Sulphonated polyurethane ionomers with new ionic diols

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The sodium or potassium salt of 4-vinyl benzenesulphonic acid was epoxidized conveniently by 3-chloroperoxybenzoic acid. Several solvent systems for the reaction were investigated and it was found that a water/ethanol mixture was most efficient at room or elevated temperatures. The epoxide formed was relatively stable and was isolated and analysed by n.m.r. and i.r.. Ring opening of the epoxide with sodium carbonate resulted in the production of the diol, potassium or sodium 4-(1,2-dihydroxyethyl) benzenesulphonate, in good yield. The new ionic diol was incorporated into polyurethane by step-growth solution copolymerization in the presence of di-n-butyltin dilaurate. Proton n.m.r., i.r., t.g.a. and the solubility of the ionomer were investigated.

(Keywords: polyurethane; ionomer; potassium 4-(1,2-dihydroxyethyl) benzenesulphonate; cationic diol)

INTRODUCTION

Polymers into which small fractions of ionic monomers have been incorporated are termed ionomers. These materials are both academically and commercially important.

Previously, sulphonated polymers have been prepared by solution sulphonation employing acetyl sulphate as the sulphonating agent, as in the method developed by Makouski *et al.*[1,2]. These polymers were subsequently neutralized. Other workers used tertiary amines such as *N*-methyl diethanolamine which were incorporated into the polyurethane prior to sulphonation with γ-propane sultone, converting the polyurethane to a polymeric zwitterion[3]. Alternatively, the urethane proton was exchanged by an initial ionization by sodium hydride[4]. The major disadvantage of these methods is that the ionic content cannot be easily controlled.

Lorenz *et al.*[5] end-capped polyethers with isocyanates, and then chain-extended with the sodium salt of *N*-(2-amino ethyl)-2-amino ethane sulphonic acid. Recently our polymer research group has synthesized the potassium and sodium salts of 1,2-dihydroxypropyl sulphonic acid (SDOL and SDPS, respectively) by an S_N2 substitution of the chloride group in 3-chloro-1,2-propanediol[6]. Using these ionic chain extenders, the ionic content in the polymer could be controlled accurately. In this paper, we report the synthesis of a more stable diol, having an aromatic group, and its use in polyurethane synthesis.

Previously, sulphonated polystyrenes were prepared by the sulphonation of the polystyrene chain with a sulphonating agent. However, we utilized the potassium and sodium salts of vinyl benzenesulphonic acid and converted the vinyl group, by a two step conversion via a relatively stable intermediate, to the diol with the sulphonate group intact. The vinyl group was readily epoxidized by 3-chloroperoxybenzoic acid. The 4-(1,2-epoxy ethyl) benzenesulphonate is relatively stable under neutral and acidic conditions but rapidly ring opens in basic conditions to the ionic diol.

A prepolymer based on polypropylene glycol 1025 (PPG) endcapped by methylene bis(4-phenyl isocyanate) (MDI) was chain extended with the ionic diol using dimethyl sulphoxide (DMSO) as solvent in the presence of a tin catalyst. The proton n.m.r. and *FT*i.r. spectra were compared with those of a non-ionic polymer using butane-1,3-diol as the hard block chain extender. The solubilities of the diols and polymers were investigated and the sodium salt of the diol was found to be much more soluble in DMSO than the potassium analogue. The thermal stabilities of the ionic diol and polymers were studied and compared with that of SDOL. The aromatic sulphonates were stable up to 320°C.

EXPERIMENTAL

Solvents and reagents

Butane-1,4-diol, BD, (BDH) was dried over 4 Å Linde molecular sieves for 2 weeks, distilled and stored over fresh molecular sieves. Polypropylene glycol 1025, PPG, (MTM) was dried over 4 Å Linde molecular sieves for 2 weeks prior to use. Methylene bis(4-phenyl isocyanate), MDI, (Bayer) was used as supplied. Di-n-butyltin dilaurate, T12, (BDH) was used as supplied. Sodium and potassium salts of 4-vinylbenzenesulphonic acid, (Fluka) were used as supplied. 3-chloroperoxybenzoic acid 85%, MCPBA, (Aldrich) was used as supplied.

The general reaction scheme of the ionic diol synthesis is given in Scheme I, where *M* is sodium and potassium.

Scheme 1 Synthesis of ionic diol. M = Na and K

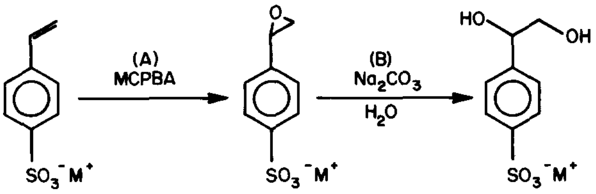

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Table 1 Solvent systems and reaction conditions employed for epoxidation

MCPBA[a] g	NVB[b] g	Water (cm^3)	Ethyl acetate (cm^3)	Ethanol (cm^3)	Acetone (cm^3)	Reaction time at 25°C	65°C
0.80	0.50	10[a]		–	–	5 days	6 h
0.80	0.50	10	10[a]	–	–	2 weeks	20 h
0.80	0.50	5	–	5	–	20 h	2 h
0.80	0.50	5	–	–	5	20 h	–

[a] MCPBA = 4-chloroperoxybenzoic acid
[b] NVB = sodium 4-vinyl benzenesulphonate
[c] Two phase reaction

Epoxidation

The quantities of material used are listed in *Table 1*. The solvent quantities and reaction conditions are also summarized.

In general, the appropriate quantities of MCPBA and the 4-vinyl benzenesulphonate (I) were dissolved in a mixture of water and another solvent. The solubility of MCPBA in water alone was very low, 0.154 g/100 g at 25°C. The solution was placed in a loosely stoppered flask and was magnetically stirred at 25°C in a water bath. Small aliquots (0.5 cm^3) of the reaction mixture were removed periodically and tested qualitatively with bromine water. Termination of the reaction was indicated by a lack of a change of colour of the bromine water from brown to colourless. The reactions were repeated at the higher reaction temperature of 65°C.

It was found that the water/ethanol (50/50%) system was by far the most efficient at ambient or elevated temperatures. Therefore, this solvent system was employed in the larger scale preparations of the epoxides.

The general procedure is now given for the synthesis of the potassium salt.

A mixture of (I) (34.0 g, 0.153 mol) and MCPBA (34.5 g, 0.200 mol) were dissolved in the mixed solvent water/ethanol (400 cm^3, 1:1 v/v). The solution was then heated at 65°C for 2 h until a bromine test was negative. The solution was allowed to cool and solvent was evaporated off by rotary evaporation.

Residual *m*-chlorobenzoic acid, MCBA, was dissolved in acetone (300 cm^3) and filtered off leaving the solid 4-(1,2-epoxy ethyl) benzenesulphonate, (II).

Epoxide ring opening

In the second stage, (II) was dissolved in distilled water (150 cm^3) and anhydrous sodium carbonate (0.500 g, 0.00472 mol) was added. The solution was refluxed for 1.5 h. Water was then evaporated off and the residue was taken up in DMSO. (The sodium salt required 150 cm^3 of DMSO and the potassium salt required 300 cm^3). The undissolved Na_2CO_3 was separated by filtration. The filtrate containing the product potassium 4-(1,2-dihydroxy ethyl) benzenesulphonate, KB (the sodium salt is denoted by NB), (III) was partially evaporated at 80°C under reduced pressure. Acetone (500 cm^3 for NB, and 1200 cm^3 for KB) was then added to precipitate the salt. The latter, a very pale yellow powder, was filtered and washed with excess acetone and dried *in vacuo* at room temperature for 1 week, % yield = 61.

Microanalysis result for KB, predicted: C 37.45%; H 3.51%; S 12.51%; found: C 37.14%, H 3.12%, S 11.98%.

FAB(–): M-alkali metal = 217 a.m.u. (H_2O–glycerol as carrier).

Polymerization

MDI (7.51 g, 0.300 mol) and PPG (10 g, 0.100 mol) were mixed and heated at 90°C with fast mechanical stirring under a nitrogen atmosphere for 1 h.

The viscous mixture was allowed to cool to 50–60°C. DMSO (20 cm^3) was added to dilute the prepolymer. KB (5.13 g, 0.200 mol) dissolved in DMSO (40 cm^3) was then added through a pressure equalizing funnel over 10 min, after which the catalyst, di-n-butyl tin dilaurate, (0.10 g), was added. The mixture was heated at 95°C with stirring for 2 h. The copolymer formed was cooled and precipitated from diethyl ether. After drying in the oven at 80°C for 3 days, the copolymer appeared as a glassy yellow solid.

Microanalysis results, predicted: C 59.51%; H 6.75%; N 3.68%; S 2.81%; found: C 59.12%; H 6.72%; N 3.67%; S 3.14%.

A non-ionic copolymer was synthesized similarly to the above but substituting KB with butane-1,4-diol.

RESULTS AND DISCUSSION

^1H n.m.r.

Proton n.m.r. spectra were recorded on a Bruker WM250 MHz spectrometer.

The proton spectra of (I), (II), and (III) of the potassium salt are given in *Figure 1a, b* and *c*, respectively. The changes are apparent as the vinyl group is converted to the epoxide and then the diol.

The vinyl protons were quite distinctive in the 5 to 7 ppm region. The aromatic protons were fairly clustered at 7.6 ppm. The epoxide however altered the appearance of the aromatic peaks. They were now more symmetrical, in the form of two doublets. The reason for this is probably that the extra electronic conjugation from the pi bonds of the vinyl group to the aromatic ring was lost on conversion. The methine proton gives a triplet at 4.5 ppm and the methylene protons give a doublet at 3.4 ppm.

Ring opening of the epoxide under basic conditions led to the required sulphonated diol. The proton n.m.r. of the latter, *Figure 1c*, was very similar to that of the epoxide except for two extra broad peaks at 5.4 and 4.9 ppm due to the hydroxyl groups.

Figure 2a and *b* shows the proton spectra of the non-ionic polymer and the ionomer, respectively.

The non-ionic polymer gave a multiplet peak at 1.7 ppm due to the central methylene protons of BD and a broad peak at 4.1 ppm corresponding to the protons at 1 and 4 positions of BD. The 1,4-disubstituted aromatic protons gave symmetrical signals at 7.1 to 7.4 ppm. A single peak for the urethane protons is at

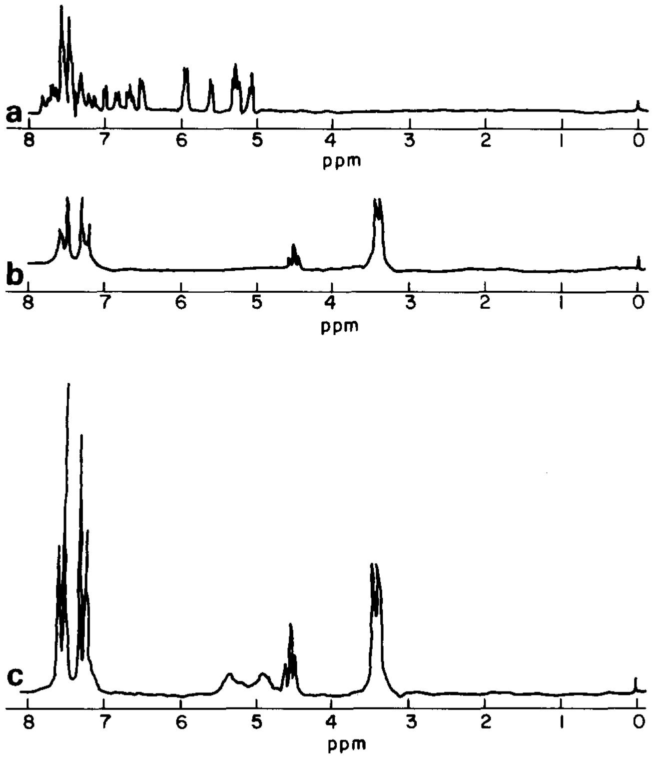

Figure 1 Proton n.m.r., potassmium salt of (a) 4-vinyl benzenesulphonic acid; (b) 4-(1,2-epoxy ethyl) benzenesulphonic acid; and (c) 4-(1,2-dihydroxy ethyl) benzenesulphonic acid

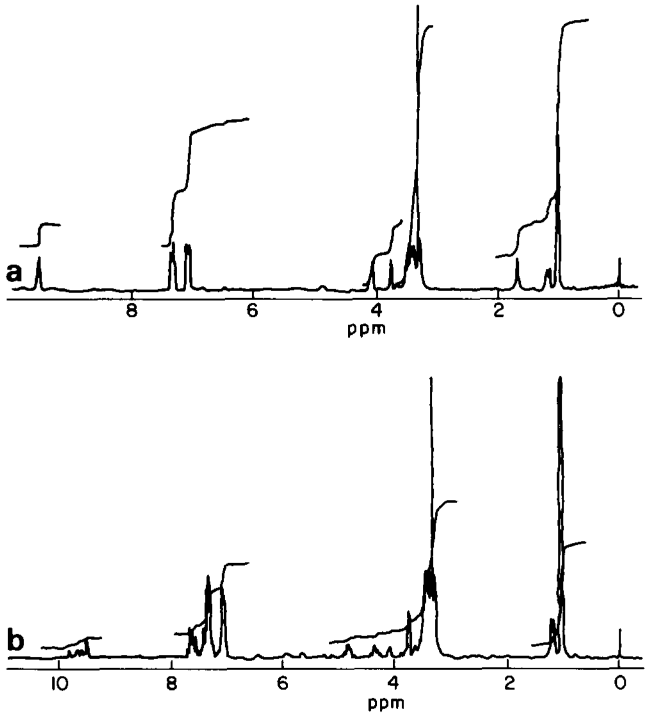

Figure 2 Proton n.m.r. (a) non-ionic polyurethane, and (b) ionomer

9.5 ppm. Integration gave a ratio of 1:4 with the aromatic protons.

The urethane protons of the ionomer gave multiple peaks in the region 9.5 to 9.9 ppm due to asymmetrical deshielding provided by the ionic diol. Between 7.0 and 7.7 ppm, two overlapping aromatic systems were observed. 1,4-disubstituted aromatic protons from MDI were between 7.0 and 7.3 ppm, whilst those of KB were between 7.4 and 7.7 ppm. The latter signals were smaller. The integration height was approximately 1/3 of the former.

FT*i.r.*

FTi.r. spectra were recorded on a Perkin Elmer 1710 *FTi*.r. spectrometer. The solid diol was dissolved in nujol and examined between NaCl plates.

The i.r. spectrum for the ionic diol showed a strong, broad band at 3500 cm^{-1}, which corresponded to the hydroxy groups of the diol. A weak, but broad band at 1650 cm^{-1} corresponding to the conjugated double bonds in the initial vinyl compound almost totally disappeared on conversion to the diol. In the fingerprint region, the typical pattern for a 1,4-disubstituted aromatic ring was disrupted by the vinyl group conjugating with the aromatic pi cloud in the starting material (I). On conversion of the functional group, the characteristic bands at 850, 820, 740, and 720 cm^{-1} appeared. The SO stretch was observed at 1210 cm^{-1}; the CS stretch at 710 cm^{-1} was masked.

The polymers were analysed in the form of thin films. Polymer solutions (5% w/v) with DMF as solvent were cast thinly onto KBr plates. After evaporation at ambient conditions for 5 h, the plates were left *in vacuo* for 24 h at room temperature before analysis.

The urethane N–H stretch at 3300 cm^{-1} was relatively sharp for the non-ionic copolymer, *Figure 3a*. The spectrum for the ionomer, *Figure 3b*, however, showed a relatively broad band at this wave number due to extra hydrogen bonding resulting from the ionic groups.

A small band at 1800 cm^{-1}, masked initially in *Figure 3a* but slightly bigger in *Figure 3b*, was probably due to the conjugated C–C aromatic bonds. Introduction of the ionic diol increased the aromatic signal by approximately 15%.

Carbonyl bands were markedly altered as a result of hydrogen bonding. *Figure 3a* showed little interchain or intrachain hydrogen bonding, with just two overlapping bands at 1700 and 1730 cm^{-1}.

The sulphonate groups of the ionomer, however, were probably able to form extensive hydrogen bonds with the urethane hydrogens. The result was two distinct bands at 1730 and 1670 cm^{-1}. New bands were also observed at 1520 and 1140 cm^{-1} in *Figure 3b*. A small overlapping band at 1480 cm^{-1} had disappeared from the spectrum of the ionomer. The SO stretch at 1210 cm^{-1} showed up as a broad band overlapping with another strong band. The fingerprint region of the spectrum of the ionomer was much more complicated due to the extra styrene ring and the sulphonate. The aromatic pattern was observed, however, with the *p*-disubstitution shown at 800 to 860 cm^{-1}. C–S stretch was shown at 710 cm^{-1}. Other bands were more difficult to assign.

T.g.a.

Thermogravimetric analysis was performed in air, using a Perkin Elmer TGA-2 coupled with a Perkin Elmer DSC 2 at 10°C min^{-1}.

Figure 4 shows the thermogravimetric results of the copolymers and KB (*Figure 4a*) under study, together with that of SDOL, (*Figure 4d*) for comparison. KB started to decompose at 320°C, which was 40°C more stable than SDOL. The non-ionic polymer, (*Figure 4b*), was stable up to approximately 270°. The ionomer,

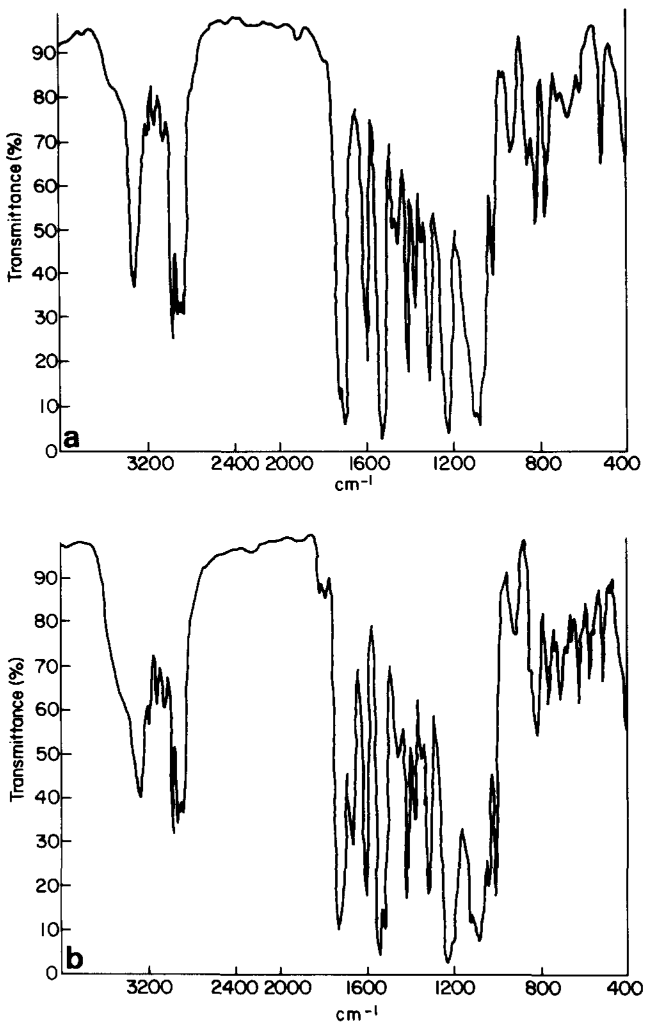

Figure 3 *FTi.r.* (a) non-ionic polyurethane, and (b) ionomer

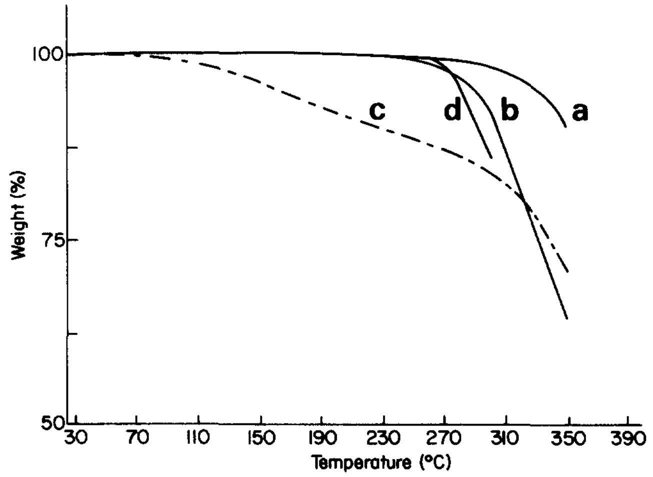

Figure 4 Thermogravimetric results of: a, the copolymers and KB; b, non-ionic polymer; c, ionomer; d, copolymers and SDOL

Table 2 Solubility

	Ionomer	Non-ionic polymer	KB[a]
Water	+	−	+
DMSO	+	+	+
DMF	+	+	−
THF	−	+	−

[a] Potassium 4-(1,2-dihydroxy ethyl) benzenesulphonate

(*Figure 4c*), was far less stable thermally. The initial weight loss from 80 to 130° was probably due to moisture absorbed by the ionomer. There was a steady weight loss of approximately 15% over the temperatures from 150 to 280°. The bulk of the ionomer decomposed at 310°.

Solubility

Some solubility results are given in *Table 2*. The ionomer was water soluble. At lower ionic incorporations than the figure quoted in the Experimental section, it would have been less likely to be soluble. It was not soluble in THF, whereas the non-ionic polymer was. Also noteworthy is that KB had about one half the solubility of that of NB (w/w) in DMSO.

CONCLUSIONS

In conclusion, we have synthesized a new aromatic and ionic diol which is more stable than those previously synthesized. The incorporation of this new diol into polyurethane by step-growth solution polymerization is relatively straightforward, and further work on this and related systems is in progress.

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