

Note

Gas chromatographic analysis of thermoplastic aromatic polyamides after alkali fusion

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Aromatic polyamides have been developed with superior thermal properties and include poly(*p*-phenyleneterephthalamide) (*e.g.*, Du Pont “Kevlar” and Enka “Arenka”) and poly(*m*-phenyleneisophthalamide) (*e.g.*, Du Pont “Nomex”). These polymers have been analysed by fusion gas chromatography (GC) by Haken and Obita¹. More complex aromatic poly(amide-imides) have also appeared. The Amoco product “A-1”, the condensation product of trimellitic anhydride, 4,4'-methylenediamine and *m*-phenylenediamine, has also been successfully analysed². A wide range of mixed aromatic polyamides and amide-imides now exists, and numerous examples of these have been described (see for example ref. 3). Commercial examples of high-modulus fibres are Teiujin “HM-50” prepared from an equimolar mixture of *p*-phenylenediamine and 3,4'-diamino-diphenylether with terephthaloyl chloride, while mixed aromatic fibres are also produced in the U.S.S.R. (*e.g.*, “SVM”³ and “Twerton”⁴).

Recently, amorphous aromatic copolyamides have been reported by Sikke-ma^{5,6}. An example is that prepared from equimolar amounts of *p*-aminobenzoic acid, *m*-aminobenzoic acid, isophthalic acid and 4,4'-methylenedianiline, although alternatives in which the 4,4'-methylenedianiline is replaced by 4,4'-sulfonyldianiline exist. This form of analogue is expected to improve back-bone flexibility, in a similar way to that claimed for “Sulfon I” and “Sulfon T”, the condensation products of 4,4'-diaminodiphenylsulfone with isophthalic or terephthalic acid, respectively⁴. The mixed aromatic copolyamides are claimed to have much better solvent resistance than other amorphous, high-temperature polymers such as polysulfones, polyetherimide and polyether sultone. These materials are stated by Akzo⁷ to be difficult to analyse and the analysis described below is believed to be previously unreported.

In this paper is described the application of alkali fusion for the analysis of an amorphous aromatic copolyamide. The fusion reaction is carried out at 300°C for 2 h by using the previously described flux-containing reagent⁸. The fragments after cleavage are converted into derivatives to allow examination by using GC.

EXPERIMENTAL

Sample

A sample of powdered HTP-1 thermoplastic aromatic polyamide provided by The Akzo Research Laboratories, Arnhem, The Netherlands, was used for analysis.

the sample contains *p*-aminobenzoic acid, *m*-aminobenzoic, isophthalic acid and 4,4'-methylenedianiline in equimolar ratios.

Alkali fusion

The alkali fusion was carried out with 200 mg of polymer samples and 13 g of potassium hydroxide-sodium acetate (95:5) according to the procedure previously reported⁸. The reaction was achieved by heating the polymer reagent mixture in a stainless-steel tube at 300°C for 2 h.

After cooling, the contents were transferred to a beaker. This was followed by the addition of sufficient concentrated hydrochloric acid to bring the pH to about 7, where the isophthalic acid was liberated as a precipitate and the 4,4'-methylenedianiline dissolved. The aminobenzoic acids remain in solution during these procedures, either as the amine hydrochloride at low pH or as the potassium salt at high pH.

The isophthalic acid fragment was filtered by using a büchner funnel and washed with hydrochloric acid and dried at 100°C. This was converted into dimethyl isophthalate by refluxing with boron trifluoride-methanol reagent according to the previously reported procedure⁸.

The filtrate containing amine fragments was rendered slightly basic by the addition of potassium hydroxide pellets to liberate the 4,4'-methylenedianiline which was recovered by extraction with 3 × 15 ml portions of chloroform. The chloroform solution was then concentrated and 3 ml of trimethylsilylimidazole (TMSI) (TRI-SIL® Z, Pierce) were added. The mixture was continuously shaken for about 15 min at 50°C and then used for the GC analysis of the 4,4'-methylenedianiline fragment as its trimethylsilyl derivative.

The remaining aqueous layer containing *p*-aminobenzoic acid and *m*-aminobenzoic acid derivatives was adjusted to a pH of 6 with a 1 M hydrochloric acid solution. The pH needs to be closely controlled to enable separation of these aminobenzoic acids, as pH < 5 or > 7 will result in reformation of soluble salts. The liberated acids were recovered by extraction with 3 × 15 ml portions of chloroform. Both fragments were converted into their trimethylsilyl derivatives using the TMSI reagent. The concentrated chloroform solutions obtained after derivatisation of the acids was then used for the analysis of *p*-aminobenzoic acid and *m*-aminobenzoic acid fragments. The analytical scheme is shown in Fig. 1.

Gas chromatography

Gas chromatography was carried out on a Hewlett Packard 5750 Research Model gas chromatograph with a flame detector and helium as carrier gas (flow-rate was 60 ml min⁻¹). The separations were performed on a 12 ft. × ¼ in. O.D., aluminium column packed with 5% SE-30 on Celatom A.W. DCMS (72-85 mesh).

The trimethylsilyl derivative of 4,4'-methylenedianiline was eluted isothermally at 252°C, while derivatives of *m*-aminobenzoic acid and *p*-aminobenzoic acid were separated at 228°C.

Dimethyl isophthalate was eluted isothermally at 220°C using the same column.

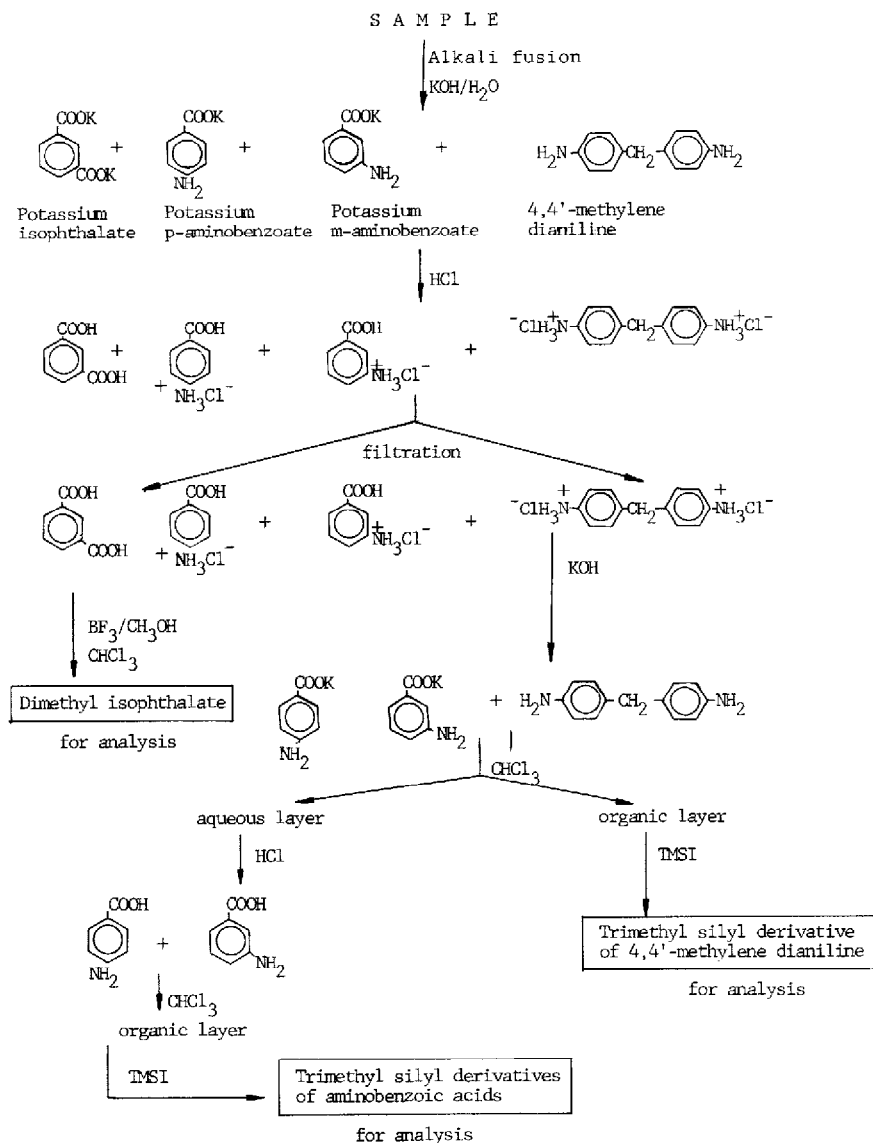


Fig. 1. Analytical scheme.

RESULTS AND DISCUSSION

The thermoplastic aromatic polyamide sample was successfully cleaved into *p*-aminobenzoic acid, *m*-aminobenzoic acid, isophthalic acid and 4,4'-methylenedianiline fragments by using alkali fusion. The cleavage was achieved after 2 h at 300°C. The fragments were readily separated by solvent extraction after adjusting the pH of the mixture as previously described.

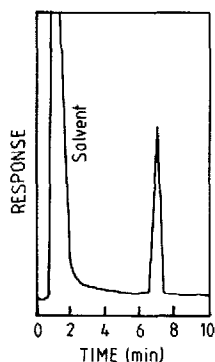


Fig. 2. Gas chromatogram showing the separation of dimethyl isophthalate.

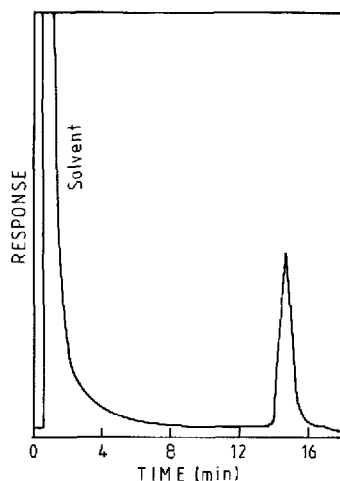


Fig. 3. Gas chromatogram showing the separation of trimethylsilyl derivative of 4,4'-methylenedianiline.

Isophthalic acid was converted into dimethyl isophthalate by using boron trifluoride-methanol reagent. The derivative obtained was separated on a SE-30 column as shown in Fig. 2.

Aminobenzoic acids and 4,4'-methylenedianiline fragments were successfully separated as their trimethylsilyl derivatives on the same column. Fig. 3 shows a chromatogram of the trimethylsilyl derivative of 4,4'-methylenedianiline obtained by using GC. Schlueter and Siggia⁹ determined the 4,4'-methylenedianiline as free amine on a free fatty acid phase column, while collaborators² have also reported the sep-

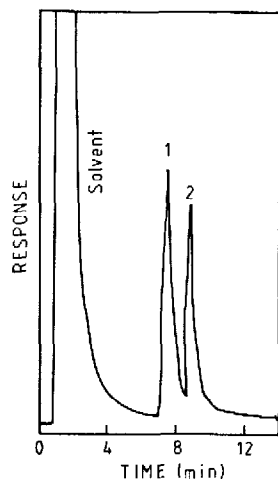


Fig. 4. Gas chromatogram showing the separation of trimethylsilyl derivatives of: (1) *m*-aminobenzoic acid and (2) *p*-aminobenzoic acid.

aration of a trifluoroacetic acid derivative of 4,4'-methylenedianiline. However, their work was performed by using liquid chromatography.

Fig. 4 shows the separation of the trimethylsilyl derivatives of the aminobenzoic acid isomers. The peaks corresponding to the trimethylsilyl derivatives of *m*-aminobenzoic and *p*-aminobenzoic acid show minor but acceptable overlap. Evaluation of various columns such as neopentyl glycol succinate, diethylene glycol succinate and Silar 10 CP was carried out before this successful result was obtained on a non-polar column.

Alkali hydrolytic fusion prior to GC has been described as a valuable method for the estimation of aminobenzoic acids, isophthalic acid and 4,4'-methylenedianiline from the thermoplastic aromatic polyamide sample.

The analyses have been carried out on a qualitative basis although it has been demonstrated that the degradative reactions¹⁰ are complete or essentially so. Errors may be introduced in the extraction steps and may be of the order of 2.0%. This, however, may be minimised or eliminated either by carrying out the reactions as indicated, where separation of various functional classes is partially conducted for convenience, or by developing an analytical scheme without such extractions. Such a procedure has been reported for the quantitative analysis of dicarboxylic acids and polyols in silicone-polyester resins¹¹. The quantitative analyses of diamines after alkali fusion has previously been reported by Schlueter and Siggia⁹ and by Glading and Haken¹².

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