

Degradation of polysulphones by alkali fusion

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ABSTRACT

The degradation of both aliphatic and aromatic polysulphones was carried out using alkaline fusion with chromatographic and spectrophotometric determination of the reaction products. The results are compared with those achieved with other functional classes of condensation polymers.

INTRODUCTION

The degradation of polymers of various functional classes as a preliminary to analysis of the reaction fragments has been carried out using hydrolytic cleavage. Many of the polymers, because of their inherent stability, require more stringent conditions than are possible using solution reaction and solid alkali has been used. The potassium hydroxide fusion reagent approximates the hemihydrate and consists of *ca.* 85% alkali.

Functional classes of polymers examined using alkali fusion include polyamides [1], polyimides [2], polyhydrazides [3], polyesters [4,5] and polyurethanes [6]. Although the analyses have largely been qualitative, the quantitative nature of the reactions has been discussed [7] and several studies concerning silicone polyesters have been reported [8,9].

The alkaline fusion procedure used is an extension of that developed by Siggia and co-workers [10], who described their procedure as fusion reaction gas chromatography (GC) [11], it being restricted to the detection of materials amenable to GC while the current procedure is applicable to all cleavage products.

The polysulphones represent a further functional

class of polymers and studies are reported using both aliphatic and aromatic homologues with the results being compared with those achieved with other functional classes of condensation polymers. The chemical cleavage of these polymers has not previously been reported and, as the structures are theoretically amenable to cleavage, the possibility of reaction as an analytical procedure is considered.

Alkyl sulphones react with alkali to produce olefins, α -bromodiethyl sulphone [12], α -bromopropyl ethyl sulphone [13] and bis(α -chloroethyl) sulphone [14] yielding *cis*-2-butene, *cis*-2-pentene and potassium 2-butene-2-sulphonate, respectively.

Rearrangement of olefinic sulphones occurs with alkali such that the position of the double bond is moved and ultimately cleavage occurs at the new site of the double bond with the formation of a saturated hydrocarbon fragment and an aldehyde. Propylene sulphone reacted with hot aqueous sodium hydroxide to produce acetaldehyde and sodium 2-methylsulphonyl-1-propanesulphonate [15–16].

Simple aromatic sulphones cleave at the sulphone link. Ingold and Jessop [17] and others [18,19] found that benzene and benzenesulphonic acid were the products of the alkaline cleavage of diphenylsulphone. Phenol was also a significant product at temperatures below the decomposition point of benzenesulphonic acid. Phenylbenzylsulphone yielded phenol and sulphur dioxide whereas ben-

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zylmethyl sulphone yielded similar products with the addition of methanesulphonic acid. Commercially available aromatic polysulphones are reported to be insoluble and not attacked by alkali. Samples were immersed at room temperature for 180 days in 10% and saturated sodium hydroxide without effect [20].

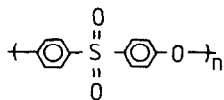
EXPERIMENTAL

Samples

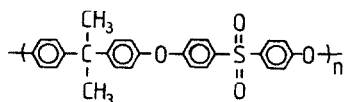
Three samples of polyolefinic sulphones, *viz.*, poly-1-(butene sulphone), poly(1-hexene sulphone) and poly 1-(cyclohexene sulphone) were used. The samples were provided by Professor J. O'Donnell of the University of Queensland.

Two commercially available types of aromatic polysulphones were used, namely the polyether sulphone Ultrason E2000 (BASF) or the ICI product Vitrex and the bisphenol A derivative of the polyether sulphone Udel P1700 (BASF) or PSOME (Amoco).

Ultrason E2000 or Vitex



Udel P1700 or PSOME



Alkali fusion procedure

Alkali fusion was carried out using 200–300 mg of polymer and 1–3 g of a prefused mixture of potassium hydroxide and 5% sodium acetate. The reaction was carried out by heating the polymer-reagent mixture in a stainless-steel, screw-capped pressure tube at various temperatures and for various times.

The reaction vessel was then allowed to cool and the reactants were placed in a 50-ml conical flask with water (30 ml). Chloroform (10 ml) was added and the mixture placed in a 100-ml separating funnel. The organic layer was separated using two aliquots of 10 ml of chloroform and then heated to

evaporate the chloroform. The chloroform/organic layer was evaporated to 2–3 ml. Gas chromatography–mass spectrometry (GC–MS) was used for analysis. The aqueous phase was evaporated to dryness and the solid also examined by infrared spectrometry. The analytical scheme is shown in Fig. 1.

Gas chromatography

For GC a Perkin-Elmer Model 8410 gas chromatograph was used. The carrier gas was helium at a flow-rate of 1000 ml min⁻¹. The column was 12 ft. × 0.25 in. O.D. aluminium packed with 10% OV-1, temperature programmed from 35°C at a rate of 15°C/min to 200°C.

Confirmatory analyses

Infrared spectrometry. Infrared spectrometry was performed with a Hitachi Model 270-30 infrared spectrometer in the region 400–4000 cm⁻¹ with the sample on a silver bromide plate.

Mass spectrometry. Chemical ionization mass spectrometry was conducted on the aqueous layer using a Finnigan Model 3200 quadrupole GC–MS system interfaced with an Incos Model 2300 data system. The ion source was maintained at 100°C by filament emission (100 mA) with source pressure of

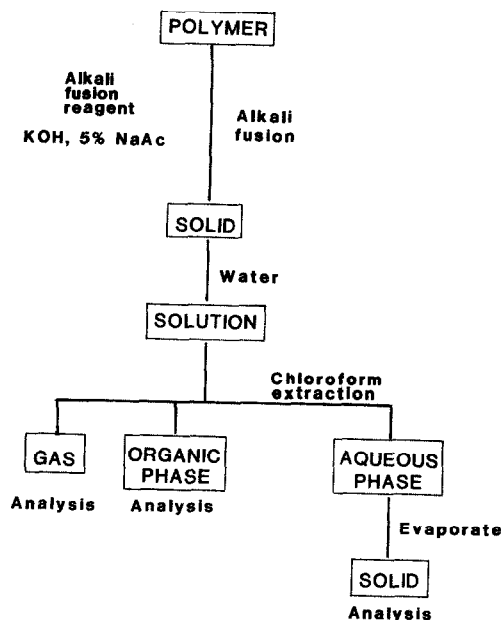


Fig. 1. Analytical scheme for alkali fusion.

0.8 Torr. A 1.5 m × 4 mm I.D. open tubular-glass column was used with methane as carrier/reagent gas at a flow-rate of 20 ml/min. The column (1.8 m × 2 mm I.D.) was packed with 2% OV-17 on Chromosorb G (100–120 mesh). The column was temperature programmed from 40°C at 10°C/min to 150°C.

NMR spectrometry. ¹H and C¹³NMR were carried out on Bruker AC300 F spectrometer operating at 300 MHz.

RESULTS AND DISCUSSION

The olefinic polysulphones were readily cleaved by reaction at 200°C for 1 h. Poly 1-(butene sulphone) and poly(1-hexene sulphone) produced 1-methyl 1,3-propanediol and 1-methyl-1,3-pentane-diol, respectively, while poly(1-cyclohexene sulphone) produced ethanol and *n*-octanol, the former predominating. The saturated ring structure of the sulphone was opened and cleavage occurred. The liberation of sulphur dioxide was apparent immediately on opening the reactors. Measurement of the gas liberated is not suitable for determination of the sulphones, however, as some reaction occurs with the potassium hydroxide with the formation of potassium hydrogensulphite. Fig. 2 shows chromatograms of the alcohols produced by cleavage of the three olefinic polysulphones.

The simpler aromatic polymer was fused at temperatures between 250 and 300°C for times up to 24 h, as shown in Table I. No cleavage occurred at

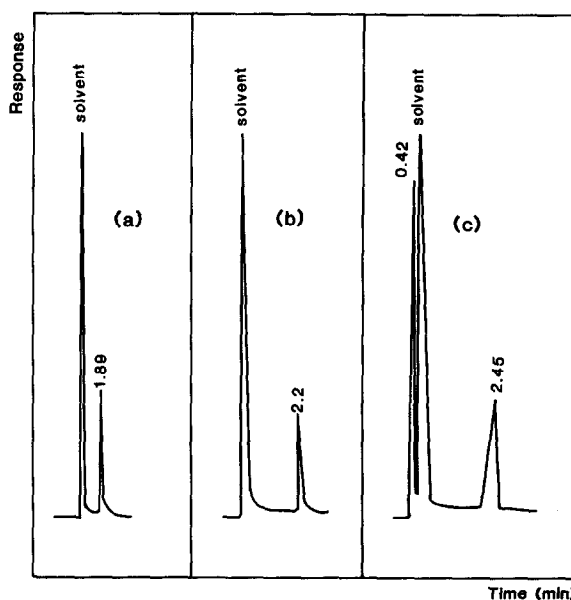


Fig. 2. Chromatograms showing reaction products of olefinic sulphones: (a) 1-methyl-1,3-propanediol from poly(1-butene sulphone); (b) 1-methyl-1,3-pentane-diol from poly(1-hexene sulphone); (c) ethanol and *n*-octanol from poly(1-cyclohexene sulphone).

short reaction times and a minimum reaction time of 6 h was necessary for degradation to occur. The polymer was cleaved at the S–C bond with liberation of sulphur dioxide. The reactions are shown in Fig. 3.

After 6 h of reaction a small amount of phenol

TABLE I

ALKALI FUSION CONDITIONS FOR SIMPLE AROMATIC POLYSULPHONES

Expt. No.	Polymer	Temperature (°C)	Time (h)	Observation
1	Ultrason E2000	300	2	Polymer did not dissolve
2	Ultrason E2000	250	4	As above
3	Ultrason E2000	350	4	As above
4	Ultrason E2000	300	6	White powder resulted, soluble in water
5	Ultrason E2000	300	12	As above
6	Ultrason E2000	280	24	As above
7	Udel P1700	280	4	White powder resulted, soluble in water to form a yellow solution
8	Udel P1700	400	4	Polymer did not dissolve
9	Udel P1700	280	12	As above
10	Udel P1700	280	24	As above

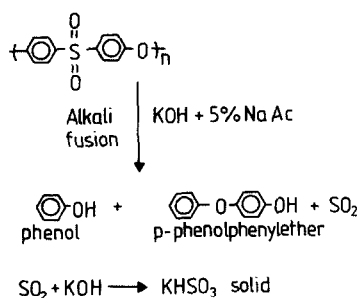


Fig. 3. Alkaline cleavage of simple aromatic polysulphone. NaAc = Sodium acetate.

was present, but on further reaction the phenol concentration increased. Fig. 4 shows chromatograms of the two reaction products at 6 and 24 h, where it was apparent that the *p*-phenol phenyl ether is degraded with further reaction. After 6 h of reaction

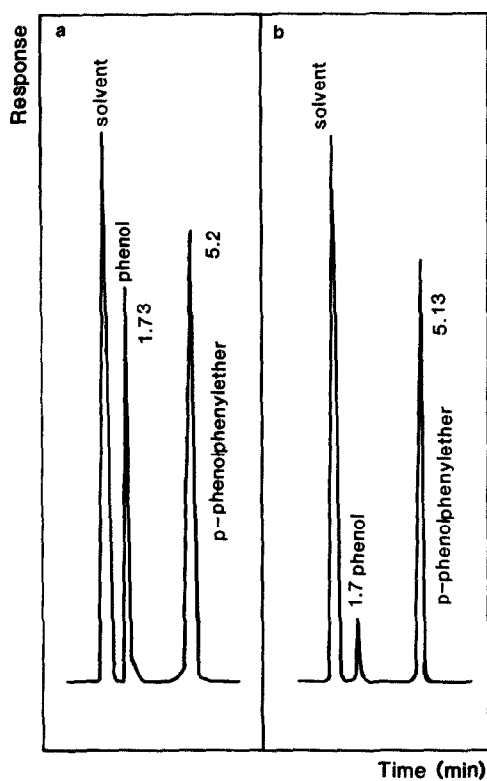


Fig. 4. Chromatograms showing cleavage products of simple aromatic polyether sulphone after (a) 6 h and (b) 24 h of reaction.

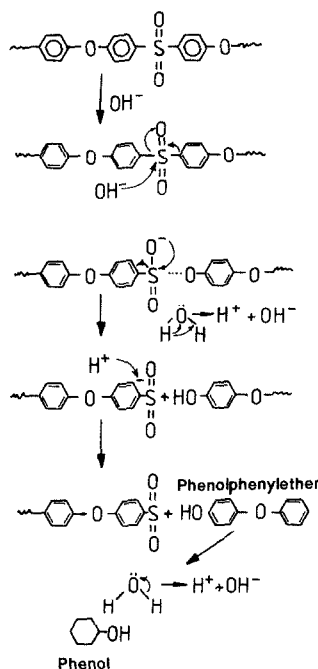


Fig. 5. Proposed degradation scheme for aromatic polyether sulphone.

sulphur dioxide could be detected on opening the reactor but with longer reaction times reaction with the alkali occurred to form potassium hydrogensulphite. The reaction scheme proposed for the degradation is shown in Fig. 5.

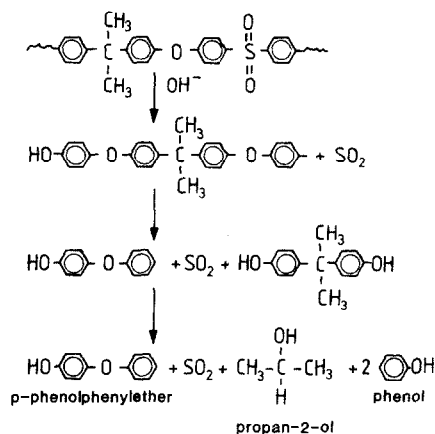


Fig. 6. Proposed degradation scheme for aromatic polyether sulphone copolymer with bisphenol A.

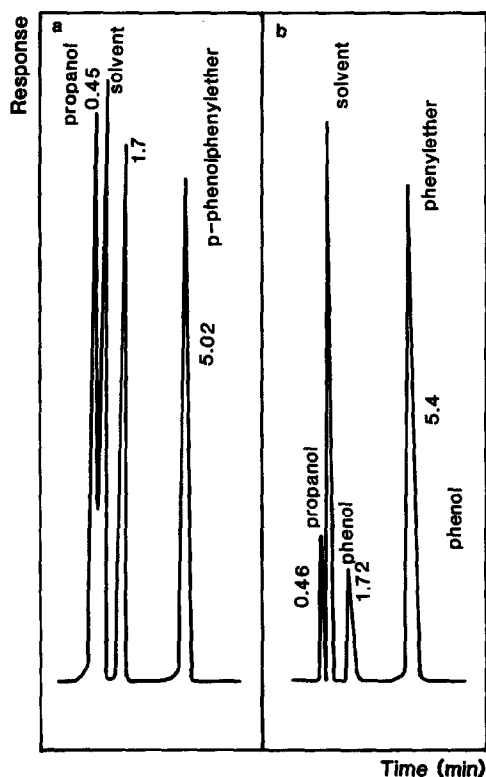


Fig. 7. Chromatogram showing cleavage products of aromatic polyether sulphone copolymer with bisphenol A after (a) 6 h and (b) 24 h of reaction.

The polysulphone copolymer with bisphenol A was examined as shown in Table I. The same constraints as with the simple polymer concerning degradation were apparent, the presence of the bisphenol A apparently not further reducing the reactivity of the volatile products were present, two as expected being common with the simple polymer, the third was 2-propanol.

The predominance of phenol at shorter reaction times was also observed. The presence of bisphenol A was also confirmed by NMR. The possible cleavage mechanism is shown in Fig. 6, which shows a chromatogram of the reaction products of the bisphenol A copolymer at 6 and 24 h, the results being in agreement with those for the simple polymer shown in Fig. 7.

The alkaline cleavage of sulphones shows that the olefinic materials are readily cleaved under the same

or milder conditions than applied to other condensation polymers. The aromatic materials, however, are much more resistant to cleavage than the other polymer systems examined and the conditions necessary are not compatible with those used in earlier studies. It is evident that the susceptibility of the two polymers to cleavage is very similar; the presence of bisphenol A in the copolymer does not further increase the resistance to cleavage as has been observed with other polymers containing bisphenol A [21].

In all of the analyses the identities of the compounds shown were confirmed by the various spectroscopic techniques. The spectra obtained are in agreement with those in available reference collections.

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