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## THE GAS CHROMATOGRAPHIC ANALYSIS OF SOME POLYCONDENSATION POLYMERS

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### SUMMARY

A method for the identification of the basic constituents of polyesters, polyimides and polyamides, alone and in combination with each other, is proposed. It consists in splitting the polymers into the parent monomers followed by their gas chromatographic analysis. For the identification of amines and polyalcohols, and for the analysis of acids, hydrazinolysis and aminolysis with tetramethylammonium hydroxide, respectively, are recommended. The reaction conditions were studied and the analysis of various polymers is discussed.

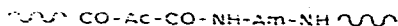
### INTRODUCTION

Polyesters, polyamides and polyimides are important polycondensation-type polymers, which have found a wide practical use.

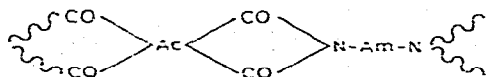
Polyesters are the condensation products of polybasic acids (Ac) and alcohols (Ao):



Polyamides are formed by the condensation of dibasic acids (Ac) and diamines (Am), or by polymerization of lactams of amino acids:



Polyimides are the final products of the reaction of polycarboxylic acid anhydrides (Ac) with diamines (Am):



If the radicals Ac and Am in polyimides are aromatic rings, the polymers possess excellent thermal stability. In order to improve their solubility and other proper-

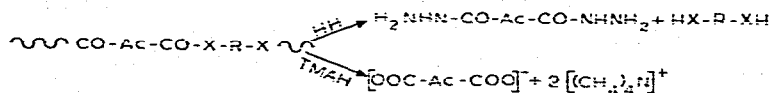
ties that are important from the point of view of applications, the polyimides are frequently combined with polyesters or polyamides. The polyester-imides and polyamido-imides obtained in this way represent a new class of polycondensation polymers with wide variations in technical properties according to their chemical structures.

For the identification of particular units, the polymer chains have to be split into the parent monomers. The splitting of polyesters is well known and easily accomplished by re-esterification reactions and alkaline or acid hydrolysis; the latter method can be also used for polyamides. The polyimide linkages are more difficult to split and require more effective reagents such as hydrazine hydrate (HH) and tetramethylammonium hydroxide (TMAH).

Although the reaction of HH with alkyl phthalimides has been known for many years<sup>1</sup>, its application to polyimides was introduced only in 1967-1968 by Dine-Hart and Wright<sup>2,3</sup>. For technical purposes, this reaction was used by Jones<sup>4</sup> as a method for cleaning and preparing printed integrated circuits. With other polymers, hydrazinolysis was applied only for the hydrolysis of poly(ethylene terephthalate) in the determination of diethylene glycol<sup>5</sup> and methyl ester end-groups<sup>6</sup>.

The pyrolysis of TMAH salts of organic acids and phenols has been proved to be a useful method for the preparation of methyl esters for gas chromatography (GC)<sup>7-14</sup>. However, we found only one mention of the splitting properties of this reagent: Bitmer *et al.*<sup>15</sup> prepared the TMAH salts of fatty acids by the aminolysis of the triglycerides with TMAH.

In the identification method proposed in this paper we utilized both HH and TMAH for splitting polycondensation polymers according to the following scheme:



where X = O or N and R = Ao or Am. In the hydrazinolysis with HH, free amines or alcohols and hydrazides are formed, while aminolysis with TMAH leads to the formation of TMAH salts of the parent acids. The reaction products of the alcohols and amines in the latter instance are not known.

## EXPERIMENTAL

### Instrumentation

A Carlo Erba (Milan, Italy) Model 2201 gas chromatograph with dual flame ionization detectors was used. Free amines, trimethylsilyl (TMS) derivatives of aminoalcohols and acid methyl esters were separated on a 120-cm long glass column of 3.5-mm I.D., packed with 3% of XE-60 on Chromosorb W AW DMCS, 0.20-0.25 mm. The temperature of the column was programmed from 80 to 200° at the rate of 5°/min. The TMS ethers of polyols were analyzed on a 1.5-m long aluminium column of 4-mm I.D., packed with 5% of SE-30 on Chromosorb W AW, 0.20-0.25 mm, with the temperature programmed from 80 to 220° at 5°/min. In some instances other special columns were used.

A simple pyrolytic device was used for the conversion of the TMAH salts of the acids being analyzed into the corresponding methyl esters. It consisted of a three-way glass stopcock with a large T-bore. One arm was wrapped with resistance wire to form an electric oven, the opposite arm was provided with a rubber stopper and the third arm, perpendicular to the first two, served as the carrier gas inlet. The liquid samples, injected in a micro-boat fixed on a 1-mm O.D. stainless-steel wire, were inserted after a short drying period by pushing the boat first through the rubber stopper and then, after opening the stopcock, into the oven. The sampling was thus accomplished without interrupting the flow of carrier gas.

### *Reagents*

Hydrazine hydrate (HH) (Ciba, Basle, Switzerland) was used as a 30% solution in water. Tetramethylammonium hydroxide (TMAH), for polarographic purposes, was obtained from Merck (Darmstadt, G.F.R.) and used as a 10% solution in water.

A model polyimide (MP) was synthesized from trimellitic anhydride and 4,4'-diaminodiphenylmethane in this Institute.

Poly(ethylene terephthalate) (PET) mat was obtained from Viledon-Werke (Weinheim, G.F.R.).

Other reagents and standards were of technical grade or better and were used as received without purification.

### *Procedures*

For hydrazinolysis, 5 mg of finely powdered sample was weighed into a glass micro-ampoule (0.35 mm I.D., 6 cm long), 40  $\mu$ l of HH was added with a Hamilton microsyringe and the ampoule was sealed over a micro-burner. After 1 h at 50° with occasional stirring, 1–2  $\mu$ l of the clear solution above the precipitate that had formed was injected into the gas chromatograph for amine analysis.

Polyamides and amide-modified polymers (amido-imides) were first hydrolyzed with 50  $\mu$ l of concentrated (37%) hydrochloric acid for 8 h at 120° in the above manner. The hydrochloric acid was then evaporated at 80–100° and 10–20 torr and the residue was treated as above.

For the analysis of polyols, their TMS ethers were first prepared. For this purpose, 20  $\mu$ l of the clear solution obtained after hydrazinolysis was transferred into another ampoule, 100  $\mu$ l of hexamethyldisilazane containing 0.5% of trichloroacetic acid was added and the ampoule was sealed and heated for 1 h at 50°. After cooling the ampoule, 2–5  $\mu$ l of the clear solution was injected into the gas chromatograph.

For aminolysis, 3 mg of finely powdered sample was weighed into a glass ampoule, 50  $\mu$ l of 10% TMAH was added and, after sealing the ampoule, it was heated for 1 h at 150°. After cooling the ampoule to room temperature, 1–2  $\mu$ l of the clear solution was injected into the micro-boat and evaporated for 2 min at 110° in a horizontal electrical oven. The boat was inserted into the pyrolytic device, first into the cold zone and then, after expelling the air, into the hot zone, which had been preheated to 340°. After 1 min, the boat was drawn out of the hot zone and the temperature programme was started for the separation of the acid methyl esters.

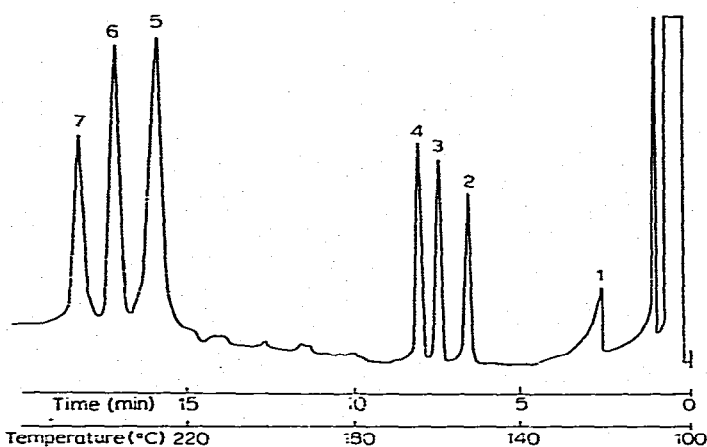


Fig. 1. Separation of free diamines on 1.2-m column packed with 3% of XE-60 on Chromosorb W AW DMCS at 100–220 (8°/min). 1 = Hexamethylenediamine; 2 = *p*-phenylenediamine; 3 = *m*-phenylenediamine; 4 = 2,4- + 2,6-toluylenediamine; 5 = naphthalenediamine; 6 = 4,4'-diaminodiphenylmethane + 4,4'-diaminodiphenyl ether; 7 = benzidine.

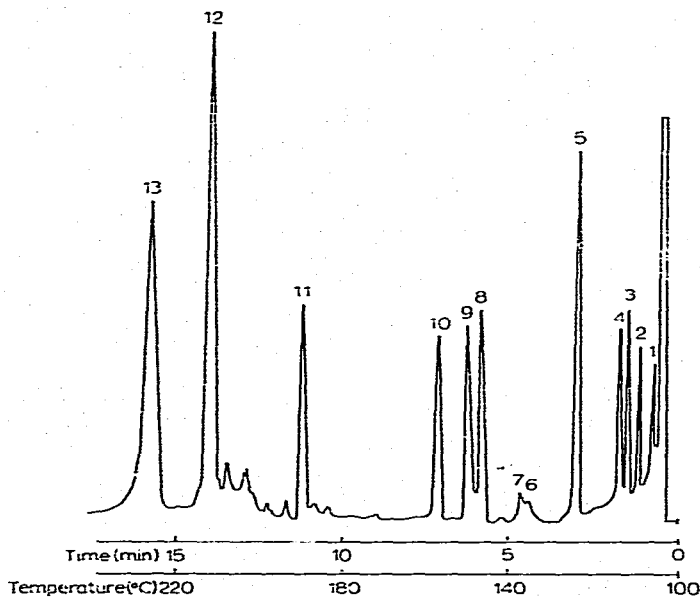


Fig. 2. Separation of methyl esters of polybasic acids. Conditions as in Fig. 1. Acid derivatives: 1 = oxalic; 2 = fumaric; 3 = maleic; 4 = itaconic; 5 = adipic; 6 = hexahydrophthalic; 7 = tetrahydrophthalic; 8 = terephthalic; 9 = isophthalic + *o*-phthalic; 10 = sebacic; 11 = trimellitic; 12 = cyclopentanetetra-carboxylic; 13 = pyromellitic.

## RESULTS AND DISCUSSION

### Gas chromatography

By using the chromatographic columns described above, we were able to separate most of the diamines, polybasic acids and polyols that occur in technical

materials (Figs. 1-3). Difficulties appeared in the analysis of alcohol-amines and phenol-amines, which, like polyols, require the deactivation of free hydroxyl groups by silylation. Under the recommended silylation conditions, only hydroxyl and carboxyl groups and not amines react, which allows them to be distinguished by either altering elution time or by an elimination technique in which the chromatograms obtained before and after silylation are compared.

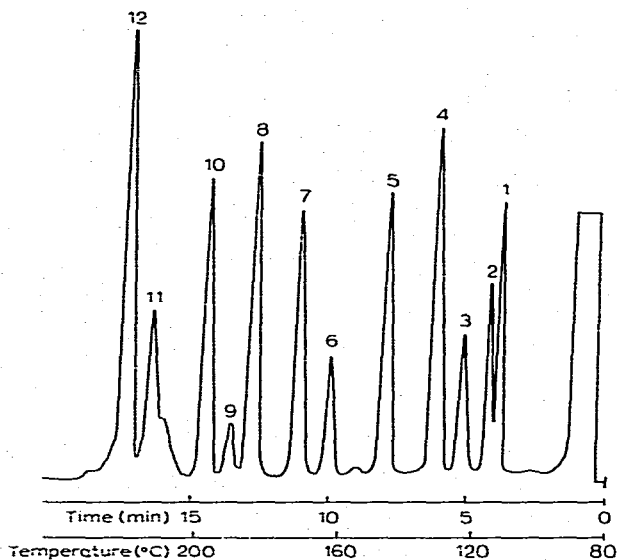


Fig. 3. Separation of TMS ethers of polyols on 1.5-m column packed with 5% of SE-30 on Chromosorb W AW at 80-220 (5 min). 1 - Ethylene glycol; 2 - 1,2-propylene glycol; 3 - 2,3-butyleneglycol; 4 - 1,3-butylene glycol - neopentyl glycol; 5 - 1,4-butylene glycol; 6 - diethylene glycol; 7 - glycerine; 8 - trimethylolethane; 9 - 1,8-octanediol; 10 - trimethylolpropane - hexanetriol; 11 - triethylene glycol; 12 - erythritol.

Under the chromatographic conditions described, some complicated polyfunctional compounds are irreversibly retained. This is the case with 3,3',4,4'-benzophenonetetracarboxylic acid methyl ester, which requires a substantially higher temperature that cannot be used with the silicone nitrile polymer phase XE-60. Lower aliphatic diamines are separated more satisfactorily either on supports modified with potassium hydroxide, on Chromosorb 103, on Tennwalt phase, or on modified carbon black (Supelco, Bellefonte, Pa., U.S.A.), which is convenient also for ethanolamines.

#### Hydrazinolysis

In order to establish the optimal conditions for hydrazinolysis, we studied the reactions of MP and technical-grade PET. First 1 mg of finely powdered or thinly cut samples was made to react in sealed ampoules with 50  $\mu$ l of the reagent at various temperatures. In defined time intervals, 1- $\mu$ l portions were injected into the gas chromatograph for the determination of 4,4'-diaminodiphenylmethane (formed from MP) or 1,2-ethanediol (formed from PET). The peak areas of parent monomers as a function of the reaction time at various temperatures are shown in Figs. 4 and 5.

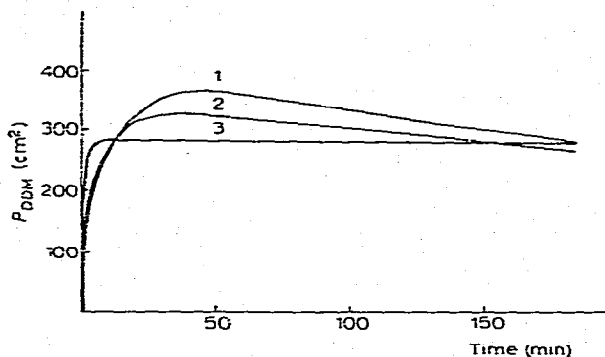


Fig. 4. Reaction rate of hydrazinolysis of a model polyimide expressed as the dependence of the peak area of 4,4'-diaminodiphenylmethane ( $P_{DDM}$ ) on reaction time. Temperature: 1, 27 ; 2, 50 ; 3, 100 .

It is obvious that the reaction with MP is very rapid and is completed in a few minutes. PET, however, reacts more slowly and the temperature dependence is more prolonged. This different behaviour results not only from the different reaction rates due to the diverse chemical structures and degrees of polymerization, but also from the form of the samples (the former was a fine powder and the latter a thinly cut mat). Hence the reaction rate is determined also by the rate of diffusion of the reagent into the sample. Therefore, occasional stirring and sufficient time must be used so as to ensure that the reaction is completed.

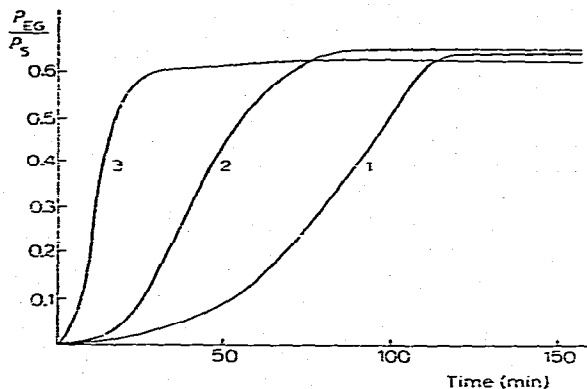


Fig. 5. Reaction rate of hydrazinolysis of poly(ethylene terephthalate) expressed as the dependence of the peak area ratio of ethylene glycol ( $P_{EG}$ ) and internal standard ( $P_S$ ) on reaction time. Temperature: 1, 25 ; 2, 35 ; 3, 55 .

The wide range of the peak areas obtained for 4,4'-diaminodiphenylmethane (Fig. 4) may be explained by its partial retention in the precipitate of trimellitic acid hydrazide. In fact, the addition of an equal amount of methanol to the reagent improved the precision. With the polyols, the presence of methanol is unsuitable because of its concurrent reaction with silylation reagent.

The excess amount of HH used is not critical: we found the same extent of reaction when 25, 50 and 100  $\mu$ l of HH was used for 1 mg of sample.

We were not able to obtain similar results with either aliphatic or aromatic polyamides which are resistant to HH.

#### Aminolysis

In order to establish the optimal conditions of aminolysis with TMAH, we proceeded in the same manner as described above. We determined the trimellitic acid trimethyl ester following the same procedure, after reaction of 1 mg of MP with 50  $\mu$ l of TMAH at various temperatures. The ratios of the peak areas of the trimethyl ester of the parent acid and the internal standard as a function of reaction time are shown in Fig. 6. Contrary to the case with hydrazinolysis, this reaction requires the use of high temperatures in order to achieve completion in a reasonable period of time. The yield of reaction products is more sensitive to excess of the reagent, and a minimum of 50  $\mu$ l of TMAH per 1 mg of sample must be used.

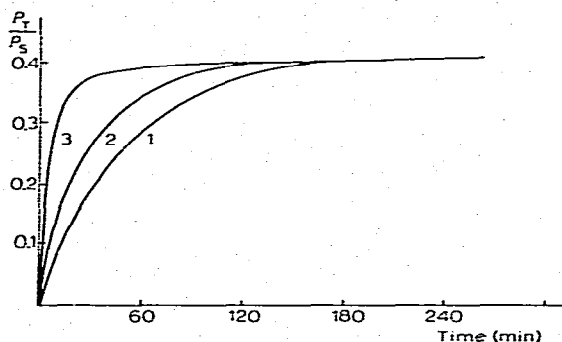


Fig. 6. Reaction rate of aminolysis of a model polyimide with tetramethylammonium hydroxide expressed as the dependence of the peak area ratio of trimellitic acid methyl ester ( $P_t$ ) and internal standard ( $P_s$ ) on reaction time. Temperature: 1, 100 ; 2, 125 ; 3, 150 .

From the quantitative viewpoint, the conditions used for the pyrolysis of the TMAH salts of acids in order to convert them into methyl esters are also important. We found that the optimal pyrolysis temperature is  $350 \pm 10^\circ$  and the drying time of the salts before pyrolysis should not exceed 2 min.

When we applied the procedure to the splitting of polyesters and polyamides, we obtained similar results. It seems that the reaction with TMAH is widely applicable and that it can be used for all classes of polymers.

#### Application to the analysis of polymers

We tested the method by analyzing the basic components in a large number of polycondensation and polyaddition polymers of known composition (model substances, defined polymers and technical materials analysed by infrared (IR) spectrometry). The polymers included polyesters and alkyds, aliphatic and aromatic polyamides, aromatic polyimides and their combinations, polyurethanes and epoxides cured with dibasic acid anhydrides. The results obtained are discussed below.

The reaction with HH is advantageous for the analysis of parent amines in polyimides and polyester-imides. Polyamides and polyurethanes remain unreacted

and first require hydrolysis with hydrochloric acid, followed by evaporation of the excess of acid and conversion of the amine hydrochlorides formed into free amines by the addition of excess of HH. Higher polyols, aminoalcohols and aminophenols must be silylated before GC analysis.

The reaction with TMAH is more universal and may serve for the identification of the acids in polyesters, polyamides, polyimides (also in their combinations) and in polyester-epoxides. On the contrary to hydrazinolysis, this reaction is inadequate for quantitative purposes.

When analyzing polyester-imides, one must take care in the identification of some polyols and diamines. After hydrazinolysis, free lower diols ( $C_2-C_4$ ) may appear on the chromatograms of amines: in this case it is useful to compare the chromatograms before and after silylation.

During the aminolysis with TMAH and the pyrolysis of salts formed, the isomerization of unsaturated acids occurs. Thus maleic and fumaric acids form the same reaction products and cannot be distinguished in this way.

In both types of splitting reaction amino acids cannot undergo subsequent GC analysis owing to the formation of non-volatile products (hydrazides with HH and unknown products with TMAH) and a different analytical method must be used in this instance.

The practical application of the methods described demonstrated that the wide range of modern heteropolymers has a very rich variety of basic components, which are particularly complicated in combinations of polymers. It is therefore advisable to combine the methods described with other identification methods, such as thin-layer, liquid and gel permeation chromatography, and especially IR spectrometry.

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