

Distribution of isomeric structures in polyisoprenes

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The ^{13}C -n.m.r. spectra of polyisoprenes were investigated. Polyisoprenes were prepared with $n\text{-BuLi/Et}_2\text{O}$, radical (emulsion polymerization), and Alfin catalysts. Poly(isoprene-4,4- d_2)s were also prepared with $n\text{-BuLi/Et}_2\text{O}$ catalysts for the signal assignments. ^{13}C -n.m.r. signals were assigned for dyad or triad sequences of *cis*-1,4-, *trans*-1,4-, and 3,4- units. Signals due to head-to-head (4,1-1,4) and tail-to-tail (1,4-4,1) linkages were also assigned. On the basis of signal assignments it was revealed that *cis*-1,4-, *trans*-1,4-, and 3,4-units were distributed almost randomly in $n\text{-BuLi/Et}_2\text{O}$ catalysed polyisoprenes. It was confirmed that radical and Alfin polyisoprenes contained about 15% of each of head-to-head and tail-to-tail linkages. It was found that radical polyisoprene had *cis*-1,4- and *trans*-1,4-units distributed randomly along the polymer chain regardless of the head and tail arrangements.

INTRODUCTION

Isoprene can be polymerized into four types of isomeric unit, *cis*-1,4-, *trans*-1,4-, 1,2-, and 3,4-units, depending on the catalysts and polymerization conditions. Thus polyisoprene can be considered as a type of copolymer consisting of these isomeric units distributed in various ways along the polymer chain. It is therefore quite reasonable to expect that the properties of polyisoprene are affected not only by the amount of isomeric units but also by the distribution of these units, as in the case of sequence distribution of monomer units in a usual copolymer.

So far, distribution of isomeric units in polyisoprene has been investigated by ozonolysis^{1,2} or pyrolysis^{3,4}. However, these methods cannot differentiate between *cis*-1,4- and *trans*-1,4-units, because both of the units are converted into the same reaction products through the main chain scission reaction. Moreover, the results obtained by these measurements should leave some ambiguity for quantitative discussion because of the concurrence of side reactions such as recombination and migration.

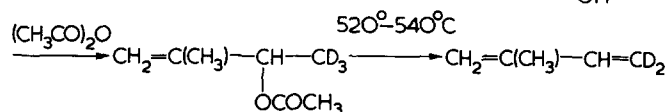
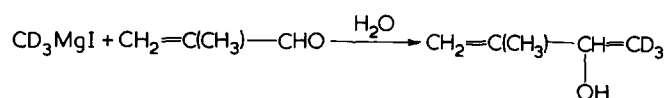
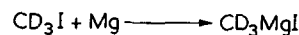
In a previous work, we have investigated the ^{13}C -n.m.r. spectra of hydrogenated polyisoprenes^{5,6}. Sequence distribution of the 1,4- and 3,4- units, arrangement of head and tail linkages, and the tacticity of the 3,4-unit were discussed for polyisoprenes prepared with various types of catalyst. We have also studied the ^{13}C -n.m.r. spectra of *cis-trans* isomerized 1,4-polyisoprenes^{7,8} and have determined the sequence distribution of *cis*-1,4- and *trans*-1,4- units in these polymers. In this work we analyse the ^{13}C -n.m.r. spectra of various types of polyisoprene and discuss the sequence distribution of *cis*-1,4-, *trans*-1,4-, and 3,4- units, and also the amount of head-to-head and tail-to-tail linkages of 1,4-units for these polymers.

EXPERIMENTAL

Monomers

Isoprene. Commercially obtained isoprene was distilled from calcium hydride under nitrogen before use.

Isoprene-4,4-d₂. Isoprene-4,4- d_2 was prepared according to the following reaction sequence:



2-Methyl-1-butene-3-ol-4,4,4-d₃. 3.84 g (0.158 mol) of magnesium turnings were placed under nitrogen atmosphere in a 100 ml three-necked round-bottom flask fitted with a dropping funnel, a reflux condenser, and a mechanical stirrer. A solution of 10 ml (0.158 mol) of methyl- d_3 iodide in 53 ml of ether was added, stirring as rapidly as the reaction would allow. After the formation of the Grignard complex, 13.2 ml (0.158 mol) of methacrolein were added dropwise and then refluxed for 2 h followed by hydrolysis with dilute hydrochloric acid. The ethereal layer was separated and dried over anhydrous magnesium sulphate, followed by distillation under reduced pressure. *2-Methyl-1-butene-3-ol-4,4,4-d₃*: b.p. $42^\circ-43^\circ\text{C}/37\text{ mmHg}$; yield, 36%.

2-Methyl-1-butene-3-yl-4,4,4-d₃ acetate. In a 50 ml two-necked round-bottom flask fitted with a reflux condenser were placed 5.85 g (0.0657 mol) of 2-methyl-1-butene-3-ol-4,4,4- d_3 , 24.8 ml (0.258 mol) of acetic anhydride, and a few drops of pyridine. The mixture was refluxed for 3 h and then neutralized with aqueous sodium carbonate. After extraction with ether, the organic layer was distilled under reduced pressure. *2-Methyl-1-butene-3-yl-4,4,4-d₃ acetate*: b.p. $25^\circ-26^\circ\text{C}/32\text{ mmHg}$; yield, 80%.

Isoprene-4,4-d₂. Isoprene-4,4- d_2 was prepared by the pyrolysis of 2.5 g of 2-methyl-1-butene-3-yl-4,4,4- d_3 acetate by passing it with a gentle stream of nitrogen through a glass tube (13 mm i.d. \times 150 mm) packed with glass beads at $520^\circ-540^\circ\text{C}$. The resultant organic layer was separated,

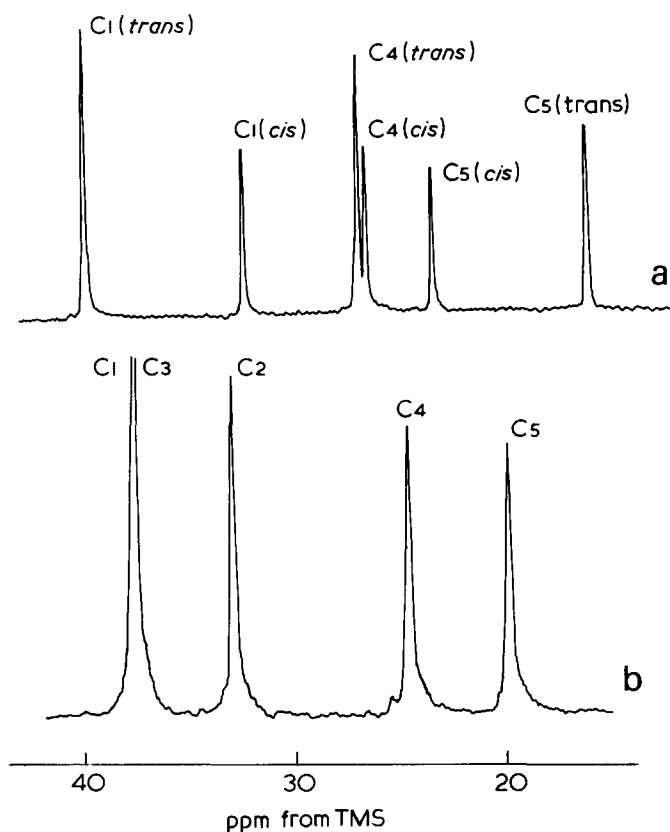


Figure 1 ^{13}C -n.m.r. spectra of (a) a mixture of *cis*-1,4 (34%) and *trans*-1,4 (66%) polyisoprenes and (b) hydrogenated 1,4-polyisoprene

neutralized with sodium hydroxide, and distilled over sodium. Yield, 65%.

Polymerization

Polymerization of isoprene and isoprene-4,4- d_2 was conducted in a glass ampoule under nitrogen using *n*-BuLi and *n*-BuLi/Et₂O as catalysts. Polymerization of isoprene was also carried out using radical (emulsion polymerization) and Alfin catalysts in conventional methods.

Hydrogenation

Polyisoprenes were hydrogenated according to the method of Sanui *et al.*⁹ using *p*-toluenesulphonylhydrazide in xylene. The hydrogenation was carried out twice in order to hydrogenate more than 98% of double bonds. The residual unsaturation was determined¹⁰ by ^1H -n.m.r. measurements, using the olefinic resonances, to be about 5 ppm.

Measurements

The ^{13}C -n.m.r. spectra were obtained at room temperature by using a JEOL-JNM PS-100 or a Varian CFT-20 spectrometer at 25 or 20 MHz, respectively. Deuteriochloroform solution (350 mg/ml) was used and chemical shifts were referred to tetramethylsilane added as an internal standard. All the spectra were proton noise decoupled and obtained with multiple scans at a pulse repetition time of 2.0 sec.

RESULTS AND DISCUSSION

Calculation of chemical shifts

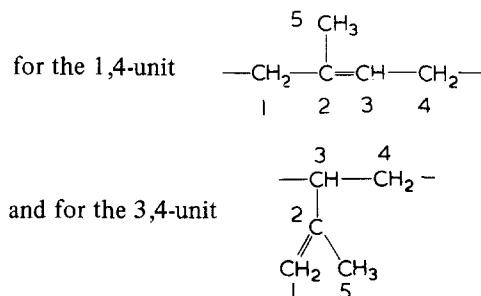
Polyisoprene containing *cis*-1,4-, *trans*-1,4-, and 3,4- units exhibits a complicated ^{13}C resonance arising from various

types of linkage. This resonance can be analysed by reference to the results of ^{13}C -n.m.r. studies of *cis*-*trans* isomerized polyisoprenes and hydrogenated polyisoprenes⁵⁻⁸.

Chemical shifts of aliphatic carbons in polyisoprene can be estimated from those of the corresponding carbons in hydrogenated polyisoprene according to the findings of Dorman *et al.*¹¹ They reported that a double bond in a mono-olefin had influence only on the chemical shift of the α aliphatic carbon and had little effect on that of the β aliphatic carbon. Therefore it can be presumed that the chemical shift of an aliphatic carbon in polyisoprene is influenced by the adjacent double bond in the same monomer unit, and is hardly influenced by the double bond in the next or more distant monomer units. The magnitude of influence by a double bond, i.e. shift factor, can be determined by the comparison of chemical shift of a carbon atom in polyisoprene with that of the corresponding carbon atom in hydrogenated polyisoprene.

Figure 1 shows the ^{13}C -n.m.r. spectra of (a) a mixture of *cis*-1,4- (34%) and *trans*-1,4- (66%) polyisoprene, and (b) of hydrogenated 1,4-polyisoprene. The shift factor of each aliphatic carbon atom in the 1,4 structure was determined by a comparison of Figure 1a with Figure 1b. The results are listed in Table 1.

Figure 2 shows the aliphatic resonances of polyisoprene containing *cis*-1,4- (57%), *trans*-1,4- (19%), and 3,4-units (24%) prepared with *n*-BuLi/Et₂O catalyst, and of hydrogenated polyisoprene. The signals observed for 1,4-polyisoprene were also detected in the spectrum of this polymer. The correspondence of aliphatic signals between polyisoprene and hydrogenated polyisoprene was deduced from Figure 1, and is indicated by solid (*cis*-1,4) and broken (*trans*-1,4) lines in Figure 2. This polymer also exhibited several sharp signals (A, B, H, L, M and Q) which were scarcely observed in the spectrum of 1,4-polyisoprene. These newly appearing signals can be attributed to carbon atoms in the sequences containing 3,4-units. For the hydrogenated polyisoprene it has been reported⁵ that the C₃ carbon of the 3,4-unit in the 1,4-3, 4-1, 4 linkage resonates at 44.39 ppm and the C₅ carbon at 19.34 ppm. On the basis of this finding, signal A (and B) in Figure 2a was assigned to the C₃ carbon of the 3,4-unit in the 1,4-3, 4-1, 4 linkage, and signal Q to the C₅ carbon. In this sequence the chemical shifts of the C₃ and C₅ carbon signals may be slightly affected by the isomeric structure of the 1,4-unit, which will be discussed later. The shift factors of the C₃ and C₅ carbons in the 3,4-unit were deduced as listed in Table 1, where the carbon atoms are denoted as follows:



The shift factor for the C₄ carbon in the 3,4-unit was assumed to be 0 ppm, because this carbon had no double bond on the α carbon, although no correspondence of signals between original and hydrogenated polyisoprene was deduced.

The shift factors obtained here showed good agreement with those obtained by Dorman *et al.*¹¹ using trisubstituted and 1,1-disubstituted ethylenes. By using the shift factors

Table 1 Shift factors for polyisoprene

Structure	Carbon	Chemical shift (ppm)			Peak	Shift factor (ppm) [‡]	
		Hy-PIP*		PIP [†]			
$\begin{array}{c} \text{5 CH}_3 \\ \\ \text{(1,4) } \text{---CH}_2\text{---C---CH---CH}_2\text{---} \\ \quad \quad \\ \text{1} \quad \text{2} \quad \text{3} \quad \text{4} \end{array}$	1	37.47	<i>cis</i>	32.08	J	-5.39 (-5.2)	
	4	24.51	<i>trans</i>	39.70	F	+2.23 (+3.4)	
			<i>cis</i>	26.36	O	+1.85 (+1.6)	
			<i>trans</i>	26.69	O	+2.18 (+1.6)	
	5	19.83	<i>cis</i>	23.25	P	+3.42 (+3.3)	
$\begin{array}{c} \text{3} \quad \text{4} \\ \quad \\ \text{(1,4) } \text{---CH---CH}_2\text{---} \\ \\ \text{2} \\ \\ \text{CH}_2 \quad \text{CH}_3 \\ \quad \\ \text{1} \quad \text{5} \end{array}$	3	44.39		47.79	A	+3.40 (-)	
	4	27.84		—	—	0.0 (0.0)	
	5	19.34		18.74	Q	-0.60 (-0.3)	
							-1.1)

* Hy-PIP, hydrogenated polyisoprene; [†] PIP, polyisoprene; [‡] values in parentheses were obtained by Dorman et al.¹¹

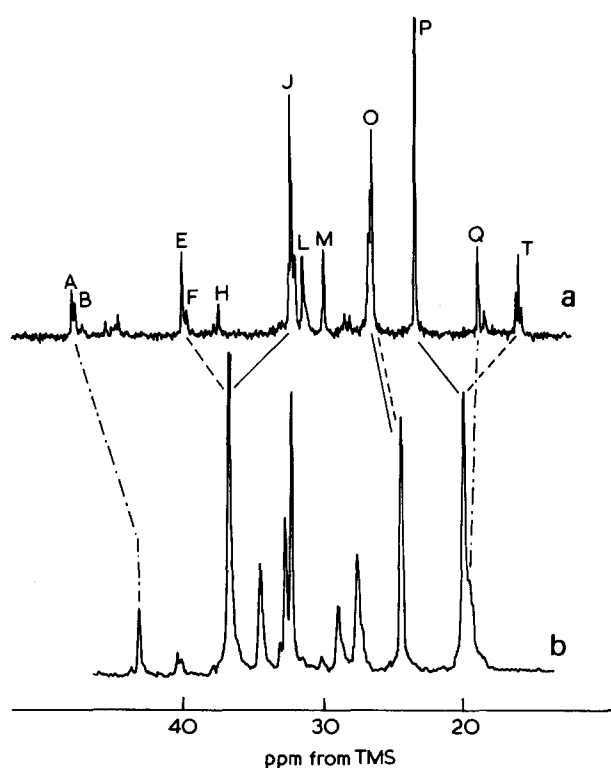


Figure 2 ¹³C-n.m.r. spectra of (a) isoprene containing *cis*-1,4-(57%), *trans*-1,4-(19%), and 3,4-(24%) units, and (b) its hydrogenate. The lines show the correspondence of the signals arising from original and hydrogenated polymers: —, *cis*-1,4; - - - - , *trans*-1,4; - · - · - · , 3,4-units

listed in Table 1, the chemical shifts of the aliphatic carbons in polyisoprene were calculated from those of the corresponding carbon atoms in the hydrogenated polymer. The results are listed in Table 2.

Assignment of signals

As shown in Table 2, the signals arising from the C₁ and C₄ carbons in the 1,4-unit and the C₄ carbon in the 3,4-unit were assumed to resonate in the range of 40–25 ppm. Differentiation between the C₁ and C₄ carbon signals can be achieved by comparison of the ¹³C-n.m.r. spectrum of polyisoprene with that of poly(isoprene-4,4-*d*₂). In the case of protonated carbon atoms, the signals appear as sharp peaks because of decoupling from the proton and their intensities

Table 2 ¹³C-n.m.r. signal assignments

Carbon atom	Signal	Assignment*	Chemical shift (ppm)		
			Obs.	Calc.	Δ(ppm)
3	A	<i>c</i> -V- <i>c,t</i>	47.79	47.79	0.00
	B	<i>t</i> -V- <i>c,t</i>	47.07	47.79	-0.72
	C	{ <i>c,t</i> -V- <i>v</i> <i>v</i> -V- <i>c,t</i>	45.35	44.83	0.52
	D		<i>v</i> -V- <i>v</i>	41.98	41.59
1	E	<i>c</i> -T	38.86	39.70	0.16
	F	<i>t</i> -T	39.70	39.70	0.00
	H	<i>v</i> -T	37.39	37.32	0.07
	J	<i>c</i> -C	32.08	32.08	0.00
	K	<i>t</i> -C	31.95	32.08	-0.13
	M	<i>v</i> -C	29.88	29.70	0.18
4	G	V- <i>v</i> (<i>m</i>)	37.55	31.96	5.59
	I	V- <i>v</i> (<i>r</i>)	32.67	30.58	2.09
	J	T- <i>v</i>	32.08	30.02	2.00
	K		31.95		
	L	{ C- <i>v</i> V- <i>c</i>	31.33	29.69	1.74
	N	V- <i>t</i>	28.21	27.84	0.37
	O	{ T- <i>c,t</i> C- <i>c,t</i>	26.36	26.36	0.00
~26.69		~26.69	~0.33		
5	P	C	23.25	23.25	0.00
	Q	<i>c,t</i> -V- <i>c,t</i>	18.74	18.74	0.00
	R	{ <i>c,t</i> -V- <i>v</i> <i>v</i> -V- <i>c,t</i>	18.04	18.01	0.03
	S		<i>v</i> -V- <i>v</i>	17.58	18.01
	T	T	15.76	15.76	0.00

* Each signal is assigned to a carbon atom in an isomeric unit denoted by a capital letter. Small letters indicate the structure of the adjacent monomer unit.

C: *cis*-1,4; T: *trans*-1,4; and V: 3,4 units; (*m*): meso and (*r*): racemic

are enhanced by nuclear Overhauser effect caused by heteronuclear decoupling. On the other hand, the signals due to deuterated carbon atoms appear as multiplets due to ¹³C-D coupling. Therefore, the signals due to the C₄ carbon can be differentiated from those of the C₁ carbon by substituting the protons attached to the C₄ carbon with deuterium. ¹³C-n.m.r. spectra of polyisoprene and poly(isoprene 4,4-*d*₂) prepared with *n*-BuLi and *n*-BuLi/Et₂O catalysts are shown in Figures 3 and 4. Signals G, I, L, N and O (indicated with arrows in Figures 3 and 4) decreased significantly in the spectra of partially deuterated polymers, which indicates that these signals had arisen from the C₄ carbon. The inten-

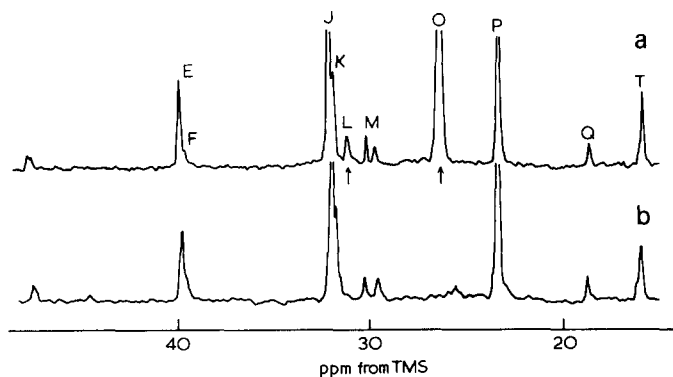


Figure 3 ^{13}C -n.m.r. spectra of (a) polyisoprene and (b) poly(isoprene-4,4- d_2) prepared with *n*-BuLi catalyst

sities of signals J and K apparently decreased in the spectra of the partly deuterated polymers, indicating that these signals were composed of two components due to C_1 and C_4 carbons overlapping each other.

Each signal from polyisoprene was tentatively assigned as shown in Table 2 on the basis of the findings described above, and also by considering the relationship between signal intensities and the fractions of isomeric units in each polymer. For signals due to the C_1 , C_3 and C_5 carbons, close agreement was obtained between the observed and calculated chemical shift values. This indicates that the simple shift factor, considering only double bonds on the α carbon, is sufficient to estimate chemical shifts of these carbon atoms. On the other hand, large differences between observed and calculated chemical shifts were detected for the signals due to the C_4 carbon adjacent to the C_3 carbon of the 3,4-unit, i.e. signals G, I, J, K and L. These differences were thought to arise from the steric effect of the pendant isopropenyl group of the 3,4-unit. A similar steric effect was also observed⁵ for hydrogenated polyisoprene.

It was found⁸ that in *cis-trans* isomerized polyisoprene the C_1 carbon displayed four signals (E, F, J and K) reflecting the dyad sequences of *cis*-1,4- and *trans*-1,4-units. The chemical shifts of these signals in the spectra of *n*-BuLi/ Et_2O catalysed polyisoprenes were found to be almost identical to those in the spectra of the isomerized polymers, indicating the validity of the assignments of these signals.

Signals G and I were assigned to the central methylene carbon (C_4) of the dyad of the 3,4-unit by considering the signal intensities and the amount of 3,4-3,4 linkage. The two signals were further assigned to the C_4 carbon in the meso- and racemic dyads of the 3,4-unit in order of increasing magnetic field by using the ^{13}C -n.m.r. spectrum of $\text{Ti}(\text{O}i\text{Bu})_4\text{-AlEt}_3$ catalysed polyisoprene in which the 3,4-units were found to combine mainly in the meso configuration⁶. In the case of hydrogenated polyisoprene the signal of the corresponding carbon atom also displayed a splitting, reflecting the dyad tacticity of the 3,4-unit.

In the sequence of 1,4-3,4-1,4, the C_3 carbon of the 3,4-unit showed two signals (A and B) reflecting the *cis* and *trans* structures of the left-hand 1,4-unit; signals A and B showed further fine splittings due to the structure of the right-hand 1,4-unit. In the case of the C_5 carbon of the 3,4-unit three signals (Q, R and S) were observed due to the 1,4 or 3,4 structure of the adjacent monomer unit, but these signals exhibited no splitting due to the structure of the adjacent 1,4-unit. Signals C, D, N, O and T also showed fine splittings. These splittings were thought to arise from the structural sequence or tacticity of adjacent or more remote

monomer units. Detailed assignments of these splittings were not conducted in this work.

Recently, Gronski *et al.*¹² have reported the ^{13}C -n.m.r. spectrum of $\text{Ti}(\text{O}i\text{Bu})_4\text{-AlEt}_3$ catalysed polyisoprene and assigned the signal due to the *cis*-1,4- and 3,4 sequences. In our previous paper it was reported that this polymer consisted mainly of *cis*-1,4- and 3,4- units with head-to-tail linkage and had the 3,4- unit connected chiefly with the meso configuration⁶. As to the sequences of the *cis*-1,4- and 3,4-units, their assignment agreed with our results listed in Table 2, although the chemical shifts of the signals were slightly different. In their experiment a signal around 37 ppm was assigned to the central methylene carbon (C_4) in the dyad of the 3,4-unit. However, this signal should be assigned to the central methylene carbon in the meso dyad of the 3,4-unit as described before.

Distribution of *cis*-1,4-, *trans*-1,4- and 3,4-units in polyisoprenes

The fractions of the *cis*-1,4-, *trans*-1,4- and 3,4-units can be determined by using either the C_1 and C_3 signals or the C_5 signals of each unit. The fraction of *trans*-1,4-unit determined by the ^{13}C -n.m.r. spectrum using the C_1 and C_3 signals or the C_5 signals was always lower than one obtained by the ^1H -n.m.r. spectrum by 3 to 8%. This discrepancy may be explained by the difference of nuclear Overhauser enhancement or spin-lattice relaxation time among carbon atoms representing these isomeric units. In the case of *cis-trans* isomerized polyisoprene the fraction of the *trans*-1,4-unit determined from the C_1 carbon signal was almost identical with the one obtained from the ^1H -n.m.r. method, although the one determined from the C_5 signal showed a lower value⁸.

Approximate fractions of the dyad or triad sequences of the *cis*-1,4-, *trans*-1,4-, and 3,4-units were obtained using signals due to the C_1 and C_3 carbons using the following equations:

$$\text{cis-trans} = E/\Sigma$$

$$\text{trans-trans} = F/\Sigma$$

$$3,4\text{-trans} = H/\Sigma$$

$$\left. \begin{array}{l} \text{cis-cis} \\ \text{trans-cis} \end{array} \right\} = [J + K - (\text{trans-3,4})]/\Sigma = [J + K - N]/\Sigma$$

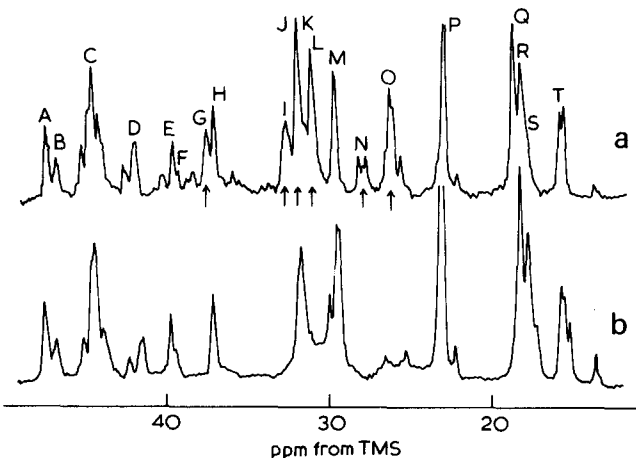


Figure 4 ^{13}C -n.m.r. spectra of (a) polyisoprene and (b) poly(isoprene-4,4- d_2) prepared with *n*-BuLi/ Et_2O catalyst

Table 3 Sequence distribution of *cis*-1,4, *trans*-1,4, and 3,4-units in n-BuLi/Et₂O polyisoprene

Sequence	BuLi/Et ₂ O							
	1/0		1/2.0		1/4.7		1/24	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
<i>cis-trans</i>	19.4	18.8	9.6	10.5	6.7	7.4	5.3	4.9
<i>trans-trans</i>			3.6	3.2	3.0	2.5	2.3	2.3
3,4- <i>trans</i>	0.0	0.6	4.6	4.1	6.2	6.0	7.6	8.0
<i>cis-cis</i>	72.0	74.6	46.9	45.6	29.6	28.8	16.7	15.4
<i>trans-cis</i>								
3,4- <i>cis</i>	5.2	2.6	12.2	13.6	16.7	17.5	15.7	17.0
<i>cis</i> -3,4-1,4			8.7	10.5	9.0	10.9	7.0	8.1
<i>trans</i> -3,4-1,4	3.4	3.2	4.4	3.2	4.8	3.7	5.2	3.8
1,4-3,4-3,4								
3,4-3,4-1,4	0.0	0.2	10.5	8.1	17.1	17.7	31.0	26.1
3,4-3,4-3,4	0.0	0.0	0.0	1.2	6.9	5.5	9.2	14.4

Calculated values were obtained on the assumption of a random distribution of the isomeric units using the fractions of these units from the relative intensities of C₁ and C₃ carbon signals

$$3,4\text{-}cis = M/\Sigma$$

$$cis\text{-}3,4\text{-}1,4 = A/\Sigma$$

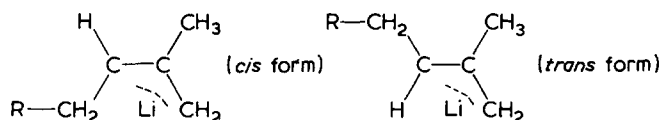
$$trans\text{-}3,4\text{-}1,4 = B/\Sigma$$

$$\left. \begin{array}{l} 1,4\text{-}3,4\text{-}3,4 \\ 3,4\text{-}3,4\text{-}1,4 \end{array} \right\} = C/\Sigma$$

$$3,4\text{-}3,4\text{-}3,4 = D/\Sigma$$

where $\Sigma = A + B + C + D + E + F + H + J + K + M - N$ and 1,4 = *cis* or *trans*. The results are listed in Table 3. The fractions of dyad or triad sequences of these isomeric units were calculated assuming a random distribution of these units using fractions of *cis*-1,4-, *trans*-1,4-, and 3,4-units obtained from the relative intensities of the C₁ and C₃ signals. The observed fractions were in good agreement with the calculated ones, which indicates that the *cis*-1,4-, *trans*-1,4-, and 3,4-units were distributed almost randomly in n-BuLi/Et₂O catalysed polyisoprenes.

From the results of Table 3 and from the ¹³C-n.m.r. study of hydrogenated polyisoprene⁶ it is concluded that *cis*-1,4-, *trans*-1,4-, and 3,4-units are randomly distributed exclusively with head-to-tail linkage in n-BuLi/Et₂O polyisoprenes. This indicates that the arrangement of head and tail is controlled by the living-end, while the structure of the terminal monomer unit is little affected by the structure of the penultimate monomer unit. Schué et al.^{13,14} and Morton et al.¹⁵ found by ¹H-n.m.r. study that the living-end of alkyl lithium catalysed polyisoprene took only two forms (*cis* and *trans*):



The formation of the 3,4-unit was interpreted by the relative electron negativity of the C₃ carbon in the living-end¹⁴ or 4,1-4,3 tautomeric system of the living-end¹⁵. They assumed that the terminal unit takes its final configuration when an adjacent monomer adds at the 1 or 3 position of the terminal lithium complex. Their proposed mechanism

was not concerned with the structural effect of the penultimate unit. Our results for sequence distribution will provide useful information to develop the study of the polymerization mechanism.

Randall¹⁶ analysed the ¹³C-n.m.r. spectra of hydrogenated polybutadiene and reported that the 1,4- and 1,2-units showed a slight alternate distribution in lithium catalysed polybutadiene. He attributed the small deviation from random distribution to a steric effect from a penultimate 1,2-unit. However, it is difficult to discuss small differences of the relative intensities of ¹³C-n.m.r. signals among different types of carbon atom.

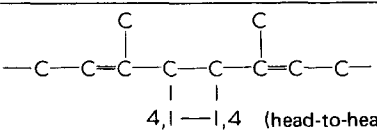
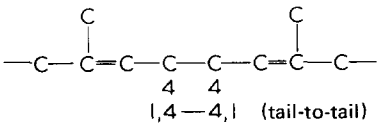
Signals due to head-to-head and tail-to-tail linkages

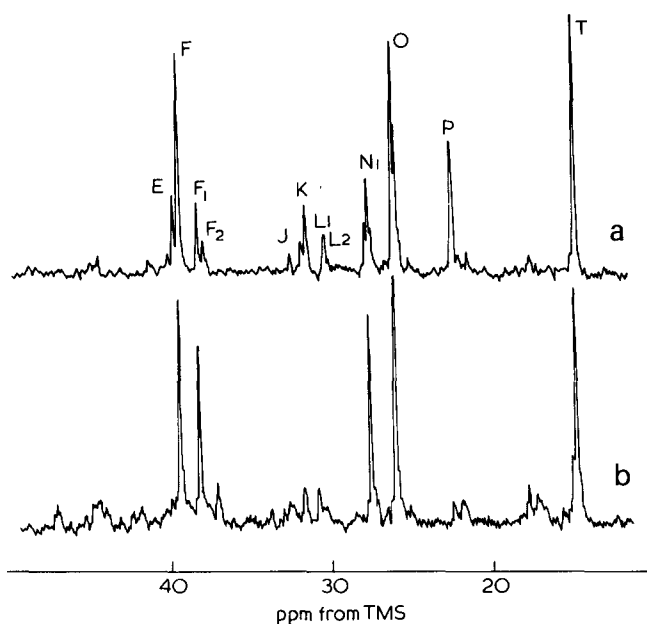
¹³C-n.m.r. spectra of polyisoprenes prepared with radical (emulsion polymerization) and Alfin catalysts are presented in Figure 5. Although radical polyisoprene contained only 7% of 3,4-unit, it exhibited strong signals around 38 ppm (F₁ and F₂), 31 ppm (L₁ and L₂), and 28 ppm (N₁), the chemical shifts of which were slightly different from those observed for n-BuLi/Et₂O polyisoprenes. These signals were thought to arise from carbons in the head-to-head (4,1-1,4) and tail-to-tail (1,4-4,1) linkages, because it was revealed that radical polyisoprene contained about 15% of both of the linkages⁶. Chemical shifts of the C₁ and C₄ carbons in these linkages were calculated using the same method as for n-BuLi/Et₂O polyisoprene. The newly appearing signals were assigned as shown in Table 4 by comparison of the observed and calculated chemical shifts, and also by considering the microstructure of this polymer, and the signal intensities. The observed chemical shifts showed close agreement with the calculated values, demonstrating the validity of the assignments. The ¹³C-n.m.r. spectrum of squalene also exhibited a signal at 28.5 ppm due to the central methylene carbon, which has a similar chemical environment to the C₄ carbon in the 1,4-4,1 linkage¹¹. This is additional evidence to support the signal assignments.

As shown in Figure 5b, Alfin polyisoprene also exhibited signals characteristic of the 4,1-1,4 and 1,4-4,1 linkages, indicating that this polymer also contained appreciable amount of these linkages. This result is consistent with the results of ¹³C-n.m.r. study of hydrogenated polyisoprene, which revealed that this polymer contained about 16% of the 4,1-1,4 and 12% of the 1,4-4,1 linkages⁶.

In the case of n-BuLi/Et₂O catalysed polyisoprenes sig-

Table 4 Signal assignments of head-to-head and tail-to-tail linkages

Linkage	Carbon atom	Signal	Sequence	Chemical shift (ppm)		
				Obs.	Calc.	Δ (ppm)
	C ₁	F ₂	<i>cis-trans</i>	38.22	36.64	1.58
		F ₁	<i>trans-trans</i>	38.51		1.87
		L ₁	<i>cis-cis</i>	30.67	29.02	1.65
		L ₂	<i>trans-cis</i>	30.94		1.92
	C ₄	N ₁		28.50	29.27	-0.77
				28.12	29.60	-1.48

Figure 5 ¹³C-n.m.r. spectra of (a) radical and (b) Alfin polyisoprenes

nals F₁, F₂, L₁, and L₂ were scarcely observed. It was difficult to detect signal N₁ in these polymers because this signal overlapped with the large signal N. The observed intensity of signal N was almost equal to the value expected from the amount of 3,4-*trans*-1,4 linkage, which indicates the absence of signal N₁ in the polymers. This finding implies that *n*-BuLi/Et₂O polyisoprenes contained a negligible amount of 4,1-1,4 and 1,4-4,1 linkages, which is consistent with the results obtained from the ¹³C-n.m.r. study of hydrogenated polyisoprene⁶.

Sequence distribution of 1,4-unit in radical and Alfin polyisoprene

On the basis of the signal assignments in Tables 2 and 4 the sequence distribution of the 1,4-unit in radical and Alfin polyisoprenes was determined using the following equations:

$$\begin{aligned}
 1,4-1,4 \text{ (cis-trans)} &= E/\Sigma \times 1,4\% \\
 \text{(trans-trans)} &= F/\Sigma \times 1,4\% \\
 \text{(cis-cis)} &= J/\Sigma \times 1,4\%
 \end{aligned}$$

Table 5 Sequence distribution of radical and Alfin polyisoprenes

Linkage	Radical PIP		Alfin PIP	
	Obs.	Calc.*	Obs.	Calc.†
1,4-1,4	<i>(cis-trans)</i>	12	11	32
	<i>(trans-trans)</i>	36	33	27
	<i>(cis-cis)</i>	4	4	7
	<i>(trans-cis)</i>	12	11	5
4,1-1,4	<i>(cis-trans)</i>	3	2	14
	<i>(trans-trans)</i>	7	7	10
	<i>(cis-cis)</i>	1	1	2
	<i>(trans-cis)</i>	3	2	2
1,4-4,1	14	14	11	8
3,4-1,4 (<i>trans</i>)	0	5	9	18

* Calculated values are obtained on the assumption of a random distribution of the isomeric units with head-to-tail (70% of 1,4-unit), head-to-head (15% of 1,4-unit), and tail-to-tail (15% of 1,4-unit) linkages.

† Calculated values are obtained on the assumption of a random distribution of the isomeric units with head-to-tail (72% of 1,4-unit), head-to-head (16% of 1,4-unit), and tail-to-tail (12% of 1,4-unit) linkages.

$$\begin{aligned}
 \text{(trans-cis)} &= K/\Sigma \times 1,4\% \\
 4,1-1,4 \text{ (cis-trans)} &= F_2/2\Sigma \times 1,4\% \\
 \text{(trans-trans)} &= F_1/2\Sigma \times 1,4\% \\
 \text{(cis-cis)} &= L_1/2\Sigma \times 1,4\% \\
 \text{(trans-cis)} &= L_2/2\Sigma \times 1,4\% \\
 1,4-4,1 &= N_1/2\Sigma \times 1,4\% \\
 3,4-1,4 \text{ (trans)} &= H/\Sigma \times 1,4\%
 \end{aligned}$$

where $\Sigma = E + F + J + K + H + 1/2(F_1 + F_2 + L_1 + L_2 + N_1)$
The results are presented in Table 5.

Each observed dyad fraction in radical polyisoprene was almost equal to the value calculated on the assumption that the *cis*-1,4-, *trans*-1,4-, and 3,4-units were randomly distributed and that 16% of both the *cis*-1,4- and *trans*-1,4-units was connected with head-to-head and tail-to-tail linkages. This result demonstrates that the *cis*-1,4 and *trans*-1,4 units were

randomly distributed along the polymer chain regardless of the head and tail arrangements. It is interesting that the random alignment of *cis*-1,4- and *trans*-1,4-units holds for head-to-tail and head-to-head linkages in radical polyisoprene.

In the case of Alfin polyisoprene it was difficult to determine the sequence distribution of *cis*-1,4- and *trans*-1,4-units because signals reflecting the sequences were not well resolved. However, it is clear that about 20% of the *cis*-1,4- and *trans*-1,4-units was combined with head-to-head linkage.

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