

Short Communication

Reactor for prechromatographic fusion reactions

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ABSTRACT

An improved design of a reactor for alkaline fusion as a preliminary to chromatographic analysis is described. The reactor allows the use of a significantly reduced sample size, minimizes leakages and facilitates the removal of the reaction products. The use of the reactor is demonstrated by the analysis of several polyester samples exhibiting increased hydrolytic stability.

INTRODUCTION

The prechromatographic degradation of many materials including some polymers using hydrolytic cleavage was developed by Siggia and co-workers [1-4] and was described as fusion reaction gas chromatography. The technique employed a device constructed from an obsolete furnace pyrolyser attached to the injection port of a gas chromatograph. The apparatus was a modification of a furnace pyrolyser [5] formerly marketed by Perkin-Elmer (Norwalk, CT, USA) (pyrolysis accessory 154-0825). For volatile degradation products a cold trap was inserted between the reactor and the chromatograph. This was immersed in liquid nitrogen during the reaction and then heated, with the contents being swept directly into the chromatograph.

Fusion reactions and chromatographic detection as pioneered by Siggia and co-workers was extended by Glading and Haken [6] with semi-microfusion conducted externally to the gas chromatograph with heating for 0.5 h at 360°C. Subsequently the

procedure with the associated work-up and derivatization has been applied to many condensation polymers possessing considerable hydrolytic stability, including polyamides [7], polyamides [8], polyurethanes [9] and polyesters [10], the polyesters having also been cross-linked using amine-formaldehyde resins [11].

The advantages of separate microfusion far outweigh those of *in situ* reaction and include the following: water necessary for the reaction remains in the reaction environment rather than tending to be preferentially swept from the reactor; the ability to conduct multiple fusions without restricting the use of the gas chromatograph or, more important, of restricting the examination to samples amenable to gas chromatography; the examination of materials normally retained in the reactor as potassium soaps or low-volatility compounds after appropriate chemical work-up and/or derivatization; the elimination of the presence of low-volatility compounds which gradually bleed or decompose into the system; the use of a diversity of chromatographic procedures, *i.e.*, gas chromatography-mass spectrometry, high-performance liquid chromatography and size-exclusion chromatography; the use of diethyl

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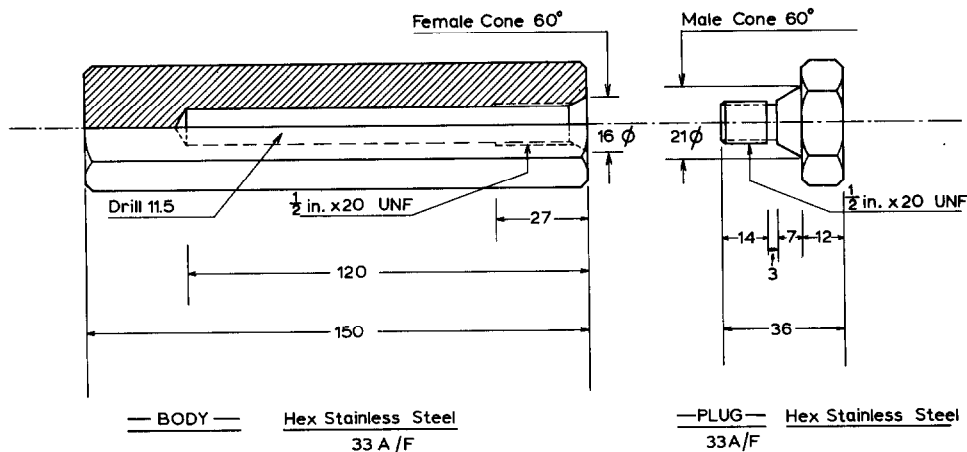


Fig. 1. Plan of stainless-steel pressure tube reactor. All dimensions in millimetres. \varnothing = Diameter.

ether cleavage in addition to hydrolysis to be carried out singly or simultaneously; and the analysis of the complete molecule rather than solely volatile cleavage products to be conducted.

The reactions were first conducted in glass pressure tubes [6] but some dissolution of silica occurred and with the determination of silica from siloxanes as an organic derivative the procedure involved interferences. The metal reactor first used consisted of a stainless-steel screw-capped pressure tube as shown in Fig. 1. The cavity in which the reaction was conducted was 120 mm \times 16 mm I.D. [12]. Limitations of the reactor included some difficulties in opening and sealing and preventing leakage during reaction. Owing to the relatively large volume of the reactor (24.0 cm³), a relatively large sample, *i.e.*, 200 mg, was used to minimize losses associated with the difficulties of removing the reactants from the reactor.

A smaller (shorter) version of the reactor shown in Fig. 1 was constructed but difficulties in preventing leakage during the reaction were greatly accentuated owing to the higher internal pressure. The diameter of the reactor was 3 mm with the total length of the cavity being 35 mm. This reactor was also unsatisfactory as it was virtually impossible to remove the melt and the finer thread of the sealing plug often could not be removed from the body.

The quantitative nature of analytical fusion reactions was demonstrated by Siggia and co-workers in

work with sulphonic acids [13], simple esters and polymeric esters [1], amides, urea and nitrile compounds [14] and polysiloxanes [3]. The initial work from this laboratory employing work-up of the potassium salts considered the quantitative examination of nylons [5] and subsequently quantitative studies of silicone polyesters [15] and cross-linked polyesters [16] were reported and the quantitative nature of the reaction was reviewed [17].

While the quantitative nature of the fusion reactions has been demonstrated, it has been shown [17] that the extraction steps in the work-up and derivatization steps introduce errors which may be as high as several percent. Recent studies [18] have eliminated or reduced the extraction steps and the losses have been reduced.

This paper reports the development of an alternative reactor which eliminates the problems previously experienced. Use of the reactor with a considerably reduced sample size, *i.e.*, 20 mg, is demonstrated with the degradation of two reactive polyesters and polyethylene terephthalate.

EXPERIMENTAL

Reactor

The stainless-steel reactor developed is shown in Fig. 2 and consists of two parts, namely the reactor shell and the flange. The reactor shell is a square stainless-steel block containing a cylindrical cavity

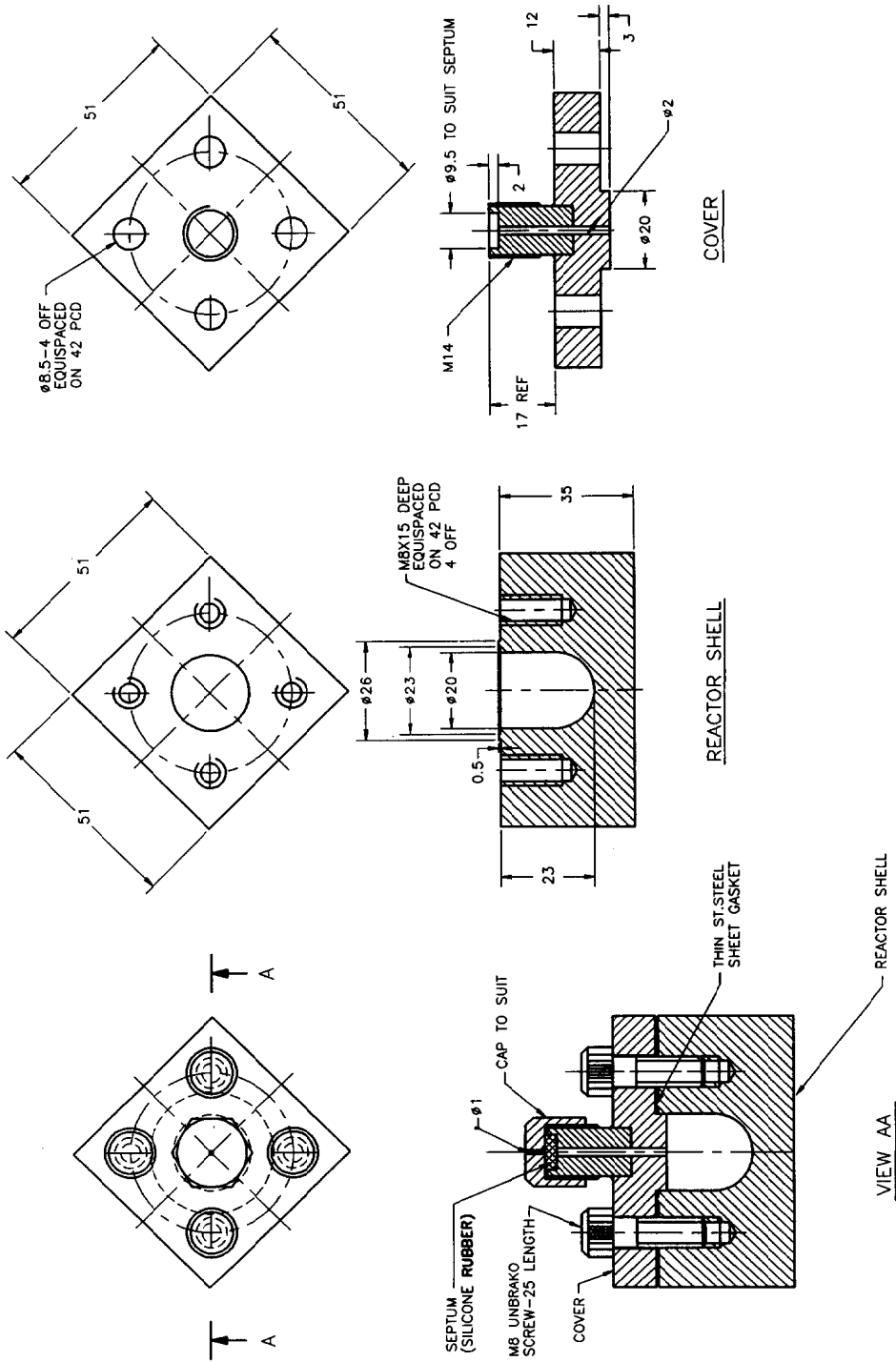


Fig. 2. Plan of improved stainless-steel reactor. All dimensions in millimetres.

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 of 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. The cover is fitted to the reactor shell by four screws.

Fusion procedure

The polyester sample (20 mg) was mixed with the fusion reagent (0.2 g) consisting of a prefused mixture of potassium hydroxide and sodium acetate (5%) and heated in the reaction vessel for 1 h at 250°C. After cooling, the contents were transferred to a beaker and dissolved in water. The polyols were then extracted with chloroform and concentrated using rotary evaporation. Acetic anhydride (2.5 ml) and 1-methylimidazole (0.5 ml) were added to the concentrated polyol extract and refluxed for 1 h. After refluxing, the contents were transferred into a separating funnel and extracted with two 20-ml portions of chloroform and washed with two 20-ml portions of water. The chloroform layer was then dried using anhydrous magnesium sulphate and concentrated to 5–6 ml in a rotary evaporator and used in the analysis.

The aqueous layer containing the resin acid components was transferred into a beaker and a dilute hydrochloric acid solution was added until the pH was 1–2. Water was then evaporated and the solid acids were dried in an oven at 105°C for 30 min. Boron trifluoride–methanol reagent (5 ml) was then added and refluxed for 1 h. Methyl esters of acid components were extracted with two 20-ml portions of toluene and then washed with two 20-ml portions of water. The toluene layer was dried with anhydrous magnesium sulphate and concentrated in a rotary evaporator to 5–6 ml and used for gas chromatographic analysis.

Gas chromatography

For gas chromatography a Perkin-Elmer Model 8410 instrument fitted with flame ionization detectors was used. The column was aluminium (12 ft. × ¼ in. O.D.) packed with 10% Silar IOCP on Chromosorb W AW DMCS. The carrier gas (helium) pressure was 20 p.s.i. (120 kPa). The polyol acetates were separated isothermally at 180°C whereas for

the carboxylate diesters the column temperature was programmed from 170 to 250°C at 8°C/min.

Samples

The samples were (1) a white crystalline solid sample of polyester based on phthalic anhydride, maleic anhydride and neopentyl glycol, (2) similar to (1) but based on propylene glycol and (3) commercially available polyethylene terephthalate film.

RESULTS AND DISCUSSION

The reactor shown in Fig. 2, owing to its broad and shallow reaction cavity, was found to facilitate handling of the sample and prevent loss of the reaction products, thus allowing smaller samples to be used. Samples of 20 mg are conveniently handled, as shown by the results reported here. Whereas this is a tenfold reduction in sample size, the actual amount of reaction product necessary for gas chromatographic examination is less than 1 µl of solution and is thus orders of magnitudes greater than available. For gas chromatography–mass spectrometry the sample requirement is much lower, it having been indicated that with modern instrumentation the identity of compounds in admixtures may be determined at about the 10^{-10} g ml⁻¹ level [19]. Leclercq *et al.* [20] have shown that identifiable mass spectra are produced with 40–60 pg of the sample. Pyrolysis gas chromatographic–mass spectrometric studies of polyacrylic esters [21] have used 800-ng (0.8-µg) samples to produce a range of components and spectra capable of interpretation for nearly 30 compounds. Similarly, forensic studies have involved samples as small as 0.5 µg in case work [22]. With the present work further significant reductions in sample size are expected by reduction of losses experienced in the work-up stages. Earlier studies [17] have shown that the hydrolytic reactions are essentially quantitative and losses and errors of at least 1–2% per extraction step are experienced.

The smaller volume of the reactor cavity, *i.e.*, 7.2 cm³, generates higher pressure during reaction, increasing the retention rate with a decrease in the reaction period necessary. The overall design prevents leakages and the four-screw system of attachment facilitates opening and closing of the reactor. The flange with the orifice allows the analysis of

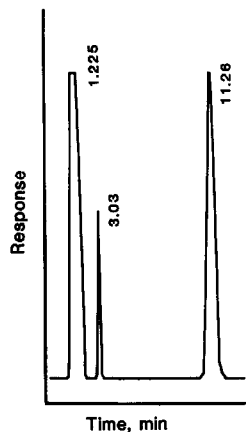


Fig. 3. Chromatogram showing peaks of solvent, diesters of maleic acid (3.03 min) and *o*-phthalic anhydride (11.26 min).

gaseous cleavage products and serves the same function as the septum incorporated into the sealing plug of the reactor shown in Fig. 1.

The separations of the acidic components of samples 1 and 2 are shown in Fig. 3 and the chromatograms of neopentyl glycol diacetate and propylene glycol diacetate from these two samples are shown in Fig. 4a and b, respectively.

The cleavage products of polyethylene terephthalate, a polyester of substantial hydrolytic stability,

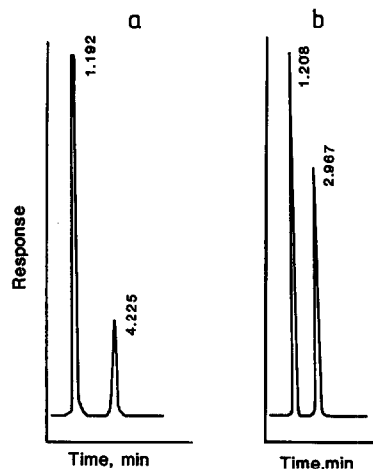


Fig. 4. Chromatograms showing solvent and diacetates of (a) neopentyl glycol (4.225 min) and (b) propylene glycol (2.967 min) from reactive polyesters.

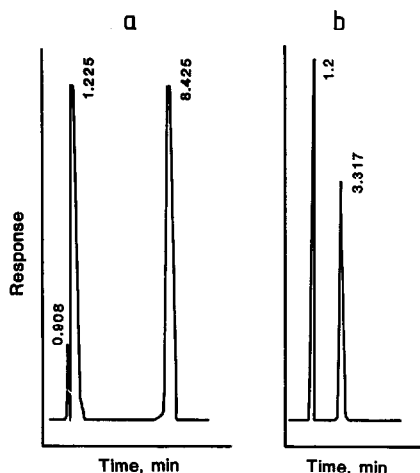


Fig. 5. Chromatograms showing solvent and (a) dimethyl terephthalate (8.425 min) and (b) ethylene glycol diacetate (3.317 min) from polyethylene terephthalate.

are shown in Fig. 5 for (a) dimethyl terephthalate and (b) ethylene glycol diacetate.

With fusion reactions the occurrence of leakages is normally extensive; basically the reactor is sealed or the volatile reaction products are essentially lost. In such a case, a high yield of non-volatile products is produced on working up and derivatizing the potassium salts whereas an almost negligible amount of volatile reaction products results. With leakages caustic residues and staining are evident on the external body of the reactor. This feature is clearly demonstrated by heating the charged reactor in an unsealed tinplate or zinc-lined can where on leakage attack and staining of the can surface are dramatic. The possibility of leakages is in any case minimized as standard analytical practice requires that multiple analyses (*i.e.*, fusions) be conducted.

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