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PYROLYSIS GAS CHROMATOGRAPHY OF CYCLOPOLYISOPRENE

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SUMMARY

Linear polyisoprene and polyisoprene containing cyclic structures in the chain both yield qualitatively identical mixtures of pyrolytic products. From the relative amount of isoprene formed during pyrolysis, the content of cyclic structures in the polymer was estimated. The results of this estimation are in agreement with high-resolution NMR analysis, while IR spectrometry gives values that are too high. In the chromatographic part of this paper, the homologous series of the α -alkenes has been used for the calculation of retention indices.

INTRODUCTION

The cyclopolymerization of isoprene is promoted by a variety of catalysts (Ziegler catalysts, Grignard reagent, etc.) which under certain conditions lead to polymers containing condensed rings of the perhydroanthracene type. The content of these structures was determined by IR spectrometry. However, because of the lack of model substances, the absorption coefficients had to be estimated, which influenced the reliability of the analysis¹⁻⁸.

There are few true analytical methods for the elucidation of the structures of polymers. Carefully controlled pyrolysis followed by gas-liquid chromatographic (GLC) analysis of the resulting mixture was expected to contribute to the knowledge of the structure of cyclopolyisoprene.

EXPERIMENTAL

Polymers

Natural crêpe rubber and the synthetic rubber Natsyn 200 were used as examples of linear polyisoprene. More than ten cyclopolyisoprenes obtained under different conditions were investigated. As all of them showed the same pattern in pyrolytic chromatograms, only three of them are included in Table III.

Sample 1 was polymerized with ethylaluminium dichloride + triphenylmethyl chloride (molar ratio 5:1) in benzene. Sample 2 was obtained with TiCl_4 + *tert.*-butyl chloride (molar ratio 1:1:1) in dichloroethane. Samples 1 and 2 were white

powders. The IR analysis indicated for both of these samples more than 85 % of cyclic structures. Sample 3 was a brown oil and was a mixture of oligomers containing 40 % of C = C bonds (linear chain corresponding to 100 %); it was obtained in benzene in the presence of sulphuric acid + triphenylmethyl chloride (molar ratio 3 : 1). All the samples used for pyrolysis were used in the solid state after grinding the powders or after grinding the rubber-like polymers cooled with liquid nitrogen.

Pyrolysis

The pyrolysis was performed in an isothermal microreactor with external electric heating (see Fig. 1). A quartz tube with an I.D. of 1 mm was attached by means of a heated tube (stainless steel, I.D. 0.25 mm), without stream splitting, directly to the capillary column. The sample support was a wire (stainless steel, diameter 0.8 mm) with one end adapted as a 4-mm long spoon with a "U" profile. The amount of sample used was about 10^{-6} g. The wire was attached by its other end to a device that allowed horizontal movement under a pressure of 2 atm. The injection was carried out by pulling the end of the wire with the sample into the preheated quartz capillary. The reaction volume was about $15 \mu\text{l}$ and the residence time in the reactor was about 2 sec. The reaction temperature was 620° . The construction details and the suitability of the operating parameters have been discussed elsewhere⁴.

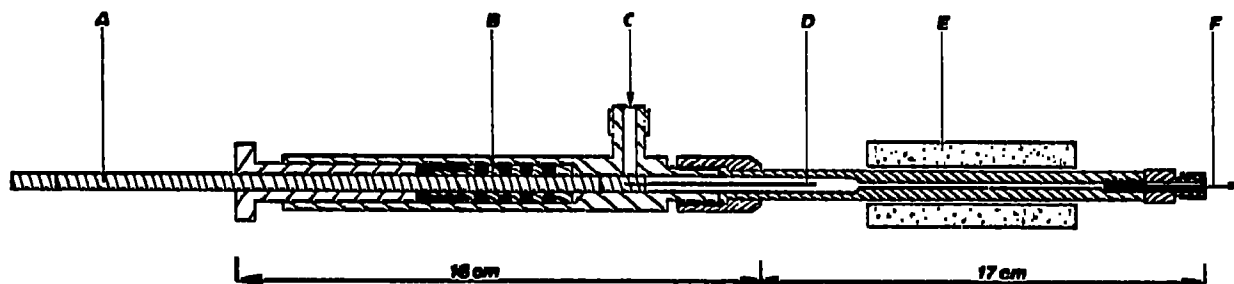


Fig. 1. Schematic diagram of the pyrolytic microreactor. A = sample support; B = tightening system; C = carrier gas inlet; D = spoon for the sample; E = external heating; F = outlet to the capillary column.

Gas-liquid chromatography

A Perkin-Elmer Model 226 chromatograph was used. The capillary (stainless steel, length 100 m, I.D. 0.25 mm) was coated with the silicone oil Emba Phase (May and Baker). The pressure of the carrier gas (nitrogen) at the entrance of the capillary was 2.22 atm and the flow-rate at 1 atm was 1 ml/min. The temperature programme comprised 15 min under isothermal conditions at 20° ; a linear temperature increase from 20° to 170° at a heating rate of $2.1^\circ/\text{min}$, and a 60 min final period under isothermal conditions at 170° .

A flame ionization detector was used. The signal was recorded with both a potentiometric pen-recorder and a magnetic tape recorder. The tapes were played back on an Infotronics integrator with a digital printing output. Under the given conditions, distinct peaks were obtained up to tridecane. The peak area was expressed as a percentage of the total peak area up to 1-undecene.

graph with the injection block and without the pyrolytic reactor was used. The substances for these mixtures were taken from the A.P.I. collection.

CALCULATION OF RETENTION INDICES BY MEANS OF 1-ALKENES

For the characterization of the positions of peaks in GLC, a number of parameters have been introduced. Because of the strong dependence of the retention time, t_x , of a substance on temperature, the retention data are often expressed as relative quantities referred to a suitably chosen reference compound. The values of t_x and t_{ref} are measured on one chromatogram.

The reproducibility of any temperature programme is poorer than the reproducibility of a given temperature. Therefore, the requirement of a suitable choice of a reference compound is, in the temperature-programmed mode, even more important than in isothermal GLC. The retention indices, I , according to VAN DEN DOOL AND KRATZ^{5,6} (eqn. 1) are often used:

$$\frac{I_x}{100} = \frac{t_x - t_z}{t_{z+1} - t_z} + z \quad (1)$$

where z is the number of carbon atoms in a normal alkane, and t_z and t_{z+1} are the retention times of normal alkanes with z and $z+1$ carbon atoms, respectively. It is again desirable to measure t_x , t_z and t_{z+1} on one chromatogram.

It is difficult to fulfil the last requirement when mixtures of pyrolytic products of solid polymers are studied. To avoid this difficulty, we tried to make use of the known property of higher n -alkanes (e.g., ditriacontane) to yield relatively large amounts of lower 1-alkenes next to small amounts of lower n -alkanes and alkadienes when pyrolyzed. The solid polymer can be easily mixed with a higher n -alkane. This mixture is pyrolyzed and in the resulting chromatogram the distinct peaks of 1-alkenes appear. We proved that the chromatogram of pyrolytic products of the mixture polymer + n -alkane is a linear superposition of the chromatograms of pyrolytic products of a pure polymer and of a pure alkane. This suggests the use of the 1-alkanes as a set of secondary standards for the calculation of the retention index, I . This calculation can be carried out in the following way. If the retention times of the bracketing 1-alkenes are denoted by t''_z and t''_{z+1} , where z is the number of carbon atoms in the reference compound, both alkene and alkane, as the case may be, then referring to Fig. 2, the index of the alkene with $z+1$ carbon atoms will be given by:

$$\frac{I''_{z+1}}{100} = \frac{t''_{z+1} - t_z}{t_{z+1} - t_z} + z \quad (2)$$

From eqns. 1 and 2, it follows that:

$$\frac{I_x}{100} = \frac{t_x - t''_{z+1}}{t''_{z+1} - t''_z} \cdot F_z + \frac{I''_{z+1}}{100} \quad (3)$$

where $F_z = (t''_{z+1} - t''_z) / (t_{z+1} - t_z)$

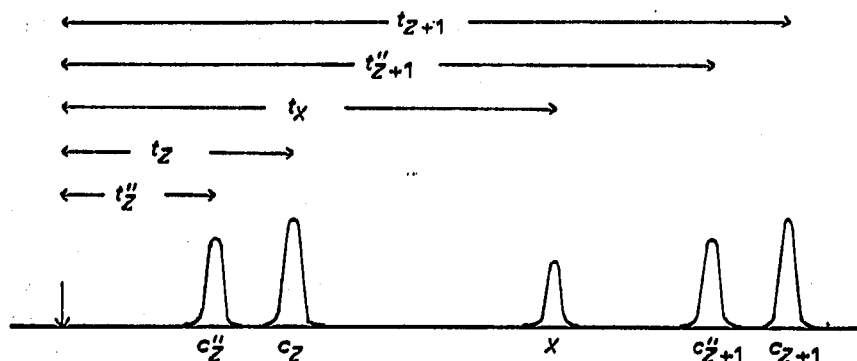


Fig. 2. Schematic diagram of a chromatogram of a mixture containing n -alkanes, 1-alkenes and x , the substance to be measured. The symbols for the substances and for the retention times are indicated.

TABLE I

COEFFICIENTS FOR CALCULATION OF RETENTION INDICES OF 1-ALKENES AND ALKANES

z	$100F_z$	I''_{z+1}	I_z
5	94.7	587.84 ± 0.12	503.2
6	100.51 ± 0.27	688.58 ± 0.13	599.85 ± 0.13
7	101.53 ± 0.10	788.81 ± 0.13	700.05 ± 0.15
8	101.44 ± 0.19	888.94 ± 0.16	799.94 ± 0.17
9	98.78 ± 0.37	987.93 ± 0.21	899.86 ± 0.34
10	97.93 ± 0.23	1088.33 ± 0.29	1000.45 ± 0.43
11	96.5	1188.17 ± 0.50	1100.0

for F_z given in Table I. The results in Table I are the mean values of at least ten experiments (except for $z = 5$ and $z = 11$).

From the data that are necessary for the calculation of F and I''_{z+1} , values of I_z (retention indices of normal alkanes calculated from the t'' values of 1-alkenes) can also be obtained. Of course, these values should not differ from 100; Table I shows good agreement.

To obtain evidence of the identity of indices I_x calculated in the usual way from eqn. 1 or from eqn. 4 by using the F and I''_{z+1} values given in Table I, we injected the model mixtures containing normal alkanes, 1-alkenes and some other substances to be expected in pyrolytic mixtures. Some of these results are given in Table II.

RESULTS

Pyrolysis of linear polyisoprene leads to chromatograms containing about 80 distinct peaks within the range investigated. In Table III are included peaks for which the area exceeded 1% of the total peak area, at least in some of the recorded chromatograms. As expected, the monomer and dimer are the main products. The higher production of monomer in Natsyn in comparison with crêpe may be due to the traces of catalyst in this technical product, which we did not purify.

TABLE II

COMPARISON OF RETENTION INDICES CALCULATED FROM EQNS. 1 AND 4

Compound	Retention index		Compound	Retention index	
	Eqn. 1	Eqn. 4		Eqn. 1	Eqn. 4
<i>trans</i> -Pentene-2	506.6	506.6	<i>trans</i> -1,2-Dimethylcyclohexane	805.0	804.1
<i>cis</i> -Pentene-2	513.6	513.6	Vinylcyclohexane	825.6	825.7
Pentadiene-1,2	542.4	542.4	4-Ethylcyclohexene	835.5	836.4
Pentadiene-2,3	551.1	551.1	<i>cis</i> -1,2-Dimethylcyclohexane	837.2	836.5
2,3-Dimethylbutene-1	564.7	564.7	1,1,3-Trimethylcyclohexane	846.2	846.5
2-Methylpentene-2	606.4	606.7	Ethylbenzene	857.4	856.8
2,3,3-Trimethylbutene-1	635.0	635.4	<i>trans, trans, trans</i> -1,2,4-Trimethylcyclohexane	862.4	862.6
Benzene	653.6	653.3	Ethylcyclohexene	874.4	875.2
2,2,3-Trimethylbutane	637.4	637.7	1,2-Dimethylcyclohexene	878.6	878.9
Cyclohexane	662.8	663.1	Styrene	885.2	885.6
Cyclohexene	677.6	677.8	1-Methyl-1-ethylcyclohexane	921.6	923.0
Methylcyclohexane	727.3	727.7	α -Pinene	944.3	945.0
Toluene	761.5	761.1	<i>p</i> -Cymene	1023.5	1024.9
1,1-Dimethylcyclohexane	793.0	792.2	Limonene	1033.8	1035.1

TABLE III

PYROLYTIC CHROMATOGRAMS OF POLYISOPRENES

Peak area as a percentage of the total peak area.

Peak	Linear polyisoprenes		Cyclopolyisoprenes		
	Natsyn	Crépe	No. 1	No. 2	No. 3
Methane	2.7	3.6	6.5	8.2	8.3
Ethene	3.1	3.1	4.8	5.0	4.2
Ethane	1.1	1.4	2.1	2.9	2.3
Propene	3.4	3.3	6.9	6.2	6.9
Butenes	2.3	2.1	4.5	4.4	6.6
Butadiene-1,3	0.7	0.9	1.8	1.2	1.0
<i>trans</i> -Butene-2	0.4	0.7	1.1	1.0	0.9
<i>cis</i> -Butene-2	0.3	0.5	0.7	0.8	0.6
2-Methylbutane	0.8	1.0	0.7	0.5	1.5
2-Methylbutene-1	2.3	2.7	2.0	1.7	2.0
Isoprene	19.5	12.5	5.1	3.5	4.5
<i>trans</i> -Pentadiene-1,3	4.2	4.4	2.4	2.5	3.3
2-Methylpentene-2	1.8	2.0	1.0	0.7	1.2
Retention index 620.1	1.0	1.2	0.5	0.4	0.4
2,3,3-Trimethylbutene-1	2.3	2.5	2.4	1.8	1.7
Benzene	0.8	1.5	4.3	3.1	1.8
Toluene	5.6	6.6	8.5	8.4	9.5
<i>p</i> -Xylene	8.6	8.8	5.6	5.8	7.3
<i>o</i> -Xylene	1.1	2.1	2.7	3.1	2.3
Retention index 993.1	5.7	4.5	4.4	3.3	5.2
Limonene	6.4	2.0	2.5	2.0	2.3

of the radicals and unsaturated fragments formed during pyrolysis. A similar cyclization is known in the pyrolysis of vinyl polymers. Chromatograms of pyrolytic

of linear polymers and only a quantitative difference was observed (Table III). The higher amount of methane can be explained by the lower stability of angular methyl groups in cyclic segments in comparison with the stability of side-methyl groups in the linear chain.

The pyrolytic mixture did not contain derivatives of cyclohexane (at least, not those derivatives that are in the A.P.I. collection). Therefore, the question was raised whether, under given conditions, the cyclic segments of the polymer were really decomposed. FABUSS *et al.*⁷ studied the pyrolysis of decahydronaphthalene, which may be considered to be a model of cyclic segments in cyclopolyisoprene. These authors also reviewed older experimental data. From their Arrhenius plot, it appears that at 610° and 2 atm, the rate constant does not exceed the value 0.01 sec⁻¹. If it is assumed that the reaction is first order, the fraction decomposed after a time t can be calculated. For $t = 2$ sec, this fraction is about 2%. It is therefore probable that in our experiments the cyclic segments did not decompose into larger amounts of compounds containing less than 11 carbon atoms (the higher compounds were not detectable).

The main difference between cyclic and linear polyisoprenes lies in the formation of monomer. The lower production of monomer in cyclopolyisoprenes supports the concept of the presence of cyclic segments in these polymers. From cyclic segments, the monomer is not formed during pyrolysis. On the other hand, the amounts both of the linear and of the cyclic polyisoprenes used for pyrolysis were always of the same order of magnitude and the relative content of monomer in pyrolytic mixtures decreased to about 3-5%. If the content of linear segments in cyclopolyisoprenes was as low as that indicated by IR analysis, a lower isoprene content than that found would be expected. This suggests that the values of absorption coefficients of the IR bands used for the determination of cyclic segments were estimated too low. The mean relative peak area for all the samples of cyclopolyisoprene investigated was 4.5%. From the comparison of this value with the value 12.5% for crêpe, it can be concluded that the content of isoprene in linear segments of cyclopolyisoprene is not less than 35%. Recently⁸, high-resolution NMR analysis showed that the content of cyclic segments is at most 50% and that these segments consist of 2-4 condensed rings. Also, the higher production of propene in the pyrolysis of cyclopolyisoprene confirms the conclusion drawn by those workers⁸ on the presence of isopropyl and isopropenyl groups in the cyclic segments.

DISCUSSION

In the work described here, we have made use of the temperature-programmed index as originally defined by VAN DEN DOOL AND KRATZ⁵. However, we have based the calculation on secondary standards present in the chromatogram, *viz.*, the 1-alkenes. The temperature-programmed retention index of these secondary standards must be measured in a separate experiment with n -alkanes present. We have shown that the values based on secondary standards agree to a high degree of precision with values based on alkanes directly. The advantage of this approach is that one list of index values for all types of compounds will suffice. However, we feel that another approach may possibly be better adapted to future needs.

define a new index based on standards already present. These standards will certainly not be the alkanes, for obvious reasons, and in many cases the 1-alkenes will be the appropriate choice. The definition we propose is:

$$\frac{I^*}{100} = \frac{t_x - t''_z}{t''_{z+1} - t''_z} + z \quad (4)$$

completely symmetrical to the index based on alkanes, where I^* is the programmed-temperature index defined on 1-alkenes; t_x is the retention time from any arbitrary zero for compound x ; t''_z is the retention time of an alkene with z carbon atoms; t''_{z+1} is the retention time of an alkene with $z+1$ carbon atoms; and z is the number of carbon atoms in the preceding alkene.

We will now obtain a set of numerical values that bear no simple relationship to the I values obtained according to VAN DEN DOOL AND KRATZ, which is a drawback. However, the values will form a self-consistent set intended for use in this special field and applicable to other fields of investigation in which the 1-alkenes are present or may be introduced.

The advantage of this approach is the presence of the reference substances in the chromatogram, which is more convenient and more precise. If the problem of conversion of I^* to I arises, the exact solution has been given in this paper, *viz.*, by establishing the I values of the reference substances first and then applying eqn. 3.

If only an estimation of the conversion is required, it can be assumed that the factor F is approximately unity. In that case, the following equations apply:

$$I_x^* - I_x \approx I_z - I''_z = 100z - I''_z$$

and

$$I_x^* - I_x \approx I_z^* - I''_z^* = I_z^* - 100''_z$$

One must either determine the VAN DEN DOOL AND KRATZ I index of an alkene or the I^* index of an alkane, which also means carrying out separate experiments or obtaining separate data. This will not be possible in an on-line pyrogram where the alkanes will not survive the pyrolysis conditions.

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