

IDENTIFICATION AND CHARACTERIZATION OF POLYMERS BY PYROLYTIC-HYDROGENATION GAS CHROMATOGRAPHY

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INTRODUCTION

Polymer analysis is one of the most difficult problems confronting the analyst, primarily because of the complexity of the molecules. Because of our interest in the application of polymers to high explosives, we undertook the development of a method capable of identifying a variety of polymers.

A review of the literature indicated that pyrolytic gas chromatography was probably the most promising technique¹⁻⁴. In the usual procedure, the volatile pyrolysis products are used as fingerprints to identify the parent polymer. Since there are many closely related polymers, fingerprinting alone is usually not sufficient for identification, although it can be so used in certain special cases^{5,6}. In the work reported here, pyrolysis has been combined with microhydrogenation so that we not only can fingerprint the volatile pyrolysis products, but also can identify the major products characteristic of the polymer sample. Polyethylene is the only polymer previously investigated by a similar technique; however, the major pyrolysis product characteristic of this polymer was not identified^{7,8}. Our method provides excellent qualitative data which are usable for quantitative analysis. Pyrograms of several representative polymers are presented to illustrate the versatility of this method.

APPARATUS AND REAGENTS

As the name implies, pyrolytic-hydrogenation gas chromatography involves three basic items, the pyrolysis unit, the hydrogenation unit, and the flame ionization gas chromatograph. The gas chromatograph and the pyrolysis unit, Models 600 C and A-425, respectively, were purchased from Varian Aerograph. The hydrogenation unit was based on the work of BEROZA⁹. A flow diagram of the apparatus is shown in Fig. 1.

Micropyrolysis unit

Several essential modifications were incorporated into the pyrolysis unit to meet our requirements. Fig. 2 is a drawing of the pyrolysis chamber and its essential parts.

The quartz sample holder is used to isolate the sample from the platinum heating coil to prolong the life of the coil, and to confine the sample in the heated

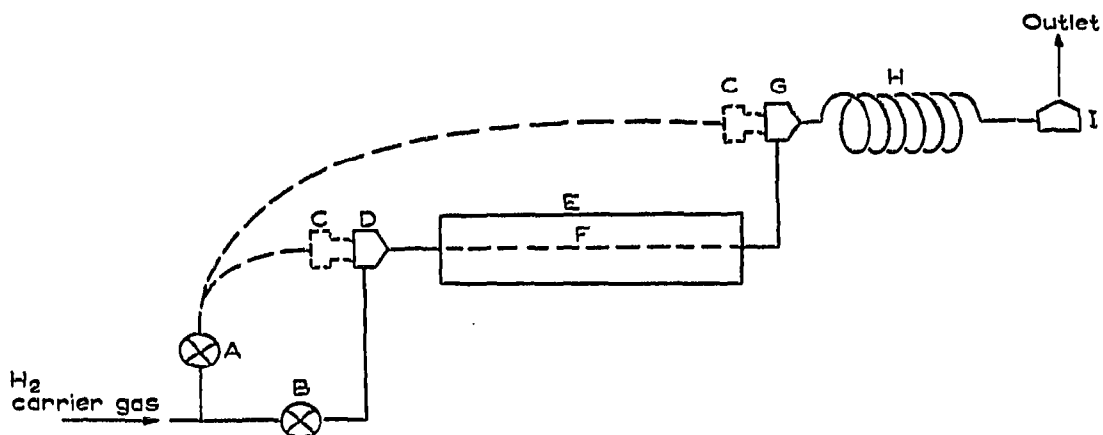


Fig. 1. Schematic flow diagram of the experimental set-up. A = On-off gas valve; B = needle valve; C = pyrolysis unit; D = sample port for hydrogenation; E = furnace; F = hydrogenation tube; G = normal sample port; H = chromatographic column; I = flame ionization detector.

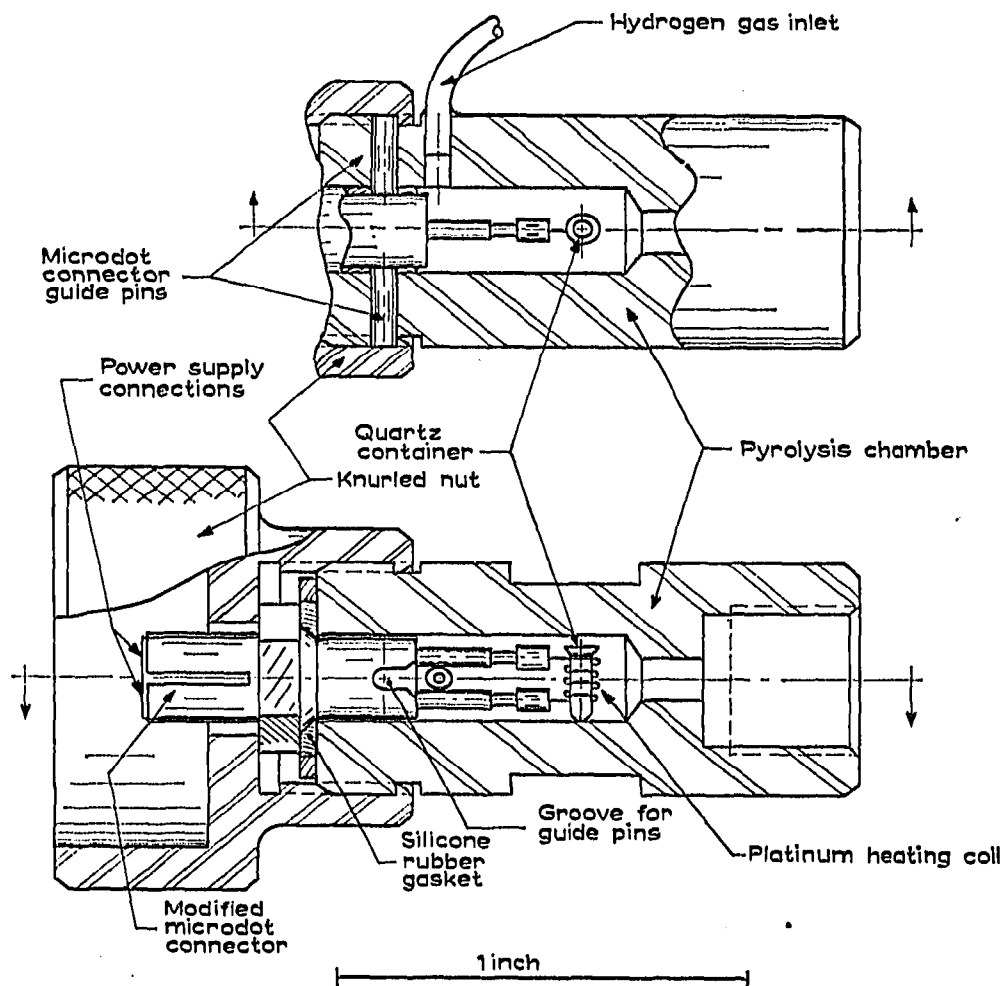


Fig. 2. Detail drawing of the pyrolysis unit.

zone during pyrolysis. With this arrangement both liquid and solid samples can be pyrolyzed for analysis.

The grooves in the Microdot connector fit two guide pins placed in the pyrolysis chamber to hold the sample container in an upright position. This minimizes sample loss while the chamber is purged with hydrogen carrier gas. With a special knurled nut and a silicone rubber gasket, the pyrolysis unit is assembled and made leak-tight. Depending on the type of pyrogram desired, the pyrolysis unit can be readily fastened either to the normal sample port for an unhydrogenated pyrogram, or to the hydrogenation sample port for a hydrogenated pyrogram, as indicated in Fig. 1. An on-off gas valve attached to the hydrogen gas line and the pyrolysis chamber serves to sweep the pyrolysis products directly into the partitioning column.

Partitioning columns

Two partitioning columns were found useful to separate the pyrolysis products, namely, a 6 ft. \times $1/8$ in. O.D. 30% tricresyl phosphate (TCP), and a 30 ft. \times $1/8$ in. O.D. 25% hexadecane (HD) column, each coated on 40/60 mesh acid-washed C-22 firebrick. The TCP column tends to group the pyrolysis products into light aliphatic, and aromatic or high boiling, products. This is advantageous since this column can be used to screen the predominant pyrolysis products from unknown polymers rapidly. Reasonably good separation of aromatic products for retention measurements is obtained on this column.

The HD column is used to separate the light aliphatic products. The 30-ft.-long column provides the necessary resolution to separate most of the C_1 to C_6 hydrocarbons.

Relative retention measurements

In order to assess the pyrolysis products, relative retention times of common aromatic hydrocarbons were measured on the TCP column, using benzene as the reference compound. A more extensive list of C_1 to C_6 aliphatic hydrocarbons were chromatographed on the HD column, and relative retention times were measured with *n*-pentane as the reference compound. Retention data are summarized in Tables I and II.

TABLE I

RELATIVE RETENTION MEASUREMENTS ON TCP COLUMN

Chromatographic conditions: Column: 6 ft. \times $1/8$ in. O.D. 30% tricresyl phosphate on 40/60 mesh acid-washed C-22 firebrick. Column temp.: 100°. Inlet temp.: 95°. Hydrogen carrier gas, flow rate 22 cc/min. Recorder speed 16 in./h. Ref. compound: benzene.

<i>Compound</i>	<i>Boiling point (°C)</i>	<i>Relative retention time</i>
Benzene (ref. compound)	80.1	1.00
Methyl methacrylate	100	1.34
Toluene	110.6	1.95
Cyclopentanone	130.6	4.47
Ethylbenzene	136.1	3.60
Isopropylbenzene	152.4	5.18
Styrene	146	5.95

TABLE II

RELATIVE RETENTION MEASUREMENTS ON HD COLUMN

Chromatographic conditions: Column: 30 ft. \times $\frac{1}{8}$ in. O.D. 25% hexadecane on 40/60 mesh acid-washed C-22 firebrick. Column temp.: 27°. Inlet temp.: 27°. Hydrogen carrier gas, flow rate 22 cc/min. Recorder speed 16 in./h. Ref. compound: *n*-pentane.

<i>Compound</i>	<i>Boiling point</i> (°C)	<i>Relative retention time</i>
Methane	-161.5	0.050
Ethylene	-103.9	0.044
Ethane	-88.3	0.070
Acetylene	-83.6	0.042
Propylene	-47.0	0.101
Propane	-42.2	0.127
Propyne	-23.0	0.115
Isobutane	-10.2	0.232
Isobutylene	-6.0	0.265
1-Butene	-5.0	0.267
1,3-Butadiene	-3.0	0.275
<i>n</i> -Butane	0.4	0.331
<i>trans</i> -2-Butene	0.9	0.347
<i>cis</i> -2-Butene	3.7	0.381
1-Butyne	8.3	0.278
2,2-Dimethylpropane	9.5	0.368
3-Methyl-1-butene	25.0	0.568
2-Butyne	27.2	0.634
2-Methylbutane	28.0	0.741
1-Pentene	30.0	0.808
2-Methyl-1-butene	31.0	0.867
2-Methyl-1,3-butadiene	34.0	0.956
<i>n</i> -Pentane (ref. compound)	35.5	1.00
2-Pentene	36.4	1.04
2-Methyl-2-butene	38.4	1.16
1-Pentyne	40.0	0.825
3,3-Dimethyl-1-butene	41.2	1.08
Cyclopentane	49.5	1.83
2,2-Dimethylbutane	49.7	1.48
4-Methyl-1-pentene	53.6-53.9	1.76
3-Methyl-1-pentene	53.6-54	1.76
<i>cis</i> -4-Methyl-2-pentene	54.2	1.89
2-Pentyne	56.0	1.73
<i>trans</i> -4-Methyl-2-pentene	57.7	2.06
2,3-Dimethylbutane	58.1	2.07
1,5-Hexadiene	60.0	2.05
2-Methylpentane	60.0	2.23
2-Methyl-1-pentene	61.5	2.47
1-Hexene	63.0	2.55
3-Methylpentane	64.0	2.57
<i>cis</i> -3-Methyl-2-pentene	65.7-66.2	3.22
2-Methyl-2-pentene	67.4	3.01
3-Hexene	67.5	2.85
<i>trans</i> -3-Methyl-2-pentene	67.6-68.2	3.60
<i>trans</i> -2-Hexene	68.0	3.02
<i>cis</i> -2-Hexene	68.8	3.21
<i>n</i> -Hexane	69.0	3.15
2,3-Dimethyl-1,3-butadiene	69.6	3.41
1,3-Hexadiene	72.0	3.58
2,3-Dimethyl-2-butene	73.0	3.97
<i>trans</i> -2-Methyl-1,3-pentadiene	74.0	4.01
Benzene	80.1	4.21
2,4-Dimethylpentane	80.5	4.41
Cyclohexane	81.4	5.37
2,4-Hexadiene	82.0	5.51
2,3-Dimethylpentane	89.8	6.72

Within a homologous series, the HD column separates the hydrocarbons in the order of their boiling points. This property can be utilized to estimate the boiling points of unknown products, as will be shown in discussing the identification of pyrolysis products from neoprene.

Microhydrogenation unit

The hydrogenation unit consists of a furnace and a 1 ft. \times 1/4 in. O.D. aluminum tube packed with 20% by weight of platinum catalyst coated on 60/80 mesh acid-washed Chromosorb W. A slight modification of BEROZA's procedure⁹ was used to prepare the catalyst.

The preparation entails the weighing of 0.737 g of chloroplatinic acid hexahydrate and 1.12 g of Chromosorb W into a 50-ml round-bottom distillation flask. About 10 ml of distilled water is added, and the mixture is heated at 90°, a Roto-vak being used to strip off the water. After 45 min a dry, yellow-colored Chromosorb W results. This material is then packed into the aluminum tubing to a column height of 9 in. Glass wool plugs placed in each end hold the packing in place. The packing should be firm, but it should be possible to insert a 25-gauge hypodermic needle easily without any obstruction. The packed tube is placed in the furnace, and a Swagelok fitting is fastened to one end to permit hydrogen to flow at a rate of 50 cc/min. The outlet gas is vented into a hood. The furnace is heated to 350° and maintained at this temperature for 1 h. The activated catalyst is swage locked into position as shown in Fig. 1. The hydrogenation catalyst is purged continuously with hydrogen, and the column temperature is maintained at 225°.

Procedure

With the pyrolysis chamber attached to the normal sample port, a weighed sample (60 to 150 μ g) is placed in the quartz container, and the pyrolysis unit is assembled with the silicone gasket and the knurled nut. The cable from the power supply is connected to the Microdot connector, and the hydrogen carrier gas valve, labeled A in Fig. 1, is turned on. The carrier gas travels from the gas cylinder, through the pyrolysis chamber and the partitioning column, to the flame detector. After the flow rate of hydrogen is adjusted to 22 cc/min at the detector outlet, the detector is ignited. The chromatograph and recorder are allowed to stabilize for a few minutes. Impressing a high current from the power supply across the platinum coil for 10 sec pyrolyzes the sample. Usually a dial setting of 95 on the power supply is sufficient to provide a maximum temperature rise of 950° inside the quartz container in 10 sec of heating. The length of heating is controlled with an electric timer which actuates the power supply. The pyrolysis products are immediately swept onto the TCP column, maintained at 100° with a sample inlet temperature of 95°.

After 1.5 h, visual inspection of the pyrogram is made to assess the predominant products. Products appearing within a few minutes on the pyrogram are primarily light aliphatic hydrocarbons, and products with longer retention times are aromatic or high boiling products. If the visual estimate indicates mostly aliphatic products, a second sample is pyrolyzed and the products are separated on the 30-ft. HD column, operated at 27°. Relative retention times of the products are measured with respect to *n*-pentane, which is chromatographed before and after each pyrolysis run. If the pyrolysis products are mainly aromatic hydrocarbons, relative retention measure-

ments are made from the pyrogram obtained from the TCP column. In this case all measurements are made with respect to the benzene peak. By comparing the retention times of the pyrolysis products with those of the authentic samples (Tables I and II), identification of the products is established.

With complex pyrograms, such as those from the rubber samples, a third sample is pyrolyzed with the pyrolysis unit attached to the hydrogenation sample port (see Fig. 1). The hydrogenated products are chromatographed on the HD column, and retention measurements are made to identify the products. By comparing both pyrograms from the HD column, and noting the disappearance or shifting of the chromatographic peaks, one can identify all the unsaturated products. The chromatographic, pyrolysis, and hydrogenation conditions are listed with each pyrogram.

RESULTS AND DISCUSSION

Several representative polymers were examined by the pyrolytic-hydrogenation gas chromatograph. Fig. 3 illustrates the pyrolysis products of polystyrene separated on the TCP column. It is immediately apparent that the products are primarily aromatic hydrocarbons. Relative retention measurements reveal that styrene monomer is the major product. By increasing the sensitivity of the gas chromatograph, it was possible to detect and identify $5 \cdot 10^{-8}$ g of this polymer via the pyrolysis products.

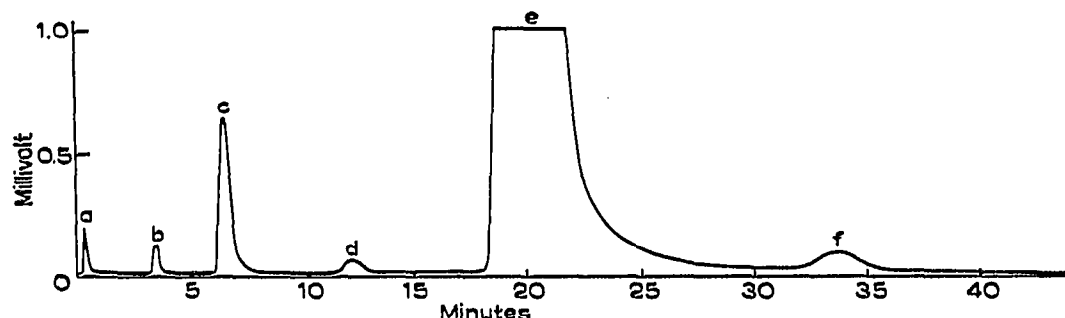


Fig. 3. Pyrogram of polystyrene. Chromatographic conditions: Column: 6 ft. \times $\frac{1}{8}$ in. O.D. 30% tricresyl phosphate (TCP) on 40/60 mesh acid-washed C-22 firebrick. Column temp.: 100° . Inlet temp.: 95° . Hydrogen carrier gas, flow rate 22 cc/min. Recorder speed: 16 in./h. Electrometer range: 10. Attenuation: \times 8. Pyrolysis conditions: Pyrolysis temp.: 950° max in 10 sec of heating. Sample size: 0.08 mg. Identification of pyrolysis products: a = light hydrocarbons; b = benzene; c = toluene; d = ethylbenzene; e = styrene (major product); f = unknown (probably a dimer).

Since no appreciable amount of aliphatic products was formed, it was not necessary to obtain a second pyrogram from the HD column.

The pyrogram of Lucite (polymethyl methacrylate) appears simple. The major pyrolysis product in Fig. 4 is methyl methacrylate monomer as identified from the retention time measurement of an authentic sample.

Included in Fig. 4 is a pyrogram of cured Eastman 910 adhesive, which is related to the acrylate polymers. The predominant pyrolysis product of Eastman 910 is methyl 2-cyanoacrylate. A chromatogram of an uncured sample made under conditions identical to those used for the pyrogram is also included here to identify the monomer. It is interesting to note that the early portion of the Eastman 910 pyrogram is identical to that produced by the products obtained from Lucite. This is not sur-

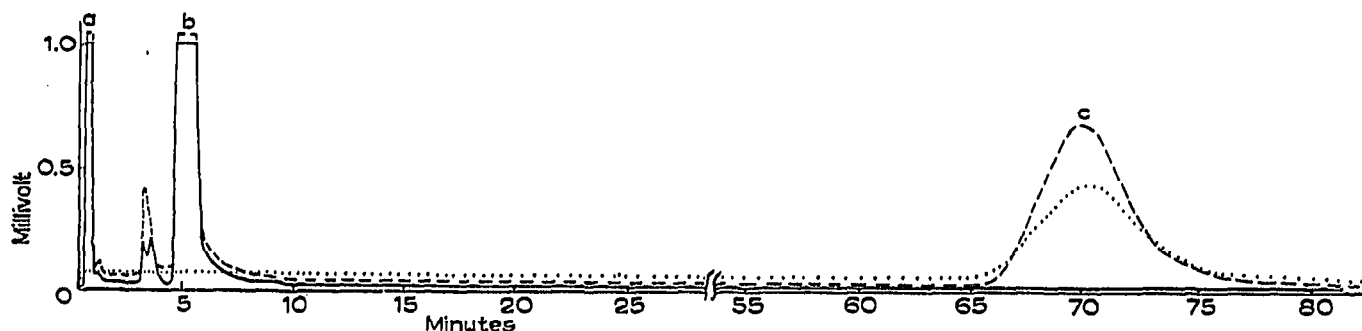


Fig. 4. Pyrograms of Lucite and Eastman 910. Chromatographic and pyrolysis conditions: same as Fig. 3. Sample size: 0.10 to 0.15 mg. (—) Lucite (polymethyl methacrylate); (---) cured Eastman 910; (····) chromatogram of uncured Eastman 910. Identification of pyrolysis products: a = C_1 to C_3 hydrocarbons; b = methyl methacrylate (major product from Lucite); c = methyl 2-cyanoacrylate (major product of Eastman 910).

prising since Lucite is added to the 910 as a filler. Although these acrylates are closely related, characteristic pyrolysis product is formed to identify the parent polymer.

Several rubber samples were also investigated. These polymers are different from those discussed previously since the pyrolysis products are primarily aliphatic hydrocarbons and they are more complex. Yet each sample forms distinct products usable for identification work. Natural and neoprene rubbers are selected for detailed discussion here.

Fig. 5 shows the pyrogram of natural rubber from the TCP column. Visual examination indicates that the products are primarily aliphatic hydrocarbons. A second sample was pyrolyzed and the products were chromatographed on the 30-ft. HD column. Fig. 6 is a tracing of the pyrogram. Relative retention times of the products were determined, and the data were compared with those in Table II. The identified products are listed in Fig. 6. 2-Methyl-1,3-butadiene (isoprene) is the major product characteristic of natural rubber.

In a complex mixture of this sort it is always necessary to verify the results with a second set of data. This was accomplished by hydrogenating the pyrolysis products from a third sample and chromatographing the hydrogenated products on the HD column (see Fig. 7). Since the hydrogenation conditions convert the unsaturated products to saturated hydrocarbons, the unsaturates should not be difficult to locate. In comparing Figs. 6 and 7 the disappearance or shifting of the corresponding chromatographic peaks is sufficient evidence to locate the unsaturated products in Fig. 6. For example, the disappearance of the three methylbutene and the 2-methyl-1,3-butadiene peaks in Fig. 7, and the appearance of a new peak identified as 2-methylbutane, verify the identities of the original peaks. Similarly propylene and propyne hydrogenate to a single product, propane. The composite peak of ethylene and acetylene converts to the anticipated product, ethane. The unresolved peak consisting of isobutylene, 1-butene, and 1,3-butadiene yields isobutane and *n*-butane, suggesting that the original peak is a mixture. Therefore, hydrogenation used in conjunction with retention time measurements is an effective method of identifying the pyrolysis products.

Fig. 8 is a pyrogram of neoprene rubber from the TCP column. At a first glance it is evident that the pyrolysis products are mainly aliphatic hydrocarbons. A second pyrogram from the HD column indicates that the major pyrolysis product is 2-chloro-

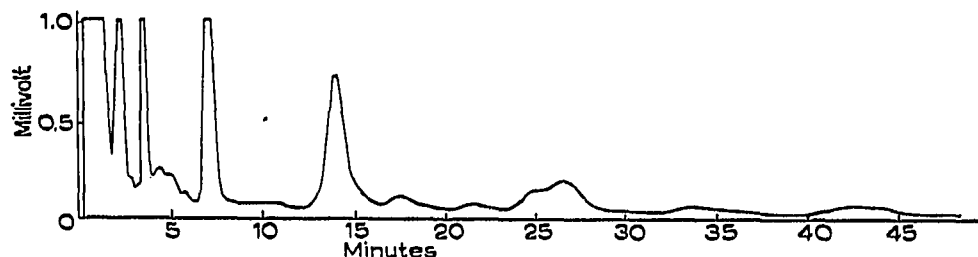


Fig. 5. Pyrogram of natural rubber from TCP column. Chromatographic and pyrolysis conditions: same as Fig. 3. Sample size: 0.10 mg.

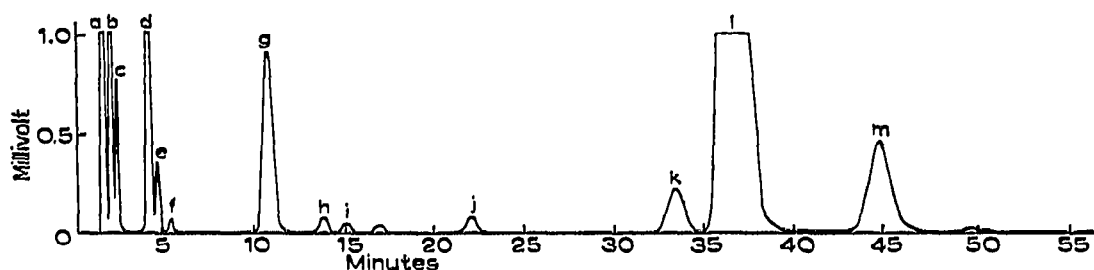


Fig. 6. Pyrogram of natural rubber from HD column. Chromatographic conditions: Column: 30 ft. \times $\frac{1}{8}$ in. O.D. 25% hexadecane on 40/60 mesh acid-washed C-22 firebrick. Column temp.: 27° . Inlet temp.: 27° . Hydrogen carrier gas, flow rate 22 cc/min. Recorder speed: 16 in./h. Electrometer range: 10. Attenuation: \times 8. Pyrolysis conditions: Pyrolysis temp.: 950° max in 10 sec of heating. Sample size: 0.13 mg. Identification of pyrolysis products: a = ethylene or acetylene; b = methane; c = ethane; d = propylene; e = propyne; f = propane; g = isobutylene, 1-butene, or 1,3-butadiene; h = *trans*-2-butene; i = *cis*-2-butene; j = 3-methyl-1-butene; k = 2-methyl-1-butene; l = 2-methyl-1,3-butadiene (major product); m = 2-methyl-2-butene.

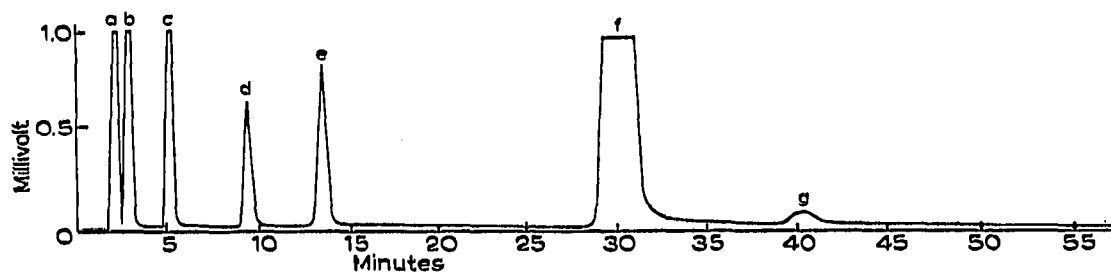


Fig. 7. Microhydrogenation of pyrolysis products from natural rubber. Chromatographic and pyrolysis conditions: same as Fig. 6. Hydrogenation conditions: Catalyst: 9 ft. \times $\frac{1}{4}$ in. O.D. aluminum tubing packed with 20% platinum coated on 60/80 mesh acid-washed Chromosorb W. Hydrogenation temp.: 225° . Sample size: 0.10 mg. Identification of hydrogenated products: a = methane; b = ethane; c = propane; d = isobutane; e = *n*-butane; f = 2-methylbutane; g = *n*-pentane.

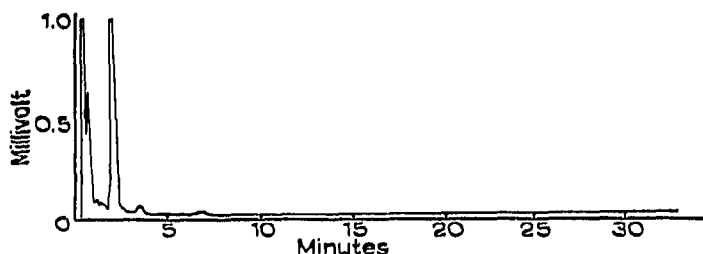


Fig. 8. Pyrogram of neoprene from TCP column. Chromatographic and pyrolysis conditions: same as Fig. 3. Sample size: 0.08 mg.

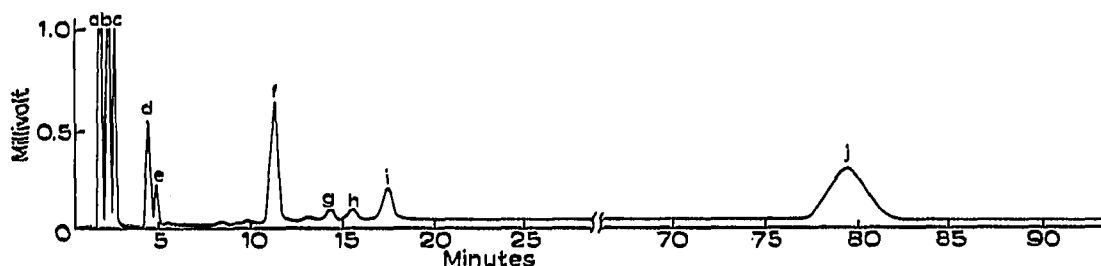


Fig. 9. Pyrogram of neoprene from HD column. Chromatographic and pyrolysis conditions: same as Fig. 6. Sample size: 0.09 mg. Identification of pyrolysis products: a = ethylene or acetylene; b = methane; c = ethane; d = propylene; e = propyne; f = isobutylene, 1-butene, or 1,3-butadiene; g = *trans*-2-butene; h = *cis*-2-butene; i = unknown; j = 2-chloro-1,3-butadiene (major product).



Fig. 10. Microhydrogenation of pyrolysis products from neoprene. Chromatographic and pyrolysis conditions: same as Fig. 6. Hydrogenation conditions: same as Fig. 7. Sample size: 0.13 mg. Identification of hydrogenated products: a = methane; b = ethane; c = propane; d = *n*-butane.

1,3-butadiene, the peak labeled "j" in Fig. 9. Since an authentic sample of this compound was not immediately available, indirect proof of its identity was established by retention time measurement and hydrogenation. Since the HD column separates products according to their boiling points, it was estimated that the boiling point of the major product was between 57 and 60°. Within this boiling range, the data in Table II suggest several possible products, e.g., *trans*-4-methyl-2-pentene, 2,3-dimethylbutane, and 1,5-hexadiene, or possibly other products not included in Table II. However, hydrogenation of the pyrolysis products (Fig. 10) produces *n*-butane. Hydrogenation products corresponding to hydrocarbons boiling between 57 and 60° are not observed. Therefore, the major pyrolysis product must be 2-chloro-1,3-butadiene (b.p. 59.4°), which would readily hydrogenate to *n*-butane. By a similar procedure, identification of the pyrolysis products associated with butyl, butadiene-styrene, and polyisoprene rubber samples was made. Table III summarizes the major pyrolysis products which can be used to identify the parent polymer samples. In all cases the pyrolysis conditions yield the monomer as the characteristic product, with the exception of butyl rubber, which yields isobutane and 2,2-dimethylpropane in addition to isobutylene (major product).

TABLE III

PYROLYSIS PRODUCTS FOR IDENTIFICATION OF RUBBER SAMPLES

<i>Sample</i>	<i>Characteristic products</i>
Natural rubber ^a	2-Methyl-1,3-butadiene
Butyl rubber	Isobutylene, isobutane, 2,2-dimethylpropane
Butadiene-styrene ^b	1,3-Butadiene or 1-butene, styrene
Polyisoprene ^a	2-Methyl-1,3-butadiene
Neoprene	2-Chloro-1,3-butadiene

^a Natural and synthetic (polyisoprene) rubbers cannot be differentiated.

^b Styrene monomer can be observed on the pyrogram from the TCP column.

KOLB *et al.* reported the pyrograms of polyethylene obtained from hydrogenation gas chromatography^{7,8}; however, exact identification of the products appearing on the pyrogram was not reported. Our pyrograms shown in Figs. 11 and 12 differ from those of KOLB *et al.* This is due in part to the chromatographic and pyrolysis conditions used to separate the volatile products. In our case the major pyrolysis product is 1-hexene. The identification of the other products is listed in Fig. 12. Hydrogenation of the pyrolysis products leads to the pyrogram in Fig. 13. Comparison of Figs. 12 and 13 confirms the identification of the products.

A more interesting polymer is the Estane 5740 X2 manufactured by B. F. Goodrich Company. Figs. 14-16 show the pyrograms from the TCP and HD columns. The pyrogram from the TCP column indicates a high boiling product as the major constituent; however, this product is not observed in the pyrogram of Fig. 15. The hydrogenated pyrogram (Fig. 16) indicates a new major product, identified as cyclopentane. To establish the true identity of the original product, the reactants used to prepare the polymer were investigated. It was found that adipic acid pyrolyzes to yield a major product identical to that in Fig. 14. It is reported in the literature that adipic acid decarboxylates at 295° in the presence of barium hydroxide to form

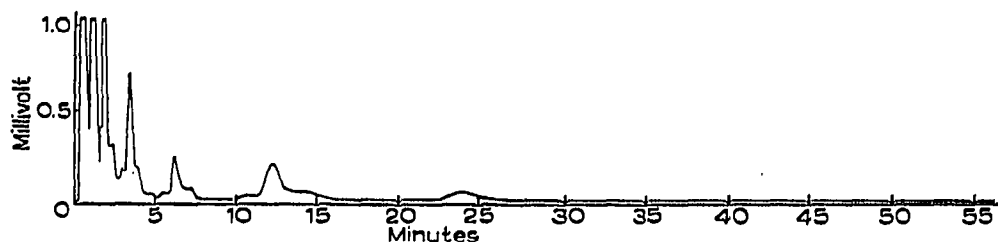


Fig. 11. Pyrogram of polyethylene from TCP column. Chromatographic and pyrolysis conditions: same as Fig. 3. Sample size: 0.07 mg.

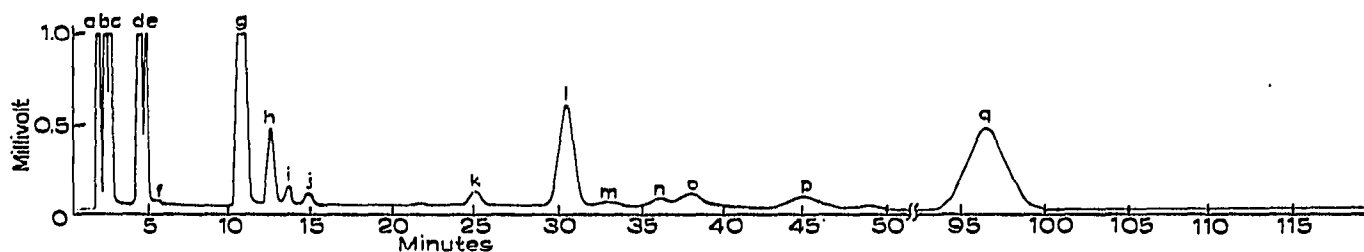


Fig. 12. Pyrogram of polyethylene from HD column. Chromatographic and pyrolysis conditions: same as Fig. 6. Sample size: 0.09 mg. Identification of pyrolysis products: a = ethylene or acetylene; b = methane; c = ethane; d = propylene; e = propyne; f = propane; g = isobutylene, 1-butene or 1,3-butadiene; h = *n*-butane; i = *trans*-2-butene; j = *cis*-2-butene; k = 2-butyne; l = 1-pentene; m = 2-methyl-1-butene; n = 2-methyl-1,3-butadiene; o = *n*-pentane; p = 2-methyl-2-butene; q = 1-hexene (major product).

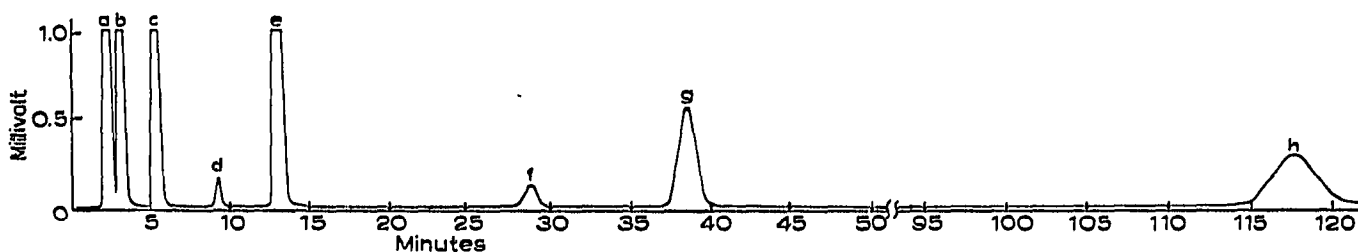


Fig. 13. Microhydrogenation of pyrolysis product from polyethylene. Chromatographic and pyrolysis conditions: same as Fig. 6. Hydrogenation conditions: same as Fig. 7. Sample size: 0.06 mg. Identification of hydrogenated products: a = methane; b = ethane; c = propane; d = isobutane; e = *n*-butane; f = 2-methylbutane; g = *n*-pentane; h = *n*-hexane.

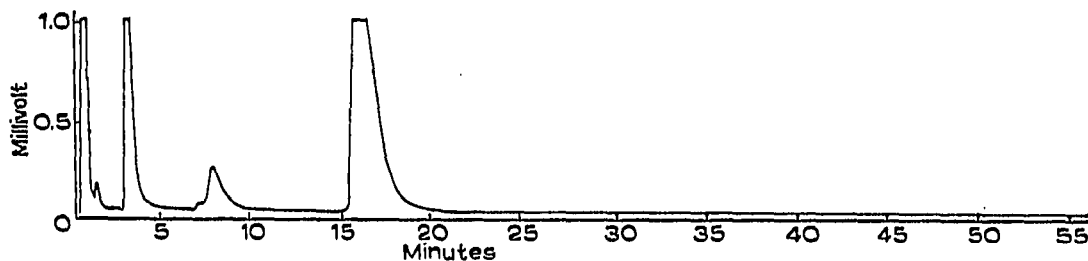


Fig. 14. Pyrogram of Estane from TCP column. Chromatographic and pyrolysis conditions: same as Fig. 3. Sample size: 0.11 mg.

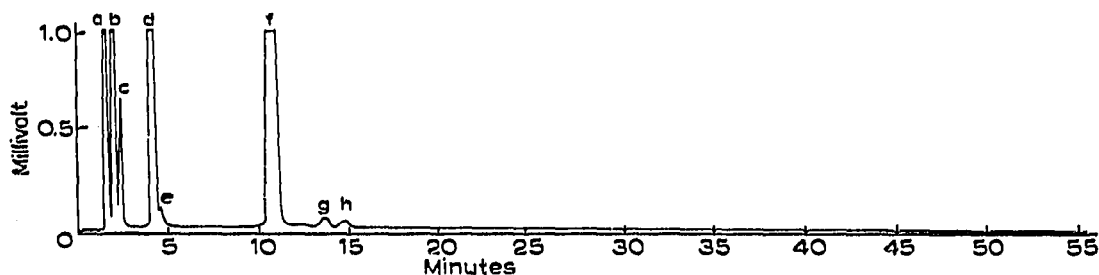


Fig. 15. Pyrogram of Estane from HD column. Chromatographic and pyrolysis conditions: same as Fig. 6. Sample size: 0.09 mg. Identification of pyrolysis products: a = ethylene or acetylene; b = methane; c = ethane; d = propylene; e = propyne; f = isobutylene, 1-butene, or 1,3-butadiene; g = *trans*-2-butene; h = *cis*-2-butene.

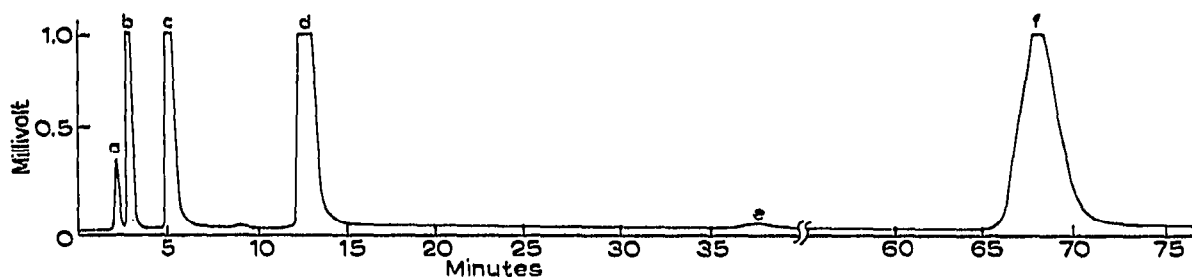


Fig. 16. Microhydrogenation of pyrolysis products from Estane. Chromatographic and pyrolysis conditions: same as Fig. 6. Hydrogenation conditions: same as Fig. 7. Sample size: 0.11 mg. Identification of hydrogenated products: a = methane; b = ethane; c = propane; d = *n*-butane; e = *n*-pentane; f = cyclopentane.

cyclopentanone¹⁰. The relative retention time of an authentic sample on the TCP column is identical to that of the major product from Estane. Cyclopentanone does not emerge from the HD column, and therefore it is not observed in Fig. 15. However, this compound hydrogenates readily to cyclopentane. Therefore, the major pyrolysis product in Fig. 14 is cyclopentanone which is characteristic of Estane 5740 X2.

It can be seen in several pyrograms that the retention times of the hydrogenated products are slightly longer than those of the corresponding saturated hydrocarbons found in unhydrogenated pyrograms. This increase in retention time is caused by the longer path length to the flame detector resulting from insertion of the hydrogenation unit. This problem is obviated by making all measurements relative to *n*-pentane.

It is evident from this study that pyrolytic-hydrogenation gas chromatography is an effective method of identifying and characterizing polymers through their pyrolysis products. The pyrograms in themselves serve as fingerprints of the parent polymer, and the identification of major pyrolysis products strengthens the analytical value of this method.

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SUMMARY

A pyrolytic-hydrogenation gas chromatograph is used to identify polymers via the identification of specific pyrolysis products. Ten polymers were successfully analyzed by this technique, and in all cases characteristic products were found. Identification of products was accomplished by retention time measurements and microhydrogenation.

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