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## CHROMATOGRAPHIC ANALYSIS OF POLYETHER BASED POLYURETHANES AFTER ALKALI FUSION\*

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### SUMMARY

An analytical procedure for the characterization of polyether polyurethanes is reported. The diamine and polyether fragments are separated by gas and gel permeation chromatography after cleavage with molten alkali. Diamines were analysed as their trifluoroacetamide derivatives. The composition of the polyethers were determined by cleavage to the corresponding polyol acetates using mixed *p*-toluene sulphonic acid-acetic anhydride reagent and separation using gas chromatography.

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### INTRODUCTION

Numerous techniques for the identification of polyurethanes and their component parts have appeared in the literature. Infrared spectrometry (IR) has been widely used<sup>1-3</sup>, but the scope of the technique is limited, and therefore unsuitable for complete analysis. In several publications<sup>4-6</sup>, pyrolysis gas chromatography has been used to compare foams containing different formulations with chemical ionization mass spectrometry being applied by Mumford *et al.*<sup>7</sup>.

O'Neil and Christensen<sup>8</sup> reviewed the available methods and highlighted the lack of a reliable systematic method. Therefore the hydrolytic decomposition of urethanes have been investigated by later workers. Hydrolysis with water under pressure was only applicable<sup>9</sup> to polyurethanes from aliphatic diisocyanates and polyvalent alcohols. Athey<sup>10</sup> studied hydrolytic degradation of some polyester and polyether urethanes and found that the latter was 5-10 times as resistant to hydrolysis than the former.

The method described by Haslam and co-workers<sup>11,12</sup> with 50% hydrochloric acid was found to give incomplete hydrolysis despite long reaction times (60 h) while side reactions also occurred. Hydrolysis of similar type of polyurethanes with 60% sulphuric acid were found to be quantitative after short reaction periods but also involved the occurrence of unfavourable side reactions<sup>13</sup>.

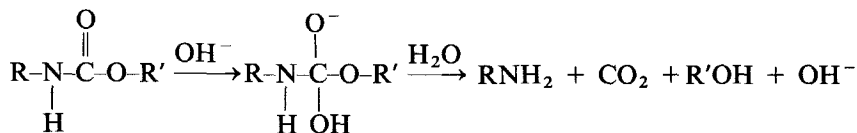
Thorough investigation by Matuszak *et al.*<sup>14</sup> have shown that polyurethanes

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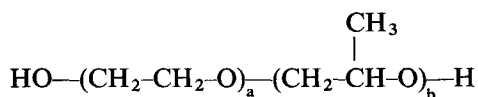
are much more susceptible to alkaline than acid hydrolysis. They propose the following mechanism for alkaline hydrolysis:



Therefore later workers utilized alkaline hydrolysis instead of lengthy acid hydrolysis. Alkaline hydrolysis is often carried out in "Parr" bomb apparatus using 2–15% aqueous sodium hydroxide or potassium hydroxide reagents<sup>15–20</sup>. The reaction was carried out at 150–350°C for 6–24 h for the complete hydrolysis and the resulting diamines, diacids, glycols or polyols from polyester and polyether polyurethane adducts have been identified by thin layer chromatography (TLC)<sup>15–19</sup>, IR<sup>19</sup>, nuclear magnetic resonance spectroscopy<sup>19</sup> (NMR) and gas chromatography (GC)<sup>19,20</sup>. No systematic procedure has been reported in the literature for complete characterization of polyether polyurethanes.

Alkali fusion, a newly-developed technique for rapid high temperature hydrolysis of condensation polymers has been extensively used by Siggia and co-workers<sup>21,22</sup> and Haken and co-workers<sup>23–29</sup> for various polymers analysis. Burford *et al.*<sup>30</sup> were able to cleave polyurethane linkages found in natural rubber crosslinked with "Novor" urethane compounds by alkali fusion.

Not only are the polyethers the most widely used polyhydroxy compound in polyurethane production but also their chemical structure can have a profound effect on physical performance, particularly in polyurethane foam. The first polyether designed specifically for polyurethane was a poly(oxytetramethylene)glycol derived from tetrahydrofuran<sup>31</sup>. At present, most of the polyethers used for the manufacture of flexible polyurethane foam are derived from propylene oxide and/or ethylene oxide. Block co-polymer of ethylene oxide and propylene oxide can be represented by the following general formula



Propylene oxide is reacted with propylene glycol or water in the presence of a basic catalyst to form a polyoxypropylene homo polymer which is then further reacted with ethylene oxide to form the block co-polymer<sup>32</sup>. The resulting polyether has a higher percentage of primary hydroxy groups than a poly(oxypropylene)glycol of comparable molecular weight. Polyoxypropylene triols are at present the most important class of polyethers used in the manufacture of polyurethanes and are made by the same general reaction, but with low-molecular-weight triols such as glycerol, tri(hydroxymethyl)propane and 1,2,6-hexanetriol rather than propylene glycol.

The proportion of oxyethylene and oxypropylene content in the polyethers have been determined by cleaving with hydrochloric acid<sup>33</sup>, hydrobromic acid<sup>34–37</sup>, hydroiodic acid<sup>38</sup>, phosphoric acid<sup>39</sup>, *p*-toluene sulphonic acid<sup>40</sup>, pyrolysis GC<sup>41,42</sup>, IR and NMR<sup>43,44</sup>. However all methods except the hydrobromic acid fusion GC

method, are unsatisfactory for the detection of basic compounds. Even the hydrobromic acid fusion method<sup>37</sup> suffers from the disadvantage that the reaction conditions (*i.e.* 150°C for 2 h) are too critical, side reactions occurring at lower temperatures or at longer times.

Several mixed anhydrides of carboxylic and sulphonic acids, as proposed by Karger and Mazur<sup>45</sup> act as reagents for the cleavage of ether linkages. Acetic and *p*-toluene sulphonic acid anhydrides powerfully<sup>46,47</sup> cleave ether linkages and also acetylate. For example, the propylene oxide adduct of glycerol splits to give glycerol triacetate and propylene glycol diacetate which are easily identified by GC<sup>46,47</sup>. This method has been successfully used to determine oxyethylene and oxypropylene content of polyethers.

We present a simple rapid and reliable analytical procedure for complete analysis of composition of polyurethane foam based on polyether and diisocyanates using alkali fusion and mixed anhydride reagent. The reactions involved in the analytical procedure are shown in Fig. 1. The advantage of alkali fusion technique is that the hydrolysis is achieved in 1 h at 250°C in molten potassium hydroxide, whereas days of refluxing with alkali in methanol is required<sup>21</sup>.

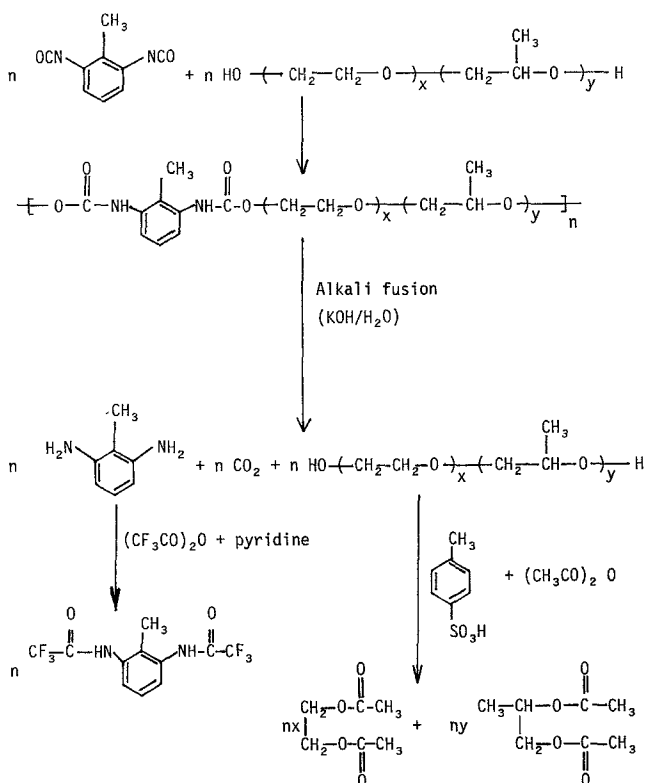


Fig. 1. Reactions involved in the analytical scheme.

## EXPERIMENTAL

*Alkali fusion*

Alkali fusion was carried out using 500 mg of polymer with 10 g of fusion flux agent (prefused mixture of potassium hydroxide containing 5% sodium acetate) prepared according to the method of Frankoski and Siggia<sup>21</sup>. The reaction was carried out by placing finely ground polymer and flux mixture in a stainless-steel reaction kettle equipped with a reflux condenser. The reaction was allowed to reflux at 250°C for 1 h with constant stirring, under nitrogen.

*Mixed anhydride reagent*<sup>46,47</sup>.

This was prepared by adding 80 g of acetic anhydride dropwise to 120 g of anhydrous *p*-toluene sulphonic acid (which had been dried under reduced pressure) contained in a 300-ml round-bottom flask. The mixture was refluxed at 125°C for 0.5 h. The product consisting of acetic *p*-toluene sulphonic anhydride was used without further purification.

*Samples*

Commercial, flexible polyurethane foam samples based on toluene diisocyanate and polyethers were analysed. These commercial samples and their substituent raw materials were supplied by Cable Makers Australia Pty Ltd.

*Separation*

After cooling the reaction mixture, the contents are dissolved in chloroform and the filtrate was extracted four times with 10-ml portions of 5 *N* hydrochloric acid.

For diamine analysis, the above solution was made alkaline and extracted four times with 10-ml portions of chloroform. The combined extracts were dried over anhydrous sodium sulphate and the solvent was partially removed under vacuum to give about 2 ml of solution of which 2  $\mu$ l was injected into the gas chromatograph. The diamines were identified by comparing their retention times with authenticated standards.

For the trifluoro acetamide (TFA) derivative preparation, diamines were recovered by removing chloroform under vacuum and dissolving the diamine in 10 ml of tetrahydrofuran containing five drops of pyridine. The mixture was cooled in an ice bath and 5 ml of trifluoroacetic anhydride (TFAA) was added. The contents were heated at 50°C for 0.5 h and 10 ml of distilled water was added to destroy unreacted TFAA. The mixture was extracted two times with 10-ml portions of chloroform. The combined organic layers were washed with 10 ml of saturated sodium bicarbonate solution. The final organic layer was dried and concentrated to a small volume for gas chromatographic analysis as above.

The polyether was recovered by evaporating the original chloroform layer which remained after the aqueous hydrochloric acid extraction. A portion of the polyether was used for the gel permeation chromatographic analysis and the other portion was refluxed at 125°C for 2 h with 10 ml of mixed anhydride reagent prepared according to the method of Tsuji and Konishi<sup>46,47</sup>. The contents were cooled and then neutralized with a saturated aqueous solution of sodium carbonate followed by

four extractions with 10-ml portions of chloroform. The combined organic layers were concentrated as above and used for gas chromatographic separation.

#### *Gas chromatography*

Gas chromatography was carried out using Hewlett-Packard 5830A Research Model gas chromatograph equipped with flame-ionization detector. Helium was used as carrier gas at a flow-rate of 75 ml/min for all separations.

#### *Diamines*

These were separated on a 12 ft.  $\times$   $\frac{1}{4}$  in. O.D. aluminium column packed with 10% Apiezon L grease on Celite AW DCMS 72-85 mesh. The detector and injection ports were maintained at 250°C and 350°C respectively. The column was operated isothermally at 205°C.

#### *Diamine TFA derivatives*

These were separated on the same column operated isothermally at 200°C. All the other conditions remained the same as above.

#### *Acetate of polyols*

These were also separated on the same column operated for 2 min isothermally at 80°C, then temperature programmed at 15°C/min to 260° and held at 260°C for 5 min. The detector and injection ports were maintained at 300°C and 350°C respectively.

#### *Gel permeation chromatography (GPC)*

The gel permeation chromatograph unit was constructed from individual Waters' modules, namely 6000A pump, U6K injector and R401 differential refractive index detector. The four columns (300  $\times$  7.8 mm I.D.) used contained  $\mu$ Styragel (10  $\mu$ m) packing of nominated exclusion limits 1000, 500 and two 100 Å. The four columns were connected in series 1000 Å, 500 Å, 100 Å and 100 Å, the last 100 Å column being connected to the detector.

The tetrahydrofuran solvent was used as the eluent at the rate of 1 ml/min which was distilled from ferrous sulphate and filtered through a 0.5- $\mu$ m Millipore FH filter before use. The antioxidant *tert.*-butylhydroxytoluene was added at a loading of 20 ppm and the solvent was kept under nitrogen blanket in the instrument reservoir. However even with these precautions, it was found necessary to use freshly distilled solvent every second day. Solutions of 200 ppm polymer were made in tetrahydrofuran and kept overnight. A volume of 500  $\mu$ l of this solution was injected and constant temperature of 20°C was maintained during separation.

## RESULTS AND DISCUSSION

Although polyether polyurethanes were found to be successfully cleaved by alkali fusion to diamines and polyethers, carbon dioxide was also liberated<sup>14</sup>, and the pressure build-up caused conventional<sup>23-29</sup> 10 mm O.D. borosilicate glass tubes to explode. Use of a stainless-steel reaction vessel overcame this problem. Although experiments described here were mainly qualitative, scope exists<sup>48</sup> for quantitative data to be obtained.

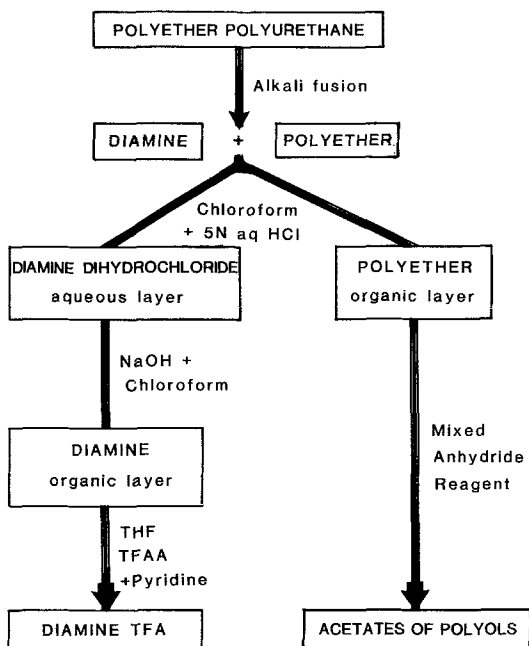


Fig. 2. Analytical scheme.

Fig. 2 shows the subsequent analytical procedure employed for the characterization of polyether polyurethanes. Fig. 3 shows the separation of 2,4- and 2,6-isomers of diamino toluene on Apiezon L column. The peak shapes were rather poor and base line separations could not be achieved. Therefore TFA derivatives of diamines were prepared leading to improved peak shapes and reduced retention times,

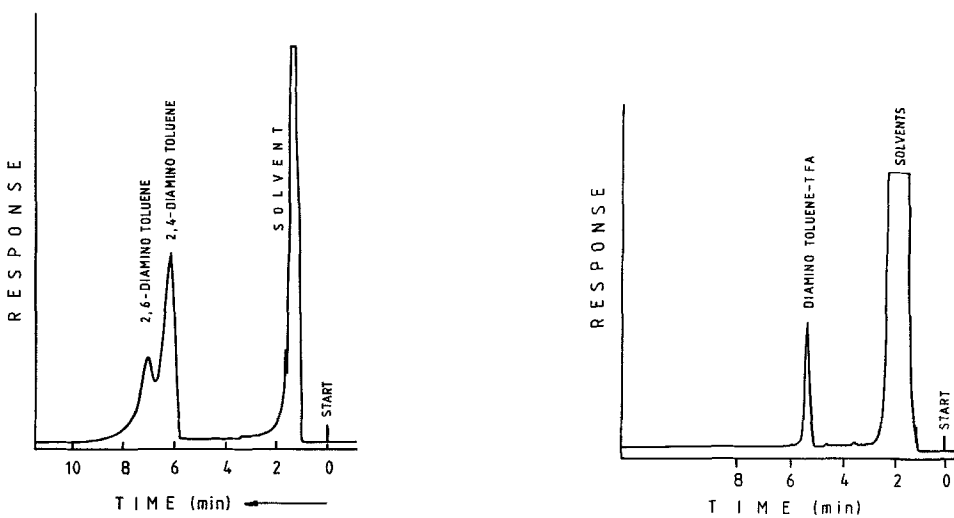


Fig. 3. Gas chromatogram showing separation of 2,4- and 2,6-diamino toluene isomers.

Fig. 4. Gas chromatogram showing separation of diamino toluene-TFA derivative.

although isomer separation was not achieved (Fig. 4). It was not possible to prepare TFA derivatives of toluene diamines by just stirring and allowing to stand with TFAA for 10 min in a vial as reported by Snyder *et al.*<sup>49</sup>. Quantitative derivatization was achieved by the aromatic amine derivatization method of Dove<sup>50</sup>.

When alkali fusion was performed in air rather than under nitrogen, several extra peaks attributable to diamine oxidation products were obtained.

Polyethers extracted from the alkali fusion procedure were separated by GPC as shown in Fig. 5. By use of appropriate standards molecular weight estimates of the original polyether used in the polyurethane manufacture could be made. However, some correction for decrease in molecular weight and increase in polydispersity caused by thermal degradation during fusion would be required. This can be done by subjecting polyethers of known original molecular weight to fusion and subsequent GPC analysis. GPC traces of constituent polyethers and the corresponding polyurethane, both after alkali fusion, were found to be identical.

Separated ethers were cleaved using mixed anhydride reagent for base compound analysis. Fig. 6 shows the gas chromatogram of acetates of polyols derived from polyethers. Peaks corresponding to ethylene glycol diacetate, propylene glycol diacetate and glycerol triacetate indicate that the polymer is the poly(oxypropylene-oxyethylene) adduct of glycerol. The peaks obtained for most of the other commercial polyethers analysed were also similar to Fig. 6 except that ethylene oxide and propylene oxide contents varied. Some polyethers were simply a co-polymer of ethylene oxide and propylene oxide.

Although the mixed anhydride reagent is a powerful acetylating agent, it was not possible to avoid the formation of some monoacetate products. Baseline separation of ethylene glycol and propylene glycol diacetates could be achieved when the temperature programming rate is reduced (*i.e.* 10°C/min or less) while other peaks will have poor shapes or not appear at all.

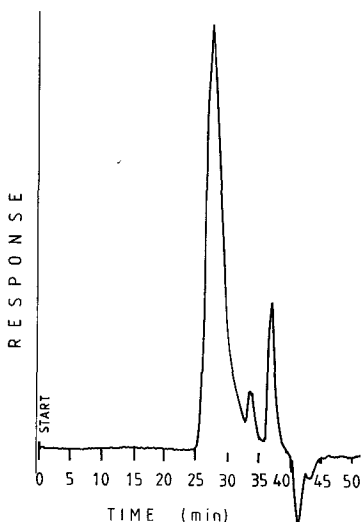


Fig. 5. Gel permeation chromatogram of polyether.

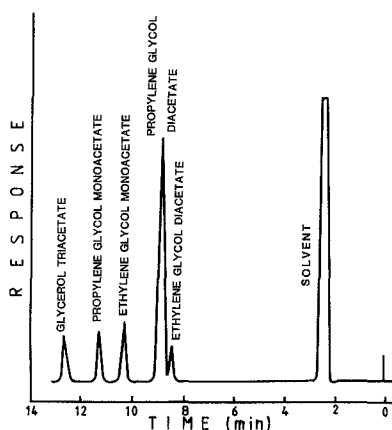


Fig. 6. Gas chromatogram showing separation of polyol acetates.

It has been demonstrated that the cleavage reaction produces near quantitative results<sup>22,29</sup>, however some of the reaction products may be subject to minor degradation as has been demonstrated with fatty polyamides<sup>24</sup> and polyhydrazides<sup>28</sup>, where minor degradation products were observed and in this case with the formation of some minor monoacetate products.

Accordingly with the analytical scheme presented, the diamine analysis has been shown to be near quantitative<sup>22,29</sup>, while the polyether analysis suffers from the difficulty that some degradation occurs. Also of more importance the chemical composition of individual deliveries of the polyethers vary slightly with the materials being purchased on analytical characteristics. The procedure however has been found satisfactory for the characterisation of polyurethane products and for the identification of the polyether used. The slightly larger scale fusion than previously employed allows sufficient polyether for further chemical analysis if required.

#### CONCLUSIONS

Alkali hydrolytic fusion of polyether polyurethanes can be achieved much more rapidly than by previous acid or other hydrolytic methods. Hydrolysis products are most conveniently analysed by GC and GPC. Diamines can be analysed by GC of both the free compounds or of the TFA derivatives.

Molecular weight of polyether hydrolysis products can be determined by GPC and the mixed anhydride reagent can be used to cleave the ether linkages for subsequent GC analysis of base acetate derivatives.

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