

CARBON-13 NMR STUDY OF MOLECULAR MOTION OF 1,2-POLYBUTADIENES IN SOLUTION

I. STRUCTURE DEPENDENCE OF MOLECULAR MOTIOM

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ABSTRACT

Proton decoupled, partially relaxed, Fourier-transform 50.3 MHz carbon-13 NMR in natural abundance was used to determine spin-lattice times (T_1) and nuclear Overhauser enhancement factors (NOE) of individual carbon of a series of 1,2-polybutadienes with different structures in solution in CDCl_3 . The structure dependence of molecular motion and the internal motion of vinyl group in 1,2-polybutadiene have been studied by nT_1 and NOE values. The nT_1 values of the carbons in *cis*-1,4-units are the highest and those of the carbons in 1,2-units are the lowest in three types of units in 1,2-polybutadiene. The nT_1 values of carbons in the same unit become greater when the adjacent 1,2-units are replaced by 1,4-units, and nT_1 values of the carbons in all units decrease sharply with the increase of content of 1,2-units in the polymers.

The fact that nT_1 values of $-\text{CH}=\text{}$ are larger than those of $=\text{CH}_2$ in vinyl group implies that there are complex internal motions of vinyl group. It is shown by calculation that the dominant factor causing the difference in nT_1 of $-\text{CH}=\text{}$ and $=\text{CH}_2$ in vinyl group is a swing of vinyl group in a plane perpendicular to the chain backbone.

In recent years carbon-13 NMR relaxation parameters such as spin-lattice (T_1) and spin-spin (T_2) relaxation times and nuclear Overhauser enhancement factor (NOE) have been used as a sensitive probe of molecular motion of polymers^[1-3]. The carbon-13 relaxation parameters for each carbon in polymers can be determined with Fourier transform (FT) NMR of carbon-13 and, therefore, the microscopic dynamics of polymer chain can be studied by FT-NMR method.

In this paper we present the results of carbon-13 spin-lattice relaxation time and nuclear Overhauser enhancement factor measurements of various carbons in a series of 1, 2-polybutadienes with different structures in solution in CDCl_3 determined by proton decoupled, partially relaxed, FT 50.3MHz carbon-13 NMR. The microscopic dynamics of chain of 1, 2-polybutadienes has been investigated.

EXPERIMENTAL

Materials

1,2-Polybutadiene samples were prepared in our laboratory. S-1 sample was prepared

at 50°C in hexane with $\text{MoCl}_4\text{OC}_8\text{H}_{17}-i\text{-Bu}_2\text{AlOC}_8\text{H}_5$ as a catalyst and other samples were prepared at 50°C in toluene-hexane (1:1) with $n\text{-BuLi}$ as a catalyst. The microstructure was regulated with tetrahydrofuran. The structure parameters of the samples are given in Table 1. The samples were further purified. The solvent is CDCl_3 and the polymer concentration is about 10%. All samples were degassed.

Table 1 Structural parameters of the samples

No.	Microstructure (%)						[η] (dl/g)
	C		T		V		
	IR	NMR	IR	NMR	IR	NMR	
L-3	41	45	52	51	7	4	3.06
V-38	28	33	51	50	21	17	3.22
V-61	24	22	27	37	49	41	3.39
V-7	19	13	24	31	57	56	3.77
V-33	13	—	20	—	67	—	3.51
S-1	8	—	10	—	82	—	3.47

Note: C, T and V represent *cis*-1,4, *trans*-1,4 and 1,2-unit, respectively.

[η] is determined in toluene at 30°C.

Carbon-13 NMR measurements

Carbon-13 NMR measurements were performed on USA Varian XL-200 FT-NMR spectrometer. The ^{13}C operating frequency is 50.3MHz and the resolution is 0.2Hz. The apparatus is equipped with an internal ^2D lock and noise modulated proton decoupler. The 90° pulse width is about 13 μsec .

NOE measurement The nuclear Overhauser enhancement factors were estimated directly by comparing the intensities of proton-decoupled and proton-coupled resonances. The ^{13}C -NMR spectra of S-1 sample with proton-decoupled and proton-coupled are shown in Fig. 1 and the peaks in the spectra are assigned according to references [4-7].

T_1 measurement Spin-lattice relaxation times (T_1) for each carbon were determined from proton-decoupled FT spectra obtained by means of the conventional 180°- t -90° pulse sequence, where t is the time interval between 180° and 90° pulses. The intensity $M(t)$ of peaks obtained from sets of such FT spectra was used to determine T_1 according to the expression

$$M(t) = M_0 [1 - 2 \exp(-t/T_1)] \quad (1)$$

where M_0 is the equilibrium intensity of the spectrum. The assumption of exponential decay in equation (1) was justified by the good linearity in the plots of $\log(M_0 - M(t))$ vs. t . The T_1 was calculated for more eight time intervals (t) by the least-squares method^[8]. Fig. 2 are the ^{13}C -NMR spectra of V-61 sample with eight time intervals (t) at 30°C.

When the error is too large, T_1 is estimated according to^[8]

$$T_1 = 1.443t_0 \quad (2)$$

where t_0 is the time interval between the 180° and 90° pulse with zero value of $M(t)$.

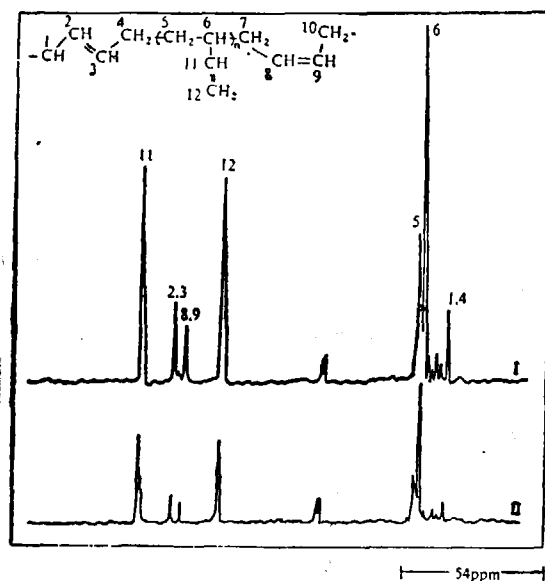


Fig. 1 ^{13}C -NMR spectra of S-1 sample
I Proton-decoupled; II Proton-coupled.

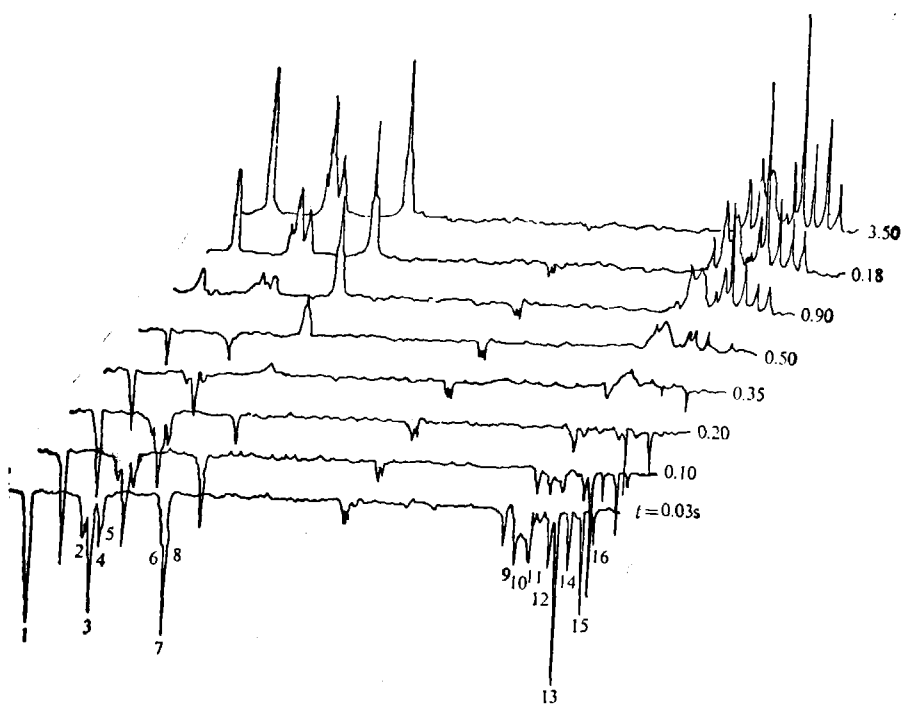


Fig. 2 ^{13}C -NMR spectra of V-61 sample with eight time intervals at 30°C
Each spectrum is the result of 60 accumulations of time-domain signals with a recycle of pulse sequence of 7 sec.

RESULTS AND DISCUSSION

1. ^{13}C -NMR spin relaxation mechanism of 1,2-polybutadiene

It is necessary to identify the spin relaxation mechanism in order to analyze the molecular motion of a polymer using NMR relaxation parameters. In analyzing carbon-13 spin relaxation, one must consider at least three possible relaxation mechanisms^[9], namely, chemical shift anisotropy, spin-rotation and ^{13}C - ^1H dipole-dipole interactions. The interaction of chemical shift anisotropy is usually negligible in carbon-13 relaxation even with non-protonated carbons and it is only at low temperature and at high magnetic field that this mechanism becomes dominant. Hence we can ignore interaction of this mechanism in our experiments. It is shown that ^{13}C - ^1H dipole-dipole interaction is dominant mechanism in macromolecules^[10]. The spin-rotation mechanism is effective only for the polymers with side group.

Carbon-13 spin relaxation mechanisms can be judged by NOE values. If the ^{13}C - ^1H dipole-dipole interaction is predominant and the extreme-narrowing condition (namely, $\omega\tau_c \ll 1$, where ω is Larmor frequency and τ_c is the correlation time) is fulfilled, the NOE has a maximum value of 2.988^[10, 11]. The NOE values of various samples are given in Table 2

Table 2 NOE values of various carbons in the samples at 30°C

1,2-unit (%)	7	21	49	57	67	82
—CH ₂ —(VCV)	2.28	3.16	3.19	3.19	—	—
—CH ₂ —(CCC)	2.82	2.80	3.08	3.75	—	—
—CH ₂ —(VTV)	2.81	2.64	2.97	2.92	—	2.53
—CH ₂ —(TTT)	2.79	2.72	2.95	3.23	—	—
—CH ₂ —(CVC)	2.94	3.08	2.75	2.95	—	—
—CH ₂ —(VVV)	—	—	2.64	3.05	3.19	2.66
—CH—(VVV)	—	—	3.00	2.90	2.99	2.59
—CH—(CVC)	3.28	2.63	2.65	—	—	—
mm	—	—	2.79	3.05	2.72	2.73
=CH ₂ (CVC, VVV) mr	2.44	2.92	2.97	2.93	2.52	2.61
rr	—	—	3.01	2.65	2.74	2.31
=CH—(CVC, VVV)	2.92	2.88	2.68	2.94	2.52	2.69
=CH—(VCV)	—	—	2.73	2.61	3.19	2.77
=CH—(CCC)	2.90	2.79	2.82	2.72	—	—
=CH—(TTT)	2.68	2.64	2.91	3.01	—	—

Three letters in bracket represent the sequence structure belonging to the considered carbon which the center letter indicates the unit that the carbon is in.

Error: 10%.

and it is seen that the NOE values for most carbons in the samples except V-33 and S-1 samples are close to the theoretical maximum value of 2.988 within experimental error. This suggests that the major relaxation mechanism is the dipole-dipole interaction. The NOE values for most carbons in V-33 and S-1 samples are smaller than 2.988 and it may be attributed to their high content of 1,2-units because the vinyl group in 1,2-unit has a high steric hindrance for the segmental motion so that the extreme-narrowing condition is not fulfilled.

2. Analysis of molecular motion

If the ^{13}C - ^1H dipole-dipole interaction is predominant and the segmental motion is isotropic, the reorientation motion of main-chain in polymers can be described by a single correlation time model^[10], and then the T_1 is given by

$$\frac{1}{T_1} = \frac{h^2}{40\pi^2} \gamma_c^2 \gamma_H^2 \sum_i r_i^{-6} [f(\omega_H - \omega_c) + 3f(\omega_c) + 6f(\omega_H + \omega_c)] \quad (3)$$

where

$$f(\omega) = \tau_c / (1 + \omega^2 \tau_c^2) \quad (4)$$

where γ_c and γ_H are gyromagnetic ratios for ^{13}C and ^1H , ω_c and ω_H are the Larmor frequencies for ^{13}C and ^1H , respectively, r_i is the distance between the carbon of interest and the i th proton, and h is Planck constant. Because of the inverse sixth-power dependence on r_i , the effect of nonbonded protons on T_1 is negligible. For the high mobile systems, the extreme-narrowing condition is fulfilled

$$(\omega_H + \omega_c)^2 \tau_c^2 \ll 1 \quad (5)$$

and eq. (3) reduces to the form

$$\frac{1}{nT_1} = \frac{h^2}{40\pi^2 r^6} \gamma_c^2 \gamma_H^2 \tau_c \quad (6)$$

where n is the number of directly bonded protons. The eqs. (3) and (6) show that the larger the nT_1 , the higher the mobility in the extreme-narrowing limit.

The nT_1 values of some carbons in various samples are tabulated in Table 3. The molecular motion of 1,2-polybutadienes is deduced from these data below.

Structure dependence of the molecular motion

From Tab. 3 it is found that the nT_1 values of carbons in *cis*-1,4-units are the highest and those of the carbons in 1,2-units the lowest in three types of units in 1,2-polybutadiene and this implies that the mobility of *cis*-1,4-units is higher than that of other units and the reorientation motion of 1,2-units is highly restricted by the vinyl group. Therefore, the dependence of the molecular dynamics of 1,2-polybutadiene on the content of 1,2-units is very great. This is why the nT_1 values of various carbons in all units decrease sharply with the increase in 1,2-units in the polymers.

It is also shown that the molecular motion is related to sequence structure. For example, the nT_1 values of the carbons in the same units become larger as the adjacent 1,2-units are replaced by 1,4-units. The dependence of molecular motion of equibinary *cis*-(1,4-1,2)-polybutadiene on the sequence structure has been investigated by Gronski et al.^[12].

Internal rotation of vinyl group

The motion velocity of $-\text{CH}=\text{}$ and $=\text{CH}_2$ in vinyl group should be the same because they are linked together by a double-bond, but the experimental results show that the nT_1

Table 3 nT_1 Values of various carbons in the samples at 30°C

1,2-unit (%)	7	21	49	57	67	82
$-\text{CH}_2-(\text{VCV})$	1.22	1.22 ^Δ	1.03	0.870 ^Δ	0.800	—
$-\text{CH}_2-(\text{CCC})$	2.47	2.19	1.97	1.77	1.50	—
$-\text{CH}_2-(\text{VTV})$	1.14	1.14	0.988	0.952	0.840	0.632
$-\text{CH}_2-(\text{TTT})$	1.86	1.63	1.35	1.23	1.04 ^Δ	—
$-\text{CH}_2-(\text{CVC})$	1.48	1.35	0.926	0.806	0.748 ^Δ	0.616
$-\text{CH}_2-(\text{VVV})$	—	—	0.970	0.862	0.746	0.532
$-\text{CH}-(\text{VVV})$	—	—	0.415	0.404	0.365	0.309
$-\text{CH}-(\text{CVC})$	1.22	1.04	1.02	0.760	0.706 ^Δ	0.662
mm	—	—	0.924	0.746	0.602	0.520
$=\text{CH}_2(\text{CVC}, \text{VVV})$ mr	1.57	1.46	0.960	0.808	0.654	0.508
rr	—	—	0.828	0.640	0.620	0.442
$=\text{CH}-(\text{CVC}, \text{VVV})$	2.84	2.39	1.18	1.04	0.705	0.604
$=\text{CH}-(\text{VCV})$	1.12	1.07	1.00	0.781	0.754 ^Δ	0.673
$=\text{CH}-(\text{CCC})$	1.57	1.25	1.33	1.33	—	—
$=\text{CH}-(\text{TTT})$	2.00	1.76	1.23	1.15	0.725 ^Δ	—
$=\text{CH}-(\text{VTV})$	—	1.16 ^Δ	1.05	0.904	0.710	0.704

Δ : T_1 value is estimated according to $T_1 = 1.443 t_0$.

Error: $\approx 10\%$.

values for the former is higher than that of the latter. This is believed to be associated with the internal rotation of vinyl group. Three models of internal rotation of vinyl group are assumed based on analysis for the structure of 1,2-unit: (1) a rotation around the C_2-C_3 axle; (2) a swing in a plane perpendicular to the chain backbone; and (3) a rotation around the C_1-C_3 axle (Fig. 3). For convenience, these three models are designed as α , β and γ motion, respectively.

The nT_1 values of the carbons in a group engaging in internal rotation can be given by^[13, 14]

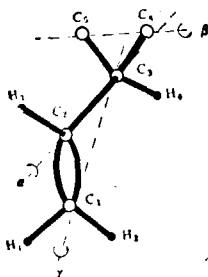


Fig. 3 Models of the internal rotation of vinyl group

$$\frac{nT_1}{n_R T_{1R}} = \frac{1}{4}(3 \cos^2 \theta - 1) + \frac{18}{5 + \rho} \sin^2 \theta \cos^2 \theta + \frac{9}{4} \frac{1}{1 + 2\rho} \sin^4 \theta \quad (7)$$

where T_1 and T_{1R} are the spin-lattice relaxation times when the relaxation is due to internal rotation and isotropic segmental reorientation of main-chain, respectively, θ is the angle between the C—H vector and the axis of rotation, and ρ

$$\rho = \frac{\tau_R}{\tau_I} \quad (8)$$

where τ_R is the correlation time of segmental reorientation of main-chain and τ_I is the effective correlation time described as the sum of two contributions as follows:

$$\frac{1}{\tau_I} = \frac{1}{\tau_R} + \frac{1}{\tau_G} \quad (9)$$

where τ_G is the correlation time of internal rotation.

The values of ρ can be evaluated from experimental data and θ can be calculated by the angle and length of various bonds in 1,2-unit. It is known that the bond angles of C—C=C and H—C—H bonds are 122° and 116° , the length of C—C, C=C and C—H bonds are $1.54\text{\AA}$, $1.33\text{\AA}$ and $1.09\text{\AA}$, respectively. From these data, it is calculated that the θ values between the C—H bond vectors of $-\text{CH}=\text{}$ and $=\text{CH}_2$ in vinyl group and the internal rotation axis are equal in α motion, 90° and 32° in β motion and 89° and 58° in γ motion, respectively. The nT_1 values of the carbons in vinyl group can be estimated by the values of ρ and θ according to eq. (7). It is clear that the α motion is not a factor causing the inequality of the nT_1 values of $-\text{CH}=\text{}$ and $=\text{CH}_2$ and, therefore, no calculation for the α motion is needed. The results calculated for the β motion are given in Table 4. From

Table 4 The calculated and observed nT_1 values for $=\text{CH}_2$ and $=\text{CH}-$ in vinyl group

1,2-unit (%)			7	21	49	57	67
$=\text{CH}_2$	20°C	cal.	1.31	1.18	0.770	0.671	0.527
		ob.	1.23	1.21	0.782	0.690	0.456
	30°C	cal.	1.70	1.45	1.06	0.800	0.677
		ob.	1.57	1.46	0.960	0.800	0.654
	40°C	cal.	1.81	1.57	1.04	0.934	0.679
		ob.	1.93	1.87	1.09	0.914	0.646
	50°C	cal.	2.00	1.63	1.35	1.18	—
		ob.	2.24	2.18	1.36	1.19	—
$=\text{CH}-$	20°C	cal.	1.58	1.86	1.02	0.884	0.306
		ob.	1.92	1.55	1.01	0.826	0.542
	30°C	cal.	2.33	2.13	0.818	0.925	—
		ob.	2.84	2.39	1.18	1.04	—
	40°C	cal.	2.79	2.96	1.36	0.985	0.646
		ob.	2.40	2.25	1.24	1.08	0.773
	50°C	cal.	3.24	3.26	2.07	1.33	—
		ob.	2.93	2.63	2.05	1.31	—

the Tab. 4 it is seen that the calculated values of nT_1 's are fairly in accord with the observed ones. The results that the nT_1 values of $-\text{CH}=\text{}$ are higher than those of $=\text{CH}_2$ in vinyl group can be also obtained by the calculation for the γ motion, but the calculated values of nT_1 are not consistent with the observed ones. This may imply that the dominant factor causing the difference in nT_1 values of $-\text{CH}=\text{}$ and $=\text{CH}_2$ in vinyl group is the β motion, namely, a swing of vinyl group in a plane perpendicular to the chain backbone.

3. Correlation time and activation energy

If the extreme-narrowing condition is fulfilled and the segmental reorientation is isotropic, the correlation time of individual carbons can be calculated by eq. (6) and those of the carbons in vinyl group must be estimated by eq. (8). The correlation times of some carbons are tabulated in Table 5.

From the temperature dependence of the correlation time we can estimate the activation energy for the motion responsible for spin-lattice relaxation by use of the relation

$$\tau_c = \tau_0 \exp(E_a/RT) \quad (10)$$

where τ_0 is the correlation time expected at infinite temperature and E_a is the activation

Table 5 Correlation time (τ_c , sec) and E_a (Kcal / mole)

1,2-unit (%)			7	21	49	57	67
$-\text{CH}_2-(\text{CCC})$	$\tau_c \cdot 10^{11}$	20°C	2.2	2.5	3.2	4.0	4.2
		30°C	1.8	2.1	2.3	2.6	3.1
		40°C	1.6	1.8	2.0	2.2	—
		50°C	1.3	1.5	1.8	2.1	2.7
	E_a		3.1	2.8	2.8	2.9	3.0
$-\text{CH}_2-(\text{TTT})$	$\tau_c \cdot 10^{11}$	20°C	3.0	3.3	4.1	4.5	5.2
		30°C	2.5	2.8	3.4	3.7	3.6
		40°C	2.1	2.3	3.1	3.1	3.1
		50°C	1.8	2.0	2.4	2.7	2.7
	E_a		3.2	3.4	3.5	3.5	—
1,2-unit (backbone)	$\tau_c \cdot 10^{11}$	20°C	4.0	4.8	6.2	7.0	7.8
		30°C	3.4	3.8	4.7	5.8	7.2
		40°C	3.0	3.2	4.3	4.7	6.6
		50°C	2.9	2.7	3.6	4.0	4.9
	E_a		2.7	3.2	3.4	3.7	3.7
Vinyl group	$\tau_c \cdot 10^{11}$	20°C	3.6	—	6.2	12	—
		30°C	2.6	2.0	5.5	8.0	—
		40°C	1.7	1.2	4.6	—	—
		50°C	1.2	1.4	2.3	—	—
	E_a		2.8	3.0	3.3	—	—

energy. The activation energy estimated from plots of $\log \tau_c$ vs. $1/T$ for some carbons are also given in Table 5.

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