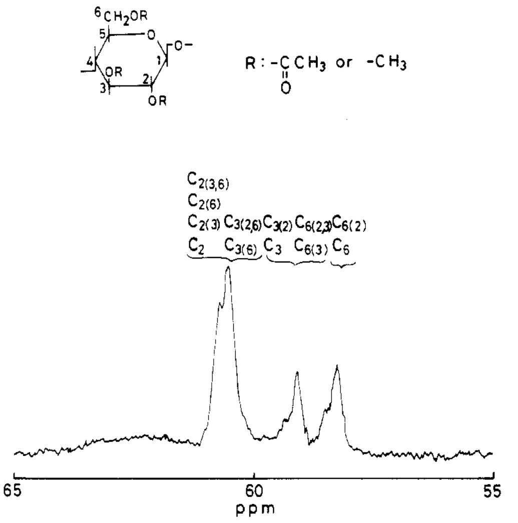


Figure 8. Proposed methoxy methyl peak assignment of acetylated methylcellulose in $CDCl_3$ at 30 °C (sample 5 in Table I, methoxy substitution position in parentheses).

Table IV
Observed and Calculated Peak Area Ratios of Methoxy Methyl Signals of Acetylated Methylcellulose Samples[a]

	obsd ratios			calcd ratios		
sample[b]	I	II	III	I	II	III
1	35	10	55	37	10	53
2	27	17	56	31	16	53
3	25	17	58	26	20	54
4	27	19	58	23	20	57
5	20	20	60	19	22	59
6	19	23	58	20	23	57
7	13	28	59	12	28	60

[a] I, II, and III correspond to signals at 58.3, 59.1, and 60.5 ppm, respectively. Fractions in percent. See also Figure 8. [b] See also Table I.

field by the change of the substituent on 6- and 3-position, respectively, from methoxy to acetyl. The proposed assignment was examined by comparing the calculated peak area ratios based on the substituent distribution results by GLC to those experimentally observed by NMR. The calculated and observed peak area ratios were found to agree satisfactorily, as shown in Table IV, strongly supporting the present assignment.

In conclusion, the present NMR technique using acetylated derivatives of cellulose ethers has proved to be a convenient and reliable method to determine the substituent distribution of cellulose derivatives. The further applications of the present technique to a series of other cellulose derivatives are now under way in our laboratory.

Registry No. Methylcellulose, 9004-67-5; methyl celluloseacetate, 51065-95-3.

References and Notes

(1) Dudley, R. L.; Fyfe, C. A.; Stephenson, P. J.; Deslandes, Y.; Hamer, G. K.; Marchessault, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 2469.
(2) Kamide, K.; Okajima, K. *Polym. J.* **1981**, *13*, 127.
(3) Miyamoto, T.; Sato, Y.; Shibata, T.; Inagaki, H.; Tanahashi, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2363.
(4) Sei, T.; Ishitani, K.; Suzuki, R.; Ikematsu, K. *Polym. J.* **1985**, *17*, 1065.
(5) Kowsaka, K.; Okajima, K.; Kamide, K. *Polym. J.* **1986**, *18*, 843.
(6) Parfondry, A.; Perlin, A. S. *Carbohydr. Res.* **1977**, *57*, 39.
(7) Takahashi, S.-I.; Fujimoto, T.; Baura, B. M.; Miyamoto, T.; Inagaki, H. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2981.
(8) DeMember, J. R.; Taylor, L. D.; Trummer, S.; Rubin, L. E.; Chiklis, C. K. *J. Appl. Polym. Sci.* **1977**, *21*, 621.
(9) Lee, D. S.; Perlin, A. S. *Carbohydr. Res.* **1982** *106*, 1.
(10) Kimura, K.; Shigemura, T.; Kubo, M.; Maru, Y. *Makromol. Chem.* **1985**, *186*, 61.
(11) Hjertberg, T.; Zadorecki, P.; Arwidsson, M. *Makromol. Chem.* **1986**, *187*, 899.
(12) Wu, T. K. *Macromolecules* **1980**, *13*, 74.
(13) Kamide, K.; Okajima, K. *Polym. J.* **1981**, *13*, 163.
(14) Goodlett, W.; Dougherty, J. T.; Patton, H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1971**, *9*, 155.
(15) Isogai, A.; Ishizu, A.; Nakano, J. *Sen-i Gakkaishi* **1984**, *40*, T-505.
(16) Reuben, J. *Carbohydr. Res.* **1986**, *157*, 201.
(17) Isogai, A.; Ishizu, A.; Nakano, J. *J. Appl. Polym. Sci.* **1986**, *31*, 341.
(18) Albersheim, P.; Nevins, D. J.; English, P. D.; Karr, A. *Carbohydr. Res.* **1967**, *5*, 340.
(19) Lindberg, B. *Methods Enzymol.* **1972**, *28*, 178.
(20) Sachse, K.; Metzner, K.; Welsch, T. *Analyst* **1982**, *107*, 53.
(21) *The Pharmacopoeia of Japan*, 10th ed.; 1981, English version p 1080; Society of Japanese Pharmacopoeia, Yakuji Nippon Ltd., 1982.
(22) *The Pharmacopoeia of Japan*, 11th ed.; 1985, Japanese version p 1242; Society of Japanese Pharmacopoeia, Yakuji Nippon Ltd., 1986.
(23) Japan Industrial Standard (JIS), L1013, 7.28-B, 1981.

Analysis of ^{13}C NMR of Polybutadiene by Means of Low Molecular Weight Model Compounds

Hisaya Sato,* Kenji Takebayashi, and Yasuyuki Tanaka

Department of Material Systems Engineering, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan. *Received February 9, 1987*

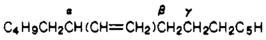
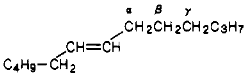
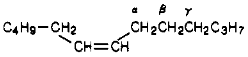
ABSTRACT: The aliphatic carbon signals of polybutadiene are assigned in terms of diad or triad sequences of cis-1,4, trans-1,4, and 1,2 units, by using model compounds corresponding to monad and diad sequences of each isomeric structure. Carbon atoms between a 1,2–1,2 linkage and a 1,4 unit showed split signals, which were assigned to the tacticity of the 1,2 diad. The sequence distributions of cis-1,4, trans-1,4, and 1,2 units were determined by using relative intensities of methylene carbon signals. Random distribution of these isomeric units was observed in polybutadienes prepared with *n*-BuLi, *n*-BuLi/Et_2O, $CoBr_2 \cdot [P(Ph)_3]/Al(i\text{-}Bu)_3 \cdot H_2O$, and radical catalysts.

Introduction

Butadiene is polymerized to yield three isomeric units; cis-1,4, trans-1,4, and 1,2 units. It is well-known that the physical properties of polybutadiene are governed by the amount and the sequence distribution of these isomeric units. The amounts of the isomeric units can be determined by infrared and ^1H NMR spectroscopies. The sequence distribution of cis-1,4 and trans-1,4 units can be determined by olefinic and aliphatic proton[1-4] or ^{13}C NMR measurement of the olefinic region for 1,4-polybutadiene.[5-7]

0024-9297/87/2220-2418$01.50/0

Table I
Structure and Chemical Shift of Butadiene Oligomers

isomers					shift factor, ppm	
symbol	structure	fraction		chem shift, ppm	this work	Conti[13]
V	 $C_4H_9CH_2\overset{\alpha}{C}H(CH{=}CH_2)\overset{\beta}{C}H_2\overset{\gamma}{C}H_2CH_2C_5H$	1-1	α	44.26	14.55	13.5
			β	35.16	5.46	5.9
			γ	26.96	−2.40	−2.4
T		1-2	α	32.71	3.00	3.0
			β	29.75	0.05	0.0
			γ	28.95	−0.41	−0.5
C		1-3	α	27.27	−2.44	−2.5
			β	29.87	0.17	0.0
			γ	29.24	−0.12	−0.5

However, these methods are not applicable to polybutadienes containing a large fraction of 1,2 units, because signals due to 1,2 units overlap with those of 1,4 units.

^{13}C NMR spectra of polybutadienes have been investigated by many researchers.[8-16] However, there remains disagreement among them concerning the assignment of some peaks, especially for peaks reflecting sequences containing polyads of 1,2 units. The discrepancy may be attributed to the fact that the spectrum consists of many peaks reflecting the sequences of the three units and the configurational sequences of 1,2 unit, overlapping each other. Hitherto, these signals have been mainly assigned on the basis of simple additivity rules of ^{13}C NMR chemical shifts established by Grant and Paul,[17] Lindeman and Adams,[18] and Roberts et al.[19] In these studies shift factors were obtained from linear or branched hydrocarbons and simple olefinic hydrocarbons. Therefore, it is principally impossible to determine the signal splittings due to tacticity. Also the chemical shifts estimated according to these empirical methods are not precise enough to assign such a complicate spectrum as that of polybutadiene.

We have already demonstrated that the anionic oligomerization of styrene followed by HPLC separation provides useful oligomers for the signal assignment of a complicated spectrum of polystyrene and have assigned ^{1}H and ^{13}C NMR spectra of polystyrene on the basis of the spectra of the oligomers.[20] In this paper some of the uncertainties in signal assignment are resolved by analyzing ^{13}C NMR spectra of various butadiene oligomers. On the basis of these signal assignments the sequence distribution of the three isomeric units are determined for polybutadienes prepared with anionic, radical, and cobalt catalysts.

Experimental Section

Butadiene oligomers were prepared by anionic oligomerization of butadiene in diethyl ether with n-butyllithium as an initiator and 1-bromopentane as a terminator. The oligomer containing one or two butadiene units, denoted monomer and dimer, respectively, were separated from the reaction mixture by GPC by using porous styrene–divinylbenzene gel with an exclusion limit of 3000 and chloroform as an eluent. The monomer and the dimer were separated into isomers by high-performance liquid chromatography (HPLC) using porous styrene–divinylbenzene gel as a stationary phase and 2,2,4-trimethylpentane as an eluent.

Polybutadienes were prepared with n-butyllithium and n-butyllithium/ethyl ether and azobis(isobutylonitrile) initiators. Syndiotactic 1,2-polybutadiene prepared with cobalt catalyst[21] was obtained from Japan Synthetic Rubber Co.

^{13}C NMR spectra were recorded on a JEOL FX-200 spectrometer (50.1 MHz) at 35 °C with a pulse repetition time of 3 s and pulse width of 10 μs (45°). Deuteriochloroform was used as a solvent and the chemical shifts were read from tetramethylsilane added as an internal standard.

Results and Discussion

Butadiene Oligomers. Butadiene oligomers were prepared by oligomerization of butadiene with butyllithium followed by termination with 1-bromopentane.

$$C_4H_9Li + n\text{-}CH_2{=}CHCH{=}CH_2 \rightarrow C_4H_9(CH_2CH{=}CHCH_2)_x\text{–}[CH_2CH(CH{=}CH_2)]_{n-x}\text{–}Li \xrightarrow{C_5H_{11}Br} C_4H_9(CH_2CH{=}CHCH_2)_x\text{–}[CH_2CH(CH{=}CH_2)]_{n-x}\text{–}C_5H_{11}$$

I

The monomer (I, n = 1) and the dimer (I, n = 2) were separated from the oligomer mixture by GPC.

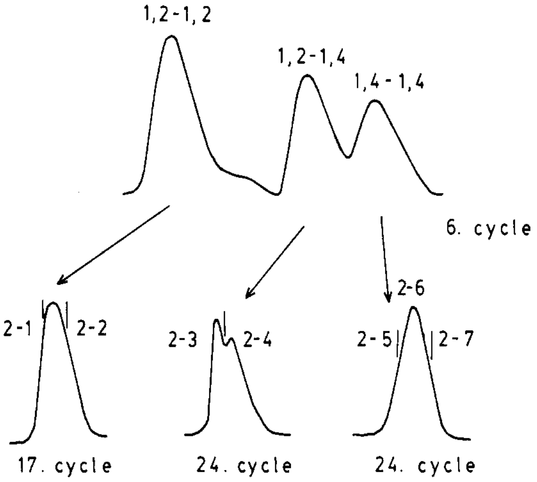


Figure 1. HPLC separation of a butadiene dimer. Column: styrene–divinyl benzene gel. Eluent: 2,2,4-trimethylpentane.

The monomer fraction was separated by HPLC into three fractions (fractions 1-1 to 1-3). These fractions were identified by ^{13}C NMR spectroscopy to be the isomers consisting of 1,2, trans-1,4, and cis-1,4 units, which are abbreviated to V, T, and C, in the eluting order. The dimer fraction obtained by GPC was separated into three groups, which were identified by ^{1}H and ^{13}C NMR measurement to be isomers containing two 1,2 units, one 1,2 and one 1,4 units, and two 1,4 units in the eluting order. The three groups were further separated into fractions 2-1 and 2-2, 2-3 and 2-4, and 2-5, 2-6, and 2-7 (Figure 1).

The signals of carbon atoms in these isomers were assigned by using selective decoupling measurements and the Lindeman–Adams equation.[18] The chemical shifts of α, β, and γ carbons of the double bond or the vinyl group in the monomer are listed in the fourth column of Table I. The contribution (shift factor) of the double bond or the vinyl group can be obtained as the chemical shift difference of the carbon between these compounds and the corresponding n-alkane. The shift factors are shown in the fifth column of Table I. Conti et al.[13] used shift factors of 1,4 units reported by Roberts et al.[19] and obtained those of 1,2 units by using the chemical shifts of carbons in 1,2-polybutadiene (the last column of Table I). Their shift factors are very similar to ours.

The expected chemical shifts of carbon atoms in all ten isomers of the butadiene dimer can be calculated by using the shift factors determined for the monomers. By comparison of the observed and expected chemical shifts of the carbon atoms in the isomer and by taking the number of 1,2 units into account, each isomer was identified and the signals were assigned. The difference between the expected and observed chemical shifts is less than 0.8 ppm for all the carbons, indicating the validity of the identification of isomer and the signal assignment.

Fractions 2-1 and 2-2 were found to be the two diastereomers of 1,2–1,2 isomers. Although the two diastereomers showed only one peak after 17 recyclings, it is revealed by ^{13}C NMR spectroscopy that their ratios are 7:3 for fraction 2-1 and 3:7 for fraction 2-2. It is expected that the meso and racemic isomers can be distinguished by the splitting pattern of the central methylene proton —CH(CH=CH$_2$)C*H*$_2$CH(CH=CH$_2$)—; the two central methylene protons in the racemic isomer are equivalent and will show A$_2$-type signals, while those in the meso isomer are unequivalent and will exhibit AB-type splitting. However, both isomers showed almost the same methylene signal. Therefore, these isomers were assigned by the elution volume considering the elution order of diastereomers in styrene oligomers,[20] i.e., the fraction eluted earlier is assigned to the racemic isomer (Vr) and the later eluting fraction to the meso isomer (Vm). The β carbon of the meso isomer showed a signal at higher magnetic field than that of the racemic isomer by 1.5 ppm. In the case of the styrene dimer the β carbon of meso isomer resonated 2.0 ppm higher than that of the racemic isomer. The chemical shift difference of the other carbons between meso and racemic isomers was less than 0.5 ppm. The chemical shift difference of the diastereomer cannot be predicted by using only the information from monomeric units.

Fraction 2-3 is presumed to contain two isomers consisting of one trans-1,4 and one 1,2 unit, i.e., VT and TV, having almost the same elution volume. Because the amount of one isomer was about 5 times that of the other isomer, the ^{13}C NMR signals of these isomers could be unequivocally distinguished by their signal intensities. The major isomer exhibited a signal at 38.26 ppm, which is characteristic of the α methylene carbon atom of the trans unit connected to the methine carbon of vinyl unit. Therefore, the major isomer was identified as the VT isomer and the minor as the TV isomer.

Fraction 2-4 is presumed to contain two isomers consisting of one cis-1,4 and one 1,2 unit, i.e., VC and CV, having the same elution volume. The ratio of the two isomers in this fraction was estimated to be 5/1 by the intensity ratio of corresponding ^{13}C NMR signals. The minor isomer exhibited a signal at 24.91 ppm, characteristic of the α methylene carbon of the cis unit linked to the methylene carbon of a vinyl unit. Therefore, the minor isomer was identified as the CV isomer and the major as the VC isomer. It is interesting that the amount of 1,2–1,4 isomer is much larger than that of 1,4–1,2 isomer in the dimer, while the amount of 1,2–1,4 linkage is same as that of 1,4–1,2 linkage in polybutadiene.

Fractions 2-5 to 2-7 of the dimer are found to be composed of four isomers having two 1,4-units, i.e., TT, TC, CT, and CC. The two methylene carbons between the two double bonds showed signals around 27.4 and 32.8 ppm; the former was assigned to one linked to the cis double bond and the latter to the trans double bond. These chemical shifts were little affected by the more remote double bonds, showing that the chemical shift of the methylene carbon signal is dependent only on the monad sequence of cis and trans units. In the case of cyclic oligomers, Mochel found a chemical shift difference between cis–cis and cis–trans methylene carbons and also between trans–trans and trans–cis methylene carbons. This chemical shift difference is confirmed to arise from the ring strain for the cyclic oligomers. The presence of ring strain of the cyclic oligomers smaller than hexamer was also reported by us.[22]

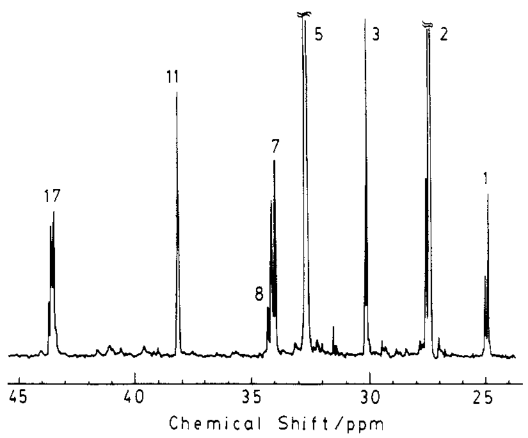


Figure 2. ^{13}C NMR spectra of polybutadiene prepared with butyllithium catalyst.

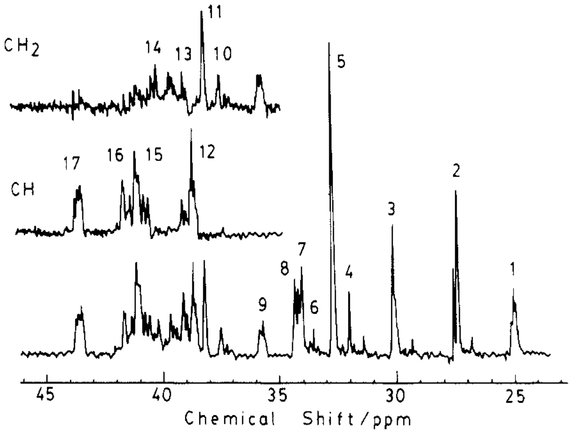


Figure 3. ^{13}C NMR spectra of polybutadiene prepared with butyllithium/ethyl ether catalyst.

The shift factor of the carbon atoms in the dimer was calculated as the chemical shift difference between the carbon in the dimer and one in the *n*-alkane. These values are listed in the fifth column of Table II. The eluting order of the dimer is consistent with that of the monomer; i.e., the isomer with 1,2 unit eluted earlier than the isomer with trans unit, which eluted earlier than the isomer with cis unit.

Polybutadiene. It has been reported that no measurable concentration of head-to-head and tail-to-tail linkages is present in polybutadiene prepared with alkyllithium catalyst by the ^{13}C NMR analysis of hydrogenated polybutadiene.[11] Therefore, only head-to-tail linkages are considered in this study. The chemical shift of aliphatic carbon atoms in polybutadiene can be calculated by adding the shift factors shown in Tables I and II to the chemical shift of polyethylene (29.71 ppm). The results are listed in Table III.

Figures 2, 3, and 4 show the ^{13}C NMR spectra of polybutadiene prepared with *n*-butyllithium (A), *n*-butyllithium/diethyl ether (B), and cobalt catalysts (C). Polymer A contained only 10% of vinyl unit and showed relatively simple spectrum because of the negligible amount of polyads of vinyl unit. Polymer B comprising

Table II
Structure and Chemical Shift of the Butadiene Dimer

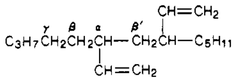
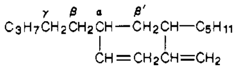
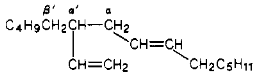
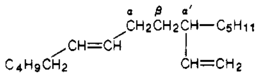
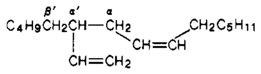
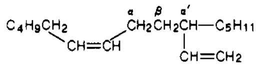
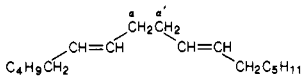
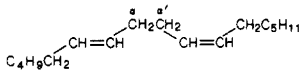
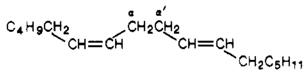
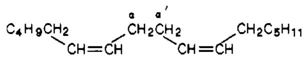
isomers				chem shift, ppm		
symbol	structure	fraction		calcd	obsd	shift factor, ppm
Vr		2-1	α	41.73	41.56	11.85
			β	35.17	35.82	6.12
			γ	26.95	26.77	−2.59
			β'	40.65	40.48	10.77
Vm		2-2	α	41.73	41.08	11.37
			β	35.17	34.31	4.61
			γ	36.95	26.61	−2.75
			β'	40.68	40.48	10.77
VT		2-3	α	38.16	38.26	8.55
			α'	44.24	44.17	14.46
			β'	34.77	34.09	4.39
TV		2-3	α	30.26	30.22	0.51
			β	35.26	34.97	5.26
			α'	43.76	43.55	13.84
VC		2-4	α	32.72	32.67	2.96
			α'	44.35	44.17	14.46
			β'	35.06	34.29	4.59
CV		2-4	α	24.86	24.91	−4.80
			β	35.37	35.08	5.37
			α'	34.91	43.70	13.99
TT		2-5	α	32.77	32.75	3.04
			α'	32.77	32.75	3.04
TC		2-6	α	32.88	32.75	3.04
			α'	27.44	27.44	−2.27
CT		2-6	α	27.37	27.44	−2.27
			α'	32.88	32.75	3.04
CC		2-7	α	27.44	27.44	−2.27
			α'	27.44	27.44	−2.27

Table III
Signal Assignment of Polybutadiene

			chemical shift, ppm		
sequence	carbon[a]	signal	calcd	obsd	Bywater[15]
C-v	4	1	24.52–24.91	24.98–25.10	24.9
C-1,4	4	2	27.44	27.42–27.57	27.35
1,4-C	1		27.44		
T-v	4	3	29.96–30.22	30.16	30.1
v-v-C(m)	1	4	31.88	31.60–32.13	32.1
1,4-v-C	1	5	32.67	32.72	32.65
T-1,4	4		32.75		
1,4-T	1		32.75		
v-v-C(r)	1	6	33.39	33.35–33.53	33.35
1,4-V-1,4	1	7	34.97–35.08	33.99–34.16	34.15
1,4-V-v(m)	1	8	34.37–34.49	34.31	34.40
1,4-V-v(r)	1	9	35.88–36.00	35.63–36.00	35.75
v-v-T(m)	1	10	37.32	37.24–37.48	37.4
1,4-v-T	1	11	38.26	38.18	38.1
v-V-v	2	12	38.68–39.16	38.57–39.13	38.6
v-v-T(r)	1	13	38.82	38.96–39.13	
v-V	1	14	39.82–41.33	39.43–41.72	38.9, 40.2, 41.8[b]
1,4-V-v	2	15	40.67–41.44	40.55–41.00	40.7
v-V-1,4	2	16	41.13–41.73	41.00–41.66	41.4
1,4-V-1,4	2	17	43.60–44.05	43.47–43.70	43.5

[a] Carbon: 1,4 unit, $-C(1)H_2C(2)H{=}C(3)HC(4)H_2-$; 1,2 unit, $-C(1)H_2C(2)H(C(3)H{=}C(4)H_2)-$. [b] Signals split due to the triad tacticity of the vinyl groups.

of 40% of vinyl unit showed complex spectrum due to the signal of vinyl polyads, which are split by the sequence length and also by the tacticity of vinyl groups. In the range 38–44 ppm, methine and methylene carbon signals overlap each other. Methine carbon signals were separately measured by the spin-echo technique (distortionless enhancement of polarization transfer: DEPT), which is shown in Figure 3. Methylene signals were obtained by subtracting the methine signal from completely decoupled spectra such that the signal around 43.5 ppm completely disappeared, because signals around this region can be assigned only to methine carbons (Figure 3c). Polymer C consisting of 84% of vinyl unit showed a simpler spectrum than polymer B, because polymer C contained a negligible amount of trans-1,4 units and the vinyl units were arranged mainly in the racemic configuration.

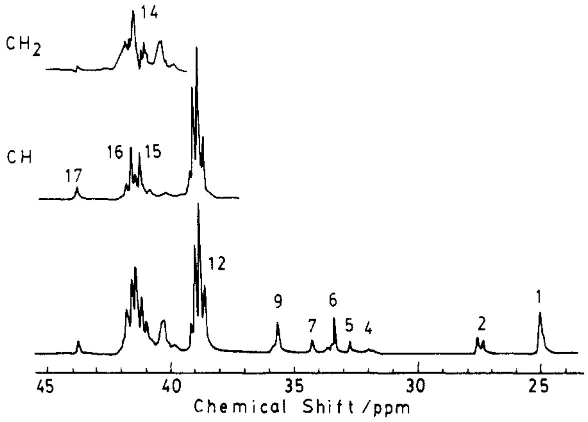


Figure 4. ^{13}C NMR spectra of syndiotactic 1,2-polybutadiene.

Table IV
^{13}C Spin-Lattice Relaxation Time (T_1) and Nuclear Overhauser Enhancement (NOE) for Polybutadiene

signal	T_1, s	NOE	signal	T_1, s	NOE
1	0.60	3.00	10	0.48	2.80
2	0.98	2.82	11	0.48	2.8
3	0.55	2.84	12	0.5	3.0
4	0.69	2.76	13	0.6	2.9
5	0.69	2.82	14	0.6	2.7
6	0.48	2.87	15	0.7	2.8
7	0.50	2.72	16	0.6	2.8
8	0.51	3.00	17	1.0	2.82
9	0.41	2.8			

These signals were assigned as shown in Table III by comparison of calculated and observed chemical shifts, considering the relative intensity and the amount of isomeric units, and also from the results of DEPT measurements.

This signal assignment is the same as that reported by Bywater,[15] except for signals 13 and 14. Signal 13 is assigned to the methylene carbon in a trans-1,4 unit next to the 1,2–1,2 (racemic) sequence, which was not assigned by Bywater. Signal 14 is the methylene carbon in a 1,2 unit flanked by two methine carbons (–$CHCH_2CH$–). This signal is presumed to be split by the tacticity of 1,2 units and to be shifted according to the sequence length of 1,2 units. Polymer C (syndiotactic 1,2-polybutadiene) also exhibited a complicated splitting. Bywater interpreted the splitting of this signal in terms of the triad tacticity of 1,2 units, which is obviously incorrect because the methylene carbon is split by the tacticity of an even number of 1,2 units. The detailed assignment of the splitting is not determined in this experiment.

The terminal methylene carbons in two or more successive 1,2 units linked to a 1,4 unit showed signals reflecting the geometric isomerism of the 1,4 unit as well as splittings due to the diad tacticity of the 1,2 units, i.e., signals 4 and 6 are assigned to 1,2–1,2-cis, signals 10 and 13 for 1,2–1,2-trans, and signals 8 and 9 for 1,4–(cis or trans)-1,2–1,2. These three pairs of the signals are separated by ca. 1.5 ppm, as expected from the dimer model. In the syndiotactic polymer signals 6 and 9, which were assigned to the racemic diad, are much larger than signals 4 and 8, indicating the validity of the identification of the two 1,2–1,2 dimers by the elution order.

The relative peak intensity is dependent on the spin–spin relaxation time (T_1) and nuclear Overhauser effect (NOE). The T_1 and NOE values of each signals were measured by using polymer B (Table IV). The T_1 values are less than 1 s. The intensity difference between the signals measured with the pulse repetition time of 6 and 3 s was less than 5%. Therefore, it can safely be said that the pulse repetition time of 3 s for the pulse width of 45° is long enough for the spin to recover the equilibrium. The NOE's are almost equal for all the signals; 2.7–3.0. These results indicate that quantitative discussion is valid for the completely decoupled spectra recorded under these conditions.

The diad sequence distribution of cis-1,4, trans-1,4, and 1,2 units can be calculated from methylene carbon signals using following equations.

$$\text{cis-1,2} = I_1/TI \tag{1}$$

$$\text{trans-1,2} = I_3/TI \tag{2}$$

$$\text{1,2-cis} = (\text{cis-1,2} + \text{trans-1,2}) - \text{1,2-trans} \tag{3}$$

$$\text{1,2-trans} = (I_{10} + I_{11} + I_{13})/TI \tag{4}$$

$$\text{cis-1,4} = {}^1\!/_2 I_2/TI \tag{5}$$

$$\text{trans-1,4} = {}^1\!/_2[(I_5 + I_4 + I_6)/TI - \text{1,2-cis}] \tag{6}$$

$$\text{1,2–1,2} = I_{14} \tag{7}$$

$$TI = {}^3\!/_2(I_1 + I_3) + {}^1\!/_2(I_2 + I_4 + I_5 + I_6 + I_{10} + I_{11} + I_{13}) + I_{14} \tag{8}$$

where, I_n indicates the intensity of signal n. In the spectra signals 13 and 14 overlapped badly, therefore, signal 13 was separated by drawing a straight baseline between the bottoms around 38.9 and 39.2 ppm. Table V shows the observed sequence distribution for polymers prepared with butyllithium, butyllithium/ether, cobalt, and radical initiators. The observed values coincided well with the calculated values assuming a random distribution of the three units. The random distribution of these units in polybutadienes prepared with alkyllithium and cobalt catalysts is also reported by Suman et al.[14] and Makino et al.,[21] respectively.

Table V
Sequence Distribution of Polybutadienes

	polymer A		polymer B		polymer C		polymer D	
sequence	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
cis-12	4.9	5.2	10.4	10.1	11.9	12.3	4.4	4.5
1,2-cis	4.5	5.2	10.1	10.0	11.7	12.3	5.1	4.5
trans-1,2	8.5	7.1	13.7	14.5	0.0	0.0	12.1	10.9
1,2-trans	8.9	7.1	13.8	14.5	0.0	0.0	11.4	10.9
cis-1,4	31.3	30.9	7.8	7.6	2.5	2.7	18.9	19.2
trans-1,4	40.9	42.4	11.7	11.0	0.0	0.0	45.6	46.4
1,2–1,2	1.1	2.1	32.3	32.3	74.2	73.3	2.5	3.6
cis	36.1		17.7		14.4		23.7	
trans	49.6		25.5		0.0		57.3	
1,2	14.3		56.8		85.6		19.0	
1,2 (by ^{1}H)	14.9		53.2		83.3		19.6	
catalyst	BuLi		BuLi/Et_2O		$CoBr_2 \cdot [P(Ph)_3]_2Al(i\text{-}Bu)_3 \cdot H_2O$		AIBN	

The characteristic signal of head-to-head 1,2 units is expected to resonate around 49 ppm and those of tail-to-tail units around 32 and 44 ppm.

$$\text{—C—C(C=C)—}\overset{1}{\text{C}}\text{(C=C)—C-1,4}$$

1, 49.31 ppm (calcd)

$$\text{—C(C=C)—C—}\overset{1}{\text{C}}\text{—}\overset{2}{\text{C}}\text{(C=C)-1,4}$$

1, 32.36 ppm (calcd); 2, 43.85 ppm (calcd)

In the spectra of polybutadiene examined no signal is observed around 49 ppm. Near 32 and 44 ppm, there are large signals 5 and 15, so that it is difficult to examine the presence of tail-to-tail linkages. However, the signal intensities of these signals are not very different from the expected values. Therefore, it can be concluded that the amount of head-to-head and tail-to-tail linkages is negligible.

The amount of 1,2 units determined by ^{13}C NMR agrees well with that determined by ^{1}H NMR measurement. The sum of intensities of signals 1 and 3 represents the fraction of *1,4*–1,2 sequence, while that of signals 7, 8, and 9 represents the fraction of 1,4–*1,2* sequence. The difference of the two values was less than 5% for the four polymers. The agreement of signal intensities is additional evidence for the validity of the signal assignment.

The triad sequence distribution of 1,2 unit can be obtained by the intensity ratios of methine signals of 17, 16 + 15, and 12, which were observed by DEPT measurement. The intensity ratios indicate that the 1,2 and 1,4 units are randomly distributed in all the polymers examined, which is in agreement with the findings obtained from methylene signals. This coincidence indicates that the methine signals of polybutadiene recorded by DEPT measurement can be used for quantitative analysis.

Acknowledgment. This work is supported by a grant from the Ministry of Education, Science and Culture, Japan; Grant 61550670 addressed to H.S.

Registry No. V, 109801-07-2; T, 6434-76-0; C, 6508-77-6; Vm, 109801-08-3; VT, 109801-09-4; TV, 109801-10-7; TT, 109801-11-8; AIBN, 78-67-1; BuLi, 109-72-8; Et_2O, 60-29-7; $CoBr_2\cdot(P(Ph_3))_2$, 14126-32-0; $Al(Bu\text{-}i)_3$, 100-99-2; polybutadiene, 9003-17-2.

References and Notes

(1) Santee, E. R., Jr.; Mochel, V. D.; Morton, M. *J. Polym. Sci., Polym. Lett. Ed.* **1973**, *11*, 453.
(2) Hatada, K.; Terawaki, Y.; Okuda, H.; Tanaka, Y.; Sato, H. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 305.
(3) Julemont, M.; Walckiers, E.; Warin, R.; Teyssie, Ph. *Makromol. Chem.* **1974**, *175*, 1673.
(4) Tanaka, Y.; Sato, H.; Hatada, K.; Terawaki, Y.; Okuda, H. *Makromol. Chem.* **1977**, *178*, 1823.
(5) Elgert, K.-F.; Stützel, B.; Frenzel, P.; Cantow, H. J.; Streck, R. *Makromol. Chem.* **1973**, *170*, 257.
(6) Conti, F.; Segre, A.; Pini, P.; Porri, L. *Polymer* **1974**, *15*, 5.
(7) Tanaka, Y.; Sato, H.; Ogawa, M.; Hatada, K.; Terawaki, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1974**, *12*, 369.
(8) Duch, M. W.; Grant, D. M. *Macromolecules* **1970**, *3*, 165.
(9) Mochel, V. D. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 1009.
(10) Araki, Y.; Yoshimoto, T.; Imanari, M.; Takeuchi, M. *Kobunshi Kagaku* **1972**, *29*, 397; *Rubber Chem. Technol.* **1973**, *46*, 350.
(11) Clague, A. D. H.; van Broekhoven, J. A. M.; Blaauw, L. P. *Macromolecules* **1974**, *7*, 348.
(12) Furukawa, J.; Kobayashi, E.; Katsuki, N.; Kawagoe, T. *Makromol. Chem.* **1974**, *175*, 237.
(13) Conti, F.; Delfini, M.; Segre, A. L.; Pini, P.; Porri, L. *Polymer* **1974**, *15*, 816.
(14) Suman, P. T., Werstler, D. D. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1963.
(15) Bywater, S. *Polymer Commun.* **1983**, *24*, 203.
(16) Ashitaka, H.; Jinda, K.; Ueno, H. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1973.
(17) Grant, D. M.; Paul E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
(18) Lindeman, L. P.; Adams, J. C. *Anal. Chem.* **1971**, *46*, 1245.
(19) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2557.
(20) Sato, H.; Tanaka, Y. *ACS Symposium Ser. No. 247*, NMR and Macromolecules, 1984, 181.
(21) Makino, K.; Ikeyama, M.; Takeuchi, Y.; Tanaka, Y. *Polymer*, **1982**, *23*, 287.
(22) Sato, H.; Tanaka, Y.; Taketomi, T. *Makromol. Chem.*, **1977**, *178*, 1993.