

Note

Gas chromatographic analysis of linear polyamides and copolyamides

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While the acidic hydrolysis of certain polyamides has been the subject of several reports¹⁻⁴ of satisfactory analytical procedures for the constituent diamine, prolonged reaction periods or elevated pressures are necessary in order to carry the sluggish reaction towards completion.

Anton¹ effected the hydrolysis of nylon samples resulting from diamine-dicarboxylic acids by refluxing for 24 h with 6 *N* hydrochloric acid at atmospheric pressure or for 4 h at 40 p.s.i. The hydrolysate was divided and the diamines were extracted with *n*-butanol from alkaline solution for examination. The methyl esters of the dicarboxylic acids were prepared with methanolic boron trifluoride and chromatographed. Nylon 6, yielding ω -aminocaproic acid, was not resolved whereas with the column conditions used nylon 6,10 and nylon 6,T could not be identified due to coincident peaks of dimethyl sebacate and dimethyl terephthalate.

Mori *et al.*² employed the same acid hydrolysis but at 130° with an additional derivative step to allow separation of the products. Nylon 6 required 2 h, nylon 6,6 4 h and nylon 11 and 12 8 h of digestion to effect cleavage. The hydrolysis products were esterified with hydrochloric acid and methanol and then subjected to reaction with trifluoroacetyl anhydride.

The same workers³ later reported a modified procedure involving a single derivative step. The method involved trimethylsilylation of the diamine hydrochlorides, the dibasic acids and the ω -aminoalkanoic acid hydrochlorides from the hydrolysate. The dried products were directly silylated with bis(trimethylsilyl)acetamine (BSA) and chromatographed. The effect of hydrochloric acid on the TMS derivative formation was eliminated by the addition of triethylamine to the reaction products. An essentially identical procedure using hydrochloric acid and TMS derivative formation was reported at about the same time by Tengler⁴.

The degradation of polyamides and polyimides using hydrazine has been reported by Mlejnek and Cveckova⁵ and earlier with polyimides by Dine-Hart and Wright^{6,7}, but the procedure, which involves a prolonged (8-h) pre-treatment with hydrochloric acid, is of little utility as it is less attractive than the method of Anton¹.

Frankoski and Siggia first applied alkali fusion to esters that are difficult to saponify⁸ and later to amides, anilides and ureas⁹. The fusion involves heating solid

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alkali with the sample in molar ratios of 50:1 or greater at 360° for 0.5 h for nylon 6,6 and 6,10, after which the liberated diamine is determined by gas chromatography. A review by Whitlock and Siggia¹⁰ discusses fusion reaction gas chromatography generally and indicates briefly the analysis of the diamines from polyimides, polyamideimides and aromatic polyamides.

Elimination of the prolonged digestion is an obvious advantage of alkali fusion although only the amino component is determined. In the work of Siggia and co-workers⁸⁻¹⁰ a reaction chamber constructed from a pyrolyser is used, which prevents the use of the gas chromatograph during the fusion.

This paper reports a rapid method for the analysis of diacid-diamine and ω -aminoalkanoic acid polyamides by the use of alkali fusion with analysis of the diamine and the methyl esters of the dicarboxylic or the ω -aminoalkanoic acids in about 45 min.

EXPERIMENTAL

Gas chromatography

The analyses were performed on a Hewlett-Packard Model 5750B research chromatograph fitted with column splitters and multi-columns in parallel with flame-ionization detection. Signals were recorded on a multi-channel recorder or an on-line computer processor.

The stainless-steel columns (2 m \times 6.35 mm I.D. were maintained isothermally at 200° and were packed with 5% diethylene glycol adipate on Chromosorb W AW DMCS for the esters and 1% Apiezon L on 60-80-mesh glass beads for the diamines.

Alkali fusion

The fusion was carried out using 0.1 g of the polymer with 1 g of the potassium hydroxide-sodium acetate reagent prepared according to the work of Frankoski and Siggia^{8,9}. The reaction was carried out in 9 mm O.D. borosilicate glass tubes that were sealed under reduced pressure. Four identical tubes could be prepared and heated in a cylindrical block of stainless steel containing four holes of appropriate diameter. The block was heated with resistance heaters, the input being suitably regulated to give a temperature of 300°. After the reaction, the tubes were removed from the heater, allowed to attain room temperature and then refrigerated to 0° before opening to prevent loss of the volatile amine.

On cooling, water was added to the reaction product and the diamine extracted with two 30-ml portions of *n*-butanol. For the diamine analyses the volume was reduced to 5 ml and 1 μ l was taken for chromatography. For the dicarboxylic acid analysis the aqueous solution was acidified with dilute hydrochloric acid and evaporated to dryness. The free acids were mixed with 10 ml of boron trifluoride-methanol reagent and heated to boiling, while aromatic diacids required refluxing for 1 h. The resulting solution of the diesters was transferred to a separating funnel containing 30 ml of water and then extracted twice with toluene. The toluene was dried over anhydrous magnesium sulphate and the volume reduced to approximately 5 ml and transferred into a volumetric flask prior to gas chromatography.

RESULTS AND DISCUSSION

Analyses were carried out on four polyamide samples produced by diamine-dicarboxylic acid condensation. The samples of nylon 6,6, 6,9, 6,10 and 6,12, which are condensation products of 1,6-diaminohexane with hexanedioic acid (adipic acid), nonanedioic acid (azelaic acid), decanedioic acid (sebacic acid) and dodecanedioic acid, respectively, were examined after fusion for 30 min.

Essentially quantitative conversions were achieved; the yields of polymer based on dimethyl ester and diamine recoveries for a series of analyses are shown in Tables I and II, respectively, together with the errors involved. The values each refer to the starting polymer calculated to 0.05 g. The chromatogram of methyl esters and of the recovery from nylon 6,9 is shown in Fig. 1, while Fig. 2 shows the separation of the 1,6-diaminohexane from nylon 6,6.

TABLE I

QUANTITATIVE DETERMINATION OF METHYL ESTERS OF DICARBOXYLIC ESTERS

Nylon	Weight of polymer (g)					Error (%)
	1	2	3	4	Average	
6,6	0.0487	0.0490	0.0485	0.0498	0.0490	-2
6,9	0.0491	0.0495	0.0496	0.0498	0.0495	-1
6,10	0.0485	0.0491	0.0487	0.0487	0.0488	-2.4
6,12	0.0480	0.0490	0.0487	0.0487	0.0486	-2.8

TABLE II

QUANTITATIVE DETERMINATION OF 1,6-HEXANEDIAMINE IN NYLON SAMPLES

Nylon	Weight of polymer (g)					Error (%)
	1	2	3	4	Average	
6,6	0.0488	0.0490	0.0489	0.0491	0.04895	2.1
6,9	0.0490	0.0492	0.0492	0.0490	0.0491	1.87
6,10	0.0491	0.0493	0.0485	0.0487	0.0489	2.21
6,12	0.0490	0.0489	0.0493	0.0490	0.04906	1.88

Analyses of copolyamides of nylons 6,6/6,10 and 6,9/6,12 were examined and compositions on the basis of methyl esters are shown in Table III.

Nylon 6, T, the condensation product of 1,6-diaminohexane and terephthalic acid, was readily cleaved, but the reaction was incomplete after 0.5 h of heating and 1.0 h was employed, after which time increased yields of the components were not obtained. The retention times of dimethyl terephthalate and dimethyl sebacate are very similar on the column used but are experienced together in polyesters and are capable of separation, as demonstrated by Jankowski and Garner¹¹, who separated the aliphatic diester and the three isomeric phthalate esters with a Ucon 50HB 280X column. The aromatic character is not common with the other simple nylons and would usually be obvious from the infrared spectrum and possibly from the reduced rate of the fusion reaction.

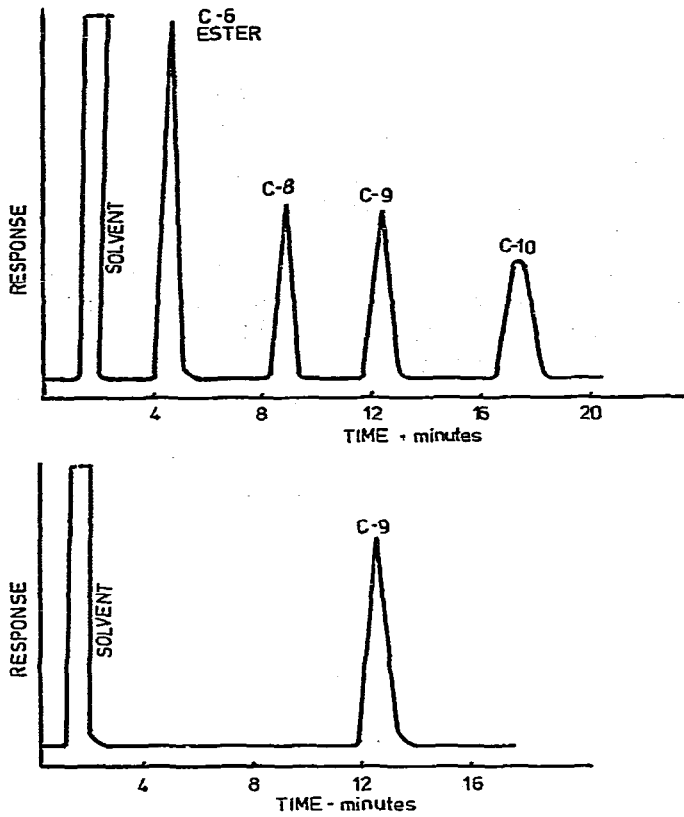


Fig. 1. Chromatograms showing separation of the methyl esters of aliphatic dicarboxylic acids and dimethyl nonanedienoate recovered from nylon 6,9.

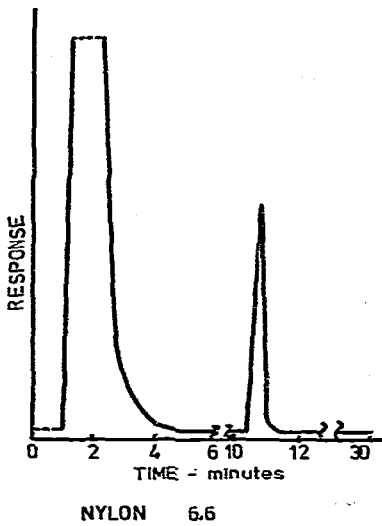


Fig. 2. Chromatogram showing 1,6-diaminohexane recovered from nylon 6,6.

TABLE III
ANALYSIS OF COPOLYAMIDES

Copolyamide	Composition (%)			Error (%)
	Actual	Analysis	Average	
Nylon 6,6/6,10	60:40	61.4:38.6; 61.2:38.8	61.3:38.7	2.16
Nylon 6,9/6,12	60:40	60.2:39.8; 61.1:38.9	60.66:39.34	1.1

Analyses of ω -aminoalkanoic acids as the methyl esters were carried out on nylon 6 (ω -aminocaproic acid), nylon 11 (ω -amino-*n*-undecanoic acid) and nylon 12 (ω -amino-*n*-dodecanoic acid) with the results as shown in Table IV.

The polyamide samples examined indicate an error in recovery of about 2% with diamine-dicarboxylic acid, ω -aminoalkanoic acid types and with several copolyamides. The losses are believed to be associated primarily with the liquid-liquid extractions that are required. Preliminary examination of products with amines and acids of high functionality and of greater molecular weight has indicated the successful use of alkali fusion, the acids being examined as the esters, while chromatography of the amines is facilitated by derivative formation, as has been used in earlier work on simpler products and in recent work by Schlueter and Siggia¹².

TABLE IV
QUANTITATIVE DETERMINATION OF METHYL ω -AMINOALKANOATES

Nylon	Weight of polymer (g)					Error (%)
	1	2	3	4	Average	
6	0.0491	0.0488	0.0490	0.0495	0.0491	1.8
11	0.048	0.0492	0.0493	0.0491	0.0489	2.2
12	0.0492	0.0489	0.0491	0.0488	0.0490	2.0

The determination is conducted without restricting the use of the chromatograph or requiring the cumbersome reactor of Siggia and co-workers. The procedure is rapid and specific and allows a complete analysis, as reported by Anton¹ in 4–24 h, to be achieved in essentially the same time as the diamine analysis of Siggia and co-workers, *i.e.*, 1–2 h, for both diamine-dicarboxylic acid and ω -aminoalkanoic acid types of polyamides.

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