Determination of the Structure of Butyl Rubber by NMR Spectroscopy

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ABSTRACT: The structure of 2,2,4,8,8-pentamethyl-4-nonene, a butyl rubber model compound, was established by ^1H and ^{13}C NMR spectroscopic methods. The results were used for the investigation of the structure of selectively deuterated butyl rubber and of butyl rubber itself. A combination of several techniques was used to assign all of the signals in these spectra. This study confirmed some of the previously published data on the structure of butyl rubber. In addition, all of the information concerning the structure of the isoprenyl units was elucidated.

Introduction

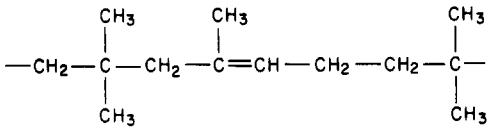
Butyl rubber is a generic name for a family of isobutylene–isoprene copolymers generally containing less than 3% incorporated isoprenyl groups. Due to its low gas permeability, good thermal and oxidative stability, and excellent moisture and chemical resistance, butyl rubber has been a product of commerce since 1942.

In addition to being used as an elastomer in its own right, butyl rubber also serves as a starting polymer for the commercial production of chlorobutyl and bromobutyl elastomers.

Problems associated with performing a detailed analysis of butyl rubber were largely due to the presence of a very small amount of the isoprenyl units in the polymer (<3 mol %).

As with all copolymers, it is desirable with butyl rubbers that the structures of both the monomeric residues and the mode of their incorporation be defined. In the case of butyl rubber, generation of the following structural information is required: (1) mode of incorporation of isobutylene units (head-to-tail or head-to-head), (2) distribution of isoprenyl units (random or block), (3) mode of incorporation of isoprenyl units (1,4, 1,2, on 3,4, and head-to-tail or head-to-head), and (4) geometry of incorporated isoprene units (*Z* or *E*). Over the years, numerous publications on the structure of butyl rubber have appeared in the literature. Largely on the basis of analogy with polyisobutylene, it was proposed that the polyisobutylene segment of butyl rubber consisted of head-to-tail-linked isobutylene units.[1]

Rehner provided information indicating that the isoprene units enter randomly into the chain in 1,4 configuration.[2] The chemical analysis of the ozone-degraded polymer did not provide any evidence for the presence of isoprenyl units enchained in the 1,2 on 3,4 mode. Furthermore, the isoprenyl microstructure 1 has gained wide acceptance.[3]



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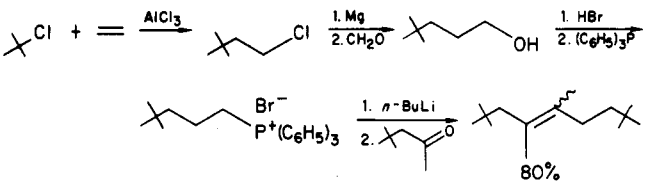
More recently, time-averaged ^1H NMR spectroscopy was used for the investigation of the structure of butyl rubber.[4] This work confirmed the type of enchainment of isoprenyl units as 1,4; however, the spectra were not of sufficiently high quality to allow the elaboration of the geometry of these units. The preliminary work on this subject, based on Fourier transform ^1H NMR studies, indicated that the geometry of the isoprenyl units in butyl rubber may vary over a wide range.[5]

Scheme I



Recently, additional papers dealing with the NMR spectroscopic investigation of butyl rubber have appeared.[6]

In spite of previous efforts, it was felt that the detailed structure of butyl rubber had not been rigorously established. With recent advances in the NMR instrumentation, we felt that it was possible to provide conclusive structural information on butyl rubber.

The objective of this work was to provide definitive information on the structure of butyl rubber by using NMR spectroscopy. Particular emphasis was placed on the mode of incorporation of the isoprene units, their geometry, and confirmation of structural features deduced in previous studies. The structure and the environment of the isoprenyl groups were emphasized because all of the curing reactions take place through this minor component. Furthermore, the halogenation chemistry of butyl rubber also takes place at these sites, and their environment has a critical influence on the outcome of halogenation reactions.[7]

In order to circumvent the problems associated with the low content of isoprenyl groups in butyl rubber, we synthesized a model compound incorporating the structural features of the proposed butyl structure and rigorously defined its structure. We then used this structural information in the interpretation of the spectra of commercial butyl rubber samples. To confirm some of the structural assignments, we also prepared and analyzed a sample of partially deuterated butyl rubber.

Experimental Section

Preparation of Samples. 2,2,4,8,8-Pentamethyl-4-nonene (2). This hydrocarbon was prepared as shown in Scheme I. The last step in the synthesis proceeded in 70% yield. A mixture consisting of 57% *Z* and 43% *E* isomers boiling at 87–90 °C (10 mmHg) was obtained. The structure of this product was confirmed by mass spectrometry (*m/e* 196.21096) and NMR spectroscopy (see the following section).

Deuterated Butyl Rubber. Specifically deuterated isoprene was prepared by the reaction of vinylmagnesium bromide with deuterated acetone, followed by dehydration. The product had a boiling point 34–36 °C (760 mmHg) and was characterized by mass spectrometry (*m/e* 73.1) and ^1H NMR spectroscopy.

Isobutylene (30 mL) and isoprene-d_5 (0.9 mL) were copolymerized in the presence of ethylaluminum dichloride in methyl chloride (120 mL) at −95 °C. The NMR spectrum of this sample is discussed in the following section.

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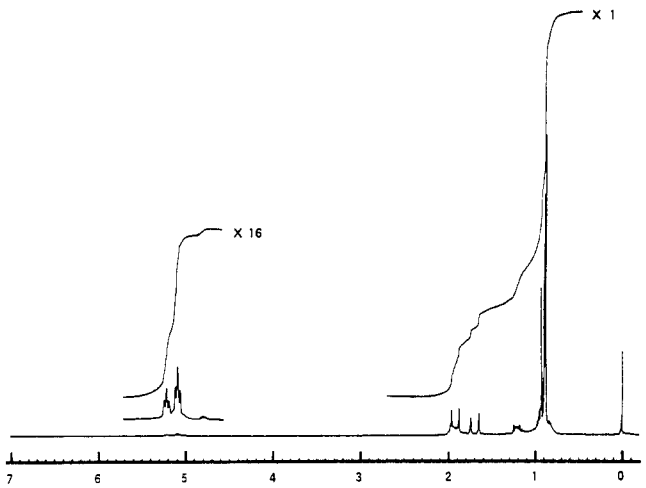


Figure 1. ^1H NMR spectrum of 2,2,4,8,8-pentamethyl-4-nonene (at 250 MHz in $CDCl_3$).

Butyl Rubber. Commercial samples were used without further purification.

NMR Measurements. Instrument. A Bruker WM-250 spectrometer was used for the experiments. The ^1H signals were observed at 250.13 MHz and the ^{13}C signals were observed at 62.89 MHz.

^1H NMR. A 2% solution of rubber samples in $CDCl_3$ and a 10% solution of the model compound in $CDCl_3$ were observed by using a 5-mm dual $^1H/^{13}C$ probe. The pulse length was 19 μs (90°) and the relaxation delay was 2 s for all ^1H spectra.

^{13}C NMR (Wide-Band Decoupled). A solution was prepared by dissolving 500 mg of butyl rubber in 10 mL of $CDCl_3$ and observed by using a 15-mm carbon probe. For the model compound, a 10% solution was also used. The pulse length was 14 μs (70°) and the relaxation delay was 5 s. For quantitative determinations, the nuclear Overhauser effect was removed by applying an inversely gated pulse sequence.

^{13}C NMR (Off-Resonance Decoupled). The same samples were observed with single-frequency decoupling, 1800 Hz off center.

^{13}C NMR (Selectively Decoupled). The same samples were observed with selected single-frequency decoupling at 3342.13 Hz (1.94 ppm), 3269.49 Hz (1.65 ppm), and 3208.50 Hz (1.41 ppm).

^{13}C (J-Modulated Spin Echo). A 90°–τ–180° pulse sequence was used, with τ = 8 ms and 5-s relaxation delay.

Results and Discussion

NMR Spectra of Model Compound 2. Prior to the synthesis of model compound **2**, we investigated the possibility of using high-isoprene-content butyl rubber as a model for conventional butyl rubber. A comparison of the ^{13}C spectra of butyl rubber samples containing 11 mol % isoprene and those containing 2 mol % isoprene indicated that the former material was not an appropriate model for commercial butyl grades. This conclusion was based on the observation that the ^{13}C spectrum of the high-isoprene-content butyl rubber contained at least three pairs of olefinic carbons, whereas the spectra of conventional butyl elastomers contain only one pair. The presence of these additional signals in the spectra of high-isoprene-content polymer is associated with more complex microstructures, such as isoprenyl units in blocks, isoprenyl units separated by one isobutylene unit, terminal isoprenyl group, etc.

The high-resolution ^1H NMR spectrum of butyl rubber model compound **2** is shown in Figure 1. An inspection of the spectrum indicates that the product consists of a mixture of isomers. After comparison with known chemical shifts of similar groups, we assigned the various signals in this spectrum as shown in Table I.

It is worth noting that at the field of 250 MHz the signals due to olefinic protons are fully resolved and appear as two individual triplets at 5.01 and 5.21 ppm. If the ^1H spectra are recorded with instruments of lower field strength (60 and 100 MHz), these two signals are not resolved but appear under a common envelope. Thus, important information about the isomeric composition of the hydrocarbon mixture is not available from this spectral region with instruments of lower field strength.

Table I
Assignment of Signals in the ^1H NMR Spectrum of the Model Compound 2

chem shift, ppm	multiplicity[a]	assignment
0.88	s	t-Bu
0.89	s	t-Bu
0.93	s	t-Bu
1.10	m	CH_2
1.65	s	CH_3, E isomer
1.74	s	CH_3, Z isomer
1.87	s and m	CH_2, E isomer
1.96	s and m	CH_2, Z isomer
5.08	t	olefinic H, E isomer
5.21	t	olefinic H, Z isomer

[a] s = singlet, m = multiplet, and t = triplet.

The signals due to the methyl groups attached to the double bond (1.65 and 1.74 ppm) of the two isomers appear at chemical shifts similar to those observed for isomeric polyisoprenes.[8] These signals were conveniently used for the determination of the isomeric composition of the mixture prior to the availability of the 250-MHz spectrometer.

As mentioned above, the synthetic procedure for the preparation of the model compound afforded a mixture of 57% Z and 43% E isomers. On treatment with thiophenol in the presence of a free radical initiator, this mixture was altered to give a mixture of thermodynamically equilibrated composition. This product contains 75% E and 25% Z isomers. In the course of this equilibration, we observed appropriate changes in the relative intensity of the signals due to the methyl and methylene protons (1.87 and 1.96 ppm) in the allylic positions.

The wide-band decoupled ^{13}C NMR spectrum of the model compound is shown in Figure 2a. Appropriate regions of this spectrum, in their expanded form, are shown in Figure 2b–d. The differentiation between the closely spaced pairs of signals and their assignment to the particular isomer was based on the relative size of the signals and on the known ratio of the two isomers of the model compound.

The assignments of the signals to particular carbon atoms were based on the known chemical shifts, the intensities of the individual signals, and the consideration of the off-resonance spectrum (Figure 3b), the selectively decoupled spectrum (Figure 4b), and the J-modulated spin–echo spectra (Figure 5). Signals due to all of the carbon atoms were correlated with the number of protons attached to them, thus enabling unambiguous assignment of the signals.

By selectively irradiating the signals centered around 1.91 ppm in the ^1H spectrum, we obtained the ^{13}C spectrum shown in Figure 4b. These signals in the ^1H spectrum are due to the methylene groups and, as is evident from Figures 3b and 4, all of the triplets in the off-resonance decoupled spectrum (Figure 3b) were collapsed into singlets. The J-modulated spin–echo spectrum (Figure 5) clearly differentiated carbon atoms with an odd number of protons (CH and CH_3 negative peaks) from those with even numbers of protons (C and CH_2 positive peaks). These experiments further confirmed the proposed assignments and allowed for the resolution of the two groups of overlapping signals.

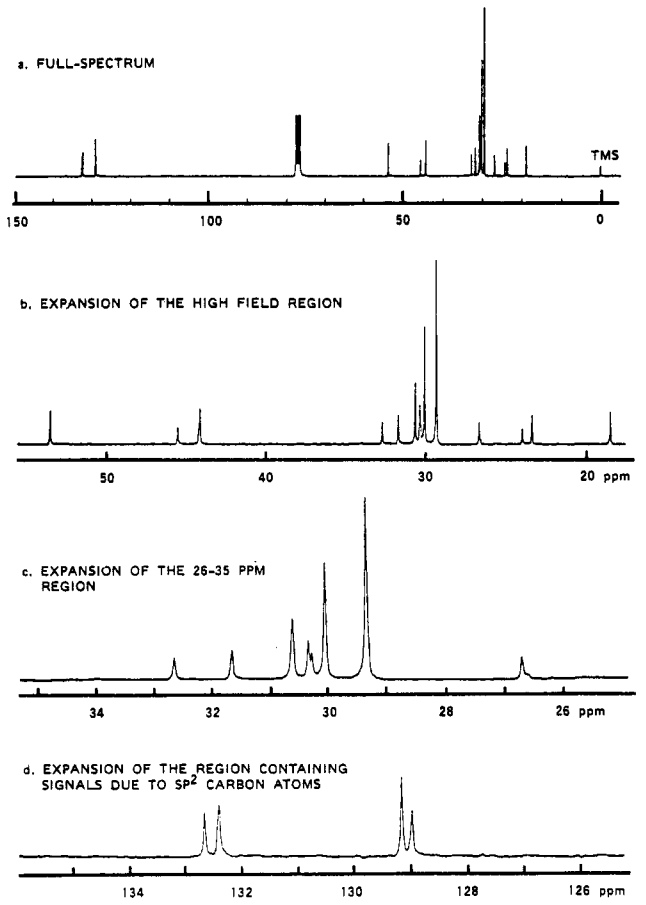


Figure 2. Wide-band ^{1}H-decoupled ^{13}C NMR spectra of 2,2,4,8,8-pentamethyl-4-nonene (at 62.8 MHz in $CDCl_3$).

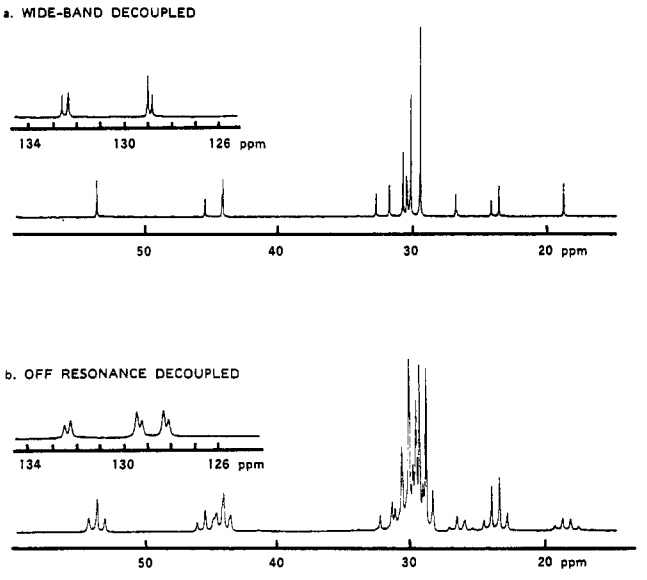


Figure 3. ^{13}C NMR spectra of 2,2,4,8,8-pentamethyl-4-nonene (at 62.8 MHz in $CDCl_3$).

The complete assignment of carbon atoms observed in the ^{13}C NMR spectrum of a mixture of isomers of the model compound 1 is shown in Table II. With the full interpretation of both ^{1}H and ^{13}C NMR spectra of 2,2,4,8,8-pentamethyl-4-nonene completed, we undertook the analysis of butyl rubber.

NMR Spectra of Butyl Rubber. The high-resolution ^{1}H spectrum of butyl rubber is shown in Figure 6. From their positions and integrated intensities, the signals at 1.11 and 1.41 ppm, observed from the lower trace of Figure 6, may be assigned to the methyl and methylene protons of the polyisobutylene units of butyl rubber.

The upper trace in Figure 6, obtained at higher amplification, features some of the signals due to the isoprenyl units of butyl rubber. From a comparison of this trace with

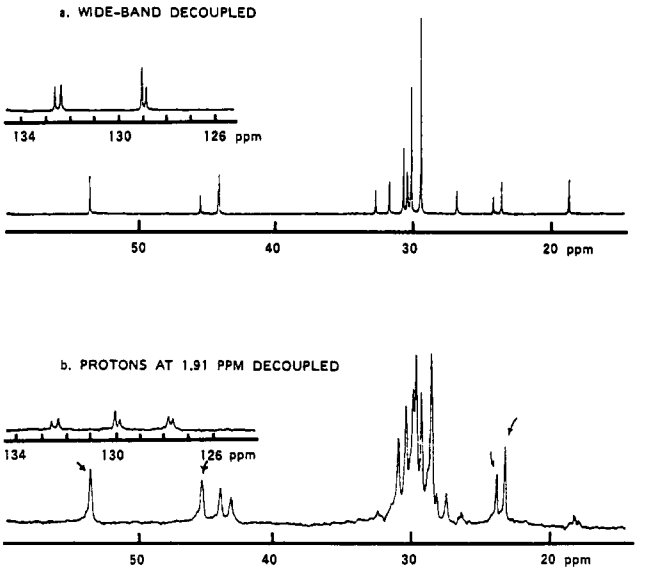


Figure 4. ^{13}C NMR spectra of 2,2,4,8,8-pentamethyl-4-nonene (at 62.8 MHz in $CDCl_3$).

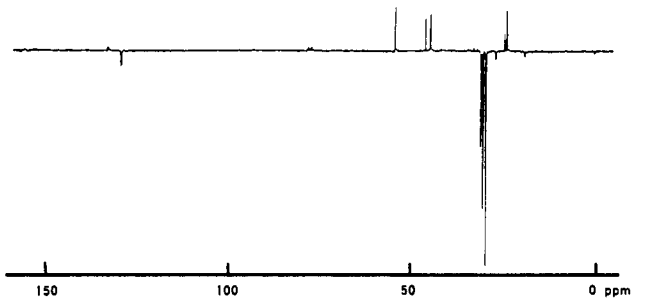
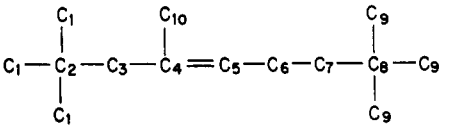


Figure 5. *J*-Modulated spin-echo ^{13}C NMR spectrum of 2,2,4,8,8-pentamethyl-4-nonene (at 62.8 MHz in $CDCl_3$).

Table II
Assignment of the Signals in the ^{13}C NMR Spectrum of the Model Compound 2



chem shift, ppm	multiplicity[a]	assignment
18.67	q	C_{10}, *E* isomer
23.47	t	C_6, *E* isomer
24.07	t	C_6, *Z* isomer
26.72	q	C_{10}, *Z* isomer
29.34	q	C_9, *Z* and *E* isomer
30.06	q	C_1, *E* isomer
30.30	s	C_8, *Z* isomer
30.34	s	C_8, *E* isomer
30.62	q	C_1, *Z* isomer
31.65	s	C_2, *E* isomer
32.64	s	C_2, *Z* isomer
44.08	t	C_7, *E* isomer
44.13	t	C_7, *Z* isomer
45.44	t	C_3, *Z* isomer
53.55	t	C_3, *E* isomer
128.92	d	C_5, *Z* isomer
129.10	d	C_5, *E* isomer
132.37	s	C_4, *E* isomer
132.67	s	C_4, *Z* isomer

[a] s = singlet, d = doublet, t = triplet, and q = quartet; from off-resonance decoupled spectrum.

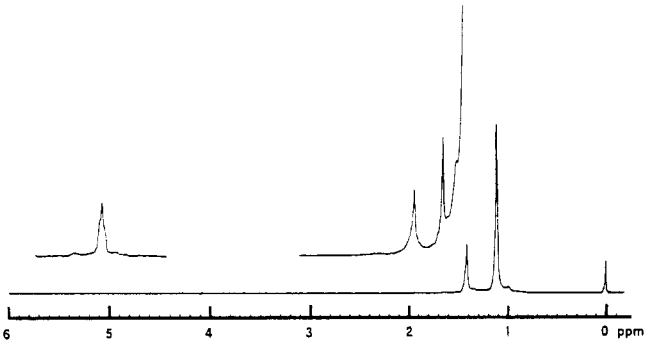


Figure 6. ^1H NMR spectrum of butyl rubber (at 250 MHz in $CDCl_3$).

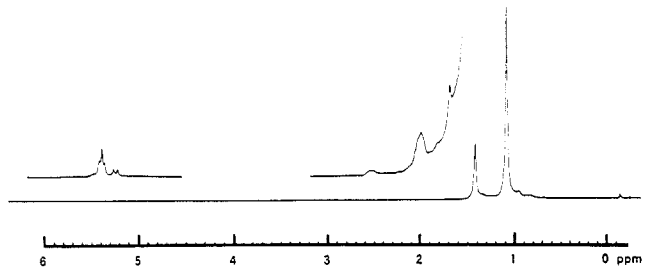


Figure 7. ^1H NMR spectrum of specifically deuterated butyl rubber (at 250 MHz in $CDCl_3$).

the spectrum exhibited by the model compound (Figure 1), it is clear that the isoprenyl units of butyl rubber are found predominantly in a single isomeric form. This can be deduced from the presence of only one signal in the 1.65, 1.94, and 5.05 ppm regions of the spectrum shown in Figure 6. The corresponding regions of the spectrum of the model compound, which is known to be a mixture of isomers, each contain a pair of signals.

In addition to providing evidence for isomeric purity of the incorporated isoprenyl units, the single triplet at 5.05 ppm also supports the exclusive incorporation of isoprenyl units in the 1,4 mode. The presence of either 1,2- or 3,4-enchained isoprenyl units in significant amounts would require the presence of additional signals in this region of the spectrum.[8]

On the basis of the previously described assignment for the model compound and comparison with the spectrum of deuterated butyl rubber (Figure 7), the signals at 1.65 and 1.94 ppm in Figure 6 can be assigned to the methyl and methylene protons of the isoprene residues, respectively. As can be seen from Figure 7, the signal at 1.65 ppm is absent and the intensity of the signal at 1.94 ppm is reduced to half of its original size in the spectrum exhibited by deuterated butyl rubber.

Prior to the synthesis of the deuterated butyl rubber and the availability of the 250-MHz instrument, the assignment of the signal at 1.65 ppm to the methyl group of the isoprene residue was confirmed by a spin-decoupling experiment. On irradiation of the olefinic proton at 5.05 ppm, the signal at 1.65 ppm became considerably sharper due to removal of long-range coupling.

The overall signal assignment from the high-resolution proton spectrum of butyl rubber (Figure 6) is summarized in Table III.

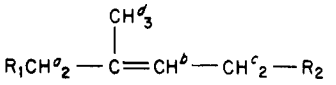
An attempt was made to draw a conclusion about the isomeric nature of the enchained isoprenyl groups of butyl rubber from the data generated by the ^1H NMR study. As discussed, the isoprenyl groups can be either in *Z* or *E* form. The ^1H NMR results presented above indicate that whereas the model compound shows two sets of signals for most of the protons of isoprenyl residues (Figure 5), only

Table III
Assignment of the Signals in the ^1H NMR Spectrum of Butyl Rubber

chem shift, ppm	multiplicity[a]	assignment
1.11	s	CH_3 of isobutylene
1.41	s	CH_2 of isobutylene
1.65	s	CH_3 of isoprene
1.94	s and m	CH_2 of isoprene
5.05	t	=CH of isoprene

[a] s = singlet, t = triplet, and m = multiplet.

Table IV
Observed Chemical Shifts (ppm) of the Protons of the Isoprenyl Residues of Butyl Rubber and Its Model Compound



	Z isomer	*E* isomer	butyl rubber
H^a	1.96	1.87	1.94
H^b	5.21	5.08	5.05
H^c	1.96	1.87	1.94
H^d	1.74	1.65	1.65

one set is present in the spectrum of butyl rubber (Figure 6). This observation strongly suggests that the double bond in butyl rubber is predominantly in one form or that the signals due to the two forms have identical chemical shifts. On the basis of the observation of the two distinctly different signals for all of the protons of the model compound, the latter possibility does not appear to be very likely.

The chemical shifts of the isoprenyl group protons for both isomers of model compound **2** and butyl rubber are presented in Table IV.

Due to the differences in the R_1 and R_2 groups in the model compound and butyl rubber, it is believed that the comparison of chemical shifts of protons H^b and H^d is critical for the assignment of the geometry of the isoprenyl units of butyl rubber. The closer agreement between the chemical shifts of these critical protons of butyl rubber and the *E* isomer of the model compound suggests that the predominant geometry of the isoprenyl groups of the polymer is *E*. A definitive proof based on ^{13}C NMR is discussed later.

While the predominant geometry of the isoprenyl residues of butyl rubber is believed to be *E*, it was of interest to investigate whether an observable quantity of *Z* isoprenyl residues may also be present in commercial elastomers. For this purpose, the 1.5–2.1 ppm region of the ^1H spectrum of butyl rubber was amplified and expanded (Figure 8a). A close examination of this region revealed that in addition to a strong signal at 1.65 ppm, which is due to the methyl protons of the *E* isoprenyl residue, there is also a weak signal at 1.70 ppm. The protons of the methyl group of the *Z* isoprenyl residues are expected to resonate at this particular field. Further evidence for the presence of *Z* isoprenyl residues was obtained from the ^1H spectrum of the deuterated butyl rubber, which was plotted in the same manner (Figure 8b). It is apparent that both of these signals (1.65 and 1.75 ppm) are missing from the spectrum as a result of the complete deuteration of the methyl groups of the incorporated isoprene.

A differential spectrum (Figure 8c) obtained by means of computer subtraction of the spectrum 8b and from spectrum 8a provides even clearer evidence of the existence of a small amount of *Z* isoprenyl residues in butyl rubber. The quantification of the *Z* and *E* isoprenyl residues in several commercial samples of butyl rubber suggests that

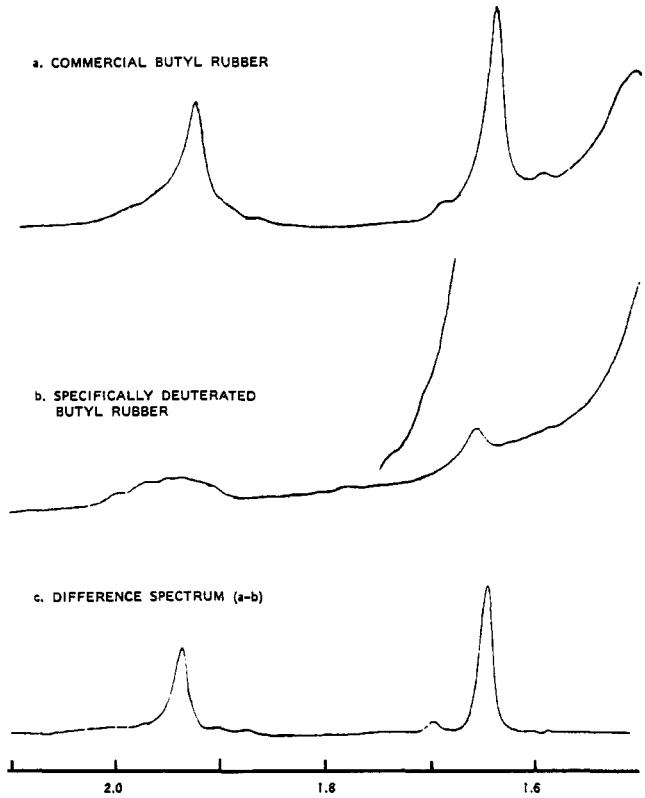
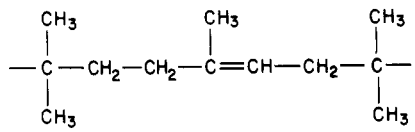


Figure 8. High-field region of the ^1H NMR spectra of butyl rubber (at 250 MHz in $CDCl_3$).

approximately 10% of the *Z* isoprenyl form is typically observed.

Finally, the observation of only one signal (5.05 ppm) in the olefinic region of the ^1H spectrum of butyl rubber (Figure 6) was taken as confirmation of the 1,4 mode of incorporation of isoprenyl residues. However, even in this mode of incorporation, two ways of attachment of isobutylene and isoprenyl units, with a different structural outcome, are possible. These are head-to-tail (**1**) and head-to-head (**3**), shown below:



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The close agreement of the chemical shifts of the isoprenyl protons in butyl rubber to corresponding protons of the model compound provides evidence that the incorporation of isoprene units into butyl rubber occurs in a head-to-tail fashion. This conclusion is further confirmed by the observation that both the model compound and the isoprene groups of butyl rubber exhibit the same unique type of halogenation chemistry.[7]

In conclusion, the detailed ^1H NMR study of the butyl rubber model compound, deuterated butyl rubber, and butyl rubber itself has provided the following information about the isoprenyl residues of butyl rubber: (1) isoprene units are incorporated in the 1,4 mode; (2) the predominant geometry of isoprenyl residues (~90%) is *E*; (3) the isoprenyl residues are attached to the isobutylene chain in head-to-tail fashion.

The wide-band decoupled ^{13}C NMR spectrum of butyl rubber, in its amplified form, is shown in Figure 9a. In addition to the three major signals, this spectrum contains a number of minor ones. The assignment of these minor signals to the isoprene-centered structure of butyl rubber

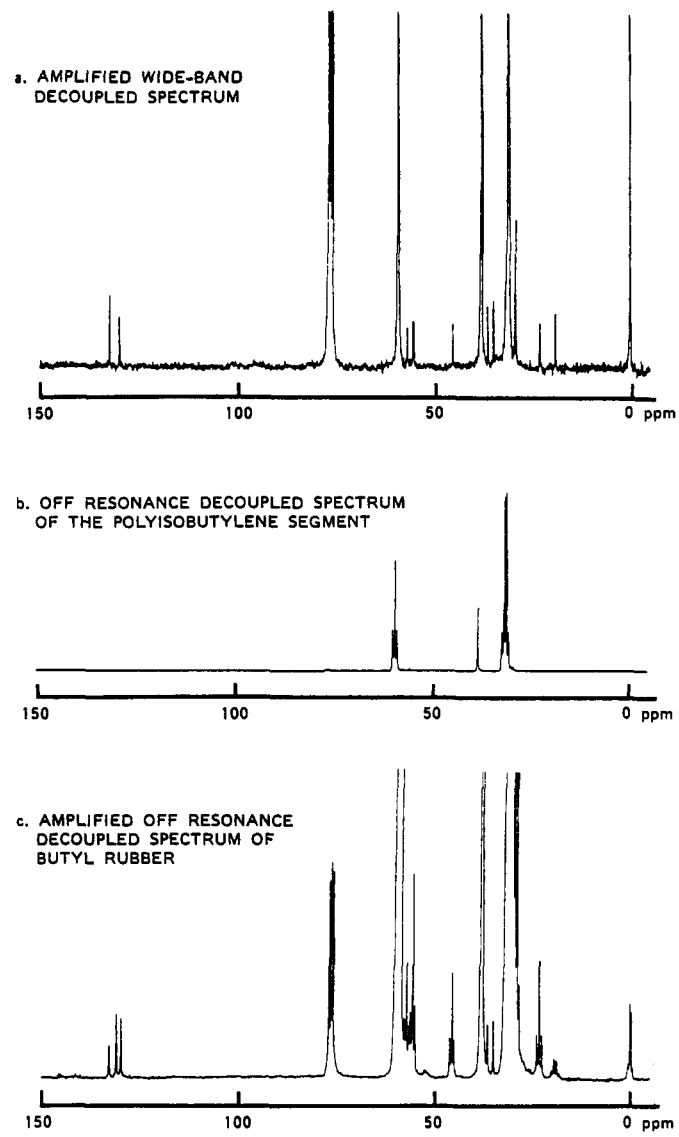

Figure 9. ^{13}C NMR spectra of butyl rubber (at 62.8 MHz in $CDCl_3$).

represented the major part of this study. This assignment was accomplished by the analysis of off-resonance decoupled and selectively decoupled spectra of butyl rubber, as well as by the application of empirical calculations.

The off-resonance decoupled spectrum of the polyisobutylene segment of butyl rubber is shown in Figure 9b. Consideration of the multiplicities of the signals permits assignment of the resonances in the following manner: the signal at 31.28 ppm is associated with the methyl group carbon atom, the signal at 38.26 ppm is due to the quaternary carbon atom bearing two methyl groups, and the signal at 59.68 ppm is due to carbon atoms of the methylene groups.

Although there were strong mechanistic indicators[9] that the polyisobutylene segment of butyl rubber is formed by head-to-tail engagement of the isobutylene units, empirical calculations[10] were carried out for both the possibilities. Table V presents a comparison of the empirically calculated ^{13}C chemical shifts for the two possible arrangements of polyisobutylene units and those observed in the spectrum of butyl rubber.

Much closer agreement between the observed chemical shifts for the polyisobutylene carbons and those calculated for the head-to-tail type of enchainment provides additional strong support for the correctness of the structure of the saturated segment of butyl rubber. A recent report

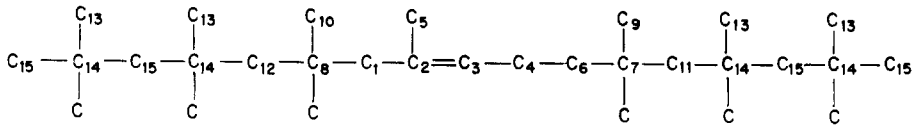

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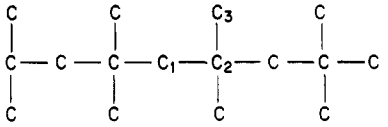
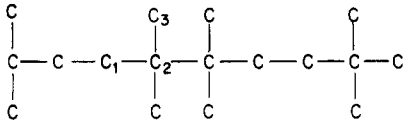
Table V
Comparison of Observed and Calculated Chemical Shifts (ppm) for the Carbons of the Polyisobutylene Segment of Butyl Rubber



head-to-tail



head-to-head

	C_1	C_2	C_3
obsd	59.68	38.26	32.28
calcd head-to-tail	54.32	36.37	29.24
calcd head-to-head	31.36	38.74	20.82

on the spectrum of the head-to-head polyisobutylene[11] lends support to previous conclusions and allows the definitive structural assignment of the polyisobutylene sequence of butyl rubber as being composed of head-to-tail-enchained isobutylene units.

For the sake of clarity, the carbon atoms of the isoprene groups of butyl rubber and their immediate polyisobutylene environment are numbered as in **4**.

A comparison of the wide-band decoupled ^{13}C spectrum of the model hydrocarbon (Figure 2a) with the corresponding spectrum of butyl rubber (Figure 9a) indicates the presence of only one isomeric form of the isoprene unit in the latter compound. This conclusion is made on the basis of the observation of only one signal at chemical shifts characteristic of carbon atoms of isoprenyl groups. The presence of two signals in each of the corresponding regions in the spectrum of the model compound, which is known to be a mixture of geometric isomers, has already been discussed.

On the basis of the consideration of the off-resonance decoupled ^{13}C NMR spectra shown in Figure 9c, it is possible to assign signals due to olefinic carbon atoms. The signal at 129.98 ppm, in this spectrum, appears as a doublet and thus must be associated with the olefinic carbon number three. In a similar manner, the signal at 132.36 ppm, which remains a singlet in the off-resonance decoupled spectrum, was assigned to the quaternary carbon atom number two.

Comparison of spectra 9a and 9c further permits the general assignment of the signals in the wide-band decoupled spectrum to methyl and methylene groups, respectively. It is clear that the signal at 19.21 ppm is due to the carbon atom of a methyl group. In the same manner, signals at 23.37, 55.81, and 45.63 ppm may be assigned to the methylene groups of isoprenyl groups and the isobutylene group attached to it.

A further assignment of ^{13}C NMR signals to particular carbon atoms was done by performing some selective decoupling experiments. By selective irradiation of given protons, the coupling effects between the protons and carbon atoms to which they are attached can be eliminated. From the interpretation of the ^1H spectrum of butyl rubber (Figure 6), it is known that the protons of both of the

Table VI
Assignment of the ^{13}C NMR Signals of Butyl Rubber

chem shift, ppm	multiplicity[a]	assignment
19.21	q	C_5, CH_3
23.37	t	C_4, CH_2
29.46	q	C_9, C_{10}, CH_3
31.28	q	C_{13}, CH_3
35.19	s	C_8, C
36.64	s	C_7, C
38.26	s	C_{14}, C
45.63	t	C_6, CH_2
55.75	t	C_{11}, CH_2
55.81	t	C_1, CH_2
57.34	t	C_{12}, CH_2
129.98	d	C_3, =CH
132.36	s	C_2, —C= from isoprene

[a] s = singlet, d = doublet, t = triplet, and q = quartet; from off-resonance decoupled spectrum.

Table VII
Comparison between Observed and Calculated[a] Values for Chemical Shifts (ppm) of the Carbon Atoms of the Isoprenyl Units

		calcd[b]	
C	obsd	head-to-tail	head-to-head
1	55.81	56.8	41.6
2	132.36	134.2[b]	123.0[b]
3	129.98	129.6[b]	140.4[b]
4	23.37	24.8	53.5
5	19.21	19.2	17.5
6	45.63	45.3	42.5

[a] Reference 11. [b] Reference 12.

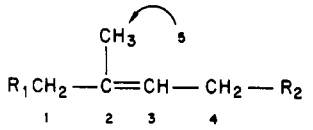
methylene groups of the isoprenyl units give signals centered around 1.94 ppm. It is also known that the protons of the methyl group of the same unit give rise to a signal at 1.65 ppm. Comparison of the selectively decoupled spectrum with that obtained under off-resonance decoupling conditions permits assignment of a signal to a given carbon atom.

The expanded off-resonance spectrum of the 0–60 ppm region of the ^{13}C NMR spectrum of butyl rubber is shown in Figure 10a. The irradiation of the proton signals centered at 1.94 ppm brings about the collapse of the two triplets appearing at 23.37 and 55.87 ppm respectively into two singlets (Figure 10b). This observation indicates that these two signals are due to the methylene carbons of the isoprenyl units of butyl rubber. They can be differentiated on the basis of the difference in chemical shifts and are assigned to C_4 and C_1, respectively.

Irradiation of the signal at 1.41 ppm (methylene protons of the isobutylene blocks) brought about the collapse of the signals at 57.34 and 55.75 ppm into singlets (Figure 10c). In this manner, these two signals can be assigned to the methylene group carbons from the neighboring isobutylene groups.

The irradiation of the signal at 1.65 ppm (Figure 10d) provided additional information. It is seen that the methyl carbon signal at 19.21 ppm is collapsed from a quartet to a doublet with residual splitting. The presence of this residual coupling suggests the presence of long-range coupling. This coupling constant was measured and found to be 7.45 Hz, in good agreement with coupling constants measured for long-range coupling in polyisoprenes (J = 7.44 Hz for E; J = 6.70 Hz for Z) under identical conditions.

Table VIII
Comparison of the Chemical Shifts (ppm) of the Isoprenyl Carbon Atoms of the Model Compound and of Butyl Rubber



	Z model	E model	butyl rubber
C_1	*45.44*[a]	*53.55*	*55.81*
C_2	132.62	132.37	132.36
C_3	128.92	129.10	129.98
C_4	24.07	23.47	23.37
C_5	*26.72*	*18.67*	*19.21*

[a] Italics indicate better fit with *E* model at C_1 and C_5.

Table IX

shielding effect	factor, ppm
G_β	+2.5
G_γ	+11.5
G_δ	+1.5

The complete assignment of ^{13}C NMR signals for butyl rubber is presented in Table VI.

By comparing the observed and calculated[11] chemical shifts for the two possible modes of isoprenyl unit enchainment, it was possible to confirm the previously established mode of incorporation of isoprene as head-to-tail. These data are shown in Table VII.

Consideration of the ^1H spectra of the model compound and butyl rubber, described above, provided an indication that the isoprenyl unit is incorporated predominantly in the *E* geometry. The ^{13}C chemical shifts of the isoprene carbon atoms of both the model compound and butyl rubber, shown in Table VIII, provide an additional strong indication that the isoprenyl units are incorporated in the *E* geometry.

Empirical Calculations. Subsequent to the full interpretation of the ^{13}C NMR spectrum of butyl rubber, we tested the applicability to this system of the empirical additive rules for prediction of chemical shifts. Two different sets of additivity parameters, one suggested by Grant and Paul for linear saturated hydrocarbons and one used by Beebe[13] for polyisoprene models, were used for the calculation of chemical shifts.

The comparison of the observed and calculated chemical shifts revealed discrepancies, the magnitude of which varied with the type of carbon atoms. The cause for these discrepancies was found to be the unusually large shielding effect of the *gem*-dimethyl group of the isobutylene unit.

The magnitude of these discrepancies was 5.0 ppm for CH_2, 23.0 ppm for C, and 2.9 ppm for CH_3. To compensate for this a set of *gem*-dimethyl parameters was introduced here as G_β, G_γ, and G_δ (Table VIII). G_β applies to CH_2, with a value of +2.5 ppm, half of the discrepancy observed since there are two *gem*-dimethyl groups at the position

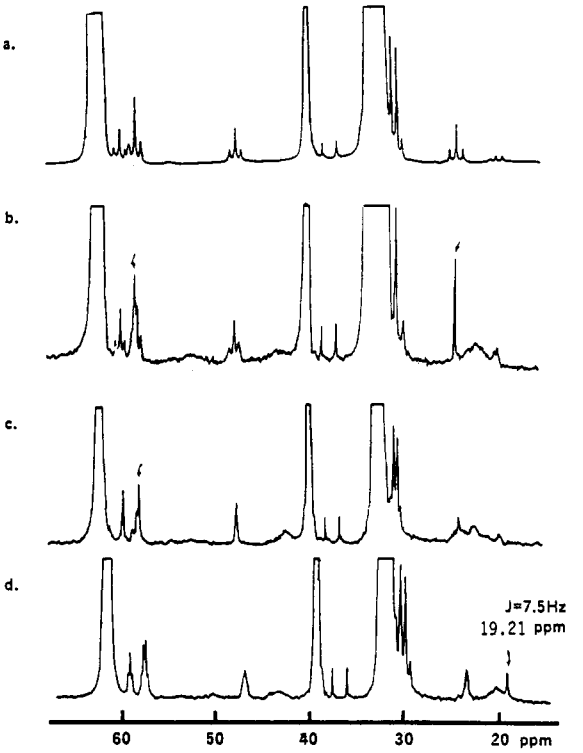


Figure 10. Amplified expanded ^{13}C NMR spectra of butyl rubber (at 62.8 MHz in $CDCl_3$): (a) expanded off-resonance decoupled spectrum; (b) same as (a) but irradiated at 1.94 ppm; (c) same as (a) but irradiated at 1.41 ppm; (d) same as (a) but irradiated at 1.65 ppm.

β to CH_2. Similarly, G_γ applies to C, with a value of +11.5 ppm, and G_δ applies to CH_3, with a value of +1.5 ppm (Table IX). From the three sets of parameters, the chemical shift values in Table X were calculated.

In most cases, the calculated values and the observed values are in close agreement. The only uncertainty is the assignment of the three narrowly spaced peaks at 55.75, 55.81, and 57.34 ppm to C_1, C_{11}, and C_{12}, respectively.

Conclusion

A detailed analysis of the ^1H and ^{13}C NMR spectra of a butyl rubber model compound, selectively deuterated butyl rubber, and butyl rubber itself was performed. By a combination of several techniques, all of the signals in both types of spectra were assigned to their respective hydrogens and carbon nuclei. The following general conclusions about the structure of butyl rubber can be made:

(1) The isobutylene units of polyisobutylene segments of butyl rubber are incorporated head-to-tail.

(2) The isoprene units of butyl rubber are incorporated head-to-tail (1,4 mode) between polyisobutylene segments.

(3) The geometry of incorporated isoprene groups is predominantly (~90%) *E*.

We believe that the information presented in this paper, in conjunction with previously published data, provides

Table X

C		β				substitutions	calcd	obsd
1	2	5	2	4	2	2° (4°), C, (D), G_β	56.8	(55.81)
4	2	2	5	2	6	C_4(D)	24.8	23.37
5	1	2	2	4	2	C_5(D), G_δ	19.2	19.21
6	2	4	2	5	2	2° (4°), G_β	45.3	45.63
7	4	2	4	2	5	4° (1°) × 2, 4° (2°) × 2, G_γ	35.5	36.64
8	4	2	5	2	4	4° (1°) × 2, 4° (2°) × 2, G_γ	32.9	35.19
9	1	3	2	4	2	1° (4°), G_δ	29.3	29.46
10	1	3	2	5	2	1° (4°), G_δ	29.6	29.46
11	2	6	2	4	4	2° (4°) × 2, G_β	55.8	(55.75)
12	2	6	2	5	2	2° (4°) × 2, G_β	56.9	(57.34)

a definitive description of all the structural features of butyl rubber, including those of the isoprenyl residues.

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Dynamics of Cubic Lattice Models of Polymer Chains at High Concentrations

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ABSTRACT: The dynamics of cubic lattice models of polymer chains are studied over a wide range of concentration by means of computer simulation. Three dynamic properties—the terminal relaxation time, the center of mass diffusion constant, and the central monomer diffusion—were studied. All three properties show clear deviations from the Rouse theory at high concentrations, but do not conform to the predictions of the reptation model.

Introduction

The dynamics of linear polymers are ordinarily discussed in terms of two models which are supposed to describe the motions of chains at the two extremes of behavior. In dilute solution the dynamics are reasonably well described by the venerable Rouse–Zimm model and its modifications.[1] The Rouse–Zimm model, however, assumes an ideal, phantom chain so neither the static nor dynamic effects of excluded volume can easily be incorporated. At the other extreme of long chains in bulk polymers the reptation model of DeGennes is ordinarily used.[2,3] The reptation model assumes that the motion of the chain is completely dominated by intermolecular entanglements so that the chain must diffuse along its contour in a snakelike fashion.

The reptation concept has been extremely fruitful. It has been elaborated into a complete theory of polymer melts by Doi and Edwards[4] and applied to a number of other problems including polymer crystallization,[5] crack healing,[6] and the Tromsdorff effect.[7] Graessley[8] has recently surveyed the theories and experimental data relevant to the reptation and Doi–Edwards theory and found qualitative agreement. DeGennes and Leger[9] have reviewed microscopic experimental probes of the reptation model and found that the data, on the whole, support the theory.

Despite the successes of the reptation model it remains controversial. Dynamic neutron scattering experiments have failed to see any evidence of reptation.[10] Computer simulation studies designed to study entanglement effects have generally failed to see reptation except in systems where a single chain is allowed to move among frozen chains or fixed obstacles.[11–15] Some of these computer studies are flawed, but the recent simulation of diamond lattice chains by Kremer[15] studied a system whose static properties indicated that it was well into the entanglement region, but the dynamic properties showed no sign of reptation. DeGennes and Leger[9] have argued that the dynamic neutron scattering studies are not able to probe a sufficiently large length scale. They have also suggested that computer simulations cannot study chains long enough to see reptation with present-day computers. At this time it seems that the question of the regime of validity of the reptation model is still unresolved.

Even if the reptation model is correct for the extreme cases of very long chains at high concentrations, chains in glassy systems, and chains trapped in networks, there is still a wide range of concentrations and chain lengths where the chain dynamics are affected by entanglements, but where the results of the reptation theory are not valid. Since there is no general theory of entanglement effects, computer simulation studies can play an important role in increasing our understanding of these effects. In this paper we report the results of an extensive computer simulation study of cubic lattice chains. Chains of lengths 12, 24, and 48 have been studied at concentrations varying from $c = 0$ (isolated chains) to $c = 0.90$. The equilibrium mean square end-to-end distance, $\langle R^2 \rangle$, and three dynamic properties—the terminal relaxation time, the center of mass diffusion constant, and the diffusion of a central monomer—have been computed. The focus has been on the chain length dependence of scaling behavior of the terminal relaxation time and the center of mass diffusion constant, and how the scaling behavior changes with concentration. We have also studied the concentration and chain length dependence of the central monomer diffusion. The central questions that we tried to answer were these: At what concentrations (if any) do deviations from the

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