Review

Degradative polymer analysis by chromatography [1]

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Abstract

The review considers the degradative analysis of polymers in association with chromatography. The work indicates very briefly the scope of polymer pyrolysis, the necessary parameters to be controlled and includes some recent advances in polymer pyrolysis with a detailed treatment of the application of chemical degradation to the identification of polymers. Pyrolytic methylation, a newer application which effectively is a combination of the two techniques described, is included. This procedure carries out in situ, part of the derivatization conducted with the chemical degradation procedure.

Keywords: Pyrolysis; Chemical degradation; Pyrolytic methylation; Reviews; Polymers

Contents

1. Introduction

A variety of factors including high molecular mass, low volatility and low solubility have re-stricted the application of the chromatographic procedures to polymer materials. Size exclusion chromatography [1–3] has been widely used for molecular weight determination but the technique is limited by solubility, stereoregularity and cross linking.

Techniques available have largely considered the whole molecule although polymer performance depends not only on molecular weight considerations, but on stereoregularity and chemical composition. In this order the application of chromatography to polymers has decreased.

Traditionally many condensation polymers were cleaved most commonly by solution hydrolysis with

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[1] Dedicated to Dr. Karel Macek on the occasion of his retirement as Foundation Editor of the Journal of Chromatography B: Biomedical Applications (1977–1996) and as an editor of the Journal of Chromatography A (1989–1993).
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the initial reactants or their derivatives being determined by gravimetric, colorimetric or spectroscopic means. Such procedures may be demonstrated by the simple alkyd resins where the work of Kappelmeier and his coworkers [4] produced the basis of procedures for the identification of phthalic anhydride (a), polyols (b) and fatty acids (c) which were soon adopted as ASTM specifications. The utility of these procedures were enhanced as the alkyd resins became more complex by the introduction in 1962 of gas chromatographic detection by Esposito [5-7].

Thermal degradation or pyrolysis has found extensive application with polymers since the first examination of an externally prepared methacrylate pyrosylsate by Davison and his coworkers in 1954 [8]. In situ pyrolysis was soon adopted and the technique has been the subject of a number of monographs [9-14]. Pyrolysis with a few exceptions does not provide quantitative results but is an extremely powerful tool particularly in association with mass spectrometry for qualitative analysis and mechanistic studies. Thermal analysis is applicable to both condensation and addition polymers and provides information concerning the chemical composition and polymer structure.

Chemical cleavage has in recent years been extended by the use of vigorous chemical reaction both in situ with gas chromatographic detection [15] of volatile reaction products and externally [16] with the examination of the reaction products or their derivatives by a variety of chromatographic and spectroscopic techniques.

A variety of pyrolysis that has been recently introduced by Challinor [17] effectively combines hydrolysis and vigorous chemical reaction. Pyrolytic methylation is conducted in the presence of a strong methylating agent such that reaction products which are of low volatility react simultaneously in the system to form volatile derivatives thus facilitating detection.

In all of these techniques the sample size is small although orders of magnitudes greater than required for mass spectrometric detection.

This work indicates very briefly the scope of polymer pyrolysis, the necessary parameters to be controlled and includes some recent advances in polymer pyrolysis with a detailed treatment of the application of chemical degradation to the identification of polymers.
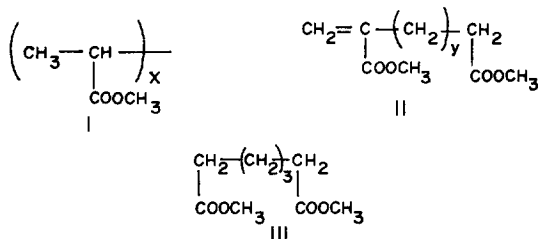
2. Pyrolysis

The major works previously mentioned show that almost every material including most polymers have been subjected to pyrolysis.

The early work on pyrolysis used a large sample, in some reports described as half as big as a pea, resulting in poor heat transfer and the production of non-reproducible results. It has long been recognized that small samples, typically less than 1 mg, good heat transfer and rapid heating of the pyrolysis element are essential in achieving reproducibility.

Improvements in separation with the general use of capillary columns and improved detection with enhanced mass spectrometry and the use of Fourier transform infra red detection have become widely accepted. With the achievement of reproducible results the applications of pyrolysis have become more sophisticated.

Microstructure determination is an area of importance and advances may be illustrated by a recent review by Tsuge and Ohtana [18] entitled " Microstructure of olefins". These are an extensively used group of synthetic polymers and structural characterization has been carried out most extensively by spectroscopic means such as ^{1}H NMR, ^{13}C NMR and FT-IR. As an alternative, in systems such as olefins which produce unsaturated degradation products, pyrolysis and hydrogenation prior to gas chromatography provides a powerful tool for microstructure determination. Pyrolysis–GC has been applied to the rapid estimation of short-chain branching in low density polyethylene, stereoregularity differences and chemical inversion of the monomer units in polypropylene and the study of sequence distributions in copolymers of ethylene and propylene.
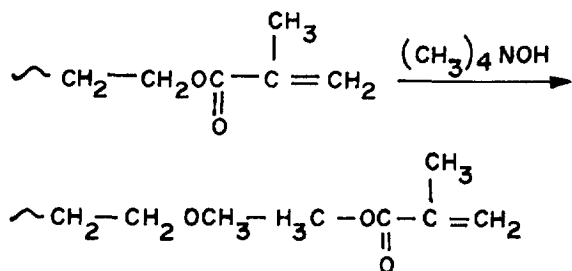
Mechanistic studies may be illustrated by the pyrolysis of the polyalkyl acrylate where unlike the polyalkyl methacrylate little monomer is produced. Rather a large variety of saturated and unsaturated homologous oligomers are produced [19,20], with polymethylacrylate (I), unsaturated (II) and saturated oligomers (III) resulting, while some analysis of tetramers was possible:

$$\left(CH_3-CH \right)_x \atop \qquad \underset{COOCH_3}{|} \qquad \underset{I}{}$$

$$CH_2= C-\left(CH_2\right)_y CH_2 \atop \underset{COOCH_3}{|} \quad \underset{COOCH_3}{|} \atop II$$

$$CH_2-\left(CH_2\right)_3 CH_2 \atop \underset{COOCH_3}{|} \quad \underset{COOCH_3}{|} \atop III$$

With improved chromatography ethyl acrylate–butyl methacrylate and ethyl acrylate–styrene–ethylmethacrylate terpolymers have recently been studied by Shuncong, Ohtani and Tsuge [21]. On pyrolysis products up to pentamers, were almost completely separated. Analysis of these higher oligomer is likely using pyrolysis and liquid chromatography. The hydrolysate being dissolved in a solution of a radical scavenger such as TEMPO (2,2,6,6-tetramethylpiperidine) which is then separated by liquid chromatography prior to mass spectrometry. While addition of the scavenger to the fragments will occur the addition would be expected to be apparent in the spectra [22].

With the pyrolysis of copolymers etc., oligomeric fragments containing combination products from the individual monomers exist. These are of value in the analysis of complex polymers as they are commonly used as multiple markers showing the presence of a particular monomer.

Pyrolysis has been used for the determination of end groups in polymer systems. Methacrylate end groups in polystyrene samples were determined by reaction with tetramethylammonium hydroxide where methyl methacrylate was split out and determined:

$$\sim CH_2-CH_2OC-C=CH_2 \xrightarrow{(CH_3)_4 NOH} \atop \underset{O}{\overset{CH_3}{\underset{||}{|}}}$$

$$\sim CH_2-CH_2\ OCH_3- H_3C-OC-C=CH_2 \atop \underset{O}{\overset{CH_3}{\underset{||}{|}}}$$

The polystyrene samples were prepared by polymerization using *sec.*- or *n*-butyl lithium as initiator. The main pyrolysate product was styrene monomer (80%) along with a considerable amount of dimers

and trimers [23]. In addition various minor fragments were produced, among which those derived from the butyl end groups were clearly distinguished.

There are several advantages of pyrolysis based techniques. Firstly, sample preparation is negligible while the time for analyses is relatively short in comparison to some other instrumental techniques. The sample size required for analysis is small making the technique suitable for forensic purposes.

The necessary size of the sample has been studied by Wheals [24] who reported that samples of lug may be used for forensic casework. The requirements for chromatography are low, less than 1 μl of a dilute solution (1%) being adequate for gas chromatographic examination. In association with mass spectrometry the sample requirement is much lower. Message [25] in 1984 indicated that with modern instrumentation the identity of compounds in admixture may be determined at 10^{-10} g/mole level. Leclercq et al. [26] have shown that identifiable mass spectra are produced with 40–60 pg of sample. Pyrolysis gas chromatographic–mass spectrometric studies of polyacrylic esters [19] carried out a decade ago used 800 ng (0.8 μg) of sample to produce a range of compounds and spectra capable of interpretation for nearly 30 compounds.

3. Chemical degradation

Chemical degradation has long been applied to some addition polymers particularly alkyd resins [4] however such procedures were time-consuming and suffered from limited sensitivity. The introduction of chromatographic detection greatly enhanced the value of such procedures, the earliest example probably being a combined Ziesel-gas chromatographic method for the determination of the composition of methacrylate–ethyl acrylate copolymers by Haslam et al. [27] in 1958. The alkoxyl groups were first converted to the corresponding alkyl iodides with hydriodic acid in phenol solution, then the iodides were trapped and separated by gas chromatography. A subsequent procedure concerned a terepolymer which included butyl maleate [28].

Analysis of alkyd resins was carried out using alcoholic hydrolysis according to the ASTM procedure [29] but with the gravimetric determination of

the reaction products being replaced by chromatographic detection in 1962 [5].

Esposito and Swann at the US Army Coatings and Chemical Laboratory continued their work and provided several analytical schemes applied to alkyd resins using chemical degradation and gas chromatographic detection.

Other early work included the acid hydrolysis of polyurethanes by Schroder [30] in 1962 and methoxy groups in cellulose by Neely and coworkers [31], the degradation of polyethers by Nadeau and Williams [32], acidic degradation of polysiloxanes by Heylmum and Piloula [33] in 1964 and acidic hydrolysis of linear polyamides by Anton [34] in 1968.

The work of Siggia and his many coworkers developed the prechromatographic reaction of many compounds including some polymers with the detection of volatile reaction products by gas chromatography. Haken and various coworkers extended the applicability of the developments of Siggia. The difference between the two group's approach was that the later work achieved complete analysis of all the reaction products. As the analyses were carried out by various techniques i.e. gas chromatography, liquid chromatography, size-exclusion chromatography and mass spectrometry the reactions were carried out in an external reactor.

Hydrolytic reactions using alkaline and acidic catalysts were used by both groups, although the work of Haken and coworkers also employed acidic cleavage of ether groups. Several polymers have been examined where the simultaneous application of both reactions was employed. In both cases qualitative analyses were most commonly reported although in both cases some quantitative analyses also have been reported.

The advantages of the external fusion are enumerated below.

(1) Fusion is more rapid, efficient and more readily controlled as the water necessary for the reaction remains in the reaction environment rather than tending to be preferentially swept in to the cold trap.

(2) Multiple fusions can be carried out in an external heater without restricting the use of a gas chromatograph, or, more important, restricting examination of that instrument.

(3) Materials that would ordinarily be retained in the reactor as soaps or low-volatile material can be examined after appropriate chemical reaction and/or derivatization.

(4) Hydrolytic degradation and cleavage of ether groups can be conducted simultaneously or separately.

(5) Other chromatographic or spectrometric techniques can be used as appropriate.

(6) All of the components of a polymer can be analyzed rather than simply those sufficiently volatile for direct gas chromatography.

Siggia and his coworkers [15] developed a procedure where vigorous hydrolytic cleavage was conducted in a reactor connected to the injector port of a gas chromatograph. The reactor was constructed from a now obsolete Perkin-Elmer 154-0825 furnace pyrolyser [35]. A small sample (1–10 mg) of polymer was fused with an excess (30 mole %) of a prefused mixture of commercial potassium hydroxide and 1–10% sodium acetate as flux in a small boat for introduction into the hydrolysis chamber. The potassium hydroxide approximates the hemihydrate and contains approximately 15% water. The reaction temperatures were within the range 200–350°C and the reaction time 0.5–1.0 h after which reaction products amenable to gas chromatography were identified.

Cellulose esters were reacted with both acids and alkalis but only acid reaction liberated a volatile product. The reaction was conducted at 170°C for 0.5 h to produce acetic acid using crystalline orthophosphoric acid [36].

The polymer materials examined by Siggia and his coworkers are listed in Table 1 together with the reaction product identified and those remained in the reaction.

The quantitative nature of both acid and alkaline fusion reactions of condensation polymers has been reported [45] and several classes of the polymers considered by Siggia and his coworkers have been conducted on a quantitative basis. A variety of esters were quantitatively cleaved by alkali fusion at temperatures between 280°C and 320° for 0.1–1.0 h. The recovery of the corresponding alcohols is shown in Table 2. Schleuter and Siggia [42] have reported the analysis of low-molecular-mass imides, polyamide, polyimides and poly (amide–imides) by alkali fusion

Table 1
Polymer materials examined by Siggia and his coworkers

Material	Product	Unidentified product of reaction	Reference
Phthalate esters	Corresponding alcohol	Alkali metal salt of acid	[15]
Polymethacrylate esters	Corresponding alcohol	Alkali metal salt of acid	[15]
Poly-chloracrylate	Corresponding alcohol	Alkali metal salt of acid	[15]
Nylon 66	Diamine	Alkali metal salt of acid	[37]
Nylon 610	Diamine	Alkali metal salt of acid	[37]
Polyacrylamide	Ammonia	[a]	[37]
Polyacrylonitrile	Ammonia	[a]	[37]
Cellulose esters	Corresponding acid	[a]	[38]
Polysiloxanes	Aliphatic or aromatic hydrocarbon	[a]	[39,40]
Polyvinyl esters	Corresponding acid	[a]	[41]
Polyamide	Diamine	Alkali metal salt	[42]
Polyimides	Diamine	Alkali metal salt	[42]
Poly(amide–imides)	Diamine	Alkali metal salt	[42]
Polyurethane esters	Diamine	Alkali metal salt	[43]
Polycarboranesiloxanes	Amine and diamine	Nil	[44]

[a] Pendant group cleaved from polymer chain.
[b] Fused with orthophosphoric acid.
[c] Fused with carbohydrazide.

Table 2
Analyses of esters and amino polymers by alkali fusion and recoveries of cleavage products

Material	Recovery (%)	Standard dev. (%)
Dialkylpthalate (C_1–C_4)	99.3	2.1
Polyalkyl methacrylate (C_1–C_3)	99.1	2.4
Polymethyl acrylate	100.7	4.6
Polyalkyl-chloroacrylate (C_1–C_3)	100.5	4.3
Nylon 66	98.4	2.1
Nylon 610	99.9	3.8
Polyacrylamide	98.5	3.1
Polyacrylonitrile	98.5	1.4
Polyimide PI-1	98.3	—
Polyimide PI-2	90.6	—
Polyimide PI-3	97.6	—
Polyamide PA-1	100.7	—
Polyamide PA-2	95.9	—
Poly(amide–imide) PA 1-1	93.9	—
Poly(amide–imide) PA 1-2	95.1	—
Poly(amide–imide) PA 1-3	98.0	—

with monomeric imides. The recovery of ammonia or benzylamine varied between 98.1 and 100.9% with relative standard deviations between 0.5 and 1.1%. With polyimides, polyamide and poly(amide–imides) appropriate aromatic diamine was recovered on yield between 98.8 and 101.2%. Mixtures of the polymers were also examined with comparable recoveries.

A variety of commercially available dimethylsiloxane products were examined by Schleuter and Siggia [40] and despite some minor uncertainty concerning purity, good agreement was achieved with the stated composition of the industrial products. While the repeating siloxane units contain 40.5% methyl groups the average of the two different terminal units is 56.1%. Therefore in a low-molecular-mass polymer the end groups have a significant effect.

The dimethylsiloxane gum SE-30 with a molecular mass of approximately $1 \cdot 10^6$ has over 1300 repeating units and represents the closest available approximation to a dimethylpolysiloxane unit. The theoretical methyl content is 40.5% and the analytical results obtained by alkali fusion is 40.47±0.24%, representing a recovery of 99.8%. The percentage recoveries for other commercial dimethylpolysiloxanes are shown in Table 3. Alkali fusion was also carried out on 15 phenylmethylsiloxanes, 5 alkyl and aryl substituted siloxanes, 4 vinyl substituted siloxanes and various copolymers. Analytical results for the particular substituents were reported but the theoretical values of the product were unknown.

While alkaline fusion caused rapid degradation of nylons of the diacid–diamine type (nylon 66 and nylon 610) in the reactor of Frankoski and Siggia [15] the procedure is not applicable to mixtures of

the two types as the same product 1,6-diaminohexane results. Similarly nylons which are condensation products of ω-aminoalkanoic acid do not provide any volatile products.

By the introduction of external fusion and derivatization both diacids in a copolyamide were determined as the dimethyl esters. Similarly the ω-aminoalkanoate soap from the type of nylon was readily identified as the methyl aminoalkanate.

A sample of 100 mg of polymer [16] was mixed with 1 g of the fusion reagent used by Siggia and Frankoski [15] and sealed under reduced pressure in a 9 mm OD borosilicate tube. Four identical tubes were heated in a cylindrical block of stainless steel fitted with resistance heaters, the input being regulated to 300°C. The tubes were removed and cooled after 0.5 h of heating water was added and the diamine was extracted with n-butanol. The extract was concentrated and examined using gas chromatography. The aqueous solution was acidified to liberate the dicarboxylic acid which was esterified with boron trifluoride–methanol reagent and subjected to gas chromatography. The reaction sequence is shown in Fig. 1, the diamine (IV) as liberated by Frankoski and Siggia [15] and the dimethyl esters (V) as extended by Glading and Haken [16].

Since the development of this procedure a number of advances have occurred with a variety of fusion reactors used. The current reactor developed by the authors [46] allows the use of a small sample [47] which makes the technique essentially comparable with pyrolysis. It has become apparent since development that advances in derivatization techniques have occurred. The direct methylation of metal salts of fatty acids with boron trifluoride–methanol reaction has been reported by Rotzsche [48] as has the trimethylsilyl derivatization of potassium and sodium salts of monobasic, dibasic and tribasic organic acids

Table 3
Analytical results for commercial polymethylsiloxanes

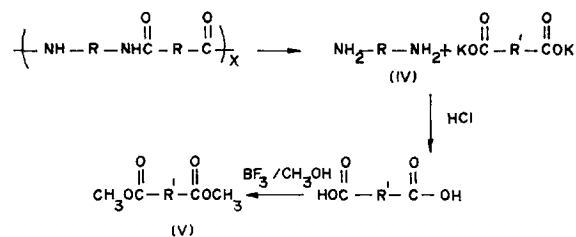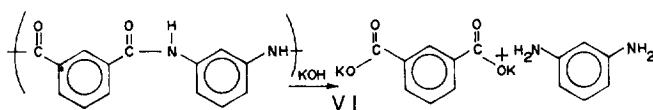| Sample	Number of repeating units	Theoretical methyl content	Result alkali fusion	Recovery (%)
SE-30	1300	40.55	40.47±0.24	99.80
SF96-20	4	45.65	39.74±0.30	87.05
SF96-50	45	41.96	40.74±0.16	97.09
SF96-100	85	40.93	40.75±0.06	99.60
DC200-100	85	40.93	41.15±0.35	100.50
GE V60000	1240	40.58	40.55±0.24	99.90

Fig. 1. Reaction scheme for polyamide analysis.

Scheme 1. Alkali fusion reaction of Nomex.

[49]. Both of these procedures have been used in subsequent fusion analysis and normally in eliminating formation of the free acid, an extraction step is unnecessary and losses are reduced.

The long-chain aliphatic or "dimer" polyamide are of considerably lower hydrolytic stability to the nylon samples and were readily cleaved by alkaline fusion. The low-molecular-mass diamines and carboxylic acids were determined by gas chromatography. The major acids present were the C_{36} "dimer" species together with the initial C_{18} species and the C_{54} "trimer" species. All these liberated acids were characterized by size-exclusion chromatography. This report [50–52] was the first example of techniques other gas chromatography being used with alkali fusion.

Polymers of considerable hydrolytic stability containing aryl group and with functionality of 3 and 4 and incorporating imide groups have been subjected to alkali fusion. Certain of these polymers were studied earlier by Schlueter and Siggia [42].

The aramid fibers are of considerable thermal and hydrolytic stability and the simplest materials are the polymers developed originally by Du Pont namely Nomex (poly m-phenyleneisophthalamide) (VI) (see Scheme 1) and Kevlar (poly p-phenyleneiso-phthalamide) (VII) (see Scheme 2). Both polymers are amenable to alkali fusion with complete cleavage in 0.5 h at 260°C [53]. The three diamine isomers were readily separated on a dimethylpolysiloxane packed column. Only two of the dimethyl phthalates were separated on a packed column, the iso and tere – on a polar cyanosiloxane packed column [54]. All three of the isomeric phthalate diesters were readily separated on a non polar (SE-30) capillary
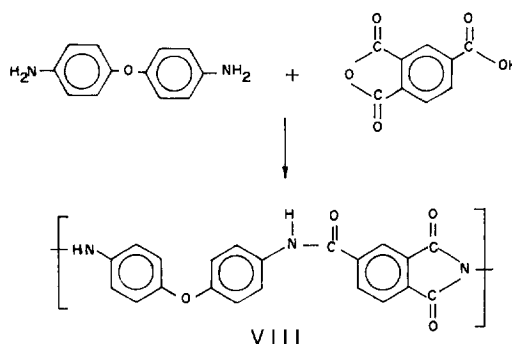


Scheme 3. Synthesis of poly(amide–imide).

column. The degradative analysis of both polymers is shown in Schemes 1 and 2.

The use of the trifunctional acid, trimellitic anhydride (1,2,4-benzene tricarboxylic acid) leads to the formation of poly (amide–imides) (VIII) (see Scheme 3). The Amoco Al polymers are aromatic homopolymers of this type. Two basic polymers are involved, designated as Al-10 and Al-11 and 4,4′-methylenedianiline and m-phenylenediamine are the diamines used.

With increased functionality acids such as 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride), polyimides are produced through poly-condensation. The Du Pont polymers Vespel and Kapton (IX) (see Scheme 4) are the condensation products with 4,4′-diaminodiphenyl ether.

The tetramethyl ester was most successfully identified by HPLC using a Bondapak C_{18} column with elution using $CH_3OH–H_2O$ (65:35, v/v), the other esters and amines or their derivatives were readily separated using gas chromatography [55].

A series of four high modulus fibers developed by
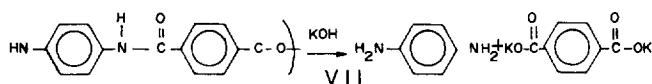
Scheme 2. Alkali fusion reaction of Kevlar.
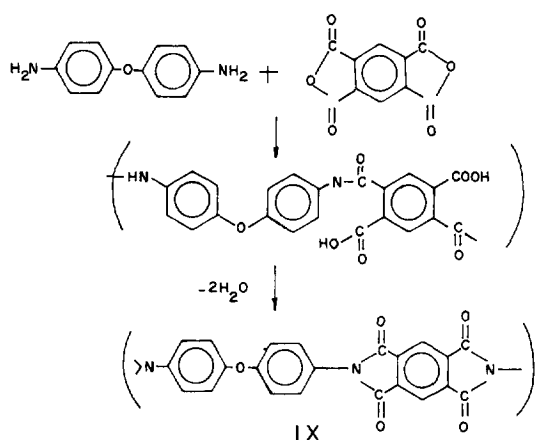
Scheme 4. Synthesis of Vespel and Kapton.

the Monsanto Company; the simplest polymer H-22 is polyterephthalhydrazide (X) while H-20 is an alternating polyhydrazide of oxalic and terephthalic acids (XI). The polymer H-202 is a copolymer produced from oxalic dihydrazide, terephthaldihydrazide (XII) and terephthaloylchloride while polymer PABH-TH-5000 is an ordered poly(amide–hydrazide) (XIII).

X

X I

X I I

X I I I
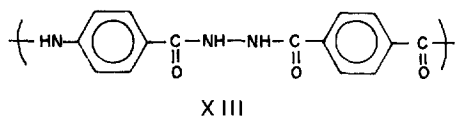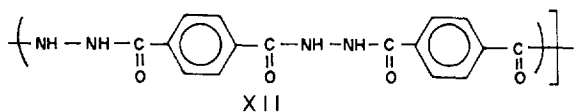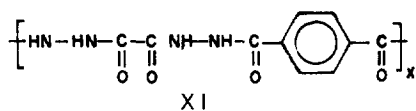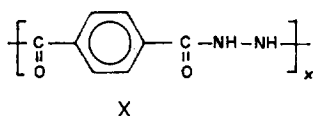
When the polyhydrazides were heated in the evacuated borosilicate tubes explosions frequently occurred due presumably to the presence of ammonia

from some trivial degradation of the hydrazine formed. The reactions were successfully conducted in longer borosilicate tubes which acted as an air condenser. The reaction temperature was (180°C) the reflux temperature of the mixture [56].

The hydrazine and the p-aminobenzoic acid were identified as the trifluoroacetamide derivatives while the oxalic acid and terephthalic acids were identified as the dimethyl esters. The analyses were carried out by gas or liquid chromatography as used previously.

Hydrolytic fusion using both acid and alkaline catalysts has been applied to the analysis of many types of polyurethanes. Acidic ether cleavage of polyether-based polyurethanes has also been reported. The major polyurethanes are the polyethers and polyester-based materials, both types have been subjected to analysis by chemical degradation using alkaline [57,58] and acid [59,60] conditions.

With the polyether materials and alkali fusion [57] a large sample of 500 mg, was used to allow recovery of the polyethers for subsequent, chemical analysis, size-exclusion chromatography and infrared spectrometry. With alkaline reaction of polyester-based urethanes the sample size was 200 mg [58] although with subsequent developments a sample reduced by about two orders of magnitude has been used [47].

The fusion reactions were carried out at 250°C for 1 h. The cooled contents of the reaction of the polyether urethane were dissolved in dichloromethane and diamine hydrochlorides and corresponding acids formed. The diamines were liberated on addition of alkali and extracted for gas chromatography of the free diamines or reacted with trifluoroacetic anhydride to from the trifluoroacetamide derivative. The polyether was recovered from the dichloromethane solution for examination.

The polyether may be cleaved chemically using an equimolar mixture of anhydrides of carboxylic and sulphonic acids, a mixture of anhydrides of acetic and p-toluenesulphonic acids as proposed by Karger and Mazur [61–63] being used. The recovered polyether was refluxed at 125°C for 2 h with 7.5 g of the mixed anhydride reagent, while the reagent is a strong acetylating agent some monoacetylated ethers were formed. The acetylation proceeded essentially to completion in the presence of 2.5% 1-methyl imidazole [59].

With the polyester-based urethanes [58] the cooled reaction products were dissolved in water and the diamines corresponding to the isocyanate used and diamine chain extenders extracted with dichloromethane. The aqueous extract was slightly acidified and the diacids extracted with dichloromethane for conversion to the dimethyl esters.

The remaining aqueous solution was rendered alkaline and the polyols extracted by prolonged liquid–liquid extraction with diethyl ether prior to gas chromatography [58]. The synthesis and chemical degradation products of polyether- and polyester-based urethanes is shown in Fig. 2 and Fig. 3.

With glycerol, pentaerythritol and other highly water soluble polyols prolonged extraction is not applicable. An alternative procedure is trimethylsilylation of the fusion products with trimethylsilylimidazole (TMSI) in dichloromethane and extraction of the individual functional classes as shown in Fig. 4. With the use of gas chromatography–mass spectrometry, the extraction steps shown can be reduced.

The acidic hydrolysis of polyether-based urethanes [59] used 100 mg of polymer refluxed with 15 g of the mixture anhydride regent for 6 h at 125°C. The cooled reaction products were dissolved in dichloromethane and then neutralised with sodium carbonate
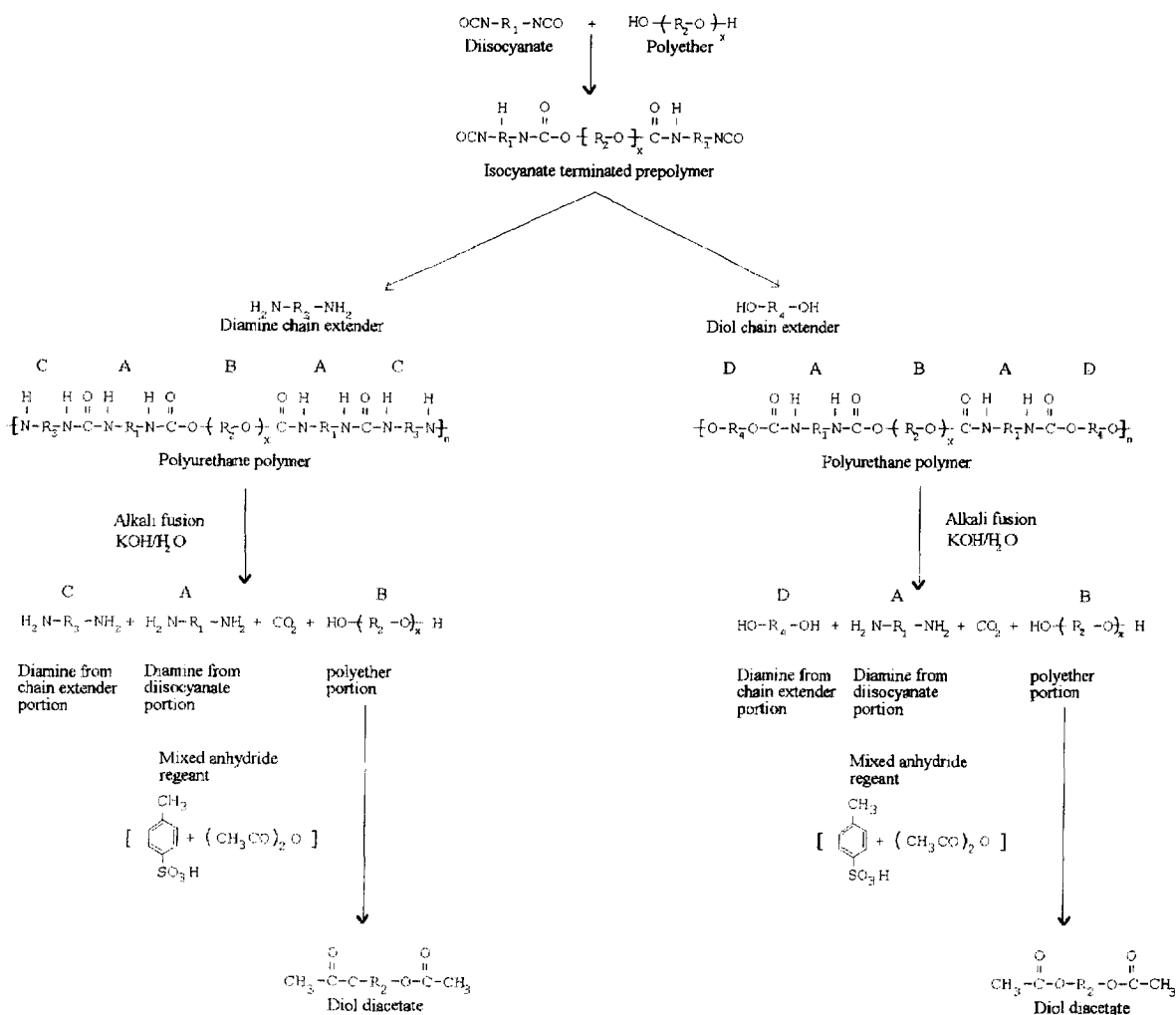

Fig. 2. Synthesis and degradation of polyether based polyurethanes.
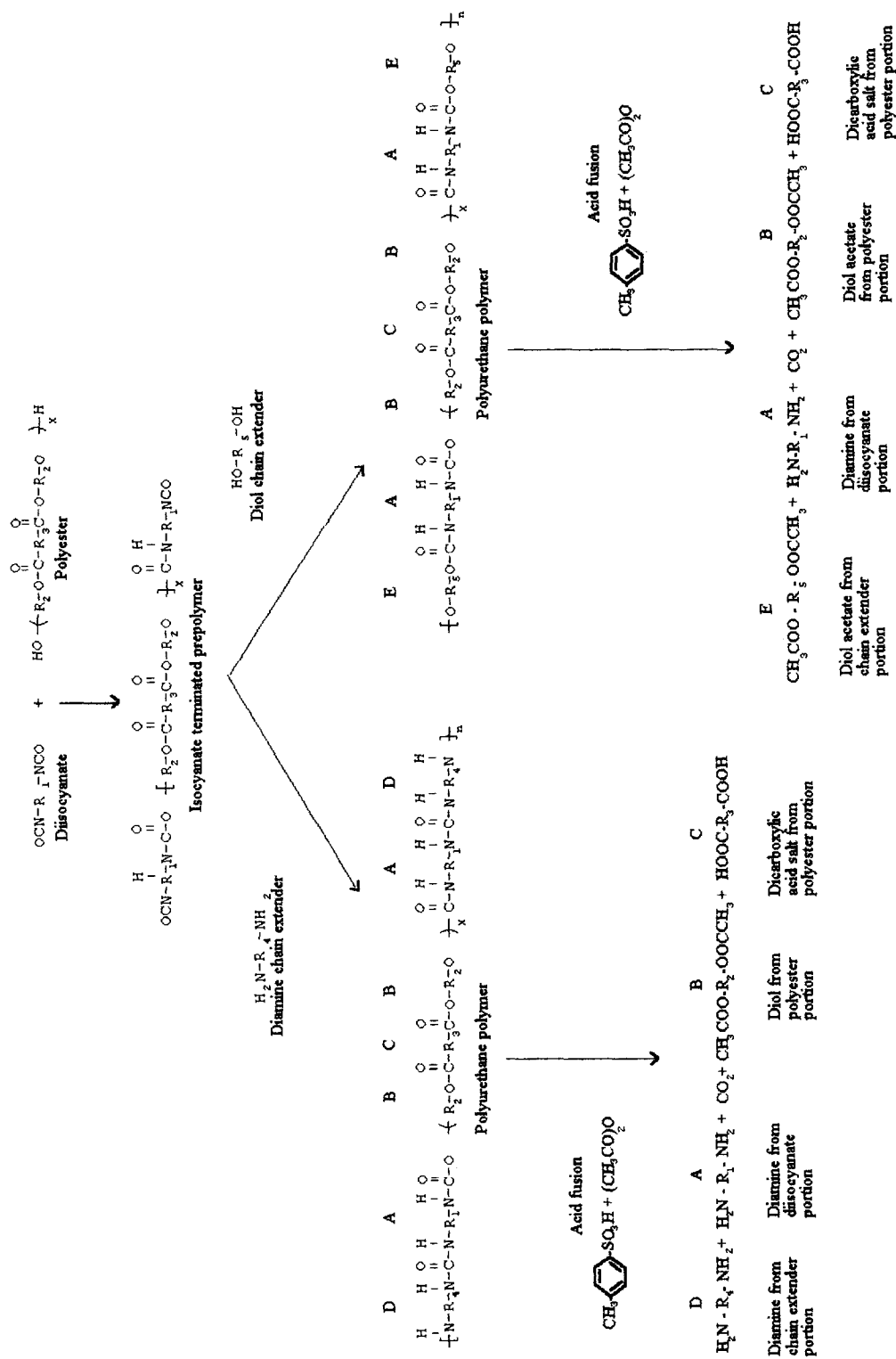
Fig. 3. Synthesis and degradation of polyester-based polyurethanes.

before extraction with dichloromethane. The organic layer was dried and the diamine hydrochlorides extracted with hydrochloric acid. After neutralisation the free diamines were extracted with dichloromethane and concentrated for gas chromatography.

The organic layer from the diamine extraction was acetylated with a mixture of acetic anhydride and 1-methylimidazole (90%, v/v). The reaction was conducted at room temperature for 10 min after which time the excess acetic anhydride was destroyed by the addition of water. The polyol acetates were extracted and concentrated for analysis. Polyester-based urethane both with amine chain extension (methylene bis-(O-chloraniline)) and diol chain extension (1,4-butanediol) have been subjected to acidic degradation [60]. The reaction proceeded much more rapidly than with polyether-based urethane and was complete in less than 3 h. The amine analysis was as for the polyether-based urethane. The organic layer remaining after the

removal of the diamines contain polyol acetates. The dicarboxylic acids were liberated from the aqueous sodium carbonate solution by acidification. The acids were extracted using dichloromethane and esterified for gas chromatography.

Commercially available oligomeric polyisocyanates are extensively used in both resins and elastomers. The products vary in molecular mass and molecular mass distribution while the isocyanate functionality varies between 2 and 4.
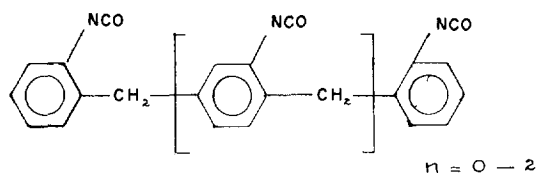
Oligomeric polyamines corresponding the oligomeric isocyanates are determined by HPLC on μPorasil (10 μm) using n-hexane–isopropanol (60:40, v/v) as eluent [64].

The analysis of four polyurethane elastomers used in medicine based on hydroxyl-terminated poly-(tetramethylene glycol), formulated on p,p'-diphenylmethane diisocyanate but with diamine and diol chain termination respectively; one diol terminated but with the saturated aliphatic analogue of MDI (hexamethylene diisocyanate) and one similarly MDI-based, but cross-linked with an acetoxysilane have been reported [65]. The analysis used procedures reported previously, with size exclusion chromatography being used to estimate the molecular mass of the polytetramethylene ether glycol used in all four products. The extent of the siloxane cross-linking was not determined although extension of the procedure in the light of analysis of silicone polyester resins [66] would allow this analysis.

The discoloration of aromatic polyurethanes is well known and acceptable materials employ saturated reactants. Glycol adipates tend to crystallize and become opaque on ageing and soft segment crystallization must be avoided with transparent polyurethanes. Polycaprolactone diols (CAPA) based on ε-caproclactone of molecular mass 2000 and a copolymer of polyhydrofuran (MW=1000) and ε-caprolactone diol 1000 (CAPA 720) 1,4-butane diol as chain extender and HMDI and MDI as diisocyanates were used. Alkaline fusion procedures
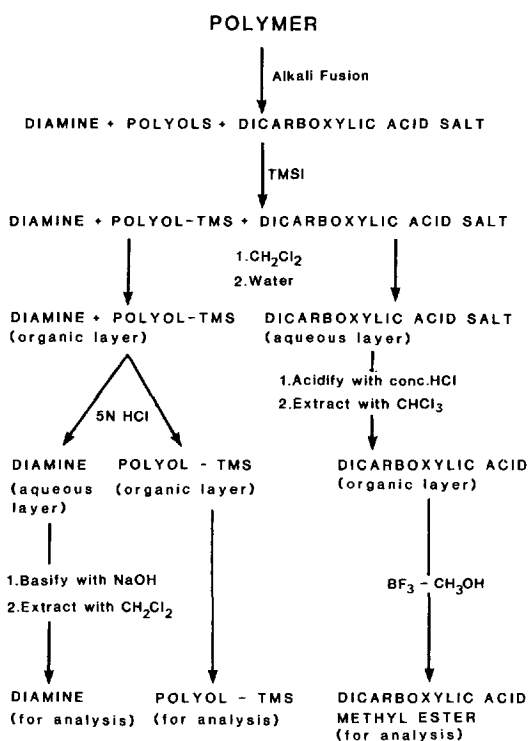

Fig. 4. Analytical scheme for polyester-based urethane foams containing tri- and tetra-functional alcohols.

largely as reported previously [59] produced the corresponding diamines and hydrocarboxylic acids. The polytetrahydrofurans from the CAPA 720 produced polyethers were determined using size exclusion chromatography using a series of μstyragel columns of various exclusion limits. The polyethers were subsequently degradated using the mixed anhydride reaction, to form 1,4-butanediol diacetate [67].

Two related urethane products have been subjected to alkaline degradation. The copolyamides of aliphatic dicarboxylic acids and arylene diisocyanates were developed by the UpJohn Co. [68]. These extremely chemical resistant polymers with high glass transition temperatures are suitable for injection molding to produce articles with good engineering properties. The polymers based on MDI and an aliphatic dicarboxylic acid fraction are readily cleaved by alkali reaction. Capillary gas chromatographic separation indicated a C_9 acid (Azelaic) as the major component together with C_{10}, C_{11}, C_{12} and C_{13} diacids. A C_{18} monocarboxylic acid used as a chain terminator was also detected. A urethane cross-linker (Novor 924) developed by the Malaysian Rubber Producers Research Association has been degraded by alkali fusion [69]. The diamine corresponding to toluene diisocyanate and *meta*-phenylene diamine, probably present as bis-maleimide, were the major products.

The degree of cross-linking and the number of secondary amine groups in polyurethane elastomers has been calculated from the determination of the tertiary amine groups by Kusz and coworkers [70]. A 10-mg sample of elastomer was dissolved in 0.5 ml tetrahydrofuran after which 200 μl of trifluoroacetic anhydride was added. The sealed reactants were heated with occasional shaking for 0.75 h at 60°C. The excess anhydride, liberated acid and the tetrahydrofuran were subsequently evaporated off in a stream of nitrogen at room temperature. An internal standard (20 mg *n*-decane) was added to the resulting solid product together with 20 mg aniline. The mixture was dissolved in tetrahydrofuran and allowed to stand at room temperature for 0.25 h. The liberated phenyltrifluoroacetamide was estimated quantitatively by gas chromatography on a non-polar packed column.

Simple aliphatic polyesters and aromatic types

based on orthophthalic acid are readily degraded by solution hydrolysis. Other polyesters based on isophthalic and terephthalic acid and liquid crystal polyesters are of greater hydrolytic stability. Like polyurethanes a wide variety of uncross-linked and cross-linked polyester systems have been subjected to prechromatographic chemical degradation. The earliest system studied [71] with alkali fusion were laminates of reactive polyesters used in fiberglass reinforced plastics which are cross-linked by reaction of ethylenic double bonds in the maleic or fumaric acids of the polyester with the styrene monomer. The analysis allowed determination of all the ester components except that portion of the dicarboxylic acid linked to the styrene. These laminate components are estimated together as unsaponifiable matter. With this analysis the silica from the fiberglass remained in solution as salts but following reports [66] with silicone alkyds, derivatives of the silica may be prepared and estimated simultaneously.

The vinyl esters incorporate properties and reactants of both polyester and epoxy resins and find use in reinforced laminates. The commonest vinyl ester was not amenable to acidic fusion as this was incomplete. However a two-stage process as has previously been employed with polyether-based urethanes allows cleavage of the terminal ester groups by alkaline fusion followed by acidic degradation of the repeating ether structure [72]. This resin is also used extensively in fiberglass laminates and analysis of these laminates is similar to FRP laminates. Other polyesters which are resistant to hydrolysis are polyethylene terephthalate and poly *n*-butylene terephthalate, both of which are readily amenable to alkaline fusion [71].

The analysis of polyester resins based on terephthalic acid, orthophthalic anhydride, adipic acid, ethylene glycol, neopentyl glycol and trimethylol propane has been reported by Qui et al. [73] using acidic degradation with phosphoric acid and acetic anhydride.

Their procedure used 100 mg of resin and 5 ml of phosphoric acid which was refluxed for 6–8 h. The reaction was continued for 1–2 h after adding 2.5 ml of acetic anhydride. Polyol acetates were formed together with free acids which were trimethylsilylated.

The acids used by these workers were selected

because earlier work by these investigators using the mixed anhydride of acetic acid and p-toluenesulphonic acid had produced two by-products, as shown below (XIV, XV), which were identified by mass spectrometry.

(XIV)   (XV)
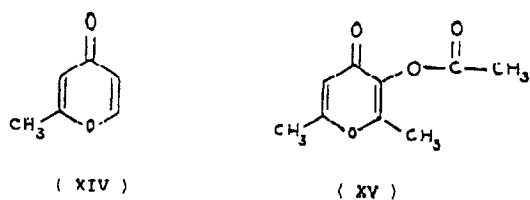
Alkyd resins containing unsaturated vegetable oil glyceride are cross linked by autoxidative polymerication. The ester components of such cross-linked alkyds are degraded by vigorous hydrolytic reactions. However the fatty acids of the vegetable oils are irreversibly cross-linked.

A smaller reactor than previously used was developed by Haken and Iddamalgoda [46] and the use of decreasing sample size has been evaluated using simple orthophthalic anhydride, maleic anhydride, propylene glycol polyester [47]. Samples of 20 mg to 2 mg were used in a series of 5 steps and ratios of phthalic anhydride/propylene glycol determined. The % recovery or the PA/PG ratio varied significantly with sample size. It is expected that an even smaller sample could be used if it could be handled.

The stainless steel reactor as shown in Fig. 5 consists of 2 parts, namely the reactor shell and the flange. The reactor shell is a square stainless steel block containing a cylindrical cavity 23 mm deep and 20 mm in diameter. The flange has an orifice (1 mm diameter) in the centre which allows entry to the cavity and combines with the main reactor cavity in the shell. The orifice is sealed with a cap fitted with a heat resistant silicone-rubber septum. A thin stainless steel gasket seals the cover and the reactor shell which are held together by four screws.

The qualitative analysis of the ester components of soya bean and coconut oil alkyds cross linked with butylated urea, butylated melamine or butylated benzoguanamide formaldehyde resins has been re-
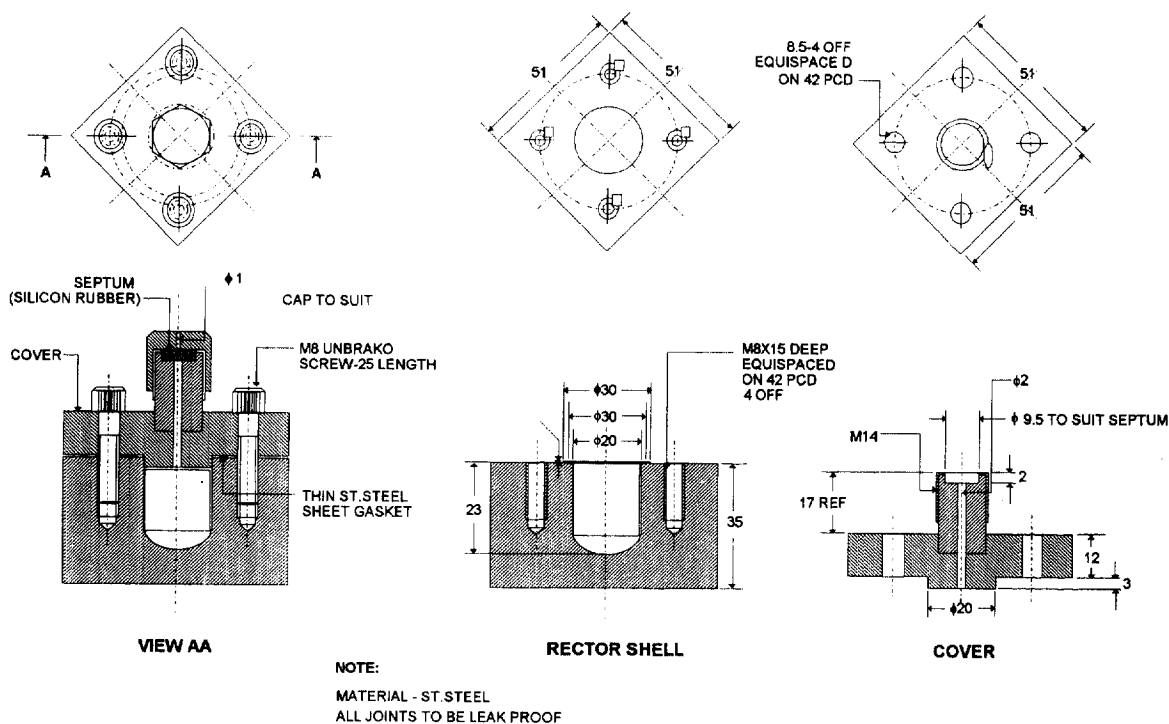

Fig. 5. Stainless steel fusion reactor.

ported [74]. Chemical cleavage of the ether links between the two resins and hydrolytic cleavage of the alkyd is achieved by acid reaction with equimolar p-toluenesulphonic acid–acetic anhydride, 85% orthophosphoric acid and acetic anhydride–acetic acid (acetic anhydride–water) (25:4, v/v) for 2, 4 and 3–4 h, respectively. It was subsequently established [75] that with trifluoroacetic anhydride–trifluorocetic acid (trifluoroacetic anhydride–water) (25:4, v/v) degradation of butylated aminoformaldehyde resin itself when used ad the cross-linker occurred with a reaction time of 2 h. The cleavage produced carbon dioxide and ammonium trifluoroacetate from the aminoplast and trifluoroacetates of the polyols are the free dicarboxylic acids from the alkyd.

The silicone modified polyester is currently the most important type. Vegetable oil modified and oil free types are available and both are normally cross-linked with aminoplast resins.

The saponification of silicone polyesters has been reported using tetramethylammonium hydroxide for 0.33 h at 100°C followed by trimethylsilylation of the liberated polyols [76]. The analysis of cross-linked systems was reported to give poor results.

The identification of both polyols and polyfuntional acids in silicone polyesters has been reported [66] using both vigorous alkaline and acid conditions. Separation and derivatization were essentially along the lines reported for polyurethanes [57–60]. The analysis of pendant alkyl and aryl groups on the co-condensed portion of the resins was effected with both alkaline and acid reaction. The reaction gas was withdrawn through a septum on the reactor and approximately 0.5 ml was injected into a Porapak Q column for gas–solid chromatographic analysis.

The analyses have generally been presented on a qualitative basis however the quantitative nature of the degradation reactions with the aggressive reagent has been studied [45]. The extraction steps introduce errors in the order of 2–5% and their minimization is desirable.

The analysis of the alkyl and aryl groups in siloxane intermediates is conducted without extraction steps by headspace analysis with an internal standard and quantitative results were obtained by Schleuter and Siggia [40].

In an attempt to minimize errors, a so-called

simultaneous determination of dicarboxylic acids and polyols was reported by Laurinatt and Hellwig [77]. The procedure was only applicable to readily hydrolyzed orthophthalic resins. Elimination of the extraction steps was achieved after hydrolysis with 1 M ethanolic alkali followed by acetylation to form derivatives of the liberated polyols.

The quantitative determination of dicarboxylic acids and polyols in silicone polyester resins [78] has been reported. The resin sample, i.e. 200 mg, was hydrolyzed with 5 ml acetic anhydride containing 15% water for 1 h. Acetic acid produced during the reaction was distilled off and the volume of liquid then reduced. On cooling boron trifluoride methanol reagent was added and the mixture refluxed for 1 h. The reaction mixture was concentrated under reduced pressure and the polyols acetylated with acetic anhydride containing 1% 1-methylimidazole. The esters formed were diluted with water and extracted with dichloromethane. After drying with anhydrous magnesium sulphate the residue was concentrated and examined by gas chromatography. The results of a series of analyses which were essentially quantitative are shown in Table 4.

The analytical procedure [78] reported above required that the silicon content be determined separately. This is readily accomplished with resins by ignition but in the presence of pigments the analysis is not possible. Alkali metal silicates have been estimated by gas chromatography as trimethylsilyl derivatives [66]. N-Trimethylsilylimidazole (TSIM) was used as for the alkali silicates but reacted only with the silicates and polyols. The use of N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) (1:1, v/v) allowed reaction with all three functional classes. The reaction scheme and a chromatogram showing the preparation are shown in Fig. 6 and Fig. 7 respectively.

A number of extremely chemical resistant liquid-crystal polyesters are finding increasing usage. The liquid-crystal copolyesters are categorized by their thermal performance into three classes.

Type I has the lowest thermal performance with heat-deflection temperature (HDT) values ranging from 82 to 216°C. Typical examples are copolyesters containing p-hydroxybenzoic acid and polyethylene terephthalate.

Table 4
Quantitative determination of uncross-linked and cross-linked silicone polyesters

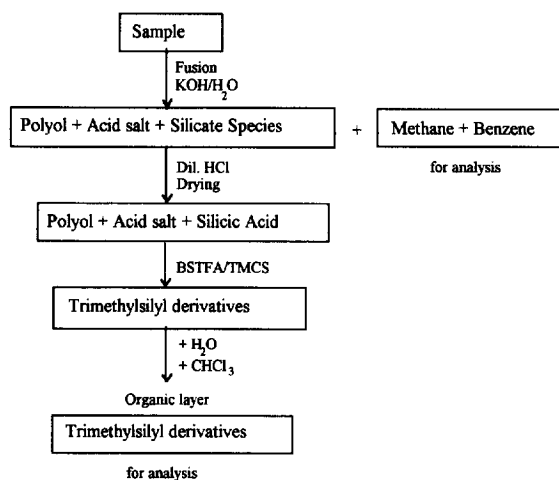| Component	Non cross-linked			Cross-linked	
	Theoretical analysis (wt%)	Expt. analysis (wt%)	Recovery (%)	Expt. analysis (wt%)	Recovery (%)
Adipic acid	21.4	20.2	95.3	19.8	91.5
Isophthalic acid	26.3	25.3	96.2	24.7	93.9
Neopentyl glycol	7.9	7.4	93.7	7.5	94.9
Trimethylol propane	44.4	42.3	95.3	42.1	94.8

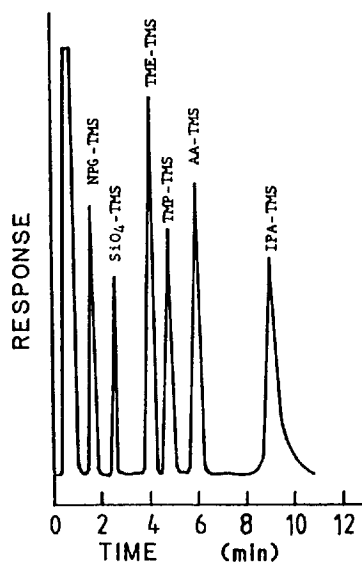Fig. 6. Analytical scheme for derivatization of silicone moiety.

Fig. 7. Chromatogram of trisilyl derivatives.

Type II polymers have HDT values from 171–214°C. Examples are products containing *p*-hydroxybenzoic acid and *p*-hydroxynaphthoic acid.

Type III polymers have HDT values from 260–354°C, terpolymer of *p*-hydroxybenzoic acid, terephthalic acid and *p,p'*-biphenyl is an example.

Analysis of these polymers using alkaline fusion has been reported [79]. Hydrolytic cleavage proceeded by a heterogenous reaction, complete reaction being indicated by solution of the sample. The reaction is facilitated when the samples are finely divided and pulverization was achieved using a Frisch Mill at reduced temperature. Milling at room temperature resulted in a rapid temperature build up with some melting and agglomeration of some samples. The heating was eliminated by mixing the sample with liquid nitrogen and gradually transferring the mixture into the operating Frisch Mill. The fusion was carried out at 250°C for 1 h. Esterification of the cooled reaction product was carried out directly. The methyl esters of the acids were extracted with dichloromethane. The fusion products were then acetylated using trifluoroacetic anhydride and the analysis were conducted using HPLC. The results were subsequently confirmed by gas chromatography–mass spectrometry.

An alternative analysis using chemical reaction of the same polymers has been reported by Ohtana et al. [80] and Satoh [81] using pyrolysis gas chromatography in association with pyrolytic methylation using tetrammonium hydroxide as extensively developed by Challinor [17].

Simple low-molecular-mass aromatic epoxy resins based on bisphenol A are readily cleaved by acidic reaction [82]. Bisphenol A glycidyl ether resin (Epon 828) which approximates the monomer and Epon 1001 where the number of repeat units approximates

two are readily degraded but the higher-molecular-mass resins are not cleaved.

The replacement of bisphenol A with bisphenol F where the central group is less hindered would be expected to facilitate cleavage. The epoxy resins studied were Epon 828, Epon 884, Epon 1001, Epon 1007 and Epon 1009 with repeating units of the monomer of 0, 0.5, 2.0, 8.5 and 12.0 respectively. The resins were examined in the uncured state and also reacted with ethylamine as a simple model compound, also 1,6-diaminohexane, 1,12-diamino-dodecane, triethylamine tetramine, tetraethylene pentamine, Versamid 125 and Versamid 140 (the condensation products of dimerised vegetable fatty acids and polyalkylene polyamines).

Epon 828 ethylamine adducts were amenable to acid cleavage products; the reaction of Epon 828 with the other simple amines produced products of which only that using 1,12-diaminododecane was cleaved by acid reaction for 16 h with p-toluenesul-phonic–acetic anhydride mixture. The very limited reactivity of the epoxy resins and the cured systems is attributed to shielding of the amenable groups due to the structure of the bisphenol A and the network formed by the amines.

Hydrolytic cleavage [83] has been applied using alkaline fusion for the analysis of a bisphenol A polycarbonate–dimethylpolysiloxane block copolymer.

While polyolefinic sulphones are readily cleaved by alkali reaction [84] to form the corresponding diols, the aromatic polysulphones are very much less reactive. The liberated sulphur dioxide is not suitable for determination as some reaction occurs with potassium hydroxide to form potassium hydrogensul-phite with aliphatic polysulphones. Reaction at 200°C for 1 h caused degradation although with aromatic polymers, temperatures to 400°C with extended reaction periods did not produce complete degradation.

A considerable number of the available condensation polymers which are theoretically capable of degradation are amenable to reaction with the agencies available.

4. Pyrolytic methylation

The term pyrolytic methylation was devised by

Kossa et al. in 1979 where the co-injection of tetramethylammonium hydroxide (TMAH) with free carboxylic acids and phenols into the injection port resulted in the formation of methyl derivatives [85–87]. This procedure was extended by Challinor [17] who conducted simultaneous pyrolysis and alkylation (SPM) by the use of the derivatising reagents, tetramethylammonium hydroxide or tetrabutylam-monium hydroxide with the polymer in the pyrolyser. Typically a 5-μg polymer sample and 2 μl of the derivatising agent was subjected to Curie point pyrolysis at 770°C. Separation of the reaction products was conducted by capillary column gas chromatography with confirmation by gas chromatography–mass spectrometry. The procedure was demonstrated with many polymer materials experienced in forensic situations. The characterization of polymers using pyrolysis in association with organic halides was reviewed by Ohtani and his coworkers in 1992 [88].

The analysis of in-situ methylated microbial fatty acids in association with pyrolysis was described by Holzer and coworkers [89]. Typically 1–5 mg of cells was scraped from an agar plate and suspended in 500 μl water. Approximately 5 μl of the suspension was transferred to a Curie point wire and 10 μl of 1% methanolic TMAH added. The methanol free wire was pyrolised at 510°C and the fatty esters identified by mass spectrometry.

A similar analysis for the rapid profiling of cellular fatty acids in whole bacterial cells has been reported by Dworzanski and coworkers [90]. Microgram amounts of bacterial cells were directly applied to a ferromagnetic wire and covered with a single drop of a methanolic solution of tetramethylam-monium hydroxide. After air drying Curie point pyrolysis was carried out and the fatty acid methyl esters were identified.

Pyrolysis and methylation of alkyd resins produced methyl esters of the polybasic acids and methyl ethers of the polyhydric alcohols. A soya bean oil pentaerythritol–orthophthalic alkyd resin produced C_8–C_{16} methyl alkanoates, tri- and tetra-methyl ethers of pentaerythritol, dimethyl ortho-phthalate and methyl benzoate, from benzoic acid used as a chain length regulator, cyclopentanone from scission of the C–O bonds of the adipic acid, dimethyl isophthalate and methyl benzoate. The fibre polyester polyethylene terephthalate produced benzene, a degradation product obtained on pyrolysis,

dimethyl terephthalate and methyl benzoate. A product indicative of the ethylene portion of the polymer was not observed [17].

Comparison of the pyrolysis residues subjected to SPM, of bisphenol A-epichlorohydrin condensate showed that the former produced three products, phenol, isopropenyl phenol and bisphenol A while the latter produced the first two products, the monomethyl ethers of all three products and the diether of bisphenol A. Pyrolysis butylation (SPB) was indicated for low-molecular-mass products and was demonstrated with vinyl acetate containing products where the acetic acid was observed as n-butylacetate. A disadvantage of the reaction was the appearance of by-products i.e. n-butanol and tributylamine. Pyrolytic butylation was also demonstrated by the formation of n-butylmethacrylate from a methacrylic acid copolymer, n-butylacetate and n-butylbutyrate from cellulose acetate butyrate and n-butyl cyanoacrylate from a cyanoacrylate adhesive [17].

The partial structure determination of alkyd resins has been reported [91]. In addition to the identification of the methyl esters of the carboxylic acids and the methyl ethers of the polyhydric alcohols, the drying oil type degree of cure and oil length can be estimated. Modifications with rosin and epoxy resins could be established. Glycerol and pentaerythritol are the most commonly used polyhydric alcohols in alkyds and the tri- and dimethyl esters and tetra-, tri- and dimethyl ethers are formed respectively. All three isomeric dimethyl phthalates were readily separated on the low polarity capillary column used. A substantial peak due to dimethyl benzoate from benzoic acid was evident. This apparently is largely due to some decarboxylation of phthalic acid although a small amount of benzoic acid may be added as a chain regulator.

Alkyds rich in linoleic, linolenic, marine oils and saturated oils are readily characterized before autoxidative polymerization. However, after drying, little remains of the linolenic acid and a multiplicity of unsaturated fish oil acids could be found. The relative proportion of unsaturated to saturated fatty acid methyl esters gives an indication of the degree of cure or age of the alkyd resin. A linseed oil–pentaerythritol–orthophthalic acid alkyd was studied over 5 months. The results show that

(a) before polymerization the ratio of 9,12,15-octadecatrienoic acid (linolenic acid) to palmitic acid

is significant but after two days polymerization, the linolenic acid has been removed by cross-linking.

(b) After two weeks the ratio of oleic acid to stearic acid starts to slowly reduce with time. After four months the concentration of oleic acid has been reduced to approximately one third of its original concentration.

(c) Nonanedioic acid begins to appear in the reaction products after three days and increases to a maximum in one month.

The oil length of an alkyd is the percentage of fatty acid glyceride present in the total resin solids. An approximation of the oil length may be obtained by considering the ratio of products from the drying oils to the aromatic products from the phthalic acids. However, some decarboxylation occurs and the value of the estimate is reduced. Several modifiers in alkyd resins may be detected. Rosin is evident as methyl dehydroabietate and epoxy resin by the products earlier mentioned. The general scope of pyrolysis methylation reactions has been reported [92] with the examination of a wide range of oxygen containing materials susceptible to hydrolytic reactions.

Phenol formaldehyde resins on pyrolytic methylation, produced a variety of phenol ethers and are readily distinguishable from epoxy resins. Proteinaceous fibers, i.e. wool and silk, are readily differentiated and the different amino acid compositions are apparent. The latter products produced phenol methylether and o-cresol methylether. Both products are attributed to hydrolysis and methylation of tyrosine, a constituent of silk.

The examination of rosin-based resins has been extensively studied: the principal acid, abietic acid contains both a conjugated diene and a carboxylic acid group both of which are readily reacted on a commercial scale. Wood rosins contain a high proportion of diterpentine and are conveniently characterized by simultaneous pyrolytic methylation [93,94]. Wood rosins are mixtures of widely varying composition, however the major acids are common.

Reaction (SPM) profiles of five wood rosin peaks are identified as methyl esters of (1) fumaric acid (2) Sandaraco–fumaric acid (3) pallstric acid (4) isofumaric acid (5) dehydroabietic acid (6) abietic acid and (7) neo-abietic acid.

para-Substituted alkylphenol resins alone or modified with rosin or its esters have produced characteristic fragments when subjected to pyrolysis

and methylation. The principal alkylphenols used are tertiary butylphenol and *para*-nonylphenol. These two phenols produce traces of the free phenols, methyl and dimethyl substituted phenols while penta-erythritol rosin esters showed peaks due to the methyl esters of dehydroabietic and abietic acids, to the tetra- and trimethyl ethers of pentaerythritol and dimethyl fumarate from maleic anhydride or fumaric acid present.

The mechanism of the reaction has been discussed by de Leeuw and Vaas [95] and Challinor [96] who has reported that the evidence indicated reaction by the following mechanisms:

The polymer when intimately mixed with tetra-methylammonium hydroxide and heated to tempera-tures above 400°C, undergoes hydrolysis by the strongly basic reagent, forming salts of the hydro-lyzed products which undergo thermal fragmentation to the methyl derivatives.

It was acknowledged that the term simultaneous pyrolysis methylation (SPM) was something of a misnomer and the process is better described as thermally assisted hydrolysis and methylation (THM).

The procedure of hydrolysis and methylation has been used by Ishida et al. [97] for the determination of rosin sizing agents on paper. The methyl esters of the rosin adduct consisting of rosin acids and fumaric acid were determined with about 1% relative stan-dard deviation. A polyester resin based on ethylene glycol, isophthalic and terephthalic acids was ana-lyzed using pyrolysis and methylation by Nishe and Okai [98].

Liquid crystalline polyesters produced from *p*-hydroxybenzoic acid and 2-hydroxy-6-naphthoic acid were subjected to pyrolysis and methylation. How-ever only partial reaction occurred. Quantitative results were achieved by introducing the methylating reagent into the pyrolyser during the hydrolysis. Similar liquid crystal polyesters based on 4-hydroxy-benzoic acid, terephthalic acid and 4,4-biphenol were also examined. Almost quantitative results were obtained using a 50-μg sample with pyrolysis at 400°C in the presence of 1 μl 25% tetramethylam-monium hydroxide. Polyesters containing 2-hydroxy-6-naphthoic acid were also examined [99,100].

Polyphenolic compounds in red wine [101] were separated by column chromatography into 3 frac-tions: (a) monomers, (b) red polymers, and (c) yellow and brown polymers (tannins). The polymers were subjected to pyrolysis including SPM. Pyrograms showing diagnostic markers for flavanoids and phen-olic acids were reported.

The characterization of various kinds of poly-carbonates has been reported by Ohtani et al. [102]. Various phenolic compounds were observed which were formed by C–C bond cleavage as well as by cleavage of carbonate linkages. The main chain almost quantitatively degraded through reactive pyrolysis at carbonate linkages to yield the dimethyl derivatives of the constituents.

The chemical characterization of the heartwood lignocellulose from selected softwoods has recently been reported by Challinor [103]. The composition of lignin-derived guaicyl and syringyl dimethoxy-and trimethoxybenzenoid compounds could be easily used to distinguish softwoods from hardwoods and, in particular gymnosperms.

References

[1] S. Mori in J. Janca (Editor), Steric Exclusion Liquid Chroma-tography of Polymers, Chromatographic Science Series, Marcel Dekker, NY, 1984, Vol. 25, Chapter 4.1.

[2] W.W. Yan, J.J. Kirkland and D.D. Bly, Modern Size Exclu-sion Liquid Chromatography, John Wiley and Son, NY, 1979.

[3] T. Provder (Editor), Chromatography of Polymers, ACS Symposium Series, Vol. 521, A.C.S, Washington, 1993.

[4] C.P.A. Kappelmeier, Chemical Analysis of Resin Based Coating Materials, Interscience, NY, 1959 and References therein.

[5] G.G. Esposito and M.H. Swan, Anal. Chem., 33 (1961) 1854.

[6] G.G. Esposito and M.H. Swan, Anal. Chem., 34 (1962) 1173.

[7] G.G. Esposito and M.H. Swan, Anal. Chem., 34 (1962) 1048.

[8] W.H.T. Davison, S. Slaney and A.L. Wragg, Chem. and Ind., London, 1961, p. 1356.

[9] G.M. Pramer, in P.E. Slade and L.T. Jenkins (Editors), Thermal Characterization Techniques, Marcel Dekker, NY, 1970.

[10] R.W. May, E.F. Pearson and D. Schothern, Pyrolysis Gas Chromatography, Analytical Science Monograph No. 3. Chem. Soc., London, 1977.

[11] V.G. Berezkin, V.R. Alishoyev and I.B. Nemirovskaya, Gas Chromatography of Polymers, Journal of Chromatography Library Vol. 10, Elsevier, Amsterdam, 1977.

[12] C.E.R. Jones and C.A. Cramers (Eds.), Analytical Pyrolysis, Elsevier, Amsterdam, 1977.

[13] S.A. Liebman and E.G. Levy (Eds.), Pyrolysis and GC in Polymer Analysis, Chromatographic Science Series. No. 29, Marcel Dekker, NY, 1984.

[14] T.P. Wampler (Ed.), Analytical Pyrolysis Handbook, Marcel Dekker, NY, 1995.

[15] S.P. Frankoski and S. Siggia, Anal. Chem., 44 (1972) 507.

[16] G.J. Glading and J.K. Haken, J. Chromatogr., 157 (1978) 404.

[17] J.M. Challinor, J. Anal. Appl. Pyrolysis, 16 (1989) 323.

[18] S. Tsuge and H. Ohtani in Reference 14, p. 77.

[19] J.K. Haken and L. Tan, J. Poly Sci. A Polymer Chem., 25 (1987) 1451.

[20] J.K. Haken and L. Tan, J. Poly Sci. A Polymer Chem., 26 (1988) 1315.

[21] M. Shumcong, H. Ohtani and S. Tsuge, J. Anal. Appl. Pyrolysis, 33 (1995) 181.

[22] T. Davis, Personal Communication, 1995.

[23] H. Ohtani, S. Ueda, Y. Tsukahera, C. Watanbe and S. Tsuge, J. Anal. Appl. Pyrolysis, 25 (1993) 1.

[24] B.B. Wheals, in E.R. Jones and C.A. Cramers (Eds.), Analytical Pyrolysis, Elsevier, Amsterdam, 1977.

[25] G.M. Message, Practical Aspects of Gas Chromatography Mass Spectrometry, Wiley-Interscience, New York, 1984.

[26] P.A. Leclercq, C.P.M. Schutjes and C.A. Cramer, in The Science of Chromatography, Elsevier, Amsterdam, 1985, p. 55.

[27] J. Haslam, J.B. Hamilton and A.R. Jeffs, Analyst, 83 (1958) 66.

[28] D.L. Miller, E.P. Samsel and I.G. Cobler, Anal. Chem., 33 (1961) 677.

[29] ASTM Specification D 531-1952, American Society for Testing and Materials, Philadelphia, PA, 1952.

[30] E. Schroder, Plaste Kautsch, 9 (1962) 121, 186.

[31] W.B. Neely, I. Noth and C.B. Roberts, Anal. Chem., 34 (1962) 1423.

[32] H.G. Nadeau and E.W. Williams, Anal. Chem., 36 (1964) 1345.

[33] G.W. Heylmum and J.E. Piloula, J. Gas Chromatography, 3 (1965) 266.

[34] A. Anton, Anal. Chem., 40 (1968) 1116.

[35] K. Ettre and P.F. Varadi, Anal. Chem., 35 (1963) 69.

[36] R.J. Williams and S. Siggia in L.R. Whitlock and S. Siggia, Sep. Pur. Methods, 3 (1974) 299.

[37] S.P. Frankoski and S. Siggia, Anal. Chem., 44 (1972) 2078.

[38] S. Siggia, L.R. Whitlock and J.C. Tao, Anal. Chem., 41 (1969) 1387.

[39] L.G. Sarto Jnr., Ph.D. Thesis, Univ. of Massachusetts, Amherst, 1982, (S. Siggia, Supervisor).

[40] D.D. Schleuter and S. Siggia, Anal. Chem., 49 (1977) 2343.

[41] R.J. Williams and S. Siggia, Anal. Chem., 49 (1977) 2337.

[42] D.D. Schleuter and S. Siggia, Anal. Chem., 49 (1977) 2349.

[43] D.G. Gibian, Ph.D. Thesis, Univ. of Massachusetts, Amherst, 1979, (S. Siggia, Supervisor)

[44] P.C. Rahn and S. Siggia, Anal. Chem., 45 (1973) 2336.

[45] J.K. Haken, J. Chromatogr., 406 (1987) 167.

[46] J.K. Haken and P. Iddamalgoda, J. Chromatogr., 600 (1992) 352.

[47] J.K. Haken and P. Iddamalgoda, Progress in Organic Coatings, 26 (1995) 101.

[48] H. Rotzsche, J. Chromatogr., 552 (1991) 281.

[49] L.-K. Ng and M. Hupe, J. Chromatogr., 637 (1993) 104.

[50] J.K. Haken and J.A. Obita, J. Oil and Colour Chem. Assoc., 63 (1980) 200.

[51] J.K. Haken and J.A. Obita, J. Chromatogr., 213 (1981) 55.

[52] J.K. Haken and J.A. Obita, J. Macromol Sci. (Chem.), A17 (1982) 203.

[53] J.K. Haken and J.A. Obita, J. Chromatogr., 244 (1982) 265.

[54] Anon Bulletin 762B Supelco Inc., Bellafonte, PA, 1976.

[55] J.K. Haken and J.A. Obita, J. Chromatogr., 244 (1982) 259.

[56] J.K. Haken and J.A. Obita, J. Chromatogr., 239 (1982) 377.

[57] P.A.D.T. Vimalasiri, J.K. Haken and R.P. Burford, J. Chromatogr., 319 (1985) 121.

[58] R.P. Burford, J.K. Haken and P.A.D.T. Vimalasiri, J. Chromatogr., 321 (1985) 295.

[59] P.A.D.T. Vimalasiri, J.K. Haken and R.P. Burford, J. Chromatogr., 355 (1986) 411.

[60] P.A.D.T. Vimalasiri, J.K. Haken and R.P. Burford, J. Chromatogr., 361 (1986) 231.

[61] M.H. Karger and Y. Mazur, J. Am. Chem. Soc., 90 (1968) 3878.

[62] M.H. Karger and Y. Mazur, J. Org. Chem., 36 (1971) 528.

[63] M.H. Karger and Y. Mazur, J. Org. Chem., 36 (1971) 532.

[64] P.A.D.T. Vimalasiri, R.P. Burford and J.K. Haken, J. Chromatogr., 351 (1986) 366.

[65] J.K. Haken, R.P. Burford and P.A.D.T. Vimalasiri, J. Chromatogr., 349 (1985) 347.

[66] J.K. Haken, N. Harahap and R.P. Burford, J. Chromatogr., 441 (1988) 207.

[67] J.K. Haken, P.A.D.T. Vimalasiri and R.P.Burford, J. Chromatogr., 399 (1987) 295.

[68] R.P. Burford, J.K. Haken and P.A.D.T. Vimalasiri, J. Chromatogr., 329 (1985) 132.

[69] R.P. Burford, J.K. Haken and J.A. Obita, J. Chromatogr., 266 (1983) 515.

[70] P. Kusz, H. Szewczyk, P. Krol and C.Z. Latocha, Kautsch. Gumme. Kunst., 41 (1988) 48.

[71] J.K. Haken and M.A. Rohanna, J. Chromatogr., 298 (1984) 263.

[72] J.K. Haken, N. Harahap and R.P. Burford, J. Coatings Technology, 62 (780) (1990) 109.

[73] W. Qui, S. Liu, F. Kanga and Z. Ni, Tuliao Gongye, 3 (1992) 44 and personal communications.

[74] J.K. Haken and M.R. Green, J. Chromatogr., 396 (1987) 121.

[75] J.K. Haken and M.R. Green, J. Chromatogr., 403 (1987) 145.

[76] J.M. McFadden and D.R. Scheung, J. Chromatogr. Sci., 22 (1984) 310.

[77] R. Laurinatt and J. Hellwig, Plaste Kautsch, 29 (1982) 710.

[78] J.K. Haken, N. Harahap and R.P. Burford, J. Chromatogr., 452 (1988) 37.

[79] J.K. Haken and P. Iddamalgoda, J. Appl. Polym. Sci., Polym. Symp., 52 (1993) 225.

[80] H. Ohtana, R. Fujii and S. Tsuge, J. High Resolut. Chromatogr., 14 (1991) 388.

[81] S. Satoh, Bunseki Kagaku, 41 (1992) 173.

[82] J.K. Haken and S. Koopetngarm, Chromatographia, 34 (1992) 276.

[83] J.K. Haken, N. Harahap and R.P. Burford, J. Chromatogr., 500 (1990) 367.

[84] J.K. Haken and M. Camamo, J. Chromatogr., 595 (1992) 283.

[85] W.C. Kossa, J. Maegee, S. Ramachandran and A.J. Walker, J. Chromatogr. Sci., 17 (1979) 177.

[86] S.J. Abraham and W.J. Criddle, J. Anal. Appl. Pyrol., 9 (1985) 53.

[87] L.D. Metcalfe and C.N. Wang, J. Chromatographic Sci., 19 (1981) 530.

[88] H. Ohtani and S. Tsuge, Kagaku (Kyoto), 47 (1992) 288.

[89] G. Holzer, T.F. Bourne and W. Bertsch, J. Chromatogr., 468 (1989) 181.

[90] J.P. Dworzanski, L. Berwald and H.L.C. Meuzalaar, Appl. Environ. Microbiol., 56 (1990) 1717.

[91] J.M. Challinor, J. Anal. Appl. Pyrol., 18 (1991) 233.

[92] J.M. Challinor, J. Anal. Appl. Pyrolysis, 20 (1991) 15.

[93] J.M. Challinor, J. Anal. Appl. Pyrolysis, 25 (1993) 349.

[94] J.M. Challinor, Proc. 12th Int. Assoc. Forensic Science, Adelaide, 1994.

[95] I.W. de Leeuw and M. Vaas, J. Anal. Appl. Pyrolysis, 26 (1993) 175.

[96] J.M. Challinor, J. Anal. Appl. Pyrolysis, 29 (1994) 243.

[97] Y. Ishida, H. Ohtani, T. Kato, S. Tsuge and T. Yano, Tappi J. 77 (1994) 177.

[98] M. Nishe and F. Okai, Japan Tokyo Koho J. P. 05, 322, 865 (93, 322, 865) (7.12.1993).

[99] S. Satoh, Bunseki Kaguku, 41 (1992) 173.

[100] H. Ohtani, R. Fujii and S. Tsuge, J. High Resolut. Chromatogr., 14 (1991) 388.

[101] G.G. Gallette and A. Asnton, Rapid Commun. Mass Spectrom., 7 (1993) 656.

[102] H. Ohtani, H. Ogasawara, S. Kawaguchi and S. Tsuge, H. Hatano, in H. Ohtani and T. Manai (Editors), International Symposium Chromatography 35th Anniv. Res. Group Liquid Chromatography, Japan, T. Hanai World Scientific, Singapore, 1995, p. 813.

[103] J. Challinor, J. Anal. Appl. Pyrolysis, 35 (1995) 93.