Carbon-13 Nuclear Magnetic Resonance of 3,4/cis-1,4-polyisoprenes Prepared with Fe(acac)₃-Al(i-Bu)₃ Catalyst

Zu Wen Qiu[a]; Xiaohong Chen[a]; Boqin Sun[a]; Zinan Zhou[a]; Fosong Wang[a]

[a] Institute of Theoretical Chemistry Jilin University Changchun, Jilin: Wuhan Institute of Physics Academia Sinica Wuhan, Hubei; Changchun Institute of Applied Chemistry Academia Sinica Changchun, People's Republic of China

PLEASE SCROLL DOWN FOR ARTICLE

CARBON-13 NUCLEAR MAGNETIC RESONANCE OF 3,4/cis-1,4-POLYISOPRENES PREPARED WITH Fe(acac)$_3$-Al(i-Bu)$_3$ CATALYST

ZU WEN QIU,* XIAOHONG CHEN, BOQIN SUN, ZINAN ZHOU, and FOSONG WANG

Institute of Theoretical Chemistry
Jilin University
Changchun, Jilin;
Wuhan Institute of Physics
Academia Sinica
Wuhan, Hubei;
Changchun Institute of Applied Chemistry
Academia Sinica
Changchun

People's Republic of China

ABSTRACT

3,4/cis-1,4-Polyisoprenes were prepared with Fe(acac)$_3$-Al(i-Bu)$_3$ catalyst. These polymers are of interest because of their higher 3,4 content and different degree of crystallinity. The ^{13}C-NMR spectra of these polymers were much more complex than those previously reported and were assigned using slightly modified empirical parameters based on Gronski et al. In order to further clarify the assignments, hydrogenation of the polymers was carried out, and the ^{13}C-NMR spectra of the hydrogenated polymers were partially assigned. Based on these assignments, it was found that the existence of long sequences of vinyl monomer units might be a favorable factor for the formation of partially crystallized

---

*To whom correspondence should be addressed at Jilin University.

127

polymer. Finally, the ^{13}C-spin relaxation times T_1, as well as their temperature dependence, were also measured in chloroform-d_1 solvent at 50 MHz, and the Arrhenius activation energy was estimated.

INTRODUCTION

In recent years, ^{13}C NMR and ^{1}H NMR have been successfully applied to the investigation of structure and sequence distributions of polyisoprenes (PIP) [1-5]. In order to clarify the assignment and sequence distribution of polyisoprenes, they were hydrogenated and investigated by Sato and Tanaka [6], and it was found that there were large differences among the ^{13}C-NMR spectra of polyisoprenes prepared with different types of catalysts. Most polyisoprene investigations have been done on *cis*-1,4- and *trans*-1,4-polyisoprenes. ^{13}C spin-lattice relaxation parameters and nuclear Overhauser factors both in bulk and in solution were determined by Hatada et al. [7]. However, relatively few investigations have so far been directed to 3,4-polyisoprenes. Gronski et al. [8] prepared 3,4/*cis*-1,4-PIP's with Ti(O-*n*-C$_3$H$_7$)$_4$/Al(C$_2$H$_5$)$_3$ catalysts and assigned the ^{13}C-NMR spectra based on empirical parameters. Up to the present, no spin relaxation parameters for 3,4-PIP have been reported.

In this work we have prepared 3,4/*cis*-1,4-PIP's with Fe(acac)$_3$-Lewis base-Al(*i*-Bu)$_3$ catalysts. The products had high 3,4 content with different degrees of crystallinity, depending on the polymerization conditions. Hydrogenated polymers were prepared by the Sanui method [9]. The ^{13}C-NMR spectra of these polymers were much more complex than those of the samples used by previous authors, but they could still be assigned by using slightly modified chemical shift parameters. ^{13}C spin relaxation times T_1, as well as their temperature dependence, were determined successfully by the usual inversion-recovery methods. These results provided us with important information about the segmental mobility of the 3,4/*cis*-1,4-polyisoprenes.

EXPERIMENTAL

Materials

Polymerization-grade isoprene was distilled under nitrogen and kept over active aluminum oxide for more than 48 h before use. Fe(acac)$_3$ was purified by repeated recrystallization. Other chemicals were of A.R. grade and were used directly without further purification.

Polymerization

Polymerization of isoprene was conducted under purified nitrogen using $Fe(acac)_3$-Lewis base-$Al(i\text{-}Bu)_3$ catalyst, as reported by Sun and Wang [10]. Chemicals were added to the reactor in the following order: benzene, isoprene, $Fe(acac)_3$, Lewis base, and $Al(i\text{-}Bu)_3$. This order should not be changed; otherwise the polymerization will not take place or the yield will be very low. Several Lewis bases were tried, and it was found that only o-phenanthroline or α,α'-dipyridyl gave good results. Typical polymerization conditions were as follows: $Fe(acac)_3$, 455 mmol/L; Lewis base, 455 mmol/L; $Al(i\text{-}Bu)_3$, 500 mmol/L. The molar ratio of $Al(i\text{-}Bu)_3$ to $Fe(acac)_3$ was varied within the range of 20 to 50. The polymerization was carried out at 10°C for a given time and was stopped by adding ethanol with 2,6-di-t-butyl-4-toluene as inhibitor. The products were purified by successive reprecipitation and were dried under vacuum at 40-50°C.

Hydrogenation

Polyisoprenes were hydrogenated twice according to the method of Sanui et al. The residual unsaturation, estimated by the ^{1}H and ^{13}C NMR olefinic resonances, was less than 3% of the double bond content.

Measurements

The degree of crystallization was determined with a Japan Rigaku 2080 large-angle diffractometer. The ^{1}H-NMR spectra were recorded with a Varian EM-390 CW NMR spectrometer. These spectra were fundamentally consistent with those obtained by previous authors, with only some minor differences, which are not yet understood. From the ^{1}H- and ^{13}C-NMR spectra, the content of 3,4 monomer units in the polymer could be estimated. ^{13}C-NMR spectra were obtained at 25 or 50 MHz using a JEOL MS 100 or Varian XL 200 NMR spectrometer. Measurements were made with 10 mm o.d. sample tubes using chloroform-d_1 as solvent. Chemical shifts were referred to tetramethylsilane added as an internal standard. The concentration of the solutions was about 18-20 wt/vol. [13]C T_1 was measured by the inversion-recovery Fourier transform method. The repetition time of (180-t-90) pulse sequence was 20 or 30 s since the longest T_1 was estimated to be 5 s. The free induction decays following 90 pulses were accumulated 80 times. [13]C-$\{^1H\}$ nuclear Overhauser enhancement was also determined by the gated decoupling method, but the results might not be very reliable due to the complexity of the spectra.

RESULTS AND DISCUSSION

Assignment of the ^{13}C-NMR Spectra

The ^{13}C-NMR spectra of these samples were much more complex than those previously reported. The ^{13}C-NMR spectra of these partially crystalline 3,4/cis-1,4-polyisoprenes were first assigned by Xie and Sun [11]. We have made a minor modification for the methylene and methine part of the spectrums. In Table 1 the empirical parameters for calculating the chemical shifts of various sequence structures are listed, while the final results are listed in Table 2. The methyl and olefinic parts of the spectra were assigned according to the results of Xie and Sun. The equation for calculating chemical shift was originally suggested by Paul and Grant [12]. Explanations for these parameters were given by Gronski et al., except for $C(\gamma_2)$ which represents the small contribution of *cis* double bond to the secondary carbon atom at the γ-position. The carbons of 3,4 units and *cis*-1,4 units are designated V_i and C_i, respectively, where $i = 1, 2, 3, 4, 5$. The carbon atoms were numbered according to Scheme 1 because small amounts of head-to-head or tail-to-tail structure actually existed, as pointed out first by Sato and Tanaka for their hydrogenated polymers (see Table 3 and Figs. 1A, 1B, 2, and 3).

TABLE 1. Empirical Chemical Shift Parameters (ppm) for the Calculation of Chemical Shifts in 3,4/cis-1,4-Polyisoprenes[a]

Values for linear alkanes	This work	Gronski [8]
$\alpha = 9.1$	$C_1(\alpha) = -7.20$	$C_1(\alpha) = -7.5$
$\beta = 9.4$	$C_4(\alpha) = 0.95$	$C_4(\alpha) = 1.0$
$\gamma = -2.5$	$3*(2°) = -6.17$	$3*(2°) = -6.2$
$\delta = 0.3$	$2°(3*) = -0.85$	$2°(3*) = -1.1$
$\epsilon = 0.1$	$C(\gamma_2)^{b} = -0.5$	

[a]Explanation for symbols of these parameters are given by Gronski et al. [8].

[b]The contribution of the *cis*-double bond to the secondary carbon atom at this position.

TABLE 2. Assignment of ^{13}C-NMR Spectra of 3,4/*cis*-1,4-Polyisoprenes

Signal	Assignments	Chemical shifts		Relative intensity[a]
		Calc	Obs	
1	VV_5V		17.75	155
2	CV_5V		18.69	102
3	CC_5V		23.46	155
4	CC_5C		23.68	55
5	C_4C	26.15	26.15	35
6	C_4VC	26.75	26.55	19
7	C_4C	28.95	28.19	9
8	CVC_1C	30.50	30.11	78
9	$VVC_1/CCVC_1V$	30.60	30.50	21
10	VVC_1V	30.70	30.73	26
11	CV_4C	30.85	31.15	34
12	VV_4C	31.75	31.99	35
13	C_4VC	32.30	32.13	39
14	CV_4VC	32.40	32.46	49
15	CC_1C/C_4VV	32.70	32.70	80
16	CC_1V	32.80	32.94	26
17	CV_4VC	33.20	33.17	16
18	VV_4C	34.55	34.41	26
19	VV_4VC/VV_4VV	35.50	35.67	26
20	VV_4VV	35.90	35.98	23
21	CV_4VC	37.00	36.49	50
22	CV_4VV	37.40	36.68	45
23	VV_4VC	37.90	37.32	65

TABLE 2 (continued)

Signal	Assignments	Chemical shifts		Relative intensity[a]
		Calc	Obs	
24	VV_4VV	38.30	38.30	88
25	b		38.93	10
26	b		39.79	13
27	CVV_3VC	41.96	41.85	72
28	VVV_3VV	42.16	42.17	200
29	CVV_3C	43.86	42.73	35
30	CVV_3C	44.16	44.54	38
31	CV_3VV	45.03	45.03	131
32	CVV_3VC	45.81	45.81	15
33	CV_3C	47.46	47.56	12
34	CV_3C	47.85	47.85	18

[a]Based on the height of Peak 28 as 200.

[b]Assigned to long-range VVV_4V with head-to-head and/or tail-to-tail linkage.
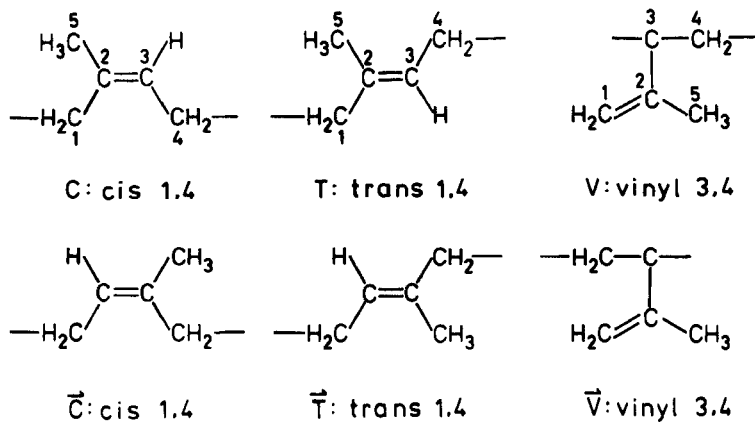
SCHEME 1.

TABLE 3. Assignment of ^{13}C-NMR Spectra of Hydrogenated 3,4/*cis*-1,4-Polyisoprenes

Signal	Chemical shifts			Assignments
	Calc[a]	Obs	Ref	
P	19.63	18.86	18.61	$VV_{1,5}V/CV_{1,5}V$
O	19.63	19.31	19.34	$CV_{1,5}C$
N	19.63	19.88	19.83	$VC_{1,5}C/VC_{1,5}V/CC_{1,5}C$
M	24.58	24.51	24.51	CC_4C/VC_4C
L'	25.08	25.09	25.00	C_4V
L''	27.52	26.26	27.42	C_4C
L	29.09	27.82	27.84	VV_4C
	28.84	28.46	28.46	C_4VC/CV_4C
K	29.09	28.99	29.32	C_4VV
J	30.46	30.41	30.58	CV_2C
J'	30.46	31.04		CV_2V/VV_2C
I	33.60	31.62	31.96	VV_4V/CV_4V
H	32.52	32.75	32.84	CC_2C
G	32.52	33.18	33.25	CC_2V/VC_2C
F	32.52	33.62	33.64	VC_2V
E'	34.22	34.40	34.31	C_1C
E	34.72	35.09	35.09	$CC_3V/VVC_1/VC_3V$
E''	34.97	35.91		VVC_1
D	37.16	37.52	37.47	$CC_1C/CC_3C/VC_3C$
C	39.52	38.59	38.13	VV_3V
B'	41.59	41.03		VV_3V
B	41.59	41.42	41.43	CV_3V/VV_3C
B''	41.99	42.55		VV_3V
A	43.66	44.35	44.39	CV_3V

[a]These values are calculated according to Linderman and Adams' empirical equation [15].
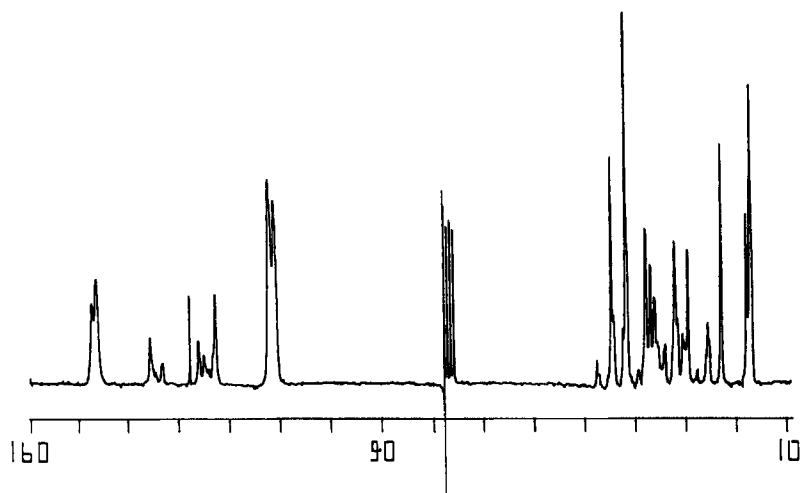
FIG. 1A. Proton noise-decoupled ^{13}C-NMR spectrum of 3,4/*cis*-1,4-poly-isoprene of Sample 1 (50.1 MHz).
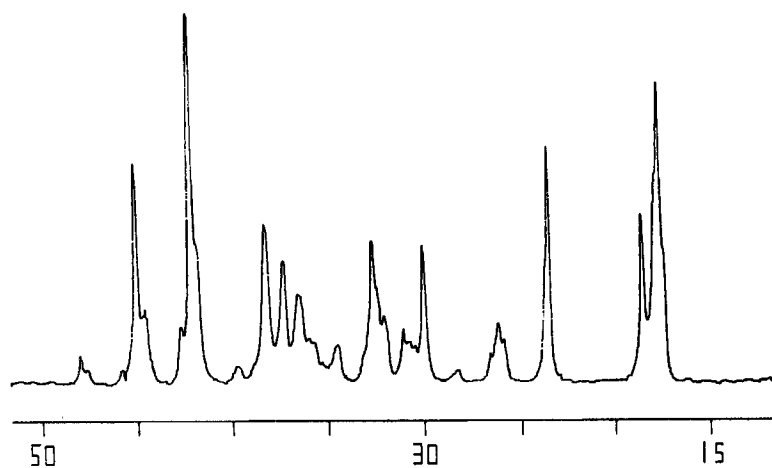

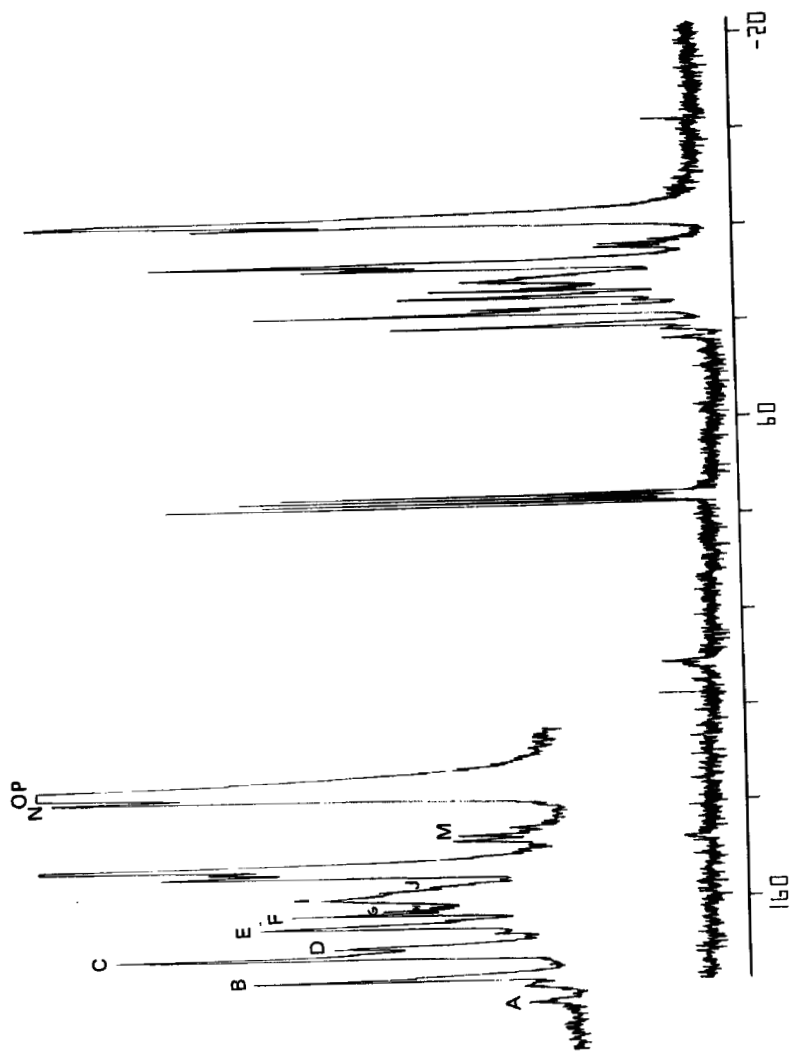FIG. 1B. Expanded spectrum in the aliphatic region (15 to 50 ppm).

FIG. 2. Proton noise-decoupled ^{13}C-NMR spectrum of hydrogenated 3,4/*cis*-1,4-polyisoprene. The expanded spectrum of the aliphatic region is shown at the top.
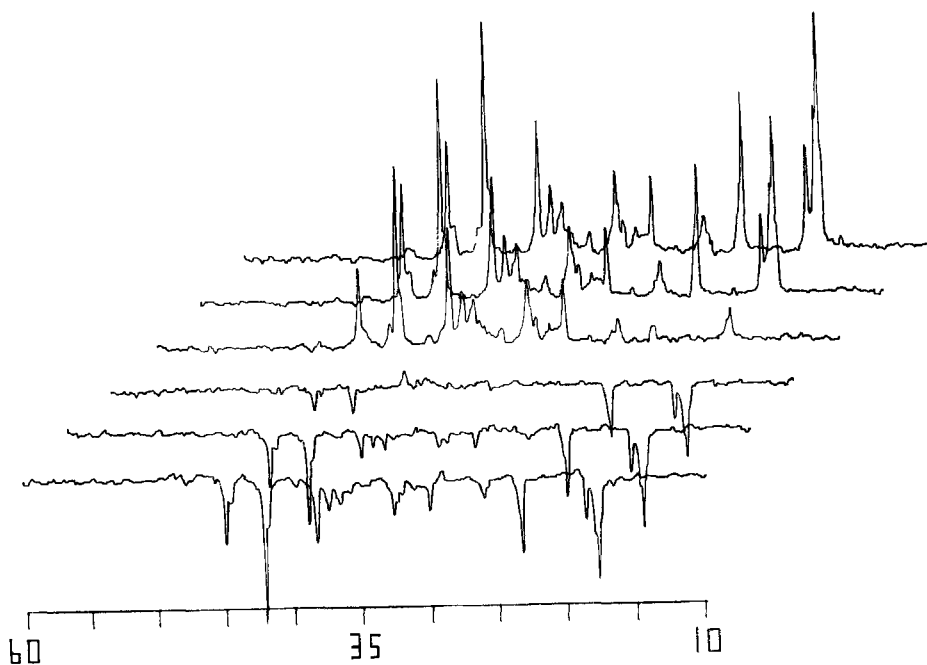
FIG. 3. Inversion-recovery Fourier transform ^{13}C spectrum of 3,4/*cis*-1,4-polyisoprene of Sample 1 at 20°C and 50.1 MHz. The repetition time of the 180-τ-90 pulse sequence was 20 s.

Relation between the ^{13}C-NMR Spectra and the Crystallinity of 3,4/*cis*-1,4-Polyisoprenes

We tried to establish the relationship between the crystallinity and the ^{13}C-NMR spectra for the solid polymer by using MAS-NMR, but we failed. However, it seems that there exists some indirect relationship between the crystallinity and the solution spectra in chloroform-d_1.

The results are listed in Table 4. It seems that long head-to-tail sequences of vinyl monomer units might be beneficial to crystallization. On the contrary, random distribution of vinyl monomer units within the polymer chain and head-to-head and/or tail-to-tail sequences will inhibit crystallization. This is in agreement with Hakathom and Brock's conjecture [14].

TABLE 4. Relations between Crystallinity and ^{13}C-NMR Signals

	Sample			
	1	2	3	4
3,4 Content	76	72	71	69
Crystallinity	33	30	18	14
Assignment	Height,[a] %			
VV_5V	57	52	49	47
CV_5V	19	19	20	24
$V(H-H/T-T)^b$	26	28	31	35
CV_4V	29	27	28	31
VV_4V	46	45	41	34
VVV_3VV	37	36	34	26
CVV_3VC	1.5	1.8	1.9	2.0
CV_3C	2.9	3.2	3.0	3.8

[a]Heights in this table represent the total heights of the structure.
[b]Some V_4's in higher field overlap C_1 and C_4. H-H means head-to-head, T-T means tail-to-tail.

^{13}C-Spin-Lattice Relaxation Time (T_1) and Its Temperature Dependence

Theoretically, spin-lattice relaxation times can only be defined for a set of noninteracting identical spin 1/2 nuclei. However, single exponential relaxation can be obtained to a reasonable degree of accuracy in proton-decoupled spectra for multispin systems and cross-correlation effects may be neglected. Unlike those of *cis*- and *trans*-1,4-PIP's, the T_1's of 3,4/*cis*-1,4-PIP are much more difficult to determine by the inversion-recovery method due to the complexity of the spectra. However, the T_1's of the stronger lines can be accurately determined. Satisfactory results were obtained and are listed in Table 5. Important conclusions may be drawn from the table: First, there seems to be no significant difference between samples of different degrees of

TABLE 5. ^{13}C Spin-Lattice Relaxation Time (T_1) and Some NOEF Values for 3,4/*cis*-1,4-Polyisoprenes[a]

Assignment	Sample			
	1	2	3	4
VV_5V	1.16	1.09	1.14	1.13
VV_5C/CV_5C	1.41	1.42	1.56	1.36
VC_5C/CC_5C	0.99	0.99	0.97	0.94
VVC_1C	0.17	0.18	—	0.15 (N2.6)
CC_1C	0.20	0.20	0.17 (N2.4)	0.17 (N2.2)
CV_4VC	0.13	—	0.13	0.13 (N2.7)
VV_4VC	0.15	0.17	0.14	0.15
VV_4VV	0.14	0.15	0.15	0.14
VVV_3VC	0.25	—	0.25 (N2.7)	0.23
VVV_3VV	0.29	0.27	0.28 (N2.7)	0.25 (N2.5)
CV_3VV	0.34	0.32	0.36 (N2.7)	0.35 (N2.7)
CV_1C	0.19	0.19	0.18 (N2.7)	0.17
CV_1V	0.18	0.17	0.21 (N2.9)	0.15
VV_1V	0.16	0.17	0.17 (N2.5)	0.14
VC_3V	0.24	0.28	0.24	0.27
VC_2V	1.92	—	2.22	2.22
VV_2V	1.83	1.87	1.90	1.87
CV_2V	2.28	2.10	—	1.91
CV_2C	2.42	—	2.73	2.24

[a]Values listed in parentheses represent the NOEF, $1 + \eta$.

crystallinity. This result is reasonable since the T_1's might only reflect the local properties of the nearest neighbor of the carbon atom concerned. Second, we found that the T_1's of 3,4/*cis*-1,4-PIP's are smaller than the T_1's of the *cis*- and *trans*-1,4-PIP's of the same concentration (20 w/v), indicating the segmental mobility of these partially crystalline 3,4/*cis*-1,4-PIP's might be less than that of *cis* and/or *trans*-1,4-PIP's. The vinyl groups in the side chains might play the role of "anchors" that lower the mobility of the segments.

The ^{13}C-T_1's of all the polymers are in the order quaternary > methyl > methine > methylene. The longest T_1's are attributed to the absence of directly bonded protons, while the rather longer T_1's are attributed to the presence of the internal rotational freedom of the methyl group, which reduces the effectiveness of the dipolar relaxation mechanism. It is especially interesting that the T_1's for VC_5C/CC_5C (0.99 0.97 0.94) are slightly smaller than those for VV_5V/VV_5C (1.16 1.41 1.41 1.36) since the latter has two rotational axes, hence is more flexible for internal rotation. The temperature dependence of the T_1's also show that the Arrhenius activation energy of the former ($E = 15.1$ kJ/mol) is slightly higher than those of the latter ($E = 11.3$, 13.3 kJ/mol).

The T_1's of methine carbons are almost twice as long as those of the methylene carbons, indicating that intramolecular DD relaxation mechanisms are dominant in these polymers. It is noteworthy that the T_1's of the $=CH_2$ carbons in the sidechain vinyl groups are about 0.18, 0.16, 0.19, slightly longer than those of $-CH-$ in the main chain (0.14, 0.15, 0.13), since the former also has some contribution of the spin rotation mechanism and reduces the effectiveness of the dipolar mechanism. This conclusion is also verified by the Arrhenius activation energies obtained from the temperature dependence measurement for the former, $E_a = 10.1, 11.4, 11.0$ kJ/mol, which are almost half of the latter, $E_a = 23.5, 20.8$ kJ/mol. It is also interesting that the activation energies, 11.6, 10.1, 11.9 kJ/mol, are half those for the T_1's of the mainchain $-CH_2-$. The true meaning of this phenomenon is not yet clear. Probably the sidechain vinyl group attacted on the methine carbon increases the rotational moment of inertia of the methine carbon, which might facilitate segmental motion and lower the activation energy.

The T_1's and activation energies of the quaternary carbon of CV_2V are longer and lower than those of the VC_2V, except for VV_2V. The reason for this exception is not clear at present. Finally, we measured the NOEF's of individual carbon atoms by the gated decoupling technique, but the results are not very reliable due to the complexity of the spectra. Only some reliable values are listed in Table 6, which indicate that the DD mechanism is dominant in 3,4/*cis*-1,4-polyisoprenes.

TABLE 6. $^{13}C\text{-}T_1$ (in seconds) of 3,4/cis-1,4-Polyisoprene (Sample 1) at Various Temperatures and the Activation Energy

Assignment	Temperature, °C			Activation energy, kJ/mol	Correlation coefficient
	20	40	50		
VV_5V/VV_5C	1.16	1.63	1.94	13.3	0.999
CV_5C	1.41	1.57	2.21	11.7	0.875
VC_5C/CC_5C	0.99	1.24	1.86	15.1	0.929
VVC_1C/CVC_1V	0.17	0.27	0.38	20.3	0.991
CC_1C/C_4VV	0.20	0.24	0.23		
CV_4VC	0.13	0.22	0.33	23.5	0.990
VV_4VC	0.15	0.26	0.23	20.8	
VV_4VV	0.14	0.19	0.20		
VVV_3VC	0.25	0.29	—		
VVV_3VV	0.29	0.37	0.43	10.1	0.997
CV_3VV	0.34	0.47	0.53	11.6	0.997
CV_1C	0.19	0.19	0.23		
CV_1V	0.18	0.18	0.29	12.3	
VV_1V	0.16	0.22	0.25	11.0	
VC_3V	0.24	0.38	0.38[a]	11.9	
VC_2V	1.92	2.89	4.28	19.9	0.979
VV_2V[b]	1.74	2.38	2.59	10.6	0.994
	1.83	2.90	3.68	18.0	0.999
CV_2V	2.28	3.04	3.26	9.6	0.991
CV_2C	2.42	2.93	3.14	6.8	0.998

[a]This value is not used for calculating the activation energy.
[b]These two lines are very close together.

REFERENCES

[1] H. Sato and Y. Tanaka, *J. Polym. Sci., Polym. Chem. Ed., 17*, 3551 (1979).
[2] Y. Tanaka and H. Sato, *Polymer, 17*, 113 (1976).
[3] Y. Tanaka and H. Sato, *Ibid., 17*, 413 (1976).
[4] Y. Tanaka, H. Sato, A. Ogura, and I. Nagoya, *J. Polym. Sci., Polym. Chem. Ed., 14*, 73 (1976).
[5] A. S. Khatchaturov, E. R. Dolinskaya, L. K. Prozenko, E. L. Abramenko, and V. A. Kormer, *Polymer, 18*, 871 (1977).
[6] H. Sato, A. Ono, and Y. Tanaka, *Ibid., 18*, 580 (1977).
[7] K. Hatada, T. Kitayama, Y. Terawaki, Y. Tanaka, and H. Sato, *Polym. Bull., 2*, 791 (1980).
[8] W. Gronski, N. Murayama, H. J. Cantow, and T. Mitamoto, *Polymer, 17*, 358 (1976).
[9] K. Sanui, W. J. Macknight, and R. W. Lenz, *J. Polym. Sci., Polym. Lett. Ed., 11*, 427 (1973).
[10] Q. Sun and F. Wang, *Collected Papers of Institute of Applied Chemistry, Academia Sinica*, 1984.
[11] D. Xie and C. Sun, Private Communication.
[12] D. M. Grant and E. G. Paul, *J. Am. Chem. Soc., 86*, 2984 (1964).
[13] M. M. Duch and D. M. Grant, *Macromolecules, 3*, 165 (1970).
[14] M. J. Brock and M. J. Hakathom, *Rubber Chem. Technol, 45*, 1303 (1972).
[15] L. P. Linderman and J. Q. Adams, *Anal. Chem., 43*, 1245 (1971).