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CHROMATOGRAPHIC ANALYSIS OF ARAMID FIBRES AFTER CHEMICAL DEGRADATION

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SUMMARY

A method of analysis is reported for certain Aramid fibres, which are the reaction products of an aromatic diamine and an aromatic dicarboxylic acid, the position of substitution of the reactants (1,3- or 1,4-) usually being the same for both functional compounds. The analysis employs cleavage of the polymers, which have high thermal and chemical resistance, using alkali fusion and extends the procedure of Siggia to allow identification of both reaction species either in their free state or as derivatives.

INTRODUCTION

Aramid fibres were defined by the United States Federal Trade Commission[1] as "a manufactured fibre in which the fibre-forming substance is a long-chain polyamide in which at least 85% of the amide linkages are attached directly to two aromatic rings". This definition does not exclude the possibility of the presence of other functional groups which may be associated with the aromatic group. Thus, within the group may be included the poly(amide hydrazides) and related copolymers developed by the Monsanto[2–8] whose analysis has recently been reported[9] and the poly(quinazolinediones) developed[10–12] and formerly marketed by Bayer[13].

The first polymer of the class, poly(*m*-phenyleneisophthalamide), currently marketed as Nomex, was developed several decades ago, followed by poly(*p*-phenyleneterephthalamide)[14–17], currently marketed as Kevlar, both developed by DuPont.

The polymers in general have extremely high chemical and thermal resistance and reaction to cleave the amide links to allow analysis is restricted, although Schleuter and Siggia[18] have effected cleavage of related polymers and identified the free diamines liberated using gas chromatography. The same work reviews the literature related to the cleavage of amide and imide linkages.

This paper reports the analysis of both reactants of the polymers. The diamines are readily examined in the free state although, as has been shown previously[19], examination may be after derivative formation if chromatography is facilitated and

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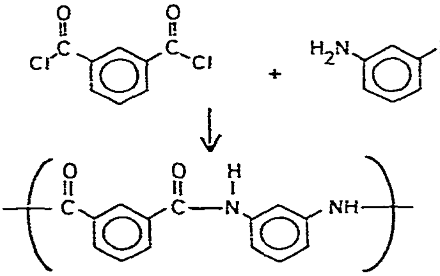
the dicarboxylic acids as methyl esters using a procedure previously reported for resinous polyamides[19]. The analyses for both reactants include the appropriate *ortho*-isomer such that the general separation characteristics of the three isomers is shown.

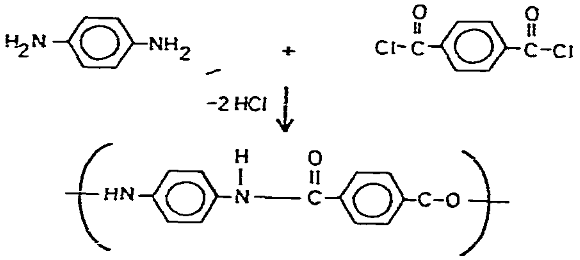
EXPERIMENTAL

Nomex is generally prepared by reaction of the reactive acid chloride. Isophthalolyl chloride and m-phenylenediamine are used:

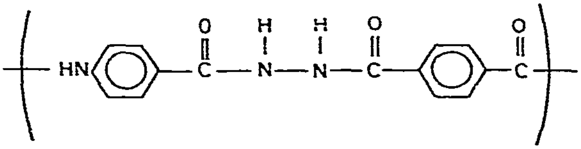


The reaction is rapid in the presence of an acid acceptor under mild conditions. Polymerization is carried out either in solution or in suspension[20].

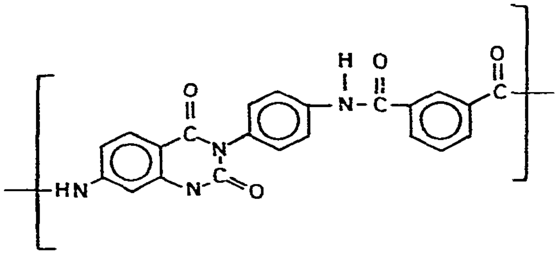
Kevlar is synthesized by the reaction of *p*-phenylenediamine with terephthaloyl chloride in hexamethylenephosphoramide and N-methylpyrridolidone (2:1) at − 10°C:



Other Aramid fibres include the poly(amide hydrazides) with a repeating unit as shown below, the analysis of which by cleavage to produce hydrazine has recently been reported[9].



Aromatic polyamides with the quinazolinedione group[10,11] in the repeating unit are a further type of Aramid fibre that has been developed but not successfully marketed. The structural unit is



FUSION REACTION

The fusion was carried out in evacuated glass tubes as in our previous work[19,21] using 0.01 g of polymer and 0.1 g of prefused potassium hydroxide containing 0.5% of sodium acetate prepared according to the procedure of Whitlock and Siggia[22]. The reaction was carried out in 10 mm O.D. borosilicate tubes heated at 260°C for 30 min.

To the cooled reaction tube was added sufficient water, *i.e.*, several millilitres, to dissolve the potassium salts. The diamine was extracted by the addition of chloroform in two portions prior to drying over anhydrous sodium sulphate. The simple diamines are readily separated as free amines on a non-polar column; however, in the presence of higher molecular weight diamines the low-molecular-weight compounds may be examined simultaneously as the trifluoroacetyl derivatives according to the analytical scheme previously reported with separation on a polyester column[19].

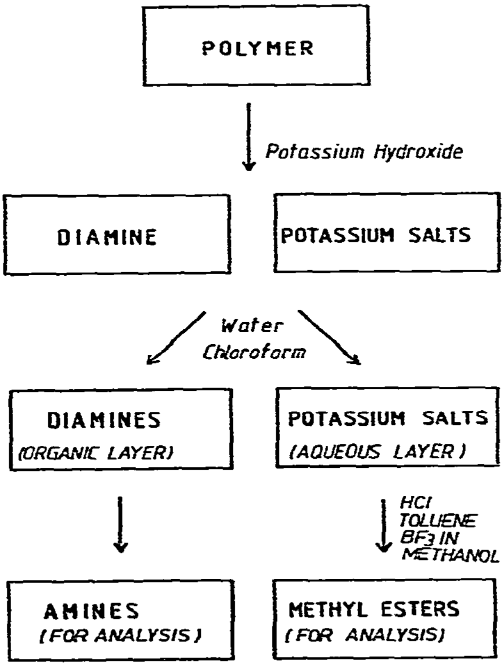


Fig. 1. Analytical scheme.

The aqueous solution from the diamine extraction was acidified with dilute hydrochloric acid and the liberated carboxylic acids were 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 the solution and the mixture was refluxed for 30 min. The resulting diester in solution was transferred into a separating funnel containing 20 ml of water and then extracted with toluene. The toluene solution was dried with anhydrous magnesium sulphate and the toluene removed under reduced pressure. Aliquots of 0.5 μl of the final solution were chromatographed.

The separation scheme is a simplification of our earlier scheme[19] and is shown in Fig. 1. *o*-Phenylenediamine and dimethyl *o*-phthalate were not recovered from polymers but were pure compounds, the latter being prepared from *o*-phthalic acid.

GAS CHROMATOGRAPHY

Gas chromatography was carried out using a Hewlett-Packard 5830A instrument. The column (6 ft. × 1/8 in., stainless steel) was packed with 10% OV-1 on Chromosorb W HP (80–100 mesh) and was operated isothermally at 120°C. Nitrogen was used as the carrier gas at a flow-rate of 32 ml/min with the injection port and detector temperatures being maintained at 125 and 250°C, respectively.

RESULTS AND DISCUSSION

The three phenylenediamine isomers were readily separated on a non-polar OV-1 column, the peaks being essentially symmetrical, as shown in Fig. 2.

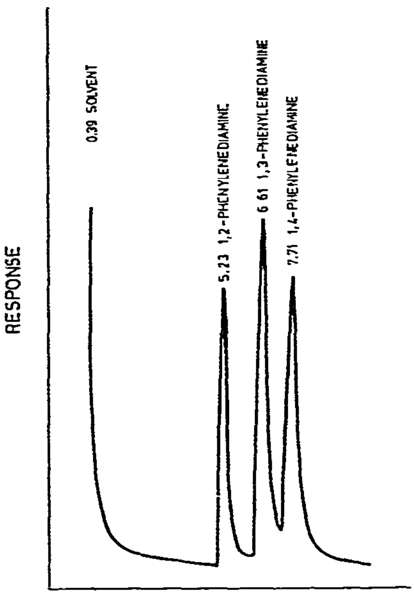
The order of elution follows the order of increasing boiling points, which are well separated (*o*- 256°C; *p*- 267°C; *m*- 284°C); because of the peak shapes the use of porous polymer columns or derivative formation is not required.

The isomeric phthalate esters are not readily capable of separation, largely owing to the similarity of their boiling points. With the same OV-1 columns the *ortho*-isomer is well resolved while the iso- and terephthalates appear as a single peak. (Note: although in an earlier paper[19] we indicated this separation, a compound was incorrectly named).

The resolution of all three isomers using a column containing Bentone 34 has been reported[23], but the separation was not shown and neither we nor Rawlinson and Deeley[24] have been able to achieve it.

The separation shown in Figure 3 is superior to that of Rawlinson and Deeley, who reported the same relative retention values for all three isomers on both polyester columns, *i.e.*, 1,4-butanediol succinate and Apiezon L.

A recent report[25] concerning the separation of various benzenecarboxylic acids and their esters has shown that on an essentially identical column, *viz.*, SE-30, dimethyl *o*-phthalate has a retention index of 1400 whereas dimethyl isophthalate and dimethyl terephthalate have values of 1495 and 1519, respectively. In a mixture the latter two isomers are not resolved, the retention index of the composite peak being between that of the individual compound peaks. The comparable values on a polyester (cyclohexanedimethanol succinate) column are *o*-phthalate 2012, isophthalate 2053 and terephthalate 2012.



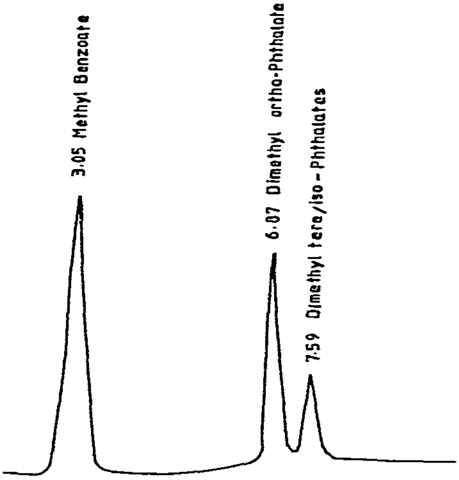


Fig. 2. Chromatogram showing separation of isomeric phenylenediamines on an OV-1 column operated isothermally at 120°C.

Fig. 3. Chromatogram showing separation of isomeric phthalate esters on an OV-1 column programmed between 160 and 250°C at 10°C/min.

There is further agreement on the separations on a non-polar column in a report of a recommended IUPAC method for the analysis of alkyd resins[26], where on a dimethylpolysiloxane (DC11) column, relative retention values of the *ortho*-, iso- and tere-esters were 1.20, 1.33 and 1.30, respectively, whereas on a mixed polyester (DEGS)-Carbowax 20M column the values for the *ortho*-, iso- and tere-esters were 1.3, 1.31 and 1.22.

Separation of the three isomers using liquid chromatography has not been successful, although separation may be effected using spectrophotometry, an ASTM procedure using ultraviolet spectrophotometry, adopted in 1961[27] and extended in 1976, being suitable for mixtures of the three isomers. Alternatively, a differential infrared analyser may be employed, as has been used for the analysis of polyester resins[28].

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