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^{13}C-NMR Spectra of Isomerized Polybutadienes

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ABSTRACT: The ^{13}C-NMR spectra of a series of polybutadienes that were obtained by isomerizing the 1,4-units in a polymer which initially contained 98% cis-1,4-units, 0.9% trans-1,4-units, and 1.1% 1,2-units were analyzed. Since the 1,2-units in the polymers could be considered to have only cis-1,4- or trans-1,4-neighbors and since the relative proportions of these were varied systematically by isomerization, the polymers provided a unique opportunity to investigate the effect of neighboring substituents on the resonances of carbons in 1,2-units. This approach enabled a number of new assignments for these resonances to be made, particularly those associated with 1,2-units centered in the four possible 1,4–1,2–1,4-triads. Resonance areas of carbons in or adjacent to 1,2-units in the polymers were in good agreement with those expected assuming a statistical distribution of cis-1,4- and trans-1,4-units.

Introduction

The ^{13}C-NMR spectra of polybutadienes have been studied by many investigators.[1–24] Resonances of aliphatic and aromatic carbons in cis-1,4-, trans-1,4-, and 1,2-units have been attributed to various structural features of the polymers and have provided monomer unit sequence distribution and stereosequence distribution information. Due to the large number of possible structural features and the overlapping of signals due to the three types of repeating units present in the polymers, it has been difficult to develop a complete set of resonance assignments for polybutadiene. Most of the assignments that have been made thus far have been developed in studies on polymers having only one or two types of repeating structures, such as polymers having only cis-1,4- and trans-1,4-units (produced by isomerization of the stereospecific forms),[4,8,10,15] equibinary copolymers containing cis-1,4- and 1,2-units,[5,7,8,10,13,15] polymers having predominantly 1,2-units,[11,16,18,19,20] and hydrogenated polymers derived from polybutadienes.[9,16,25]

The establishment of assignments for the resonances of the carbons of 1,2-units has been particularly difficult because of interference by resonances of cis-1,4- and trans-1,4-units in the aliphatic carbon region and because pairs of contiguous 1,2-units can have meso- or racemic-configurations. Structural features of polybutadienes that contain contiguous 1,2-units can thus be responsible for carbon resonances that reflect diad and triad configurations as well as repeating unit sequencing. By investigating the carbon spectra of polybutadienes with high 1,2-unit contents and the spectra of model butadiene dimers and by applying spin-echo techniques to simplify the interpretation of the spectra, assignments for many resonances of diads and triads with contiguous 1,2-unit enchainments have been made.[20] Detailed assignments have yet to be made for resonances of single 1,2-units, however. No information is available concerning the influence of neighboring unit structure on the carbon resonances of 1,2-units in 1,4–1,2–1,4-triads of polybutadienes. The purpose of this paper is to report the results of 100-MHz ^{13}C-NMR studies on polybutadienes obtained by isomerizing a predominantly *cis*-1,4-polybutadiene that contained a small proportion of 1,2-units. The isomerization reaction enabled the configurations of 1,4-units that were neighbors to the 1,2-units to be varied systematically. By correlating the resonance patterns of carbons in 1,2-units and in units adjacent to them with the compositions of the isomerized polymers, it has been possible to make additional assignments for the ^{13}C-NMR spectra of polybutadienes.

Table I
Conditions Used To Prepare Isomerized Samples and Characteristics of the Products

	reaction					
sample	temp (°C)	time (h)	mole ratio PBD/sulfone	% cis[a]	% trans[a]	T_m (°C)
A				98.0	0.9	−5.4
B	140	49	0.573	96.7	2.5	−9.4
C	132	428	0.573	95.7	2.8	−10.3
D	140	112	0.573	94.3	4.6	−14.7
E	140	210	0.573	90.3	8.7	−25.0
F	160	26	0.573	84.0	14.5	
G	140	140	0.131	75.5	22.5	
H	140	168	0.129	71.4	27.0	
I	140	168	0.067	56.4	42.5	
J	140	216	0.050	33.5	65.5	

[a] Determined by IR.

Table II
Percentage of 1,4-Units Having a Trans Configuration in Isomerized Polybutadienes

	analysis method		
polymer	NMR[a]	NMR[b]	IR
C	3	5	3
D	5	6	5
E	10	11	9
F	15	15	15
G	24	25	23
H	28	28	27
I	44	44	43
J	65	64	66

[a] Resonance of aliphatic carbons of 1,4-units. [b] Resonance of olefinic carbons of 1,4-units.

Experimental Section

High-*cis*-1,4-Polybutadiene. A 24.4% solution of butadiene (1.36 mol) in hexane was polymerized at 30 °C during 21 h using a catalyst prepared in situ from nickel boroacylate (0.025 mmol), triisobutyl aluminum (1.25 mmol), and a 1:2 BF_3/hexanol complex (1.25 mmol).[26] The reaction mixture was diluted with hexane containing 0.15 g of butylated hydroxytoluene (BHT) and evaporated to dryness. The yield was nearly quantitative. Infrared[27] and NMR analysis indicated the polymer to contain 98.0% cis-1,4-, 0.9% trans-1,4-, and 1.1% 1,2-units. The mo-

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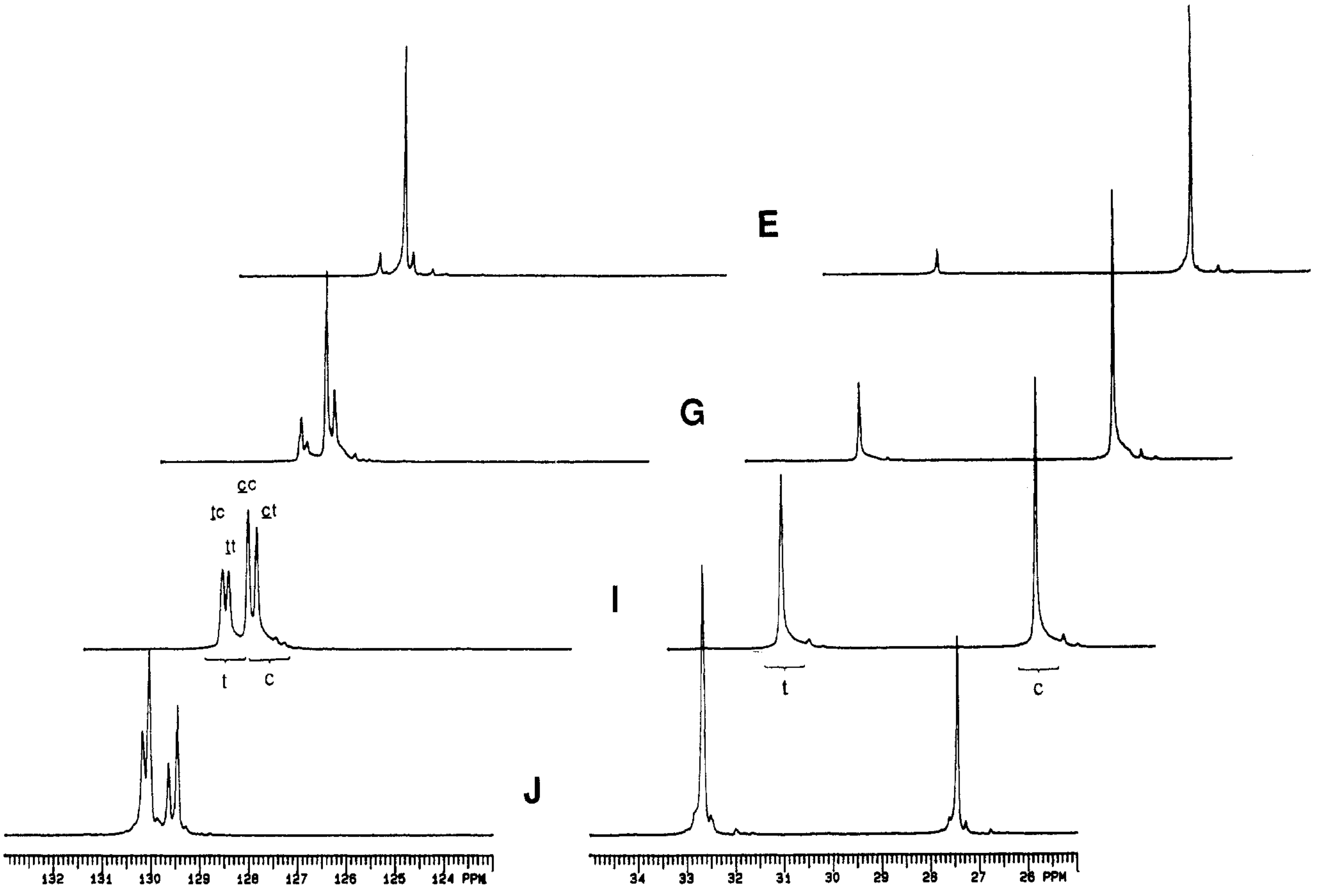


Figure 1. ^{13}C-NMR spectra of isomerized polybutadiene samples E, G, I, and J.

lecular weight of the polymer, determined by gel permeation chromatography was 175 000.

Isomerization of *cis*-1,4-Polybutadiene. The cis–trans isomerization of double bonds was accomplished by heating a solution of the polymer in toluene with butadiene sulfone.[28,29] The reactions were conducted in heavy-walled glass tubes that were sealed with crown caps since the reaction temperature (130–160 °C) was above the boiling point of toluene. The conditions employed to prepare the various polymers are given in Table I, along with polymer characterization data. At the end of each isomerization reaction, the solution was cooled to room temperature, additional BHT was added, and the solution was poured into methanol to precipitate the polymer. The polymer was then collected and dried. The ratios of cis-1,4- to trans-1,4-units in the polymers were determined by ^{13}C-NMR, using the olefinic carbon region (cis, 129.2-129.8 ppm; trans, 129.8–130.3 ppm) and the aliphatic carbon region (cis, 27–28.2 ppm; trans, 32.2–33.4 ppm). The compositions of the polymers were also determined by infrared analysis, using the standard procedure.[22] As can be seen in Table II, all three methods yielded equivalent results. The polymers were also characterized by DSC. Melting endotherms were detected for polymers with more than 90% 1,4-cis-units. The melting points for these samples are given in Table I.

NMR Measurements. The ^{13}C-NMR spectra were recorded on a Varian XL-400 spectrometer at 50 °C. $CDCl_3$ was used as the solvent and internal reference (77.0 ppm for center line). Polymer concentrations were 10% (w/v). The following acquisition parameters were used: spectral width 20618.6 Hz, acquisition time 0.728 s, pulse width 17.5 μs (45°), digital points 30 016, repetition delay 10 s. Depending on the sample, 3500–7000 transients were collected.

Peak areas were determined by cutting and weighing resonance areas and also by digitally integrating using software provided with the spectrometer. These two approaches yielded resonance areas that agreed within 5% relative. Average values from five area measurements on each spectrum were used.

Nomenclature similar to that employed in previous studies[10,13,16] on the NMR spectra of polybutadienes will be employed in the following discussion. Cis-1,4-, trans-1,4-, and 1,2-units will be repesented by c, t, and v, respectively. The unit in a monomer sequence that is responsible for an observed resonance will be written in italics, and numbers will be used to distinguish olefinic carbons of 1,4-units in the vicinity of 1,2-units, according to the following convention.

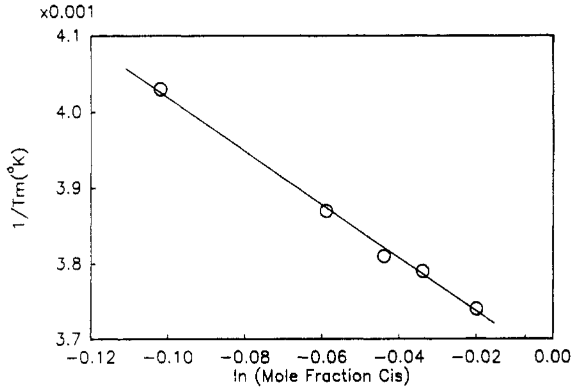


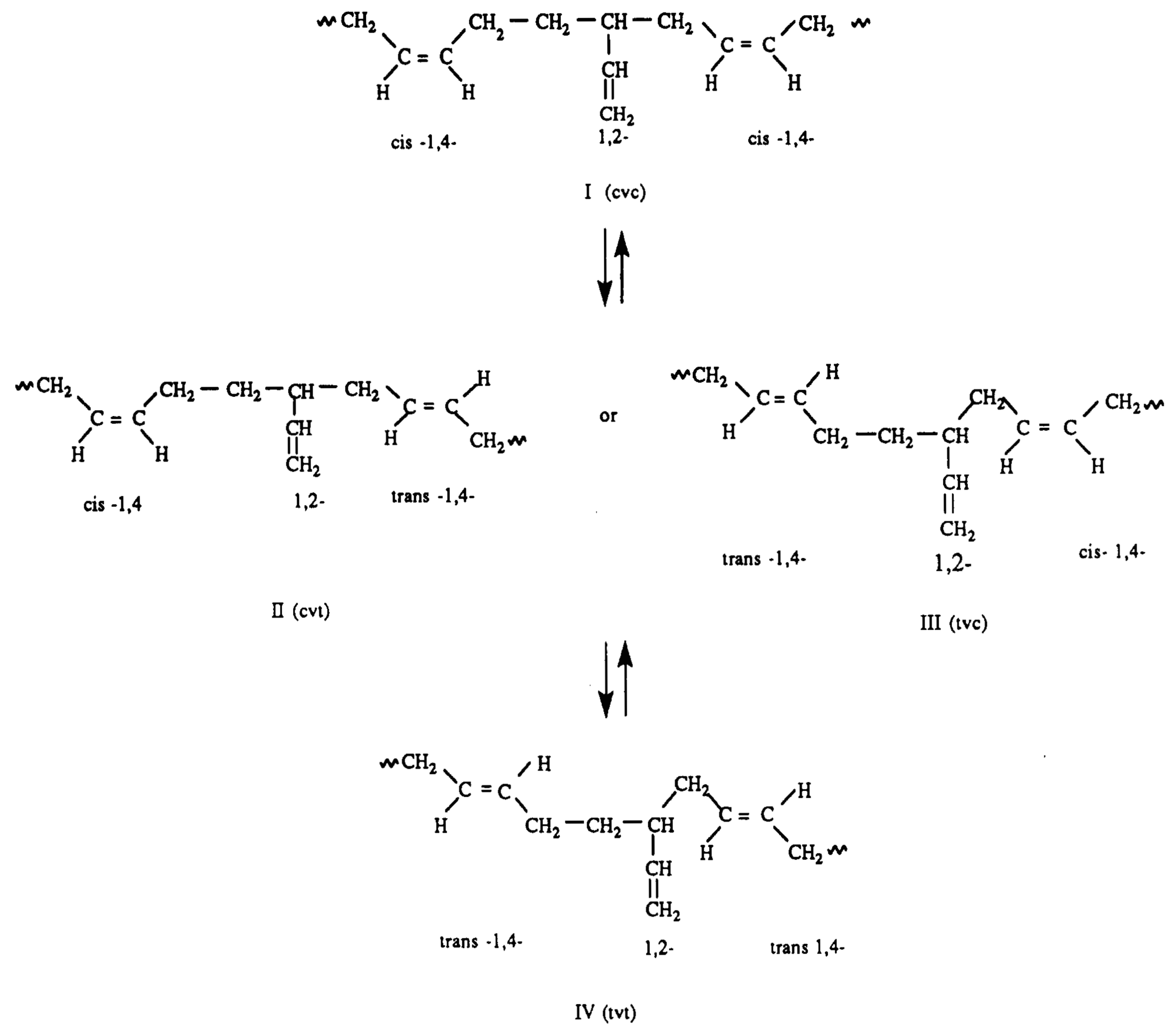
Figure 2. Plot of $1/T_m$ versus ln (mole fraction cis) for isomerized polymers.

$$\sim\mathrm{CH_2CH(1){=}CH(2)CH_2CH_2CH(CH{=}CH_2)CH_2CH(3){=}CH(4)CH_2}\sim$$

Results and Discussion

Isomerization. The procedure of Cunneen and Watson[29] was used to isomerize a polybutadiene sample that initially contained 98.0% cis-1,4-, 0.9% trans-1,4-, and 1.1% 1,2-units. This process yielded polymers containing from 0.9 to 65% trans-1,4-units. Figure 1 shows the 100-MHz ^{13}C-NMR spectra of a series of isomerized polymers. The extent of isomerization of cis-units to trans-units was easily measured from resonances that had been previously assigned to cis-1,4- and trans-1,4-units in the polymers. Previous studies have established that the isomerization process occurs cleanly and randomly. The random character of the isomerization process is supported by the melting behavior of polymers that contained more than

Scheme I



90% cis-1,4-units. Figure 2 shows a plot of the reciprocals of the melting points (T_m) observed for the polymers versus the mole fraction of cis-1,4-units present. The plot is linear, and a heat of fusion (ΔH_m) of 2.32 kJ/mol can be calculated from its slope. This value agrees with the published value of ΔH_m = 2.51 kJ/mol obtained in a similar manner.[30] The intercept of the plot shown in Figure 2 corresponds to a T_m value of 271.3 K for a polymer containing 100% cis-1,4-units.

Since the isomerization (actually equilibration) of cis-1,4- and trans-1,4-units occurs randomly, the changes that are expected to occur in the vicinity of the 1,2-units are given in Scheme I. Assuming the isomerization process occurs randomly, Bernoullian statistics can be used to calculate the relative proportions of structures cvc, cvt, tvc, and tvt from the relative amounts of cis-1,4- and trans-1,4-units present. If x represents the fraction of 1,4-units that are cis-1,4-units, the relative amounts of these structures, designated f_{cvc}, f_{cvt}, f_{tvc}, and f_{tvt} may be calculated as follows:

$$f_{cvc} = x^2$$

$$f_{cvt} = f_{tvc} = x(1 - x)$$

$$f_{tvt} = (1 - x)^2$$

Triad fractions of vinyl-centered triads so calculated were used to interpret appropriate resonance patterns of the isomerized polymers.

NMR Results. Table III catalogues the resonances observed in the spectra and includes assignments developed in this work as well as those made previously. Resonance patterns of individual carbons will be discussed in detail in the following sections.

Aliphatic Carbon Resonances. The aliphatic carbon resonance region is dominated by the resonance of the methylene carbons present in *cc* + *ct* (≈27.5 ppm) and *tt* + *tc* (32.7 ppm) diads. The relative areas of these two resonance regions provided a reliable measure of the ratio of cis-1,4- to trans-1,4-units in the polymers. This approach does not take into account resonances of *cv* and *tv* diads and would not be applicable to polymers with high 1,2-unit contents. However, it works well in the present study because the 1,2-contents are low. Figure 3 shows the resonance observed in the 32.4–33.0 region, where the methylene carbon resonance of trans-units is observed. A relatively sharp resonance at 32.66 ppm is observed in the spectra of polymers A–C, which have predominantly cis-1,4-structure. The spectrum of polymer C is provided in Figure 3 to depict this. It is reasonable to assign this signal to *tc* diads. In the spectra of polymers with higher trans-contents several other signals appear slightly downfield from the 32.66 ppm signal. Their intensities relative to the 32.66 ppm signal increase as the proportion of trans-structure increases. It seems reasonable to attribute them to *tt* sequences. Since two resonances develop, units that are adjacent to *tt* sequences may also influence this resonance region.

Table III
Signal Assignments of Isomerized Polybutadienes

peak[a]	carbon[b]	assignment	chemical shift (ppm)
1a	CH_2	*c*v*t*	24.92
1b	CH_2	*c*v*c*	25.02
	CH_2	*cc* + *ct*	27.46
2a	CH_2	*t*v*t*	30.10
2b	CH_2	*t*v*c*	30.17
3	CH_2	*tt* + *tc*	32.66, 32.68, 32.70
4	CH_2	vc	32.76
5a	CH_2	*tvt*	34.08
5b + 5c	CH_2	*tvc* + *cvt*	34.18, 34.23
5d	CH_2	*cvc*	34.37
	CH_2	v*t*	38.14, 38.17
6a	CH	*tvt*	43.46
6b + 6c	CH	*tvc* + *cvt*	43.54, 43.59
6d	CH	*cvc*	43.69
7a	CH_2=	*tvt*	114.08
7b	CH_2=	*tvc* + *cvt*	114.16
7c	CH_2=	*cvc*	114.26
	CH(3)=	v*ct*	127.88
	CH(3)=	v*cc*	128.06
	CH(3)=	v*tt*	128.38
	CH(3)=	v*tc*	128.52
8	CH(1)=	*c*v	129.28
9	CH=	*ct*	129.44, 129.46, 129.48
10	CH=	*cc*	129.63, 129.65
11	CH(1)=	*t*v	129.87
12	CH=	*tt*	130.01, 130.03, 130.05, 130.07
13	CH=	*tc*	130.14, 130.16, 130.18
	CH(4)=	v*t*	130.49
14	CH(2)=	*t*v	131.28
15a	CH=	*cvc*	142.63
15b	CH=	*cvt* + *tvc*	142.69
15c	CH=	*tvt*	142.75

[a] New assignments are designated by number–letter combinations. Signals that are identified in figures are numbered. [b] Olefinic carbons of 1,4-units adjacent to 1,2-units are identified by the following numbering scheme: $-CH_2CH(1)=CH(2)CH_2CH_2CH(CH=CH_2)-CH_2CH(3)=CH(4)CH_2-$.

Empirical shift calculations reported by others[20] have predicted that the vc resonance should occur near 32.72 ppm, but a signal corresponding to this resonance has not been reported previously. The spectra of samples A and B contain a signal at 32.76 ppm that corresponds well to this calculated chemical shift. This signal is obscured by the resonance of *tt* diads in the spectra of polymers having more than 10% trans-1,4-units, which may explain why it was not observed previously.

In addition to the intense resonances due to methylene carbons of cis-1,4- and trans-1,4-units, several minor resonances due to carbons in or adjacent to 1,2-units are observed in the spectra. Their resonance patterns vary with the cis/trans ratio as can be seen in Figure 4. Resonances of the methylene carbons of 1,4-units that are attached to 1,2-units (*c*v, *t*v, vc, and v*t*) have been assigned previously to signals observed near 25, 30, 33, and 38 ppm, respectively. The spectra in Figure 4 contain two resonances in most of these general areas. This suggests that the resonances are due to sequences larger than diads. For example, the spectra of polymers A–F (97–85% cis) contain predominantly a signal at 25.02 ppm in this region. In the spectra of polymers with appreciable trans-contents (polymers G–J) an additional signal is present at 24.92 ppm. The relative intensities of the signals at 24.92 and 25.02 ppm are directly proportional to the relative amounts of trans- and cis-units in the polymers, as can be seen in Table IV (signals 1a and 1b). Accordingly, it is reasonable to assign the resonances observed at 24.92 and 25.02 ppm to *c*v*t* and *c*v*c* sequences. Similarly, the spectra of polymers A–F do not contain a significant signal near 30 ppm, signifying little or no *t*v, but signals at 30.10 and 30.17 ppm are present in the spectra of the polymers with significant trans-contents. On the basis of the good correspondence of the relative areas of these signals with the relative amounts of cis- and trans-units present in the polymers (Table IV, signals 2a and 2b), the signals at 30.10 and 30.17 ppm are assigned to *t*v*t* and *t*v*c* sequences, respectively. Due to interference by resonances of *tt* carbons, the vc region (32.76 ppm) could not be investigated when the polymers had appreciable trans-contents. However, the v*t* region seemed to contain resonances at 38.14 and 38.17 ppm. Due to their very close proximity, no attempt was made to measure their relative intensities. On the basis of qualitative changes in the shape of the 38 ppm resonance pattern with the trans-content of the polymers, the signals at 38.14 and 38.17 ppm are tentatively attributed to *c*v*t* and *t*v*t* sequences, respectively.

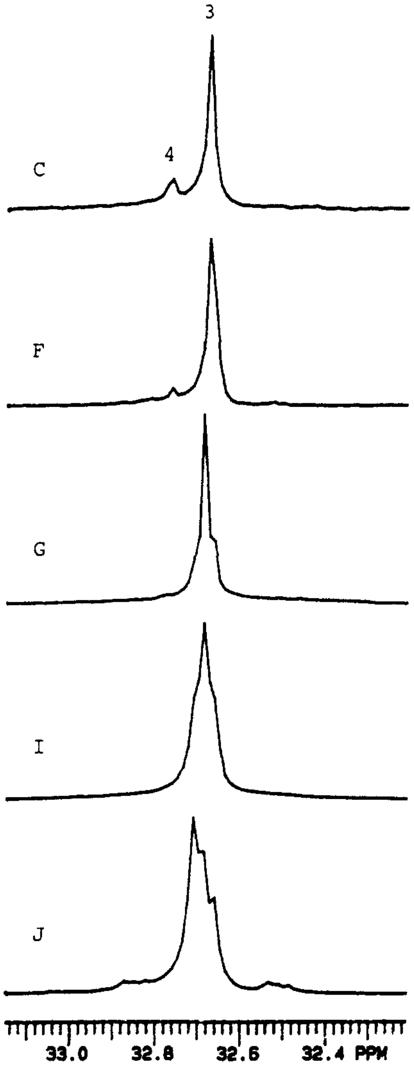


Figure 3. Expanded ^{13}C-NMR spectra of the aliphatic resonances (3 and 4) of isomerized polybutadiene samples C, F, G, H, I, and J.

The resonance patterns of aliphatic carbons of 1,2-units in the polymers each consist of up to four resonances corresponding to the four possible 1,2-unit-centered triads (*cvc*, *cvt*, *tvc* and *tvt*). The resonance of the methine carbons of 1,2-units occurs at ~34 ppm. A single resonance (5d, 34.37 ppm) predominates in this region in the spectra of samples A–C, enabling it to be assigned to *cvc*. In the spectrum of sample J, the predominant signal (5a) occurs at 34.08 ppm, and this may be assigned to *tvt*. Between the resonances at 34.08 and 34.37 ppm is a broad resonance area that is attributed to *cvt* and *tvc* resonances. If the isomerization process is truly random, signals for these resonances should have equal intensities. It appears that two resonances may contribute to this region, but they are not of equal intensity. It may be that the resonances of

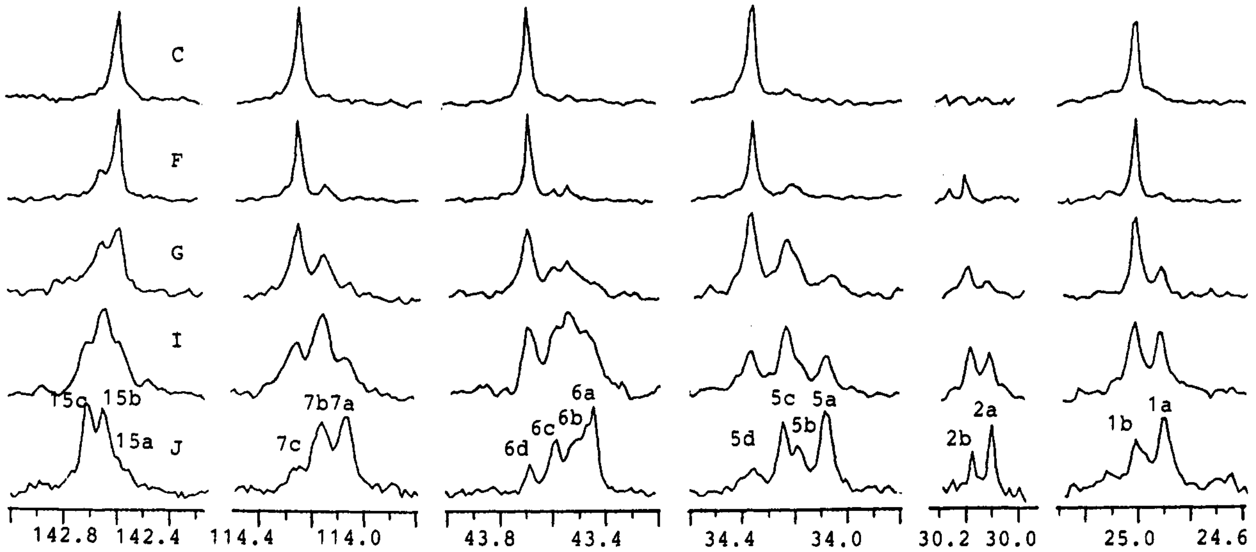


Figure 4. Expanded ^{13}C-NMR spectra of resonances (1, 2, 5–7, and 15) of isomerized polybutadiene samples C, F, G, I, and J.

Table IV
Observed and Calculated Resonance Areas of Isomerized Polybutadienes

	obsd (calcd) resonance areas				
resonance region	C (3% trans)	F (15% trans)	G (24% trans)	I (44% trans)	J (65% trans)
1a	0.05 (0.03)	0.12 (0.15)	0.22 (0.24)	0.45 (0.44)	0.60 (0.65)
1b	0.95 (0.97)	0.88 (0.85)	0.78 (0.76)	0.55 (0.56)	0.40 (0.35)
2a			0.28 (0.24)	0.45 (0.44)	0.64 (0.65)
2b			0.72 (0.76)	0.55 (0.56)	0.36 (0.35)
5a	0.01 (0.01)	0.05 (0.02)	0.09 (0.06)	0.22 (0.19)	0.41 (0.42)
5b, 5c	0.08 (0.05)	0.25 (0.26)	0.36 (0.36)	0.49 (0.50)	0.46 (0.46)
5d	0.91 (0.94)	0.70 (0.72)	0.55 (0.58)	0.29 (0.31)	0.13 (0.12)
6a,b	0.07 (0.04)	0.14 (0.15)	0.26 (0.24)	0.47 (0.44)	0.63 (0.65)
6c	0.04 (0.03)	0.10 (0.13)	0.18 (0.18)	0.23 (0.25)	0.26 (0.28)
6d	0.89 (0.93)	0.76 (0.72)	0.56 (0.58)	0.30 (0.31)	0.11 (0.12)
7a	0.01 (0.01)	0.03 (0.02)	0.08 (0.06)	0.19 (0.19)	0.44 (0.42)
7b	0.07 (0.05)	0.27 (0.26)	0.35 (0.36)	0.52 (0.50)	0.47 (0.46)
7c	0.92 (0.94)	0.70 (0.72)	0.57 (0.58)	0.29 (0.31)	0.09 (0.12)
20a	0.92 (0.94)	0.71 (0.72)	0.56 (0.58)	0.28 (0.31)	0.15 (0.12)
20b	0.07 (0.05)	0.26 (0.26)	0.35 (0.36)	0.52 (0.50)	0.42 (0.46)
20c	0.01 (0.01)	0.03 (0.02)	0.09 (0.06)	0.20 (0.19)	0.43 (0.42)

cυt and *tυc* sequences are not resolved and that signal noise is responsible for the apparent presence of two resonances of unequal intensity in some of the spectra. Since the relative areas of signals 5a, 5b + 5c, and 5d agree well with triad fractions calculated from the cis-contents of the polymers (Table IV) as described above, it is reasonable to assign them to *tυt*, *cυt* + *tυc*, and *cυc* triads, respectively. Similarly, four resonances are observed for the methylene carbons of vinyl-units (43.4–43.8 ppm). The resonance at 43.69 ppm (6d) is predominant in this region in the spectra of polymers with high cis-contents (e.g., polymers C and F). On this basis and the good correlation of its relative area with that expected for *cυc* triads, this signal is assigned to *cυc* triads. Resonances at 43.54 and 43.59 ppm (6b and 6c) appear to have approximately equal intensities in many of the spectra. Since *tυc* and *cυt* triads should be present in equal amounts in the polymers and since it is reasonable to expect their resonances to occur between those of *cυc* and *tυt* triads, the resonances at 43.54 and 43.59 ppm are collectively assigned to *tυc* and *cυt* triads. They cannot be assigned individually at this time. The relative area of the resonance at 43.59 ppm agrees with triad fractions calculated for either *tυc* or *cυt* triads (Table IV). Similarly, the relative areas of the resonances at 43.54 and 43.46 ppm (6a and 6b), measured collectively, agree with the sums of triad fractions calculated for *tυt* and either *tυc* or *cυt* triads. On this basis, the resonance at 43.46 ppm is attributed to *tυt* triads.

Table V
Ratios of 1,2-Unit-Related Aliphatic Carbon Resonances to 1,4-Unit Methylene Carbon Resonances (×100)[a]

	ratio					
polymer	CH_2- (1a & 1b)[b] (*c*v)	CH_2- (2a & 2b)[b] (*t*v)	CH_2- (4)[b] (v*c*)	CH_2 (v*t*)	CH_2- (5a–d)[b] (υ)	CH- (6a–d)[b] (υ)
C	0.47	nd[c]	0.46	nd[c]	0.46	0.44
F	0.39	0.03	0.43	0.04	0.41	0.40
G	0.37	0.11	nd[c]	0.09	0.50	0.45
I	0.25	0.21	nd[c]	0.21	0.51	0.45
J	0.21	0.26	nd[c]	0.27	0.46	0.42

[a] Observed areas under resonances of CH_2(*cc* + *ct*) and CH_2(*tc* + *tt*) are added to be 100%. [b] Assigned peaks or sequences are in parentheses. [c] nd = not detectable.

Table V compares the resonance areas observed for various resonances associated with vinyl structure. The areas are expressed as ratios of the areas of interest to the sum of the areas due to methylene carbons of 1,4-units (signals at 27.46 and 32.66–32.70 ppm). These relative areas are very consistent internally and with a 1,2-content of approximately 1 mol % (theoretical ratio = 5.0×10^{-3}). This provides support for the assignments and demonstrates that the 1,2-units were not affected by the isomerization procedure.

Olefinic Carbon Resonances. The four major olefinic resonances observed for the polymers are shown in Figure 5. These have been assigned in previous studies on polymers with predominantly 1,4-structure to *ct* (peak 9), *tt* (peak 10), *cc*, (peak 12), and *tc* (peak 13) diads. Although single resonances have been indicated in the past, the high signal/noise ratios required for the present study enable fine structure to be recognized in each of these major resonances. This may some day be interpreted in terms of monomer triad sequences. For example, signals at 129.63 and 129.65 ppm that contribute to peak 11 might be assigned to ccc and tct triads, respectively. In general, however, the fine structure is not sufficiently well-defined to be analyzed in this study. Table IV lists the chemical shifts of peaks and shoulders observed in each of these major resonances.

Also of interest in Figure 5 are the resonances of trans-units next to vinyl-units (peaks 11 and 14) that are present in the spectrum of polymer J. These have been assigned previously.[10,26]

The resonances of the olefinic carbons of 1,2-units occur at ~114 (=CH_2) and ~142 (–CH=) ppm. Figure 4

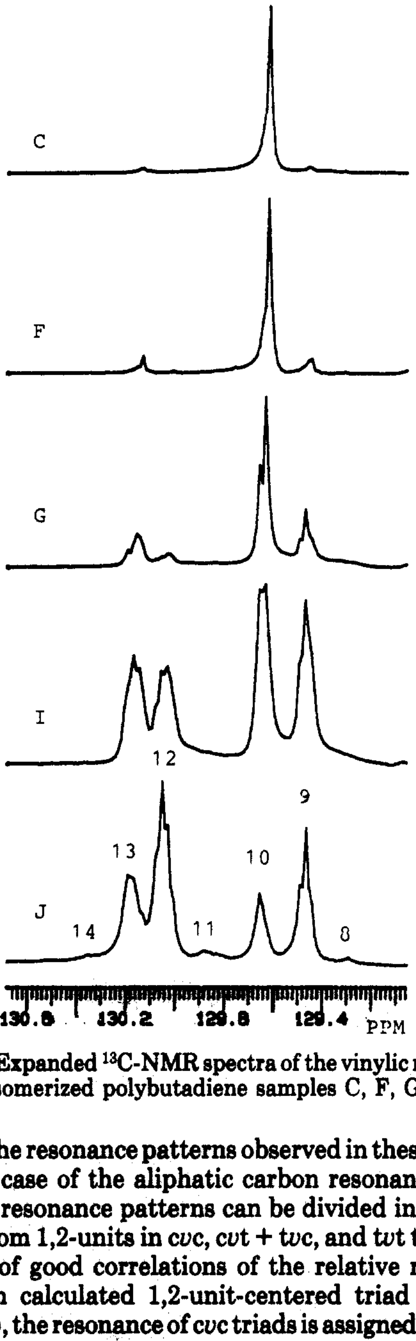


Figure 5. Expanded ^{13}C-NMR spectra of the vinylic resonances (8–14) of isomerized polybutadiene samples C, F, G, I, and J.

contains the resonance patterns observed in these regions. As in the case of the aliphatic carbon resonance of 1,2-units, the resonance patterns can be divided into contributions from 1,2-units in *cvc*, *cvt* + *tvc*, and *tvt* triads. On the basis of good correlations of the relative resonance areas with calculated 1,2-unit-centered triad fractions (Table IV), the resonance of *cvc* triads is assigned to signals at 114.26 (7c) and 142.63 (15a) ppm, that of *cvt* + *tvc* triads is assigned to signals at 114.16 (7b) and 142.69 (15b) ppm, and that of *tvt* triads is assigned to signals at 114.08 (7a) and 142.75 (15c) ppm. It is interesting that the line ordering occurs in different directions for the (–CH=) and (=CH$_2$) carbons.

Minor resonances that are due to cis-1,4- or trans-1,4-units in the vicinity of 1,2-units occur in the 128–131 ppm region. These have been assigned previously[10] and are listed in Table III. Due to the presence of other strong signals in the region, these resonances are difficult to study.

Conclusions

All of the carbon resonances of isolated 1,2-units in polybutadiene can provide information about the configurations of 1,4-units that are adjacent to the 1,2-units. Table III lists chemical shift assignments developed in this study for the methine (6a–d), methylene (5a–d), saturated methine (7a–c), and unsaturated methylene (15a–c) carbons of 1,2-units in *cvc*, *tvc* + *cvt*, and *tvt* triads.

The resonances of the methylene carbons of 1,4-units next to isolated vinyl-units previously observed as signals for cv (24.9 ppm) and *t*v (30.1 ppm) diads have now been identified as four signals (24.92, 25.02, 30.10, and 30.17 ppm) which are attributed to *c*v*t*, *c*v*c*, *t*v*t*, and *t*v*c*, in order of increasing chemical shift. Finally, fine structure has been noticed in the olefinic carbon resonances associated with 1,4–1,4-diads (peaks 9, 10, 12, and 13) that may eventually be the source of triad sequence distribution information.

In all cases where resonance area measurements could be made, the results obtained in this study were consistent with calculations made assuming that the isomerization reaction occurs randomly. Chemical shifts observed for previously assigned resonances were in good agreement with previously reported values.

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