Vulcanization of Butadiene Rubber by Means of Cyclic Disulfides. 2. A 2D Solid State HRMAS NMR Study on Cross-Link Structures in BR Vulcanizates

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ABSTRACT: Vulcanizates of high *cis*-butadiene rubber (BR) obtained by using several cyclic disulfides such as 1,2-dithiacyclooctane, 1-oxa-4,5-dithiacycloheptane, and 2,3,12,13-tetrathia-[4,4]-metacyclophane, were studied by means of high-resolution magic angle spinning (HRMAS) *solid state* NMR spectroscopy in order to determine cross-linking sequence and overall molecular structure. DEPT-135 HRMAS spectra recorded at 60 °C provided the multiplicity of 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 HRMAS COSY and TOCSY (*to*tal *c*orrelation *s*pectroscop*y*) experiments. Comparison of these results with *solution* NMR data on hexyl disulfide grafted BR and previously described work on a *cis*,*cis*,*cis*-1,5,9-cyclododecatriene (*ccc*-1,5,9-CDT) based model system led to the elucidation of the entire network structures. The ^{13}C chemical shifts found experimentally appeared to be in good agreement with chemical shifts calculated for the proposed structures. It was shown that cross-linking proceeds by means of *addition* of the cyclic disulfides to the carbon double bonds of BR instead of α *substitution*.

Introduction

Although sulfur vulcanization of BR has been known for many years[1] the exact mechanism viz. by either *addition* at or *substitution* α to the olefinic double bonds remains one of the major topics of interest in rubber chemistry.[2] Several attempts were made to elucidate the overall molecular structure, either by using model compounds[3,4] or by studying the vulcanizates themselves.[5] We were especially interested in the relationship between the type of cross-link and mechanical properties in vulcanizates of high *cis*-1,4-polybutadiene (BR).[6] It was assumed that the kind of cross-links could be varied in a controlled way by using cyclic disulfides, resulting in well-defined networks. To gain more insight in the cross-linking of BR with cyclic disulfides, a model compound vulcanization study was carried out.

In a first attempt to gain insight into the structure of BR networks, a low molecular weight model for BR, i.e., *cis*,*cis*,*cis*-1,5,9-cyclododecatriene (*ccc*-1,5,9-CDT), **1**, was vulcanized using the cyclic disulfide 1-oxa-4,5-dithiacycloheptane. *Solution* NMR proved that bis(alkyl) cross-link structure **2** (Figure 1) was formed due to *addition* of the cyclic disulfide to the carbon double bonds in the model compound.[7] The other possible reaction mode leading to **3**, the formation of cross-links resulting from α *substitution* analogous to accelerated sulfur vulcanization of model compounds,[8] was not observed in the present study.

On the basis of these results, the vulcanization of BR was investigated in greater detail using several cyclic disulfides such as 1,2-dithiacyclooctane, 1-oxa-4,5-dithiacycloheptane and 2,3,12,13-tetrathia-[4,4]-metacyclophane as vulcanizing agents (Figure 2). To discriminate between the possible cross-link structures in the BR vulcanizates, *solid state* NMR was employed due to the low solubility of the resulting products in organic solvents. Compared to the solution NMR used previously, however, the stronger dipolar interactions and variations in the bulk magnetic susceptibility[9] lead to a significant broadening of the proton signals, and the application of 2D $^{1}H-^{1}H$ NMR techniques will become more troublesome.

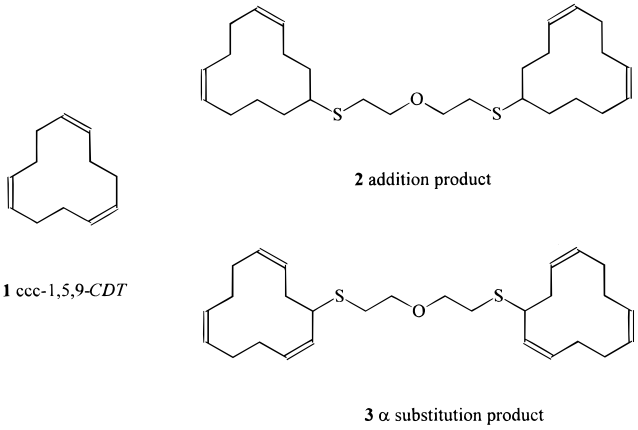

Figure 1. Possible cross-link structures in the 1-oxa-4,5-dithiacycloheptane vulcanization of *ccc*-1,5,9-CDT.

The application of spectral editing techniques such as DEPT and ESCORT/SEMUT,[10] on the other hand, was proven to be very useful in the characterization of BR, SBR, and NR vulcanizates. Pioneering work by Koenig and co-workers[11,12] showed that DEPT/^{13}C-GHPD in combination with ^{13}C chemical shift calculations yielded valuable information on cross-link structures, main chain modifications, and pendent groups.

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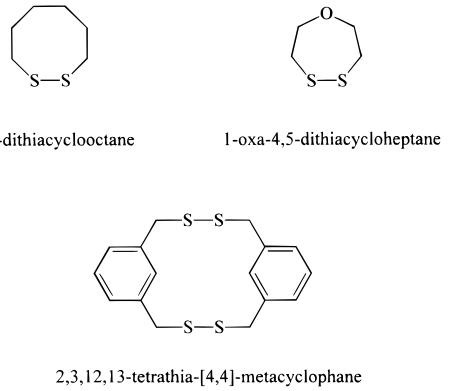
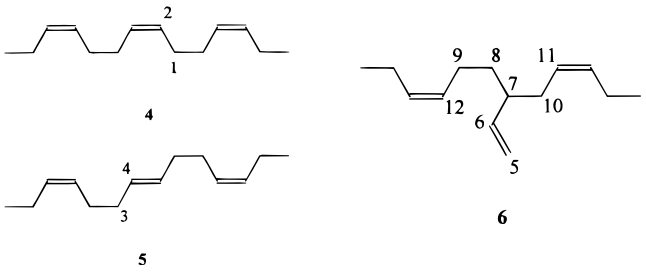


Figure 2. Cyclic disulfides used for vulcanization of BR.

Table 1. Components Used in the Vulcanization of BR

component phr	1	2	3	4
BR	100	100	100	100
hexyl disulfide	8.0			
1,2-dithiacyclooctane		3.0		
1-oxa-4,5-dithiacycloheptane			3.0	
2,3,12,13-tetrathia[4,4]-metacyclophane				2.0
ZDMC	10.0	6.7	6.7	6.7
1,12-diaminododecane	8.0	4.4	4.4	4.4

Table 2. ^{1}H and ^{13}C Chemical Shift Assignment of High *cis*-BR for Structural Units 4−6



assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	2.03	27.3	26.9
2	5.33	129.6	127.7
3	1.97	32.6	31.7
4	5.37	130.1	129.5
5	4.80	115.0	112.3
6	5.60	143.0	143.1
7	2.00	43.6	40.1
8	1.30−1.50	34.2	28.1
9	2.00	24.9	24.2
10	2.00	32.6	36.5
11	5.30	129.8	128.4
12	5.30	130.1	130.2

A disadvantage in the application of ^{13}C NMR spectroscopy in the analysis of vulcanizates is the low sensitivity for detection of the small amount of cross-links present in the vulcanizates. ^{1}H NMR is far more sensitive for the detection of the limited amounts of cross-links present and it has been shown that narrow ^{1}H-line shapes due to reduction of anisotropic mobility could be obtained using the proper experimental conditions. These examples include tissue samples,[13] lipids,[14] dispersed solids,[15] polymeric gels,[16] and swollen resins.[17] These last two classes include cross-linked elastomers[18] *swollen to equilibrium* under the conditions of high-resolution magic angle spinning *(*HRMAS*)* solid state NMR. Moreover, Komoroski and co-workers[19] found from an explorative solution NMR study on supramolecular guayule triterpene that 2D-NMR techniques such as C,H−COSY, H,H−COSY, and INADEQUATE

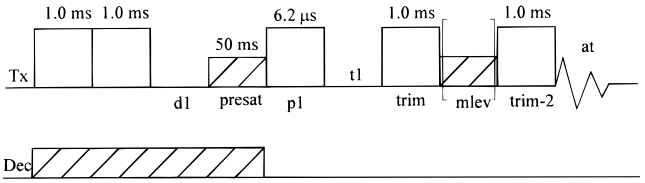


Figure 3. HRMAS TOCSY pulse sequence used for double simultaneous irradiation experiments.

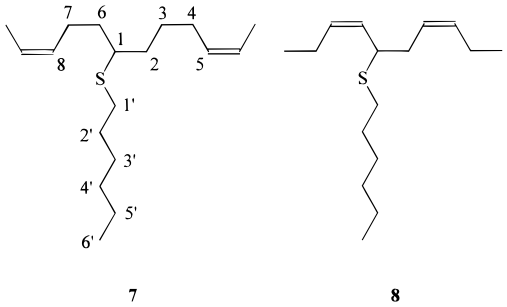


Figure 4. Possible structures and numbering scheme of hexyl disulfide grafted BR.

provide additional information on the cross-link structures present in the vulcanizates.

In the present paper, the application of several of these techniques in the elucidation of the molecular network structures of BR vulcanizates formed after reaction with several cyclic disulfides is described. To investigate the applicability of the above-mentioned techniques under HRMAS NMR conditions, the reaction of BR with hexyl disulfide was also studied, since grafts will be formed instead of cross-links. Because of the absence of cross-links, these BR grafts can be analyzed with *both* solution and HRMAS 2D NMR spectroscopy, allowing straightforward comparison. In addition, to extract long-range through bond contacts the use of clean-TOCSY techniques under HRMAS conditions is introduced.

Experimental Section

Materials. 1,12-Diaminododecane (Aldrich) and ZDMC (zinc *dim*ethyl dithio*c*arbamate, Perkacit-ZDMC, Flexsys) were used without further purification. 1,2-Dithiacyclooctane, 1-oxa-4,5-dithiacycloheptane, and 2,3,12,13-tetrathia-[4,4]-metacyclophane were prepared as reported elsewhere.[20,21,22] Bis-(hexyl) disulfide was synthesized by a method similar to that used for the cyclic disulfides. High *cis*-BR (Cariflex BR 1200) was obtained from Shell (M_n = 140 000, M_w = 393 000, and M_z = 770 000).

Vulcanization of BR. The vulcanizing components were mixed with BR into slabs on a laboratory size two-roll mill (Swabenthan) with an average mill-speed of 20 rpm and a friction ratio of 1:1.13 at a temperature of 50 °C for 10 min.

The compound recipes used are given in Table 1. The slabs were vulcanized into thin sheets with a thickness of approximately 1.5 mm in a hydraulic press during 1 h at 140 °C and a mold pressure of 15 MPa. Vulcametric experiments were performed in order to establish if cross-linking had taken place. A Göttfert 65.87 Elastograph was used, and experiments were performed according to standard methods.[23] After 1 h at 140 °C the cyclic disulfide compounds showed an increase in rheometer torque, whereas for the hexyl disulfide compound no increase was observed, indicating that no cross-linking had occurred.

Prior to NMR analysis the cyclic disulfide BR vulcanizates were extracted with cyclohexane, acetone, and dichloromethane for 24 h using a Soxhlet apparatus in order to remove any unwanted impurities. Residual solvents were removed by

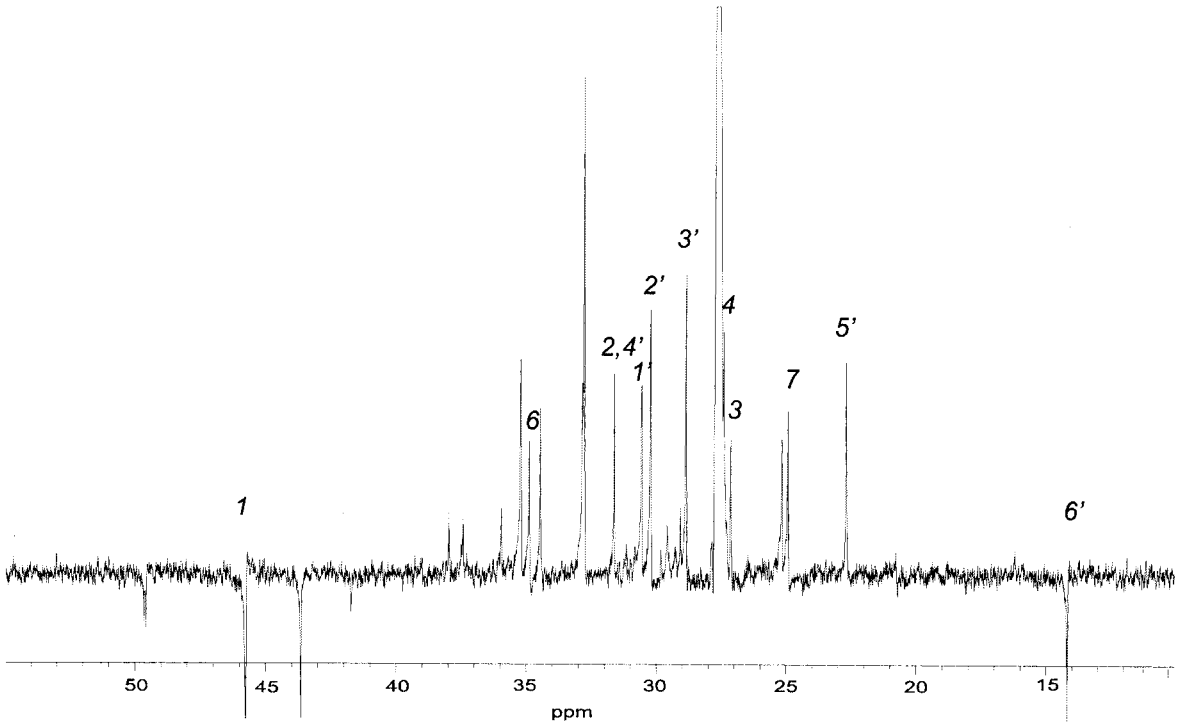


Figure 5. Solution ^{13}C DEPT-135 spectrum of hexyl disulfide grafted BR recorded in $C_2D_2Cl_4$ at 60 °C. Spectrum shows CH/CH_3 down and CH_2 up.

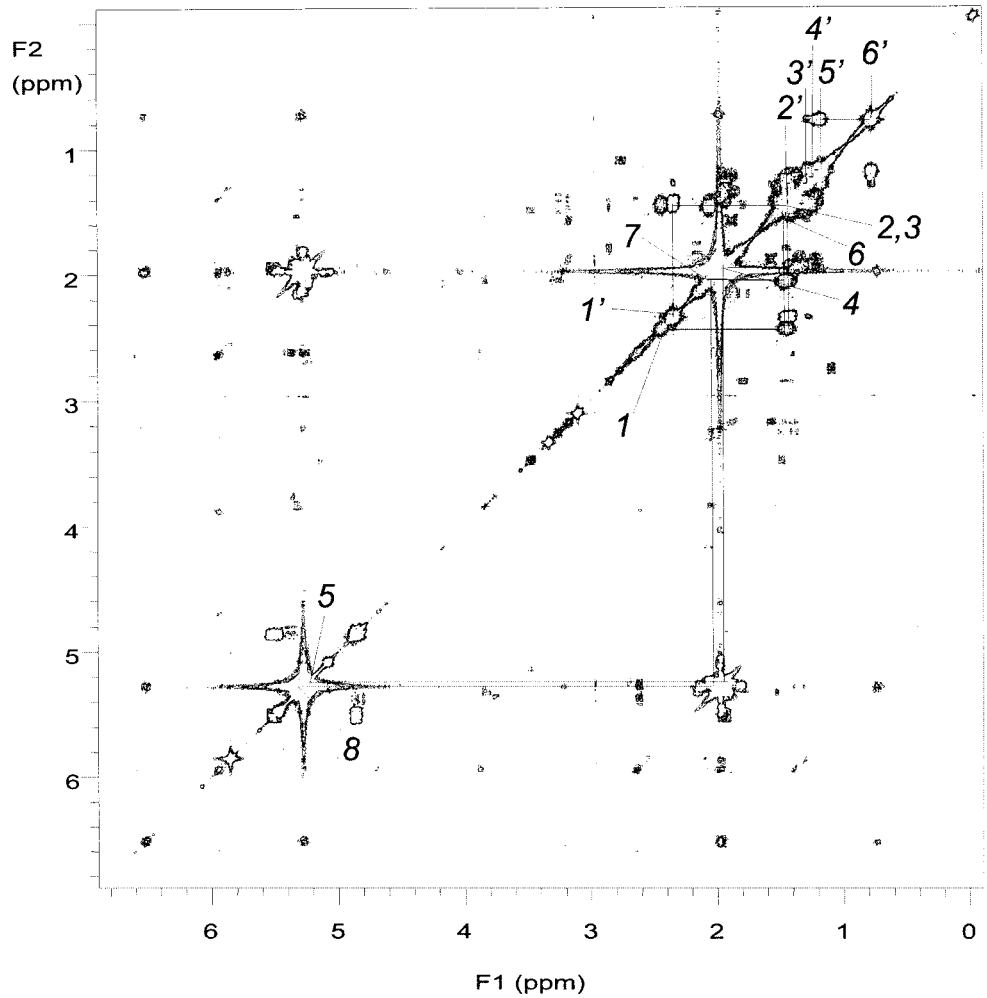
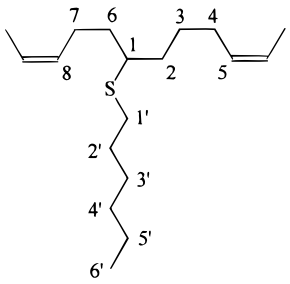


Figure 6. Solution COSY NMR spectrum of hexyl disulfide grafted BR recorded in $C_2D_2Cl_4$ at 60 °C.

drying the samples for 12 h at reduced pressure. The bis(hexyl) disulfide reaction product was purified by precipitation of a 1% solution in chloroform into a 10-fold volume of methanol. The product was filtered and dried as described above.

Table 3. ^{1}H and ^{13}C Chemical Shift Assignments of Hexyl Disulfide Grafted BR (Compound 7)



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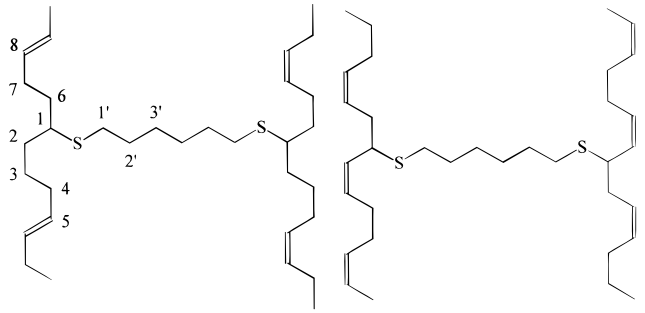
assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	2.43	45.6	44.6
2	1.40	30.5	33.1
3	1.38	27.3	28.1
4	1.94	27.5	28.3
5	5.22	130.0	130.5
6	1.48	34.8	34.1
7	2.13	24.8	24.8
8	5.28	130.0	130.5
1′	2.38	30.5	30.0
2′	1.42	30.0	29.7
3′	1.27	31.3	29.4
4′	1.22	29.0	24.8
5′	1.18	22.5	23.1
6′	0.78	14.2	13.9

NMR Spectroscopy. NMR experiments were performed using a Varian Unity 400 WB NMR spectrometer operating at 400 and 100 MHz for ^{1}H and ^{13}C, respectively. Solution NMR experiments were carried out on uncured BR dissolved in $C_2D_2Cl_4$ at 60 °C. ^{1}H, ^{13}C, COSY,[24] DQF−COSY,[25] clean-TOCSY (MLEV17),[26] NOESY,[27] HETCOR,[28] and HMQC[29] experiments were used for the assignment of the ^{1}H and ^{13}C resonances. All 2D spectra were collected as 2D hypercomplex data.[30] 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. The ^{13}C spectra of dry vulcanizates were recorded after 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 spectra were obtained after acquiring 128 increments with 1800 scans per increment. The ^{1}H 2D NMR 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 to 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 spectra were accumulated with 512 increments and 32 scans per increment. 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. 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 (Figure 3).



9 **10**

Figure 7. Possible structures and numbering of the 1,2-dithiacyclooctane BR vulcanizate.

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

Results and Discussion

A. Assignment of High *cis*-BR. The ^{1}H and ^{13}C NMR resonance assignments of uncured high *cis*-BR were established in order to distinguish between resonances arising from uncured BR and from cross-links or main chain modifications in the vulcanizate samples. The molecular structure of BR was determined by means of NMR and it was shown that the high *cis*-BR used consisted of 96.5% cis (**4**), 1.5% trans (**5**), and 2% vinyl units (**6**) (see Table 2 for structures).

The ^{13}C and ^{1}H NMR assignments of uncured high *cis*-BR recorded at 60 °C in $C_2D_2Cl_4$ solution were extracted from DEPT-135, COSY, DQF−COSY, and HMQC NMR spectra (not shown).

The ^{13}C DEPT-135 NMR spectrum showed a methine (*CH*) resonance at δ 43.6 ppm, which was assigned to carbon 7 in vinyl structure **6**. The corresponding ^{1}H signal at δ 2.0 ppm (HMQC) was used as the *key frequency* to establish the main chain connectivities of the vinyl structure and corresponding chemical shifts by means of COSY and/or DQF−COSY walks. The diastereomeric protons attached to carbons 8 and 10 gave rise to heavily coupled AB systems located at δ 1.3−1.5 and around δ 2.0 ppm, respectively. Using this procedure, the resonances at δ 4.8 and δ 5.6 ppm were assigned to the respective olefinic protons 5 and 6. The protons attached to carbons 9, 10, 11, and 12 were extracted from the COSY spectra using the same strategy. Once the ^{1}H NMR chemical shifts were assigned, HMQC connectivities readily afforded the corresponding carbon chemical shifts. The chemical shifts found were shown to be in good agreement with known literature values,[31,32] the determined chemical shifts were all within 2 ppm compared to the calculated values found for the cis and trans monomer units. Larger deviations were, however, found for the vinyl structure. Branching strongly influences the conformation of the polymer backbone, determining the experimentally obtained values and making comparison with calculated values that do not incorporate conformational effects less accurate.

B. Assignment of Hexyl Disulfide Grafted BR. Hexyl disulfide grafted BR was used as a model for cyclic disulfide BR vulcanizates. The compound showed upon vulcanization no increase in rheometer torque (140 °C for 1 h) and, moreover, remained soluble in $C_2D_2Cl_4$. Because of the absence of cross-links in the graft,

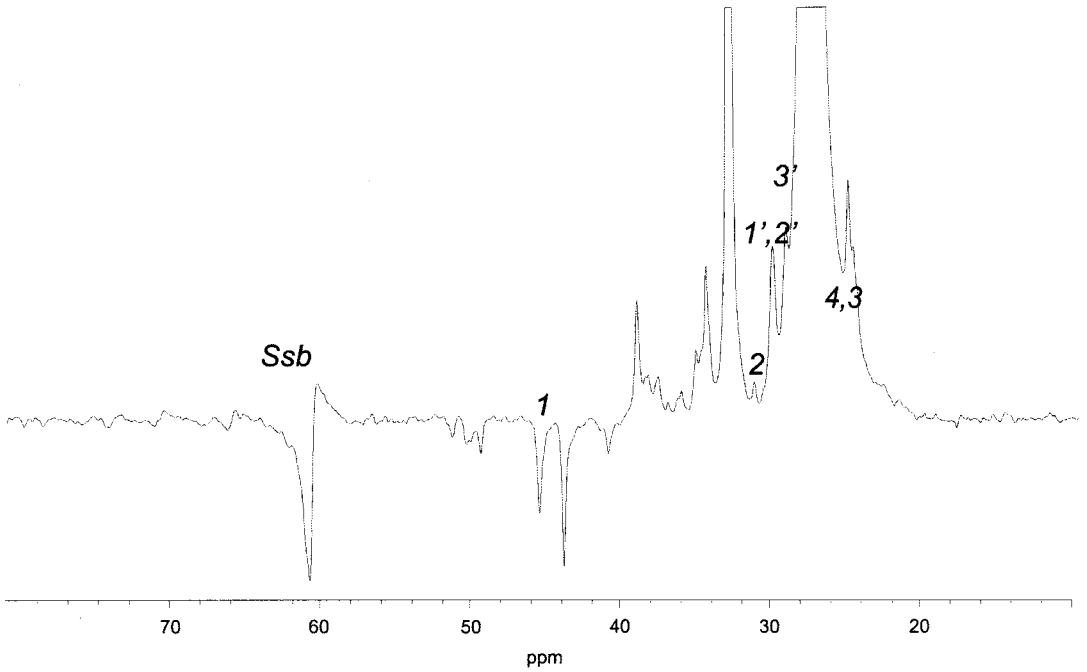


Figure 8. ^{13}C DEPT-135 HRMAS NMR spectrum of the 1,2-dithiacyclooctane BR vulcanizate. Spectrum shows CH/CH_3 down and CH_2 up.

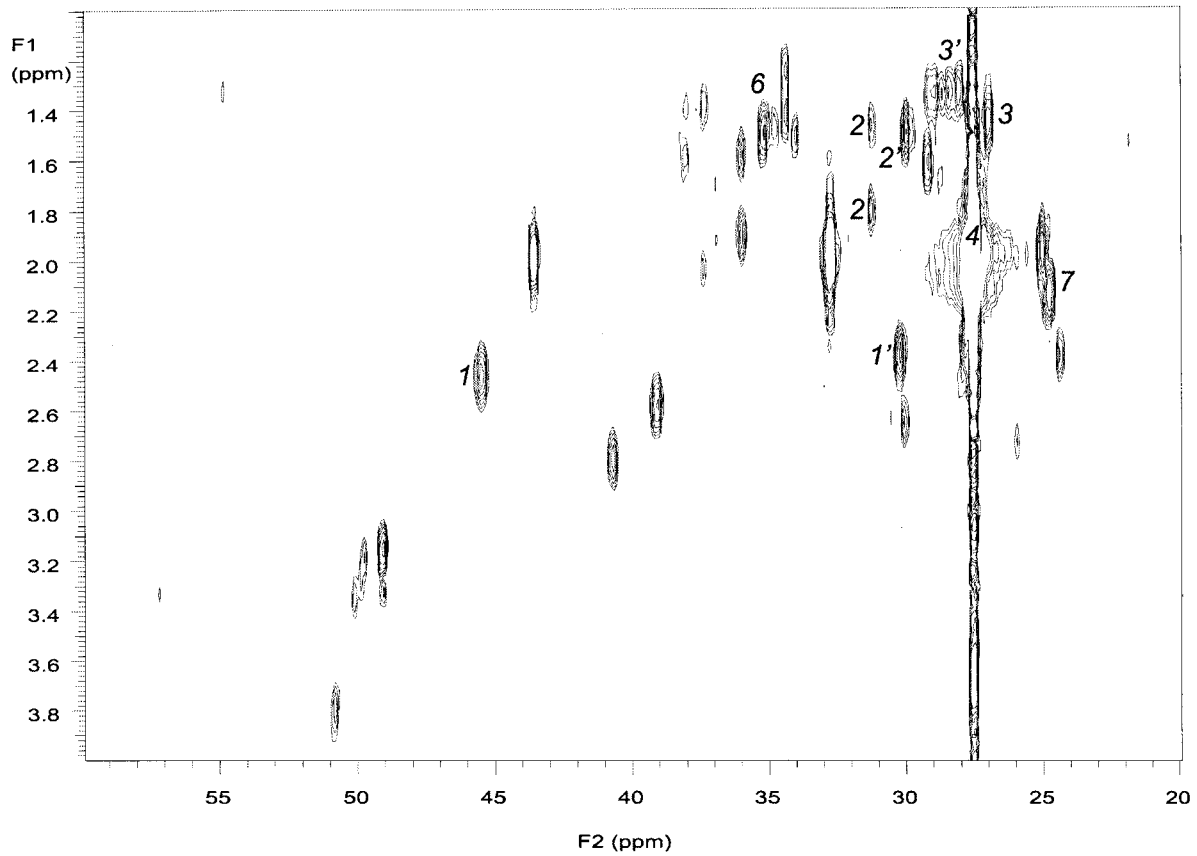


Figure 9. HETCOR HRMAS NMR spectrum of the 1,2-dithiacyclooctane BR vulcanizate, $J_{CH} = 127$ Hz, recorded at 60 °C.

the product could be used for both solution and HRMAS NMR analysis, allowing comparison with the NMR data obtained for the BR vulcanizates as well as for the vulcanizate of the model compound *ccc*-1,5,9-CDT (vide supra). As expected, the HRMAS NMR spectra showed significant line broadening compared to the solution NMR spectra. Only solution NMR data are presented here.

If hexyl disulfide reacts with BR in a similar way as the model compound *ccc*-1,5,9-CDT with the cyclic disulfide (see Figure 1), graft **7** formed due to addition or the α-substituted product **8** will be found instead of cross-linked structures (Figure 4).

Discrimination between methine, methylene, methyl, and quaternary carbons was possible using ^{13}C DEPT-135 spectroscopy. In Figure 5 the aliphatic region of the

solution ^{13}C DEPT-135 spectrum of hexyl disulfide grafted BR is shown.

The upon grafting introduced methine moiety and the corresponding NMR signals were used as a starting point in the elucidation of the graft structure. Although several methine signals were present in the region δ 40−50 ppm, the only resonance which shifted upon the use of different cyclic disulfides was situated between δ 45−46 ppm (see, e.g., the various ^{13}C MAS DEPT NMR results).[33] It is therefore likely that the methine ^{13}C resonance at δ 45.6 ppm originated from the grafted structure. The methyl resonance located at δ 14.2 ppm arises from a side reaction product of hexyl disulfide itself.

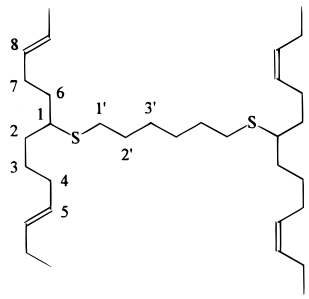
The ^{13}C chemical shifts were mapped to the corresponding ^{1}H resonances by means of HETCOR/HMQC NMR techniques. Methine resonance 1 resulting from the formation of hexyl monosulfide grafts was situated at ^{13}C and ^{1}H chemical shifts of δ 45.6 and δ 2.43 ppm, respectively. The very large signals residing at δ 2.00 and δ 5.30 ppm originated from the cis units in the polymer main chain (see Figure 6). Compared to these signals, resonances arising from *cross-linked moieties* were only present in *extremely low abundance* (less than 5%), clearly imposing difficulties in the straightforward assignment.

The absence of neighboring contacts between methine proton 1 and the olefinic region in the COSY spectrum (Figure 6) clearly excluded the formation of alkenyl pendent groups as shown for structure **8** (Figure 4). Instead, alkyl pendent groups were formed indicating the formation of addition product **7**.

Next-neighboring protons 2 and 6 were hard to identify as they showed significant overlap. Detailed analysis showed, however, that neighbor 2 was residing at δ 1.40 ppm whereas the signal at δ 1.48 ppm was assigned to proton 6. Additional evidence for structure **7** was obtained by employing TOCSY techniques, as the total main chain spin system of **7** could be assigned without ambiguity starting from proton 1. The methine resonance (proton 1) at δ 2.43 ppm showed two long-range through bond contacts with methylene protons situated at δ 1.94 and δ 2.13 ppm (TOCSY). These methylene protons showed direct contacts (COSY) with both the olefinic and aliphatic region and were assigned to protons 4 and 7. Exact discrimination between these protons was based on the cross signals to the aliphatic region at δ 1.38 and δ 1.48 ppm. The ^{1}H NMR resonance located at δ 1.94 ppm showed a cross signal to the aliphatic region at a chemical shift of δ 1.38 ppm (proton 3); this resonance belonged to proton 4. Consequently, the resonance residing at δ 2.13 ppm that exhibited a cross signal with proton 6 at δ 1.48 ppm was assigned to proton 7. The side chain visualized by the protons 1′−6′ was also readily identified. Performing through bond walks in the TOCSY and COSY spectra led to the definite conclusion that proton 3′ and 4′ coincided at apparently δ 1.22−1.27 ppm. A unique assignment of the corresponding ^{13}C resonances was consequently troublesome, and the ^{13}C assignments presented in Table **3** were partly based on chemical shift calculations.

Small traces of several side products were also identified[34] and were likely to be formed due to decomposition of the vulcanization accelerator. Although no attempts were made to present the results to date, they have been shown, however, to be of importance for the characterization of the grafted products.

Table 4. ^{1}H and ^{13}C Chemical Shift Assignments of the 1,2-Dithiacyclooctane BR Vulcanizate 9



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assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	2.51	45.5	44.6
2	1.42/1.80	32.1	33.1
3	1.55	27.1	28.1
4	1.94	27.6	28.3
5	5.35	130.0	130.5
6	1.50	35.3	34.1
7	2.10	25.0	24.8
8	5.27	130.0	130.5
1′	2.35	30.3	29.7
2′	1.50	30.1	29.0
3′	1.25	28.5	27.9

The calculated chemical shift values agreed very well with the observed chemical shifts despite the introduced sulfur heteronucleus and branching (Table 3). Moreover, due to the limited number of input chemical shift values, no attempts were undertaken to "train" the program in order to obtain better fits.

The 1D and 2D NMR results strongly suggest that only one type of pendent group was formed upon grafting, yielding product **7** (Figure 4), resulting from addition to the double bonds instead of α substitution.

C. Assignments of Cross-Link Structures in Cyclic Disulfide BR Vulcanizates. 1,2-Dithiacyclooctane BR Vulcanizate. In the elucidation of cross-link structures present in the 1,2-dithiacyclooctane BR vulcanizate, the same strategy was followed as for the elucidation of the molecular structure of the hexyl disulfide BR graft. Cross-link structures resulting from addition or α substitution are shown in Figure 7. However, due to insolubility of the vulcanizate, the 2D NMR techniques previously used were now applied to samples spun under the magic angle and in the solid state (HRMAS NMR spectroscopy).

Comparison of the solution ^{13}C DEPT-135 spectra of hexyl disulfide grafted BR (Figure 5) with the ^{13}C DEPT-135 HRMAS spectra of the 1,2-dithiacyclooctane BR vulcanizate as shown in Figure 8 confirmed the formation of the *same type* of methine carbon located at δ 45.5 ppm.

Therefore, it is suggested that the underlying mechanism of cross-link formation leading to structure **9** in the cyclic disulfide vulcanizate (Figure 7) is comparable to that of the grafting of the linear hexyl disulfide onto the BR polymer chains.

From the HETCOR HRMAS spectrum (Figure 9) it became evident that the methine ^{1}H resonance of interest (proton 1) was located at δ 2.51 ppm. Neighboring protons 2 and 6 were assigned on the basis of ^{13}C chemical shift calculations in combination with HETCOR spectroscopy. For carbon 6 a ^{13}C chemical shift of δ 34.1 ppm was calculated (Table 4), experimentally

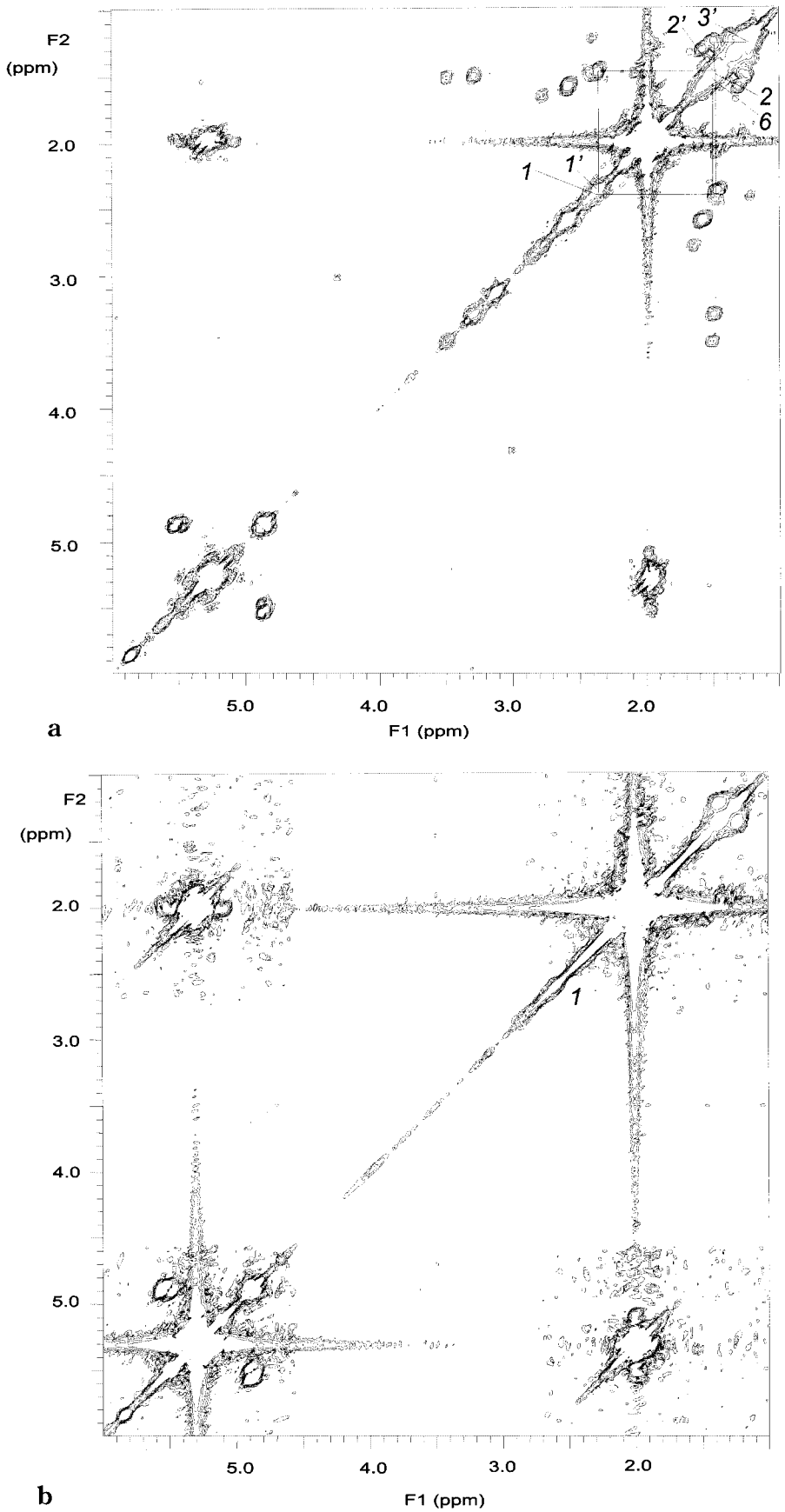


Figure 10. COSY HRMAS NMR spectra of a sample swollen to equilibrium ($C_2D_2Cl_4$, a) and a dry sample (b) of the 1,2-dithiacyclooctane BR vulcanizate.

(HETCOR) ^{13}C and ^{1}H chemical shifts of δ 35.3 and δ 1.50 ppm were found. The experimental ^{13}C chemical shift of neighbor 2, δ 32.1 ppm, agreed very well with the calculated value (δ 33.1 ppm). The corresponding protons, being diastereotopic, were residing at δ 1.42 (2^a) and δ 1.80 ppm (2^b).

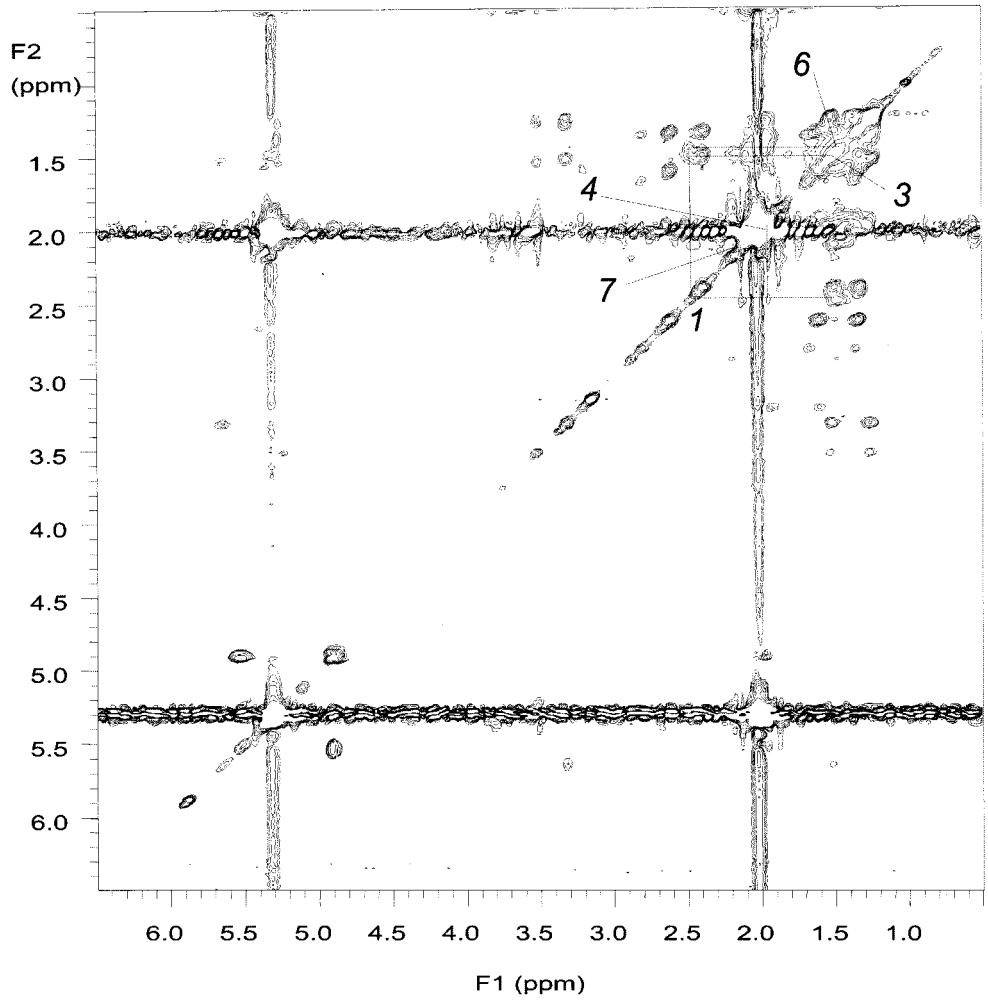


Figure 11. TOCSY HRMAS NMR spectrum of a swollen sample of the 1,2-dithiacyclooctane BR vulcanizate, recorded using a mixing time $\tau_{mix} = 60$ ms.

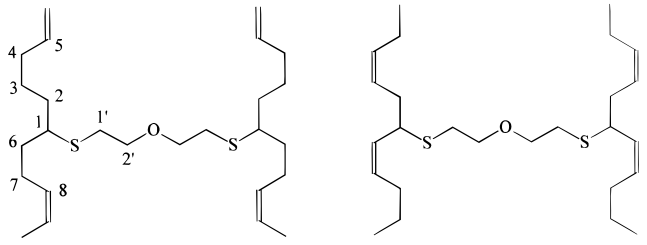
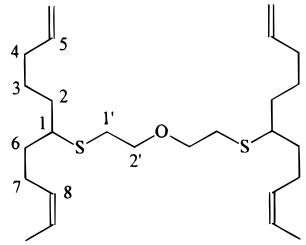


Figure 12. Possible structures and numbering of the structures **11** and **12** in the 1-oxa-4,5-dithiacycloheptane BR vulcanizate.

It is difficult to establish the *J*-coupled network of the plain vulcanizate by means of COSY NMR experiments as no cross signals were observed for dry samples (Figure 10). Swelling of the vulcanizate, however, reduced the residual dipolar coupling to a considerable extent, resulting in more liquidlike behavior yielding sharp signals in solid state ^{1}H NMR spectra. As a result, high-resolution 2-dimensional COSY, relayed-COSY and clean-TOCSY HRMAS NMR spectra were obtained.

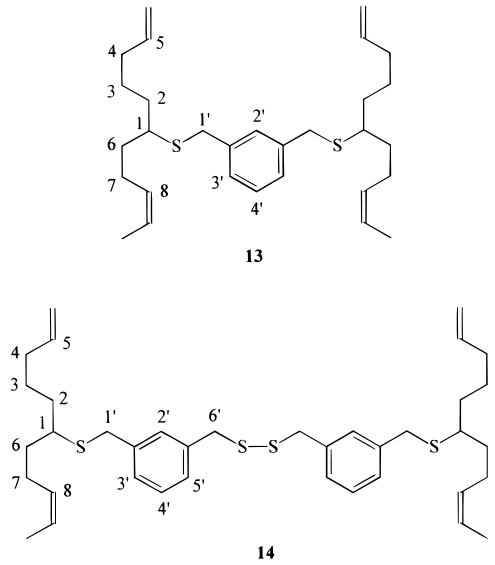
In Figure 10 a significant improvement in resolution upon swelling of the vulcanizate in the COSY HRMAS NMR experiment is shown. Contrary to the COSY spectrum of the dry sample the spectrum of the highly swollen network shows several contacts of interest. This improvement in resolution and the ability to record spectra in the locked mode when swollen in deuterated solvents, clearly allowed the recording of high-resolution 2D HRMAS solid state NMR spectra over a long period

Table 5. ^{1}H and ^{13}C Chemical Shift Assignments of Structure 11



11

assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	2.50	45.6	44.6
2	1.42/1.80	31.4	33.1
3	1.54	27.1	28.1
4	1.94	27.6	28.3
5	5.28	130.1	130.5
6	1.48	33.0	34.1
7	2.08	24.8	24.8
8	5.28	130.1	130.5
1′	2.55	29.8	32.7
2′	3.54	71.2	70.3

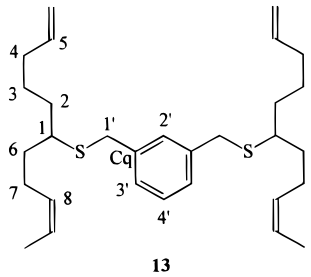


13

14

Figure 13. Possible structures and numbering protocol of the 2,3,12,13-tetrathia-[4,4]-metacyclophane BR vulcanizate.

Table 6. ^{1}H and ^{13}C Chemical Shift Assignments of Structure 13



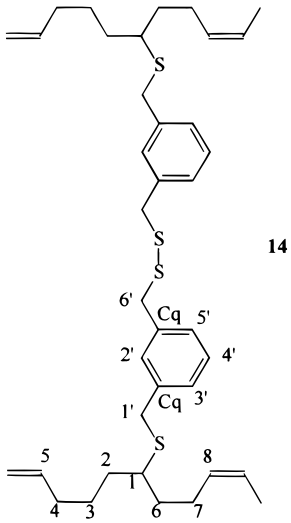
13

assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	2.38	45.1	45.5
2	1.44/1.68	31.4	33.3
3	1.47	27.0	28.1
4	1.96	27.4	28.3
5	5.30	129.9	130.5
6	1.43	34.9	34.3
7	2.12	24.9	24.8
8	5.30	129.9	130.5
1′	3.49	35.2	38.4
2′	6.98	127.8	127.7
3′	7.13	128.4	126.5
4′	7.03	127.3	128.7
C_q	-	137.4	136.2

of data acquisition required for the recording of 2D NMR spectra. The quality of the resulting spectra strongly depended upon the degree of swelling; swelling to equilibrium afforded the highest resolution.

COSY walks yielded the next neighbor contacts from the proton located at δ 2.50 ppm (proton 1), affording the shifts of protons 2 and 6 at δ 1.42/1.80 and δ 1.50 ppm, respectively. The absence of direct contacts between proton 1 and the olefinic region excludes the formation of alkenyl pendent groups and hence of vulcanization due to α substitution. Additional information was obtained from experiments employing long-range *J*-couplings. Some long-range through bond contacts could be obtained from relayed-COSY spectra using delay times up to 100 ms. However, at higher mixing times magnetization was lost due to T_2 relaxation, causing the complete disappearance of cross signals. Given these drawbacks, the earlier mentioned

Table 7. ^{1}H and ^{13}C Chemical Shift Assignments of Structure 14



14

assignt	^{1}H shift (ppm)	^{13}C shift (ppm)	^{13}C calcd shift (ppm)
1	2.38	45.1	45.5
2	1.44/1.68	31.4	33.3
3	1.47	27.0	28.1
4	1.96	27.4	28.1
5	5.30	129.9	130.5
6	1.43	34.9	34.3
7	2.12	24.9	24.8
8	5.30	129.9	130.5
1′	3.49	35.2	38.4
2′	6.98	130.7	127.7
3′	6.90	124.8	126.5
4′	7.40	130.5	128.7
5′	6.93	126.8	127.7
6′	3.42	43.7	38.4
C_q	-	137.4	136.2
C_q	-	138.3	138.1

TOCSY HRMAS pulse sequence should be a more convenient alternative to establish the *J*-coupled network. Since TOCSY is a phase sensitive measurement, T_1 noise due to the extremely large signals of the main chain, forms a serious problem in recording high quality 2D spectra. To overcome this problem in the dynamic range, single or simultaneous irradiation of the two main peaks was performed. A presaturation pulse on the observe channel was used to diminish the aliphatic resonance located at δ 2.00 ppm while the decoupler channel was used for irradiation of the olefinic resonance residing at δ 5.35 ppm (see Experimental Section for details).

TOCSY HRMAS spectroscopy provided the (long-range) ^{1}H through bond contacts between proton 1 with protons 3 and 7 at δ 2.51, δ 1.55, and δ 2.10 ppm, respectively. Since two long-range contacts were observed, the formation of a symmetric main chain product could be excluded. COSY HRMAS spectroscopy provided contacts of 4 (δ 1.94 ppm) with 5 (δ 5.35 ppm) and 7 (δ 2.10 ppm) with 8 (δ 5.27 ppm). It also provided the contact of proton 3 (δ 1.55 ppm) with proton 2 at δ 1.42/1.80 ppm that is only faintly visible due to its diastereotopicity. The combination of COSY and TOCSY HRMAS spectroscopy also led to the assignment of the complete ^{1}H spin system of the bridging fragment. Proton 1′ was located at δ 2.35 ppm. Its neighboring proton 2′ was residing at δ 1.50 ppm (COSY). TOCSY provided neighbor 3′ at δ 1.25 ppm. From TOCSY spectroscopy it also became clear that a symmetrical

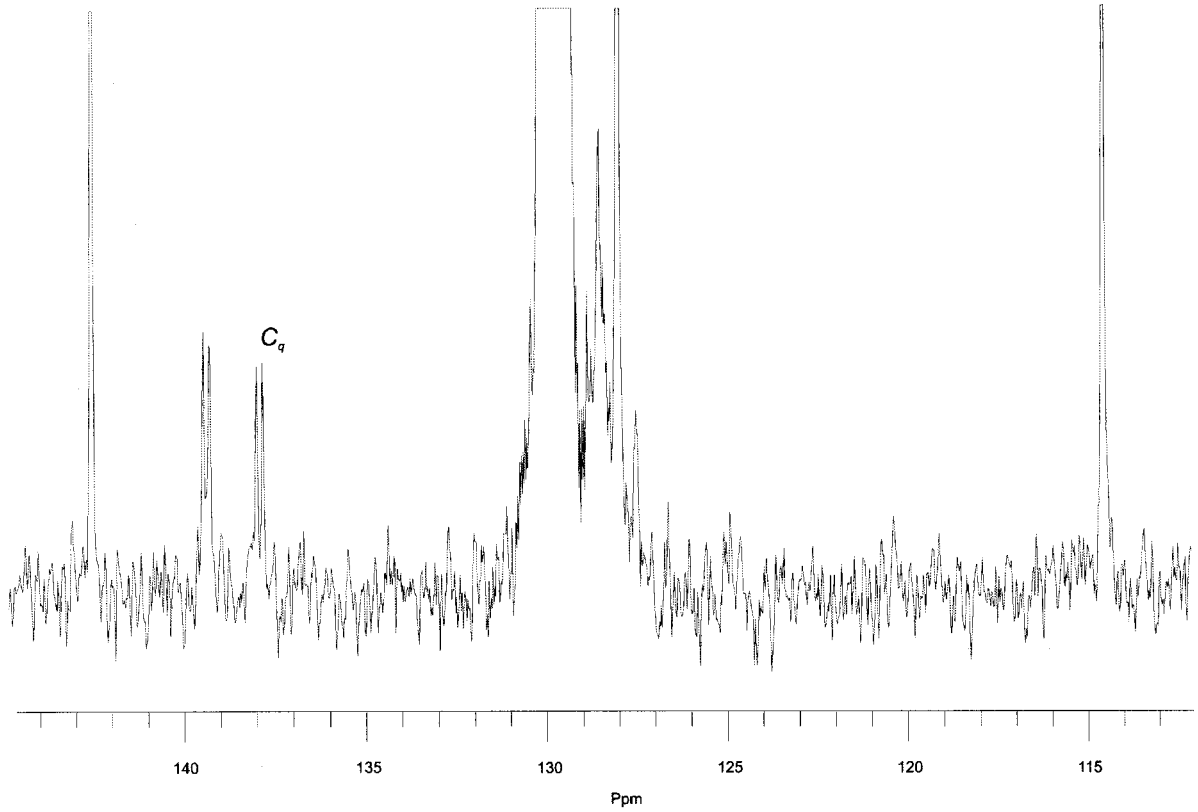


Figure 14. Olefinic part of the ^{13}C GHPD HRMAS NMR spectrum of the 2,3,12,13-tetrathia-[4,4]-metacyclophane BR vulcanizate.

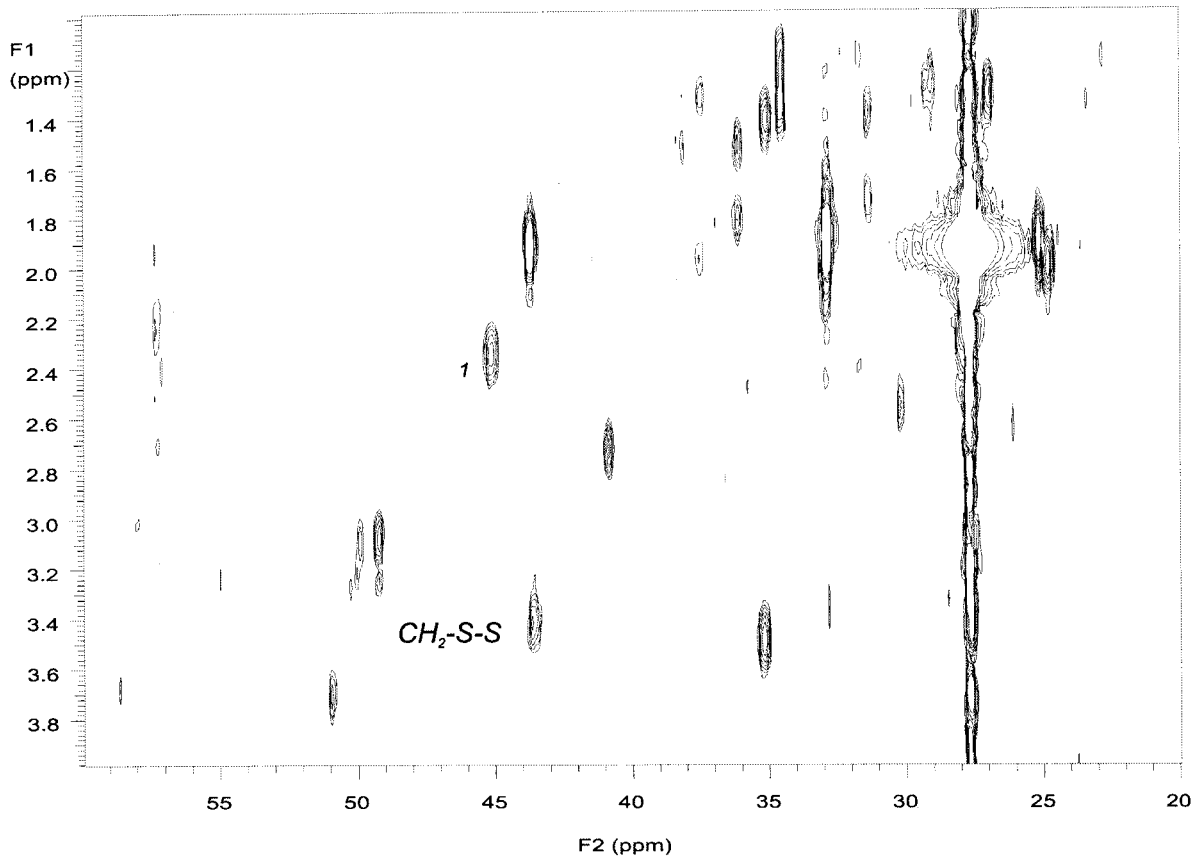


Figure 15. HETCOR HRMAS NMR spectrum of the 2,3,12,13-tetrathia-[4,4]-metacyclophane BR vulcanizate, recorded at 60 °C.

cross-link unit was formed, since no more cross-peaks were visible, not even at mixing times longer than 90 ms, thereby proving the bis(alkyl) nature of cross-link structure **9**. The ^1H resonances were mapped to the corresponding ^{13}C resonances employing HETCOR HR-MAS spectroscopy.

The complete ^{1}H and ^{13}C chemical shifts of structure **9** are summarized in Table 4. The ^{13}C chemical shifts were in good agreement with ^{13}C chemical shift calculations. The resemblance between the solution NMR data of the thiohexyl graft **7** (Table 3) and HRMAS NMR data of cross-link **9** was apparent. These findings suggest that the underlying mechanism of graft or cross-link formation is identical.

1-Oxa-4,5-dithiacycloheptane BR Vulcanizate. The cross-link structures, which might have been formed, are presented in Figure 12.

In correspondence with the assignment for the BR vulcanizate formed after reaction with the cyclic disulfide 1,2-dithiacyclooctane, the newly introduced methine ^{13}C-resonance (1) was found at δ 45.6 ppm in the ^{13}C DEPT-135 HRMAS NMR spectrum. Furthermore, the presence of (at least) two different $^{13}CH_2O$ resonances situated at δ 69.5 and δ 71.2 ppm (2′) suggested the presence of two (slightly) different materials.

The corresponding ^{1}H resonances were assigned using HETCOR HRMAS techniques. Proton 1 was situated at δ 2.50 ppm, while proton 2′ was found at δ 3.54 ppm. The assignments were performed analogous to that of the 1,2-dithiacyclooctane BR vulcanizate by combining COSY and TOCSY HRMAS techniques on swollen vulcanizates. Again, only a product formed due to addition at the carbon double bonds of BR was found, yielding **11** as the vulcanizate product.

It became clear that the main chain protons did not shift much upon formation of a different cross-link structure (**9** vs **11**); e.g., neighboring protons 2 and 6 were found at δ 1.42/1.80 and δ 1.48 ppm, respectively. The ^{1}H and ^{13}C chemical shifts found as well as the calculated chemical shifts are summarized in Table 5.

The $^{13}CH_2O$ resonance at δ 69.5 ppm showed a corresponding proton resonance at δ 2.95 ppm. Its chemical shift is indicative for methylene protons located α to a disulfide bond. Since these resonances were not observed in hexyl disulfide grafted BR, we suggest that these originated from dithiamethylene units formed upon ring oligomerization and/or polymerization of 1-oxa-4,5-dithiacycloheptane. The larger rings formed were trapped within the vulcanizate and are therefore not extractable upon workup.

2,3,12,13 Tetrathia-[4,4]-metacyclophane BR Vulcanizate. Following the same strategy as used for the other cyclic disulfide BR vulcanizates, it was shown that in the 2,3,12,13-tetrathia-[4,4]-metacyclophane BR vulcanizate cross-links were formed due to addition to the carbon double bonds of BR (**13** in Figure 13).

The ^{13}C and ^{1}H chemical shift assignments are collected in Table 6. It was shown that upon the vulcanization of BR with 2,3,12,13-tetrathia-[4,4]-metacyclophane a second cross-link structure was formed, which was assigned as structure **14** (Figure 13). Cleavage of only one of the two disulfidic bonds present in 2,3,12,13-tetrathia-[4,4]-metacyclophane, leaving the other disulfide intact, might also lead to cross-linking with BR. The aliphatic region of the DEPT-135 HRMAS spectrum shows a distinct methylene resonance at δ 43.57 ppm, which was proposed to originate from the CH_2 group (6′) next to the remaining disulfide bond in **14**.

The ^{13}C DEPT-135 spectrum of the 2,3,12,13-tetrathia-[4,4]-metacyclophane BR vulcanizate was supplemented by a direct polarization ^{13}C spectrum (*GHPD* ^{13}C NMR) in order to assign the aromatic quaternary ^{13}C atoms present in the cross-link/pendent group (Figure 14).

Four different quaternary carbon signals were observed, indicating the formation of at least four different xylene containing side chain structures, either as pendent groups or cross-links. On the basis of the chemical shift data and chemical shift calculations they were assigned to structures **13** and **14** (Tables 6 and 7).Finally it can be stated that upon comparison of the various ^{13}C DEPT spectra of the vulcanizates arising from reaction of BR with cyclic disulfides, several differing methine resonances were found in the chemical shift range δ 40−46 ppm. These were ascribed to the methine resonances originating from the cyclic disulfide pendent groups or cross-links.

However, the other parts of the methine region (δ 40−50 ppm) were very much superimposable, suggesting the occurrence of the same pendent groups or cross-link structures in all compounds. The structures might be similar to those formed during tetramethylthiuram disulfide TMTD/ZnO accelerated sulfur vulcanization.[35] Decomposition of the zinc salt is a prerequisite for this to occur.

D. Conclusions. The HRMAS solid state NMR study on BR vulcanizates supports the conclusion drawn earlier from model compound vulcanization studies on *cis*,*cis*,*cis*-1,5,9-cyclododecatriene, that cyclic disulfides form cross-links by addition to the carbon double bonds under the influence of ZDMC and primary amines. It is possible to discriminate between products due to α *substitution* or *addition* to the double bond by combining various 1D and 2D solution NMR techniques on dry (native) as well as swollen vulcanizates. DEPT HRMAS spectra provided the ^{13}C-resonances with the corresponding multiplicity, which served as a starting point for all the studies presented (methine key resonance). Interpretation of HETCOR HRMAS spectra led to the assignment of the corresponding ^{1}H chemical shifts and proton positions. Finally, COSY and TOCSY HRMAS spectra showed unambigiously that addition of the cyclic disulfide to the double bonds leads to the observed cross-linking and allowed the elucidation of the entire molecular network.

^{1}H and ^{13}C chemical shifts found by means of HRMAS solid state NMR were compared to the chemical shifts of hexyl disulfide grafted BR obtained using solution NMR. General agreement between the corresponding chemical shifts was found. Furthermore, ^{13}C chemical shift calculations for the graft structure and the various cross-link vulcanizate structures appeared to compare well with the data experimentally observed.

The various NMR experiments presented clearly open up the possibility to study rubber vulcanizates on a molecular level, providing valuable information about cross-link structure and the underlying mechanism of their formation in greater detail.

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