^{13}C n.m.r. determination of units formed by irregular addition in polyisoprene

A. S. Khatchaturov, E. R. Dolinskaya, L. K. Prozenko, E. L. Abramenko and V. A. Kormer
S. V. Lebedev All-Union Synthetic Rubber Research Institute, 198035, Leningrad, USSR

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^{13}C n.m.r. spectroscopic data obtained for model compounds imitating regular and irregular addition of monomer units in linear polyisoprene are compared with the chemical shifts calculated using the empirical regularities found for the branched alkanes and alkenes and a good correlation is established. The validity of the results obtained was confirmed by investigation of the carbon spectra of hydrogenated and unhydrogenated polyisoprenes which contain chain fragments with irregular addition of units. Samples of hydrogenated polyisoprene are shown to give resonance lines that correspond to the methylene carbons of head-to-head and tail-to-tail addition and show chemical shifts at 34.62 ppm and 27.61 ppm, respectively. For the unhydrogenated polyisoprenes, the methylene carbons of *trans*- and *cis*-units in head-to-head addition were found to absorb at 38.6 ppm and 31.4 ppm, respectively, with those in the tail-to-tail addition of both isomers absorbing at 28.4–28.8 ppm. The latter findings offer a practical means of characterizing irregularities in polyisoprenes.

INTRODUCTION

The structural parameters of the macromolecules of natural and synthetic rubbers can be characterized reasonably well by using spectroscopic techniques, in particular n.m.r. analysis. The amount of 3,4-units and the ratio of *cis–trans* isomers in the case of 1,4-addition are determined quite reliably from the proton n.m.r. spectra at frequencies above 250 MHz. Examination of the carbon n.m.r. spectra yields extensive, though not always quantitatively unambiguous, information about other more detailed structural parameters of polyisoprene, such as the presence of 1,4–3,4–1,4 and isomeric (*cis–trans*) diad sequencies[1,2].

There are also more subtle characteristics of the polymer chain microstructure, such as the regularity of asymmetrical monomer units addition in polymerization, i.e. the occurrence of 'regular' (head-to-tail), 'irregular' (head-to-head and tail-to-tail) types of addition.

There are some reasons to suggest that the polymer's properties are affected by these irregularities, which is why knowledge of the character and the percentage of disturbances will be helpful in an attempt to upgrade the structure and properties of a synthetic rubber. Up until now, no known spectroscopic method, apart from the indirect and not very reliable ozonolysis technique, could approach a solution of this difficult analytical problem.

It is the purpose of this work to detect the irregularities in the structure of synthetic polyisoprene rubbers by n.m.r. spectroscopic analysis. Even the latest developments of the n.m.r. technique provide no chance of success in proton spectra. It is only the carbon n.m.r. spectra, with their great range of chemical shifts, relatively narrow lines and high sensitivity of a spectral line position to the type of molecular surroundings for the given carbon atom, that provide a chance of detecting the separate lines corresponding to regular and irregular additions in macromolecule chain fractions.

Our research was carried out in three stages. We first tried to reveal respective lines in the carbon n.m.r. spectra of unsaturated polyisoprenes by calculating their position with the help of empirical regularities found for the ^{13}C n.m.r. spectra of branched alkanes and alkenes. The data obtained were then compared with the ^{13}C n.m.r. spectra of specially synthesized low molecular weight model compounds, and next with some specially prepared samples of polyisoprene–Alfin and radical known to contain an irregular addition in the chain. Finally, we compared the carbon n.m.r. spectra of the hydrogenated polyisoprenes and those simulated for polyalkanes with various amounts of methylene carbons bounded by tertiary carbon atoms in their chains.

Similar results obtained in all three studies contribute further to the validity of the above considerations.

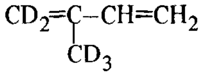
EXPERIMENTAL

Sample A of a low molecular weight polyisoprene was prepared using an Alfin catalyst[3].

Sample B of an oligomer of isoprene with molecular weight 2500–3000 was prepared by free radical polymerization using azo-compounds as initiators.

Sample C of a polyisoprene was synthesized with π-allylnickel iodide catalyst[4].

Deuterated isoprene



$$CD_2{=}\underset{\displaystyle CD_3}{\underset{|}{C}}{-}CH{=}CH_2$$

was synthesized[5] through the intermediate[6] 2-methyl-2-oxy-butene-3. Deuteroacetone-d_6 was used as a starting deuterated product.

Sample D of a deuterated oligomer of isoprene (~40 monomer units) was prepared using n-butyllithium in benzene solution.

All the polyisoprene samples were hydrogenated using *p*-toluene sulphonylhydrazine in *p*-xylene[7,8].

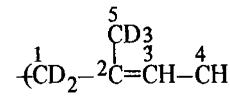
^{13}C n.m.r. spectra were obtained at room temperature using a Bruker HX-270 spectrometer operating at 67.88 MHz. Samples for the n.m.r. investigations were prepared as 20–30% w/v solutions in deuterochloroform and charged into 10 mm o.d. tubes. Stabilization was provided by using a deuteron signal. Spectra were taken in a pulse regime, the pulse spacing being 10–15 sec, and the number of scans being of the order of several hundreds or more. The spectrum region corresponding to 12 kHz was placed in an 8K computer store. The ^1H and ^2D n.m.r. spectra, which will be described below, were recorded at 270 MHz and 13.82 MHz.

The chemical shifts of the resonance lines due to all nuclei were measured on δ-scale relative to TMS.

RESULTS AND DISCUSSION

Assignment of ^{13}C n.m.r. methylene lines in polyisoprene

Natural rubber and gutta–percha were among the first polymers for which carbon n.m.r. spectra data were obtained[9]. At present these spectra are well studied, though the correctness of assignment of the methylene carbons C_1 and C_4 signals is questionable[10]. In this case it is impossible to make a distinction by selective proton decoupling, and other approaches do not give an unambiguous answer. Bearing in mind the ultimate goal of our work we think the proper assignment of all the signals in polyisoprene is a problem of primary importance. With this end in view we have carried out the asymmetrical deuteration and subsequent polymerization of isoprene monomer. This method is cheaper and more productive than that proposed in ref 10, i.e. the examination of the ^{13}C n.m.r. spectra of a ^{13}C-isotope-enriched rubber sample. As a result the low molecular weight polyisoprene D having the structure



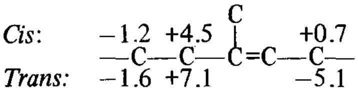
$$-\!\!(\overset{1}{C}D_2-{}^2\overset{\overset{5}{CD_3}}{\overset{|}{C}}=\overset{3}{C}H-\overset{4}{C}H_2)\!\!-_n$$

was obtained, with the protons at carbons C_1 and C_5 being substituted by deuterons. The validity of this structure determination was substantiated by ^1H (including a homonuclear double resonance) and ^2D n.m.r. spectra analyses of sample D[11]. The proton spectrum demonstrated the absence of a methyl group line as well as the half-intensity of a methylene group line. The deuteron spectrum of sample D[11] exhibited the presence of two lines at 1.6 and 2.1 ppm, with the intensity ratio close to the relative numbers of deuterium atoms. An undeuterated polyisoprene sample was prepared under the same conditions as were used for D. As evidenced by its proton spectrum, the polymer contained about 10% 3,4-units, with the *cis–trans* ratio for the 1,4-units being 65/35.

Unambiguous assignment of the methylene carbons C_1 and C_4 signals has been performed using the proton-decoupled ^{13}C n.m.r. spectrum of D (*Figure 1*). Under these experimental conditions the proton-carrying carbons are free from interaction with their protons and their signals are of singlet character. As for the deuteron-carrying carbons, they keep interacting with the deuterons, so their absorption lines appear as typical multiplets: a triplet for $=CD-$, a quintet for $-CD_2-$, and a septet for $-CD_3$. The spectrum clearly shows that for the *cis*-isomer a singlet at 26.45 ppm is due to the methylene carbon C_4, a multiplet at 32.0 ppm to the methylene carbon C_1 and a septet in the vicinity of 22.5 ppm to the deuteromethyl carbon C_5. The respective lines for the *trans*-isomer are observed at 26.6 ppm, 39.5 ppm and 15.3 ppm. The spectrum shows also the lines corresponding to 3,4 units: the multiplets for C_1 and C_5 at 111 ppm and 18 ppm, respectively, and the singlets for C_2, C_3 and C_4 at 147.5, 48 and 31 ppm, respectively. Consequently, the doubts expressed in ref 10 are not confirmed experimentally.

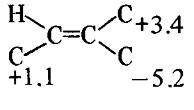
Identification of carbon resonance lines corresponding to polyisoprene chain fragments having irregular additions

Searching for the ^{13}C n.m.r. lines corresponding to the chain fragments having head-to-head and tail-to-tail monomer additions requires the localization of the potential spectral regions for a carbon of each type. To this end we have utilized the regularities found empirically for the carbon n.m.r. spectra of substituted alkenes[12]. We have used two approaches[13]. The first included the estimation of the effect of methyl substitution on the position of resonance lines (deviation in ppm) of the β and γ carbons in alkenes:



This estimation was made on the basis of comparison data between the ^{13}C n.m.r. spectra of 2-hexene and 2-heptene and those of the 3- and 2-methyl derivatives of both these compounds. To ascertain the applicability of these parameters for the polymers, we have calculated the spectra of *cis-* and *trans*-polyisoprenes from the respective spectra of polybutadiene. The discrepancy between the observed and calculated values was not more than ±0.5 ppm. This permitted the chemical shifts of methylene carbons C_1 in the chain fraction having approaching methyl groups (head-to-head addition) and of methylene carbons C_4 in the fraction with remote methyl groups (tail-to-tail addition) to be calculated on the basis of the same ^{13}C n.m.r. spectrum of polybutadiene. We obtained the values 30.8 ppm (*cis*-unit) and 39.4 ppm (*trans*-unit) for carbons C_1 and about 28.0 ppm (both isomers) for carbons C_4.

In another approach[13] the branched polyalkanes having an adequate number of methylene groups (2, 3 or 4) between the tertiary carbons were taken as the basis for consideration. The ^{13}C n.m.r. spectra of these alkanes are known from experimental data and can be calculated using the additive spectral parameters of chemical shifts[14,15]. Then double bonds are 'introduced' into these polyalkanes to estimate the change in the methylene carbon chemical shifts. For this purpose the data on shifts of resonance lines of saturated carbons in 1,2,2-trisubstituted alkenes relative to those of respective alkanes were used[12]:



The applicability of these alkenation parameters for polymers can be checked by 'calculating' the carbon spectra

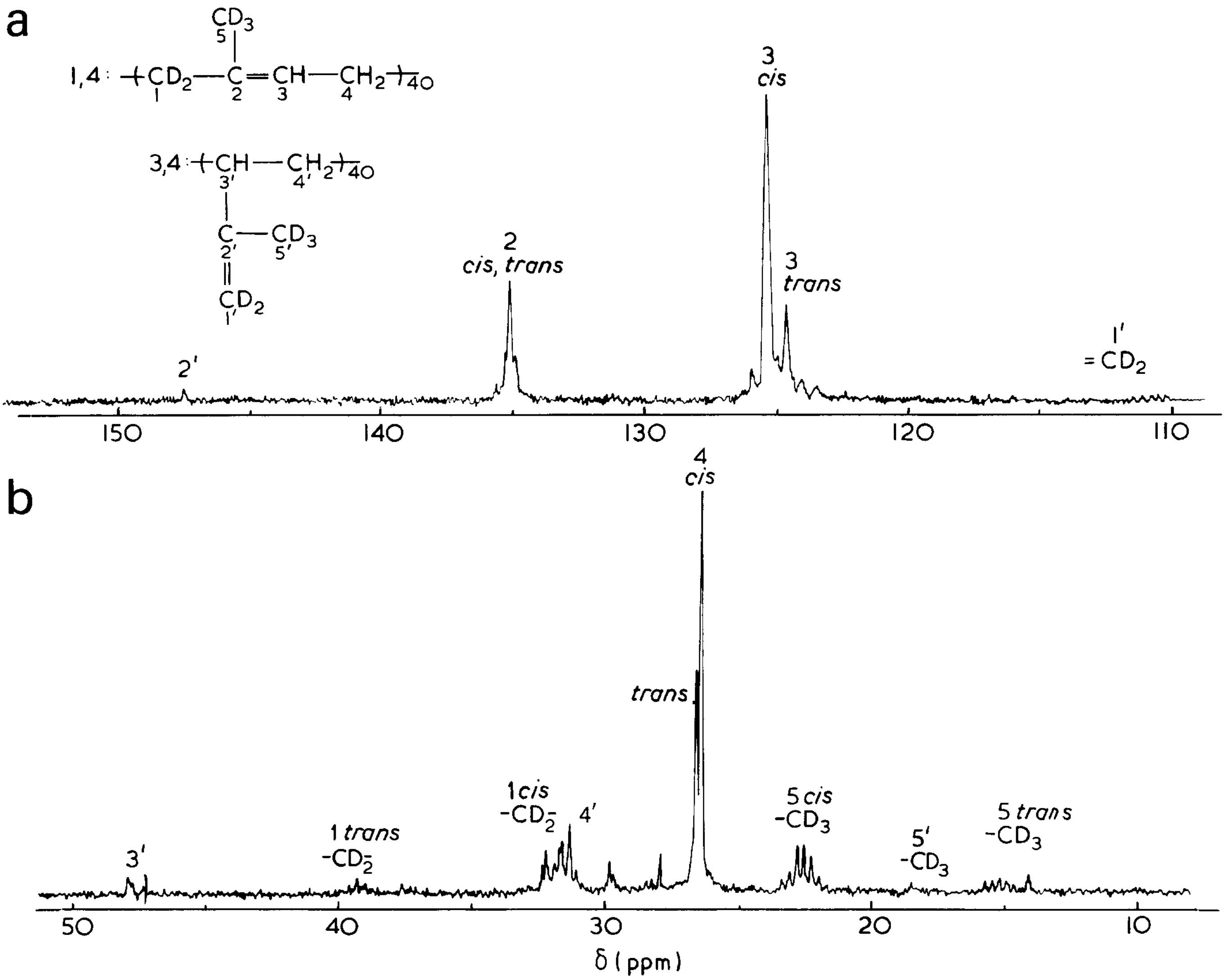
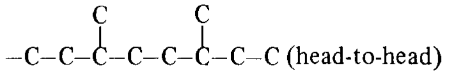


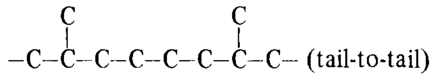
Figure 1 ^{13}C n.m.r. spectrum (67.88 MHz) with proton decoupling of polyisoprene-d_5 $(\text{–}CD_2\text{–}\underset{\underset{CD_3}{|}}{C}\text{=}CH\text{–}CH_2\text{–})_n$ in $CDCl_3$ at room temperature. (a) olefinic region; (b) the aliphatic region. Figures denote the assignment of lines to carbons in 1,4-monomer units (figures with primes denote carbons in 3,4-units)

of *cis*- and *trans*-polyisoprene from the spectrum of polyalkane, wherein every fourth carbon atom in a macromolecule chain is a tertiary one. The obtained values of chemical shifts for carbons C_1 and C_4 in *cis*- and *trans*-isomers closely resemble those found experimentally. For this reason the above correction parameters of alkenation were applied to the polyalkanes of the type:



$$\text{–C–C–}\overset{\overset{C}{|}}{C}\text{–C–C–}\overset{\overset{C}{|}}{C}\text{–C–C (head-to-head)}$$

and



$$\text{–C–}\overset{\overset{C}{|}}{C}\text{–C–C–C–C–}\overset{\overset{C}{|}}{C}\text{–C– (tail-to-tail)}$$

As a result, the chemical shifts were calculated to be at 30.0 ppm (*cis*-unit) and 38.4 ppm (*trans*-unit) for carbon C_1 in head-to-head addition and at about 28.4 ppm (for both isomers) for carbon C_4 in tail-to-tail addition.

In our opinion, the second approach is more valid because it is based on more reliable starting data on chemical shifts for polyalkanes and the parameters of alkenation.

This implies that the data obtained in both approaches are fairly close to each other, which further contributes to their reliability. Hence the lines characterizing head-to-head addition are to be searched for in the vicinity of 30.0 ± 1.0 ppm (for a *cis*-isomer) and of 38.4 ± 1.0 ppm (for a *trans*-isomer), while those characterizing tail-to-tail addition in the region of 28.4 ± 0.5 ppm for both isomers.

Model compounds

In a previous paper[16] several low molecular weight compounds modelling various types of addition of isoprene units are described. *Figure 2a–d* depicts the alkyl parts of ^{13}C n.m.r. spectra of 4,7-dimethyldecadiene-3,7 (I), squalene (II), 2,6,11,15-tetramethylhexadecatetraene-2,6,10,14-d_{12} (diheranyl) (III) and 4,8-dimethyldodecadiene-4,8 (IV). The preparation of these compounds and the assignment of all intensive lines are reported in ref 16. We shall deal here exclusively with the signals of carbon atoms from

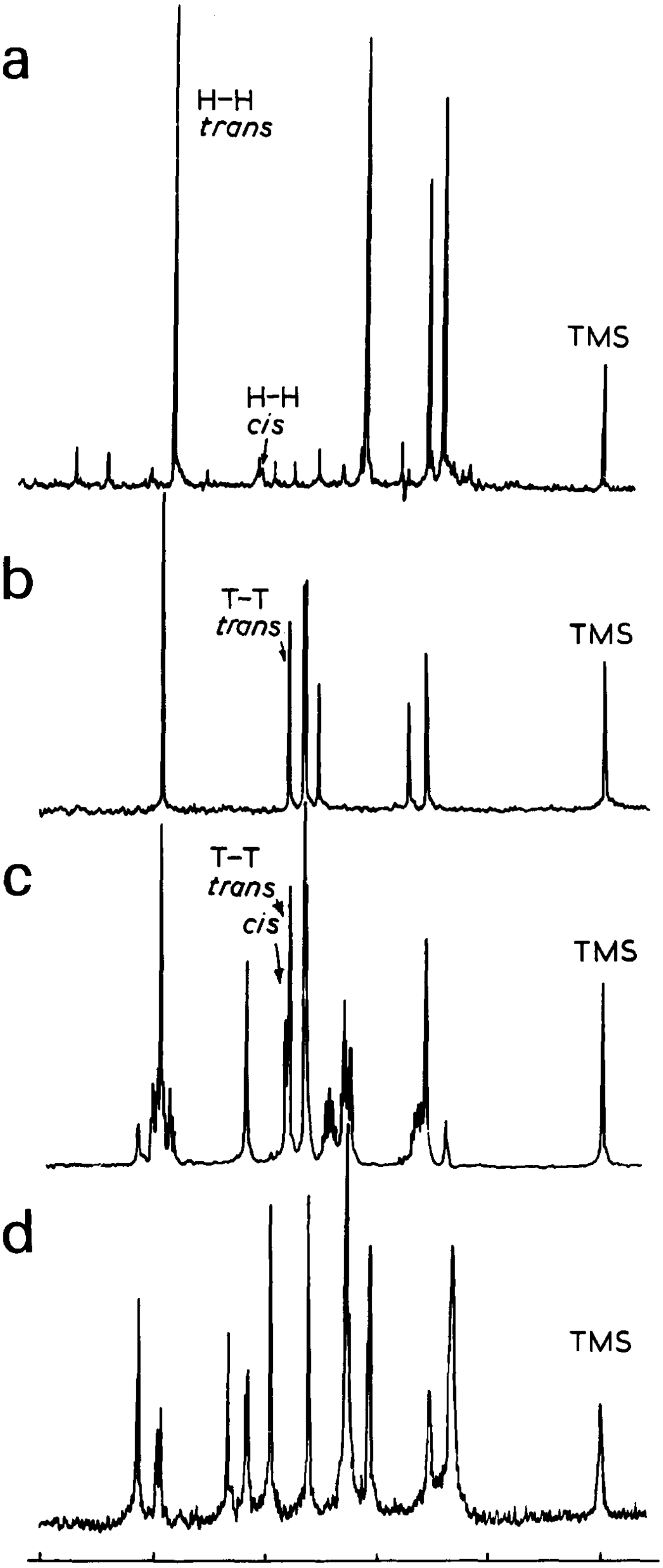


Figure 2 Aliphatic part of ^{13}C n.m.r. spectra with proton decoupling of model compounds (a) I, (b) II, (c) III and (d) IV (see text) in $CDCl_3$. Content of *trans*-isomer for compound I is 90%, for compound II 100%, for compound III 66%, and for compound IV 55%

those parts of the molecules where head-to-head and tail-to-tail addition are imitated.

The only model of head-to-head addition is represented by compound I (*Figure 2a*). The line corresponding to the carbons C_1 in a *trans–trans* linkage (in I these are carbons 5 and 6) appears at 38.64 ppm. As evidenced by the proton n.m.r. spectrum of compound I [16], it consists practically entirely of *trans*-isomers. At the same time, however, the presence of a slight amount of *cis*-isomer should not be overlooked; according to the data in ref 13, an absorption line corresponding to the carbon C_1 of a *cis*-isomer in head-to-head addition might be in the vicinity of 31.5 ppm. The intensity of this line should be nearly one order lower than that of a line at 38.64 ppm.

Tail-to-tail addition is modelled in two compounds: the well known squalene (II, *Figure 2b*) (pure *trans*-isomer) and in diheranyl (III, *Figure 2c*) (*trans*- and *cis*-isomer mixture with the ratio ~60/40). In squalene the carbon of the tail-to-tail addition resonates at 28.42 ppm, while that in diheranyl gives in the same region two absorption lines, at 28.22 ppm and 28.47 ppm. These two lines may be assigned to the *trans*- and *cis*-isomers, respectively.

Compound IV in *Figure 2d* does not contain methylene fractions of the tail-to-tail or head-to-head types. Note that the regions from 27.5 to 30 ppm and from 34 to 40 ppm are free from absorption lines.

In this way, the examination of ^{13}C n.m.r. spectra of the model compounds yields practical values of chemical shifts for the lines which correspond to methylene carbons in head-to-head addition, 38.6 ppm (linkage of *trans–trans* isomers) and 31.5 ppm (linkage of *cis–cis* isomers), as well as for those in tail-to-tail addition, 28.5 ppm and 28.7 ppm (apparently, linkages of *trans–trans* and *cis–cis* isomers) in the low molecular weight compounds. These findings are exactly consistent with the conclusions in ref 13 concerning the arrangement of the absorption lines of methylene carbons in irregular addition of monomer units.

^{13}C n.m.r. spectra of hydrogenated polyisoprene

Hydrogenated polyisoprene of a regular structure (i.e. with head-to-tail addition of monomer units) represents a set composed of regular, repeating sequences of three methylene carbons bounded by tertiary carbons each bearing methyl groups. Chemical shifts of the methylene carbon lines in ^{13}C n.m.r. spectra of branched alkanes are very sensitive to their position with respect to the point of branching. There exist good empirical relationships allowing the position of these absorption lines in the ^{13}C spectrum to be calculated with sufficient accuracy[14,15]. These regularities have already been utilized to advantage for the structural characterization of ethylene–propylene and alternating butadiene–propylene copolymers[17,18]. Using the additive parameters of substitution one can calculate the positions of resonance lines corresponding to all the types of isoprene unit addition. Application of this method to the investigation of a regular polyalkane, wherein every fourth carbon in a chain is a tertiary one, yields the chemical shift at 37.16 ppm for the carbons nearest to the point of branching, and that at 24.58 ppm for those in a middle position. These results closely resemble the experimental data[1,19]. So, in view of the possibility of predicting unambiguously the proper position of methylene carbon absorption lines with this method, it should be regarded as quite helpful also for determining the fragments of chains having irregular addition of monomer units in polyisoprene. The number of methylene carbons in between the tertiary carbons in these fragments in hydrogenated polyisoprenes may be either two (head-to-head addition) or four (tail-to-tail addition).

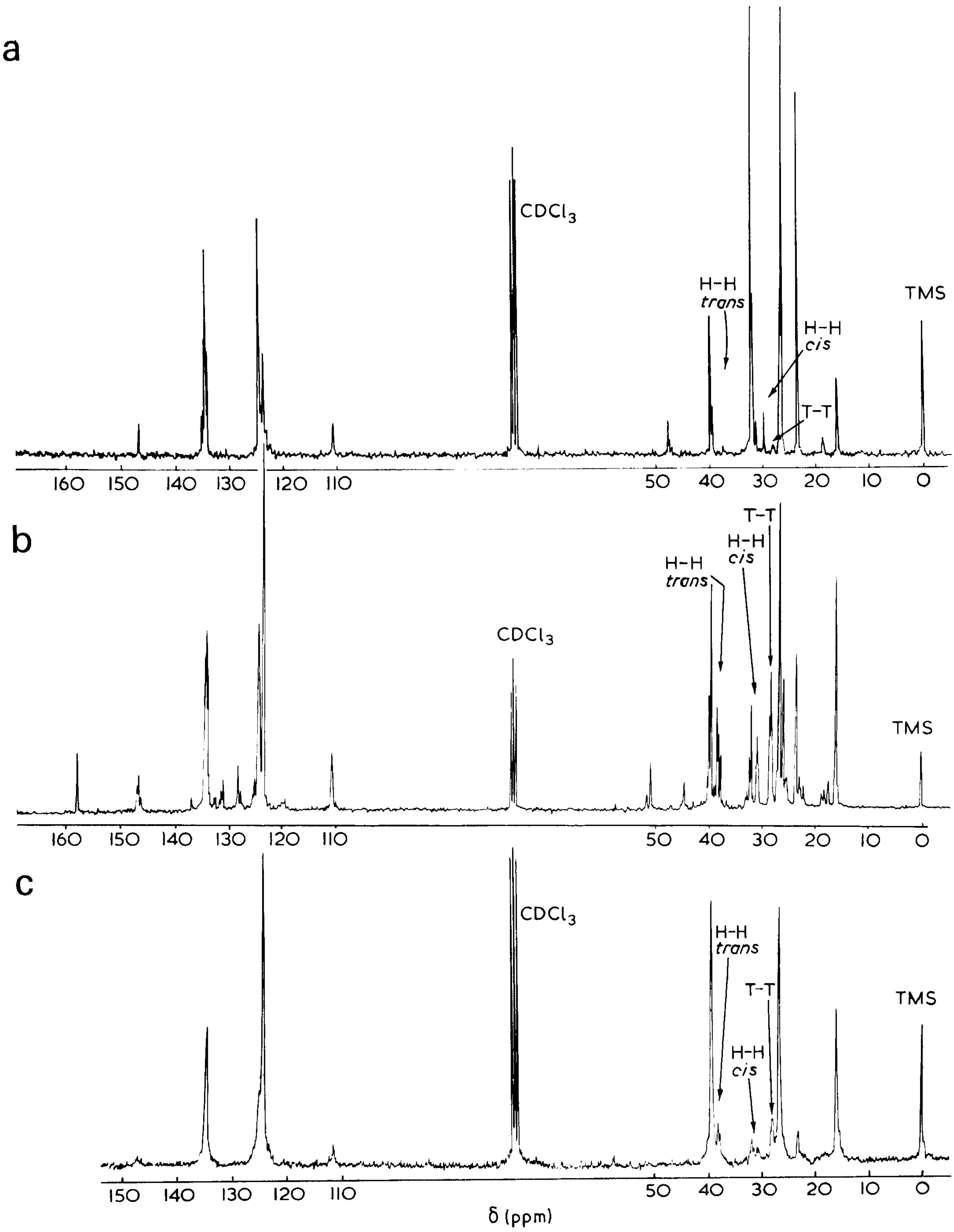


Figure 3 ^{13}C n.m.r. spectra of irregular rubbers in CDCl$_3$. (a) sample A; (b) sample B; (c) sample C. *Cis/trans* isomer ratio for sample A is 4, for sample B is 1/3 and for sample C is 1/9

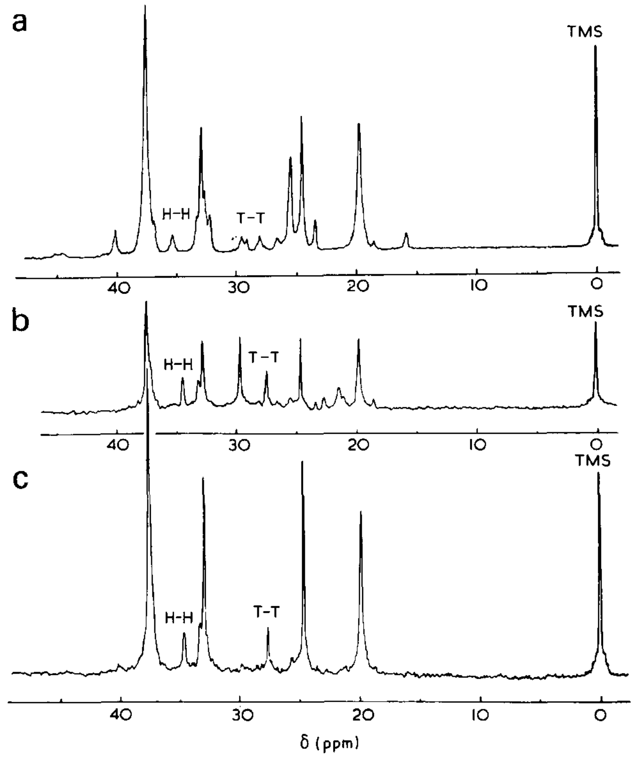


Figure 4 Aliphatic part of ^{13}C n.m.r. spectra of hydrogenated samples: (a) A; (b) B; (c) C. Solutions in $CDCl_3$

Calculation performed for the fragments having the head-to-head type of addition by using the additive parameters of substitution described above gives the chemical shifts of two equivalent methylene carbons at 34.22 ppm. In the fragments having tail-to-tail addition the methylene carbons nearest to the point of branching should absorb at 36.91 ppm (practically overlapping the similar carbon lines in the spectrum of a regular hydrogenated polyisoprene), with the central carbons absorbing at 27.27 ppm. So the lines at 34.22 ppm and 27.27 ppm should be treated as being representative of the fragments having head-to-head and tail-to-tail addition, respectively.

Certainly, in the spectrum of a hydrogenated polymer, any information about the isomeric structure of a macromolecule is obscured.

Carbon spectra of polyisoprene

To check the data we searched for the lines corresponding to the fragments having irregular addition of monomer units in the ^{13}C n.m.r. spectra of some polyisoprenes and their hydrogenated analogues. The samples used were some inverted monomer units (prepared with the help of allylnickel iodide or Alfin catalyst systems or using azo-initiators), and also those having a regular structure (natural and synthetic cis-1,4-polyisoprene). *Figure 3* demonstrates the ^{13}C n.m.r. spectra of irregular rubbers, the samples A, B and C.

The spectra of the respective hydrogenated analogues are illustrated in *Figure 4*. Spectra of regular polymers are not shown because they contain practically no lines assigned to the fragments of irregular addition.

It is evident from *Figure 4c* that the ^{13}C n.m.r. spectrum of hydrogenated sample C contains lines at 27.64 and 34.64 ppm, which correspond to the methylene carbons of the fragments having tail-to-tail and head-to-head addition. The peaks account for nearly 17 and 19%, respectively, of the specific area of a single carbon, i.e. they correspond to the percentage of monomer units involved in irregular addition. Since each addition involves carbons of two monomer units, the above percentages account for 8.5 and 9.5%, respectively, of the irregular tail-to-tail and head-to-head additions. The spectrum of unhydrogenated sample C (*Figure 3c*), roughly 90% of which is accounted for as *trans*-isomer, exhibits the presence of a strong line at 28.38 ppm (tail-to-tail addition, *trans*- and *cis*-isomers), a weaker line at 38.68 ppm (head-to-head addition, *trans*-isomer) and even weaker lines at 31.2 and 31.0 ppm (head-to-head addition, *cis*-isomer). The areas of these lines account for nearly 16, 13 and 4% of the specific area of a single carbon, i.e. correspond to 8, 6.6 and 2% tail-to-tail and *trans*- and *cis*-isomers head-to-head addition.

Also, in the ^{13}C n.m.r. spectrum of hydrogenated polyisoprene sample B (*Figure 4b*) there are lines corresponding to the irregular additions, at 27.61 ppm and 34.62 ppm. Their areas make up nearly 23 and 21% of the area of a single carbon, corresponding to 11.5 and 10.5% of the irregular tail-to-tail and head-to-head types of addition. The spectrum of this unhydrogenated polymer B (*Figure 3b*), roughly 75% of which is accounted for as *trans*-isomer, is rich in lines due to the presence of a variety of types of isoprene unit additions (including non-linear ones) typical of the radical polymer. In the spectrum region corresponding to tail-to-tail addition one can observe two overlapping lines at about 28.55 and 28.34 ppm (*cis*- and *trans*-isomers). Lines at 37.85, 38.29 and 38.55 ppm (*trans*-isomer) and two lines near 30.92 ppm (*cis*-isomer) correspond to head-to-head addition. The relative intensities of these three groups of lines account for roughly 26, 14 and 13% of the specific intensity of one carbon line, corresponding to 13, 7 and 6.5% tail-to-tail, and *trans*- and *cis*-isomer head-to-head addition. The line splitting is caused not only by the presence of non-linear chain fragments but also by the presence of both *trans*- and *cis*-isomers in the irregular additions.

In the ^{13}C n.m.r. spectrum of hydrogenated polymer A (*Figure 4a*) the lines corresponding to macromolecule chain fragments with irregular addition appear slightly downfield – at 27.9 ppm (tail-to-tail) and 35.2 ppm (head-to-head) – accounting for nearly 10 and 11% of the area of specific carbon, i.e. for 5 and 5.5% of the irregular tail-to-tail and head-to-head addition.

The spectrum also involves other strong lines, probably due to the combination of linear and branched fragments in a polymer chain, which of course distort the area ratios.

The spectrum of the unhydrogenated sample A (*Figure 3a*), whose *trans*/*cis*-isomer ratio is about 1/4, shows a rather weak line at nearly 28.5 ppm (tail-to-tail addition), a very weak line at ~38.6 ppm (head-to-head addition, *trans*-isomer), and also a line at 31.42 ppm (head-to-head addition, *cis*-isomer). The intensities of these lines are comparatively low, and account for 8, ~1 and 7%, respectively, of the specific carbon intensity, i.e. for only 4 and 3.5% of the tail-to-tail and *cis*-isomer head-to-head types of addition.

On the whole, the spectrum of sample A differs markedly from those of samples B and C, which may well be attributed to the more regular chain of the former.

According to our data, the ^{13}C n.m.r. spectra of hydrogenated and unhydrogenated samples of regular rubbers – natural and synthetic polyisoprenes – do not show any detectable lines corresponding to irregular addition units.

Table 1 ^{13}C n.m.r. line positions of methylene carbons in model compounds and polyisoprenes in the chain fragments with irregular units additions.

	Chemical shifts (in ppm from TMS)			
	Head-to-head		Tail-to-tail	
Compound	*Cis*	*Trans*	*Cis*	*Trans*
Calculated models: I	30.8	39.4	28.0	
II	30.0	38.4	28.4	
Model compounds:				
I 90% *trans*	31.5	38.64	–	–
II 100% *trans*	–	–	–	28.42
III 66% *trans*	–	–	28.77	28.51
Polyisoprene sample A: *cis/trans* = 4	31.43 (29.93)	38.5	28.5	
Polyisoprene sample B: *cis/trans* = 1/3	30.92	~38.3	28.55	28.34
Polyisoprene sample C: *cis/trans* = 1/9	31.1	38.68		28.38
Calculation for hydrogenated polyisoprene chain	34.22		27.27	
Hydrogenated radical polyisoprene	34.62		27.61	

CONCLUSIONS

This work has not been aimed at the quantitative analysis of the content of polyisoprene chain fragments having irregular unit addition. Our intention was to determine the potential regions of chemical shifts of the carbon resonance lines corresponding to these structures using model compounds and empirical spectral regularities, and next, on the basis of these findings, to detect the pertinent lines in the spectra of samples which were known beforehand to contain inverted chain fragments. The results of our investigations are reasonably concordant (*Table 1*). So we suggest that, to analyse polyisoprene for irregularity of the addition of the monomer units, it is possible to use both hydrogenated samples, giving lines at 34.6 ppm and 27.6 ppm representative of head-to-head and tail-to-tail addition respectively, and unhydrogenated ones.

By using unhydrogenated samples we avoid the additional difficult procedure of hydrogenation and retain information concerning the isomeric structure of a polymer.

Comparison between the data obtained allows one to conclude that, in the ^{13}C n.m.r. spectra of unhydrogenated polyisoprenes, the methylene carbon lines corresponding to the fragments having irregular additions of the tail-to-tail type should appear at about 28.5 ppm (for both isomers), while those corresponding to the fragments of the head-to-head irregular addition type should be at nearly 31.4 ppm (for the *cis*-isomer) and at 38.6 ppm (for the *trans*-isomer). The deviation found for the first value does not exceed ±0.5 ppm, while that found for the two others is within ±1 ppm.

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