Vulcanization of Butadiene Rubber by Means of Cyclic Disulfides. 3. A 2D Solid State HRMAS NMR Study on Accelerated Sulfur Vulcanizates of BR Rubber

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ABSTRACT: Sulfur vulcanizates of high *cis*-butadiene rubber (BR) obtained by using different curing systems such as conventional (CBS) and efficient sulfur (sulfur donor, TMTD) vulcanizing systems were investigated in detail using high-resolution magic angle spinning (HRMAS) solid state NMR spectroscopy in order to identify the type of cross-linking sequence and overall molecular structure. DEPT-135 HRMAS spectra recorded at 60 °C provided the different ^{13}C-resonances; interpretation of the HETCOR HRMAS spectra yielded the corresponding ^{1}H frequencies. Direct and long-range through bond homonuclear connectivities were obtained from COSY and TOCSY HRMAS experiments, whereas NOESY HRMAS experiments provided the dipolar through space interactions. Comparison of these results with solution NMR data on a BR model compound vulcanizate led to the elucidation of the entire network structure. The ^{13}C chemical shifts found experimentally appeared to be in good agreement with chemical shifts calculated for the proposed structure. Using the described vulcanizing systems, it was shown that cross-linking proceeds by means of α *substitution* rather than *addition* in contrast with our studies on cyclic disulfides based vulcanization reactions of BR. By using CBS or TMTD as vulcanizing agents, differentiation in sulfur cross-link length could be established. Moreover, the presence of several *cyclic sulfides* in the vulcanizates was observed and a mechanism for their formation is suggested.

Introduction

The elucidation of cross-link structures present in sulfur vulcanized high *cis*-1,4-polybutadiene (BR) is important for the study of structure−property relationships of BR vulcanizates. The generation of evidence for the presence and nature of cross-link moieties, formed either by means of *addition* at or *substitution* α to the olefinic double bonds, is in this perspective probably the most difficult yet very important problem to address.[1]

The use of 2D high-resolution magic angle spinning (HRMAS) solid state NMR techniques,[2] allowed us to gain insight into both the structure and the underlying mechanism of cross-link formation on a molecular level. Previous results on the vulcanization of a model compound (*cis*,*cis*,*cis*-1,5,9-cyclododecatriene, *ccc*-1,5,9-CDT) appeared to be in good agreement with 2D solution NMR data of a BR graft,[3] indicating the formation of alkyl cross-links. NMR analysis led to the entire elucidation of the molecular structure and it was concluded that addition had occurred instead of α substitution. When high *cis*-BR was vulcanized with cyclic disulfides, alkyl cross-links were also formed, probably by addition to the double bonds.[4]

On the other hand, in accelerated sulfur vulcanization, the formation of alkenyl cross-links is greatly enhanced due to increased α substitution, as shown by Koenig and co-workers.[5] These results suggest that different reaction mechanisms must operate, depending on the reagents used and/or the reaction conditions employed.

Table 1. Compounds Used in the Accelerated Sulfur Vulcanization of *cis*-1,4-BR

component	composition **1** (phr)	composition **2** (phr)
BR	100	100
CBS	4	
TMTD		10
S_8	8	
ZnO	5	5
SA	5	

To study the effect of the type of curing system, the conventional (*N*-cyclohexyl-2-*b*enzothiazole *s*ulfenamide, CBS) and efficient sulfur (sulfur donor, *t*etra*m*ethyl*t*hiuram *d*isulfide, TMTD) vulcanizing systems were investigated in more detail by exploiting several 2D HRMAS solid state NMR techniques. The results obtained will be compared with and serve as part of our ongoing research on the structural modification of cross-linking and the corresponding material properties.

Experimental Section

Materials. Stearic acid (SA, Aldrich), sublimated sulfur (S_8, Merck), zinc oxide (Merck), *N*-cyclohexyl-2-benzothiazole sulfenamide (Perkacit-CBS-c, Flexsys), and tetramethylthiuram disulfide (Perkacit-TMTD-c, Flexsys) were used without further purification. High *cis*-BR (Cariflex BR 1200) was obtained from Shell (96.5% cis, 1.5% trans, and 2% vinyl-content, M_n = 140 000, M_w = 393 000 and M_z = 770 000).

Vulcanization of BR. The compound recipes used are given in Table 1. Sample preparation was carried out as described previously.[3] The t_{90} times were determined from vulcametry and used in the vulcanization of the samples. The CBS and TMTD samples were vulcanized at a pressure of 15 MPa and at temperatures of 150 and 140 °C, respectively.

NMR Spectroscopy and ^{13}C Chemical Shift Calculations. NMR experiments were performed using a Varian Unity

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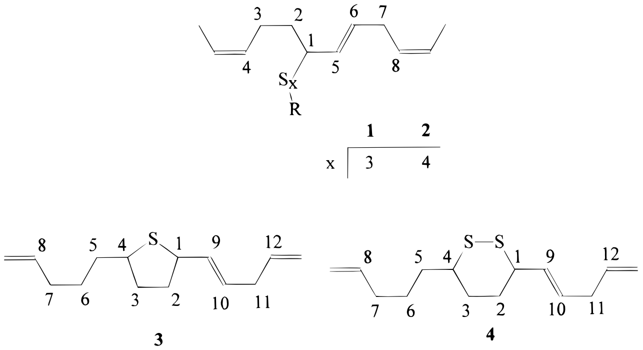


Figure 1. Possible structures in the CBS BR vulcanizate as found using NMR.

400 WB NMR spectrometer operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively. ^{1}H, ^{13}C, COSY,[6] DQF−COSY,[7] clean-TOCSY (MLEV17),[8] NOESY,[9] HETCOR,[10] and HMQC[11] NMR experiments were used for the assignment of the ^{1}H and ^{13}C resonances. All 2D spectra were collected as 2D hypercomplex data.[12] After weighting with shifted sine−bell functions, the COSY and HETCOR data were Fourier transformed in the absolute value mode while the DQF−COSY, clean-TOCSY (MLEV17), and HMQC data were transformed in the phase-sensitive mode. All data processing was performed using standard Varian VnmrS/VnmrX software packages.

For the solid state NMR experiments, a Jakobsen-design probehead was used in combination with a Sørensen heating apparatus and a Varian rotor speed control unit. The 5 mm ZrO_2 spinners were spun under the magic angle with a speed of 4 kHz and a temperature of 60 °C. Typical $\pi/2$ pulse angles ranged from 4.4 to 5.2 μs and from 5.5 to 6.7 μs for ^{1}H and ^{13}C, respectively. The ^{13}C spectra of dry vulcanizates were recorded after careful molding using a recycle time of 5 s or more and gated high power decoupling (GHPD) during acquisition. Usually, the accumulation of 3000−5000 transients resulted in DEPT-135 and ^{13}C spectra with good signal-to-noise ratios. High quality HETCOR HRMAS spectra were obtained after acquiring 512 increments with 800−1200 scans per increment and 4096 data points in both dimensions. All ^{1}H NMR 2D experiments were performed on vulcanizates swollen in $C_2D_2Cl_4$, using a recycle time of 2 s. The deuterium signal was used for locking by tuning the X-channel on the deuterium frequency. The accumulation of 32−64 scans was sufficient to obtain good signal-to-noise ^{1}H spectra. COSY, DQF−COSY, and TOCSY HRMAS NMR spectra were accumulated with 512 increments and 32 scans per increment, typically. In the clean-TOCSY experiments the mixing time of the MLEV17-pulse was arrayed between 30 and 100 ms. The T_1 noise in the phase-sensitive experiments, caused by the two large peaks due to the BR main chain, could be reduced through *simultaneous* selective irradiation of these peaks.[3] The aliphatic CH_2 peak was irradiated using a 500 ms presaturation pulse while the intensity of the olefinic CH peak was reduced using decoupler irradiation.

In addition to the experiments described, NOESY (*n*uclear *O*verhauser *e*nhancement *s*pectroscop*y*) HRMAS NMR spectra, recorded in order to extract through space interactions, were acquired at 10 °C with 512 increments and 32 scans per increment.[13] The mixing time was arrayed between 100 and 200 ms. NOE cross-peaks result from through space dipolar interactions.[13] The intensity is determined by several factors including the internuclear distance.[14]

The ^{13}C chemical shifts were calculated using the commercially available software program ACD/CNMR version 2.51.

Assignment of Structures in the CBS BR Vulcanizate

During the elucidation of the molecular networks obtained after cross-linking, it became evident that *non*-cross-linked main chain modifications were also formed.

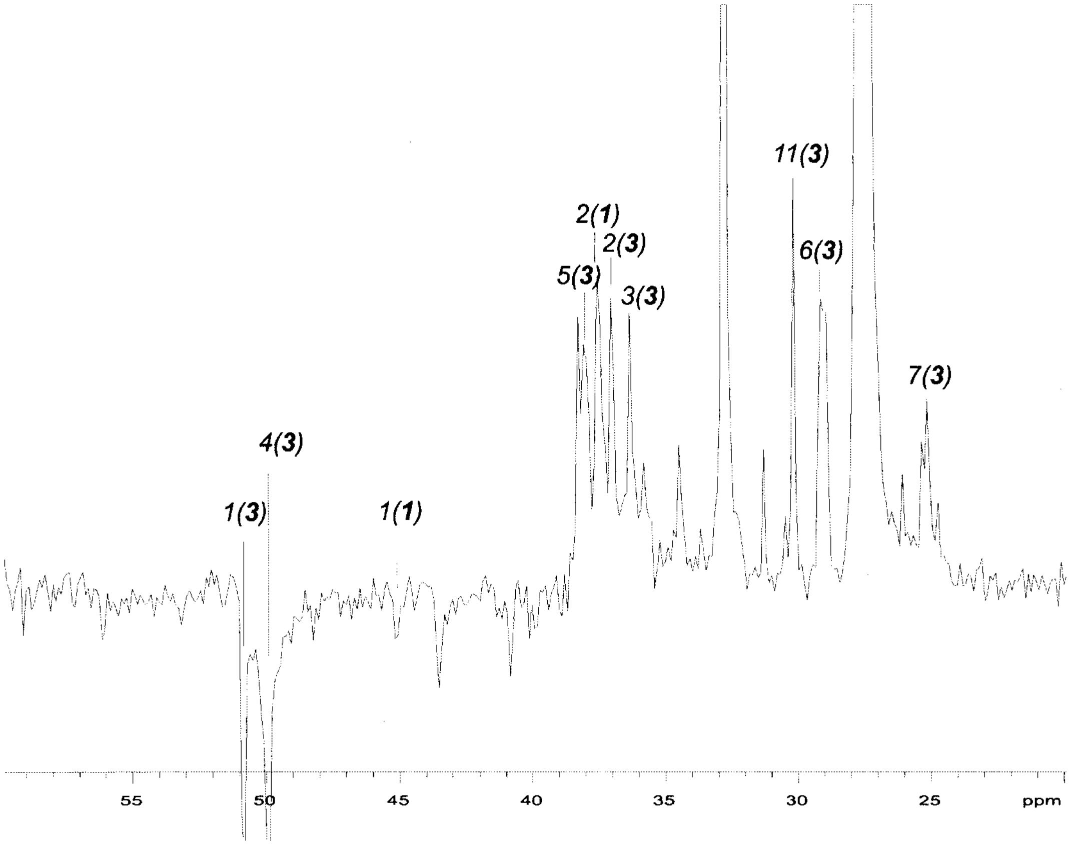


Figure 2. ^{13}C DEPT-135 HRMAS spectrum of the CBS BR vulcanizate recorded at 60 °C using J_{CH} = 127 Hz, typically. Structure selection is given in parentheses. Spectrum shows CH/CH_3 down and CH_2 up.

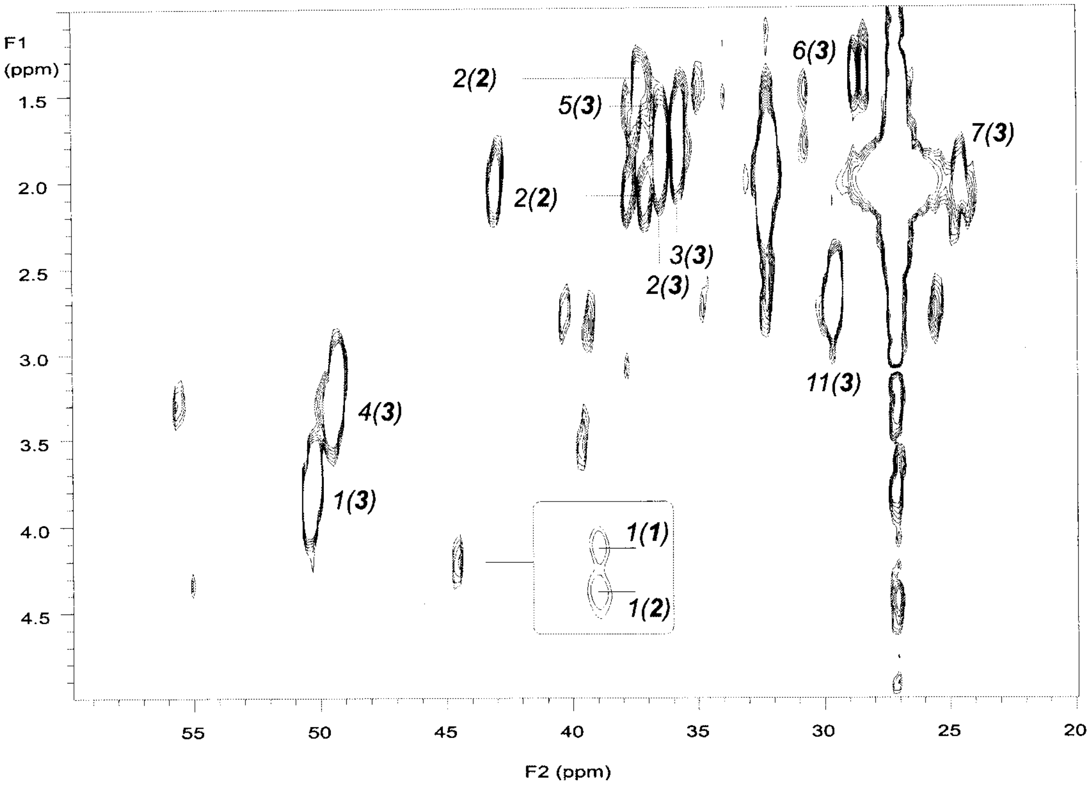


Figure 3. HETCOR HRMAS spectrum of the CBS BR vulcanizate recorded at 60 °C using J_{CH} = 127 Hz, typically. Relevant signals are given for structures **1** (**2**) and **3**. Structure selection is given in parentheses.

To discriminate between these two, they will be treated separately.

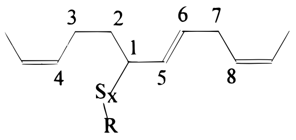
Cross-Linking. To elucidate the cross-link structures in the CBS BR vulcanizate, the same NMR strategy was used as for the assignment of the cross-link structures in the various cyclic disulfide BR vulcanizates described previously.[3,4] Various cross-link structures have been found for the conventional sulfur vulcanization of BR or corresponding model olefins. It is possible that, in the CBS BR vulcanizate studied, cross-links are present resulting from addition, α substitution, vicinal cross-linking, or α substitution accompanied by allylic rearrangement. The NMR data suggested the formation of structures **1** and **2** formed during the CBS vulcanization (Figure 1). Also cyclic structures **3** and **4** were identified and will be treated separately (vide infra).

DEPT-135 HRMAS spectroscopy was utilized to extract the newly introduced methine and methylene resonances (Figure 2). Because of the large resemblance between structures **1** and **2** on one hand and **3** and **4** on the other, correlations identified for **1** and **3** are given in parentheses for comparison purposes.

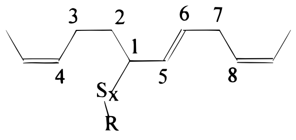
It should be noted that the assignment of the defined spin system to either structure **1** or **2** is arbitrary, whereas the assignment of spin systems to structure **3** or **4** is not.

Several resonances were visible in the methine area between δ 35.0 and δ 60.0 ppm. Combining the results of various DEPT-135 spectra with the 1D ^{1}H NMR data showed that the ^{13}C methine resonances 1 of structures **1** and **2** coincided at δ 44.9 ppm (Table 2). This is most clearly visible in the HETCOR HRMAS spectra, which showed for this methine ^{13}C resonance at δ 44.9 ppm two faintly distinct and uncorrelated proton signals at δ 4.14 and δ 4.19 ppm (Figure 3, inset). Hence, this single ^{13}C resonance (in fact, two coalescing signals) should be attributed to two (slightly) chemically different methine groups.

Table 2. ^{1}H and ^{13}C Chemical Shift Assignment of Structures 1 and 2[a]



1 x = 3



2 x = 4

	assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	1	4.14	44.9	46.6
	2	2.14/1.45	32.8	32.4
	3	1.69	27.6	20.7
	4	5.49	130.4	133.0
	5	5.36	132.8	133.1
	6	5.43	129.1	130.7
	7	2.72	30.0	31.8
	8	5.31	131.6	128.4
2	1	4.19	44.9	47.8
	2	2.02/1.85	37.5	31.3
	3	1.51	31.3	20.7
	4	5.16	130.2	133.0
	5	5.31	130.2	136.5
	6	5.42	128.4	130.7
	7	2.71	26.1	31.9
	8	5.21	129.7	128.4

[a] The structure assignment **1** or **2** is chosen arbitrarily (see text for explanation).

The COSY HRMAS spectrum shown in Figure 4 provided two through bond correlations from proton 1 of structure **1** at δ 4.14 ppm to the neighboring diastereomeric protons 2 at δ 2.14/1.45 ppm, which are anisochronous, and to proton 5 resonating at δ 5.36 ppm. On

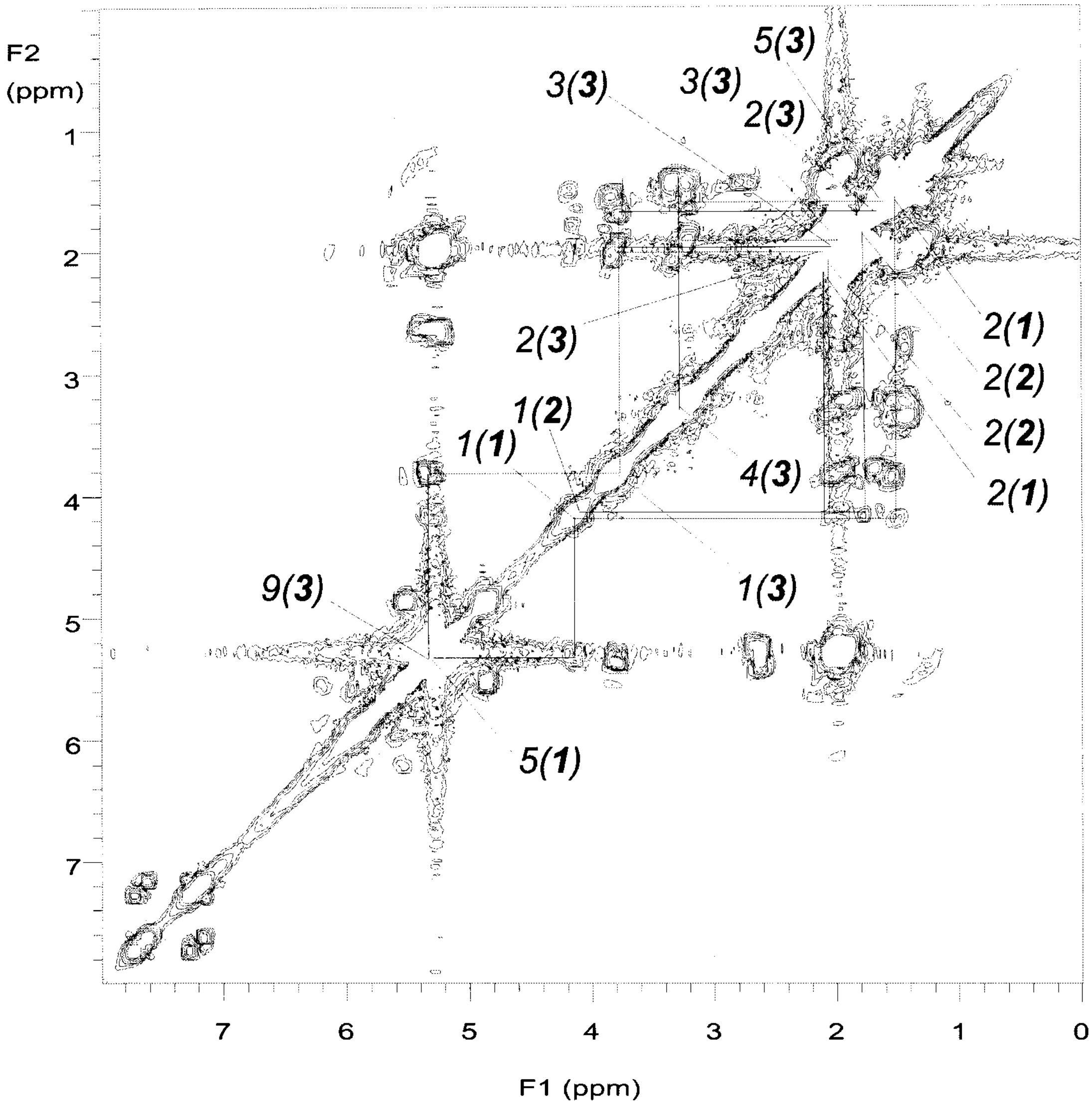


Figure 4. COSY HRMAS spectrum of the CBS BR vulcanizate swollen in $C_2D_2Cl_4$. Relevant signals for structures **1** (**2**) and **3** are selected. Structure selection is given in parentheses.

the basis of these results not only was the formation of an alkenyl methine functionality confirmed but also the presence of structures formed due to addition, α substitution, or vicinal cross-linking could be excluded (vide supra).

The TOCSY spectrum shows, besides somewhat higher resolution compared to the COSY spectrum, the contacts between proton 1 and the protons 2 as well as proton 3 (δ 1.69 ppm) of structure **1**. Several resonances and connectivities belonging to structure **3** were also identified, such as between proton 1 and the protons 4, 9, 10, and 11.

It appeared, unfortunately, not possible to extract the complete cross-link structure from COSY and TOCSY HRMAS (Figure 5) spectra solely, due to severe overlap of several proton resonances in the aliphatic region below δ 2.00 ppm.

NOESY HRMAS spectroscopy proved to be a useful technique in order to overcome this problem and provided conclusive evidence for the assignment of the resonances of protons 1 and the protons 4 and 9, which were recognized as arising from cyclic structure **3** (Figure 6). A NOE correlation was also observed between methine proton 1 and proton 7 residing at δ 2.72 ppm belonging to structure **1**. Several other less relevant contacts were also observed.

COSY HRMAS spectroscopy showed that, for proton 7, only olefinic neighbors were found in accordance with structure **1**, thereby excluding structures formed by means of a straight α substitution (vide supra). Structure **1** could result from α substitution followed by a shift of the double bond, although the exact mechanism of formation remains unclear at date.

The chemical shift assignment of structure **2** (vide supra) was carried out analogously starting from proton 1 residing at δ 4.19 ppm. The resemblance between structures **1** and **2** is clear, and although two separate spin systems can be identified, no conclusive evidence could be generated for the assignment to either structure **1** or **2**. ^{13}C chemical shifts were calculated for cross-links with increasing length x of the sulfur cross-link. The closest agreement between experimentally found and calculated ^{13}C chemical shifts was found for trisulfidic structure **1** and tetrasulfidic structure **2** (Figure 1). It should be noted that the agreement between calculated and experimentally observed chemical shifts was poorer for the alkenyl structures presented above than for alkyl structures shown previously.[3] The influ-

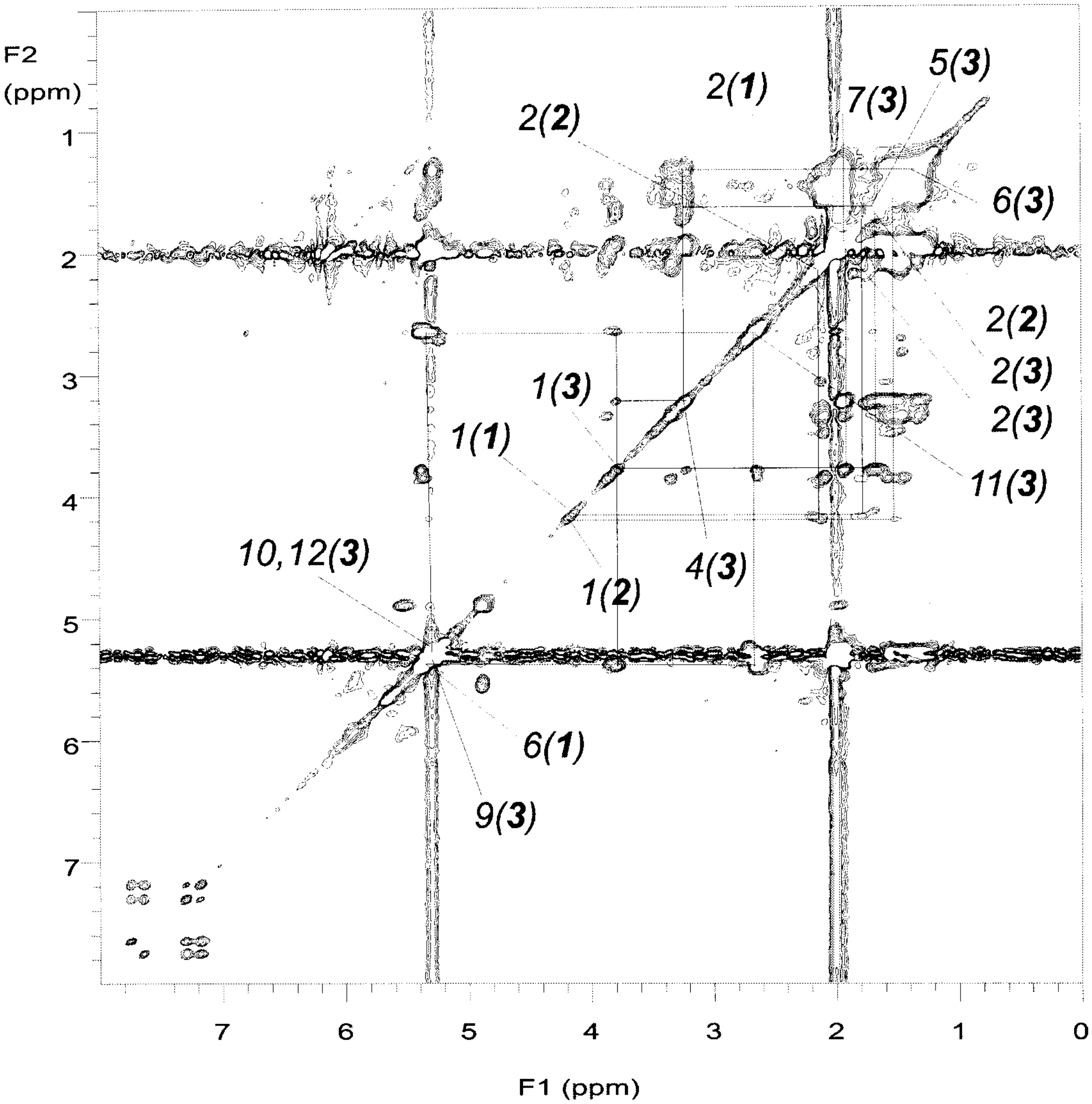


Figure 5. TOCSY HRMAS spectrum of the swollen CBS BR vulcanizate. The spectrum was recorded using $\tau_{mix} = 60$ ms. Relevant signals for structures **1** (**2**) and **3** are selected. Structure selection is given in parentheses.

ence of the longer and more electronegative sulfur cross-link can less easily be calculated. The ^{1}H and ^{13}C chemical shift assignments of cross-link structures **1** and **2** are summarized in Table 2.

Cyclic Sulfide Main Chain Modifications. Cyclic sulfide main chain modifications were suggested to be formed during reversion.[15,16] Several authors have demonstrated the formation of cyclic main chain modifications in conventional vulcanization of either BR or corresponding model compounds. The structures **5**, **6**, and **7** in Figure 7 have been proposed as possible cyclic main chain modifications.[17] In contrast, our NMR data strongly suggested the formation of unsymmetrical structures **3** and **4** in the CBS BR vulcanizates studied (Figure 1).

Combination of DEPT-135 and HETCOR HRMAS spectroscopy yielded the assignment of the ^{13}C resonances and showed that the ^{1}H and ^{13}C methine resonances of 1 (structure **3**) were located at δ 3.78 and δ 50.9 ppm, respectively.

COSY analysis provided subsequently the neighbors of proton 1, which are protons 9 and 2. Proton 9 was found in the olefinic region residing at δ 5.37 ppm and the neighboring protons 2, diastereotopic and anisochronic, were located at δ 1.91 and δ 1.69 ppm. These findings suggested the formation of an alkenyl methine functionality, thus excluding the formation of structure **5**.

From the TOCSY HRMAS spectra the long-range contacts from 1 with protons 11 and 4 located at, respectively, δ 2.67 and δ 3.21 ppm were extracted. Resonance 11 showed only contacts with the olefinic region in correspondence with the methylene group in structure **3**. Structure **3** could be the result of α substitution followed by an allylic rearrangement. From the COSY HRMAS spectra, it became clear that 4 is an alkyl methine proton since only contacts into the aliphatic region were found. Its neighbor 5 was situated at δ 1.62 ppm, and diastereotopic neighbors 3 were found at δ 1.86 and δ 1.58 ppm. Since proton 4 was assigned to an aliphatic methine group which differs from methine group 1 (different chemical shifts were observed for these protons), the formation of symmetrical cyclic sulfidic structures such as **5** and **7** could be excluded. Although a linear structure with two adjacent methine groups is also feasible, strong indications for the formation of cyclic structures were obtained from the NOESY HRMAS spectra. NOE correlations were observed between the protons 1 and 4 (Figure 6), indicating the presence of structure **3** (Figure 8). While

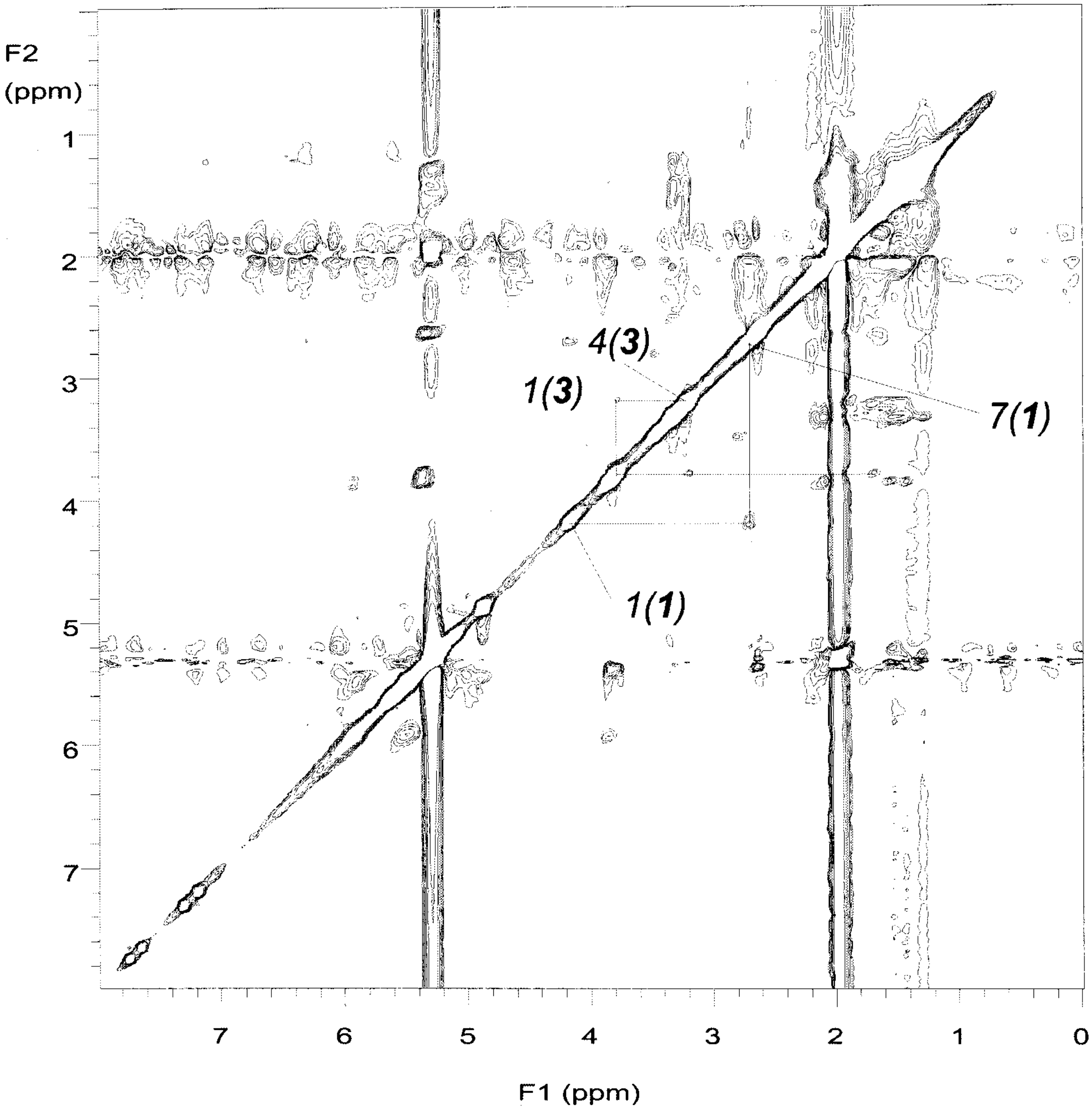
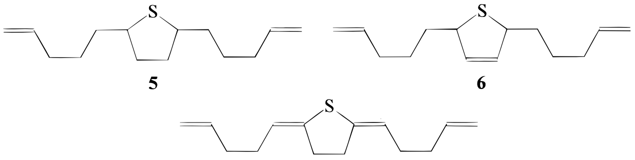


Figure 6. NOESY HRMAS spectrum of the swollen CBS BR vulcanizate. The spectrum was recorded at 10 °C using $\tau_{mix} = 125$ ms. Relevant signals for structures **1** (**2**) and **3** are selected. Structure selection is given in parentheses.



5 6 7

Figure 7. Proposed cyclic structures in the CBS BR vulcanizate.

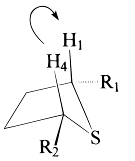


Figure 8. NOE contacts between protons 1 and 4 found for structure **3**.

NOE correlations were anticipated for this structure when protons 1 and 4 were situated at the same side of the relatively rigid ring system, no or small cross-signals are expected for the noncyclic structures.

Figure 5 shows that a TOCSY walk almost identical with that for structure **3** could be performed starting from the ^{1}H resonance located at δ 3.84 ppm. These ^{1}H resonances shifted slightly downfield in comparison with the corresponding resonances in structure **3** and were tentatively attributed to cyclic structure **4**. Proof for this cyclic structure could, however, not be obtained from the NOESY HRMAS spectra (Figure 6) since a NOE contact comparable to the one that led to the assignment of structure **3** was not observed for structure **4**. The higher conformational flexibility in the larger six-membered ring system in structure **4** probably prohibits the observation of NOE contacts between the protons 1 and 4 at ambient temperatures. The assignment of resonances belonging to either structure **3** or **4** is partly based on this argument. Tables 3 and 4 show the good agreement between ^{13}C chemical shifts found experimentally and the calculated values derived for structures **3** and **4**.

Furthermore, from the intensities of the ^{1}H signals, it was concluded that upon CBS BR vulcanization a large amount of cyclic structures was formed compared to the cross-linked products. Of these cyclic structures, structure **4** is formed predominantly (65%).

The cyclic structures observed in the polymer backbone have been suggested to be formed from intermediate episulfides, as shown in Figure 9.[14,15] We propose that in the CBS BR vulcanizate the cyclic sulfidic

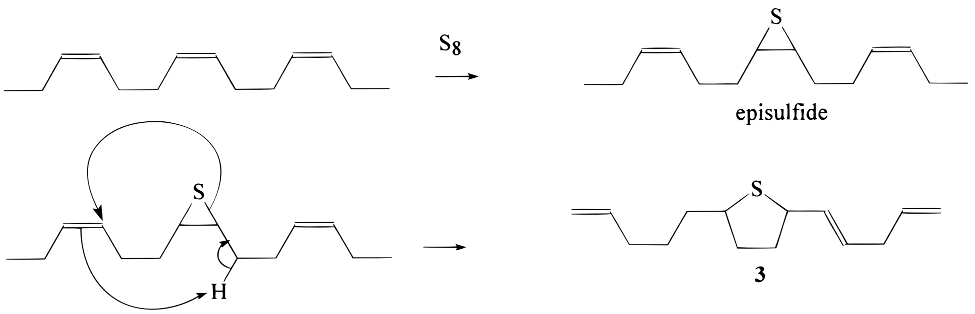


Figure 9. Possible mechanism for the formation of cyclic sulfide structures in the polymer backbone.

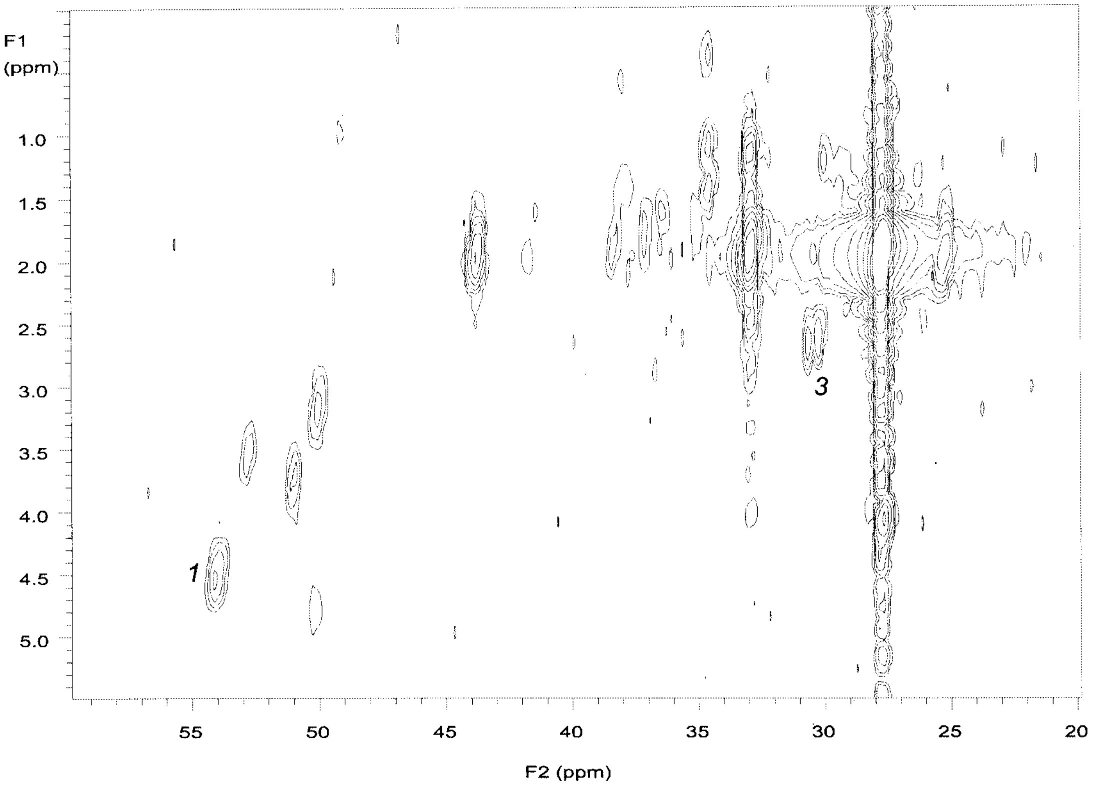
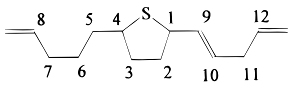


Figure 10. HETCOR HRMAS spectrum of the TMTD BR vulcanizate recorded at 60 °C using J_{CH} = 127 Hz.

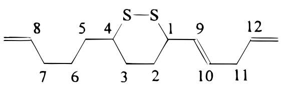
Table 3. ^{1}H and ^{13}C Chemical Shift Assignment of Structure 3



3

assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	3.78	50.9	45.5
2	1.91/1.69	37.0	26.4
3	1.86/1.58	36.3	32.8
4	3.21	49.9	54.3
5	1.62	37.5	34.4
6	1.28	29.0	27.6
7	1.90	25.0	27.2
8	5.31	129.6	127.7
9	5.37	133.7	123.0
10	5.29	130.0	128.4
11	2.67	30.0	33.0
12	5.31	132.8	135.8

Table 4. ^{1}H and ^{13}C Chemical Shift Assignment of Structure 4



4

assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	3.84	51.0	45.5
2	2.02/1.52	38.3	26.4
3	2.04/1.40	37.5	32.8
4	3.34	50.0	54.3
5	1.62	37.5	34.4
6	1.26	29.0	27.6
7	1.90	25.0	27.2
8	5.29	129.6	127.7
9	5.36	133.7	133.9
10	5.28	130.0	126.7
11	2.67	30.0	33.0
12	5.31	132.8	135.8

structures **3** and **4** (Figure 7) were formed by a process of elimination−addition of these episulfides. The intermediate episulfides were formed by sulfuration of the double bonds in BR. Elimination of a proton α to the episulfide leads to ring-opening of the three-membered ring system, hereby releasing significant ring strain (Figure 9).

Subsequently, nucleophilic attack of the formed sulfur anion to a nearby double bond yielded structure **3**. Correspondingly, structure **4** was formed from a four-

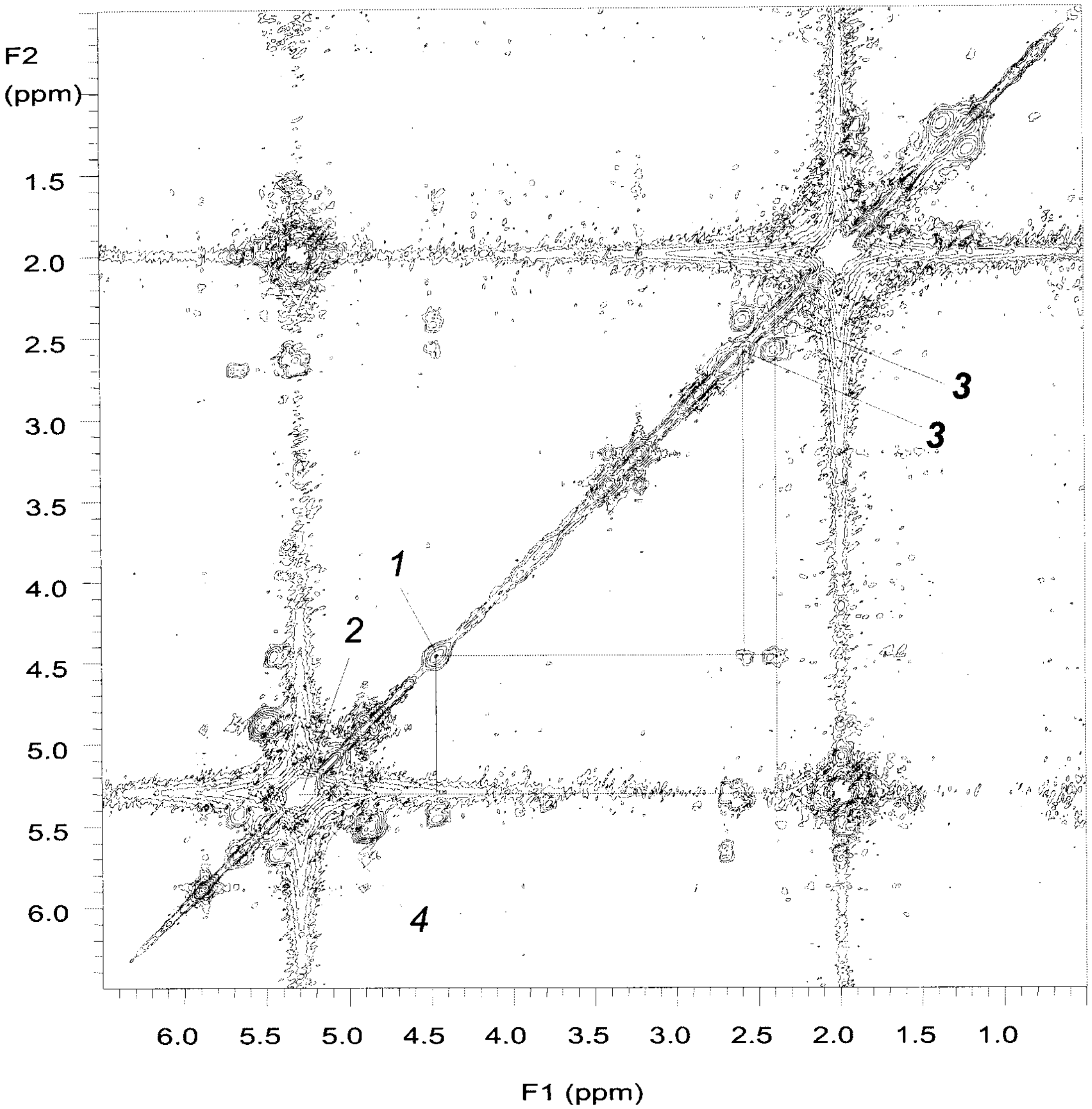


Figure 11. COSY HRMAS spectrum of the TMTD BR vulcanizate swollen in $C_2D_2Cl_4$.

membered heterocyclic ring system containing two adjacent sulfur atoms.

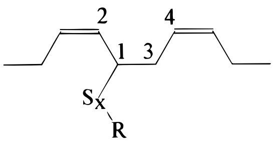
Assignment of Structures in the TMTD BR Vulcanizate

Gregg and Lattimer studied the sulfur-donor vulcanization of 1,5,9,13-cyclohexadecatetraene (CHT) and found mainly mono- and disulfidic bis(alkenyl)-cross-link structures due to exclusive α substitution.[16,17] According to Smith and Koenig, who studied TMTD vulcanized BR by solid state NMR, several other cross-link structures were formed as well.[18] The NMR data of our TMTD BR vulcanizate, however, strongly suggested the formation of cross-links of type **8** (Table 5). The DEPT-135 HRMAS spectrum obtained for the TMTD vulcanizate appeared to be in excellent agreement with the DEPT-135 spectra of corresponding vulcanizates as recorded by Smith and Koenig.[18] The methine ^{13}C resonance used for the assignment of cross-link structure **8** was located at δ 54.0 ppm (Table 5), whereas from HETCOR HRMAS spectroscopy it was evident that the corresponding ^1H resonance was situated at δ 4.48 ppm (Figure 10).

COSY HRMAS analysis provided the next neighbors 2 and 3 (Figure 11). Olefinic methine resonance 2 was located at δ 5.42 ppm, whereas the neighboring methylene protons 3 were diastereotopic and found at, respectively, δ 2.38 and δ 2.55 ppm thus excluding structures due to mono or double addition.

Since the other neighbor of the methylene protons 3 was situated at δ 5.40 ppm, it could be concluded that structure **8** (Figure 11) was formed entirely due to α substitution of an allylic hydrogen atom by a sulfur bridge, without an accompanying shift of the nearby double bond. Therefore, the resonance at δ 5.40 ppm could be ascribed to proton 4.

Table 5. ^1H and ^{13}C Chemical Shift Assignment of Structure 8



8

x = 1

assignt	^1H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	4.48	54.0	41.5
2	5.42	130.0	124.1
3	2.38/2.55	29.0	31.5
4	5.40	131.1	123.6

Although not as clearly visible as in the COSY HRMAS spectra of the CBS vulcanizates, the type of resonances earlier assigned to structures **3** and **4** (Figure 1) were also observed in the COSY spectra of the TMTD vulcanizates, indicating the formation of similar cyclic main chain modifications. Comparison of the ^{1}H intensities of the cyclic sulfidic main chain modification resonances with those from, e.g., the vinyl protons of BR revealed that these modifications were only present in (very) small amounts in the TMTD vulcanizate. The experimentally observed and calculated ^{1}H and ^{13}C resonances belonging to structure **8** are summarized in Table 5.

Conclusions

It was shown that accelerated sulfur vulcanization of BR using CBS and TMTD resulted mainly in alkenyl cross-links and several types of main chain modifications. This contrasts with the formation of alkyl cross-links found for the cyclic disulfide vulcanization of BR in our earlier study.[3,4] In the CBS BR vulcanizate, introduction of the cross-links as well as main chain modifications were caused by a process of α substitution accompanied by allylic rearrangement of the double bond, whereas the cross-links in TMTD vulcanized BR were entirely formed due to α substitution. The cross-links differed not only in nature but also in the length of the sulfur-bridging entity. While CBS vulcanization yielded mainly tri- and tetrasulfidic cross-links, the TMTD vulcanization resulted primarily in monosulfidic cross-links.

In addition to the formation of cross-links, the presence of alkenyl cyclic sulfides in the vulcanizate was observed in both types of vulcanizates. It is suggested that these main chain modifications could be the result of an elimination−addition sequence of reactions proceeding from intermediate episulfides.

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