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CHROMATOGRAPHIC ANALYSIS OF THERMOPLASTIC, MEDICAL-GRADE, POLYETHER-BASED POLYURETHANE ELASTOMERS

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SUMMARY

An analytical procedure is described for rapid qualitative analysis of medical-grade polyether-based polyurethane elastomers. The elastomers are conventionally the complex reaction product of an isocyanate-terminated linear polyether prepolymer with either a diamine or a diol chain extender. The polymer is cleaved into the corresponding diamine, polyether, diol, or hydrocarbon by molten alkali fusion at high temperature. These fragments are analysed by gas and gel-permeation chromatography, after separation by a liquid–liquid extraction procedure. Polyethers are further cleaved into the corresponding polyol acetates by using a mixed anhydride reagent, before gas chromatographic analysis.

INTRODUCTION

Polyurethane elastomers are elastomeric materials produced by the rearrangement polymerisation of diisocyanate and polyols[1]. Their three main constituents are: (i) a diisocyanate; (ii) a long-chain hydroxy-terminated polyol, either as a polyester or as a polyether; (iii) a chain extender, which is often a short-chain glycol or a diamine. Polyethers have now assumed a dominant role in the commercial production of polyurethanes. A particularly important use of polyurethane elastomers is in the medical area[2] where implant devices are required to withstand continual and long-term flexing. Artificial hearts and bladders of this type have withstood 150 million cycles without failure and show considerable promise[3–5].

The first polyether specifically designed for polyurethane elastomer manufacture was polyoxytetramethylene ether glycol (PTMEG) derived from tetrahydrofuran[6]. Although polyurethanes derived from PTMEG exhibits outstanding physical properties, the cost of PTMEG restricts its use to specific applications. At present, most of the commercially available polyethers are derived from ethylene oxide and/or propylene oxide. Linear, glycol-initiated propylene oxide–ethylene oxide block copolymers find some commercial use in the production of elastomers. Linear polyethers having molecular weights close to 2000 have been preferred for elastomers,

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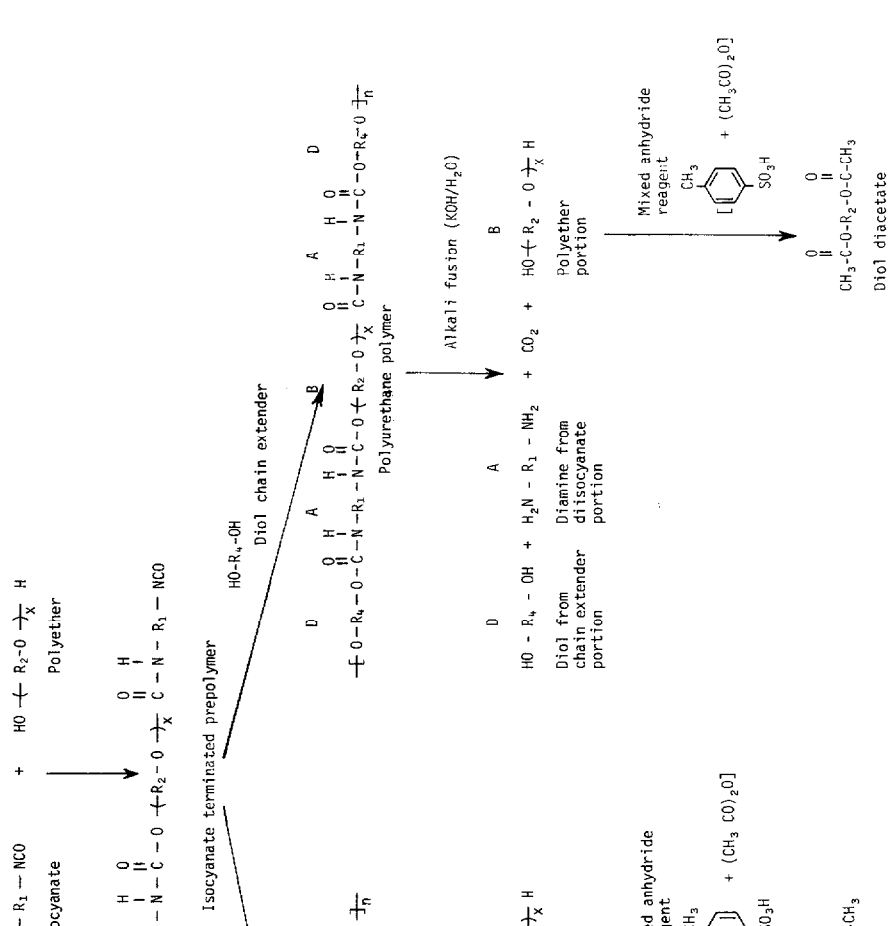

Fig. 1. Reactions involved in the analytical scheme.

whereas slightly branched ones of similar molecular weight are preferred for flexible foams, and more highly branched polyethers for rigid foams and chemically resistant coatings[1].

The chemical analysis of polyurethanes is difficult because of the stability of the urethane linkage and often because of a three-dimensional structure of the polymer. Available classical methods only provide simple qualitative tests for a few constituents[7]. Infrared spectrometry (IR)[8–10] has been widely used to identify the type of diisocyanate and the functional groups present in polyurethanes. Nuclear magnetic resonance spectroscopy (NMR)[11] shows some potential for the determination of structural groups, but use is limited because the sample must be dissolved prior to examination. Therefore, the scope for these instrumental techniques is restricted and unsuitable for complete polymer analysis. Pyrolysis gas chromatography (GC)[12–14], together with chemical ionization mass spectroscopy[15], have been used but are also unsuitable for the complete analysis.

As direct methods of analysis are not capable of identifying all the constituents, the hydrolysis of the polymer, followed by examination of the fragments, is at present the most complete and proven approach. Hydrolysis with water[16] under pressure was only applicable to polyurethane from aliphatic diisocyanates and polyvalent alcohols. Athey[17] studied the hydrolytic degradation of some polyester and polyether urethanes and found that the latter was 5–10 times as resistant to hydrolysis than the former.

Hydrolysis with 50% aqueous hydrochloric acid[18,19] was found to be incomplete even, after 60 h of refluxing, while side reactions also occurred. Hydrolysis of similar type of polyurethanes with 60% sulphuric acid[20] was found to be quantitative after short reaction periods but also involved unfavourable side reactions. Matuszak *et al.*[21] have investigated the hydrolysis under various conditions and found that the urethane linkage is much more susceptible to alkaline than acid hydrolysis. Alkaline hydrolysis[22–27] has subsequently been used, usually in a Parr bomb apparatus with 2–15% aqueous sodium hydroxide or potassium hydroxide reagents. The reaction is usually carried out at 150°C for 16 h, and the resulting products have been identified by thin-layer chromatography (TLC), IR, NMR and GC. No systematic procedure has been reported in the literature for complete analysis of polyether-based polyurethane elastomers.

Alkali fusion, a recently developed technique for high-temperature hydrolysis of condensation polymers, has been widely used by Siggia and co-workers[28,29] and by Haken and co-workers[30–40] for various polymer analyses, including polyurethane foam analysis.

The present work describes a simple, rapid, reliable, analytical procedure for complete analysis of polyether-based polyurethane elastomers, involving alkali fusion of the polymer, followed by acid cleavage of the polyether with mixed anhydride reagent.

The mixed anhydride reagent[41,42] was used to cleave polyethers, because reported methods, using hydrochloric acid[43], hydrobromic acid[44–47], hydriodic acid[48,49], *p*-toluenesulphonic acid[50], pyrolysis GC[51,52], IR, and NMR[53,54], were found to be unsatisfactory for complete analysis of the polyether. The main advantage of the alkali fusion procedure is that the hydrolysis is achieved in 2 h at 250°C in molten alkali fusion reagent, whereas refluxing for days with alkali in methanol

TABLE I

COMMERCIALLY AVAILABLE MEDICAL-GRADE POLYURETHANE ELASTOMERS[4]

Sample No.	*Name*	*Supplier*	*Description*
1	Biomer	Ethicon (Somerville, NJ, U.S.A.)	Linear, segmented, aromatic, polyether-based, ethylenediamine-extended
2	Pellethane, 2663 Series	Upjohn Chemical (North Haven, CT, U.S.A.)	Linear, segmented, aromatic, polyether-based, butanediol-extended
3	Tecoflex	Thermo Electron (Waltham, MA, U.S.A.)	Linear, segmented, aliphatic, polyether-based, butanediol-extended
4	Cardiothane	Kontron (Everett, MA, U.S.A.)	Crosslinked, aromatic, polyether-based, urethane silicone copolymer

is required[25]. All the reactions involved in the analytical scheme are shown in Fig. 1.

Thermoplastic urethane elastomers

Polymers analysed include the four important polyether-based polyurethane elastomers commercially available for medical applications. The composition and structures of the polymers are not disclosed by the manufacturers but have been suggested in various reports[2–5], and details are shown in Table I. The polymer structures are shown in Figs. 2–5 and are confirmed or modified by the work reported here.

Conventional elastomers are cross-linked by primary valency bonding, while thermoplastic elastomers are cross-linked by secondary valency bonding, such as Van der Waals interactions, dipole interactions or hydrogen bonding. These bonds break down at elevated temperatures but are reconstituted on cooling. The thermoplastic

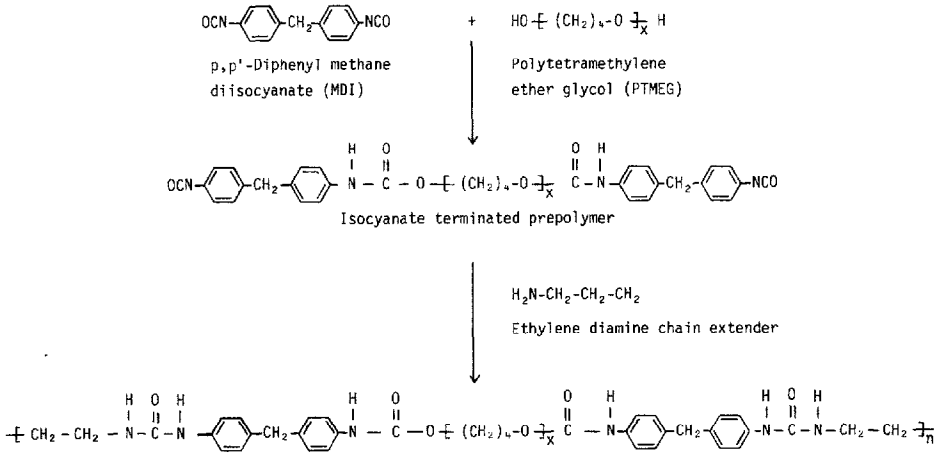

Fig. 2. Molecular architecture of Biomer.

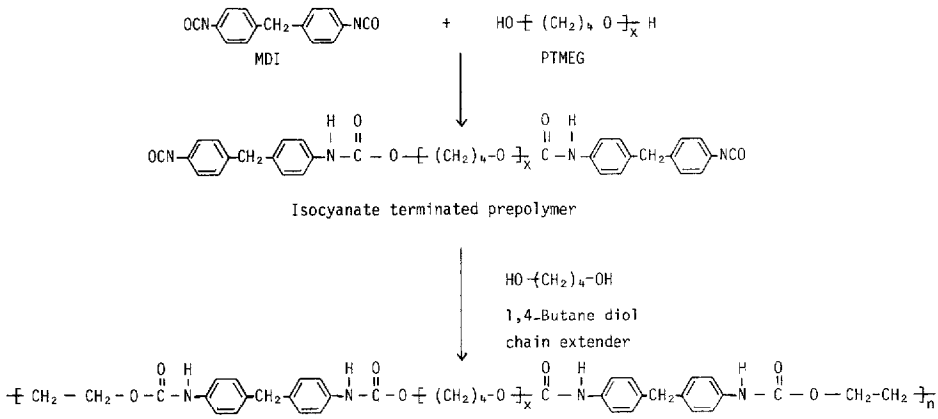

Fig. 3. Molecular architecture of Pellethane.

elastomers are segmented copolymers possessing hard and soft segments and the structure of polyurethane elastomers of this type has generally been described by Bonart[55].

The samples shown in Table I are of four important types. Samples 1 and 2 are aromatic in character but with diamine and diol chain extension. Sample 3 is similar to sample 2, but the isocyanate is saturated. Sample 4 is cross-linked with a reactive silane.

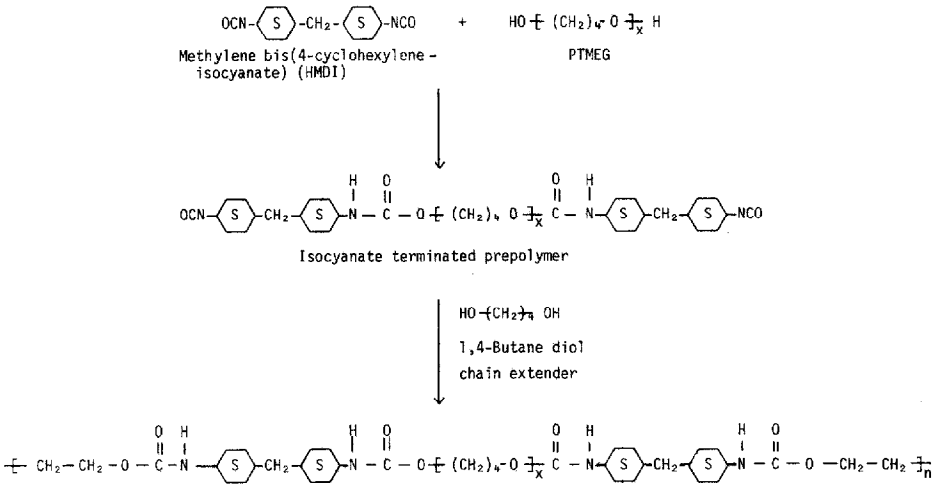

Fig. 4. Molecular architecture of Tecoflex.

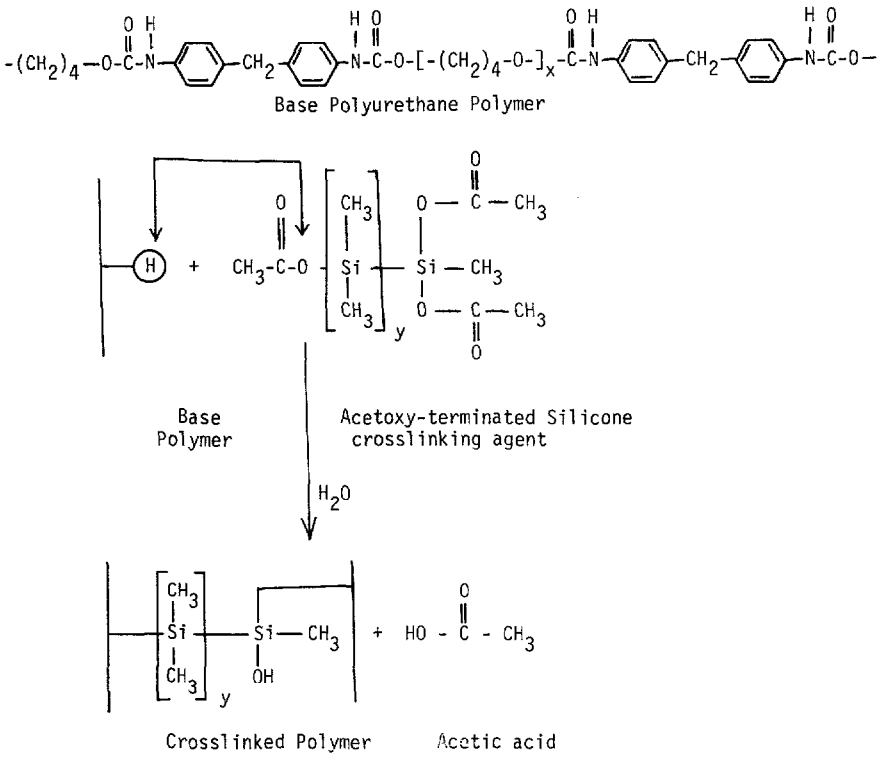

Fig. 5. Cross-linking of Cardiothane.

EXPERIMENTAL

Alkali fusion

Alkali fusion was carried out using 200 mg of polymer with 15 g of fusion flux reagent (prefused mixture of potassium hydroxide containing 5% sodium acetate) prepared according to the method of Siggia and co-workers[28,29]. Hydrolysis was achieved by heating the finely ground polymer–reagent mixture in a stainless-steel screw-cap pressure tube at 250°C for 2 h.

Separation procedure

After the tube had cooled its contents were dissolved in water and transferred to a separating funnel and extracted with four 15-ml portions of dichloromethane. The remaining aqueous solution was saturated with potassium carbonate and extracted with ether in a liquid–liquid extraction apparatus for at least 6 h. Suitable apparatus has been described[56]. The ether extract was dried over anhydrous sodium sulphate and concentrated to a small volume (2 ml) the for GC analysis of diol chain extender.

The combined organic extract was then extracted with three 10-ml portions of aqueous (5 *M*) hydrochloric acid. The combined aqueous extract was made alkaline by adding sodium hydroxide pellets and was then extracted with three 10-ml portions of dichloromethane. The combined organic extract was dried and concentrated to a small volume for the GC analysis of diamines corresponding to diisocyanate and diamine chain extender.

The polyether was recovered by evaporating the original dichloromethane extract remaining after the aqueous hydrochloric acid extraction. A portion of the polyether was used for gel-permeation chromatography (GPC) and the other portion was refluxed at 125°C for 2 h with 10 ml of mixed anhydride reagent. This was prepared by refluxing an equimolar mixture of *p*-toluenesulphonic acid and acetic anhydride for 0.5 h[41,42]. The reaction mixture was cooled and then neutralized with a saturated aqueous solution of sodium carbonate, followed by extraction with three 10-ml portions of chloroform. The combined organic extracts were dried and concentrated for the GC analysis of polyol acetates resulting from the polyether cleavage.

GC

GC was carried out in a Hewlett-Packard 5830A Research Model gas chromatograph with flame ionization detection.

Diamines

These were separated on a 5 ft. × 1/8 in. O.D. stainless-steel column, packed with 10% XE-60 on Chromosorb W AW DMCS, 80–100 mesh, with helium as carrier gas at a flow-rate of 30 ml/min. The detector and injector were maintained at 250°C and 300°C respectively. The separations of methylene bis-(4-cyclohexylene amine) (HMDA) and *p,p'*-diphenylmethane diamine (MDA) were carried out isothermally at 210°C and 230°C respectively.

Diamine–trifluoroacetamide

These were separated on a 4 ft. × 1/4 in. O.D. aluminium column packed with 4% SE-30 on Chromosorb W AW DMCS. The detector and injector were maintained at 250°C and 300°C, respectively. The column was operated 2 min isothermally at 120°C, then temperature-programmed at 15°C/min to 260°C, held at 260°C for 5 min. A helium carrier gas flow-rate of 70 ml/min was maintained during the separations.

Polyol acetate

This was separated on a 12 ft. × 1/4 in. O.D. aluminium column packed with 10% Apiezon L grease on Celite AW DCMS (72–85 mesh). The detector and injector were maintained at 200°C and 250°C, respectively. The column was operated isothermally at 165°C, using a helium carrier gas flow-rate of 70 ml/min.

Diol

Separation of 1,4-butanediol was carried out on a 4 ft. × 1/8 in. O.D. stainless-steel column, packed with Porapak Q (80–100 mesh), with a helium carrier gas flow-rate of 30 ml/min. The injection port and detector were maintained at 250°C and 300°C, respectively. The column was operated isothermally at 235°C.

Methane

This was separated on the same Porapak Q column operated isothermally at 30°C, with a helium carrier gas flow-rate at 25 ml/min. The injector and detector temperatures were maintained at 100°C and 150°C, respectively.

GPC

The gel-permeation chromatograph was constructed from individual Waters modules, namely a Model 6000A pump, a Model U 6K injector, and a Model R 401 differential refractive index detector. The four-column system used consisted of 300 × 7.8 mm I.D. stainless-steel columns, packed with μ-Styragel (10 μm) packing having nominal exclusion limits of 1000, 500, 100, and 100 Å, respectively. The columns were connected in series so that the last 100 Å column was connected to the detector.

The eluent used was tetrahydrofuran (THF) at a flow-rate of 1 ml/min. The solvent was distilled from ferrous sulphate and filtered through a 0.5-μm Millipore FH filter before use. As antioxidant, 20 ppm *tert.*-butylhydroxytoluene was added to the solvent, which was kept under a nitrogen blanket in the solvent reservoir. Polyether solutions (200 ppm) were prepared in THF solvent, and an aliquot of 500 μl of this solution was injected. Constant temperature of 20°C was maintained during separation.

RESULTS AND DISCUSSION

Polyether-based polyurethane elastomers were successfully cleaved into diamine, polyether, and diol fragments. Alkali fusion reactions are usually carried out at 200–350°C. The reaction time could be considerably shortened by using higher temperatures. But the fusion temperature was limited to 250°C, due to degradation of 1,4-butanediol at higher temperature in the presence of the fusion reagent.

The diamines corresponding to the diisocyanate portion of the polymers were successfully separated by GC. Thus, MDA was separated from Pellethane, Biomer, and Cardiothane, and HMDA was isolated on a XE-60 column. Identity of the

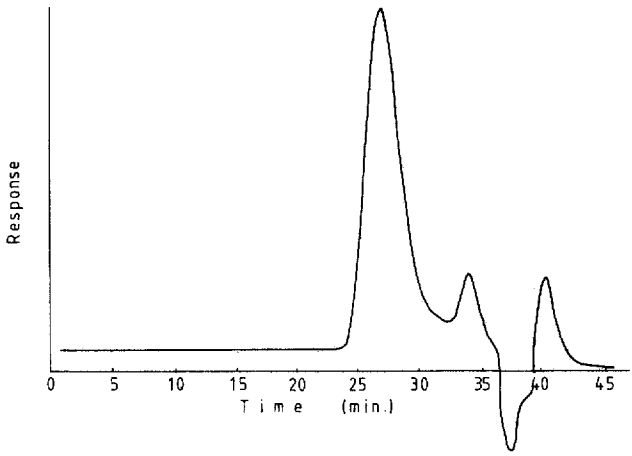

Fig. 6. Liquid chromatogram showing separation of PTMEG.

diamines were confirmed by mass spectrometry. The ethylene diamine chain extender could not be detected with the diamines above, as it is lost during the extraction and concentration stages. To detect ethylene diamine from Biomer, the fusion products were converted to trifluoroacetic acid (TFA) derivatives using TFA anhydride reagent. A suitable procedure has been described[57]. The ethylenediamine–TFA derivative and the MDA–TFA derivatives were separated on a SE-30 column. Similarly, 1,4-butanediol could be separated from Pellethane and Tecoflex on a Porapak Q column.

The alkali fusion reaction GC has been applied for the determination of alkyl and aryl groups in polysiloxanes by Schlueter and Siggia[58]. The method involved the quantitative cleavage of all organic substituents bonded to silicon, producing the corresponding hydrocarbons. Alkali fusion of Cardiothane produces methane from its methylsilicone cross-links. This was detected by injecting 0.5 ml of gas, collected over the reaction medium, into a Porapak Q column.

Polyethers, produced from alkali fusion were separated by GPC, as shown in Fig. 6. By use of appropriate standards, molecular weight estimates of the original polyether used in the polyurethane manufacture were made. However, some correction for decrease in the molecular weight and increase in polydispersity caused by thermal degradation during fusion is required[39].

The separated polyethers were cleaved into polyol acetates using mixed anhydride reagent and 1,4-butanediol diacetate was isolated from all four polymers analysed. This confirmed the identity of the PTMEG used in the manufacture of all four polymers.

CONCLUSIONS

Hydrolysis by alkali fusion of polyether-based polyurethane elastomers is achieved much more rapidly than by previously reported hydrolytic methods. The hydrolysis products are conveniently analysed by GC and GPC. The molecular weight of polyether obtained after hydrolysis, is determined by GPC, and a mixed anhydride reagent is used to cleave the polyether into corresponding polyol acetates for subsequent GC analysis.

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REFERENCES

1 J. H. Saunders and K. C. Frisch, *Polyurethanes: Chemistry and Technology, Part 1 Chemistry*, Interscience, New York, 1962.
2 H. M. Leefer and R. M. Wright, *Rubber Chem. Technol.*, 56 (1983) 523.
3 M. Szycher, V. Poirier and J. Keiser, *Trans. Am. Soc. Artif. Intern. Organs*, 23 (1977) 116.

4 M. Szycher, V. L. Poirier and D. Dempsey, *Am. Chem. Soc. Rubber Dev. Chicago, Prepr.*, 5 (1982) 1–18.
5 M. Szycher, V. L. Poirier and D. Dempsey, *Elastomerics*, March (1983) 11–15.
6 C. M. Barringer, *Teracol 30, Polyalkylene Ether Glycol Bulletin*, 11R-1-Dupont, 1956.
7 P. Wright and A. P. C. Cumming, *Solid Polyurethane Elastomers*, MacLaren, London, 1969.
8 W. H. T. Davison and P. J. Corish, *J. Chem. Soc.*, (1955) 2428.
9 O. Kinoshita, *Shikizai Kyokaishi*, 44 (1971) 273.
10 D. J. David and H. B. Staley, *Analytical Chemistry of Polyurethanes*, Wiley-Interscience, New York, 1969.
11 E. G. Brame, C. Ferguson and G. J. Thomas, *Anal. Chem.*, 39 (1967) 517.
12 C. Read, *Br. Polym. J.*, 6 (1974) 1.
13 F. D. Hileman, K. J. Voorhees, L. H. Worjcik, M. M. Birky, P. W. Ryan and I. N. Einhorn, *J. Polym. Sci.*, 13 (1975) 571.
14 D. Thorburn Burns, E. W. Johnson and R. F. Mills, *J. Chromatogr.*, 105 (1975) 43.
15 N. A. Mumford, D. A. Chatfield and I. N. Einhorn, *J. Polym. Sci.*, 23 (1979) 2099.
16 H. Rinke, *Ger. Pat.*, 951 268 (1956).
17 R. T. Athey, *Rubber Age (N.Y.)*, 86 (1965) 705.
18 J. Haslam and H. A. Willis, *Identification and Analysis of Plastics*, Illiffe Books, London, 1965.
19 J. Haslam and M. Clasper, *Analyst (London)*, 76 (1951) 33.
20 H. Winterscheidt, *Seifen Oele Fette Wachse*, 15 (1954) 404.
21 M. L. Matuszak, K. C. Frisch and S. L. Reegen, *J. Polym. Sci.*, 11 (1973) 1683.
22 J. L. Mulder, *Anal. Chim. Acta*, 38 (1967) 563.
23 P. J. Corish, *Anal. Chem.*, 31 (1959) 1303.
24 P. Fijolka, R. Gnauck and G. Schulz, *Plaste Kautsch.*, 19 (1972) 751.
25 B. Dawson, S. Hopkins and P. R. Sewell, *J. Appl. Polym. Sci.*, 14 (1970) 33.
26 B. Dawson, S. Hopkins and P. R. Sewell, *J. Appl. Polym. Sci.*, 14 (1970) 45.
27 L. Li Gotti, R. Piacentini and G. Bonomi, *Mater. Plast. Elastomeri*, 36 (1970) 213.
28 S. P. Frankoski and S. Siggia, *Anal. Chem.*, 44 (1972) 507.
29 L. R. Whitlock and S. Siggia, *Sep. Purif. Methods*, 3 (1974) 299.
30 J. K. Haken and J. A. Obita, *J. Macromol. Sci. Chem.*, A 17, 2 (1982) 203.
31 J. K. Haken and J. A. Obita, *J. Oil Colour Chem. Assoc.*, 63 (1980) 194.
32 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 213 (1981) 55.
33 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 244 (1982) 259.
34 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 244 (1982) 265.
35 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 239 (1982) 377.
36 G. J. Glading and J. K. Haken, *J. Chromatogr.*, 157 (1978) 404.
37 R. P. Burford, J. K. Haken and J. A. Obita, *J. Chromatogr.*, 268 (1983) 515.
38 J. K. Haken and M. A. Rohanna, *J. Chromatogr.*, 298 (1984) 263.
39 P. A. D. T. Vimalasiri, J. K. Haken and R. P. Burford, *J. Chromatogr.*, 319 (1985) 121.
40 R. P. Burford, J. K. Haken and P. A. D. T. Vimalasiri, *J. Chromatogr.*, 321 (1985) 295.
41 K. Tsuji and K. Konishi, *Analyst (London)*, 96 (1971) 457.
42 K. Tsuji and K. Konishi, *Analyst (London)*, 99 (1974) 54.
43 R. W. Morgan, *Ind. Eng. Chem. Anal.*, 18 (1946) 500.
44 A. Mathias and N. Mellor, *Anal. Chem.*, 38 (1966) 472.
45 J. B. Stead and A. H. Hindley, *J. Chromatogr.*, 42 (1969) 470.
46 R. M. Smith and M. Dawson, *Analyst (London)*, 108 (1980) 85.
47 I. I. Kaduji and J. B. Stead, *Analyst (London)*, 101 (1976) 728.
48 T. Ramstad, T. J. Nestrick and R. H. Stehl, *Anal. Chem.*, 50 (1978) 1325.
49 T. Kudawara and H. Ishicoatari, *J. Soc. Chem. Ind. Jpn*, 68 (1965) 2133.
50 A. Cervenka and G. T. Merrall, *J. Polym. Sci., Polym. Chem. Ed.*, 14 (1976) 2135.
51 E. W. Neumann and H. G. Nadeau, *Anal. Chem.*, 35 (1963) 1454.
52 T. F. Portzman, *Anal. Chem.*, 36 (1964) 108.
53 R. A. Griff and P. W. Flanagan, *J. Am. Oil Chem. Soc.*, 85 (1963) 2446.
54 K. Konishi and Y. Kanoh, *Bunseki Kagaku*, 15 (1966) 1110.
55 R. Bonart, *Polymer*, 20 (1979) 1389.
56 *Labware and Scientific Equipment Catalogue*, Corning, Laboratory Division, Storne, Staffordshire, Q 24, 1981.
57 R. A. Dove, *Anal. Chem.*, 39 (1967) 1188.
58 D. D. Schlueter and S. Siggia, *Anal. Chem.*, 49 (1977) 2343.