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ANALYSIS OF RESINOUS OR FATTY POLYAMIDES USING GAS AND GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

A general procedure for the rapid analysis of resinous polyamides is reported. The various acidic and amine fragments are identified after cleavage with molten alkali. Mono- and dicarboxylic acids are analysed as methyl esters and the diamines either in the free state or as trifluoroacetyl derivatives.

INTRODUCTION

While resinous polyamides have been available for several decades[1,2] their analysis has only recently been reported [3–5]. The absence of a reliable systematic procedure has been highlighted by O'Neill and Christensen[3,4] in a report of a study in which methods for high-molecular-weight diacid–diamine condensates of the nylon type were employed. The report shows the procedures to be in part repetitive, extremely time consuming and unsuitable for routine characterization. The five IUPAC samples were subsequently re-examined[5] using chromatographic procedures, which had also recently been applied to nylon analyses[6], and acceptable results were achieved in a fraction of the time previously required.

The present work reviews the analysis of polyamide materials and presents an analytical procedure generally applicable to resinous polyamides. Several complications that have been encountered since the early work[5] are discussed. The analysis of free diamines is of use for the determination of residual reactant and is also included.

Resinous polyamides

Resinous polyamides are either of the reactive or non-reactive type. The latter, having essentially stoichiometric proportions of the acidic and amino compounds, are used in printing inks, coatings and as the modifier to achieve the thixotropic character of alkyd enamels[7]. The reactive polyamides are used for cross-linking epoxide systems and are of greater importance; containing an excess of amino groups, they have terminal primary and secondary amine groups, both of which are reactive towards the epoxide group.

Polyamide analysis

High-molecular-weight linear polyamides have been analysed after cleavage by prolonged acid hydrolysis[8-14], and some of the procedures have employed chromatography to identify the fragments[6,11-14]. Diacid–diamine condensation products have been hydrolysed by refluxing with 6 *N* hydrochloric acid for 24 h at atmospheric pressure or for 4 h at 40 p.s.i.[8]. These conditions are representative of those used in the IUPAC study[3,4]. The hydrolysate is then divided and the free amines extracted with *n*-butanol from alkaline solution for chromatography. The dicarboxylic acids are extracted with diethyl ether and the dimethyl alkanoates prepared with methanol–boron trifluoride.

The same hydrolysis reagent was used by Mori *et al.*[12] at 130°C but an additional derivative step was included to allow identification of ω-amino acid type polyamides as the trifluoroacetyl (TFA) derivatives of the liberated ω-aminoalkanoic acids. With this procedure, the time required to effect hydrolysis was 2 h for nylon 6, 4 h for nylon 66 8 h for nylons 11 and 12. The same workers later reported a simplified procedure with a single derivative step, where trimethylsilylation of the diamine hydrochlorides, the dibasic acids and the ω-aminoalkanoic acid hydrochlorides from the hydrolysis was carried out simultaneously[13].

Hydrazine has been employed by Mlejnak and Cveckova[15] for the degradation of amides and imides, but with an 8-h pre-treatment with hydrochloric acid the method is thus less attractive than simple acid digestion alone.

The rapid hydrolysis of various polymeric systems[16] including amides and imides has been effected using fusion with solid alkali and flux. The solution reactions are limited by the concentration of base present and the reaction temperature possible. The procedure involved heating the polymer with 1 50 mole % excess of solid alkali and flux (1–10 %) in a device attached to the injection port of a gas chromatograph, into which the liberated amine was passed for identification.

The rapid hydrolysis was subsequently employed by Glading and Haken[6], but externally to the chromatograph, after which derivatives of the diamines, dicarboxylic acids or ω-aminoalkanoic acids were prepared. The analysis required 1–2 h and provided quantitative results. This procedure was applied to a re-examination of the IUPAC samples, and with minor modification and extension forms the basis of the present work.

Simple fatty polyamides have been examined using gas chromatography (GC) by (1) reaction GC with formation of the corresponding nitrile using a polyester–phosphoric acid column[17-19], (2) formation of methyl esters or trifluoroacetyl derivatives[20] or (3) direct examination[21-24].

EXPERIMENTAL

Samples

The polyamide samples remaining from the IUPAC study[4] or made up to the IUPAC formulations were used for the determination of the acids and diamines present. Other diamines and acidic compounds were determined in polyamides prepared in the laboratory where the free amine concentration was maintained as in the reactive IUPAC formulation E of composition: 63.0 % (w/w) common dimer acid A, 2.6 % (w/w), tall oil fatty acid, 24.0 % (w/w) triethylenetetramine and 10.4 % (w/w)

tetraethylenepentamine. The common dimer acid A had the following composition: 11.9% monomeric monocarboxylic acid, 3.9% dimeric monocarboxylic acid, 66.2% dimeric dicarboxylic acid and 18.0% trimeric carboxylic acids. The acids and diamines were present as 10% of each sample synthesized.

Gas chromatography

An F & M Model 810/29 gas chromatograph with flame ionization detectors was used for all GC separations with helium as carrier gas.

Diamine-TFA derivatives. These were separated on an aluminium column (2 m × 3 mm I.D.) packed with 5% (w/w) neopentyl glycol succinate on Gas-Chrom Q (100–120 mesh). The column and injection port were maintained at 220°C.

Tall oil fatty acids. The acids as methyl esters were separated on an aluminium column (1.2 m × 6 mm O.D.) packed with 6% OV-1 silicon gum rubber on Gas-Chrom Q (100–120 mesh). The column was operated at 200°C.

Low-molecular-weight monobasic esters. These were separated on the same column as the tall oil esters but the column was operated at 70°C.

Dimer acid esters. Separation was attempted using the OV-1 column with temperatures ranging between 150 and 250°C with isothermal and programmed operation. The dicarboxylic dimer esters were readily separated into mono- and trimeric compounds using gel permeation chromatography. This separation was considerably better than that achieved GC and was used throughout this work.

Mono- and dibasic acid modifiers. These were separated as methyl esters on the samecolumn programmed between 160 and 250°C at 10°C/min.

Diamines. These were examined using the following porous polymer columns: (1) Porapak Q (1 m × 3 mm O.D.) operated both isothermally and temperature programmed between 180 and 250°C at 6°C/min[25]; (2) Tenax GC (1.5 × 3 mm O.D.)[26] programmed from 100 to 300°C at 15°C/min then held isothermally for 2 min.

Gel permeation chromatography

The gel permeation chromatograph was constructed from individual Waters modules, namely the 6000A pump, U6K injector and R-400 differential refractive index detector. The columns used contained μStyragel packing of nominal exclusion limits 10^5, 10^4, 10^3, 500 and 100 Å.

The tetrahydrofuran (THF) solvent was distilled from potassium metal and filtered through an 0.05-μm filter before use. The antioxidant *tert.*-butylhydroxytoluene (BHT) was added at a rate of 25 ppm and the solvent was kept under nitrogen gas in the instrument reservoir. However, even with these precautions it was found necessary to use freshly distilled solvent every second day. 0.1% (w/v) solutions of standards were used. A constant temperature of 21°C was maintained.

Alkali fusion

Alkali fusion was carried out using 0.01 g of polymer with 0.1 g of a prefused mixture of potassium hydroxide and 0.5% sodium acetate prepared according to the work of Whitlock and Siggia[16]. The reaction was carried out in borosilicate glass tubes (10 mm O.D.) that were sealed under vacuum. Three identical tubes were prepared and heated in a cylindrical stainless-steel block containing four holes of

suitable diameter. The block was heated by resistance heaters, and the input current regulated to give a temperature of 260°C. The temperature was monitored by placing a thermometer in one of the four holes. The reaction mixture was allowed to reflux for 30 min and then allowed to cool to room temperature.

Separation

For the diamine analysis, each tube was cut open and 2 ml trifluoroacetic anhydride (TFAA) were added to the reaction mixture. The liberated free amine in the tube reacts with TFAA forming the amine-TFA derivative[20]. The reaction was usually complete after 15 min of stirring and standing. The excess of TFAA was destroyed by adding sufficient water which also dissolved the potassium salt in the tube. The amine-TFA derivative was dissolved by adding THF (6 ml) to the mixture which was then extracted with two 20-ml portions of chloroform.

The extracted solution was dried over anhydrous sodium sulphate and filtered. The solvents were partially removed under vacuum to give approximately 2 ml of solution. A 2-μl volume of this solution was chromatographed. The diamines were identified by comparing their retention times or separation temperatures, depending
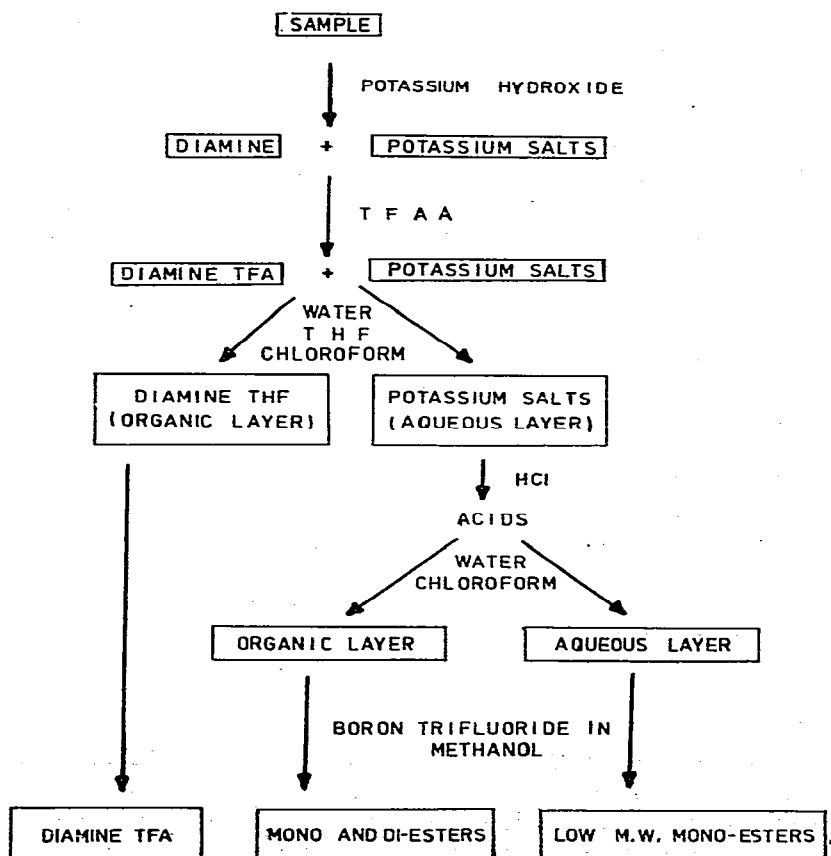

Fig. 1. Analytical scheme.

whether isothermal or temperature programmed operation was used, with the TFA derivatives of known diamines.

For the carboxylic acid analysis, the aqueous solution remaining from the above extraction was acidified with dilute hydrochloric acid and the liberated carboxylic acid extracted with two 20-ml portions of toluene. The toluene solution was dried using anhydrous magnesium sulphate and the volume was reduced under vacuum to about 10 ml. Boron trifluoride–methanol reagent (20 ml) was added to this solution and the mixture refluxed for 30 min. The resulting diester solution was transferred to a separating funnel containing 20 ml water and then extracted with toluene. The toluene solution was dried with anhydrous magnesium sulphate and the toluene removed under vacuum. Aliquots (0.5 μl) of the final solution were chromatographed. Low-molecular-weight monobasic acids which are soluble in water are identified by taking the aqueous solution remaining after the toluene extraction and esterifying as above. The separation scheme is shown in Fig. 1.

RESULTS AND DISCUSSION

The application of the procedure is illustrated by considering a reactive polyamide, i.e., the IUPAC sample E, which forms the basis of the various samples prepared for this study. Fig. 2 shows a chromatogram of the TFA derivatives of triethylenetetramine and tetraethylenepentamine, while Fig. 3 shows the separation of the dimer acids achieved by gel permeation chromatography. Dimer acid methyl
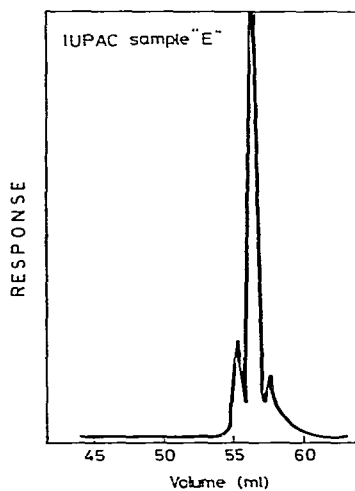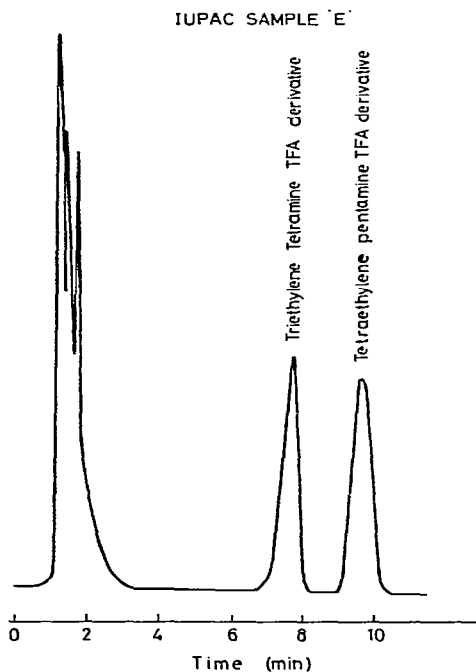

Fig. 2. Chromatogram showing TFA derivatives of triethylenetetramine and tetraethylenepentamine.

Fig. 3. Gel permeation chromatogram showing separation of methyl esters of dimer acids into C_{18}, C_{38} and C_{54} components.

esters have been examined by GC[27,28] on polysiloxane gum columns at high temperature. Separation of the monomer (C_{18}) and dimer (C_{36}) components is satisfactory, but separation of the trimer component (C_{54}) is very poor and gel permeation chromatography is preferred. Separation of the tall oil methyl esters[29-33] is a typical fatty acid analysis and Fig. 4 shows such a separation with a polysiloxane gum column; greater resolution of the component fatty acids may be achieved using a polyester column.
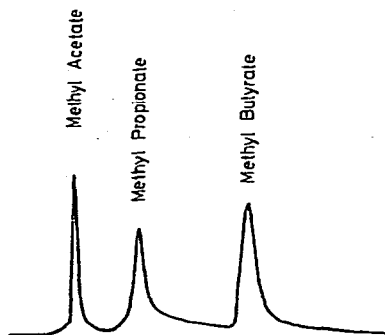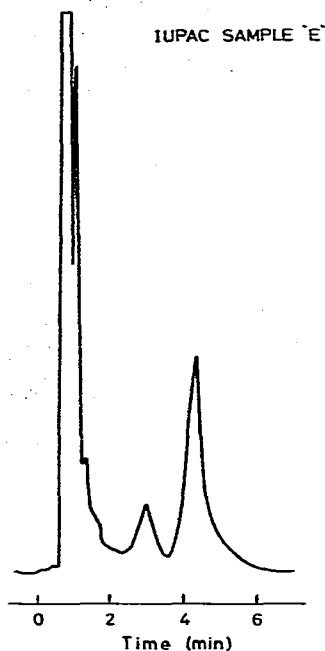

Fig. 4. Gas chromatogram of tall oil fatty esters using an OV-1 column operated at 200°C.

Fig. 5. Chromatgram showing separation of simple aliphatic esters using an OV-1 column operated at 70°C.
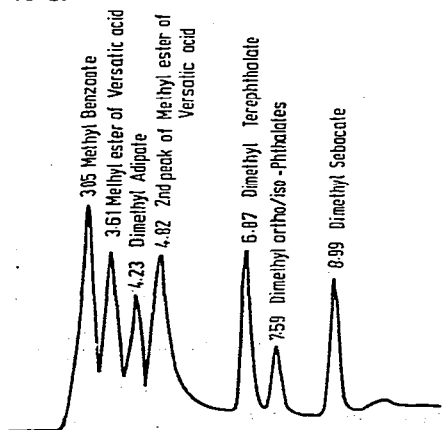

Fig. 6. Chromatogram showing separation of acidic modifiers on an OV-1 column programmed between 160 and 250°C at 10°C/min. Numbers above the peaks refer to computer-produced retention values and are of no relevance to the present paper.

The low-molecular-weight acids used as chain terminators are recovered by the procedure for water soluble acids shown in the analytical scheme (Fig. 1). Fig. 5 shows a chromatogram of the separation of the three simple acids.

Other acids used in polyamides include benzoic acid, methyl benzoate being the first peak appearing on the chromatogram (Fig. 6). Versatic acids, commercially available mixed synthetic branched chain acids (Shell Chemicals), have found limited use in resin making and the product Versatic 911 is shown in Fig. 6 as two peaks due to the C_9 and the C_{11} components respectively. Separation of the common resin acid oorthophthalic is shown, while the two isomers iso- and tere-phthalic acids are super-imposed. Resolution of the three isomers has been reported using bentone 34[34], however the method has not been successfully used in the laboratory[35]. Separation of the aliphatic dicarboxylic esters has been achieved and these are included in Fig. 6.

Separation of all of the diamines as TFA derivatives is shown in Fig. 7, where it is apparent that the propylene derivative is eluted before the ethylene derivative due apparently to the different nature of the TFA substitution, while the peaks of the diethylenetriamine and 1,6-diaminohexane derivatives are superimposed.
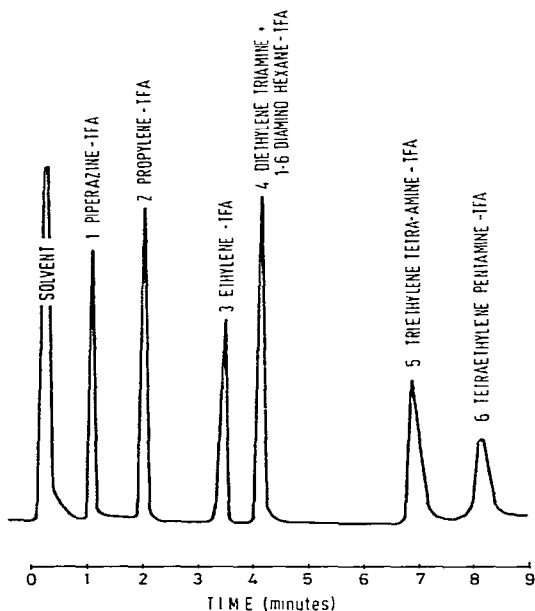

Fig. 7. Gas chromatogram of polyamide diamine-TFA derivatives. For explanation of numbers above the peaks see legend to Fig. 1.
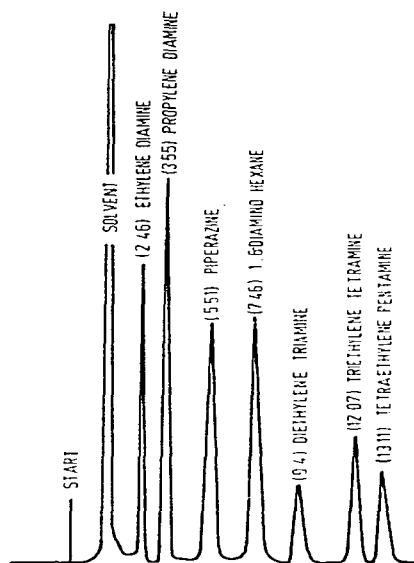
Fig. 8. Gas chromatogram of polyamide diamines. For explanation of numbers above the peaks see legend to Fig. 1.

A chromatogram of a separation of the free amines on a Tenax GC column is shown in Fig. 8, where all of the amines are resolved with little overlap.

CONCLUSION

The analysis of resinous polyamides using alkaline hydrolytic fusion is shown to require a fraction of the time for the usual prolonged acid hydrolysis. Separation of

the amino constituents has been effected both by GC of the liberated diamines and of the diamine-TFA derivatives. In addition to analysis of the dimer constituent and of the conventional fatty acids, separation of a variety of mono- and dicarboxylic acids used as modifiers has been achieved.

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