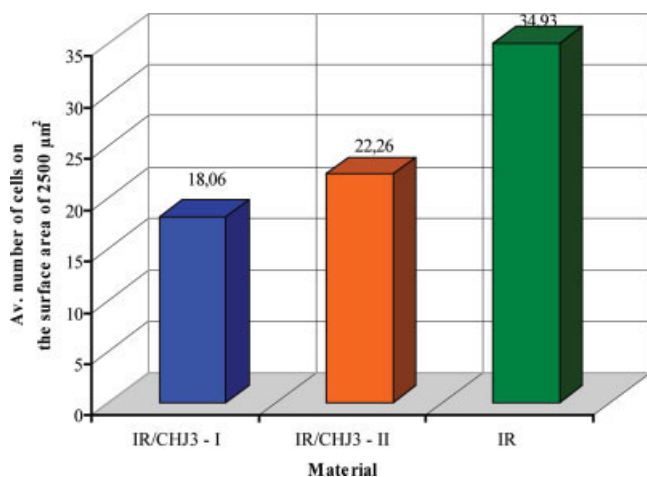


**Figure 12** Surface energy of IR vulcanizates. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

The volume resistance of polyisoprene modified with  $\text{CHI}_3$  does not change significantly. It can be explained by a high extent of crosslinking produced by the postvulcanization oxidation, possibly blocking partially conjugated double-bond structures of macromolecular chains (see the previously postulated mechanisms of modification/crosslinking) from cooperation with iodine species in a charge transfer.<sup>32</sup>

#### Bacteriostaticity

The modification considerably improves the bacteriostaticity of rubber, which has to be mainly associated with the strong hydrophilization of its surface. Despite about a 20% variation between specimens I and II, the greater than 50% depreciation in the number of bacteria present on the surface of  $\text{CHI}_3$  vulcanizates in comparison with a peroxide one is apparent (Fig. 13).



**Figure 13** Bacteriostaticity of IR vulcanizates. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Another reason that has to be taken into account when we are trying to explain this is an increase in the surface microroughness of the vulcanizates. Iodine vulcanization does not result in such an increase in the microroughness, which could affect contact-angle data; however, apart from killing, it can influence the accommodation of 5- $\mu\text{m}$  bacteria on the material surface.

## CONCLUSIONS

$\text{CHI}_3$  can be effectively applied to the modification/crosslinking of diene rubbers. The mechanism of the chemical reaction between rubbers and  $\text{CHI}_3$  is mainly of a radical character. Throughout the elastomers studied, IR was found to exhibit the highest reactivity toward  $\text{CHI}_3$ , although the kinetics of the  $\text{CHI}_3$  vulcanization of IR differ significantly from the others. The modification of IR with a relatively small amount of  $\text{CHI}_3$  changes significantly the properties of the elastomer. Apart from a considerable degree of crosslinking of *cis*-macromolecules taking place, *cis*-*trans* isomerization is one of the main results of the modification. A significant hardening of the material after vulcanization, resulting from thermal aging, can be explained by its additional crosslinking with oxygen species. The modification of IR by an admixing of  $\text{CHI}_3$  leads to an alternative thermoplastic material, which exhibits higher surface energy and bacteriostaticity, for new potential fields of application.<sup>33</sup>

## References

- Fettes, E. M. *Chemical Reactions of Polymers*; Mir: Moscow, 1967; Vols. 1 and 2.
- Yurovskii, V. S.; Krasnov, A. P.; Afonicheva, O. V.; Komornitskii, V. K.; Pashkina, T. I. *Kautsch Rezina* 1999, 1, 23.
- Dogadkin, B. A. *Chemistry of Elastomers*; WNT: Warsaw, 1976.
- Schildknecht, C. E. *Vinyl Polymers*; PWTech.: Warsaw, 1956; pp 294 and 391.
- Dobrosz, K.; Matysiak, A. *Plastics*; The State Technical Publishers: Warsaw, 1985; p 187.
- Bielinski, D.; Slusarski, L.; Włochowicz, A.; Slusarczyk, C. *J Appl Polym Sci* 1998, 67, 501.
- Polish Farmakopea, 4th ed.; Polish Pharmaceutical Society: Warsaw, 1993; Vol. 2, p 636.
- Rubber Technologist's Handbook*; De, S. K.; White, J. R., Eds.; Rapra Technology: Shawbury, United Kingdom, 2001; Chapter 2.10.
- Barson, C. A.; Bevington, J. C.; Hunt, B. J. *Polymer* 1996, 37, 5699.
- Owen, E. D.; Al-Moh'd, H. S. M. *Polymer* 1997, 38, 3533.
- Dai, L.; White, J. W. *Synth Met* 1995, 69, 563.
- Yildirim, P.; Erman, B. *Synth Met* 1997, 88, 231.
- Kwiatkowski, W. M.Sc. Thesis, Technical University of Lodz, 2005; Chapter 6.1.
- Atkins, P. W. *Concepts in Physical Chemistry*; Oxford University Press: London, 1995.
- Flory, P. J. *J Chem Phys* 1943, 11, 521.

16. Bielinski, D.; Slusarski, L.; Affrossman, S.; O'Neil, S.; Pethrick, R. A. *J Appl Polym Sci* 1997, 64, 1927.
17. Tanaka, Y. *J Appl Polym Sci Appl Polym Symp* 1989, 44, 1.
18. Moneva, L.; Dimitrov, R. *Kautsch Gummi Kunstst* 1991, 44, 330.
19. Salomon, G.; van der Schee, A. C.; Katelaar, J. A.; van Eyk, B. *J Polym Sci* 1954, 14, 181.
20. [www.micromaterials.co.uk](http://www.micromaterials.co.uk).
21. Kuczynski, J. *Polimery* 1990, 35, 219.
22. Yang, N. C.; Marolewski, T. A. *J Am Chem Soc* 1968, 90, 5644.
23. Oliver, J. P.; Rao, U. V. *J Org Chem* 1966, 31, 2696.
24. Steel, C.; Zard, R.; Hurwitz, P.; Cohen, S. G. *J Am Chem Soc* 1964, 86, 679.
25. Prygiel, A.; Cander-Felczynska, J.; Slusarski, L. *Polimery* 1991, 36, 143.
26. Dostovalova, V. I.; Velichko, F. K.; Amriev, R. A.; Bondarenko, O. P.; Freidlina, R. K. *Izv Akad Nauk Ser Kim* 1987, 12, 2719.
27. Kiura, T.; Fujita, M.; Sohmiya, H.; Ando, T. *Ultrason Sonochem* 2002, 9, 205.
28. Rado, R. *Polymer Reactions Initiated by Peroxides*; WNT: Warsaw, 1974.
29. Eskina, M. V.; Khachaturov, A. S.; Krentsel, L. B.; Litmanovitch, D. A. *Eur Polym J* 1990, 26, 181.
30. Golub, M.; Heller, G. *Can J Chem* 1963, 41, 937.
31. Brydson, J. A. *Rubber Chemistry*; Applied Science: London, 1978; p 128.
32. Chiang, C. K.; Druy, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmid, A. G.; Park, Y. W.; Shirakawa, H. *J Am Chem Soc* 1978, 100, 1013.
33. Bieliński, D. M.; Ślusarski, L.; Głąb, P. *Pol. Pat. P-376571* (2005).