

CHROM. 14,918

ALKALI FUSION REACTION GAS CHROMATOGRAPHY OF AROMATIC POLYIMIDES, AROMATIC POLYAMIDES AND AROMATIC POLY(AMIDES-IMIDES)

J. K. HAKEN* and J. A. OBITA

Department of Polymer Science, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

(Received March 23rd, 1982)

SUMMARY

An extension of the procedure applicable to the analysis of the acidic and amino components of linear diacid–diamine condensates following cleavage using alkali fusion is reported. Separation of the methyl esters of mono-, di- and tricarboxylic aromatic acids is achieved using gas chromatography and the esters of the tetracarboxylic acids using liquid chromatography. The separation of the aromatic diamines as the trifluoroacetyl derivatives is achieved using liquid chromatography as an alternative to gas chromatography of the free diamines using a porous polymer column.

INTRODUCTION

Alkali fusion reaction gas chromatography of aromatic polyimides and aromatic polyamides with resultant analyses of the aromatic diamines has been reported by Schlueter and Siggia¹. The alkali fusion was carried out by heating the polymer with the sample in molar ratios of 50:1 or greater at 360°C for 0.5 h. A reactor constructed from a furnace pyrolyser available commercially² a decade ago was attached to the injection port of the chromatograph. The procedure employed determined the liberated amine while the polyfunctional acid remained in the reactor as the potassium salt³. The method has been extended using dicarboxylic acid–diamine condensates⁴, ω -aminoalkanoic types⁴ and fatty polyamides^{5,6} to the examination of both types of reactants.

The procedure developed (1) eliminated the restriction of availability of the chromatograph and use of the cumbersome reactor; (2) allowed the recovery and identification of the dicarboxylic acid as a suitable derivative; and (3) allowed recovery of the diamine, the chromatography of which is often improved by examination of a derivative or by the use of liquid chromatography.

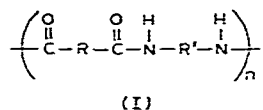
The procedure indicated is shown to be applicable to complex aromatic polyimides and aromatic polyamides, the tri- and tetracarboxylic acids being determined as their methyl esters using gas and liquid chromatography, while the separation of several aromatic amines is demonstrated using liquid chromatography. Polyamides and poly(amide-imides) are previously reacted with hydrazine hydrate following preliminary digestion with acid⁷. The di-, tri- and tetracarboxylic acids are determined

by reaction with aqueous tetramethylammonium hydroxide with pyrolysis of the resulting salts to produce volatile methyl esters.

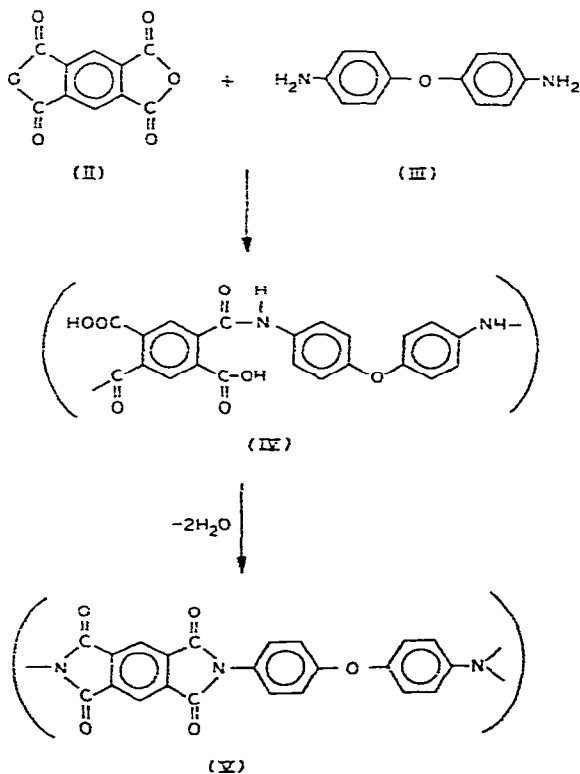
In this work the separation of the methyl esters of mono-, di- and tricarboxylic acids has been achieved using gas chromatography and the esters of tetracarboxylic acid using liquid chromatography. The separation of the aromatic diamines 4,4'-methylenedianiline and 4,4'-diaminodiphenyl ether is effected using liquid chromatography.

EXPERIMENTAL

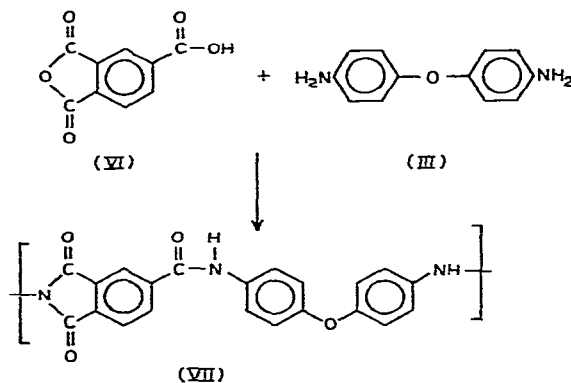
The polymers used in our earlier studies⁴⁻⁶ were linear condensation products of dicarboxylic acids and diamines. A representative polymer (I) is shown below.



where R is a methylene group or an aromatic ring and R' is a methylene group. Both R and R' may, however, be methylene groups or a simple or coupled aromatic system and examples are indicated. In addition to the polyamide linkage $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{NH} \end{array}$ it has been shown that the polyamide linkage $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}-\text{N} \end{array}$ may be cleaved by the same hydrolytic reaction¹.



For polymers of acids with higher functionality the polyimide is often produced through the polycondensation of 1,2,4,5-benzenetetracarboxylic dianhydride (II) (pyromellitic anhydride) with 4,4'-diaminodiphenyl ether (III) to form a polyamide carboxylic acid intermediate (IV), which is converted by dehydration and ring closure into the polyamide (V). This polymer is representative of the DuPont material available in various forms as Vespel and Kapton.



The use of the 1,2,4-benzenetricarboxylic acid (VI) (trimellitic anhydride) in place of pyromellitic anhydride (II) leads to the formation of poly(amide-imides) (VII). The Amoco AI polymers are aromatic homopolymers of this type. Two basic polymers are involved designated, as AI-10 and AI-11, where 4,4'-methylenedianiline and *m*-phenylenediamine are the diamines used⁸.

Fusion reaction

The fusion reactions were carried out in borosilicate tubes (10 cm × 6 mm O.D.) sealed under reduced pressure and heated for 0.5 h in a stainless-steel block at 250°C. The fusion reagent used was commercial potassium hydroxide containing about 15% of water with 1% of sodium acetate as a flux. About 0.05 g of polymer was fused with a 100% excess of reagent. The separation scheme employed has been detailed previously⁶ and is shown schematically in Fig. 1.

Gas chromatography

Gas chromatography was carried out using a Hewlett-Packard 5830A instrument with flame-ionization detection. The methyl esters were separated on a 6% SE-30 on Gas-Chrom Q column (1.2 m × 6 mm O.D. stainless steel), operated for 3 min isothermally at 160°C, then temperature programmed at 10°C/min to 240°C and held at 240°C for 5 min.

Liquid chromatography

Liquid chromatography was carried out using a Gowmac Model 80/20 instrument equipped with an ultraviolet detector operating at 254 nm. A Bondapak C₁₈ column (25 cm × 6 mm O.D.) was used, elution being effected with methanol-water (65:35) at a flow-rate of 1.5 ml/min.

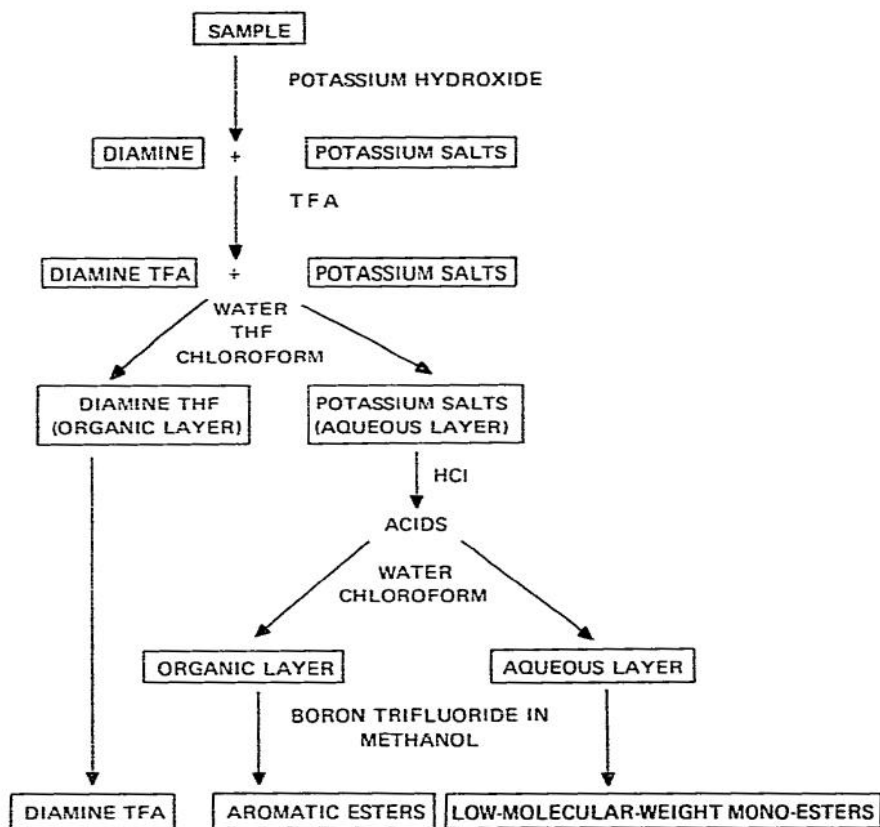


Fig. 1. Analytical scheme. THF = Tetrahydrofuran.

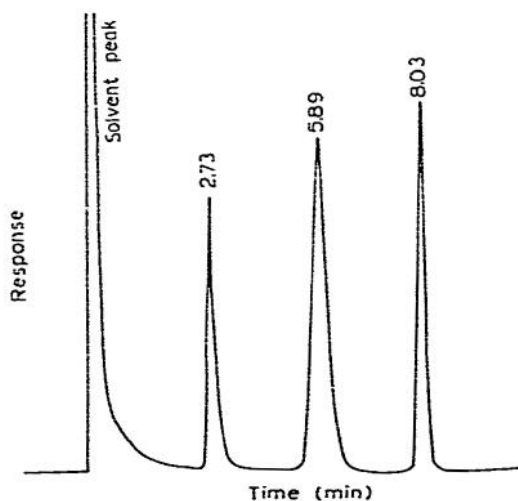


Fig. 2. Gas chromatogram showing separation of methyl esters of benzoic acid, terephthalic acid and 1,2,4-benzenetricarboxylic acid.

RESULTS AND DISCUSSION

The methyl esters of the tri- and tetracarboxylic acids recovered from the various polymers via the procedure shown in Fig. 1 were examined using gas chromatography. The monobasic acid ester and a dibasic ester (dimethyl terephthalate) were added to show a general separation. As indicated previously⁶, the three isomeric phthalate esters were not resolved by gas chromatography and subsequent examination has shown that the use of liquid chromatography with a variety of operating conditions still allows resolution into only two peaks. The separation shown in Fig. 2 indicates acceptable resolution of the mono-, di- and triesters, whereas the tetraester appears as an ill-defined bump and is unsatisfactory. Two of the isomeric triesters (unidentified) have been resolved by Rawlinson and Deeley⁹, and recently the separation of both the 1,2,4-tri- and the 1,2,4,5-tetracarboxylic esters have been reported¹⁰ using a non-polar column (6% SE-30) comparable to that used in this work, temperature programmed from 80 to 260°C at 8°C/min with a final isothermal period of 10 min at 260°C and a polyester column (6% cyclohexanedimethanol succinate) operated isothermally at 260°C, which is above the recommended maximum operating temperature. A good peak shape was achieved by these authors for the tetracarboxylic ester but could not be reproduced in our laboratory.

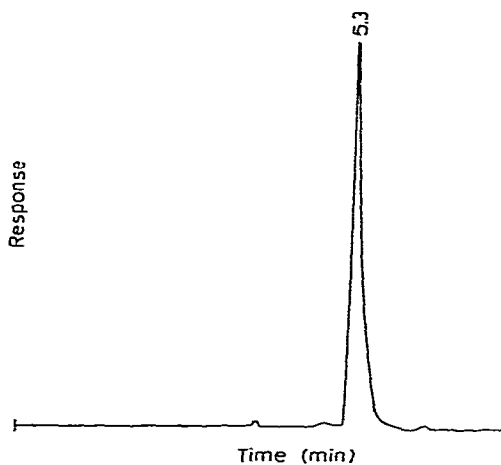
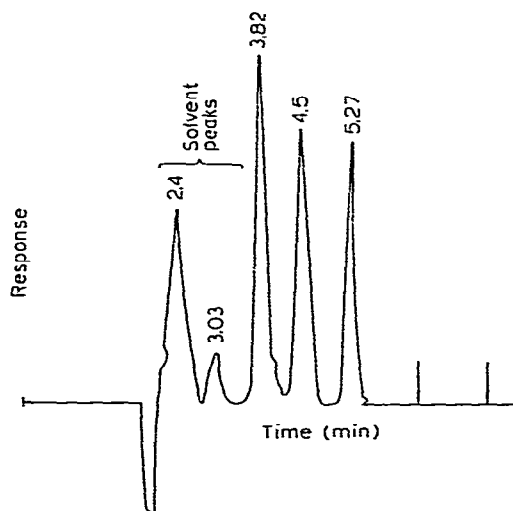


Fig. 3. Liquid chromatogram showing separation of methyl esters of terephthalic acid, 1,2,4-benzenetricarboxylic acid and 1,2,4,5-benzenetetracarboxylic acid.

Fig. 4. Liquid chromatogram showing elution of TFA derivative of 4,4-methylenediamine.

The same three di-, tri- and tetraesters were readily separated using liquid chromatography (Fig. 3).

The diamines recovered from polyamides and polyimides can be determined in a number of ways depending both on their molecular weight and on the analytical procedure to be used for the ester determinations. Schleuter and Siggia¹ determined

m-phenylenediamine, 4,4'-methylenediamine and 2,4-toluenediamine as free amines on an FFAP column, aliphatic polyamines from nylon materials⁴ and fatty polyamides^{5,6} have been determined as free amines on porous polymer columns (Porapak Q and Tenax GC) and as trifluoroacetyl (TFA) derivatives on a polyester column, and hydrazine and *p*-aminobenzoic acid from polyhydrazides have been examined as TFA derivatives by both gas and liquid chromatography¹¹.

Fig. 4 shows the separation of a representative TFA derivative of an aromatic diamine, *i.e.*, 4,4'-methylenediamine, achieved using liquid chromatography.

REFERENCES

- 1 D. D. Schleuter and S. Siggia, *Anal. Chem.*, 49 (1977) 2349.
- 2 L. Ettre and M. Varida, *Anal. Chem.*, 36 (1963) 69.
- 3 L. R. Whitlock and S. Siggia, *Separ. Purif. Methods*, 3 (1974) 135.
- 4 G. J. Gladding and J. K. Haken, *J. Chromatogr.*, 157 (1978) 404.
- 5 J. K. Haken and J. A. Obita, *J. Oil Colour Chem. Ass.*, 63 (1980) 200.
- 6 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 213 (1981) 55.
- 7 O. Mlejnek and L. Cvečková, *J. Chromatogr.*, 94 (1974) 135.
- 8 *Amoco AI Polymers for Temperature Resistant Applications*, Bulletin D1073, Amoco Chem. Corp., Chicago, IL.
- 9 J. Rawlinson and E. L. Deeley, *J. Oil Colour Chem. Ass.*, 50 (1967) 373.
- 10 E. A. Kruglov, L. G. Tsysheva, G. D. Kharlamovich and T. V. Portnova, *J. Anal. Chem. USSR*, 35 (1980) 92.
- 11 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 239 (1982) 377.