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### An Analytical Scheme for Resinous Polyamides

J. K. Haken<sup>a</sup>; J. A. Obita<sup>a</sup>

<sup>a</sup> Department of Polymer Science, The University of New South Wales, Kensington, Australia

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## An Analytical Scheme for Resinous Polyamides

J. K. HAKEN and J. A. OBITA

Department of Polymer Science  
The University of New South Wales  
P.O. Box 1, Kensington 2033, Australia

### ABSTRACT

The analyses of resinous polyamides has been very limited; the sole available work would appear to be a cooperative IUPAC study where the overall results were generally poor, particularly considering the effort devoted to the study. The examinations reported employed chemical analyses of the samples as received and after hydrolysis, together with instrumental analyses using IR and NMR spectroscopy and gas and gel permeation chromatography. A successful procedure for the rapid analyses of these IUPAC polyamides has been developed in which cleavage is carried out using alkali fusion rather than the prolonged acidic hydrolysis procedures previously used. The various acidic and amine fragments produced have been identified after formation of methyl esters of the dicarboxylic acids and trifluoroacetyl derivatives of the diamines using gas and gel permeation chromatography. The limitations of examination of the free diamines is described.

### INTRODUCTION

Resinous or fatty polyamides are condensation polymers of polymeric fatty acids with di- or polyamines. Their properties depend on the polyamine used, the polymeric acid, and its modification with

other acids. The resinous polyamides differ from the usual diacid-diamine type of nylon polyamide in that the major component is a dimer acid, a 36-carbon dibasic acid, which influences the physical properties particularly enhancing the solubility. The products were developed in the 1940s at the Northern Regional Research Laboratories of the U.S. Department of Agriculture firstly using ethylene diamine [ 1 ], which has become the major diamine component, and subsequently with other polyamines and with the addition of monobasic and other dibasic acids [ 2 ].

Resinous polyamides are of two types: The nonreactive polyamides, with essentially stoichiometric quantities of amine and acid, find use in printing inks, various minor coating applications, and as the modifier to achieve the thixotropic character of alkyd enamels [ 3 ]. The reactive polyamides employ an excess of the amine with the resulting product having terminal primary and internal secondary amine groups. The products are used as cross-linking agents for epoxy systems, the epoxy group reacting with both primary and secondary amine groups to form secondary and tertiary amino compounds.

A recent IUPAC cooperative study [ 4, 5 ] has highlighted the lack of a reliable systematic method of analysis for fatty polyamides, and a study of the literature failed to show any analytical procedures for the materials. The procedures indicated in the report [ 4 ] are in part repetitive, extremely time consuming, of limited accuracy, and generally unsuited for any type of routine characterization. While some information was obtained by preliminary chemical and spectroscopic examination, prolonged acid hydrolysis was necessary to produce the reactant acid for chromatographic analysis and the amine compounds for spectrophotometry.

Acid hydrolysis of polyamides, mainly higher molecular weight linear materials of the nylon type, has been studied by various workers [ 6-12 ], and some of the procedures have employed chromatography to facilitate the analyses [ 9-12 ]. Anton [ 9 ] hydrolyzed the nylon samples resulting from diamine-dicarboxylic acid condensation by refluxing for 24 h with 6 N HCl at atmospheric pressure or for 4 h at 40 psi. The former conditions are representative of those used in the IUPAC study. The hydrolysate was divided and the diamines were extracted with n-butanol from alkaline solution. Dicarboxylic acids were methylated with methanol/boron trifluoride and chromatographed. Mori and co-workers [ 10 ] employed the same acid hydrolysis but at 130°C with an additional derivative step to allow separation of the products. Nylon 6 required 2 h, nylon 66 4 h, and nylons 11 and 12 8 h of digestion to effect cleavage. The hydrolysis products were esterified with hydrochloric acid and methanol and then reacted with trifluoroacetyl anhydride (TFA). The same co-workers [ 11 ] reported a modified procedure involving a single derivative step. The method involved trimethylsilylation of the diamine hydrochlorides, the dibasic acids, and the  $\omega$ -aminoalkanoic acid hydrochlorides from the hydrolysate. The dried products were directly silylated with bis(trimethylsilyl)acetamide (BSA) and chromatographed. The effect of hydrochloric

TABLE 1. Composition of Polyamides used in IUPAC Study

Polyamide	Component	Weight percent
A	Methyl epoxy stearate	16.0
	Tall oil fatty acids	37.3
	Tetraethylene pentamine	46.0
B	Common dimer acid A <sup>a</sup>	73.8
	Tall oil fatty acid	9.1
	Diethylene triamine	15.1
	p-tert-Butyl phenol novolak	2.0
C	Common dimer acid B <sup>a</sup>	80.0
	Propionic acid	6.0
	Hexamethylene diamine	9.0
	Ethylene diamine	5.0
D	Distilled dimer acid A <sup>a</sup>	63.4
	Azelaic acid	17.3
	Ethylene diamine	6.1
	Piperazine	13.2
E	Common dimer acid A <sup>a</sup>	63.0
	Tall oil fatty acid	2.6
	Triethylene tetramine	24.0
	Tetraethylene pentamine	10.4

<sup>a</sup>The common dimer acid A contained (determined by GC by the supplier) monomeric monocarboxylic acid 11.9%, dimeric monocarboxylic 3.9%, dimeric dicarboxylic 66.2%, and trimeric 18.0%. Common dimer acid B gave 7.0, 4.7, 70.7, and 17.6% for the same components. For the distilled dimer acid the corresponding figures were 7.1, 0.7, 92.2, and 0.0%.

acid on the trimethylsilyl derivative formation was eliminated by the addition of triethylamine to the reaction products. An essentially identical procedure, using hydrochloric acid and trimethylsilyl derivative formation, was reported at about the same time by Tengler [12].

The degradation of polyamides and polyimides using hydrazine has

been reported by Mlejnak and Cveckova [13] but the procedure, which involves a prolonged (8 h) pretreatment with hydrochloric acid, is of little utility as it is less attractive than the method of Anton [9].

The rapid hydrolysis of amides and imides has been effected by Siggia and various co-workers [14-16] using fusion with solid alkali and flux. The solution reactions have been limited by the concentration of base present and the reaction temperature possible. The procedure involved heating the polymer with a 50 mol% excess of solid alkali and flux (1-10%) within a device attached to the injection port of a gas chromatograph, into which the liberated amine was passed for identification. The reduced hydrolysis period was subsequently employed by Glading and Haken [17] in an analytical procedure for both diamine-dicarboxylic acid and  $\omega$ -aminoalkanoic acid-type polyamides requiring 1 to 2 h and providing quantitative results. The IUPAC study considered five fatty polyamides of known composition as shown in Table 1, these being the usual type of condensation products of low molecular weight, polyfunctional amines with difunctional dimer acid materials.

The present paper shows application of the alkali fusion procedure to the standard polyamides and demonstrates that considerable improvement of the analytical procedure is possible.

## EXPERIMENTAL

### Samples

The polyamides A, C, and D were samples remaining from the IUPAC study while the materials B and E were produced in the laboratory by simple condensation according to the formulation shown in Table 1 and using a procedure suggested by an international producer. The dimer acid used was Empol 1022 (Unilever-Emery). The products A and E, with significantly higher amine content, are of the reactive type.

### Gas Chromatography

An F and M model 810/29 gas chromatograph with flame ionization detector was used for all gas chromatographic separations with helium as carrier gas.

Diamine-TFA Derivatives. These were separated on a 2 m  $\times$  3 mm i.d. aluminum column 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. These were separated on a 1.2 mm length of aluminum column (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 operated isothermally at 130°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 monomeric, dimeric, and trimeric compounds using gel permeation chromatography. This separation was considerably better than that achieved by gas chromatography and was used throughout the work.

Diamines. These were examined using the porous polymers Porapak Q and Tenax GC. (1) The Porapak Q column (1 m × 3 mm o.d.) was operated both isothermally and temperature programmed 180-245°C at 60°/min [18]; (2) the Tenax GC column (1.5 m × 3 mm o.d.) was operated at 300°C [19].

### Gel Permeation Chromatography

The gel permeation chromatograph unit was constructed from individual Waters modules, namely, the 6000A pump, U6K injector, and R-400 differential refractive index detector. The columns used contained  $\mu$ -Styragel packing of nominated exclusion limits 10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, 500, and 100 Å.

The tetrahydrofuran solvent (THF) was distilled from potassium metal and filtered through a 0.05  $\mu$ m filter before use. The antioxidant tertiary butyl hydroxy toluene (BHT) was added at a loading of 25 ppm and the solvent was kept under a nitrogen blanket 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 were used for all standards. 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 Siggia and his co-workers [20]. The reaction was carried out in 10 mm o.d. borosilicate glass tubes that were sealed under vacuum. Three identical tubes were prepared and heated in a cylindrical block of stainless steel 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 half an hour and then left to cool to room temperature.

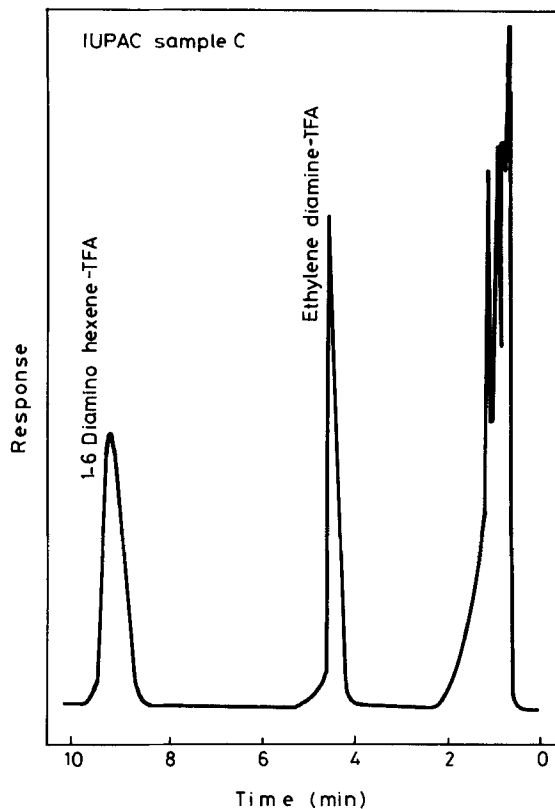


FIG. 1. Gas chromatogram showing separation of TFA derivatives of 1,6-diaminohexane and ethylene diamine.

### Separation

For the diamine analysis, each tube was cut open and TFA (2 mL) added to the reaction mixture. The liberated free amine in the tube reacts with TFA, forming an amine-TFA derivative. The reaction was usually complete after 15 min of stirring and standing. The excess TFA 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  $2 \times 20$  mL portions of chloroform. The extracted solution was dried over anhydrous sodium sulfate and filtered. The solvents were partially removed under vacuum to give approximately 2 mL of solution of which  $2 \mu\text{L}$  was chromatographed. The diamines were identified by comparing their retention times or separation

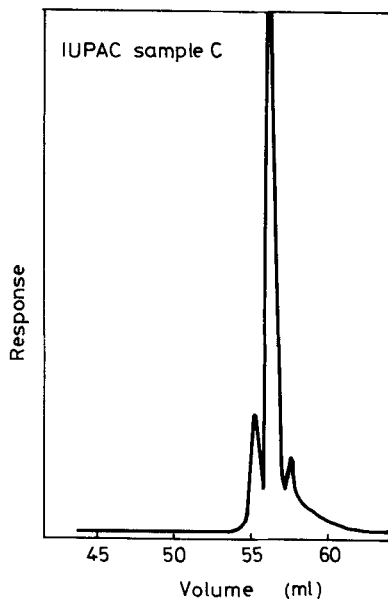


FIG. 2. Gel permeation chromatogram of dimer acid methyl esters.

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

For the dicarboxylic acid analysis, the aqueous solution remaining from the above extraction was acidified with dilute hydrochloric acid and the liberated dicarboxylic acid extracted with  $2 \times 20$  mL portions of toluene. The toluene solution was dried, using anhydrous magnesium sulfate, and the volume reduced under vacuum to about 10 mL. Boron trifluoride-methanol reagent (20 mL) was added to this solution and the mixture refluxed for half an hour. The resulting solution of the diester was transferred to a separating funnel containing 20 mL of water and then extracted with toluene. The toluene solution was once more dried over anhydrous magnesium sulfate and the volume reduced under vacuum until all the toluene was removed.  $0.5 \mu\text{L}$  of the final solution was chromatographed.

For low molecular weight monobasic acids, which are soluble in water, the aqueous solution remaining after the toluene extraction above was esterified as above and chromatographed.

## RESULTS AND DISCUSSION

The analyses have been conducted generally on a qualitative basis, although it has been shown with conventional linear polyamides [17]



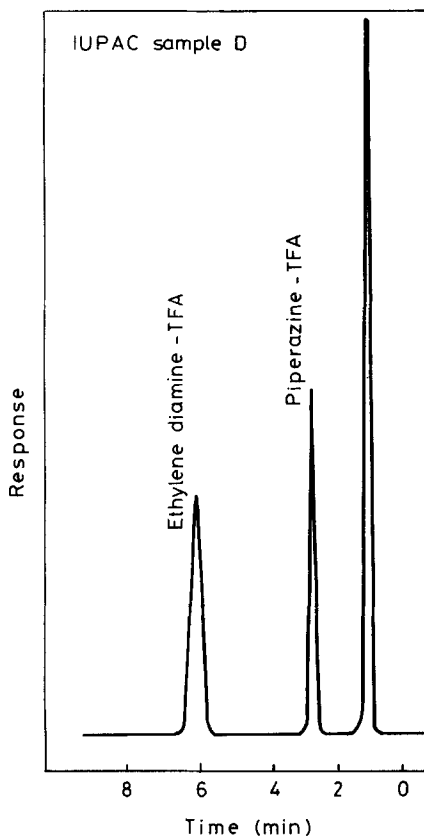


FIG. 3. Gas chromatogram showing separation of TFA derivatives of ethylene diamine and piperazine.

that essentially quantitative results were achieved with diamines and simple dicarboxylic acids. It will be indicated elsewhere [21], in a general analytical scheme for polyamides, that the diamines and modifying monocarboxylic acids are essentially quantitatively cleaved. Recovery of the fatty materials is less clear cut as, while both tall oil fatty acids and dimer acids have been separated by gas chromatographic procedures, the recovery after cleavage of a resin is less satisfactory as oxidative and isomerization reactions will always occur to some extent during the thermal fusion reaction and with the alkali used in the analysis [22-24]. Despite the possibility of these reactions, the procedures reported clearly show the presence of tall oil and dimer acids in the samples considered with near quantitative results.

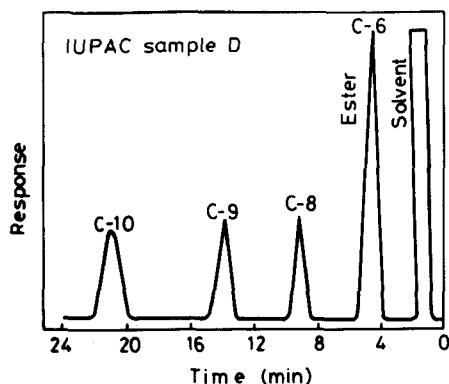


FIG. 4. Chromatogram showing separation of the methyl esters of aliphatic dicarboxylic acids.

Tall oil fatty acids have been examined as methyl esters by several groups of workers [25-29], and the procedures applicable to fatty acid esters generally, with separation on polyester columns, are readily applied. The separation of dimer acids by gas chromatography has been the subject of several reports [30, 31], all using polysiloxane gum columns at high temperatures. These procedures provide quite poor separation of the dimer esters. Gel permeation chromatography, which provides a much superior separation, has been used such that the monomer (C18), dimer (C36), and trimer (C54) components may each be estimated.

The diamines were successfully separated as the TFA-derivatives on packed columns while the free amines were not eluted. The diamines were, however, separated with porous polymer columns, ethylene diamine and piperazine being well separated using Porapak Q but triethylene pentamine and tetraethylene pentamine were not eluted. This is similar to results achieved by Casselman et al. [18]. All of the amines of interest were eluted from a Tenax GC column; the peak shapes of the higher amines were rather poor and unsuitable for quantification.

The procedure developed was demonstrated using the IUPAC samples. Separations of tall oil fatty acids and tetraethylene pentamine from Sample A were carried out without difficulty. The methyl epoxy stearate was not separated by gas chromatography; this result is in agreement with the earlier report of O'Neill and Christensen [5], who indicated that the common ring-opening reaction of amine-epoxy would occur such that the ester would not be recovered after the hydrolysis. The use of gel permeation chromatography produced a peak which did not coincide with the dimer ester and is further indication of the formation of an addition compound.

Sample B was separated with derivatives of diethylene triamine

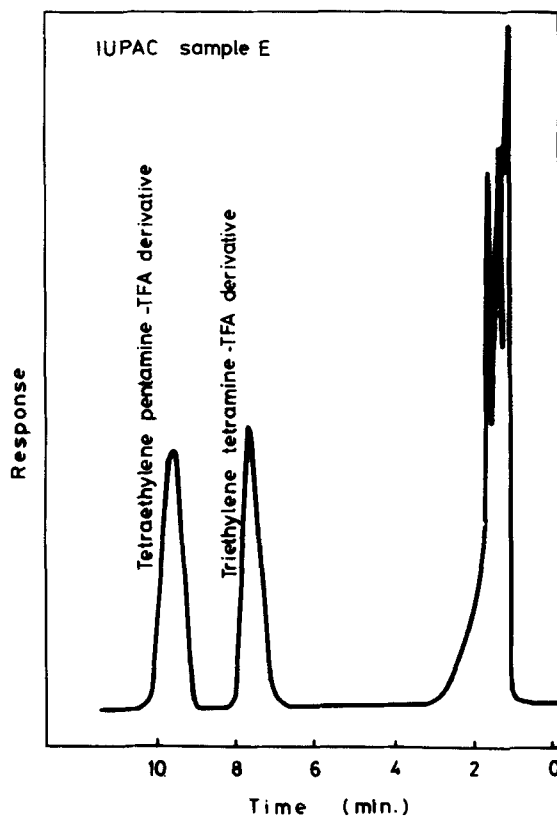


FIG. 5. Gas chromatogram showing separation of TFA derivatives of triethylene tetramine and tetraethylene pentamine.

and of tall oil esters, being determined by gas chromatography, while monomer, dimer, and trimer components of the dimer acids were examined using gel permeation chromatography. The antioxidant, *p*-tert-butyl phenol novalac, was not detected by the analysis.

The diamines present in Sample C were readily resolved and the chromatogram is shown in Fig. 1, while Fig. 2 shows the separation of the dimer esters by gel permeation chromatography. The methyl propionate was identified by chromatography of the extract containing water-soluble esters.

The analysis of Sample D paralleled that of Sample C; the separation of ethylene diamine and piperazine is shown in Fig. 3. The azelaic acid was readily detected by gas chromatography, it having been estimated quantitatively previously [17] as a component of nylon 610, and is shown in Fig. 4.

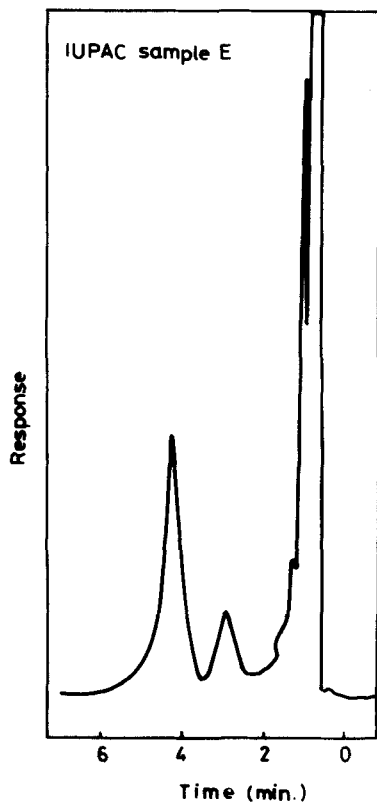


FIG. 6. Gas chromatogram of tall oil fatty esters.

Figure 5 shows a chromatogram of the derivatives of triethylene tetramine and tetraethylene pentamine from Sample E. The dimer acids were separated by gel permeation chromatography; Fig. 6 shows the gas chromatographic separation of the tall oil acid methyl esters.

### CONCLUSION

The alkali fusion procedure employed for the hydrolysis of the polyamide is much quicker, i.e., 30 min, than the prolonged acid hydrolysis used previously with nylon samples and adapted by the IUPAC collaborators. Separation of the hydrolysis products by chromatographic means is considered to be more satisfactory for

the diamines than the spectroscopic methods previously used [4]. Similarly, gel permeation chromatography has been found to be more valuable for resolution of the components of dimer acids than high temperature gas chromatography on a nonpolar stationary phase.

The procedure reported is believed to be generally applicable and provides within a few hours an analysis which is in part quantitative and in part semiquantitative with the well-known constraints indicated.

A number of other components have been found in commercially available resinous polyamides that have been examined, and polyamide analysis generally has been considered elsewhere [21].

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