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CHROMATOGRAPHIC ANALYSIS OF POLYESTER-BASED POLYURETHANE ELASTOMERS AFTER ALKALI FUSION

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SUMMARY

An analytical procedure is described for rapid qualitative and quantitative analysis of polyester-based polyurethane elastomers. The elastomers are conventionally the complex reaction product of an isocyanate-terminated linear polyester prepolymer cross-linked with either a diamine or a diol chain extender. The polymer is cleaved into the corresponding diamine, dicarboxylic acid and glycol fragments by molten alkali fusion at high temperature. These products are analysed using gas and liquid chromatography, after separation using a liquid-liquid extraction procedure. Dicarboxylic acids are converted to dimethyl ester derivatives before gas chromatographic analysis while diisocyanate is examined as the diamines and diols, as liberated.

INTRODUCTION

Polyurethanes are among the most versatile of all polymer systems with extensive commercial applications in such areas as flexible and rigid urethane foams, elastomers, coatings, adhesives and films.

During the initial development of polyurethanes, polyesters were the most commonly used type of polyol. Polyesters are still widely used in the manufacture of polyurethanes. The most common ingredients of polyesters for urethane applications are adipic acid, phthalic anhydride, simple glycols and triols. The glycols used generally include, ethylene, propylene, 1,3-butylene, 1,4-butylene and diethylene glycol. The triols are usually glycerol, 1,2,6-hexanetriol, trimethylol propane and trimethylol ethane. Pentaerythritol may be used as a suitable source of crosslinking in some cases.

Acceptable control of urethane polymer formation is obtained when the polyester contains only terminal hydroxyl groups as reactive sites¹ and preferred polyesters have been those with very low free acidity and very low water content. Linear polyesters having molecular weights close to 2000 have been preferred for elastomers,

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slightly branched ones of similar molecular weight for flexible foam and elastic coatings, and more highly branched ones for rigid foams and the most chemically resistant coatings.

Numerous techniques have been utilized for the identification of polyurethane polyesters. The direct instrumental techniques such as Infra-red (IR) spectrometry¹⁻³ and nuclear magnetic resonance (NMR) spectroscopy^{4,5} have been widely used, but the scope of these techniques is limited and unsuitable for complete characterization. Pyrolysis-gas chromatography⁶⁻⁸ has also been widely used and found to be unsuitable for the identification of all of the constituents in the polymer or by quantitative analysis.

As direct methods of examination are not capable of identifying all the constituents, methods involving hydrolysis have become established and allow identification of the separated hydrolysis fragments. The hydrolysis of urethane linkages has been thoroughly investigated. Hydrolysis with water under pressure is only applicable to polyurethanes from aliphatic diisocyanates and polyvalent alcohols⁹. Athey¹⁰ investigated hydrolytic degradation of some polyester and polyether-based polyurethanes and found that the latter were 5 to 10 times as resistant to hydrolysis than the former. Hydrolysis under acidic conditions (*i.e.* with 50% hydrochloric acid) required longer reaction times (60 h) and yielded some undesirable side products^{11,12}.

Investigation by Matuszak *et al.*¹³ has shown that polyurethanes are much more susceptible to alkaline hydrolysis than acid hydrolysis. Alkaline hydrolysis has subsequently been used, usually in a Parr bomb apparatus, using 2-15% aqueous sodium hydroxide or potassium hydroxide reagents^{4,5,14-17}. The reaction is usually carried out at 150°C for 16 h and the resulting diamines, diacids and glycols from polyester based polyurethanes have been identified by thin-layer chromatography (TLC), IR, NMR and gas chromatography (GC)^{4,5}.

Alkali fusion, a newly-developed technique for rapid, high temperature hydrolysis of condensation polymers, has been widely used by Siggia and co-workers^{18,19} and Haken and co-workers²⁰⁻²⁷ for various polymer analysis including a recent work on polyether-based polyurethanes. Alkali cleavage of the polymer was followed by acid cleavage of the polyether diols.

A simple, rapid and reliable procedure for the complete analysis of polyurethane elastomers based on polyesters using alkali fusion is reported. The reactions involved in the analytical procedure are shown in Fig. 1. Both systems, where cross-linking is achieved with diols or diamines, are included, while methylene bis(*ortho*-chloroaniline) (MBCA) is widely used, its analysis has not been previously reported. The advantage of the alkali fusion procedure is that the hydrolysis is achieved in 2 h at 200°C, whereas days of refluxing are required with alkali in methanol^{4,5}.

EXPERIMENTAL

Samples

Commercially available polyester-based polyurethane samples, with compositions summarized in Table I, were used for the analysis.

Alkali fusion

Alkali fusion was carried out using 200 mg of polymer with 10 g of fusion flux

TABLE I
COMPOSITION OF POLYESTER-BASED POLYURETHANE SAMPLES ANALYSED

TDI = Toluene diisocyanate; MDI = *p,p'*-diphenylmethane diisocyanate; MBCA = methylene bis(*ortho*-chloroaniline).

Sample No.	Diisocyanate	Polyester		Cross-linker
		Glycol(s)	Dicarboxylic acid	
1	TDI	Ethylene glycol	Adipic acid	MBCA
2	TDI	Ethylene glycol, 1,4-butanediol	Adipic acid	MBCA
3	TDI	Ethylene glycol, 1,2-propanediol, 1,4-butanediol	Adipic acid	MBCA
4	MDI	Ethylene glycol	Adipic acid	1,4-Butanediol
5	TDI	Ethylene glycol, 1,2-propanediol	Adipic acid	MBCA

reagent (prefused mixture of potassium hydroxide containing 56 sodium acetate) prepared according to the method of Frankoski and Siggia¹⁸. 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.

Separation procedure

After cooling and opening the stainless-steel tube, the contents was dissolved in water and transferred to a separating funnel and extracted four times with 20-ml portions of dichloromethane. Evaporation of the combined dichloromethane extracts give diamines corresponding to the diisocyanate portion and chain extender portion of the polymer for chromatographic analysis.

The remaining aqueous solution was rendered slightly acidic using concentrated hydrochloric acid, and extracted with chloroform. Evaporation of the chloroform extract gives the dibasic acid from the polyester backbone. The dibasic acid was converted to its dimethyl ester by adding 5 ml of boron trifluoride-methanol reagent and refluxing for 1 h. The unreacted reagent was destroyed by adding water and the methyl ester was extracted with chloroform and concentrated to a small volume (2 ml) for gas chromatographic analysis. The aqueous solution remaining was then made alkaline by the addition of sodium hydroxide pellets and saturated by adding potassium carbonate. This solution is extracted with diethyl ether in a liquid-liquid extraction apparatus for at least 5 h. Suitable apparatus has been described²⁸. The diethyl ether extract was dried over anhydrous sodium sulphate and concentrated to a small volume for GC analysis. The separation scheme is shown in Fig. 2.

Gas chromatography

Gas chromatography was carried out using a Hewlett-Packard 5830A Research Model gas chromatograph with flame-ionization detection.

Diamines. These were separated on a 4 ft. × 1/8 in. O.D. stainless-steel column

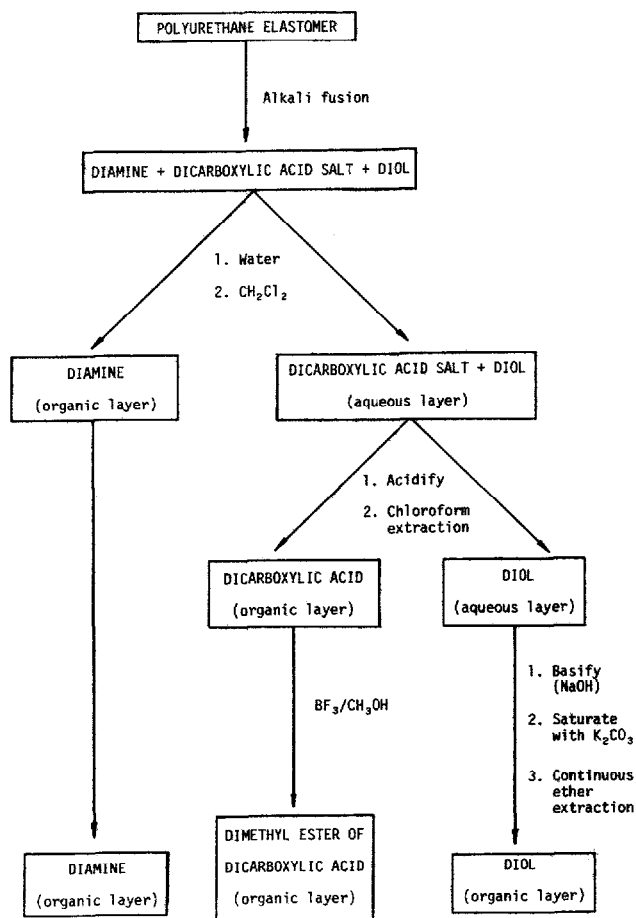


Fig. 2. Analytical scheme.

packed with 10% XE-60 on Chromosorb W AW DMCS 80–100 mesh, using helium as carrier gas out a flow-rate of 40 ml/min. The detector and injection ports were maintained at 250°C and 300°C, respectively. The column was temperature programmed from 150 to 275°C at 20°C/min and held at 275°C for 5 min.

Methyl esters of dicarboxylic acids. These were separated on a 12 ft. × ¼ in. O.D. aluminium column packed with 10% Apiezon L grease on Celite AW-DMCS, 72–85 mesh. The detector and injection ports were maintained at 180°C and 200°C, respectively. The column was operated isothermally at 165°C using helium as carrier gas at a flow-rate of 70 ml/min.

Glycols. Separation of glycols were carried out on the 4 ft. × 1/8 in. O.D. stainless-steel column packed with Porapack Q, using helium as carrier gas at a flow-rate of 35 ml/min. The injection port and detector were maintained at 250°C and 280°C, respectively. The column was operated 2 min isothermally at 200°C and then temperature programmed at 6°C/min to 250°C and held at 250°C for 5 min.

Liquid chromatography

The separation of 2,4- and 2,6-diaminotoluene was carried out by liquid chromatography (LC).

The liquid chromatography system was constructed from individual Waters modules, namely 6000 A pump, U6K injector and 440 variable wavelength differential flow UV absorbance detector and Edward Instrument 10 mV recorder. Separations were carried out on a reversed-phase Ultrasphere-octyl (Brownlee Labs. RP 8-SPHERI-5) 250 × 4.6 mm I.D. column. Operating conditions were: flow-rate 1 ml/min; temperature 20°C; UV detector at 254 nm; injection volume 10 μl from 100 ppm solution. The mobile phase used was acetonitrile-water (10:90) containing 0.001 M sodium dihydrogenphosphate and 0.003 M disodium hydrogenphosphate, pH 7.4.

RESULTS AND DISCUSSION

Polyester-based polyurethane elastomers were successfully cleaved into diamine, dicarboxylic acid and glycol fragments using alkali fusion. The initial fusion reactions were carried out with polyether-based polyurethanes in a stainless-steel reactor fitted with a reflux condenser²⁷. An inert (nitrogen) atmosphere was maintained over the reaction medium to avoid possible oxidation of fragments formed. The use of a stainless-steel screw-cap pressure tube completely filled with polymer-reagents mixture eliminated the necessity of using an inert atmosphere.

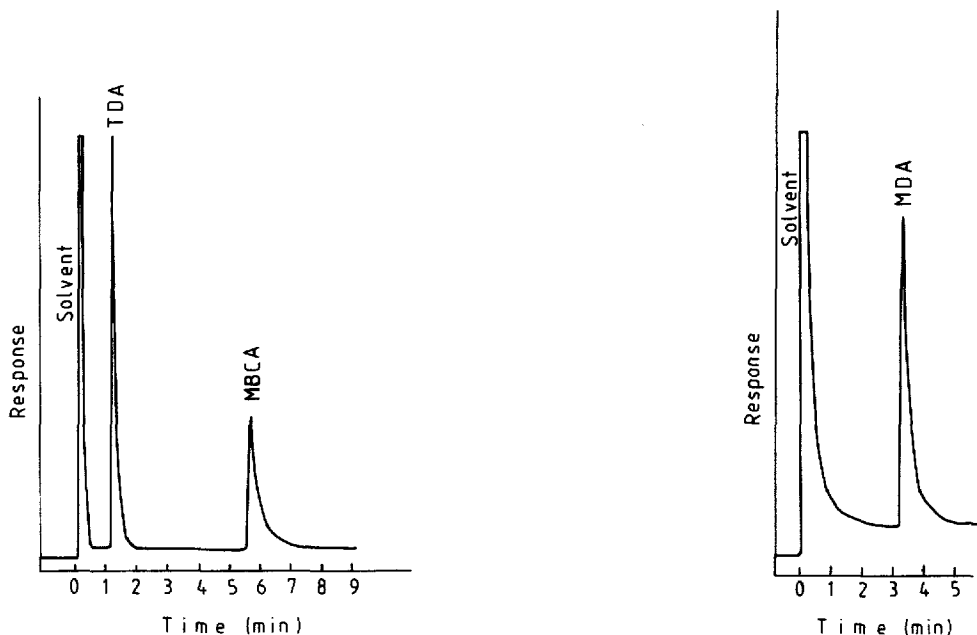


Fig. 3. Gas chromatogram showing the separation of toluene diamines (TDA) and methylene bis(*ortho*-chloroaniline) (MBCA). Conditions: 4 ft. × 1/8 in. O.D. stainless-steel column packed with 10% XE-60 on Chromosorb W AW DMCS, 80–100 mesh; carrier gas, helium; flow-rate, 40 ml/min. The detector and injection ports were maintained at 250 and 300°C, respectively. The column was temperature programmed from 150°C to 275°C at 20°C/min and held at 275°C for 5 min.

Fig. 4. Gas chromatogram of *p,p'*-diphenylmethane diamine. Conditions as in Fig. 3.

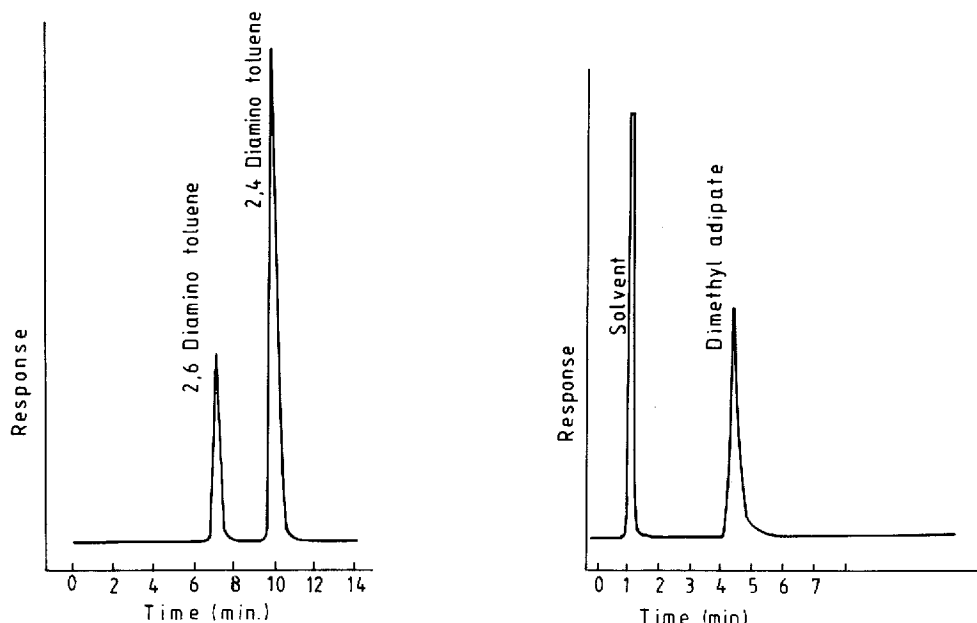


Fig. 5. Liquid chromatogram showing the separation of 2,6- and 2,4-diaminotoluene. Conditions: reversed-phase Ultrasphere-octyl column, 250×4.6 mm I.D.; flow-rate, 1 ml/min; temperature, 20°C ; UV detector set at 254 nm; injection volume $10 \mu\text{l}$ from 100 ppm solution. Mobile phase, acetonitrile-water (10:90) containing 0.001 M sodium dihydrogenphosphate and 0.003 M disodium hydrogenphosphate (pH 7.4).

Fig. 6. Gas chromatogram of dimethyl adipate. Conditions: 12 ft. \times 1/4 in. O.D. aluminium column packed with 10% Apiezon L grease on Celite AW-DCMA, 72-85 mesh. The detector and injection ports were maintained at 180°C and 200°C , respectively. The column was operated isothermally at 165°C using helium as carrier gas at a flow-rate of 70 ml/min.

Alkali fusion reactions are usually carried out at $200\text{--}350^\circ\text{C}$. The reaction time could be considerably reduced by using high temperature. In this work, we observed some undesirable side reactions when very high temperatures (*i.e.* 300°C) were used or the water content of the fusion reagent was low. For example, adipic acid, formed by hydrolysis of the polyester portion of the polyurethane, undergoes a cyclic condensation reaction to form cyclopentanone²⁹. Most of the glycols formed also undergo degradation reactions at very high temperatures in the presence of alkali fusion reagent. Hence fusion reaction conditions were limited to 200°C for 2 h, using alkali fusion reagent containing 25% water to prevent undesirable side products.

The diamine corresponding to the diisocyanate portion of the polymers and chain extender portion were successfully separated by GC. Fig. 3 shows the separation of toluene diamines (2,4- and 2,6-isomers) and methylene bis(*ortho*-chloroaniline) (MBCA) from sample No. 1. Similar chromatograms were obtained for the other samples except sample No. 4. Fig. 4 shows the chromatogram of *p,p'*-diaminodiphenylmethane obtained from sample No. 4. Separation of 2,4- and 2,6-diaminotoluene was unsuccessful using GC, but was achieved using liquid chromatography (Fig. 5). This chromatogram was used for the quantitative estimation of isomer content of toluene diisocyanate used for the manufacture of the polymer. Conditions

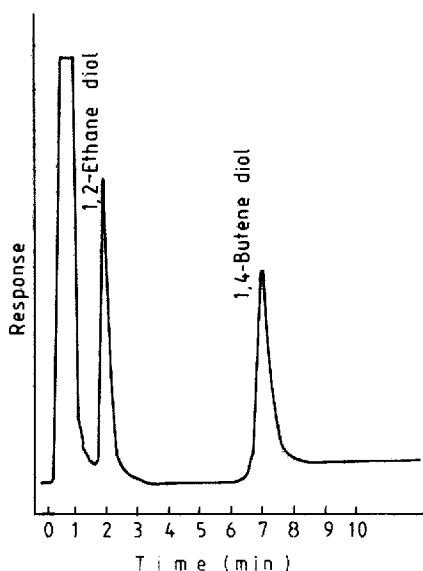


Fig. 7. Gas chromatogram showing the separation of 1,2-ethanediol and 1,4-butanediol. Conditions: 4 ft. \times 1/8 in. O.D. stainless-steel column packed with Porapak Q, using helium as carrier gas at a flow-rate of 35 ml/min. The injection port and detector were maintained at 250°C and 280°C, respectively. The column was operated 2 min isothermally at 200°C and then temperature programmed at 6°C/min to 250°C and held at 250°C for 5 min.

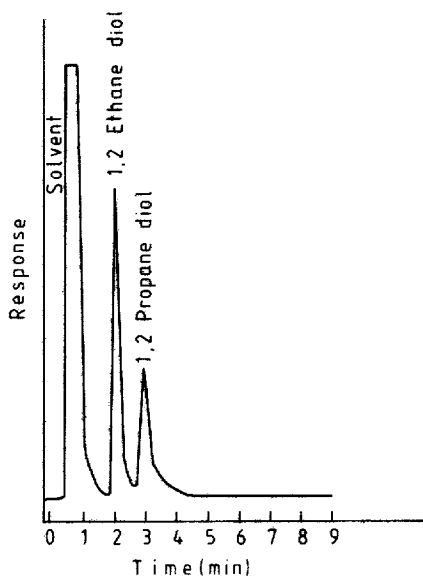


Fig. 8. Gas chromatogram showing the separation of 1,2-ethanediol and 1,2-propanediol. Conditions as in Fig. 7.

used were similar to that reported by Snyder and Breder³⁰. MBCA was not eluted under these conditions.

Derivatization of dicarboxylic acids into their methyl esters was used for GC identification of dicarboxylic acids²⁰⁻²³. Adipic acid was converted to its dimethyl ester using boron trifluoride-methanol reagent. Separation of dimethyl adipate on Apiezon L column is shown in Fig. 6.

Low-molecular-weight glycols present in all samples were successfully separated by GC on Porapak Q, porous polymer column. Figs. 7 and 8 show the separation of glycols from sample No. 4 and 5 respectively. These chromatograms could be used to estimate glycol proportions used in polyester manufacture.

CONCLUSIONS

Alkali hydrolytic fusion of polyester-based polyethanes is much faster than conventional solution hydrolysis methods. Complete qualitative and semi-quantitative analysis of polyurethane polymers could be achieved in a few hours. The hydrolysis fragments are conveniently analysed by GC and LC. Non-volatile fragments such as dicarboxylic acids are converted to a suitable volatile derivative before GC analysis.

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