

Note

High-performance liquid chromatographic analysis of polymeric polyisocyanate based polyurethanes after alkali fusion

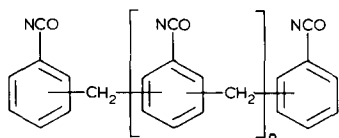
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Polyurethane materials have been known for more than 25 years. Their outstanding and varied properties have led to many applications. They are used as flexible and rigid foams, fibres, elastomers, coatings, adhesives and thermoplastic and thermosetting resins.

Until the 1970's most rigid and semi-rigid foam systems were based on a toluene diisocyanate (TDI) prepolymer or quasi-prepolymer process. With the advent of oligomeric polyisocyanates (OPIs) or poly(methyl phenyl isocyanate) "one-shot" methods can be used to make rigid and semi-rigid urethane foams. The OPIs are manufactured by phosgenation of aniline-formaldehyde condensates and may be represented by



The commercial products currently available vary primarily in their molecular weight and molecular weight distribution and hence isocyanate functionality varies from 2 to 3. They are always specifically designed for particular applications. Isocyanates with lower functionality (*i.e.* close to 2) are preferred for semi-rigid foam formulations while certain rigid foam applications require an isocyanate with higher functionality¹. The flexibility of preparation of OPIs allows such variability and so a versatile range of polymers can be produced.

The analysis of polyurethanes after alkali fusion has been the subject of our recent reports²⁻⁵ where diamine fragments corresponding to diisocyanates (including *p,p'*-diphenylmethanediamine) have been successfully separated on an XE-60 column using gas chromatography (GC). Although OPI based polyurethanes could be cleaved into corresponding polyamines by alkali fusion the subsequent separation of higher polyamines (*i.e.* $n = 1, 2$ etc.) could not be achieved by GC. This is because

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of their low volatility due to their high polarity together with high molecular weight. Liquid chromatography overcomes this problem although an unsuccessful attempt at separation was reported by Mumford *et al.*⁶ while size-exclusion chromatography (SEC) has been used to separate the OPI raw material itself⁷.

This paper reports a rapid and reliable analytical procedure for the qualitative and quantitative analysis of OPI-based polyurethanes after alkali fusion.

EXPERIMENTAL

Samples

Rigid polyurethane foam samples based on OPI were prepared in our laboratory by a "one-shot" process, using formulations given in Table I.

TABLE I
FOAM SAMPLE FORMULATIONS

	Parts (w/w)	
	1	2
Poly(methyl phenyl isocyanate) (Desmodur VL, Bayer)	100	100
Polyether	70.2*	48.5**
Silicone surfactant (DC-193, Dow Corning)	1.5	2.9
Trichlorofluoromethane	23.6	29.3
Amine catalyst (triethylene diamine)	2.6	2.5

* Glycerol based.

** Pentaerythritol based.

Alkali fusion

Alkali fusion was carried out using 500 mg of polymer with 15 g of fusion flux reagent (prefused mixture of potassium hydroxide containing 5% sodium acetate). The hydrolysis was accomplished by placing finely ground polymer reagent mixture in a stainless-steel screw cap pressure tube heated at 200°C for 2 h.

Acid fusion

Acid fusion was carried out by refluxing 300 mg of polymer and 30 g of mixed anhydride reagent (prepared by refluxing equimolar mixture of *p*-toluenesulphonic acid acetic anhydride reagents for 0.5 h^{8,9}) mixture for 6 h.

Separation procedure

After cooling and opening the stainless-steel tube, the contents were dissolved in water and transferred to a separating funnel and extracted with 3 × 20 ml portions of dichloromethane. The combined organic extracts were dried over anhydrous sodium sulphate and extracted with 2 × 20 ml portions of 5 M hydrochloric acid. The combined aqueous extract was rendered slightly acidic using sodium hydroxide pellets

and liberated polyamines were extracted with 3×20 ml portions of dichloromethane. The polyamines corresponding to OPI were recovered by evaporating the combined, dichloromethane extracts under reduced pressure.

Size-exclusion chromatography

The size-exclusion chromatograph unit was constructed from individual Waters modules, namely 6000A pump, U6K injector, R 401 differential refractive index detector. The four columns (300×7.8 mm I.D.) used contained μ Styragel ($10 \mu\text{m}$) packing of nominated exclusion limits 1000 and 100 \AA . The four columns were connected in series, two 1000 \AA and two 100 \AA , the last 100 \AA column being connected to the detector.

The tetrahydrofuran (THF) solvent was distilled from ferrous sulphate and filtered through a $0.5\text{-}\mu\text{m}$ Millipore FH filter before use at a flow-rate of 1 ml/min. The antioxidant *tert.*-butylhydroxytoluene was used at a loading of 20 ppm. Solutions of 200 ppm polymeric amines in THF were analysed. A volume of $250 \mu\text{l}$ of this solution was injected and constant temperature of 20°C was maintained during separation.

High-performance liquid chromatograph (HPLC)

The liquid chromatography system was also constructed from individual Waters modules, these being a 6000A pump, U6K injector, 440 variable wavelength differential flow UV absorbance detector, and Edwards Instruments 10-mV recorder. Separations of polyamines were carried out on a μ Porasil ($10 \mu\text{m}$) (Waters Assoc.) 250×4.6 mm I.D. column. Operating conditions were: flow-rate, 1 ml/min temperature, 20°C ; UV detector set at 254 nm; injection volume, $10 \mu\text{l}$ from 50 ppm solution. The mobile phase used was *n*-hexane-isopropanol (60:40).

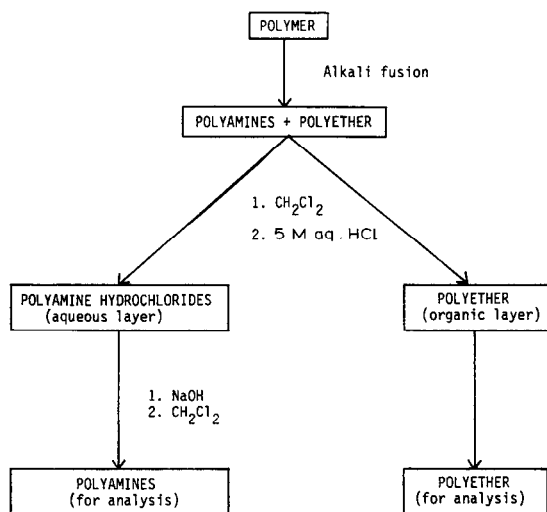


Fig. 1. Analytical scheme.

RESULTS AND DISCUSSION

OPI-based polyurethanes could be successfully cleaved into polyamines corresponding to OPI and polyether fragments using both alkali or acid fusion. Alkali fusion was carried out at 200°C for 2 h while acid fusion (using *p*-toluenesulphonic acid and acetic anhydride reagent) was carried out at 125°C for 6 h. Therefore alkali fusion is preferred to acid fusion due to the shorter reaction period needed. The polyamines formed after alkali fusion were successfully separated from the other fragments using the liquid-liquid extraction procedure shown in Fig. 1.

Separation of these polyamines were attempted on an XE-60 column and on a Tenax-GC column by GC.

Only 4,4'-diphenylmethanediamine (*i.e.* $n = 0$ analogue) was eluted whilst higher polyamines (*i.e.* $n = 1, 2$ etc.) remained uneluted. Therefore liquid chromatography was used to effect the separation.

Fig. 2 shows the SEC separation of all three polyamines present. Resolution is not sufficient for accurate quantitative analysis of PPI. Hence HPLC was used, and Fig. 3 shows the separation of polyamines by this procedure (HPLC). Base-line separation of all three polyamines were achieved, indicating this method could be used for accurate quantitative and qualitative analysis of polyamines corresponding to OPI.

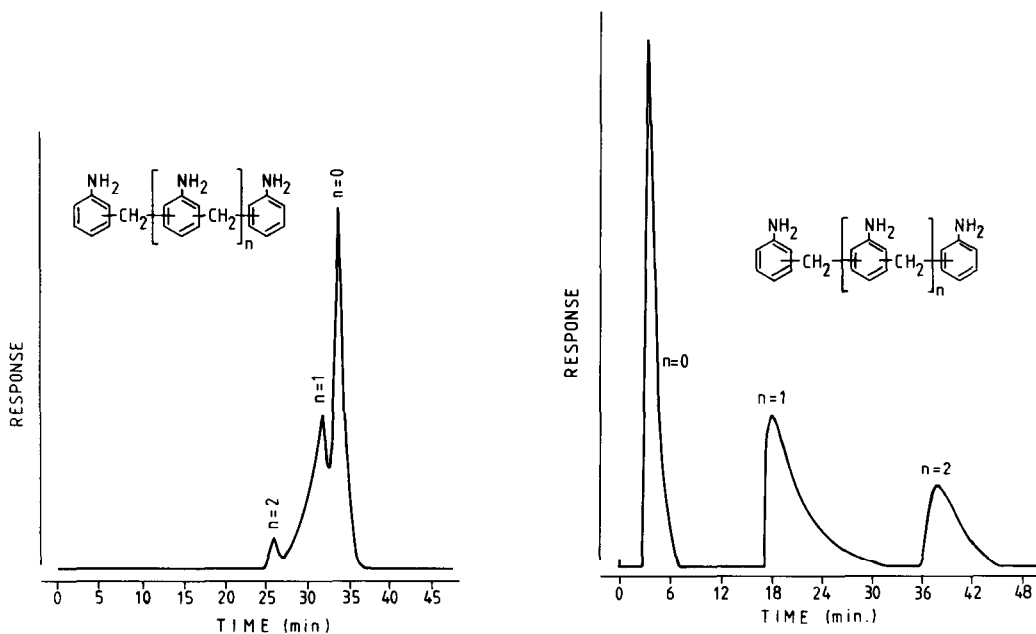


Fig. 2. Chromatogram showing the separation of oligomeric polyamines by size-exclusion chromatography.

Fig. 3. High-performance liquid chromatogram showing the separation of oligomeric polyamines.

CONCLUSIONS

Alkali hydrolytic fusion of OPI-based polyurethanes is much faster than conventional solution hydrolysis methods or acid fusion. HPLC is ideally suited for the subsequent qualitative and quantitative analysis of polyamines corresponding to OPI.

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