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Structural Dependence of Carbon-13 NMR Spin-Lattice Relaxation Times of 1,4-Polyisoprenes

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Summary

Carbon-13 spin-lattice relaxation times, T_1's, were measured for cis-1,4, trans-1,4 and cis-trans isomerized polyisoprenes in chloroform-d_1 at 25 MHz and mainly at 27°C. Cis-polyisoprene generally showed longer T_1 than the trans-polymer except for methyl carbon, showing the greater segmental mobility of cis-polymer chain. The T_1 of methyl carbon was longer for the trans-polymer than for the cis-polymer. This indicates the greater freedom of the internal rotation of methyl group in trans-polyisoprene. The segmental motion was found not to be isotropic, especially for cis-polyisoprene. The T_1's of the main chain carbons in cis-trans isomerized polyisoprenes increased with increasing content of the cis-unit.

Introduction

Carbon-13 NMR spectra of 1,4-polyisoprenes in solid state have been studied above their glass transition temperatures (KOMOROSKI et al. 1977; SCHAEFER 1972) and the ^{13}C spin-lattice relaxation times(T_1's) of individual carbons were found to be longer for trans-polyisoprene than for cis-polyisoprene. The reverse relationship was reported for 1,4-polybutadiene in both solid and solution (GRONSKI and MURAYAMA 1976).

In this work we measured the ^{13}C-T_1's of cis-1,4, trans-1,4 and cis-trans isomerized polyisoprenes in chloroform-d_1 and found that the cis-polyisoprene showed generally longer T_1 than the trans-polymer except for the methyl carbons. The ^{13}C-T_1 of methyl carbon was longer for trans-polymer than for cis-polymer.

Experimental

The samples of cis- and trans-polyisoprenes were a synthetic, commercial product (cis-1,4: 97%, trans-1,4: 2%, 3,4: 1%) and a gutta percha (trans: 100%), respectively.

Cis-trans isomerized polyisoprenes were prepared

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in benzene from cis- or trans-polyisoprene by UV-irradiation (CUNNEEN et al. 1959). The irradiation was carried out at 18°C on about 2% solution containing diphenyl disulfide (0.2 ∿ 2.0 wt% of the polymer) by using a high-pressure mercury lamp for 4 to 180 min under nitrogen pressure. The isomerized polyisoprene was purified by repeated reprecipitations from benzene solution with acetone. Microstructures of the polymer samples were determined by ^{1}H NMR spectroscopy (TANAKA et al. 1971). ^{13}C NMR spectra were recorded by a JNM-FX-100 Fourier transform NMR spectrometer (JEOL) at 25 MHz on a chloroform-d_1 solution in 10mm o.d. NMR sample tube. The concentration of the solution was 7 wt/vol% if not specified in the text. ^{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 100 sec. The free induction decays following 90° pulse were accumulated 50 or 100 times. ^{13}C-^{1}H nuclear Overhauser enhancement was determined by the gated decoupling method. For the measurement in solid state, the cylinders were cut from the polymer samples and fitted snugly into the NMR sample tube. The cylindrical samples were covered with methanol-d_4 in order to avoid the air gaps between the sample and the tube and also to give the deuterium NMR signal for the magnetic field-locking system.

Results and Discussion

In Figure 1 are shown the ^{13}C NMR spectra of cis-, trans- and cis-trans isomerized (cis-1,4: 55%, trans-1,4: 44%, 3,4: 1%) polyisoprenes measured in chloroform-d_1 at 27°C. The peak assignments are indicated in the Figure. Relatively large shifts between the spectra of cis- and trans-polyisoprenes were observed on the resonances of CH_3 and CH_2(1) carbons. The signals due to the CH_2(1) carbon of the isomerized polymer split into four peaks, which had been assigned to cis-trans, trans-trans, cis-cis and trans-cis dyad sequences in the order of increasing magnetic field (TANAKA and SATO 1976).

The ^{13}C-T_1 and NOE for cis- and trans-polyisoprenes were measured in chloroform-d_1 at 27°C and are shown in Table 1. The T_1's for both polymers were in the order of quaternary > methyl > methine > methylene carbon. Much longer T_1 of quaternary carbon is attributed to the absence of the directly bonded proton. Despite the presence of three directly bonded protons, the methyl carbons showed fairly long T_1's. This should be due to the internal rotational freedom of the methyl group, which reduces the effectiveness of dipolar coupling to directly bonded protons. The T_1 of the methyl carbon is longer for the trans-polymer than for the cis-polymer. The results indicate the greater

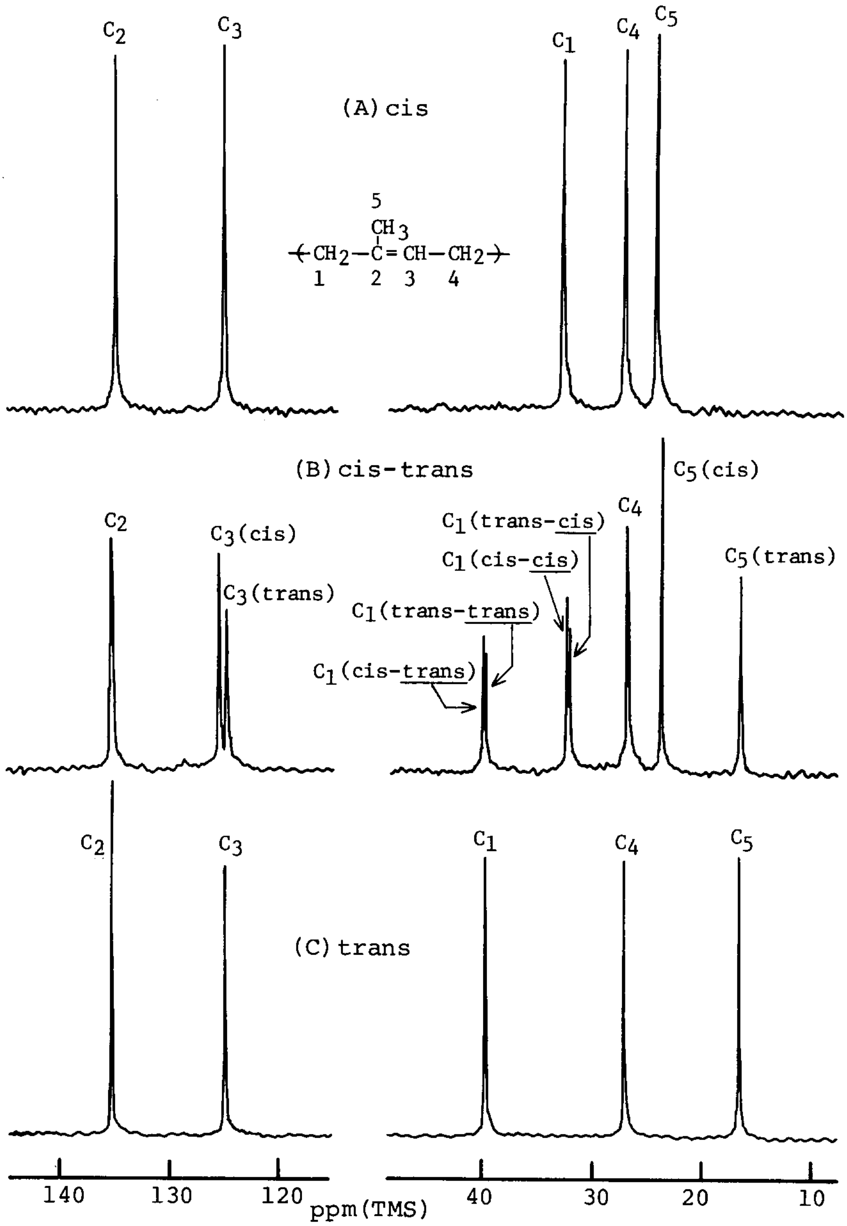
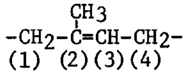


Fig. 1 ^{13}C NMR spectra of 1,4-polyisoprenes measured in $CDCl_3$ at 27°C and 25.05 MHz.
(A) cis-1,4: 97%, trans-1,4: 2%, 3,4: 1%
(B) cis-1,4: 55%, trans-1,4: 44%, 3,4: 1%
(C) trans: 100%

TABLE 1

^{13}C Spin-Lattice Relaxation Time(T_1), and Nuclear Overhauser Enhancement(NOE) for cis-1,4 and trans-1,4 Polyisoprenes[a] in Chloroform-d_1 at 27°C

Polymer		CH_3	$CH_2(1)$	$CH_2(4)$	$=\overset{\vert}{C}H(3)$	$-\overset{\vert}{C}=(2)$
cis-1,4	T_1[b]	1.95	0.60	0.75	0.97	6.20
	NOE	3.19	3.41	3.19	3.46	3.29
trans-1,4	T_1[b]	3.88	0.53	0.56	0.96	6.03
	NOE	2.77	2.77	3.14	2.85	2.84

[a] 

$-\underset{(1)}{CH_2}-\underset{(2)}{\overset{CH_3}{\overset{\vert}{C}}}=\underset{(3)}{CH}-\underset{(4)}{CH_2}-$

[b] In second.

freedom of the internal rotation of methyl group in trans-polyisoprene compared with that in cis-polyisoprene since the difference between the T_1's of the corresponding vinyl carbons of cis- and trans-polymers is not so large.

The longer relaxation times for the methylene carbons of cis-polyisoprene compared to trans-polymer show the greater segmental mobility of cis-polymer chain. This is consistent with Huggins'idea (HUGGINS 1946) that a swinging-door type of rearrangement of only two chain atoms can take place in cis-polyisoprene, but not in trans-one, since the rotation about any of the single bonds in the trans-polymer requires the simultaneous motion of many chain atoms.

The ratio of the T_1 of methine carbon to that of methylene carbon is lower than 2.0, especially for cis-polyisoprene, and nearly independent on the temperature of measurement (cf. Table 2) and the concentration of solution (cf. Table 3). The T_1 of $CH_2(1)$ carbon differs from that of $CH_2(4)$ carbon and the difference is much larger for cis-polyisoprene compared to trans-one. The results mean that the segmental motion of 1,4-polyisoprene, particularly cis-polyisoprene, is not isotropic.

The ^{13}C NOE's for cis- and trans-polyisoprenes were close to the theoretical maximum of 2.988 at 27°C (Table 1), indicating the predominance of dipolar relaxation. The NOE values for the carbons of cis-polyisoprene slightly exceeded the theoretical maximum, and may indicate that the additional relaxation mechanism was involved.

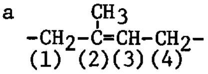
The ^{13}C-T_1's of cis- and trans-polyisoprenes were measured in chloroform-d_1 at several temperatures and are given in Table 2. The T_1 values increased with an increase in the temperature of measurement. From the Arrhenius plot the activation energies for the reorientations of the carbons were estimated as shown in the Table. Slightly lower activation energies for the main chain carbons in the cis-polymer indicate a less restricted segmental mobility of cis-polymer chain. A

TABLE 2

^{13}C-T_1(sec) of cis-1,4 and trans-1,4 Polyisoprenes[a] at Various Temperatures and the Activation Energy(KJ/mol)

Polymer	Temp. (°C)	CH_3	$CH_2(1)$[b]	$CH_2(4)$[b]	$=\overset{\vert}{C}H(3)$	$-\overset{\vert}{C}=(2)$
cis-1,4	27	1.95	0.60(1.6)	0.75(1.3)	0.97	6.20
	45	2.30	0.83(1.4)	0.94(1.3)	1.18	8.69
	55	2.97	0.91(1.5)	1.13(1.2)	1.35	10.44
	ΔE	12	13	12	10	16
trans-1,4	27	3.88	0.53(1.8)	0.56(1.7)	0.96	6.03
	45	4.48	0.67(1.8)	0.71(1.7)	1.23	9.24
	55	5.87	0.87(1.5)	0.91(1.5)	1.34	12.41
	ΔE	12	15	14	10	21

[a]



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

(1) (2)(3) (4)

[b] The values in parentheses represent the ratio of the T_1's of methine and methylene carbon.

greater freedom of the internal motion of methyl group in trans-polyisoprene is not reflected in the activation energy although the true meaning is not clear at present.

It was reported by Schaefer that the ^{13}C-T_1's in solid state at 40°C and 22.6 MHz of the carbons of trans-polyisoprene were all longer than those of the corresponding carbons of cis-polyisoprene. This is nearly reverse to the results of the present work obtained in solution at 27°C, although the temperatures of measurement were slightly different with each other. The concentration dependence of ^{13}C-T_1 of cis- and trans-polyisoprenes were investigated in chloroform-d_1 at 27°C in the concentration range of 7 to 52 wt/vol%. The results are given in Table 3. The T_1 decreased with an increase in the concentration of solution. However, the microstructure dependence of the T_1 was independent of the concentration of solution, that is, the T_1 of methyl carbon was longer for trans-polymer

TABLE 3

Concentration Dependence of ^{13}C-T_1(sec) of cis-1,4 and trans-1,4-Polyisoprenes in Chloroform-d_1 at 27°C

Polymer	Conc. w/v%	CH_3	$CH_2(1)$[a]	$CH_2(4)$[a]	$=\overset{\vert}{C}H(3)$	$-\overset{\vert}{C}=(2)$
cis-1,4	7	1.95	0.60(1.6)	0.75(1.3)	0.97	6.20
	19	1.82	0.57(1.5)	0.67(1.3)	0.84	6.16
	29	1.68	0.42(1.4)	0.45(1.3)	0.60	5.61
	44[b]	1.25	0.29(1.4)	0.32(1.3)	0.41	4.04
trans-1,4	7	3.88	0.53(1.8)	0.56(1.7)	0.96	6.03
	23	3.29	0.42(1.9)	0.44(1.8)	0.81	5.35
	34	2.61	0.32(2.0)	0.37(1.8)	0.65	4.76
	52[b]	1.76	0.22(1.9)	0.23(1.8)	0.41	2.94

[a] The values in parentheses represent the ratio of the T_1's of methine and methylene carbon.

[b] These samples are somewhat inhomogeneous.

TABLE 4

^{13}C-T_1 and T_2 of Solid Polyisoprenes[a] at 27°C

Polymer		Temp(°C)	CH_3	CH_2(1)	CH_2(4)	=CH(3)	-C=(2)
cis-1,4	T_1/ms	27	327	44	50	61	607
		40[c]	350	50	55	95	700
	T_2/ms[b]	27	36	16	18	23	40
trans-1,4	T_1/ms	27	597	74	73	109	882
		40[c]	450	85	85	160	950
	T_2/ms[b]	27	12	4	5	4	3

[a] Samples were covered with methanol-d_4.

[b] $T_2 = (\pi \times \text{half-height line width})^{-1}$.

[c] Data taken from the literature (SCHAEFER 1972).

and the T_1's of chain carbons were longer for cis-polymer regardless of the concentration. The ^{13}C-T_1 and spin-spin relaxation time, T_2, were measured in solid state at 27°C since the measurements by Schaefer (SCHAEFER 1972) were carried out at 40°C and those in solution by us were done at 27°C. The results are substantially in agreement with the Schaefer's if the difference in the temperature of measurement is taken into account (Table 4). So it is clear that the structural dependence of ^{13}C-T_1 for solid polyisoprene is different from that for polyisoprene in solution. The true meaning for this phenomenon is not clear at present but should be clarified in the future.

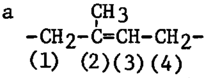
In Table 5 are given the ^{13}C-T_1's of several cis-trans isomerized polyisoprenes measured in chloroform-d_1 at 27°C. The methyl carbon in trans-unit showed consistently longer T_1 than that in cis-unit and the T_1 values in each unit are nearly constant regardless of the cis-trans composition of the polymer. The T_1's of methyl carbons in two trans-units of 2,5,9-trimethyl-cis, trans, trans-1,5,9-cyclododecatriene, the cyclic trimer of isoprene, are 8.8 and 8.7 sec, respectively,

TABLE 5

^{13}C-T_1 in Second for cis-trans Isomerized Polyisoprene[a] in Chloroform-d_1 at 27°C

cis %	CH_3		=CH(3)		$CH_2(1)$[b]				CH_2(4)	-C=(2)
	cis	trans	cis	trans	c - c	t - c	c - t	t - t		
0	—	3.88	—	0.96	—	—	—	0.53	0.56	6.03
23[c]	2.20	3.45	0.68	1.01	0.41	0.49	0.58	0.46	0.50	7.12
55[d]	2.11	3.81	0.68	1.26	0.54	0.57	0.74	0.67	0.65	7.07
63[d]	2.17	3.91	0.81	1.25	0.58	0.59	0.84	0.82	0.67	7.49
73[d]	2.15	4.56	0.86	1.26	0.62	0.57	0.83	0.89	0.65	7.62
97	1.95	—	0.97	—	0.60	—	—	—	0.75	6.20

[a]



$\underset{(1)}{-CH_2}-\underset{(2)}{\overset{CH_3}{C}}=\underset{(3)}{CH}-\underset{(4)}{CH_2}-$

[b] c-c: cis-cis, t-c: trans-cis, c-t: cis-trans, t-t: trans-trans.

[c] Prepared from gutta percha.

[d] Prepared from commercial cis-polyisoprene (cis-1,4: 97%, trans-1,4: 2%, 3,4: 1%).

and longer than that of the methyl carbon in the cis-unit (5.0 sec). These results indicate that the internal rotation of methyl group is dominated only by the geometry of the double bond, to which it is attatched, and scarcely affected by the structure of neighbouring monomer units. On the other hand, the T_1's of the backbone carbons depended on the cis-trans composition of the polymer and increased with an increase in the cis-unit content indicating that the segmental mobility of 1,4-polyisoprene increases, as a whole, with an increase in the cis-content. The T_1 for the methine carbon in trans-unit was longer than that in cis-unit of the same polymer and the T_1 for the $CH_2(1)$ methylene carbon in trans-trans dyad was also longer than that in cis-cis dyad. This should be noteworthy and rather strange since the T_1's of these carbons in trans-polyisoprene was shorter than those of the corresponding carbons in cis-polyisoprene. However, similar phenomenon was observed for cis-trans polybutadiene and was explained by the effect of rotational barrier of the neighbouring monomer unit (GRONSKI and MURAYAMA 1976). The relatively lower activation energy for the T_1 of trans-unit in cis-trans polybutadiene was explained as the effect of the lower rotational barrier of the neighbouring cis-unit, and vice versa (GRONSKI and MURAYAMA 1976). Similar explanation might be applied to the results of our cis-trans isomerized polyisoprenes, although the more detailed study should be needed.

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References

J. I. CUNNEEN, G. M. C. HIGGINS, and W. F. WATSON: J. Polym. Sci., 40, 1 (1959)

W. GRONSKI and N. MURAYAMA: Makromol. Chem., 177, 3017 (1976)

M. L. HUGGINS: J. Polymer Research, 1, 1 (1946)

R. A. KOMOROSKI, J. MAXFIELD, and L. MANDELKERN: Macromolecules, 10, 545 (1977)

J. SCHAEFER: Macromolecules, 5, 427 (1972)

Y. TANAKA, Y. TAKEUCHI, M. KOBAYASHI, and H. TADOKORO: J. Polym. Sci., A2, 43 (1971)

Y. TANAKA and H. SATO: Polymer, 17, 113 (1976)

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