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Incorporation of Isoprene in Isobutylene/Isoprene Copolymers: NMR Identification of Branching in Butyl Rubber

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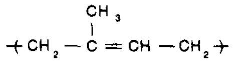
ABSTRACT: This paper describes a detailed investigation of the structure of butyl rubber by one- and two-dimensional NMR methods. Butyl rubber is a copolymer of isobutylene with 1−3 mol % isoprene and is prepared by cationic polymerization. Our goal was to determine secondary methods of isoprene incorporation other than 1,4-addition. Possibilities include 1,2-, 3,4-, or 4,3-addition. We found no evidence for structure arising from either of these possibilities, although there have been previous reports of 1,2-addition in the literature. We present the first identification of a second type of structure, however, which is a branch point in the polymer chain. This minor structure presumably results from 1,4-addition followed by rearrangement and subsequent isobutylene addition to form the branch point. The minor structure is present in both commercial butyl materials and laboratory isobutylene/isoprene copolymers polymerized at various temperatures. The amount of the minor branched isoprene species increases relative to the 1,4-addition product with increasing polymerization temperature. We discuss GPC and rheological data which suggest that the branch point detected by NMR is associated with long-chain branches.

I. Introduction

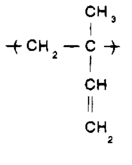
Butyl rubber is a copolymer of isobutylene with isoprene, prepared by cationic polymerization and usually having ca. 1−3 mol % isoprene.[1] Butyl rubber and its halogenated derivatives are important large-volume commercial products. The vulcanization process determines the final properties of the elastomer, and the number of potential cross-linking sites is determined by the incorporation of isoprene. A knowledge of the types and quantity of unsaturated structures formed by isoprene incorporation is important since small variations can have a significant impact on vulcanization.

In this paper, we report for the first time the structure of a second type of unsaturated isoprene moiety formed during the copolymerization of isoprene and isobutylene. This species gives rise to a branch point in the polymer chain. The chemistry leading to this structure is not obvious from first principles of carbocationic polymerization. Previous spectroscopic work has shown that the isoprene is predominantly incorporated (ca. 90−95%) in an *E*-1,4-enchained head-to-tail arrangement,[2−5] thereby producing a strictly linear polymer backbone. It is expected that isoprene may also incorporate via 1,2- or 4,3-addition, with the 1,2 addition favored sterically. These three modes of isoprene incorporation are schematically represented below.



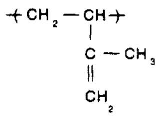
$+CH_2-\overset{CH_3}{C}=CH-CH_2+$

1,4 addition



$+CH_2-\overset{CH_3}{\underset{CH=CH_2}{C}}+$

1,2 addition



$+CH_2-\underset{C(CH_3)=CH_2}{CH}+$

4,3 addition

Vukov and co-workers,[2] as well as Rose and co-workers,[3] found no evidence for 1,2- or 4,3-enchained isoprene using both ^{13}C and ^1H NMR. In contrast, Cheng et al. assigned ^1H NMR resonances at 4.93 ppm to the olefinic vinylene hydrogens of 1,2-enchained isoprene.[4] In a recent paper discussing the kinetics of unsaturation epoxidation, Puskas and Wilds also reported the presence of 1,2-enchained isoprene using the same 4.93 ppm peak.[5] Kennedy and co-workers have also assigned 1,2- and 4,3-structures based on a relatively low-field NMR investigation of the living polymerization of isoprene and isobutylene.[6] In each case, structural assignments were made on the basis of conventional one-dimensional spectra. Isoprene is a dilute comonomer (typically 1.5 mol %), and the complete characterization of even more dilute isoprenyl species is not trivial. In this paper, we use ^1H and ^{13}C homonuclear and natural-abundance heteronuclear two-dimensional methods at high field strengths (500 MHz) to clarify the inconsistencies in previous reports on butyl structure and report a second branched isoprene moiety which is consistent with the NMR data. No 1,2- or 4,3-enchained isoprene is observed. We demonstrate that the ratio of the major 1,4-enchained isoprene and the minor isoprenyl derivative is dependent upon polymerization temperature. At higher polymerization temperatures, isoprene is incorporated exclusively as the minor branched derivative.

II. Experimental Section

Commercial butyl samples were prepared in methyl chloride using aluminum chloride and organoaluminum chloride initiators at −110 °C.[1] Laboratory copolymer samples were prepared at −30, −50, and −80 °C using ethylaluminum dichloride catalysts in a 60/40 (v/v) methyl chloride/hexane solvent mixture and ca. 2 mol % isoprene feed. Deuterated copolymer was prepared at −50 and −30 °C via the copolymerization of isobutylene-d_8 (CDN isotopes, 98.5% d) and isoprene.

Butyl samples were dissolved in chloroform to make 1−2 wt % solutions for ^1H NMR and 10 wt solutions % for ^{13}C NMR study. Selected butyl materials from many sources were examined, and the results here are representative. All data were obtained at a field strength corresponding to 500-MHz ^1H NMR frequency. Standard ^1H NMR one-pulse experiments

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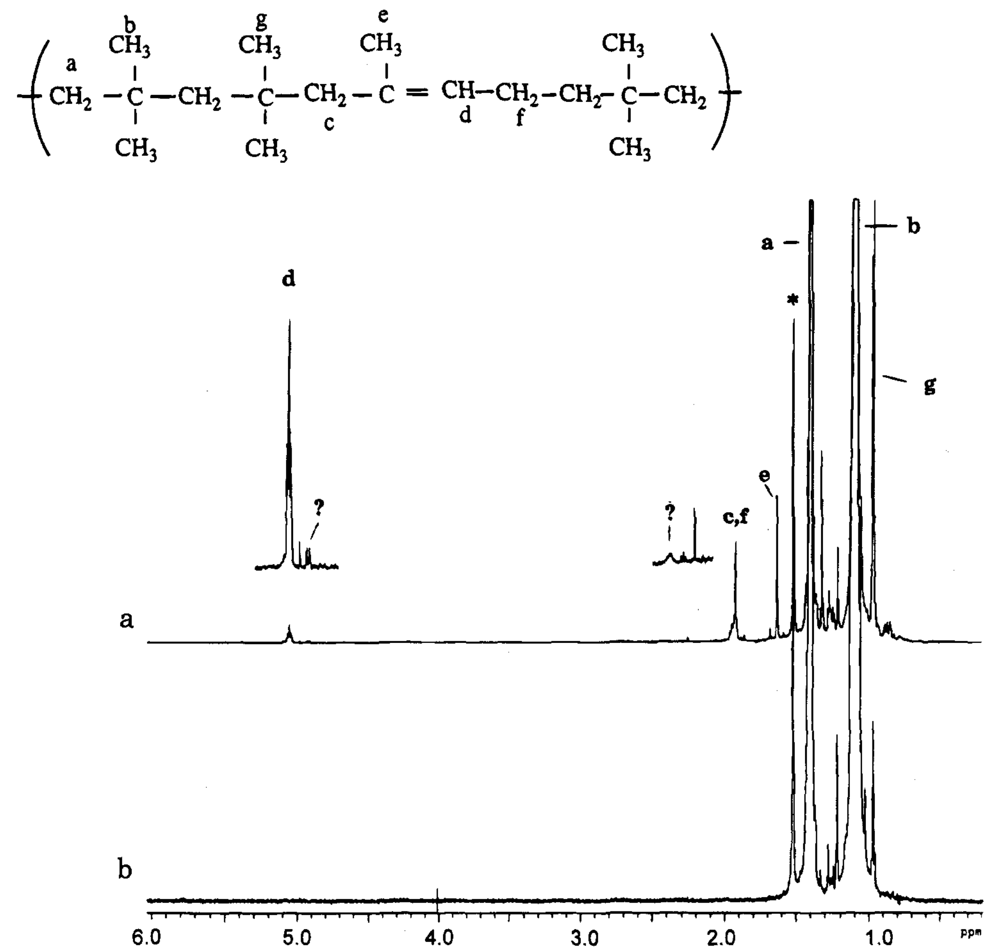


Figure 1. 500-MHz ^{1}H NMR spectrum of (a) commercial butyl rubber and (b) polyisobutylene. The peaks are labeled according to the structure, and the asterisk denotes a peak arising from residual water in chloroform.

were acquired using a 45° pulse, 5 s recycle delay, and 2 s acquisition time. ^{13}C NMR spectra were collected with NOE using a 90° pulse, 20 s recycle delay, and 2 s acquisition time. Two-dimensional COSY data were acquired using the standard two-pulse sequence[6,7] with either phase cycling for P-type peak selection or phase-sensitive hypercomplex acquisition using the method of States and Haberkorn.[9] A sweep width of 4288 Hz was used in each dimension, with 512 t_1 increments and 32 transients/increment. Hypercomplex phase-sensitive inversely detected heteronuclear multiple-quantum coherence (HMQC)[9,10] data were collected using a proton sweep width of 6000 Hz and a carbon sweep width of 20 000 Hz, with 128 t_1 increments and 64–256 scans/increment. The data were processed with sine-bell apodization. The spacing between the initial BIRD sequence and the basic HMQC sequence was 0.2 s.

III. Results

The ^{1}H NMR spectrum of butyl rubber is shown in Figure 1 along with the structure of the major 1,4-isoprenyl species. A spectrum of pure polyisobutylene is shown in the bottom trace for reference. All of the assigned resonances have been reported previously.[2] The olefinic methine hydrogens of the 1,4-isoprene give rise to a triplet at 5.05 ppm. The doublet at 4.93 ppm (with 9.5 Hz splitting) has previously been assigned in only one report to olefinic methylene hydrogens arising from isoprene polymerized via 1,2-enchainment.[4] However, the absence of a clear olefinic methine signal suggests that this assignment is questionable. Cheng and co-workers suggested that the methine signal was hidden by the 5.05 ppm triplet from 1,4-enchained isoprene.[3] Indeed, selective decoupling experiments which collapse the 5.05 triplet reveal a peak at 5.09 ppm which is of the appropriate intensity required for a methine of 1,2-enchained isoprene (not shown). The sharp singlet at 5 ppm is from an additive.

The phase-sensitive COSY spectrum for butyl rubber is shown in Figure 2 for the 1.5–5.5 ppm region. As expected from the structure and assignments in Figure 1, the 5.05 ppm triplet from 1,4-isoprene shows two strong correlations to the allylic methyl and methylene hydrogens at 1.65 and 1.95 ppm, respectively. The structure responsible for the 4.93 ppm doublet is in question, and it is these correlations which are most interesting. Two correlations involving the 4.93 ppm doublet are observed. Both of these correlations involve peaks only in the aliphatic region; there is no correlation to the 5.05 triplet or any other peaks in the olefinic region. This data alone excludes 1,2-enchained isoprene as a possible structure. The correlations which are observed show connectivity with a broad singlet at 2.44 ppm and a sharp singlet at 1.72 ppm. Selective irradiation of the 2.44 ppm resonance resulted in the collapse of the 4.93 ppm doublet to a singlet (not shown), which indicates that the 2.44 ppm resonance arises from one proton. Conversely, if the 4.93 ppm doublet is irradiated, the 2.44 ppm peak still resembles a broad multiplet due to additional couplings (vide infra), and therefore it is not possible to directly distinguish the 4.93 ppm peak as due to olefinic methylene or methine hydrogens.

Since spectral editing experiments lend themselves most readily to ^{13}C observation, heteronuclear correla-

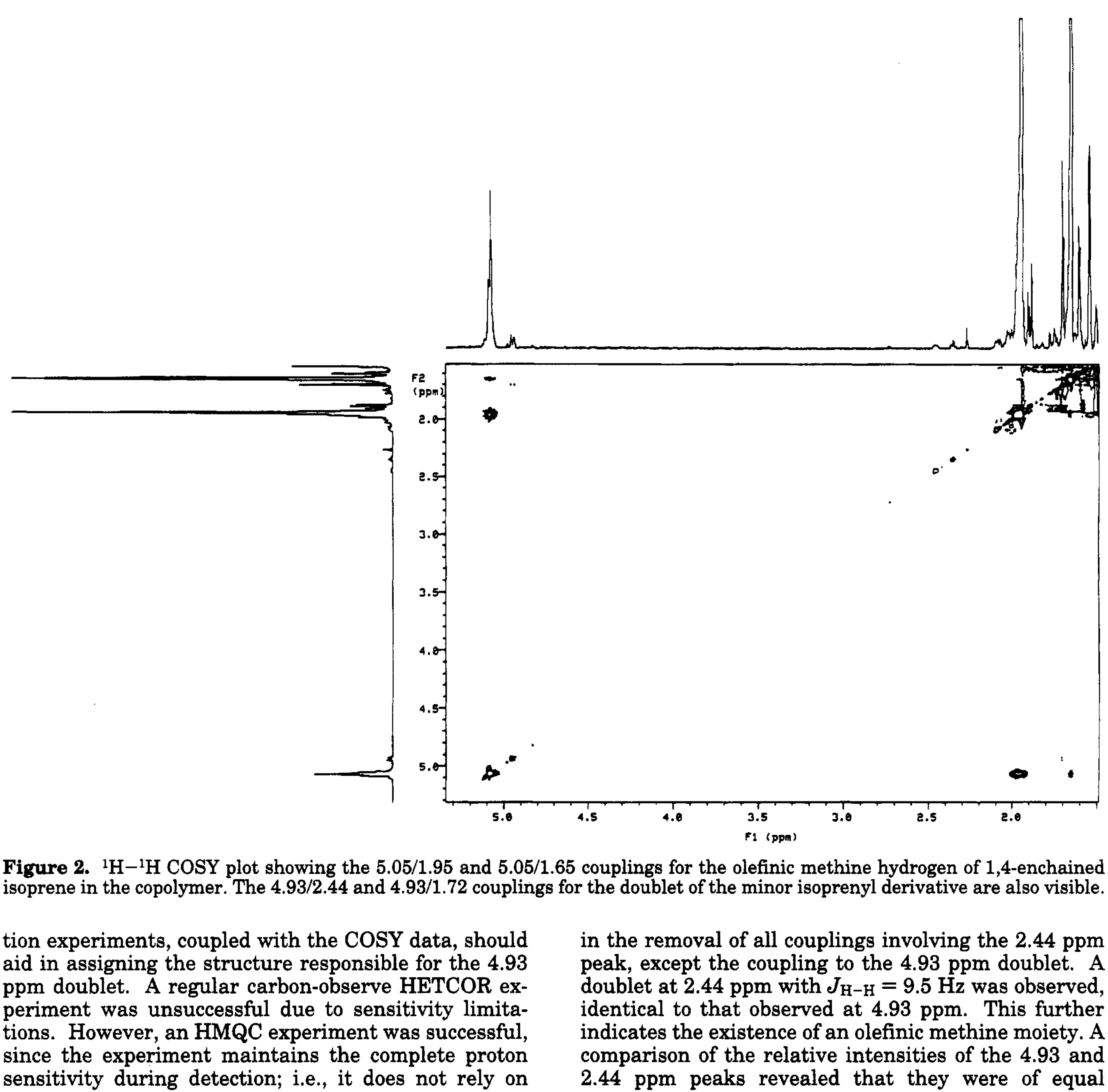


Figure 2. $^1H-^1H$ COSY plot showing the 5.05/1.95 and 5.05/1.65 couplings for the olefinic methine hydrogen of 1,4-enchained isoprene in the copolymer. The 4.93/2.44 and 4.93/1.72 couplings for the doublet of the minor isoprenyl derivative are also visible.

tion experiments, coupled with the COSY data, should aid in assigning the structure responsible for the 4.93 ppm doublet. A regular carbon-observe HETCOR experiment was unsuccessful due to sensitivity limitations. However, an HMQC experiment was successful, since the experiment maintains the complete proton sensitivity during detection; i.e., it does not rely on polarization transfer for generation of observable magnetization. The results of this experiment are shown in Figure 3 for the olefinic carbon and hydrogen regions. The protons are detected in t_2 in the absence of ^{13}C decoupling, so the proton signals in F_2 appear as doublets with the appropriate J_{C-H}. The 1,4-isoprene triplet is correlated to a carbon shift of 130 ppm, whereas the 4.93 ppm proton doublet in question is directly bonded to a carbon with a chemical shift of ca. 140 ppm. The 130 ppm peak was previously assigned to the olefinic methine carbon from 1,4 isoprene incorporation.[2,3] ^{13}C NMR data and an attached proton test (APT) experiment indicated that the carbon signal at 140 ppm was from an olefinic methine carbon (see below). The HMQC establishes that the 140 ppm carbon methine signal and the 4.93 ppm olefinic hydrogen signal are due to a second unsaturated methine moiety in the polymer, while again ruling out isoprene incorporated in a 1,2- or 4,3-vinylene arrangement.

This assignment was confirmed in additional selective decoupling ^1H NMR experiments in which the aliphatic region from 1 to 1.7 ppm was saturated. This resulted in the removal of all couplings involving the 2.44 ppm peak, except the coupling to the 4.93 ppm doublet. A doublet at 2.44 ppm with $J_{H-H} = 9.5$ Hz was observed, identical to that observed at 4.93 ppm. This further indicates the existence of an olefinic methine moiety. A comparison of the relative intensities of the 4.93 and 2.44 ppm peaks revealed that they were of equal intensity. Recall that the methine hydrogen at 4.93 ppm was also coupled to hydrogens at 1.72 ppm in the COSY plot. The resonance at 1.72 ppm was 3 times the integrated intensity of each of the 4.93 and 2.44 ppm peaks. While the data indicate a secondary structure in which isoprene is incorporated similar to 1,4-enchained isoprene, but with a aliphatic methine instead of methylene adjacent to the olefinic methine, additional information concerning where this structure occurs (in the chain vs end group) and if this structure leads to branching is required.

A series of isobutylene/isoprene copolymers were synthesized at −80, −50, and −30 °C to help address the questions raised above. Shown in Figure 4 are the ^1H NMR spectra for the copolymers synthesized at −80 and −50 °C, along with commercial butyl synthesized at −110 °C for reference. As may be seen from examining the olefinic region of the spectrum (specifically the 4.93 ppm doublet and the 5.05 ppm triplet), the relative fraction of the isoprene feed which is incorporated as the secondary structure increases as the polymerization temperature increases. At the highest temperature,

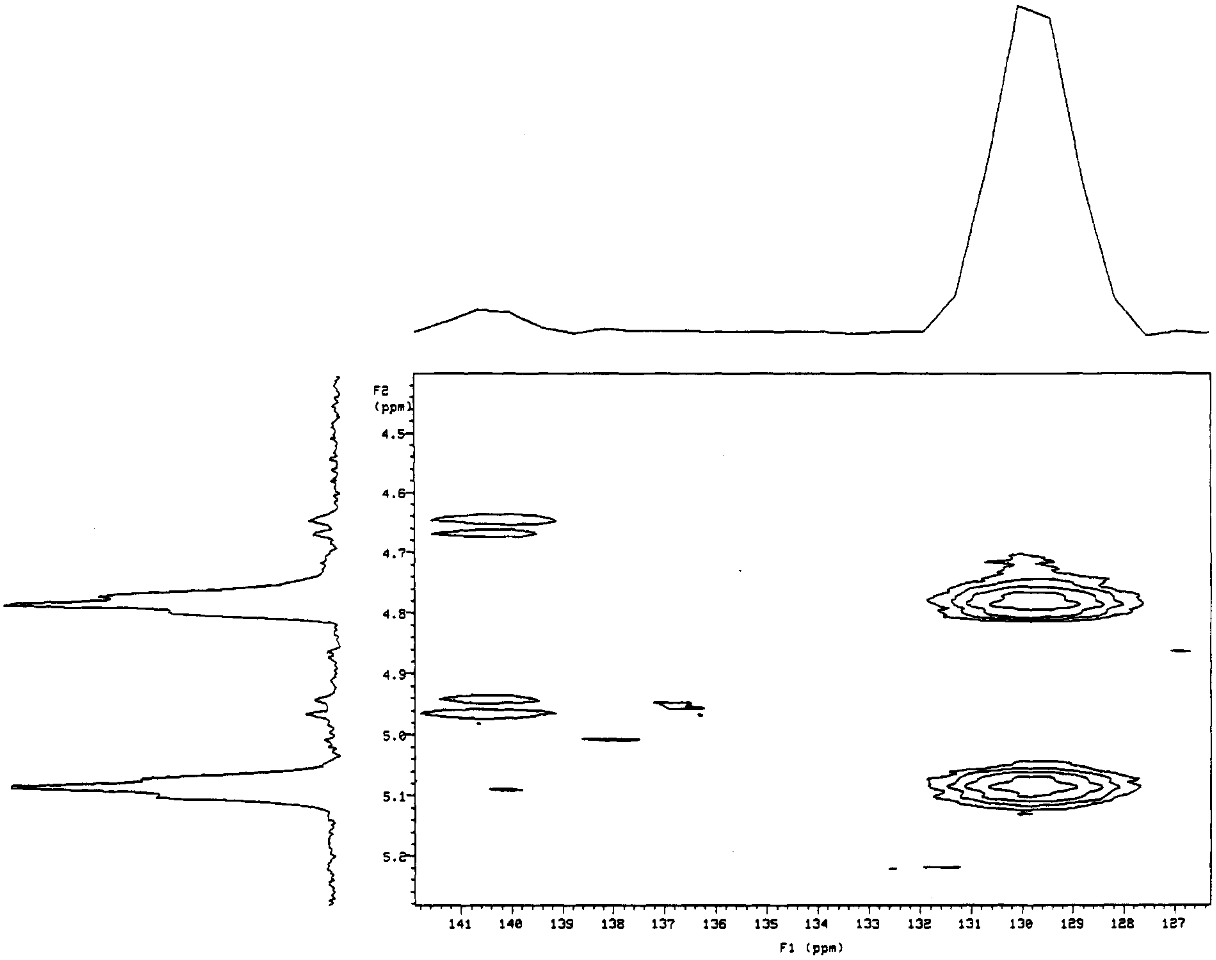


Figure 3. $^1H-^{13}C$ HMQC spectrum of the olefinic region of the polymer in Figure 2. The proton signals are detected in the absence of carbon decoupling.

isoprene is incorporated as the secondary structure only. The signals associated with the minor unsaturated species (4.93, 2.44, 1.90, and 1.72 ppm) are not observed in polymerizations of isobutylene alone, verifying that this species is derived from isoprene incorporation. The signal at 1.90 ppm is assigned to the methylene group adjacent to the quaternary olefinic carbon of the minor structure (i.e., the C_1 methylene of isoprene), based on comparisons with the 1.95 ppm signal for the same methylene group in 1,4-enchained isoprene. The lower intensity signals observed in the olefinic region arise from chain terminations of isobutylene, as recently discussed by Kennedy[12] and verified in our own experiments (spectra not shown).

The ^{13}C NMR spectra of commercial butyl copolymer and polymer synthesized at −50 °C are shown in parts a and b of Figure 5, respectively. The olefinic regions have been expanded to reveal the signals arising from isoprene incorporation in either of the two forms. The intense signals at 130 and 132.5 ppm observed for the commercial butyl polymer have been previously assigned to the olefinic methine and quaternary carbons of 1,4-enchained isoprene.[2] No signals are observed in the 110−120 ppm region, further dismissing the presence of 1,2- or 4,3-enchained material. Based on the proton NMR data presented above, the spectrum of the −50 °C polymer (Figure 5b) should only have carbon signals arising from the secondary isoprene structure in the polymer. Two olefinic signals are observed at 127 and 140 ppm. The APT test indicated that the 127 ppm signal was due to a quaternary carbon, while the 140 ppm peak was from a methine carbon. We also note that comparison of the 50−60 ppm range of parts a and b of Figure 5 reveals signals arising from methylene carbons whose intensities approximate the intensities of the respective olefinic carbons. More signals of equal intensity are observed in this region of Figure 5b for the polymer containing only the secondary isoprenyl derivative.

Two copolymer materials were prepared at −50 °C and −30 °C using isobutylene-d_8 as the comonomer. Figure 6 shows the ^1H spectrum of the isobutylene-d_8/isoprene copolymer made at −50 °C. In contrast to the sample of Figure 4c polymerized at −50 °C, there remains some 1,4-enchained isoprene signals for the deuterated synthesis, suggesting an isotope effect. Most importantly, the 2.44 ppm aliphatic methine signal which appears as a broad multiplet in Figure 6 (and previous spectra) is a sharp doublet with the same 9.5 Hz splitting observed for the 4.93 ppm olefinic methine signal. This result indicates that isoprene is incorporated in the secondary structure such that the aliphatic methine is coupled to other hydrogens from adjacent isobutylene units, in addition to the olefinic coupling to the 4.93 ppm peak. As mentioned earlier, selective irradiation of the aliphatic region of the spectrum also collapsed the 2.44 ppm peak to a doublet, but the deuteration results demonstrate that the additional couplings arise from isoprene−isobutylene spin interactions.

A two-dimensional COSY experiment on the same deuterated copolymer of Figure 6 should unequivocally

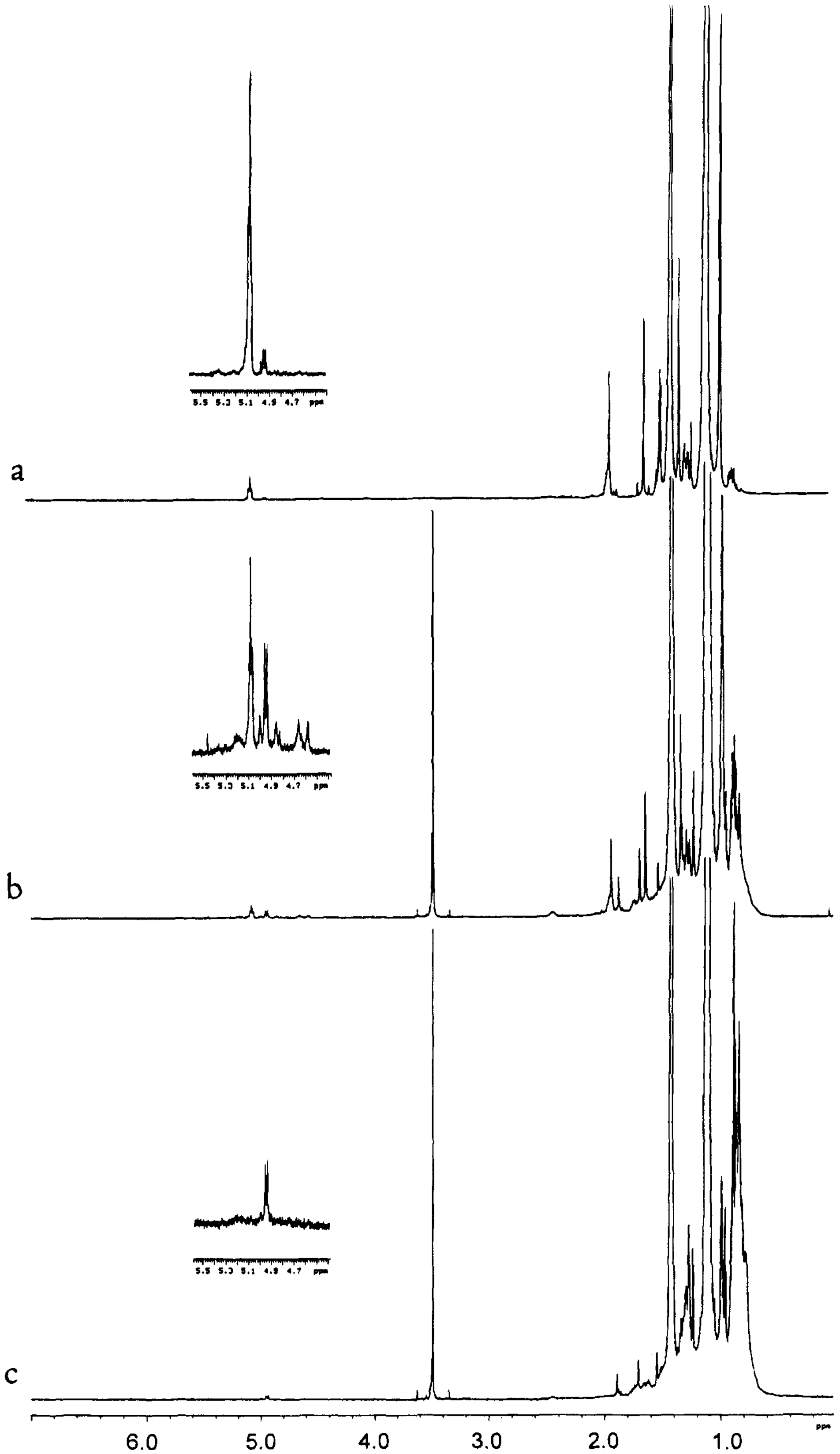


Figure 4. ^{1}H NMR spectra for isobutylene/isoprene copolymers synthesized at (a) −110 °C (commercial butyl), (b) −80 °C, and (c) −50 °C. The signal at 3.5 ppm in b and c is from methanol. Note that the ratio of the 4.93, 1.90, and 1.72 ppm peaks to the 5.05, 1.95, and 1.65 peaks, which is fractional at −110 °C, becomes infinite at −50 °C.

establish the couplings of all isoprene hydrogens, since there are no isobutylene protons. The results are shown in Figure 7. Although this plot is similar to that shown in Figure 2, there is an additional correlation observed between the 4.93 ppm doublet and a singlet at 1.90 ppm. Recall the 1.90 ppm peak was previously assigned to the aliphatic methylene of isoprene α to the quaternary olefinic carbon, and the COSY results confirm this assignment. Note that the 4.93/2.44 ppm coupling is the strongest, with the weaker cross-peak intensity observed for the 4.93/1.90 and 4.93/1.72 ppm correlations. Presumably, the 4.93/1.90 ppm correlation be-

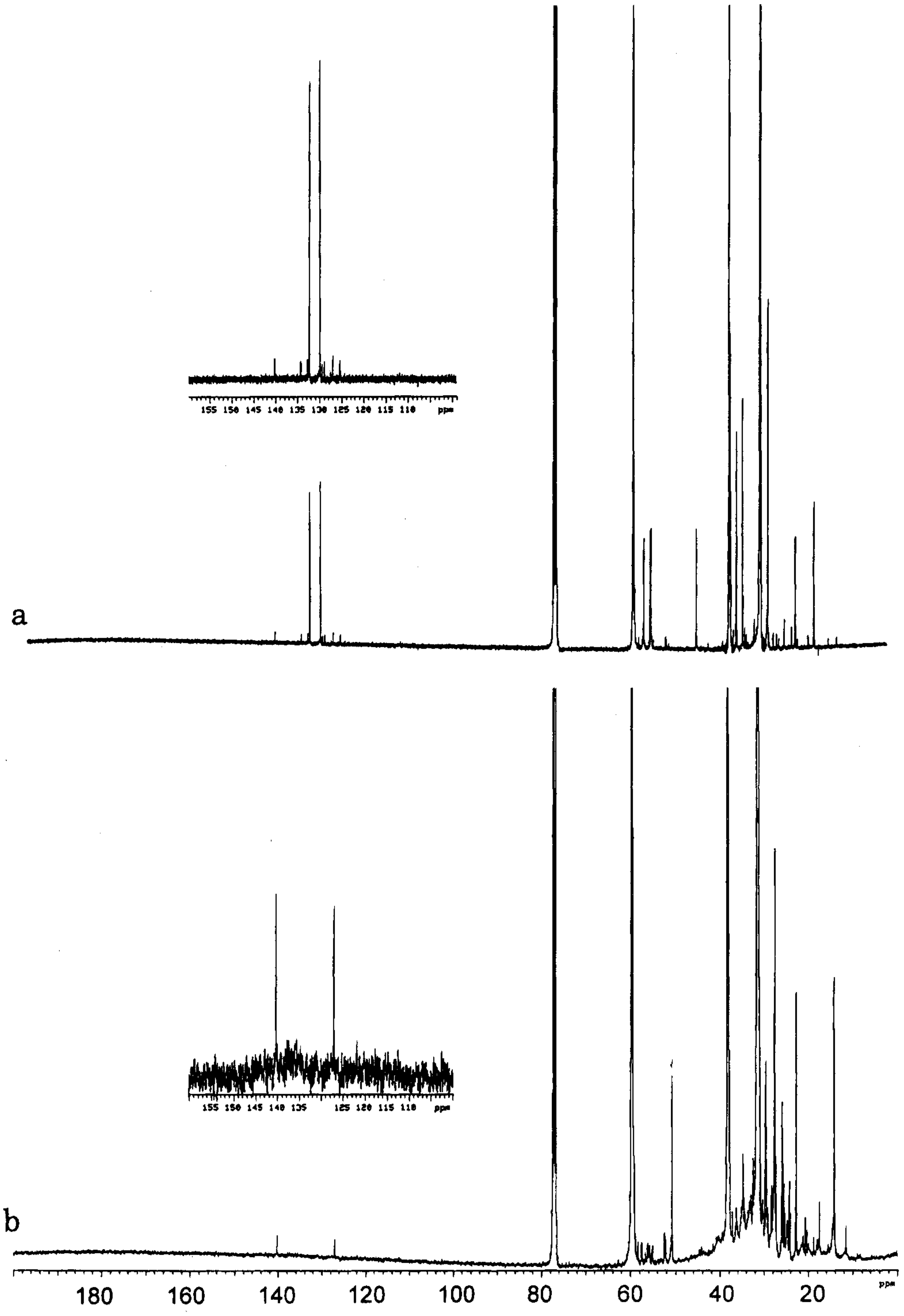
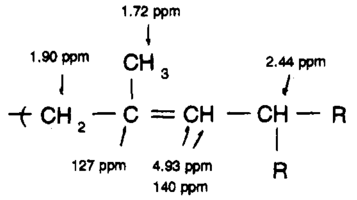


Figure 5. ^{13}C NMR spectra for (a) −110 °C commercial copolymer and (b) −50 °C copolymer. These are the same samples as in parts a and c of Figure 4. See text for discussion.

comes visible in this experiment since there is a higher concentration of the minor species, and four-bond couplings to isobutylene methyl groups are now removed, resulting in a more intense methylene signal. HMQC data (not shown) for the aliphatic hydrogen and carbon regions of the deuterated copolymer revealed a correlation between the peak at 1.90 ppm in the proton spectrum and 56 ppm in the carbon spectrum. Recall, based on proton data alone, the 1.90 peak had been previously assigned to the isoprene methylene group α to the quaternary olefinic carbon. Knowledge of the carbon shift of this species proves useful in the discussion of side-chain chemical shifts below.

IV. Discussion

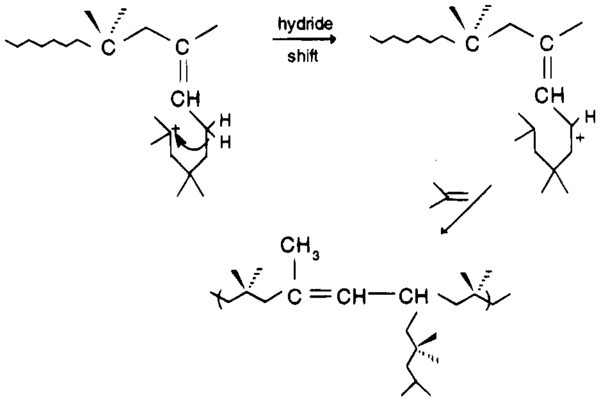
The proposed structure of the secondary isoprene species in butyl rubber is shown below.



The proton chemical shifts of the olefinic methine (4.93 ppm) and the aliphatic methine (2.44 ppm) compare favorably with values of 4.9 and 2.42 ppm for the same hydrogens in the model compound 2,4-dimethyl-2-pentene. Although the NMR data presented above specifically demonstrated that the aliphatic methine carbon C4 was bonded to hydrogens in the α position arising from isobutylene repeat units, the length and structure of additional isobutylene repeat units could not be determined, hence the "R" notation. There are several possibilities for the R groups. One possibility is a short or long branch from the main polymer backbone associated with each secondary isoprene structure. Alternatively, the R groups could be a cyclic ring or derivative that occurs as a result of rearrangements at the chain end. We will address this latter possibility first.

Number-average molecular weights were determined by gel-permeation chromatography for several commercial butyl copolymer samples. Typically, M_n is 130 000−150 000 for the commercial butyl materials under investigation. Assuming one olefin repeat unit per chain, calculations of the degree of polymerization based on the normalized intensity of the secondary isoprene structure peak at 4.93 ppm yielded M_n values of ca. 50 000−75 000. A similar calculation for the laboratory sample polymerized at −80 °C resulted in an M_n value of 7160, while GPC results were 18 437. The factor of 2−3 deviation indicates that the minor structure is present in amounts greater than that required to terminate each chain. We therefore do not attribute the minor isoprenyl structure to chain ends.

The formation of a side chain may occur via a backbiting mechanism, hydride transfer, or alkyl shift to generate an allylic carbocation in the chain. Isobutylene could then attack this center and generate a growing polymer chain, leaving a branch of finite length. From the NMR identification of the aliphatic methine moiety at 2.44 ppm in the proton spectrum and 140 ppm in the carbon spectrum, a branch point exists. The NMR analysis of the polymer prepared with isobutylene-d_8 revealed that isobutylene repeat units are α to the branch point carbon. Several signals are observed in the 52−60 ppm region of Figure 5b which are of the correct intensity required for isobutylene methylene groups α to the branch point. One mechanism which could produce a side chain composed of two isobutylene repeat units is shown below.



Here, the growing chain end backbites, abstracting a hydride ion to form a more stable allylic carbocation. Isobutylene attacks to continue chain growth, and a methyl-substituted five-carbon side chain remains. Chemical shift calculations were carried out for the side- and main-chain α methylene carbons to the branch point using the Grant and Paul parameters.[13] The resulting values for the α carbons of the side chain and the main chain were 52.9 and 53.7, respectively. Two methylene carbon signals are observed in Figure 5b at 52.1 and 52.5 ppm. A similar calculation for the α methylene of the side chain produced a 57.2 ppm shift. Again, signals are observed in this region of the spectrum. While these calculations do not prove the existence of the structure shown above, when considered along with the complete NMR data, they are in every way consistent.

Consideration of substituent effects on chemical shifts also explains the respective differences between the carbon shifts for the olefinic quaternary and methine carbons of the 1,4-structure and the secondary structure (see Figure 5a,b). The quaternary olefinic carbon in the 1,4-structure has a chemical shift of 132.5 ppm, while the chemical shift for the quaternary carbon of the minor species was 127 ppm. One would expect an upfield shift for this carbon in the minor species, since there is an additional γ substituent. Similarly, the olefinic methine carbon of the minor species has a chemical shift of 140 ppm, compared to 130 ppm for the 1,4 structure. The Grant−Paul parameters predict a downfield shift of 9.78 ppm upon introduction of an additional β group.[13]

We have demonstrated that the presence of the secondary structure is not associated with end groups, thereby ruling out the association of only methyl groups as the R substituents above. We have also shown that the R groups arise from isobutylene, ruling out any isoprene-isoprene addition. However, there still remains the question of the exact structure of the R substituent. In an attempt to unequivocally determine if the species α to the branch point are two methylenes or one methylene and one methyl, the signal for the olefinic methine hydrogen (4.93 ppm) was selectively irradiated. Only the couplings between the branch point methine hydrogen and the R groups should remain. The resulting splitting pattern for the branch point methine hydrogen (2.44 ppm) is shown in Figure 8. The pattern appears to be a heptet, which would imply that the R groups were methyls. However, the splitting is only 3.6 Hz, far less than the ca. 6−8 Hz expected for a $CH-CH_3$ hydrogen−hydrogen coupling.[14] This implies that the pattern does not arise from a first-order AMX spin system. A spin simulation program was used to fit the multiplet shown in Figure 8a. Based on the presence of methylene signals in the 55−60 ppm region of the carbon spectrum and the calculations described in the preceding paragraph, we assume initially that the α substituents are two methylene groups. An ABCDX spin system was used to model the experimental spectrum, with the 2.44 ppm aliphatic methine treated as X, and the methylene hydrogens from the two groups as AB and CD. The calculated spectrum is shown for comparison in Figure 8b, with a splitting between multiplet peaks of 3.6 Hz. Calculated coupling constants and line frequencies are summarized in Table 1. The model not only provides excellent agreement with the experimental data but also is consistent with the expected coupling behavior for the structure of the minor species. If one of the R groups is a short side chain and the other is the polyisobutylene backbone, the branch point carbon is a chiral center. If both R groups are long polyisobutylene chains, the branch point is a prochiral center. In either case, the hydrogens of the α methylene groups are magnetically

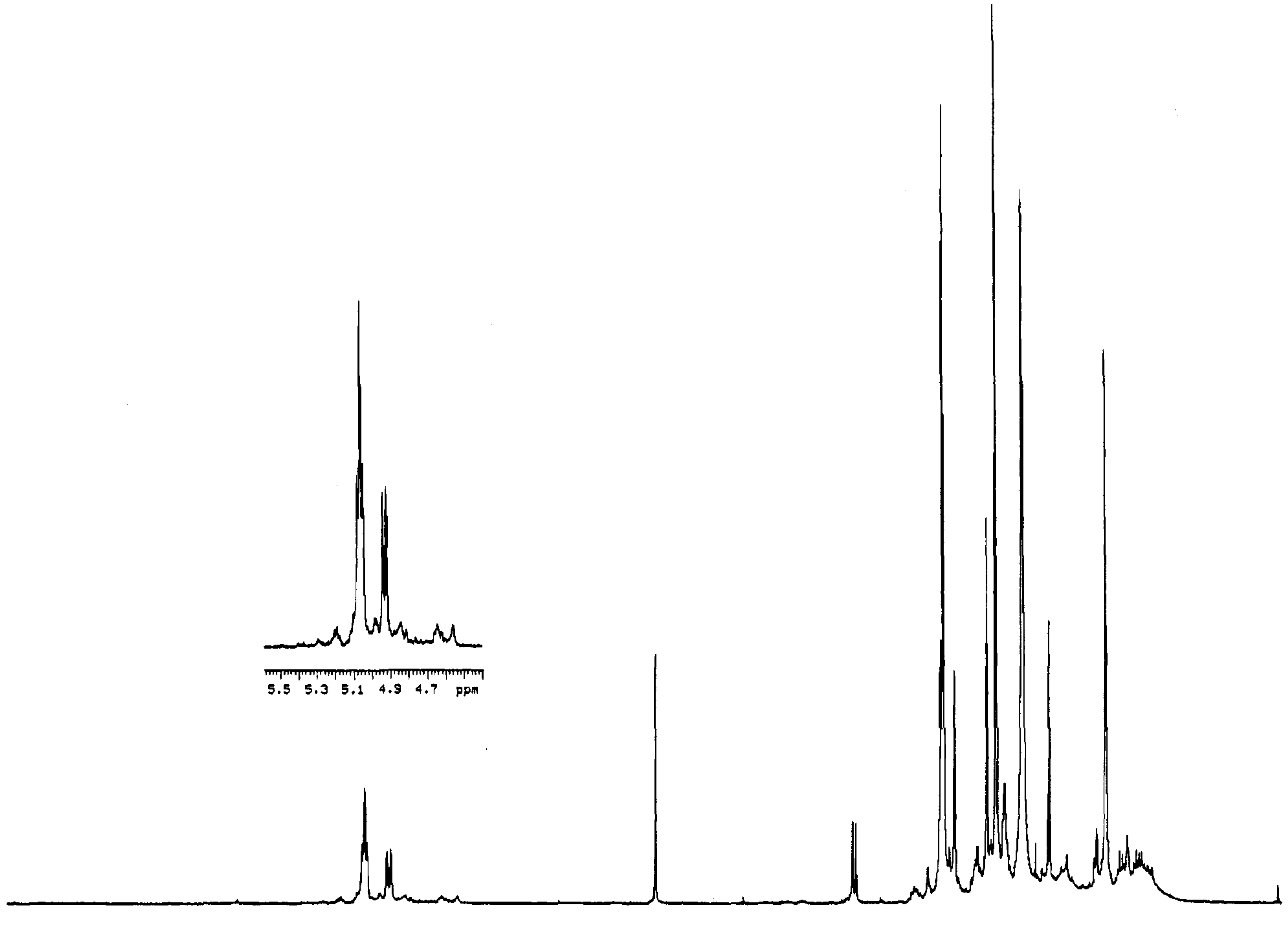
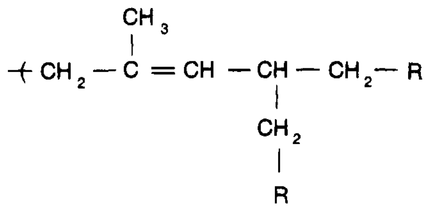


Figure 6. ^{1}H NMR spectrum for an isobutylene-d_8/isoprene copolymer polymerized at −50 °C. Note that the 2.44 ppm signal is now a sharp doublet. The 3.5 ppm peak is from residual methanol. The relative intensity of the 4.93, 2.44, 1.90, and 1.72 ppm peaks is 1:1:1.9:3, as expected for their assignments as CH:CH:CH$_2$:CH$_3$ groups.

inequivalent. Geminal couplings must be considered within each methylene group, as well as axial−axial (trans) and axial−equatorial (gauche) vicinal couplings to the methine hydrogen. Examination of the calculated couplings constants in Table 1 reveals that the values for geminal and vicinal couplings are well within expected limits.

The above exercise strongly suggests that isobutylene methylene groups are attached to the branch point methine group, as in the following structure.



$$-\!\!\left(CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-\underset{\underset{\underset{\displaystyle R}{|}}{\displaystyle CH_2}}{\underset{|}{CH}}-CH_2-R\right.$$

Earlier, we discussed a possible mechanism by which a short five-carbon branch could form. While we were unable to specifically identify NMR evidence for the presence of a short- or long-chain branch, data obtained using dual-detection gel permeation chromatography and rheological methods suggest that the branch is indeed a long-chain branch. Briefly, the comparison of chromatograms obtained using standard differential refractometer (DRI) to that obtained using a low-angle laser light scattering (LALLS) detector provides accurate molecular weight relationships independent of hydrodynamic volume. If the molecular weight detected by the LALLS detector is significantly greater than that detected by the (DRI) detector, this indicates the presence of branches which are of significant molecular weight, i.e., long-chain branches. A plot showing both the LALLS chromatogram and the DRI chromatogram is shown in Figure 9 for the copolymer synthesized at −80 °C. This material contained 0.50 mol % of the secondary isoprene species, which is 2−3 times more than that of commercial butyl polymers. The M_w from the LALLS detector was 79 887, while the DRI detector indicated an M_w of 67 191. This is a difference of ca. 20%, which indicates that this polymer has long-chain branches. A similar comparison for a commercial butyl sample revealed only a 1% difference in the molecular weight from the two detectors. These data provide strong evidence that the branch point we have confirmed by NMR is associated with long-chain branches. Sosky and co-workers have reported zero-shear viscosity (η_0) measurements on commercial butyl rubbers.[15] Comparisons of the slope of log η_0 vs log M_w for butyl and linear polyisobutylene polymers reveal a 7.3 power law relationship for butyl and the standard 3.4 power law for the linear polyisobutylene. This divergence from the 3.4 power for butyl also suggests that long-chain branching exists in butyl rubber.

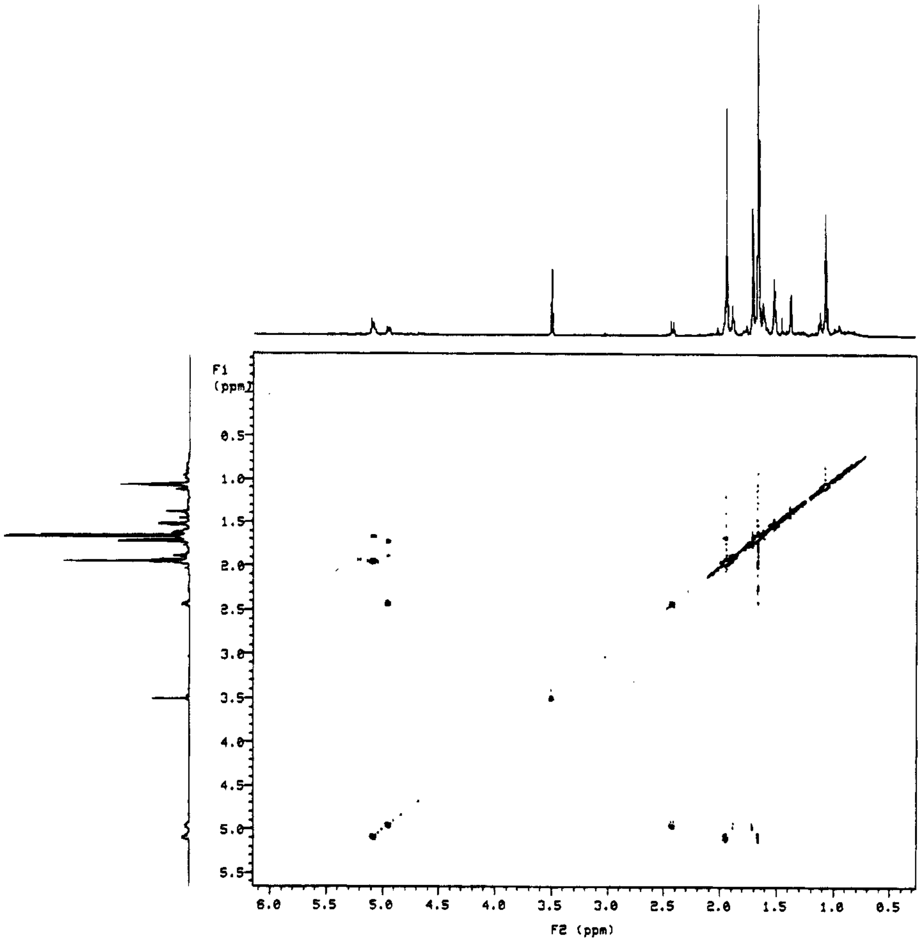


Figure 7. $^1H-^1H$ COSY plot of the isobutylene-d_8/isoprene copolymer in Figure 6.

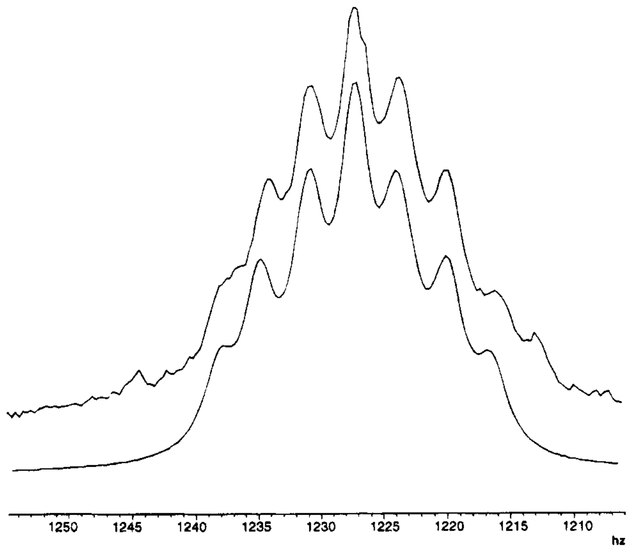


Figure 8. Comparison of experimental (top) and simulated (bottom) spectra for the 2.44 ppm proton peak obtained while selectively irradiating at 4.93 ppm. See text for details.

Table 1. Comparison of Experimental and Simulated Parameters of the ABCDX Model for $-CHCH(CH_2)_2$ Spin System Multiplet Acquired under Selective Irradiation Conditions

	frequency (Hz)		intensity (au)	
line	obsd	calcd[a]	obsd	calcd
1	1216.8	1216.8	0.33	0.32
2	1220.8	1220.5	0.58	0.55
3	1224.5	1224.2	0.81	0.78
4	1227.9	1227.8	1	1
5	1231.5	1231.2	0.82	0.78
6	1235	1235.2	0.59	0.55
7	1238.2	1238.0	0.29	0.30

[a] rms frequency error = 0.18 Hz. Calculated coupling constant values: $J_{AB} = -9.1$; $J_{CD} = -9.2$; $J_{AX} = 7.4$; $J_{CX} = 7.3$; $J_{BX} = 3.5$; $J_{DX} = 3.2$.

Finally, we comment on the possibility that the branched species is only present in a low molecular weight oligomeric phase. The DRI chromatogram in Figure 9 for the −80 °C copolymer shows an additional sharp peak at a retention volume of 38 mL (all peaks at retention volumes greater than 40 mL arise either from small molecule additives or column artifacts not associated with the polymer sample). Although the peak is extremely sharp, it could arise from a low molecular weight oligomeric phase. The minor isoprenyl derivative species could be associated exclusively with the presence of this oligomeric phase. A rather crude attempt to address this possibility involved dissolving some commercial butyl copolymer in chloroform and then precipitating the polymer by adding acetone. No change in the relative concentration of the minor species occurred, in contrast to what one might expect if any low molecular weight oligomers remained in solution. This result is ambiguous, so future plans include using GPC to isolate only the higher molecular weight polymer. NMR analysis of this fraction would then confirm the absence or presence of the minor species.

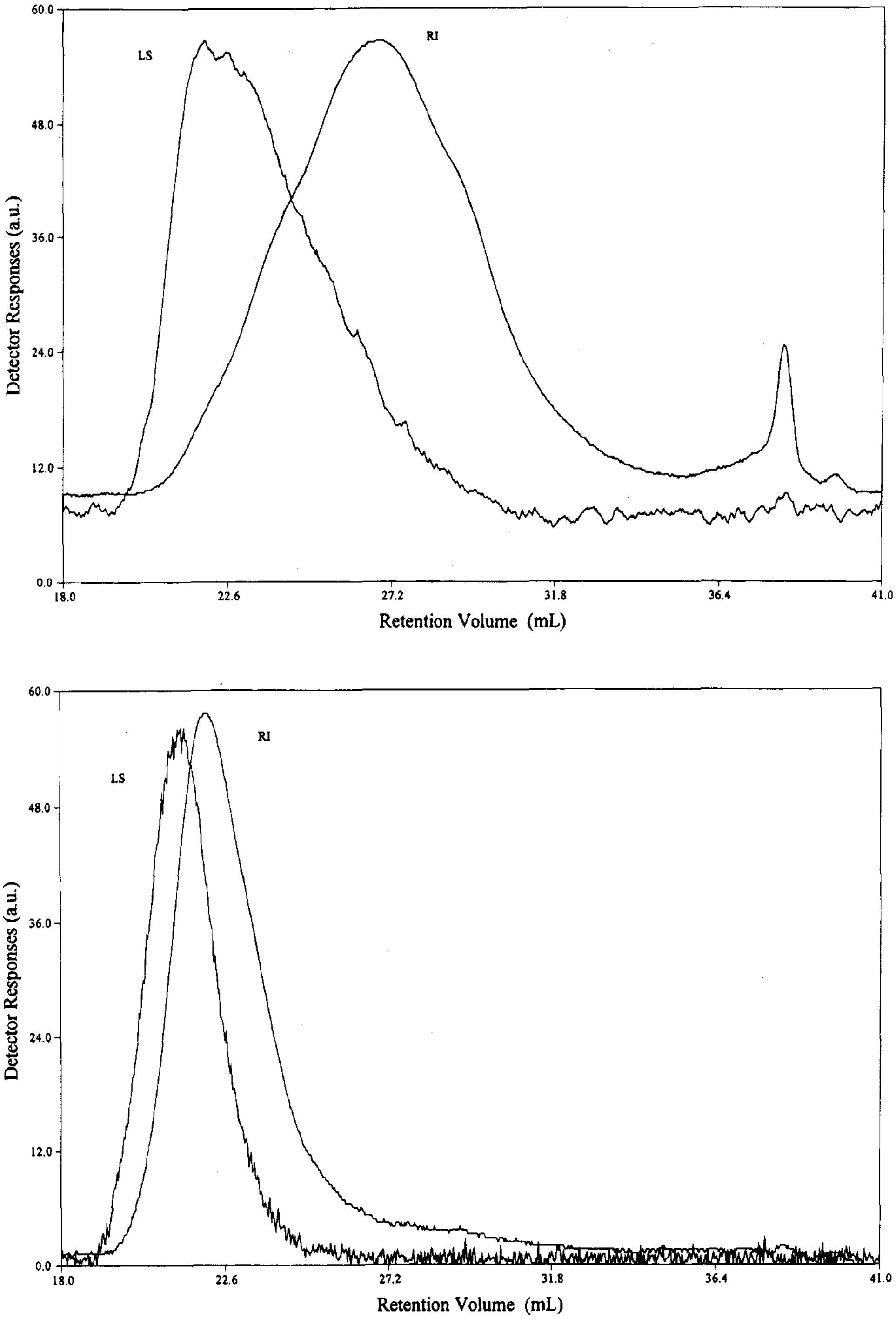


Figure 9. Dual-detector GPC chromatograms for the copolymer synthesized at −80 °C (top) and commercial butyl polymer (bottom). The LALLS trace is the upper trace in each plot. All signals at retention volumes greater than 40 mL arise from either small-molecule additives or column artifacts not associated with the polymer.

Conclusions

We have identified that branch points exist in cationically polymerized isoprene/isobutylene copolymers as well as the commercial butyl rubber copolymers using one- and two-dimensional NMR methods. No evidence was found for 1,2 or 4,3 isoprene addition. These branch points are not associated with end groups but rather occur at isoprene units in the chain whose structure is modified from the predominant 1,4 isoprene addition product. The relative concentration of this minor isoprene species to that of the 1,4-enchained isoprene increases with increasing polymerization temperature. Although specific NMR data proving the existence of short-chain vs long-chain branches was not obtained, GPC and rheological measurements suggest that the branches are long-chain branches. Complete confidence for the assignment of long-chain branches would require a systematic rheological investigation of several copolymers with varying concentrations of the minor species.

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