NMR STUDY OF THE STRUCTURE
OF CATIONICALLY POLYMERIZED POLYISOPRENE

E.Drahorádová[a], D.Doskočilová[b] and B.Matyska[a]

[a]Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2, and
[b]Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6

Dedicated to the 65th anniversary of the late Academician R. Brdička.

The structure of cyclopolyisoprenes, the products of cationic polymerization of isoprene, has been studied by NMR. The cyclopolymerization process can be roughly characterized by the determination of the relative amount of olefinic protons. From the relative amounts of different types of double bonds in the polymer, the average length of cyclic segments can be estimated. The cyclic segments contain a large amount of methyl groups bound on saturated carbon atoms, and on the basis of this finding their structure is discussed.

Polymerization of isoprene catalyzed by Lewis or Brönsted acids leads to the formation of polymers the properties of which differ considerably from those of conventional rubberlike dienes like natural rubber, balata, 3,4-polyisoprene etc[1]. Infrared spectra of these polymers exhibit only weak traces of bands characteristic of monomer units added in 1,4; 3,4 or 1,2 position[2]. An important property of these polymers is the reduced content of double bonds as compared with e.g. natural rubber and other polyisoprenes. According to the conditions of polymerization, it varies between 10 to 50% of the value found in the linear forms[3]. The great reduction of the content of double bonds indicates the formation of cycles in the polymer chain. The molecular weights of cyclopolyisoprenes can be easily modified by reaction conditions and range from 136 (dimer) to several milion.

The actual structure of these products of cationic polymerization (cyclopolymers) has not been proved explicitly, and it can differ according to the conditions of polymerization. The differences concern especially the content of linear forms of addition, the number of cycles in one sequence, the number and position of substituents, of residual double bonds and probably also the size of the cycles. Such a polyisoprene must always be regarded as a copolymer with alternating linear and cyclic sequences of various length.

The characterization of cyclopolyisoprenes has so far been based only on the determination of residual double bonds by the ICl method and further on data concerning the amount of monomer units added in the 1,4-cis and trans, 1,2- and 3,4-positions as obtained from infrared spectra[4]. Infrared data about the content of linear forms are, however, useful only for comparison purposes[5]. Several attempts at a more detailed characterization of the products of cationic polymerization have been described[6–8].

An indirect evidence of the cyclic structure of acid catalyzed polyisoprene is provided by

a comparison of its infrared spectra with those of cyclized natural rubber, balata and synthetic 3,4-polyisoprene. The physical properties (solubility, density, infrared spectra) of all cyclization products are very close to the properties of polymers obtained by cationic polymerization[9].

NMR spectroscopy has so far not been applied to the study of the structure of cyclopolyisoprene. However, there exist a number of NMR studies of cyclized polydienes[10-18]. Cyclized polyisoprenes[17,18] were found to be formed by condensed six-membered rings joined either by methylene groups or by linear isoprene units with the average number of cycles in one cyclic segment between two and three.

As infrared spectra of cycloisoprenes can yield only rather inaccurate data about the content of cyclic structures in various samples, and in no case can any information be obtained from them about the length and type of cyclic segments, we have attempted to apply NMR spectroscopy to the solution of this problem. From NMR spectra measured at 60 and 80 Mc sufficiently detailed information could not be obtained, and for this reason the results of this work are based mainly on the analysis of 220 Mc spectra of three representative samples of cyclopolyisoprene, selected according to 60 Mc NMR spectra, infrared spectra and molecular weight. To aid in the interpretation of polymer spectra, 220 Mc spectra of two different mixtures of cyclic isoprene dimers prepared under similar conditions as one of the studied polymers, and the spectrum of limonene were also measured.

EXPERIMENTAL

Polymerization conditions and general characterization of the studied polymer samples are summarized in Table I and of the oligomer samples in Table II.

The content of units added in 1,4-position was determined from the intensity of the infrared band at 840 cm^{-1}. This band corresponds to the $=$C—H vibration of both the *cis* and *trans* forms of the —C$=$CH— group, with different absorption coefficients in each form[20]. In Table I, values calculated with the coefficients of the *trans* form are given. Values calculated with the coefficients of the *cis* form are shown in parentheses. The contents of units added in position 3,4 and 1,2 were determined from the intensities of bands at 888 and 910 cm^{-1} (*cf.*[20]).

NMR spectra were measured on the spectrometers Jeol 3-60 at 60 Mc, Tesla BS 487 at 80 Mc and on the spectrometer Varian HR 220 at 220 Mc. 10% solutions of the oligomers or polymers in CCl$_4$ with hexamethyldisiloxan as internal standard were used for the measurement. All spectra were scanned at room temperature.

Infrared spectra were measured on the Zeiss UR 10 spectrometer by the KBr pellet technique.

RESULTS

NMR Spectra

NMR spectra of two mixtures of dimers of different composition, of one mixture of trimers measured at 80 Mc, and of one cyclopolymer measured at 60 Mc are shown in Fig. 1. In all these spectra two groups of bands are distinctly separated:

the bands of apliphatic protons in the range $9.5-7.6\tau$ and the bands of olefinic protons in the range $5.5-4.6\tau$. The spectrum of the polymer similarly as the spectrum of the mixture of trimers and one mixture of dimers exhibit a very prominent band of protons in CH_3—$\overset{|}{\underset{|}{C}}$— groups at τ 9·1, indicating the presence of cycles[10-19]. From the spectrum of cyclopolyisoprene the content of olefinic protons can be determined very precisely, and it is found to be much lower than in linear polyisoprene, as expected in a polymer with a high content of cyclic structures. The spectra of the mixtures of dimers contain a large number of bands due to the presence of several

TABLE I

Polymerization Conditions and Properties of the Cyclopolyisoprene Samples[a]

Condition	Sample		
	I	II	III
Polymerization: Catalyst	H_2SO_4	$TiCl_4$ + t-BuCl	$TiCl_4$ + t-BuCl
Conc. of catalyst mol. l^{-1}	$3.3 . 10^{-2}$	$1.7 . 10^{-3}$ + $1.5 . 10^{-3}$	$5 . 10^{-3}$ + + $5 . 10^{-3}$
Conc. of isoprene mol. l^{-1}	1·3	1·7	2·0
Polymerization time, min	60	75	180
Mol. w.	400—600	$2.5 . 10^5$	$1.2 . 10^6$
[η] (toluene 25°C) dl. g^{-1}	—	0·05	0·06
Content of C=C (%) (see[b])	40	60	30
Content of 1,4-trans addition (%) (IR) (see[c])	cannot be determined	74.5 (17)	18 (4)
Content of 1,2 + 3,4 (%) (IR)	cannot be determined	2·9 (0·9 + 2)	0·7

[a] Polymerized at $T = 25°C$ in CH_2Cl_2; [b] Determined by the ICl method; [c] Contents of the 1,4-trans-addition was calculated under the assumption that cis-forms were completly absent. Figures in parentheses represent the contents of the 1,4-cis addition assuming analogically that no trans-units were formed.

different compounds. Analogous bands appear also in the mixture of trimers and probably also in the polymer, indicating a similar structural composition in the series. In the polymer, of course, the bands are broader and can no longer be resolved. Detailed interpretation of the 60 and 80 Mc spectra even of the dimers is not possible because of serious band overlapping.

220 Mc NMR spectra of limonene and of both above mentioned mixtures of dimers are shown in Fig. 2. In agreement with previous results[21,22] the lines in the spectrum of limonene are interpreted as follows: τ 8·37 as methyl protons in the group CH_3—C=C—, τ 8·29 as methyl protons in the group CH_3—C=CH_2, τ 8·05 as —CH_2—C=, τ 5·33 as CH_2=C— and τ 4·66 as —CH=C—. In the spectra of the mixtures of dimers, the appearance of three methyl doublets (τ 9·03, 9·00 and 8·78) indicates the presence of at least three further components with three different types of methyl groups bound to saturated carbon atoms, in addition to limonene. The doublets at τ 9·03 and 9·00 can be interpreted as isopropyl groups in gama and beta position with respect to a ring double bond[23], and the third as a methyl group bound directly to the ring in beta position to a double bond[24,25]. In addition to the bands appearing in limonene in the range of olefinic protons, the mixtures of dimers exhibit a further band at τ 4·75 corresponding probably to a different type of monosubstituted

TABLE II

Conditions of Preparation and Properties of Low Molecular Weight Isoprene Oligomers[a]

Condition	Sample		
	IV	V	VI
Conc. of isoprene mol/l	2·5	2·9	2·9
Polymerization time min	180	60	60
Mol. w.[b]	136	136	—
Content of C=C (%) (ICl)	—	80	60
B.p.[c]	35—68°C at 20 mm Hg	up to 30°C at 10 mm Hg	75—90°C at 10 mm Hg

[a] Concentration of polymerization catalyst (H_2SO_4) was $1·12 . 10^{-2}$ mol . 1^{-1}, reaction medium CH_2Cl_2. [b] As determined by mass spectroscopy, samples IV and V contain predominantly dimers with traces of trimers, sample VI predominantly trimers with some higher oligomers. [c] Polymerization product distilled under reduced pressure; the studied samples represent fractions boiling in the range indicated.

ring double bond, and a band at τ 4·49 corresponding to a double bond of type —CH=CH—.

220 Mc spectra of three typical cyclopolymer samples are shown in Fig. 3. These spectra were interpreted on the basis of an analysis of NMR spectra of linear poly-isoprenes, by comparison with 220 Mc NMR spectra of cyclic dimers, and in agreement with a number of references[10-18,23,26-28]. The spectra of cyclopolymers are quite complicated, but in spite of this, some prominent bands appear in the range of aliphatic protons: the band at τ 9·09 corresponding to methyl groups bound to a saturated carbon atom, the band at τ 8·42 corresponding to groups CH_3—$\overset{\mid}{C}$=$\overset{\mid}{C}$— and the band at τ 8·06 corresponding to groups —CH_2—$\overset{\mid}{C}$=$\overset{\mid}{C}$—. In the range of olefinic protons there appear three partially overlapping bands corresponding to three types of olefinic protons: the band at τ 5·35 corresponds to CH_2=$\overset{\mid}{C}$— groups which can appear in isopropenyl or exomethylene groups in cyclic segments, or in isopropenyl
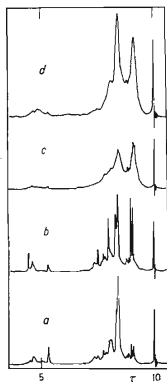

FIG. 1

NMR Spectra

a,b 80 Mc NMR spectra of two mixtures, *IV* and *V* of cyclic isoprene dimers; *c* 80 Mc NMR spectrum of a mixture of cyclic trimers; *d* 60 Mc NMR spectrum of cyclopolyisoprene *I*.
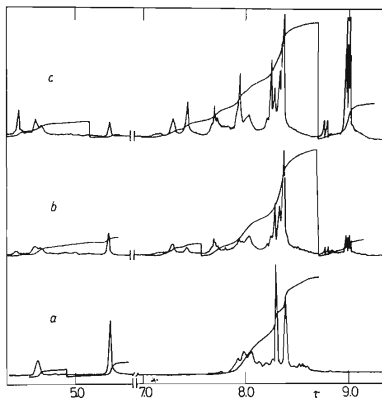
FIG. 2

220 Mc NMR Spectra

a Limonene, *b,c* two mixtures of cyclic isoprene dimers (samples *IV* and *V*).

groups in linear segments formed by 3,4-addition, the band at τ 4·95 corresponding to $-\overset{|}{CH}=C-$ protons in linear segments formed by 1,4-addition, and the band at τ 4·75 corresponding to $-CH=\overset{|}{C}-$ protons in cyclic structures. 1,2-addition can be excluded because of the absence of the band at τ 4·45 $(CH_2=C\underline{H}-\overset{|}{C}-)$.

In addition to this qualitative interpretation, some quantitative data about the structure of the studied cyclopolymers may also be obtained (Table IIIA). By integration of the sum of the olefinic and the sum of the aliphatic protons, the relative amount of residual olefinic protons can easily be obtained. Under the assumption that the polymer does not contain tetrasubstituted double bonds, the reduction of the content of olefinic protons can be used to characterize roughly the cyclization process. For the determination of the relative amount of monomer units in cyclic and linear segments, the relative amount of different types of olefinic protons has to be determined (Table IIIA). The distribution of monomer units into cyclic and linear segments, calculated from the data of Table IIIA, is given in Table IIIB. The content of linear forms (1,4-addition) was calculated from the content of olefinic protons absorbing at τ 4·95. The content of units formed by 3,4-addition was calculated from the intensity of the band at τ 5·35 and is given separately, because this kind of addition can occur both in linear and in cyclic segments. It was assumed that all remaining monomer units are contained in cycles. The numbers in row 3 (Table IIIB) thus represent the minimum, and the sum of the numbers in rows 2 and 3 (Table IIIB) the maximum number of monomer units in cyclic segments.

From the data of Table IIIA, the amounts of some characteristic groups in cyclic segments have also been calculated, and are given in Table IIIC. From the content of olefinic protons in cycles, the average length of cyclic segments can be estimated. The transition from a cyclic to a linear segment must always be connected with the appearance of one double bond in the sequence of cycles, either on the first, or on the last cycle of the segment (with the exception of segments at the end of the chain). Consequently, the number of double bonds in cycles is equal to the number of cyclic segments; if the total number of monomer units in cycles is known, (Table IIIB), the average length of a cyclic segment can be calculated and this is given in Table IIID. In the last row of Table IIID, the average number of all methyl groups in one cyclic segment is given, calculated under the assumption that the unsaturated unit in the cyclic segment carries one methyl group on the double bond.

INFRARED SPECTRA

In the range $500-2000$ cm^{-1}, the infrared spectra of all the studied samples of cyclopolyisoprenes exhibit only two strong bands (1382 and 1458 cm^{-1}) of the symmetric

TABLE III

Structural Characteristic of Cyclopolyisoprenes from NMR Data

Structure		Sample		
		I	II	III
A. Proton type[a]	τ			
Aliphatic				
Total	9.5 — 7.6	92	91	93
CH_3 on saturated carbon	9.09	27	25	38
Olefinic				
Total	5.3 — 4.6	8	9	7
In cycles	4.75	2	1	3
In $CH_2=C-$	5.35	2	1	0
In linear units	5.0	4	7	4
B. Addition type (%)				
1,4		32	56	32
3,4		8	4	0
Other (cyclic)		60	40	68
C. Characteristic group				
(Number per 100 monomer units in cyclic segments)				
$-CH=C-$		23	18	35
$CH_2=C-$		12	9	—
CH_3-C-		120	160	153
D. Average number of cycles		3 — 4[b]	3 — 4	2
Average number of all $-CH_3$ groups per one cyclic segment		5	7	5.6

[a] Content of characteristic groups expressed as % of protons of corresponding type from the total number of protons. [b] Due to low molecular weight, end groups cannot be neglected; in the calculation, two double bonds in one cyclic segment were considered.

and antisymmetric bending CH_3 vibration and of the scissoring CH_2 vibration. The absorbance ratio E_{1460}/E_{1382} is lower in our cyclopolymer samples ($1\cdot29$ to $1\cdot37$) than in linear polyisoprene ($1\cdot6-1\cdot7$). In the sample *I* the band at $1\,382\;cm^{-1}$ is clearly split with a shoulder at $1\,368\;cm^{-1}$, indicating the presence of geminal methyl groups. The appearance of the very weak band at $1\,178\;cm^{-1}$ which might correspond to a skeletal $\begin{smallmatrix}C\\ \\C\end{smallmatrix}\!\!>\!\!C\!-\!C$ vibration indicates that the geminal methyls are present in the form of an isopropyl group. In samples *II* and *III* the splitting of the $1\,382\;cm^{-1}$ band is not observed. All other bands in the spectra of the cyclopolymers studied are very weak, but still the bands at 848, 888 and $910\;cm^{-1}$ are quite clear. The amounts of units added in positions 1,4-, 3,4- and 1,2- estimated from the intensities of these bands are given in Table I. For reasons discussed above these values do not agree with NMR data but, at least qualitatively, a higher content of linear forms found from NMR is generally manifested by a higher intensity of the infrared bands.

DISCUSSION

Even though the structure of cyclopolyisoprenes cannot be completely determined from NMR spectra, a number of new findings could be obtained from them. The determination of the total content of double bonds by integration of NMR bands is probably more reliable than the determination of unsaturation by other methods.

The only unverified assumption in this determination is the absence of tetrasubstituted double bonds, but this assumption is present also in the determination of unsaturation by the ICl method or from infrared spectra. The content of double bonds in cyclopolyisoprenes determined from NMR spectra is considerably higher than that resulting from the ICl method. Nevertheless, the loss of unsaturation is large and indicates the presence of cyclic structures.
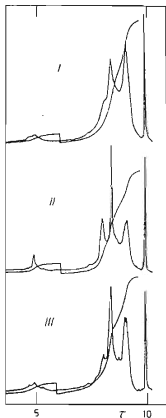
FIG. 3

220 Mc NMR Spectra of Cyclopolyisoprenes *I*, *II* and *III*

A further finding confirming the presence of cycles is the appearance of the very prominent band of methyl groups bound to a saturated carbon atom (τ 9·09). Such methyl groups cannot be formed by linear addition of isoprene. The NMR method makes it possible to differentiate between double bonds in linear and cyclic segments, and thus to determine the relative content and average length of cyclic sequences. The samples studied by us contained 40—70% of monomer units in cycles, with an average cyclic segment composed of 2—4 cycles. From NMR spectra, the linear segments in cyclopolyisoprenes are formed mostly by 1,4-addition, possibly partly also by 3,4-addition (Table III*B*). 1,2-Addition can be excluded.

Although NMR spectra indicate the presence of certain characteristic groups in cyclic segments, the structure of these segments cannot be completely determined from them, because it is evidently not unique. As in the oligomeric fractions the presence of mono-, di- and triterpenes[6], *i.e.* of compounds with a different number of cycles can be determined, it must be assumed that also in the polymers formed under similar conditions an analogous distribution of segment lengths will be present. Besides this, NMR spectra of mixtures of dimers and trimers indicate that various segments contain different functional groups (isopropyls, isopropenyls, *etc.*). As seen from Fig. 1, there exists a direct relation between the spectra of low oligomers and of polymers prepared under similar conditions, supporting the assumption about the presence of various structures of cyclic segments in cyclopolymers.

All studied samples contained a large amount of methyl groups bound to a saturated carbon atom. In sample *I*, each third saturated monomer unit in a cyclic segment contains one additional methyl group (Table III*D*). Because the molecular weight of this sample is low, it contains a large portion of molecules with only one cyclic segment, or molecules which are purely cyclic. A typical chain segment conforming to the results given in Table III*C* and *D*, could have the structure
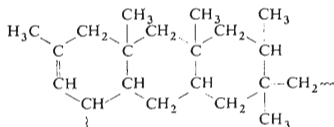

or
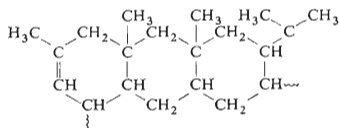
If such a segment stands at the end of a chain (approximately one half of all cyclic segments), then the last ring should contain an exomethylene, isopropenyl or double bond in the ring.

Both remaining samples contain an average of two methyl groups on saturated carbon atoms in each saturated monomer unit in a cyclic sequence. The presence of such a large number of methyl groups on saturated carbon atoms can be explained only by the addition of monomer in position 1,3- or 2,3- during polymerization. The chemical shift of the methyl groups (τ 9·09) indicates a six-membered ring structure. In order to generate an additional methyl group on a saturated carbon atom in each addition step, the cyclic segment cannot contain only six-membered rings if it is longer than three monomer units (bicyclic form), and it must be assumed that also five-membered rings are formed. Methyl groups on saturated carbon in five membered rings are expected to absorb at τ 9·3. In our spectra no separate peak appears in this region, but in spite of this we do not think that the assumption of the presence of five-membered rings is in contradiction with our NMR spectra; the methyl band at τ 9·1 is very broad and has an upper limit distinctly above τ 9·3.

A typical cyclic segment of polymers *II* and *III* could then be represented as follows:
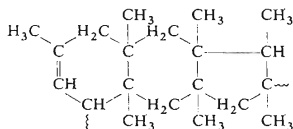
All these are of course not the only possible structures — based on NMR spectra — a variety of other structures, corresponding to the great variety of oligomers found, should also be considered, as discussed above.

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