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## Note

### Gas chromatographic analysis of isocyanate-based copolyamide resins

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The synthesis of novel copolyamides from aliphatic/aromatic dicarboxylic acids and arylene diisocyanate has been reported by the Upjohn Company<sup>1</sup>. These copolyamides are highly amorphous and characterized by high glass transition temperatures. The materials can be injection moulded to give tough transparent articles with good engineering performance.

These polymers are, in general, extremely chemically resistant. The amide linkages are difficult to cleave by simple hydrolysis, which is difficult and prolonged as indicated by Dawson *et al.*<sup>2</sup>. Rapid hydrolysis of amides and imides using alkali fusion was reported by Siggia and co-workers<sup>3-6</sup>, the free diamines being identified by gas chromatography (GC). Glading and Haken<sup>6</sup> applied alkali fusion to nylon-type polyamides and found that quantitative results could be obtained using both diamine and dicarboxylic acid fragments. They also reviewed the literature relating to the cleavage of polyamides. The alkali fusion procedure was later applied to the analysis of resinous polyamides<sup>7-9</sup>, aramid fibres<sup>10</sup>, polyhydrazides<sup>11</sup> and polyurethanes<sup>12,13</sup> by Haken and coworkers.

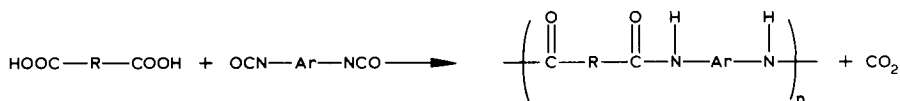
This paper reports the analysis of new types of copolyamide resins based on isocyanates using an alkali fusion procedure. The diamines are readily examined in the free state although, as has been shown previously<sup>7-11</sup>, the chromatography of some diamines is facilitated after derivative formation. The dicarboxylic acids were chromatographed as their dimethyl ester derivatives.

## EXPERIMENTAL

### *Samples*

Two thermoplastic resins, Isonamid-7030<sup>14</sup> and Isoplast<sup>15</sup> (available from Upjohn), based on *p,p'*-diphenylmethane diisocyanate (MDI), were used for the analysis. These polymers are believed to be manufactured according to a patent<sup>1</sup> that describes the synthesis of novel copolyamides from aliphatic/aromatic dicarboxylic acids and arylene diisocyanates as shown below. The raw materials used in this polymer synthesis were azelaic acid and/or isophthalic acid and MDI and/or toluene diisocyanate (TDI)<sup>1</sup>.

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### *Fusion reaction*

The alkali fusion was carried out in stainless-steel pressure tubes, using 100 mg of finely ground polymer and 1.5 g of alkali fusion reagent (a pre-fused mixture of potassium hydroxide containing 5% of sodium acetate), prepared according to the procedure of Siggia and co-workers<sup>3,4</sup>. The reaction was carried out at 300°C for 1 h.

### *Separation procedure*

To the cooled reaction tube was added sufficient water (several millilitres) to dissolve the potassium salts. The diamine was then extracted with four 10-ml portions of dichloromethane. The combined organic extract was dried over anhydrous sodium sulphate and filtered. The solvent was then partially removed under vacuum to give approximately 1 ml of solution, of which a 1- $\mu$ l volume was chromatographed. The diamines corresponding to diisocyanates were identified by comparing their retentions with those of authentic standards.

For dicarboxylic acid analysis, the aqueous solution remaining after the above extraction was acidified with dilute hydrochloric acid and the liberated carboxylic acids were extracted with four 10-ml portions of chloroform. To the dried chloroform extract were added 20 ml of boron trifluoride-methanol reagent and the mixture was refluxed for 1 h. The resulting solution, containing the dimethyl esters of dicarboxylic acids, was washed with water, dried, concentrated and chromatographed. The separated dicarboxylic acids were identified by mass spectrometry. The separation scheme is shown in Fig. 1.

### *Gas chromatography*

GC was carried out using a Hewlett-Packard 5830A instrument with flame ionization detection.

### *Diamines*

These were separated on a 4 ft.  $\times$  1/8 in. O.D. stainless-steel column packed with 10% XE-60 on Chromosorb W AW DMCS. The column was operated isothermally at 235°C using helium as the carrier gas at a flow-rate of 30 ml/min.

### *Methyl esters of dibasic acids*

These were separated on a BP-10 vitreous silica capillary column (25 m  $\times$  0.3 mm I.D.) (Scientific Glass Instruments, Ringwood, Victoria, Australia). The column was operated isothermally at 60°C for 1.5 min, then programmed at 10°C/min to 265°C.

## RESULTS AND DISCUSSION

Isocyanate-based copolyamide resins were successfully cleaved into diamine and dicarboxylic acid fragments using alkali fusion. These fragments were conve-

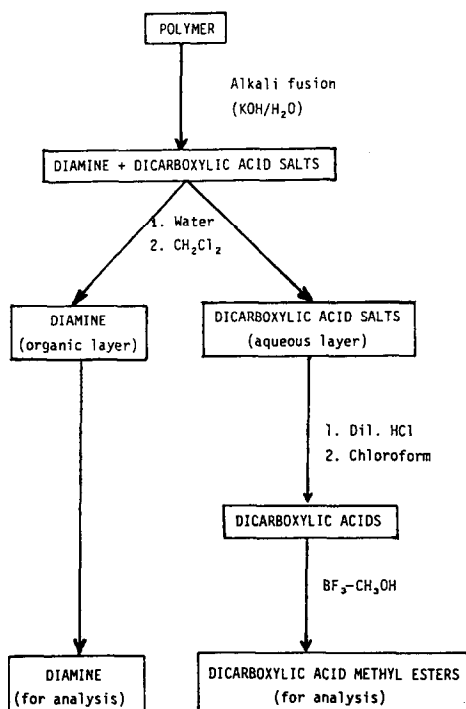


Fig. 1. Analytical procedure.

niently separated by liquid-liquid extraction and a derivatization procedure as shown in Fig. 1. The diamines corresponding to the diisocyanate portion of the polymers were successfully separated by GC. Fig. 2 shows the separation on an XE-60 column of *p,p'*-diphenylmethanediamine (MDA) extracted from Isonamid.

The dicarboxylic acids were converted into their methyl ester derivatives using boron trifluoride-methanol reagent. Fig. 3 shows the separation on a BP-10 capillary column of the dicarboxylic acid methyl esters obtained from Isonamid. The major

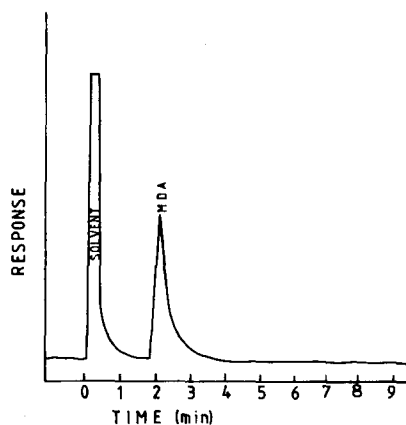


Fig. 2. Chromatogram showing the separation of *p,p'*-diphenylmethane diamine (MDA).

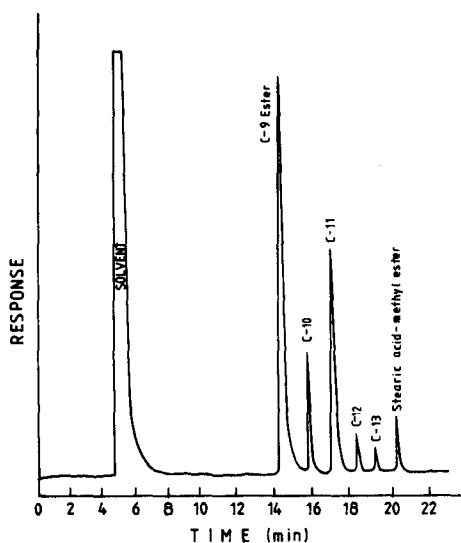


Fig. 3. Chromatogram showing the separation of dicarboxylic acid methyl esters.

acid present is azelaic acid ( $C_9$ ), but peaks and mass spectra consistent with  $C_{10}$  (sebacic acid,  $C_{11}$ ,  $C_{12}$  and  $C_{13}$  dicarboxylic acids were detected, as also was a peak corresponding to methyl stearate or a  $C_{17}$  monocarboxylic acid with a pendant methyl group. The acid fraction from Isoplast was essentially the same. Similar chromatograms were obtained for diamine and dicarboxylic acid methyl esters obtained from Isoplast.

Neither isophthalic acid nor toluenediamine corresponding to TDI were detected during the analysis of Isonamid and Isoplast, both being alternative materials indicated within the patent<sup>1</sup>. The detection of stearic acid as its methyl ester confirms its use as a capping agent as described in the relevant patent<sup>1</sup>.

## CONCLUSIONS

Alkali hydrolytic fusion of isocyanate-based copolyamide resins is faster than conventional solution hydrolysis methods. Complete qualitative and quantitative analysis can be achieved in a few hours. The hydrolysis fragments are conveniently analysed by GC. Non-volatile fragments such as dicarboxylic acids are converted into a suitable volatile derivative before GC analysis.

## ACKNOWLEDGEMENTS

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