

# Solid-State $^{13}\text{C}$ -NMR Investigations of Crosslinked Structure Modifications in Elastomers during Heating Treatment

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**ABSTRACT:** The chemical modifications occurring during the thermal degradation of sulfur-cured natural rubber were investigated with  $^{13}\text{C}$ -NMR. Samples of vulcanized rubbers were heat-aged at 70°C under an air (oxidative) environment for 3, 7, and 21 days. Changes were analyzed by the measurement of the variations of the concentrations of dif-

ferent C-S<sub>x</sub>-C crosslinked structures during the thermooxidative process through the intensity of the related NMR lines in the 10–70-ppm range. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 3–8, 2003

**Key words:** rubber; NMR; degradation

## INTRODUCTION

The literature contains much information on the degradation of rubber by different agents, such as oxidation and heat. Most degradation analyses are performed with physical or chemical methods on a macroscopic level. The pioneering works of Mori and Koenig<sup>1</sup> and Gronski and coworkers<sup>2,3</sup> showed the efficiency of high-resolution, solid-state, magic-angle spinning (MAS)  $^{13}\text{C}$ -NMR spectroscopy for the characterization of natural rubber (NR) vulcanizates on the molecular level. Our aim in this study was to use this method to try to clarify the network structure behavior of sulfur vulcanizates under thermooxidative conditions. Some preliminary results were previously published.<sup>4</sup> As the physical properties of these materials are determined to a large extent by the distribution of C-S<sub>x</sub>-C sulfidic crosslinks of various ranks  $x$ , both conventional vulcanization (CV) and efficient vulcanization (EV) systems were studied. According to the literature, in the former case, the vulcanizate contains mostly polysulfidic crosslinks; in the later case, there are mainly monosulfidic crosslinks.

In this study, the changes in the concentrations of different C-S<sub>x</sub>-C crosslinked structures were examined for the two classes of vulcanizates as a function of the oxidative treatment. The results were compared with those reported in a recent work by Parker and Koenig.<sup>5</sup>

## EXPERIMENTAL

### Vulcanizates

The NR grade used was SMR-CV60. Two batches were prepared in a laboratory two-roll mill. The formulations are given in Table I. No antioxidant was added to magnify the oxidative effects. The two systems were cured at 160°C. The curing times (38 and 18.75 min for the EV and CV systems, respectively) were established by the usual rheometry according to ISO Standard 3417 and corresponded to  $T_{100}$  (100% of the maximum measured torque). Air-aging accelerated tests were achieved on 2-mm-thick pieces in a multicellular oven at 70°C for 3, 7, and 21 days.

### NMR measurements

The  $^{13}\text{C}$ -NMR spectra were recorded at room temperature on a Bruker Avance 300 spectrometer at 75.47 MHz with a 4-mm cross-polarization (CP)/MAS probe.

Figure 1 shows three different  $^{13}\text{C}$ -NMR spectra for the NR sample obtained with a pulse width of 90° (4

TABLE I  
Formulations

	EV	CV
NR	100	100
ZnO	3	3
Stearic acid	1	1
Sulfur	0.3	6
DTDM <sup>a</sup>	6	—
DPG <sup>b</sup>	—	1

<sup>a</sup> 4,4'-Dithiodimorpholine.

<sup>b</sup> Diphenylguanidine.

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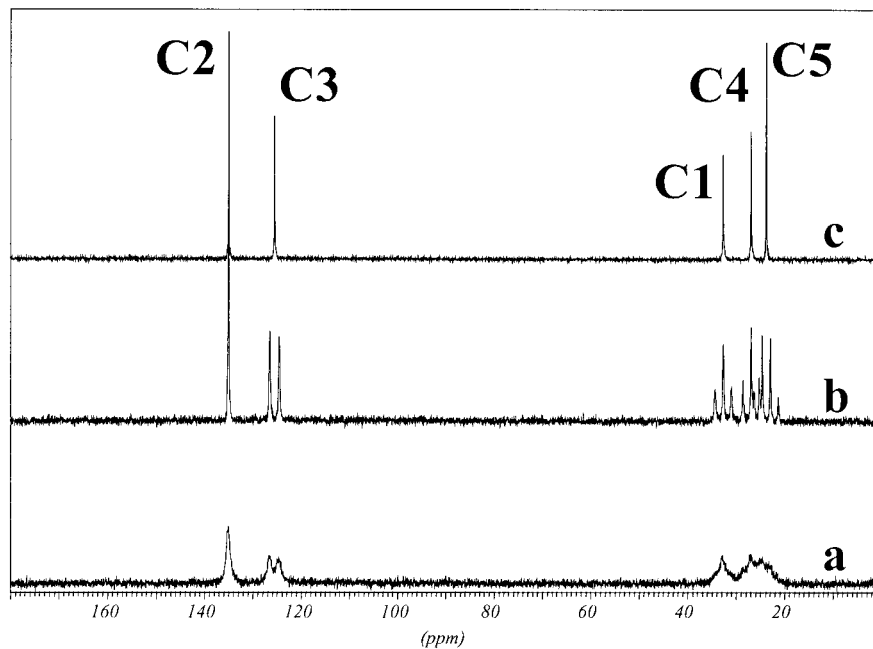


Figure 1  $^{13}\text{C}$ -NMR spectra of NR: (a) static, (b) MAS, and (c) MAS and  $^1\text{H}$  decoupling.

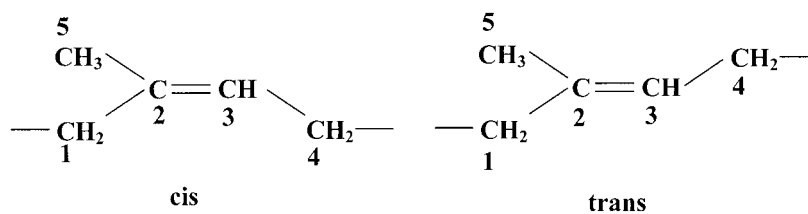


Figure 2 1,4-Polyisoprene units (cis and trans).

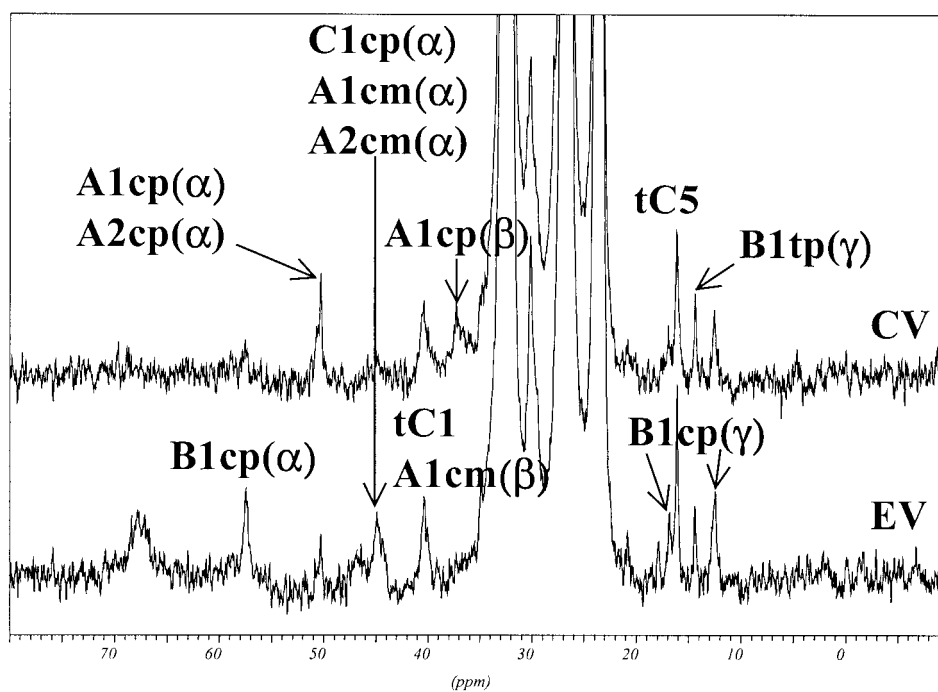


Figure 3  $^{13}\text{C}$ -NMR spectra of sulfur-vulcanized NR for EV and CV systems.

TABLE II  
Chemical Shift and Nomenclature of Structures  
Occurring on Vulcanization of NR  
in CV and EV Systems

Chemical Shift (ppm)	CV	EV	Structure
12.5	+	+	B1cp( $\gamma$ )
14.4	+	+	B1tp( $\gamma$ )
16.1	+	+	tC-5
16.9	+	+	B1cp( $\gamma$ )
37.3	+		A1cp( $\beta$ )
40.4	+	+	tC-1, A1cm( $\beta$ )
44.8		+	C1cp( $\alpha$ ), A1cm( $\alpha$ ), A2cm( $\alpha$ )
50.4	+	+	A1cp( $\alpha$ ), A2cp( $\alpha$ )
57.6		+	B1cp( $\alpha$ )

A + sign indicates the existence of a line in the related MMR Spectrum.

$\mu$ s) applied with a repetition time of 6 s. A spectral width of 20 kHz and 16K data points were used for data collection. At the bottom of the figure, the spectrum obtained with a static sample is presented. The lines are broad but less so than those in solid glassy polymers. In the middle, the MAS (10 kHz) spectrum gives evidence for multiplets that are fingerprints of  $J$  couplings between  $^1\text{H}$  and  $^{13}\text{C}$ . At the top is shown the high-resolution spectrum obtained from a combina-

tion of MAS (10 kHz) and  $^1\text{H}$  decoupling (60-kHz radio-frequency field strength). The five NMR lines are connected to the five  $^{13}\text{C}$  atoms of the monomer unit.

All the experiments discussed in this article were achieved in the last way with 10,000 transients. The spectra were calibrated with respect to the  $\text{CH}_2$  ( $\gamma$ ) resonance of the *cis*-1,4-isoprene unit (Fig. 2), which was set to 32.5 ppm to facilitate a comparison with the chemical-shift determinations in previous works by Mori and Koenig<sup>1</sup> and Gronski and coworkers.<sup>2,3</sup>

The dominant resonances at 134.8, 125.3, 32.5, 26.7, and 23.6 ppm were related to the five carbon atoms C1, C2, C3, C4, and C5, respectively, of the *cis*-1,4-isoprene unit (Fig. 2). Extra, very small resonances near 16 and 40 ppm allowed us to evaluate the trans-isomer proportion to less than 1%. This may be seen as the threshold of detection.

Line widths and intensities were determined for all the samples with WIN-NMR Bruker software.

## RESULTS AND DISCUSSION

### Vulcanization

During the vulcanization, several different crosslinked structures were formed. They could be observed in the

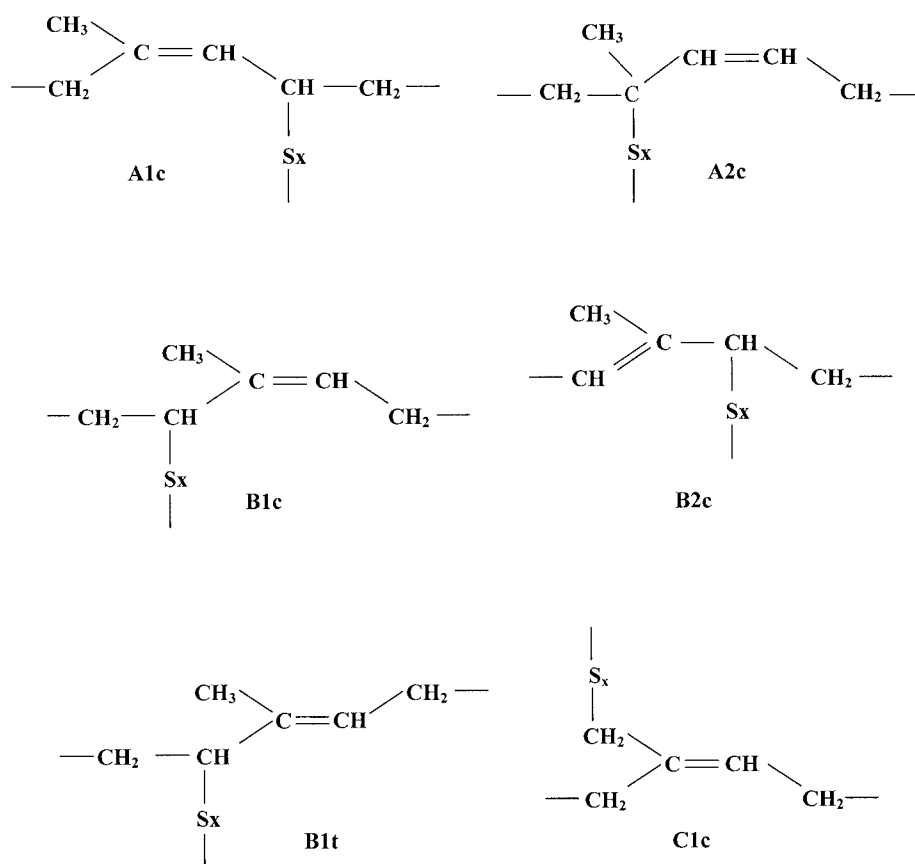


Figure 4 Possible structures occurring during the vulcanization of NR.

$^{13}\text{C}$ -NMR spectra of the 100% cure systems in the range 10–70 ppm, as shown in Figure 3.

In the NMR spectrum, only monosulfidic and polysulfidic linkages could be differentiated.<sup>1</sup> The fingerprints (line position and related structure) of the two types of vulcanization were quite different. They are summarized in Table II, with the main differences bolded.

In the labeling of the peaks, the first letter and number represent the structure (Fig. 4), with c or t for cis or trans isomer and p or m for polylinkages or monolinkage, and the Greek letter is the proximity of the crosslinked carbon. The symbols tC-1 and tC-5 stand for the carbon numbers 1 and 5 of the trans isomer.

### Thermal heating under air

Aging effects were investigated in detail on the vulcanizates in the high state of cure through the variation of the relative intensities of the crosslink resonances and the line widths of the C1, C2, C3, C4, and C5 resonances directly related to the polyisoprene network.

In Figure 5(a,b) are presented the variations of the line widths of these NMR lines related to the C1, C2, C3, C4, and C5 carbons for the CV and EV systems, respectively.

Figures 6 and 7 show the evolution the NMR line intensities related to the various crosslinked carbon peaks versus the heating time (0, 3, 7, or 21 days) for the CV and EV systems, respectively.

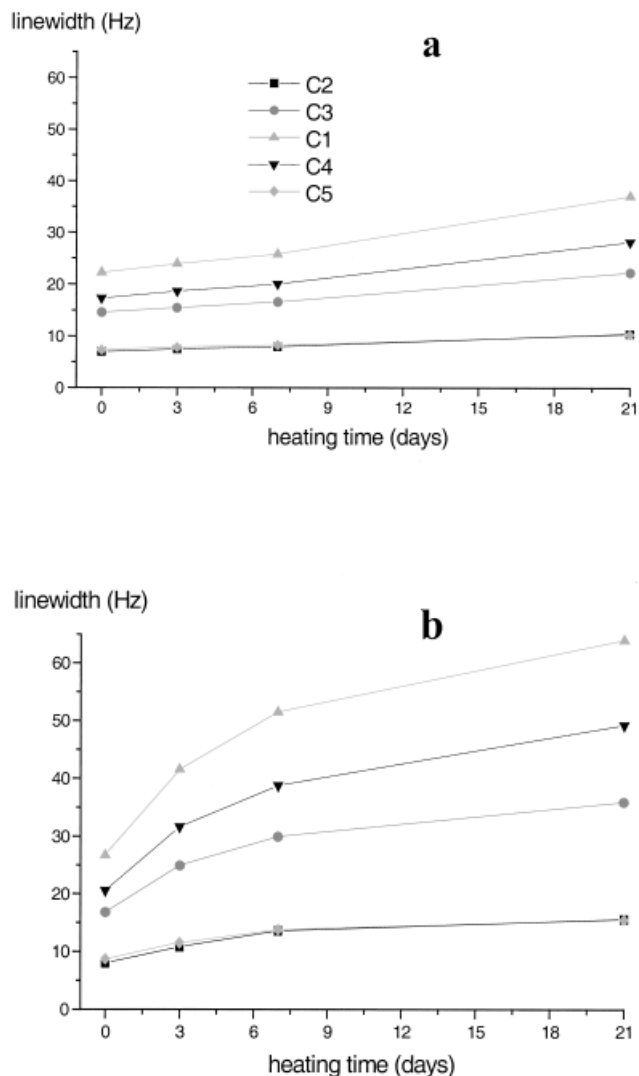
### Decomposition of the polysulfidic linkages

According to a previous attribution by Koenig,<sup>1</sup> these crosslinks correspond to resonances at 12.5, 14.4, 16.9, 37.3, 50.4, and 57.6 ppm.

For the CV system, the NMR peaks at 37.3 and 50.4 ppm, related to A1cp and A2cp carbons, showed the fastest degradation rate. They nearly disappeared after 3 days of heating. In the same time, an increase in A-type monolinkages was observed that could indicate that polylinkages were reduced with respect to monolinkages, and a new peak appeared at 57.6 ppm that was previously attributed to B1cp carbons. This result raises the question of peak assignments for the 57.6-ppm structure, which could be related to B1cm structures.

The degradation rate for the B1cp (12.5, 16.9, and 57.6-ppm) structures was similar in the CV and EV systems but slower than that for the A polylinkages. These B linkages disappeared only after more than 7 days of heating treatment.

However, for the CV and EV systems, no degradation of the 14.4-ppm B1tp structure was observed even



**Figure 5** Line-width variations under thermal aging: (a) EV and (b) CV systems.

for the longest heating time. This result makes questionable the previous attribution of the 14.4-ppm peak to a polysulfidic linkage. A similar assumption was recently suggested.<sup>4</sup>

### Decomposition of the monosulfidic linkages

The monosulfidic linkages were observed at 40.4 ppm and 44.8 ppm. As the 40.4-ppm peak was also due to the C1 carbon of the trans isomer, we only discuss the latter one. It was seen only in EV systems. Its degradation rate was rather low because it disappeared for a heating time longer than 7 days. This rate was the same as that observed for the B1cp structures. This result reinforces the question about the previous attribution of the corresponding peaks.

### Cis–trans isomerization

The results showed that the 16.1-ppm (tC-5) line was unaffected by the thermal treatment. The 40.4-

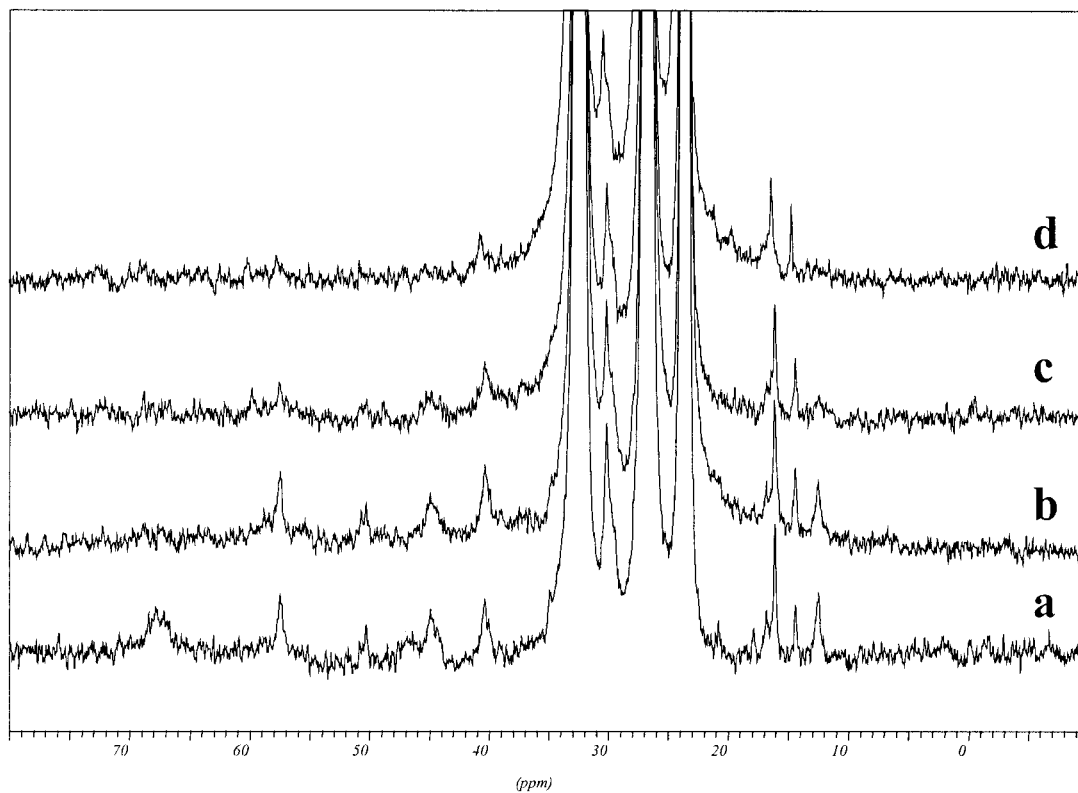


Figure 6  $^{13}\text{C}$ -NMR spectra under thermal aging for an EV system: (a) 0, (b) 3, (c) 7, and (d) 21 days.

ppm [tC-1, A1cm( $\beta$ )] line intensity decreased, but this may be attributed to the destruction of the sulfidic A1cm( $\beta$ ) crosslinks. These peaks, together

with the 14.4-ppm peak, were the only structures that remained after 21 days of heating. It may be concluded that the structures resulting from the

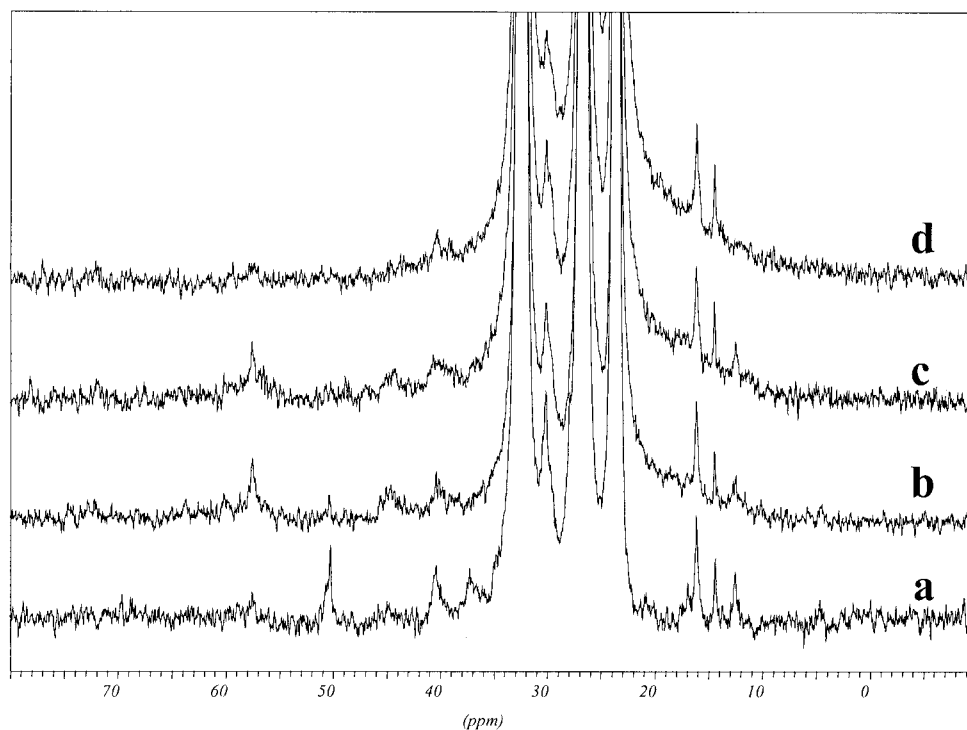


Figure 7  $^{13}\text{C}$ -NMR spectra under thermal aging for a CV system: (a) 0, (b) 3, (c) 7, and (d) 21 days.

cis–trans isomerization were insensitive to the thermooxidative treatment.

### Line broadening

During the thermal treatment, the C1, C2, C3, C4, and C5 resonances directly related to the polyisoprene network became broader, but the effect was much more pronounced for CV systems than that for EV systems. Moreover, the broadening occurred in quite different manners for the two types of vulcanizates: for the EV systems, the relative line broadening rate was nearly constant, about 0.02 per day; for the CV system, this rate was much greater for the first heating periods (0.1–0.19 between 0 and 3 days and 0.07–0.09 between 3 and 7 days) and was quite similar for the last period. The lines that were the most strongly affected by broadening were connected to the C1 and C4 carbons.

If the line broadening is assumed to be related to distributions of isotropic chemical shifts and to dipolar interactions, which may not be completely averaged, these last results mirror an increasing rigidity of the polyisoprene network in agreement with increasing modulus values.

Because thermooxidative treatment leads to the destruction of sulfidic crosslinks, as demonstrated by our measurements and other experimental evidence, the increasing network rigidity must be attributed to crosslinks resulting from the heating process, such as C–C crosslinks resulting from the recombination of macroradicals. That more important broadening was found in the CV system rather than in the EV system can be related to the larger measured crosslink density in the former vulcanizate.

### CONCLUSIONS

The experimental results showed that monosulfidic and B polysulfidic crosslinked structures had better stability under thermooxidative aging than A polysulfidic structures. The A polysulfidic linkages decomposed within 3 days of treatment into monolinkages. The cis–trans-isomerization structures were the most stable.

From the line broadening, which was related to the increasing rigidity of the polyisoprene network and the destruction of the sulfidic crosslinks, it may be suggested that the formation of C–C crosslinks took place in the first period of the heating treatment, especially for the CV system. Nevertheless, they were not found in our experiments because of the long spin–lattice relaxation ( $T_1$ ) of the related  $^{13}\text{C}$  nuclei.

This study showed the efficiency of solid-state  $^{13}\text{C}$ -NMR for studying vulcanizate structures on the microscopic level. Moreover, some of the results gave evidence for discrepancies with some previous peak attributions, especially the B1cp ones (12, 17, and 57 ppm), which, according to our results, behaved instead as monosulfidic crosslinks. This requires further investigation.

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