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Solid-State ^{13}C NMR Study of Accelerated-Sulfur-Vulcanized ^{13}C-Labeled ENB−EPDM

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ABSTRACT: Accelerated-sulfur-vulcanized ^{13}C-labeled EPDM with and without carbon black and extender oil was analyzed using ^{13}C solid-state NMR to determine the chemical structure of the network. High-resolution solid-state ^{13}C NMR reveals that sulfur cross-linking takes place at the allylic positions of the ENB independent of the presence of carbon black and oil. From the integrated intensities of the ^{13}C signals, the conversion of ENB into a cross-link can be quantitatively determined during the vulcanization process. The ENB conversion for gumstock EPDM is ~10% after 10 min of vulcanization at 150 °C, which is a typical optimum vulcanization time in commercial applications. In the presence of carbon black the ENB conversion is marginally faster and reaches ~12% in 10 min, while a maximum conversion of ~20% was obtained. The efficiency of the ENB conversion was ~20% less at 150 °C and ~30% less at 180 °C in the compound with carbon black and oil compared to the compound without carbon black and oil. The substitution at the 9-position of ENB is always preferred over each of the two 3-positions. In turn, the substitution on the 3-exo position is always preferred over the 3-endo position, which is different from earlier model studies. When the material is heated for extended periods (10−20 min), oxidation and reversion of the cross-links starts to occur. Reversion is enhanced upon a temperature increase to 180 °C and yields a 4,5,6,7-tetrahydro-4,7-methanobenzo[*b*]thiophene compound. The length of the sulfur bridge in compound A and B is rather short, i.e., 1 or 2.

Introduction

Ethylene−propylene−diene elastomers (EPDM) are commercially produced by terpolymerizing ethylene, propylene, and a small amount (usually between 4 and 8 wt %) of a diene monomer, viz. 2-ethylidene-5-norbornene (ENB) or dicyclopentadiene (DCPD).[1−3] The saturated polymer backbone of EPDM is resistant to oxygen or ozone attack and degradation by heat and UV radiation. Hence, EPDM is used for high temperature and outdoor applications such as coolant tubes, automotive sealings, and window profiles. The residual unsaturation present as a side group of the polymer chain is essential for sulfur vulcanization of EPDM.

The specific aim of this investigation is to resolve the chemical structure of the cross-links in sulfur-vulcanized EPDM. In the past, sulfur vulcanization has been investigated using low-molecular-weight model compounds.[4−6] The main advantage of model compounds is the absence of the polymer backbone, overcoming the solubility problem, and the possibility to use HPLC and GC for separation and MS and NMR in solution for identification. The focus of that research was the elucidation of the sulfur vulcanization mechanism of polydiene rubbers. A generally accepted reaction mechanism for sulfur vulcanization was established, involving the subsequent formation of active sulfurating species, pending cross-link precursors and sulfur cross-links. The sulfur vulcanization system of ENB containing EPDM has been studied using 2-ethylidene-norbornane (ENBH).[7,8] It was shown that accelerated sulfur vulcanization of ENBH involves the allylic carbon atoms C(3) and C(9) (Figure 1).

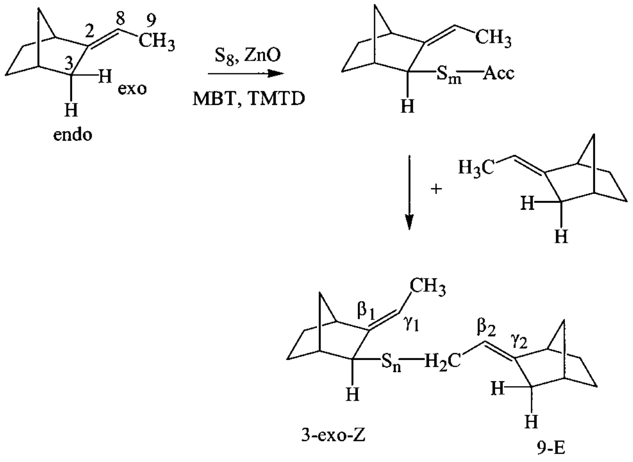

Figure 1. Accelerated sulfur vulcanization of ENBH (Acc = accelerator residue; 3-exo-*Z* and 9-*E* are just examples).

A different approach is the direct analysis of the rubber itself. In this respect IR and Raman spectroscopy have often been used to elucidate the cross-link structures of vulcanized polydiene and EPDM elastomers. For IR and Raman spectroscopy studies, there is a clear limitation when large amounts of carbon black are applied, as is common practice in technical rubber goods. Solid-state ^{13}C NMR spectroscopy does not have this disadvantage and has proven to be a powerful method for the investigation of structural changes upon vulcanization of the real rubber system with and without carbon black, since the chemical network can be ob-

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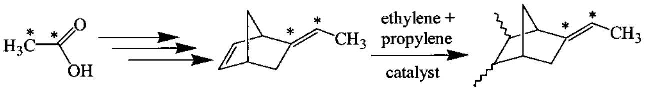


Figure 2. Synthetic scheme for preparation of 2,8-$^{13}C_2$ ENB labeled EPDM.

Table 1. Vulcanization Formulations of the ENBH Model and the ^{13}C-Labeled EPDM

material	model (phr)[a]	compound A (phr)	compound B (phr)
ENBH	100.0		
2,8-$^{13}C_2$-ENB EPDM		100.0	100.0
carbon black (N330)			66.4
oil (Sunthene 4240)			51.0
TMTD (Perkacit TMTD)	1.0	1.3	1.3
MBT (Perkacit MBT)	0.5	0.6	0.6
sulfur	1.5	1.9	1.9
ZnO	5.0	6.4	6.4
stearic acid	1.0	1.3	1.3

[a] Per hundred rubber.

served directly.[9] The diene monomer content of EPDM is usually low, i.e., less than 10 wt %, which corresponds with ~1 C═C for every 100 carbon atoms. Consequently, it is difficult to use solid-state ^{13}C NMR to characterize reaction products of EPDM involving the unsaturation of ENB.

An effective way to enhance both the selectivity and the sensitivity of NMR is selective isotope labeling of the reactive species. The natural abundance of ^{13}C is ~1%. When a ^{13}C label is introduced, the ^{13}C NMR signal is enhanced by almost 2 orders of magnitude. It is generally thought that sulfur cross-linking of elastomers involves sulfur substitution on the α-positions of the double bond.[10] Labeling with ^{13}C at the 2- and/or 8-positions is expected to provide optimum conditions for investigating the chemistry of vulcanization of EPDM. Placing the labels at the double bond has the additional advantage that the signals from the labels will be well resolved. In contrast, the aliphatic part of the ^{13}C NMR spectrum of EPDM already contains a large number of partially overlapping signals, which makes labeling studies involving aliphatic carbons very complex. Finally, the introduction of two ^{13}C labels yields a doublet fine structure as a result of the ^{13}C−^{13}C J coupling, which will be of help in the analysis of the NMR response and can be used in double quantum filtering techniques such as 2D-correlation spectroscopy. By monitoring the intensities of the ^{13}C resonances that appear upon sulfur cross-linking, the conversion of the third monomer can be followed in time. Recently, a synthetic scheme for the specific labeling of ENB and its incorporation in a labeled EPDM was presented (Figure 2).[11] This ^{13}C-labeled ENB−EPDM is here used to study the sulfur vulcanization of EPDM. In practical applications carbon black and oil are added to the EPDM to enhance the mechanical properties. The influence of these additives on the ENB conversion will also be investigated.

Experimental Section

2-Ethylidenenorbornane (ENBH) was used to model EPDM. The formulation of the model vulcanization was adapted from ISO-4097 with tetramethylthiuram disulfide (TMTD) and 2-mercoptobenzothiazole (MBT) as accelerators (Table 1). The model vulcanization experiment was performed using a 10 mL glass tube with a 3 mm thick wall. To prevent evaporation of volatile fractions, the tube was closed with a Teflon screw cap. The vulcanization reaction was started by placing the tube in a hot oil bath equilibrated at 150 °C. The mixture was vigorously stirred during the course of the reaction. The reaction was quenched after 2 h by transferring the reaction vessel from the oil bath into a stream of cold water. Chloroform was added to the reaction mixture to dissolve the organic fraction containing the vulcanization products. The inorganic solid material was removed by filtration and analyzed by NMR to verify that all organic material was extracted. A yellow-brown residue remained after evaporation of the chloroform. This residue was purified by column chromatography using Silicagel 60 as the stationary phase. First a yellow-brown product was eluted with a retardation factor $R_f = 0.8$, using n-pentane as the mobile phase. It contained the model vulcanizate and was analyzed by solution NMR spectroscopy. In addition, another product with a retardation factor of $R_f = 0.6$ was obtained and was analyzed by solution NMR spectroscopy. This second fraction was discarded since contained the vulcanization intermediates shown in Figure 1 that were of no interest to our current investigation.

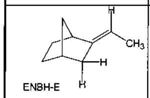
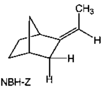
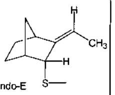
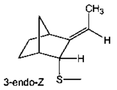
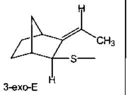
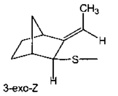
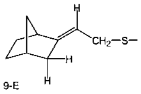
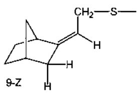
To study reversion, 50 mg of the model vulcanizate was mixed with 500 mg of n-heptadecane in a glass ampule of 10 mL. The ampule was subsequently cooled with ice, flushed with argon and sealed under vacuum. The vulcanization reaction was started by placing the ampule in a salt bath equilibrated at 200 °C. The reaction was quenched after 1 h by transferring the ampule into a stream of cold water. The reaction product was isolated by column chromatography using Silicagel 60 as the stationary phase. With n-pentane as the mobile phase, a light yellow product was eluted with a retardation factor $R_f = 0.8$. The obtained product, 4,5,6,7-tetrahydro-4,7-methonobenzo[b]thiophene was identified with solution NMR. Another fraction was obtained with a retardation factor $R_f = 1.0$, which was identified as ENBH. The silicagel contained no organic material after elution.

1D and 2D NMR spectra of the low-molecular-weight model reaction products were recorded at room temperature with a Bruker DMX-600 using deuterated chloroform as the solvent. Tetramethylsilane (TMS) was added as an internal standard for calibration of the ^{1}H NMR chemical shifts. ^{13}C chemical shifts are given relative to TMS using the signal from the natural abundance ^{13}C in the solvent as an internal standard ($\delta = 77.0$ ppm). COSY,[12] HMQC,[13] and HMBC[14] data were recorded at 600 MHz for ^{1}H and 125 MHz for ^{13}C. The data were averaged in 2048 points in the t_2 dimension. The number of increments was 512 and the number of transients was between 16 and 32. The data were Fourier transformed in the time proportional phase increment (TPPI) mode after being weighted with sine-bell functions shifted by $\pi/2$. For processing of the data, the Bruker Xwinnmr software package was used.

Compounding of the labeled EPDM was done by mixing the $^{13}C_2$-2,8-ENB−EPDM with all other ingredients according to the formulation in Table 1 in a 5 cm^3 mini-extruder at 80 °C for 10 min. ^{13}C-labeled EPDM compounds (~50 mg) were cured into 1 × 1 cm pieces with a thickness of 1 mm using a template in a hydraulic press at a pressure of 10 MPa at 150, 180 and 210 °C. In addition to these compounds, two other compounds were prepared. The first was a compound with 4 parts per hundred rubber (phr) bis(dimethyldithiocarbamato)zinc(II) (ZDMC) and 2 phr TMTD. The second was a compound with 5 phr sulfur. The first compound was prepared by dissolving 100 mg of $^{13}C_2$-2,8-ENB−EPDM and the ingredients into a boiling mixture of 200 mL of n-hexane and 25 mL of chloroform under reflux for 12 h. The second compound was prepared by dissolving 100 mg of $^{13}C_2$-2,8-ENB−EPDM and the ingredients into a boiling mixture of 200 mL of n-hexane and 25 mL of acetone under reflux for 12 h. After removal of the solvent by evaporation, both mixtures were dried under high vacuum for 2 h.

Solid-state ^{13}C NMR spectra of labeled EPDM were recorded either with a Bruker AMX-500 spectrometer operating at 125 MHz ^{13}C frequency or with a Bruker DSX-750WB spectrometer operating at 188 MHz ^{13}C frequency. Various spinning frequencies between 4.5 and 9.0 kHz were used. Solid-state ^{13}C NMR spectra were recorded at 70 °C in order to enhance the mobility of the polymer chains leading to a better spectral

Table 2. ^{1}H and ^{13}C NMR Chemical Shifts of the ENBH Model Vulcanizates

crosslink structure	δ_i C(2) (ppm)	δ_i C(8) (ppm)	δ_i H(3) (ppm)	δ_i H(8) (ppm)	δ_i H(9) (ppm)
 ENBH-E	145.7	111.6	1.79 (endo) 2.10 (exo)	5.22	1.62
 ENBH-Z	147.7	110.8	1.74 (endo) 2.05 (exo)	5.02	1.48
 3-endo-E	145.2	116.7	4.10–4.35	5.38	1.62
 3-endo-Z	144.4	117.1	4.05–4.10	5.36	1.69
 3-exo-E	145.0	119.2	3.60–3.80	5.46	1.65
 3-exo-Z	144.1	119.7	3.85–3.95	5.50	1.74
 9-E	152.7	111.1	1.90–2.20	5.14	3.40–3.75
 9-Z	152.2	111.5	1.95–2.20	5.35	3.30–3.55

resolution for rubber materials.[9] The solid-state ^{13}C NMR data were calibrated using the $^{13}CH_2$ response with $\delta = 29.98$ ppm of the long ethylene sequence as an internal reference. At 70 °C a maximum ^{13}C T_1 of ~1.3 s was measured with a saturation recovery experiment[15] on the C(2) carbon of the reinforced vulcanized labeled compound. The C(2) carbon of the 9*E*/*Z* structures as given in Table 2 had the longest ^{13}C T_1. The presence of carbon black increased the ^{13}C T_1 by ~0.2 s compared to the gumstock compound. Solid-state ^{13}C NMR spectra were recorded with a recycle delay of 10 s and inverse gated proton decoupling to allow complete relaxation of the nuclei between scans. The 90° ^{13}C pulse length was 6 μs.

Spectra were deconvoluted with Lorentzian lines using the CERN (Geneva, Switzerland) Minuit fitting package.[16]

Results and Discussion

Assignment of Signals. The ^{13}C NMR data for $^{13}C_2$-2,8-ENB–EPDM and natural abundance EPDM are shown in Figure 3, parts A and B, respectively. The olefinic region in Figure 3A is dominated by the response from the ^{13}C labels in the double bond at C(8) and C(2). Two strong doublets at $\delta = 110.7$ and $\delta = 146.6$ ppm are observed, each with a splitting of ~75 Hz, which is a characteristic value for two carbon labels connected by a double bond. In addition, partially resolved weak doublet signals, also with a characteristic double bond splitting of ~75 Hz, are observed at $\delta = 111.3$ and $\delta = 145.6$ ppm. The observation of two strongly overlapping doublets at around 111 and 146 ppm is attributed to the presence of both the *E* and *Z* isomers of the ENB in the EPDM. The observation of these doublets is important, they validate a similar observation with enhanced resolution with solution NMR spectroscopy.[11] From the integrated intensities of the two signals, we calculate an *E*/*Z* ratio of 8.3, which agrees with earlier results[11] but contrasts with the *E*/*Z* ratio of ~3 for commercial EPDM. This discrepancy is caused by the different synthesis routes of each of the samples. The aliphatic region of the ^{13}C NMR spectra was assigned using the tables provided by Carmen et al.[17] and Randall.[18]

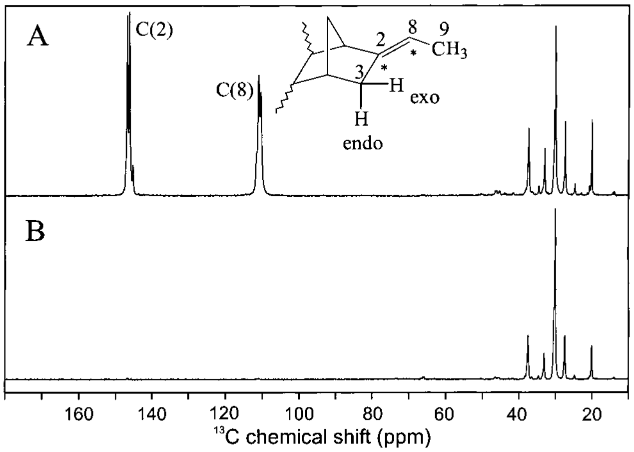


Figure 3. ^{1}H-decoupled ^{13}C MAS NMR spectra of labeled (A) and unlabeled EPDM (B).

Sulfur vulcanization involves substitution at the α-positions next to the residual double bond of ENB. The subsequent difference in chemical environment is sufficient to induce a shift of both labeled carbon signals. This shift enables a direct analysis of the chemical structure of the cross-link. The downfield region of a ^{13}C NMR spectrum collected from a vulcanized labeled EPDM is presented in Figure 4B. The cross-linked EPDM gives rise to weak broad responses around 117 and 151 ppm. In addition, the integrated signal intensity of the ENB unsaturation not participating in cross-linking is somewhat less than the unsaturation in the same sample before the reaction (Figure 4A). The aliphatic part of the NMR spectrum appears unchanged after cross-linking (data not shown). This can be expected, since the amount of third monomer in the system is only 8 wt % and the amount of ENB involved in sulfur substitution appears quite low. In addition, the double bond between the two ^{13}C labels is not converted during vulcanization.

In the past, ^{1}H NMR in combination with HPLC has been used to analyze ENBH model vulcanizates and six different cross-link microstructures were identified (Table 2).[7] These results are in agreement with our own results obtained at a much higher NMR frequency. The higher NMR frequency, 600 instead of 300 MHz, made the assignment possible without use of HPLC separation, which is very time-consuming. In all these structures an α-hydrogen was substituted by a sulfur bridge. The structures have been assigned according to the position of attachment of the sulfur atom and a corresponding nomenclature was introduced, i.e., 3-exo, 3-endo, and 9. In addition, the conformation of the double bond, *E* or *Z*, is included. The length of the sulfur bridge usually varies between one and five sulfur atoms. The ^{1}H assignment of the various cross-link structures obtained with higher magnetic fields can be used to obtain the assignment of the ^{13}C responses via heteronuclear correlation techniques. Since the C(8) carbons are directly bonded to the only olefinic ^{1}H present in ENB, the C(8)–H correlations are well-resolved in a single HMQC experiment (Figure 5). The assignment of the response from the quartenary C(2) carbons is

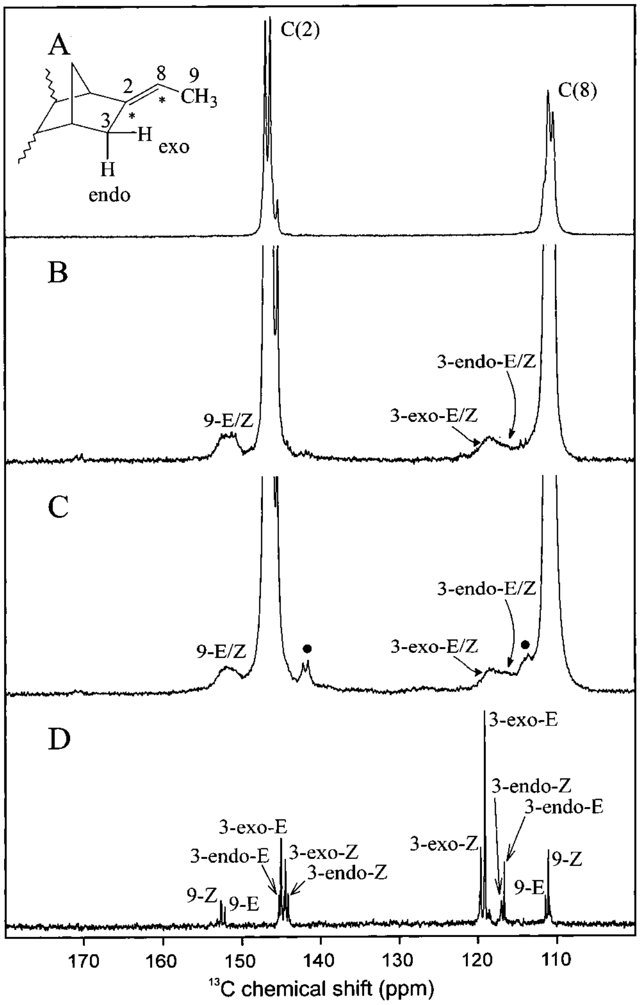


Figure 4. ^{1}H-decoupled ^{13}C MAS NMR spectra of labeled EPDM (A), labeled EPDM cross-linked for 30 min at 150 °C (B), labeled EPDM cross-linked in the presence of carbon black and oil for 30 min at 150 °C (C), and the ENBH model vulcanizate, liquid NMR (D).

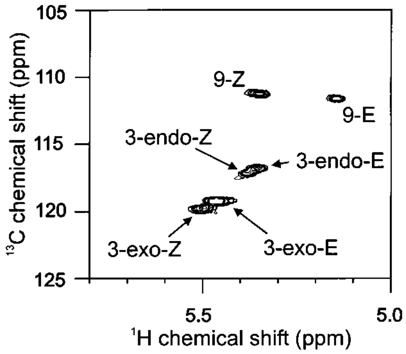


Figure 5. Olefinic region of a 2D ^{13}C−^{1}H NMR spectrum of the ENBH model vulcanizate.

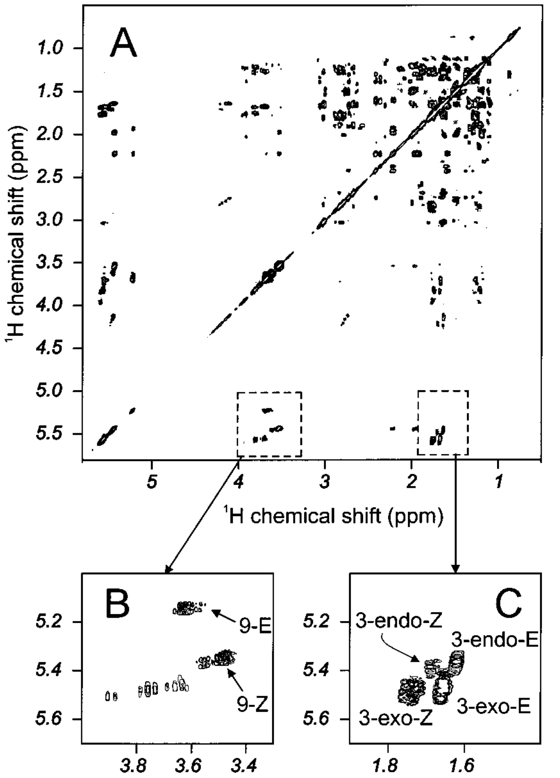


Figure 6. ^{1}H−^{1}H COSY NMR spectrum of the ENBH model vulcanizate (A), enlarged section of the cross-peaks from the 9-*E*/*Z* model vulcanizates (B), and enlarged section of the cross-peaks from the 3-endo-*E*/*Z* and 3-exo-*E*/*Z* model vulcanizates (C).

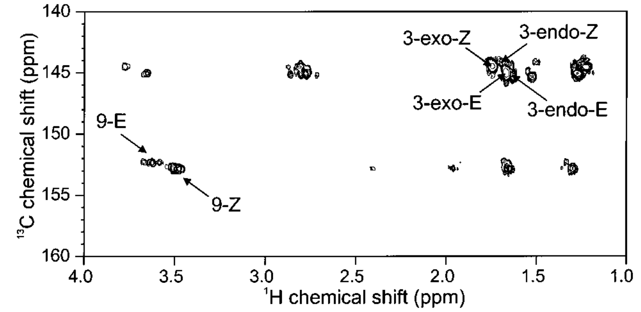


Figure 7. Long-range 2D ^{13}C−^{1}H NMR spectrum of the ENBH model vulcanizates (A). The data reveal long-range correlations of the 9-*E*/*Z*, the 3-endo-*E*/*Z* and the 3-exo-*E*/*Z*.

more complicated. In the ^{13}C NMR spectrum of the model vulcanizates, eight quartenary signals are observed around 145 ppm (Figure 4D). The assignments of the ^{1}H resonances at the 9-position can be obtained from a straightforward ^{1}H−^{1}H COSY NMR experiment (Figure 6). The ^{1}H atoms at the 9-position have a small 3-bond *J* coupling of ~5 Hz with the C(2) carbons. This long-range coupling can be exploited in a HMBC experiment to assign the C(2) responses (Figure 7). The other correlations in this spectrum have arisen from $^{5}J_{CH}$ couplings. This leads to the final ^{13}C NMR assignment for the ENBH model vulcanizate, which is summarized in Table 2.

It is remarkable that the length of the sulfur bridge has only a small influence on the ^{13}C chemical shift (~0.2 ppm) of the olefinic carbons of the model vulcanizates. In addition, sulfur substitution has an effect of 1−2 ppm on the ^{13}C chemical shift of the β-carbon, which is small compared to the effect of 4−5 ppm on the γ-carbon (Figure 1). This agrees with unpublished results by Hahn.[19] Using the ^{1}H assignments of the model vulcanizate, the amount of substitution on the 3-exo, 3-endo, and 9-positions can be determined. This analysis reveals that the fraction with substitution on the 3-exo is higher than the fraction with 3-endo substitution, while the component with substitution at the 9-position is less, which is in agreement with earlier data.[7]

Next, the assignment of the ^{13}C NMR signals for the ENBH model system is used to analyze the ^{13}C NMR spectrum of the cross-linked EPDM rubber in Figure 4B. Taking into account some additional inhomogeneous broadening of ~30−50 Hz due to, e.g., bulk anisotropic susceptibility variations or somewhat restricted motions in the polymer, the model study leads to the assignments presented in Figure 4B. The line broadening was determined using the fitting program and was compared to the line widths observed in the same way for the unfilled samples. The resolution is not sufficient to resolve the *E* and *Z* configurations of the various vulcanization structures. In addition, the signal from the sulfur-substituted ENB overlaps with the response from the unreacted ENB and the difference in chemical shifts of the signals from the quartenary C(2) carbons in the vulcanization products 3-endo-*E*/*Z* and 3-exo-*E*/*Z* and the quartenary C(2) carbons of the unreacted ENB is less than 1 ppm (Table 2). In addition, the ^{13}C resonances of the carbons C(8) of vulcanization products 9-*E*/*Z* are superimposed on the signals of the C(8) carbon of the unreacted ENB. Despite a considerable overlap, discrimination between substitution on C(3)-endo, C(3)-exo, and C(9) is still possible.

The methodology of ^{13}C enrichment in conjunction with high-resolution magic-angle spinning (HR-MAS) NMR allows not only for the first time a detailed study of sulfur vulcanization of pure EPDM but also an investigation of the effect of a common filler, carbon black, on the chemistry of cross-linking. The ^{13}C NMR spectrum in Figure 4C of the compound with carbon black and oil is very similar to the data presented in Figure 4B. This shows that the effect of carbon black and oil on the cross-link structure is limited. The presence of the carbon black gives rise to somewhat broader lines (~45−80 Hz), because the mobility of the polymer chains is restricted by adsorption to the carbon black surface.[20] There is no evidence for excessive line broadening. This might be expected since the susceptibility difference of the carbon black filler compared to EPDM can cause a disturbance in the local magnetic field,[21,22] especially where the polymer chains are in close contact with the carbon black. However, this is not observed and is in line with earlier studies on polydiene rubbers.[23]

In Figure 4C, there are additional signals indicated with ● at 114 and 142 ppm, which have not been observed in the gumstock compound. These signals are observed in the compound with carbon black before cross-linking and therefore arise from structures that have been formed during the mixing procedure. These resonances have also been observed on peroxide-cured $^{13}C_2$-ENB-labeled EPDM and provide evidence for radical formation during mixing with carbon black.[24] This indicates that the reinforced compound has already slightly scorched before the actual vulcanization step, while it still can flow when it is being cured in the hydraulic press. These results provide strong evidence that the carbon black contains radicals and/or generates radicals during the mixing step, when high shear forces are applied.

ENB Conversion. The cross-linking process was followed in the two compounds A and B at two different temperatures, viz. 150 and 180 °C. Since the distinction between the *E* and *Z* isomers cannot be made in solid-state NMR spectra due to insufficient resolution, three main structures regarding sulfur substitution, i.e., 3-endo, 3-exo, and 9, are distinguished. By application of curve fitting to the solid-state spectra, the conversion of ENB can be determined in time, assuming that the total integral over the olefinic region is constant. For every ^{13}C NMR spectrum the region between 180 and 100 ppm was deconvoluted with a superposition of Lorentzian lines. The dataset collected from the sample vulcanized for 30 min at 180 °C was first deconvoluted and the integrated intensities, the line widths and the chemical shifts of the various signals were determined. Subsequently, the other spectra in the series with different vulcanization times were analyzed for each signal, while keeping the line widths and the chemical shifts fixed to their values. This leaves the integrated intensities of the signals as the only free parameters and they can be determined with a relative error of ±10% in terms of the ENB conversion. Note that ENB conversion refers to sulfur substitution at the allylic position, while the double bond remains.

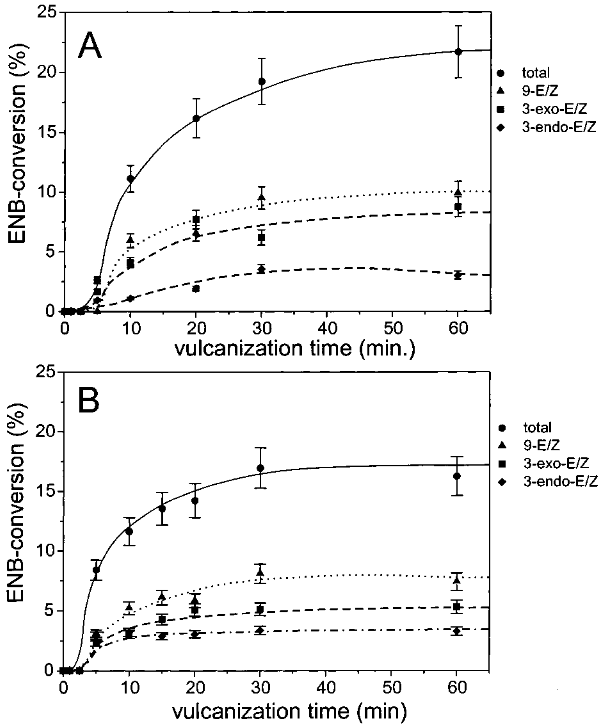


Figure 8. ENB conversion vs cure time for labeled EPDM. The samples were cross-linked at 150 °C, without carbon black and oil (A) and with carbon black and oil (B). The lines are guides to the eye.

Parts A and B of Figure 8 represent the ENB conversion of compounds A and B, respectively, at 150 °C for curing times up to 120 min. The bars indicate the errors from the deconvolution procedure. The ENB conversion is limited to ~22% for the gumstock compound (A) and to ~17% for the compound with carbon black and oil (B). This is relevant for commercial applications, since ENB is the most expensive monomer of EPDM.

Parts A and B of Figure 9 represent the ENB conversion of compounds A and B, respectively, at 180 °C for curing times up to 60 min. The ENB conversion is limited to ~19% for the gumstock compound (A) and to ~14% for the compound with carbon black and oil (B). The higher temperature of 180 °C has a tremendous influence on the rate of vulcanization as is expected. The maximum ENB conversion is already obtained after 10 min at 180 °C vs 60 min at 150 °C. However, the total amount of ENB conversion at 180 °C is lower compared to the one at 150 °C.

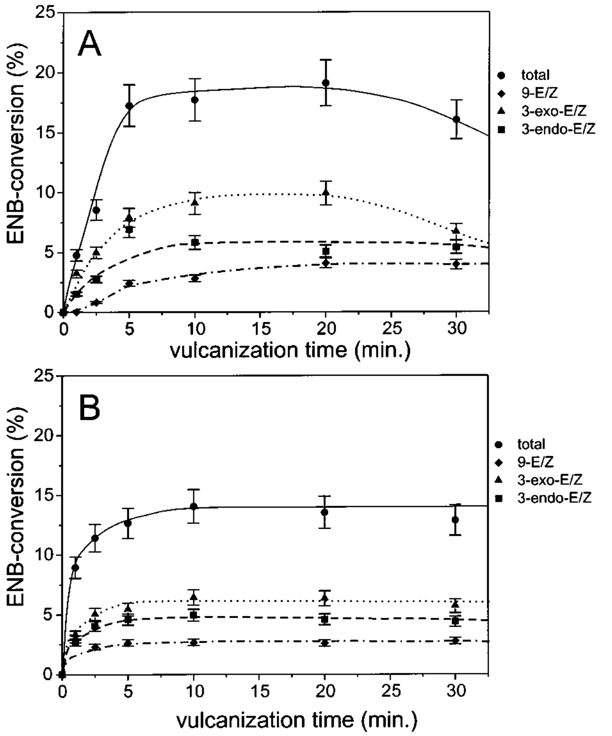


Figure 9. ENB conversion vs cure time for labeled EPDM. The samples were cross-linked at 180 °C, without carbon black and oil (A) and with carbon black and oil (B). The lines are guides to the eye.

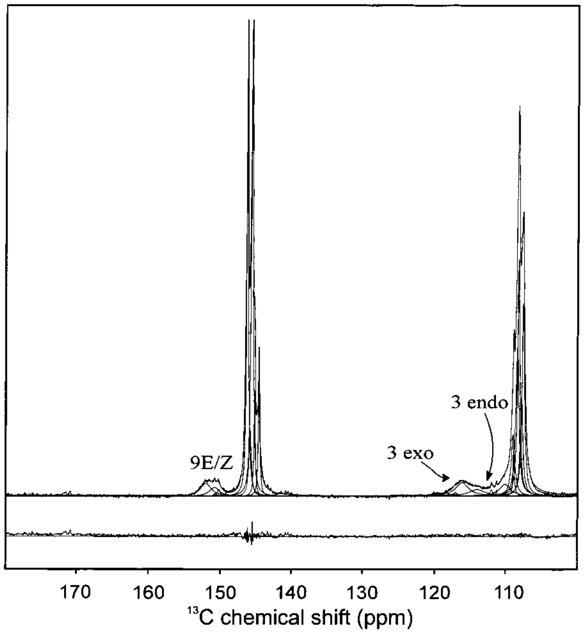


Figure 10. Fit of labeled EPDM cross-linked for 120 min at 150 °C.

According to the ^{13}C NMR studies presented here, most of the ENB is not converted during accelerated sulfur vulcanization, which is clearly illustrated in an example of one the fits from vulcanized carbon-13 labeled EPDM (Figure 10). This is in contrast with data obtained with wide line ^{1}H NMR relaxation studies.[25] In these studies, a first analysis of cross-link formation was presented by fitting ^{1}H time domain signals with a superposition of T_2-broadened responses. It is evident that the accuracy of the ^{13}C experiments presented here is better, since direct analysis of the vulcanization reaction is possible due to the selective isotope enrichment and the large ^{13}C chemical shift dispersion.

The observation that vulcanization of the carbon black reinforced compound yields a lower degree of ENB conversion than for the gumstock compound (22 vs 17%) is in line with data obtained from ^{13}C NMR for polydiene rubbers.[23] In contrast, the initial ENB conversion and buildup of cross-links appears more rapid in the presence of carbon black. For instance, after 5 min curing time, the ENB conversion of compound A is ~3% and of compound B ~8%. A significant difference is also observed upon 1 min curing at 180 °C (Figure 9). The ENB conversion for compounds A and B is ~5% and ~9%, respectively. At 180 °C the total ENB conversion for compound A is thus ~30% higher than that for compound B. This provides strong evidence that on one hand the carbon black promotes the vulcanization at the start of the vulcanization experiment, while on the other hand it appears to suppress the cross-linking process at longer time scales. The samples are too small (1 mm thick) to note a difference in heat transfer from the press to the sample and it is therefore concluded that the carbon black influences the reaction kinetics. The carbon black surface can act either as a catalyst, mainly during the earlier stages of the vulcanization or as a inhibitor at the end of the vulcanization. The inhibitor effect is probably due to restricted mobility in the system or due to adsorption of vulcanization chemicals at the surface on the carbon black.

From Figures 8 and 9, distinct differences in chemical reactivity of the three types of α-hydrogens can be observed. In Figure 8A, for instance, the amount of sulfur substitution on the 9-position is at most ~10%, while sulfur substitution on the 3-exo position and 3-endo position yield ~8% and ~3%, respectively. Similar trends are observed at higher temperatures (180 °C) and in the presence of carbon black and oil. It shows that substitution at the 9-position is preferred over each of the two 3-positions, however the sum of the fractions with substitution at the 3-position is larger than the component with substitution at the 9-position. In addition, the substitution at the 3-exo position is always preferred over the 3-endo position. Earlier studies have already indicated that there is no direct relationship between the number of α-hydrogens present in an EPDM and the reactivity of these hydrogens toward sulfur substitution.[26] Thus, the preference for the 9-position cannot be explained in this way. It should be related to a difference in chemical reactivity of each of the allylic positions. The experimental observation from Figures 8 and 9 that the 3-exo is preferred over the 3-endo is surprising, since for model vulcanizates the 3-endo position is preferred over the 3-exo position. This difference between the model and the real system may be due to additional steric hindrance at the 3-endo position in the polymer system. This illustrates the intrinsic limitation of the model studies.

Oxidation and Reversion. In the spectra of compound A vulcanized at 180 °C and for very long vulcanization times (approaching 120 min) at 150 °C, a buildup of some additional signals at 171, 122, and 120 ppm is observed, which cannot be attributed to a sulfur cross-link structure (Figure 11A,B). In addition, the broad signal around 152 ppm exhibits fine structure and consists of two doublets at 150 and 152 ppm. The sharp signal at 150 ppm indicates breakdown of the polysulfidic cross-links into a monosulfidic cross-link, since its

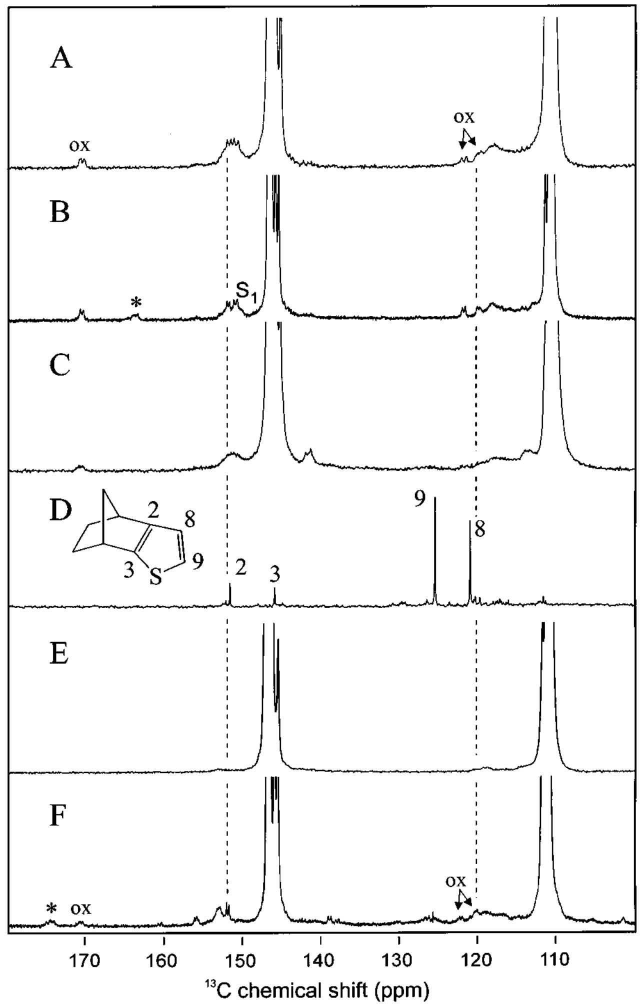


Figure 11. ^{1}H-decoupled ^{13}C MAS NMR spectra of labeled EPDM cross-linked for 120 min at 150 °C (A) and for 30 min at 180 °C (B), of labeled EPDM cross-linked for 30 min at 180 °C with carbon black and oil (C), of the thiophene model (D), of labeled EPDM cross-linked with ZDMC and TMTD for 20 min at 150 °C (E), and of labeled EPDM cross-linked with pure sulfur for 120 min at 150 °C. Asterisk: spinning sideband of the ENB response at 110 ppm. ox: oxidation product. S_1: monosulfidic cross-link.

intensity increases with cure time and the signal shifts upfield when a cross-link consists of only one sulfur atom. The signal is indicated with S_1. The signal around 171 ppm with a J_{C-C} coupling of 58 Hz, indicated with ox, strongly suggests the presence of a labeled carbonyl due to oxidation of the double bond in the cross-linked ENB or non-cross-linked ENB. It was shown with an ultrahigh field ^{13}C$-$^{13}C COSY experiment that the upfield signals at ~120 and ~122 ppm correlate with the carbonyl response at ~171 ppm (Figure 12). This shows that two different carbonyl structures are present at 171 ppm. The correlations with the two olefinic signals indicate that carbonyls are connected by a single bond to unsaturated carbons. The J_{C-C} couplings of 58 and 61 Hz of the signals at ~120 and ~122 ppm, respectively, are consistent with the delocalization of electrons in double bonds. There are two possibilities to form such oxidation products. First, ENB as it is incorporated in EPDM can be oxidized directly due to the presence of oxygen in the rubber sample. However, heating EPDM in the absence of cross-linking chemicals does not lead to the formation of these oxidation products. If the oxidation products are formed directly from ENB$-$EPDM, the presence of the cross-linking chemicals should catalyze a specific reaction to form the carbonyl structures. Alternatively, oxidation of the sulfur cross-link structures can also lead to carbonyls. Both explanations are plausible.

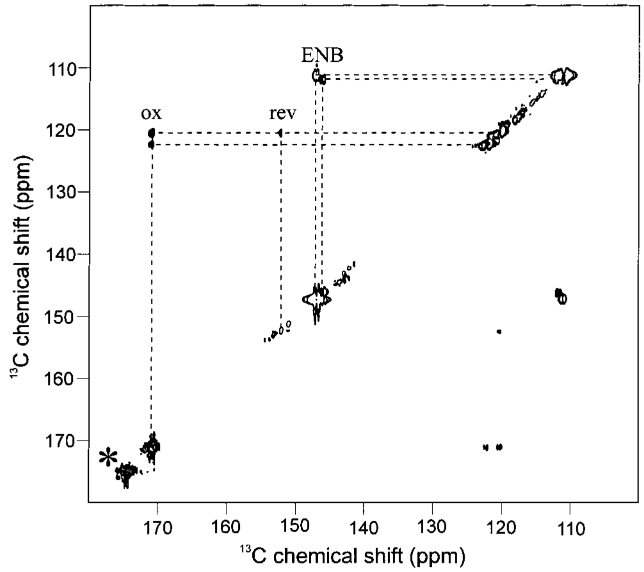


Figure 12. TPPI phase-sensitive ^{13}C$-$^{13}C COSY MAS NMR spectrum recorded at ultrahigh field with proton-decoupling during acquisition of the labeled EPDM after cross-linking at 180 °C for 20 min. The use of a wide-bore ultrahigh field spectrometer, operating at 188 MHz ^{13}C frequency and 750 MHz ^{1}H frequency, allows the unambiguous assignment of the reversion and oxidation product signals, indicated with ox and rev, respectively. Asterisk: spinning sideband.

The signals at 120 ppm also match with signals at 152 ppm with a J_{C-C} coupling of ~61 Hz. The ^{13}C$-$^{13}C COSY experiment reveals that these two signals are indeed from adjacent carbons (Figure 12) and that there are in fact two superimposed doublets at 120 ppm, since the signal has two sets of correlations in the 2D experiment. The response at ~120 ppm is split by a J_{C-C} coupling of ~61 Hz, which is characteristic for a delocalized system like a thiophene.[27] Formation of thiophenes was also observed when polysulfidic cross-link products were thermally treated at higher temperatures (180$-$220 °C).[28,29] The ^{13}C NMR spectrum of a thiophene model, viz. 4,5,6,7-tetrahydro-4,7-methanobenzo[*b*]thiophene, is presented in Figure 11D. The ^{13}C response from the model at 152 and 121 ppm corresponds well with the signals at 152 and 120 ppm, respectively. The signals are only slightly shifted due to interactions of the model thiophene with the solvent. This close correspondence of the shift value provides strong evidence that in the rubber system a thiophene structure is formed. The signal intensity from the labels in this thiophene structure increases with curing time at 180 °C. This probably explains the lower intensity of the 3-exo, 3-endo, and 9 signals at 180 vs 150 °C. The detection of a thiophene compound is important, since it indicates reversion, leading to a deterioration of mechanical and elastic properties. Distinct differences are observed in the ^{13}C NMR spectrum of compound B (Figure 11C). The signal intensities of the thiophene in compound B are much less than for compound A (Figure 11B). In addition, the signal of the carbonyl oxidation product is less intense for the compound with carbon black and oil, both of which are correlated to nonconverted ENB signals. Since the ENB conversion was lower in the presence of carbon black and oil, this suggests a correlation between the maximum efficiency of the ENB conversion and the formation of both oxidation and reversion products.

The downfield region of a ^{13}C NMR spectrum collected from ZDMC and TMTD vulcanized labeled EPDM is presented in Figure 11E. This cross-linked EPDM gives rise to the same weak broad responses around 117 and 151 ppm as presented in Figure 11B. The intensity of these signals is, however, much lower compared to the vulcanizations in the presence of sulfur. TMTD vulcanizates are known for their very short sulfur bridges, one or two sulfur atoms.[4] Since the ^{13}C NMR spectrum obtained from the TMTD-vulcanizate (Figure 11E) and the spectra obtained from compound A and B are very similar, it can be concluded that the sulfur bridge length for compounds A and B is short indeed, i.e., 1 or 2. However, the ENB conversion for compounds A and B is much higher.

Unaccelerated Sulfur Vulcanization. The downfield region of a ^{13}C NMR spectrum collected from pure sulfur-vulcanized labeled EPDM is presented in Figure 11F. The signals corresponding to the thiophene compound and the oxidation products are also observed in this spectrum. The broad signals at 118 and 154 ppm are assigned to the same structures as obtained from accelerated-sulfur vulcanization; however, the former signals are slightly shifted downfield. In addition, new unidentified signals can be observed at 156, 138, and 126 ppm in the downfield region. The downfield shift of 2 ppm of the allylic sulfur-substituted moieties can be explained by the fact that the sulfur bridge in the nonaccelerated system is much longer than for the accelerated system. Nonaccelerated sulfur vulcanization involves also substitution at the α-positions, but in addition it also results in addition to the double bond ($S_8 + 2$ olefins → alkenyl−S_n−alkyl).[30] The sulfur bridge length for nonaccelerated sulfur vulcanization is known to be very long compared to accelerated sulfur vulcanization.[30] The sulfur cross-link with only one sulfur atom has the most upfield chemical shift (Figure 11B). The longer the sulfur bridges the more downfield the chemical shift of the ^{13}C response will be, which is exactly what is observed here. The fact that a sulfur cross-link can consist not only of allylic sulfur-substituted moieties, but also of ENB moieties with sulfur added to the double bond in the aliphatic region of the ^{13}C NMR spectrum at chemical shifts in the range 50−70 ppm (data not shown) cannot be the explanation for the difference in chemical shift, since the distance between the two ENB moieties involved in a cross-link is too large.

Conclusions

Using isotope labeling and NMR, we find that accelerated sulfur vulcanization of ^{13}C labeled EPDM occurs at the allylic positions of ENB. This is in agreement with model studies with low-molecular-weight olefins. The chemical structures of the cross-links that are formed have been analyzed with ^{13}C NMR. Three main structures can be identified, with sulfur substitution on the 9, 3-endo, and 3-exo positions. From the integrated intensities of the ^{13}C NMR signals, the maximum conversion of ENB is estimated at 22% of the total ENB content.

According to NMR measurements, the cross-link structure is not significantly affected by the presence of carbon black and oil. The presence of carbon black initially promotes cross-linking, while the final yield of ENB conversion is lower. The total conversion of ENB is ∼20% lower at 150 °C and ∼30% lower at 180 °C in the presence of carbon black and oil. The ENB conversion in 10 min at 150 °C, which is a characteristic time scale in vulcanization applications, is only 10% of the total amount of ENB in the polymer. This is important, since it suggests that there is still ample room for improvement of the conversion efficiency of ENB, which is the most expensive monomer of EPDM.

Upon prolonged heating at higher temperatures, oxidation and reversion of sulfur-vulcanized EPDM occurs. The decrease in cross-link density is accompanied by the formation of a thiophene compound. From data of the vulcanization with TMTD and pure sulfur, it can be concluded that the sulfur cross-links in compound A and B have sulfur bridges with only one or two sulfur atoms.

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Note Added after ASAP Posting

This article was released ASAP on 1/26/2002 with an error in line 13 of the abstract (material replacing reaction). The correct version was posted on 2/26/2002.

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