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## CHROMATOGRAPHIC ANALYSIS OF AROMATIC POLYHYDRAZIDES, OXALYL ARYLENE POLYHYDRAZIDES AND AROMATIC POLY-(AMIDE-HYDRAZIDES) AFTER ALKALI FUSION

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### SUMMARY

A procedure which allows rapid analysis of aromatic polyhydrazides, oxalyl arylene polyhydrazides and aromatic poly(amide-hydrazides) is reported. The various acidic and amino components are identified after derivatization following cleavage with molten potassium hydroxide rather than by prolonged hydrolysis with hydrochloric acid, as has generally been employed with nylon-type polyamides. Degradation of the poly(amide-hydrazides) produce the salt of *p*-aminobenzoic acid and the analytical scheme developed allows derivatization without an additional step. Modification of the fusion procedure previously reported is required for use with all the polyhydrazides.

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### INTRODUCTION

The traditional method of analysis of aliphatic polyamides of the nylon-type<sup>1</sup> has usually employed acidic hydrolysis followed by chemical or instrumental analysis. With 6 *N* hydrochloric acid hydrolysis of Nylons 11 and 12 required a digestion period of 8 h at 130°C to effect cleavage while aromatic materials, less susceptible to hydrolysis require even longer periods of digestion.

Frankoski and Siggia<sup>2</sup> employed alkali fusion with amides, anilides and ureas. The procedure with Nylon 6,6 and 6,10 involves heating solid alkali with the sample in molar ratios of 50:1 or greater at 360°C of 0.5 h. The fusion was carried out in a reactor constructed from a furnace pyrolyser attached to a gas chromatograph, the liberated diamine, 1,6-diaminohexane, being determined by gas chromatography with the dicarboxylic acid remaining in the reactor as the salt. The procedure was extended for the same type of dicarboxylic acid-diamine condensate, for  $\omega$ -aminoaliphatic acid-types of nylon<sup>3</sup> and for fatty polyamides<sup>4</sup> to allow examination of both the acid and the amine components.

The procedure developed (1) eliminated the restricted availability of the chromatograph and use of the cumbersome reactor; (2) allowed recovery and identifi-

cation of the dicarboxylic acid as a suitable derivative; and (3) allowed recovery of the diamine, chromatography of which is often improved by examination of a derivative or by the use of liquid chromatography.

Schlueter and Siggia<sup>5</sup> have used a fusion reactor for the identification of aromatic diamines derived from a variety of aromatic polyamides, polyimides and poly(amide-imides) and have included a substantial bibliography of earlier analytical reports.

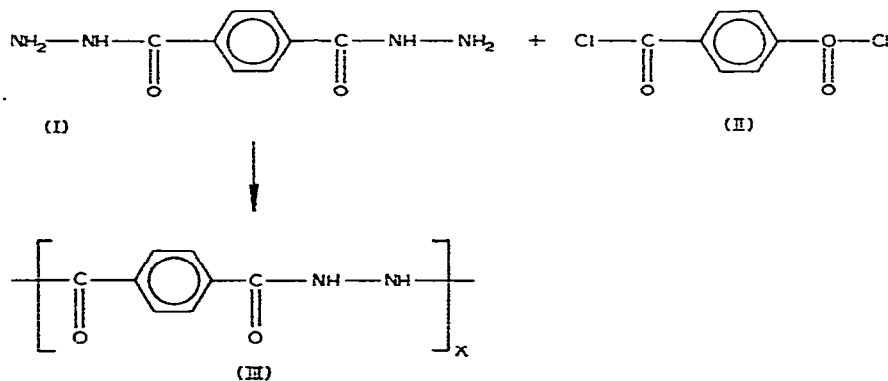
The examination of derivatives of amines from the same types of polymers and of the tri- and tetracarboxylic acids used has been recently reported<sup>6</sup>.

A series of related high-modulus fibres produced by the Monsanto Company comprise both aromatic polyamides and aromatic (amide-hydrazides)<sup>7,8</sup>. Frazer and co-worker have described the synthesis of aromatic polyhydrazides<sup>9,10</sup> and alternating oxalyl/arylene polyhydrazides<sup>11,12</sup> prepared by low-temperature solution polycondensation of the corresponding hydrazides and the acid chlorides in hexamethylphosphoric triamide containing dissolved lithium chloride. The same condensation being subsequently reported using N,N-dimethylacetamide<sup>13</sup> as solvent.

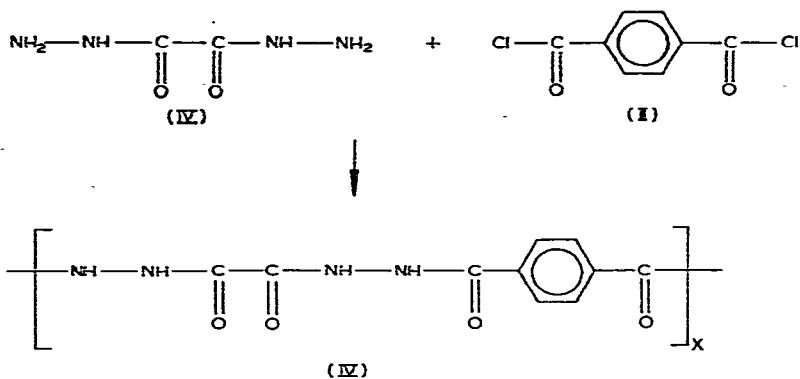
The literature does not contain any procedures for the analysis of the polyhydrazides and related polymers and the procedure using alkali fusion and chemical derivatization is reported. Degradation of the poly(amide-hydrazides) produces the salt of *p*-aminobenzoic acid and an alternative reaction scheme to that previously reported is employed to allow a single derivatization step.

## EXPERIMENTAL

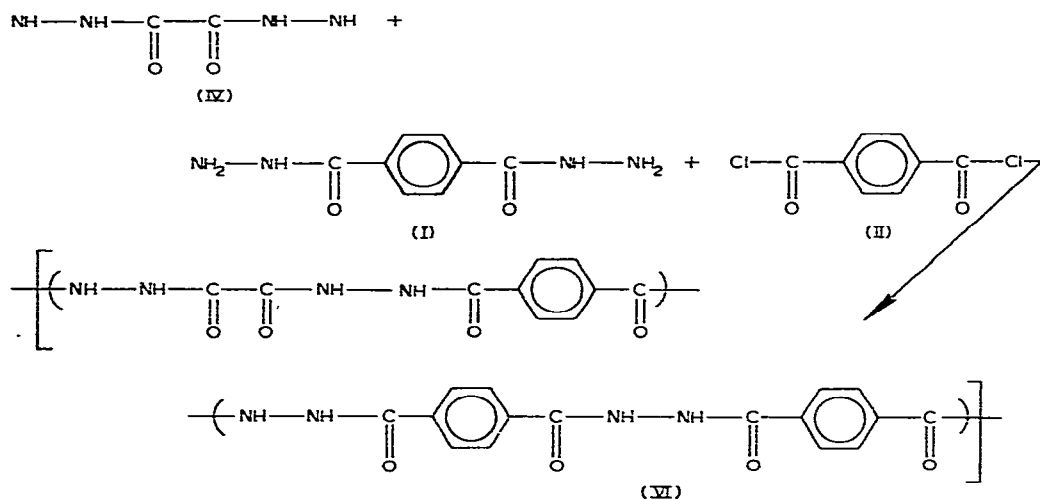
The polymer H-22 was produced from terephthaldihydrazide (I) and terephthaloyl chloride to form poly(temphthalhydrazide) (III).



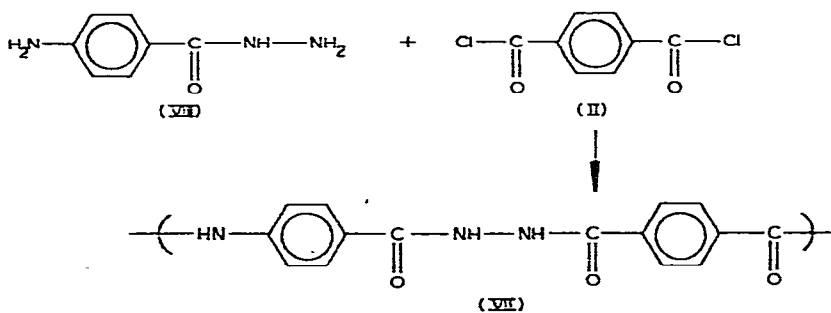
The polymer H-20 was produced from oxalic dehydrazide (IV) and terephthaloyl chloride (II) to form the alternating polyhydrazide of oxalic and terephthalic acids (V).



The polymer H-202 is a random copolymer produced from oxalic dihydrazide (IV), terephthaldihydrazide (I) and terephthaloyl chloride (II).



The polymer PABH-TX-500 is an ordered poly(amide-hydrazide) (VII) formed by the reaction of *p*-aminobenzhydrazide (VIII) with terephthaloyl chloride (II).



### Fusion reaction

The fusion reactions carried out by Siggia and co-workers<sup>2,5</sup> and by Haken and co-workers<sup>3,4,6</sup> were performed in sealed systems. When the polyhydrazides and their copolymers were heated as in our earlier works, *i.e.* in borosilicate tubes that had been sealed under reduced pressure, violent explosions generally occurred which were due presumably to some minor degradation of the hydrazine at the high temperatures (250–300°C) used. The analyses were carried out successfully by placing the appropri-

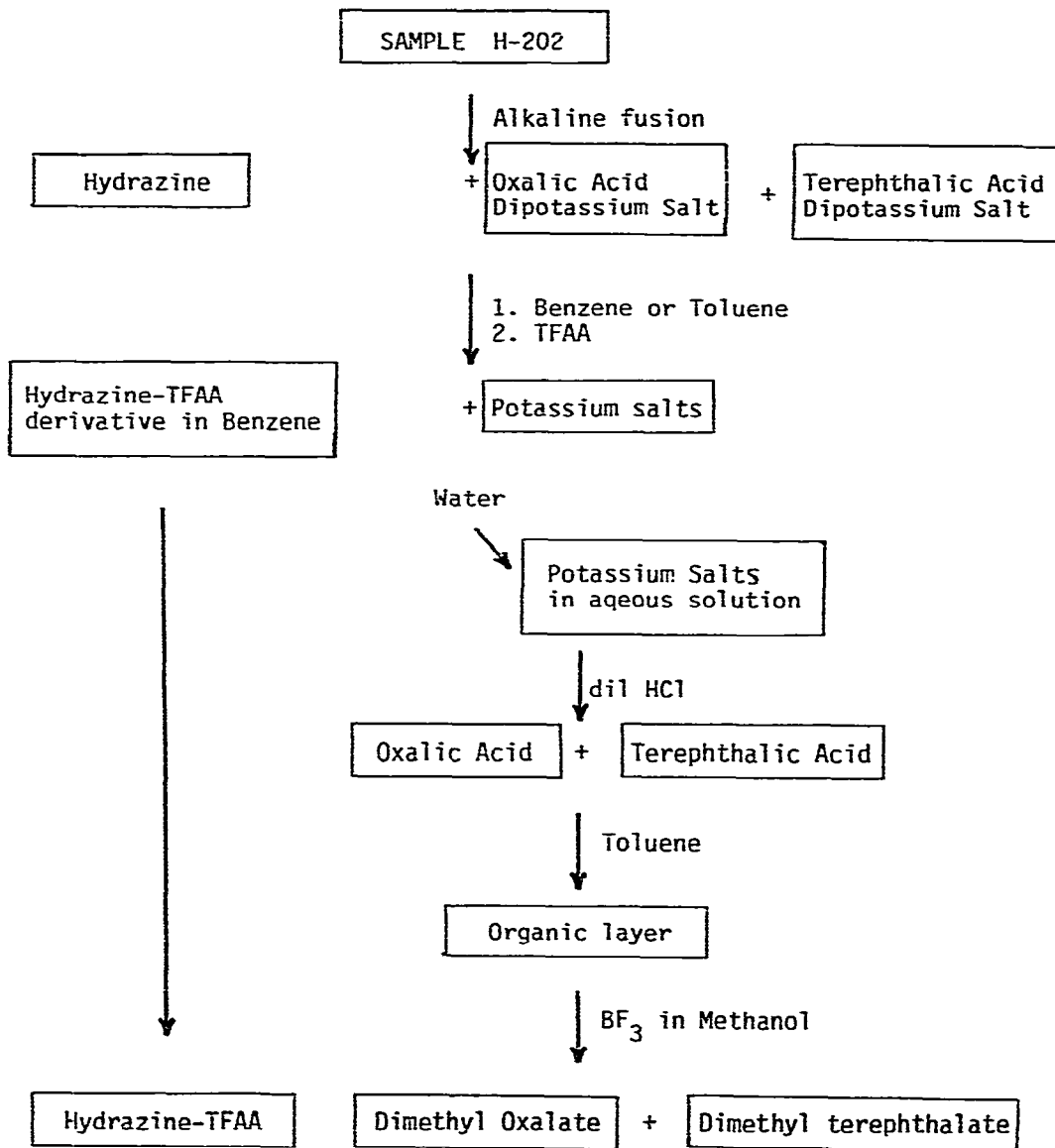


Fig. 1. Analytical scheme for H-202.

ate quantities of polymer and fusion mixture in a suitable microflask fitted with an air condenser or, alternatively, in a 25 cm × 6.0 mm borosilicate tube set in a stainless steel block heated with resistance heaters as described previously<sup>3,4,6</sup>.

After fusion for 0.5 h at the refluxing temperature of the mixture, *i.e. ca.* 180°C, after which time all of the polymer had dissolved, the reaction mixture was cooled and separated according to the scheme shown in Fig. 1. The scheme for the copolymer H-202 was also applicable to the polymers H-20, H-22 and PABH-TX-500. With PABH-TX-500 trifluoroacetic anhydride (TFAA) reacts with the potassium salt of *p*-aminobenzoic acid to form the TFAA derivative. The derivative is water soluble and was recovered according to Fig. 1. It was identified after esterification.

#### *Gas chromatography*

An F & M 810/29 gas chromatograph fitted with flame-ionization detectors was used with columns and temperature as indicated below, and with helium as carrier gas.

*Diamine TEAA 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 was programmed between 180 and 22°C at 8°C/min with the final temperature being held for 3 min.

*Dimethyl esters.* These were separated on an aluminium column (1.2 × 6 mm O.D.) packed with 6% OV-1 silicone gum rubber on Gas-Chrom Q (100–120 mesh). The column was programmed from 160 to 240°C at 10°C/min. The initial temperature was held at 160°C for 3 min after injection.

#### *Liquid chromatography*

The liquid chromatograph was a Gowmac Model 80/20 instrument equipped with a UV detector operating at 254 nm.

A Bondapak C<sub>18</sub> column (25 cm × 6 mm O.D.) was used. For elution methanol–water mixtures were used in the proportions and with the flow-rates shown in the relevant figures.

## RESULTS AND DISCUSSION

The hydrazine cleaved from all four polymers was readily resolved as the TFAA derivative on the polyester column previously used for diamines. The separation gave a near-symmetrical peak (shown in Fig. 2), elution being much faster than with the corresponding derivatives of the higher-molecular-weight diphenyldiamines. The conditions selected allowed reasonably rapid elution of the higher-boiling TFA derivative of the *p*-aminobenzoic ester. Although some tailing was evident, this could be greatly reduced by starting the programme at a considerably lower temperature. Separation could also be readily achieved using liquid chromatography, as shown in Fig. 3. The derivative dissolved in methanol, was eluted methanol–water (65:35) that had been filtered and degassed.

The terephthaloyl group that is also present in all four polymers was determined as dimethylterephthalate and the separation is shown in Fig. 4. The same figure shows the separation of dimethyl oxalate produced by cleavage of the alternating polyhydrazide of oxalic and terephthalic acids (H20) and from the random copoly-

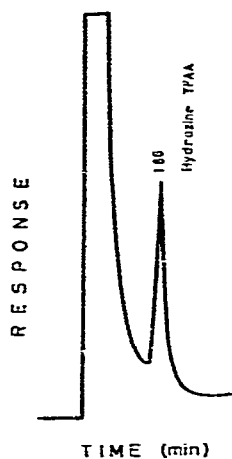


Fig. 2. Gas chromatogram showing separation of the hydrazine TFAA derivative.

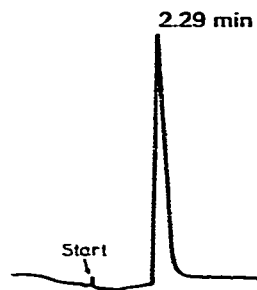


Fig. 3. Liquid chromatogram showing separation of the hydrazine TFAA derivative. Eluent: methanol-water (65:35). Flow-rate: 2 ml/min. Pressure: 1500 p.s.i.

mer produced from oxalic and terephthalhydrazides with terephthaloyl chloride (H202).

Fig. 5 shows separation of the TFAA ester derivative of *p*-aminobenzhydrazide from the poly(amide-hydrazide) PABH-TX-500.

While the separation of the TFAA derivative of hydrazine has been shown using liquid chromatography, it is apparent that the technique could also be successfully used for the other separations shown. The separation of dimethyl terephthalate by liquid chromatography has been shown previously<sup>6</sup> in a work which also reported separation of esters of 1,2,4-benzenetricarboxylic and 1,2,4,5-benzenetetracarboxylic

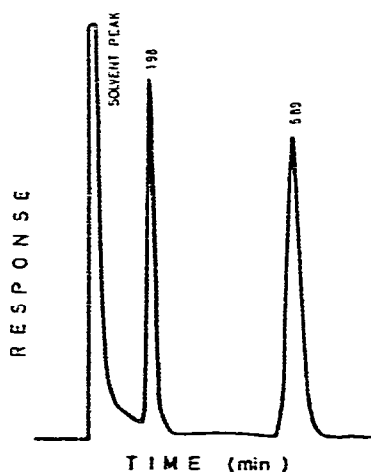


Fig. 4. Gas chromatogram showing separation of diesters of oxalic and terephthalic acids.

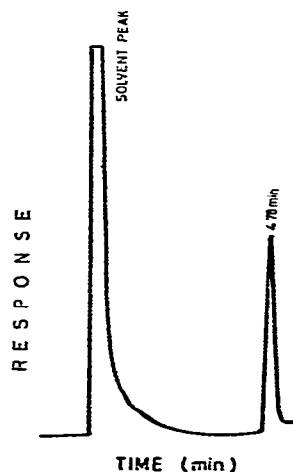


Fig. 5. Gas chromatogram showing separation of the TFAA ester derivative of *p*-aminobenzoic acid.

acids. The same work also reported separations of the TFAA derivatives of several 4,4'-diaminodiphenyl compounds using the same Bondapak C<sub>18</sub> column.

The quantitative aspects of the method have not been definitely determined for the polyhydrazides, this being due in part to the difficulties encountered in establishing the purity of the samples. On the reasonable assumption that the samples are of high purity, near quantitative results were achieved, the error being  $\pm 2-3\%$  which is comparable with earlier results<sup>3,5</sup> from alkali-fusion analyses. Schleuter and Siggia<sup>5</sup> have showed some minor degradation of aromatic diamines by identifying ammonia. Using the same procedure it was evident that the hydrazides produced little ammonia, although other minor products were evident.

#### ACKNOWLEDGEMENT

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