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SHORT COMMUNICATION

^{13}C-NMR of Polyisoprenes: Sequence Distribution of *cis*-1,4 and *trans*-1,4 Units

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^{13}C-NMR spectroscopy has been applied to analyze the sequence distribution of isomeric structures of diene polymers. Some reports have been published on the sequence distribution of 1,2 and 1,4 units or *cis*-1,4 and *trans*-1,4 units in polybutadienes.[1-3] As for polyisoprene, however, few investigations have been made on the sequence distribution of isomeric structures using this technique, although Duch, *et al*, reported the assignment of ^{13}C-NMR signals of the *cis*- and *trans*-polyisoprenes.[4]

In this work, we have studied the ^{13}C-NMR spectra of *cis—trans* isomerized 1,4-polyisoprenes and found new signals attributed to *cis—trans* dyad linkage, which enable us to discuss quantitatively the sequence distribution of *cis*-1,4 and *trans*-1,4 units along the polymer chain.

Isomerization of polyisoprene (gutta percha and synthetic *cis*-1,4-polyisoprene) was carried out in benzene solution at 20°C under nitrogen atmosphere with the irradiation of a high pressure mercury lamp using thiobenzoic acid as an activator. Natural abundance ^{13}C-NMR spectra were obtained on a JEOL JNM-PS PFT 100 spectrometer equipped with a Fourier transfer accessory at 25.1 MHz. About 15% (w/v) solution in $CDCl_3$ was used. All the spectra were proton noise-decoupled and obtained with multiple scans and with pulse repetition time of 3.0 sec.

It has been reported that chicle contains *cis*- and *trans*-polyisoprenes:[5] thus chicle polyisoprene shows signals at 32.25 and 134.85 ppm due to the *cis* polymer and at 39.67 and 134.38 ppm due to the *trans* one (Figure 1 a). These chemical shift values are almost in agreement with

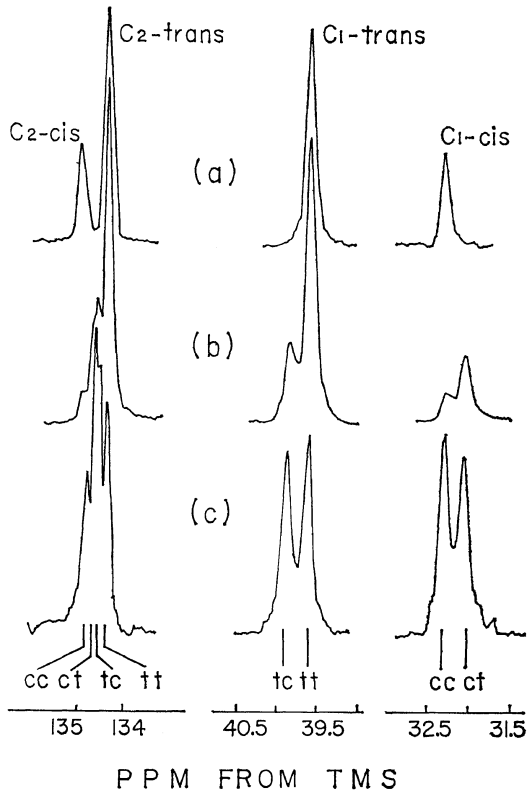

Figure 1. ^{13}C-NMR spectra of 1,4-polyisoprenes: (a), chicle polyisoprene; (b), isomerized gutta percha; (c), isomerized *cis*-1,4-polyisoprene. The symbols C_1 and C_2 correspond to $-\underline{C}H_2-C(CH_3)=CH-CH_2-$ and $-CH_2-\underline{C}(CH_3)=CH-CH_2-$, respectively.

those obtained by Duch, *et al*,[4] who assigned these four peaks to C_1-*cis*, C_1-*trans*, C_2-*trans*, and C_2-*cis* in the ascending order of chemical shifts. The symbols C_1 and C_2 correspond to $-\underline{C}H_2-C(CH_3)=CH-CH_2-$ and $-CH_2-\underline{C}(CH_3)=CH-CH_2-$ in monomer units. Isomerized gutta percha exhibits four signals, corresponding to those of C_1-*cis*, C_1-*trans*, C_2-*cis*, and C_2-*trans* (Figure 1 b). It is noteworthy that each of the C_1-*cis* and C_1-*trans* splits into two peaks and the C_2 signal appears as two doublets in the spectrum of isomerized gutta percha. Similar splittings were also clearly observed in the spectrum of isomerized *cis*-polyisoprene (Figure 1 c). The signals due to the other carbons, however, did not provide any information on the *cis—trans* sequences. The crystallinity of the *trans* polymer drastically decreased through isomerization and, moreover, the isomerized *cis*-polyisoprene displayed no crystallinity due to long *trans* sequence, even though it has 50.0% *trans*-1,4 units (Figure 2). These results indicate the production of *cis—trans* linkages by isomerization. And since the viscosity change due to the *cis—trans* isomerization is not so large, the cleavage reaction of the main chain may be negligible (Table II). Consequently, the newly appearing signals are attributed to the C_1 or C_2 carbons in *cis—trans* linkage and each peak is tentatively assigned as shown in Table I.

The fractions of dyad sequences (*trans—trans*, *trans—cis*, *cis—trans*, and *cis—cis*) of isomerized polyisoprenes were measured using C_1 NMR signals according to the above assignment. The observed values are in close agreement with the calculated ones, assuming the random distribution of *cis* and *trnas* units specified by a single

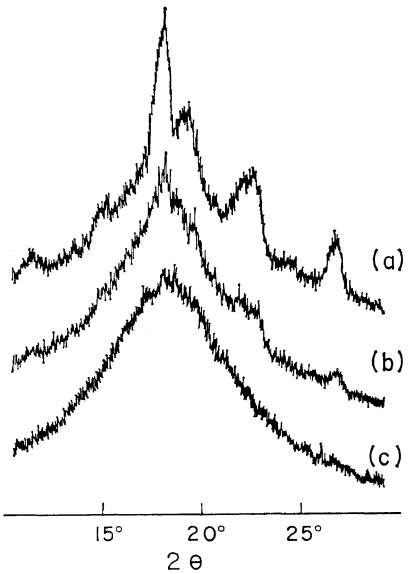

Figure 2. X-ray diffraction patterns of 1,4-polyisoprenes: (a), gutta percha; (b), isomerized gutta percha; (c), isomerized *cis*-1,4-polyisoprene.

Table I. Assignments of the signals of polyisoprene

Carbone	Chemical shift, ppm from TMS			
	trans—trans	*trans—cis*	*cis—trans*	*cis—cis*
C_1[a]	39.67	39.91	32.01	32.25
C_2[a]	134.38	134.55	134.68	134.85

[a] The symbols C_1 and C_2 correspond to $-\underline{C}H_2-C(CH_3)=CH-CH_2-$ and $-CH_2-\underline{C}(CH_3)=CH-CH_2-$, respectively.

Table II. Sequence distributions of 1,4-polyisoprenes

Sample	*trans*	*cis*	Fractions of dyad sequence				$[\eta]$[a]
			trans—trans	*trans—cis*	*cis—trans*	*cis—cis*	
Chicle	66.1	33.9	66.1	0	0	33.9	—
Isomerized gutta percha	78.4	21.6	60.0 (61.5)[b]	18.4 (16.9)	15.3 (16.9)	6.3 (4.7)	2.62
Isomerized *cis*-polyisoprene	50.0	50.0	24.9 (25.0)[b]	25.1 (25.0)	24.6 (25.0)	25.4 (25.0)	2.20
Gutta percha	100	0	—	—	—	—	1.55
cis-Polyisoprene	3	97	—	—	—	—	3.60

[a] Viscosities were measured in toluene solution at 30°C.

[b] The values in parentheses are calculated assuming a random distribution of *cis* and *trans* units.

parameter (Table II).

In the spectrum of chicle polyisoprene, the absence of the splitting in the C_1 and C_2 signals indicates that chicle contains both pure *cis*- and *trans*-polyisoprenes. This finding is in accordance with the result obtained by Schlesinger[5] with solvent extractions.

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