Synthesis and characterization of some polyurethane ionomers

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Polyurethane ionomers based on either poly(propylene glycol), PPG, or poly(ethylene glycol), PEO, and di-(4-isocyanatophenyl) methane, MDI, butane-1,4-diol and *cis*-2-butene-1,4-diol have been synthesized and characterized. Attempts to convert the unsaturated polyurethanes directly to ionomers by reaction with *N*-chlorosulphonyl isocyanate, CSI, followed by hydrolysis, failed due to the more favoured reaction of CSI with the labile hydrogen on the urethane linkage. Therefore, the *cis*-2-butene-1,4-diol was first converted to the dibenzoate which was then treated with CSI to form the β-lactam derivatives. Subsequent hydrolysis of these derivatives with tetra-n-butyl ammonium hydroxide solution produced ionic derivatives whilst at the same time regenerating the terminal –OH groups. These ionic diol intermediates were then used for synthesizing the polyurethane ionomers.

Keywords Polyurethane; ionomers; synthesis; characterization; modification; *N*-chlorosulphonyl isocyanate

INTRODUCTION

Segmented polyurethanes are linear block copolymers consisting of 'soft' and 'hard' segments. The soft segments are derived from low molecular weight, flexible, aliphatic polyesters or polyethers, while the hard segments are formed by strongly hydrogen bonded urethane blocks. These materials have found widespread commercial applications as paints, varnishes, surface coatings, fibres and insulating materials[1–3]. More recently, polyurethanes have been used in medical equipment and for implantations for support and substitution[4–6]. The low clotting tendencies of polyurethanes[7] makes them particularly useful in biomedical applications. In order to further improve the blood compatibility of these polymers, negatively charged ionic groups, which are characteristic of the anti-clotting polysaccharide, heparin, are incorporated into the polymer backbone. It has been suggested that anionic surfaces retard or eliminate blood clotting[8] and that the negatively charged films are less thrombogenic than either the uncharged or positively charged films[9]. Therefore, membranes with negatively charged groups should inhibit platelet adsorption when in contact with blood and hence reduce the risk of thrombosis. No polyurethane ionomer containing both $-COO^- N^+(But)_4$ and $-NHSO_3^- N^+(But)_4$ groups has been reported previously in the literature.

This paper describes the synthesis and characterization of ionic polyurethanes derived either from poly(propylene glycol) or poly(ethylene glycol), with di-(4-isocyantophenyl)methane, butane-1,4-diol and an ionic derivative of *cis*-2-butene-1,4-diol.

EXPERIMENTAL

Reagents

Cis-2-butene-1,4-diol (Aldrich Chemicals Co. Ltd.) was dried with Linde molecular sieve, type 5A for 48 hours. It was then fractionally distilled under reduced pressure (b.pt. 135°C/15 mm Hg). Butane-1,4 diol (BDH Chemicals) was dried with sodium metal and was then fractionally distilled under nitrogen at reduced pressure (b.pt. 145°C/0.5 mm Hg).

N-chlorosulphonyl isocyanate, CSI, (Aldrich Chemicals Co. Ltd.), 98% pure) was fractionally distilled under reduced pressure using a glass helix-packed column. CSI is a colourless liquid which fumes slightly in moist air. Di-(4-isocyanatophenyl)methane, MDI, (Bayer Ltd., as 'Desodur 44MS'), undergoes chemical changes on storage because of uretidione and isocyanurate formation. It was purified by fractional distillation using a jacketed Vigreux column under reduced nitrogen pressure (b.pt. 150°C/0.1 mm Hg) to give a white crystalline solid (m.pt 38°C).

Poly(propylene glycol), PPG, (BDH Chemicals), was dried in a vacuum oven at 120°C for 5 hours. This was to remove traces of water (w/w = 0.3%) present in the poly(propylene glycol) which readily react with isocyanate groups and could lead to a subsequent inbalance of molar equivalence of reactants.

Poly(ethylene glycol), PEO, (Union Carbide), contains water, and traces of a basic catalyst used during its synthesis. The presence of these impurities leads to gel formation during preparation of the polyurethanes if used directly. The PEO was purified by heating to about 80°C in a conical flask on a hot plate, while stirring with a magnetic stirrer. A slight excess of concentrated hydrochloric acid was then added to neutralize the basic impurities. The excess hydrochloric acid and moisture were then removed under vacuum at 80°C for 6 hours.

Tetra-n-butylammonium hydroxide solution (Hopkin and Williams), approximately 0.1M solution in toluene/methanol was used as supplied.

Pyridine (BDH Chemicals), was dried by refluxing over potassium hydroxide pellets and then fractionally distilled under nitrogen (b.pt. 115°C/760 mm Hg).

Dimethyl sulphoxide, DMSO, (Hopkin and Williams),

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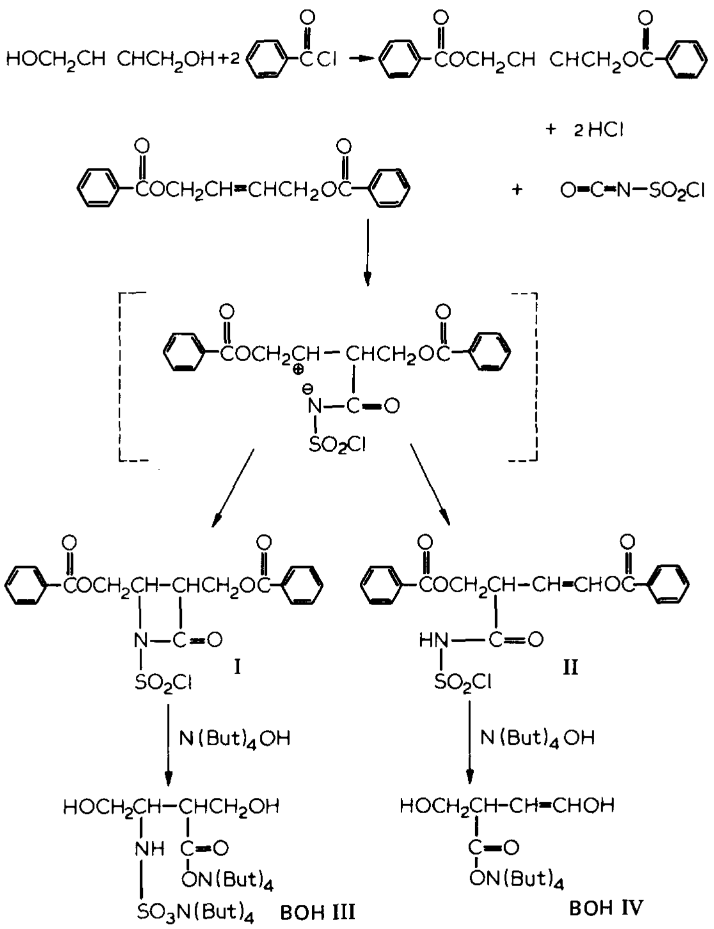


Figure 1 Main reactions leading to the formation of ionic diol intermediates

was purified first by drying with Linde Molecular sieve, type 5A, for 24 hours and then stirred over barium oxide for another 24 hours. The dried DMSO was fractionally distilled under nitrogen at reduced pressure (b.pt. 53°C/1 mm Hg).

4-Methylpentane-2-one (Aldrich Chemical Co. Ltd.), was purified by stirring over calcium hydride for 48 hours before fractional distillation under nitrogen (b.pt. 114°C/760 mm Hg).

Benzoyl chloride (Hopkin and Williams), was purified by fractional distillation under nitrogen at reduced pressure.

Benzene (Hopkin and Williams), was purified by stirring over calcium hydride for 48 hours and stored overnight over sodium wire. It was then fractionally distilled under nitrogen (b.pt. 80°C/760 mm Hg).

Commercial sodium metal (BDH Chemicals), in liquid paraffin was freshly cut and dried between filter papers before use. Anhydrous barium oxide and calcium hydride (BDH Chemicals), were used as received.

Oxygen-free nitrogen (B.O.C.), was dried by passing it through a series of columns containing sulphuric acid, anhydrous calcium chloride, potassium hydroxide and silica gel.

Preparation of the ionic diol from cis*-2-butene-1,4-diol*

Synthesis of dibenzoate derivative, (DB). Benzoyl chloride (81.73 g) was gradually added to a solution of *cis*-2-butene-1,4-diol (24.90 g) dissolved in pyridine (15 cm^3) in a round bottomed flask, cooled in an ice-bath. The reaction mixture was then refluxed for 1 hour, and after cooling to room temperature, it was treated with dilute sulphuric acid to dissolve the pyridine salt and precipitate the *cis*-2-butene,1,4 dibenzoate, (**DB**). The dibenzoate was washed with sodium hydrogen carbonate solution, followed by water. It was recrystallized from aqueous ethyl alcohol and dried in a vacuum oven (m.pt. 68°C).

Found: C, 72.89%; H, 5.44%; Calculated C, 72.97%; H, 5.40%.

Reaction of CSI with dibenzoate derivative (DB) to give N*-sulphonyl chloride derivatives (BOS).* The dibenzoate (6.45 g) was dissolved in benzene (50 cm^3) and the solution added to a continuously stirred solution of *N*-chlorosulphonyl isocyanate, CSI, (4.10 g) in benzene (20 cm^3) in a resin flask equipped with a stirrer, thermometer, condenser and dropping funnel. The reaction mixture was kept at 40°C for 5 hours. At the end of this period, the solvent and any unreacted CSI were removed at low temperature, under reduced pressure. Two principal derivatives, the α-β-disubstituted β-lactam-*N*-sulphonyl chloride (I) and the β-γ-unsaturated carbonamide-*N*-sulphonyl chloride (II) were formed; and their structures are shown in *Figure 1.*

Found: C, 48.77%; H, 4.02%; N, 2.89%; S, 9.01%; Cl, 6.85%; Calculated C, 52.12%; H, 3.65%; N, 3.20%; S, 7.31%; Cl, 8.11%.

The discrepancy between the actual microanalytical results and those calculated from structures I and II, suggest the formation of byproducts, which are discussed later.

Hydrolysis of the N*-sulphonyl chloride derivatives, (I) and (II).* The *N*-sulphonyl chloride derivatives (3.0 g) were hydrolysed with 0.1 M tetra-n-butylammonium hydroxide solution in methanol/toluene (275 cm^3) for 6 hours. The solvents were removed using a rotary evaporator under reduced pressure. A dark brown viscous liquid, BOH, consisting predominantly of two ionic diols, BOH(III), and BOH(IV), shown in *Figure* 1, was obtained.

Found: C, 64.39%; H, 11.65%; N, 4.83%; S, 2.78%; Calculated (assuming BOH(III) and BOH(IV) only are formed in the molar ratio 70:30) C, 62.45%; H, 11.39%; N, 5.91%; S, 4.50%.

The assumption of I and II being formed in the molar ratio 70:30 will be discussed later.

Synthesis of polyurethane ionomers, PUM, PUN, SHE/2 and SHE/3

A modification of the method described by Lyman[10] and others[11] was used to prepare the polyurethane ionomer, PUM. A 500 cm^3 resin flask was equipped with a stirrer, condenser, drying tube, thermometer, dropping funnel and a nitrogen inlet. The apparatus was flamed out under nitrogen. A solution of poly(propylene glycol) (51.250 g) in DMSO (40 cm^3) was added to a well stirred solution of MDI (25.020 g) in 4-methyl-pentan-2-one (40 cm^3) in the reaction flask. The mixture was stirred for 2 hours at 90°C and then cooled to 60°C. Butane-1,4-diol (4.012 g) in DMSO (10 cm^3) was added over about 10 min with stirring and once addition was complete the reaction mixture was maintained at 90°C for another hour. It was then cooled to 60°C and the ionic diols, (BOH), (3.857 g) were then added continuously with stirring over one hour at 90°C.

The concentration of free isocyanate groups present in the mixture was determined by reacting a sample with an excess of dibutylamine and then back titrating with a standard hydrochloric acid solution. Butane-1,4-diol (0.246 g) was then added to give an equimolar overall concentration of isocyanate and hydroxyl groups in the reaction mixture. Towards the end of the reaction a slight excess of butane-1,4-diol was added to ensure hydroxyl end groups on the resulting polymer. The polymer was precipitated into water and then reprecipitated from *N*,*N*-dimethyl formamide solution into water. It was dried in a vacuum oven for 5 days at 40°C. Found: C, 63.57%; H, 8.58%; N, 3.52%; S, 0.44%; Calculated (based on the assumption that onlv the two products, BOH, *Figure 1*, react with NCO) C, 64.66%; H, 8.47%; N, 3.56%; S, 0.40%.

A further polyurethane ionomer, (PUN), based on di-(4-isocyanatophenyl)methane, poly(ethylene glycol), butane 1,4-diol and the ionic diol (BOH) was also synthesized by an analogous process. Found: C, 60.19%; H, 7.15%; N, 4.33%; S, 0.52%; Calculated (based on similar assumptions as for PUM), C, 60.75%; H, 7.44%; N, 4.70%; S, 0.56%.

Some of the $-N^+(But)_4$ groups in the polyurethane ionomer were exchanged with Na^+ or K^+ by stirring a solution of PUM and sodium or potassium chloride in aqueous DMF at 25°C for 4 hours and then reprecipitating twice into distilled water. The ionomers SHE/2 and SHE/3 represent the original PUM with $N(But)_4^+$ ions replaced by Na^+ and K^+, respectively.

Synthesis of non-ionic polyurethane copolymers

The following high molecular weight linear polyurethanes were also prepared by the above method.

(i) PUI, based on MDI and PPG with a molar ratio of OH/NCO groups equal to 1.67. Found: C, 61.62%; H, 9.43%; N, 1.70%; Calculated C, 63.11%; H, 9.54%; N, 1.83%.

(ii) PU2, based on MDI and *cis*-2-butene-1,4 diol with a molar ratio of OH/NCO groups equal to 0.77. Found: C, 67.45%; H, 4.60%; N, 8.28%; Calculated C, 68.78%; H, 4.39%; N, 8.88%. and

(iii) PUA, based on PPG (51.250 g), MDI (25.020 g), *cis*-2-butene-1,4 diol (0.237 g) and butane-1,4-diol (4.258 g) were prepared in a similar way to the ionic polyurethane PUM, except that the butane-1,4-diol was added in one step and, since equimolar concentrations of -OH and -NCO groups were involved, no back-titration was necessary.

The final polymer was end-capped using a slight excess of butane 1,4-diol, as for PUM. Found: C, 61.26%; H, 8.52%; N, 4.23%; Calculated C, 61.64%; H, 8.19%; N, 4.84%.

Infra-red i.r.

I.r. measurements were performed with a Perkin–Elmer 157G spectrophotometer using thin films of polyurethane cast from THF and the reaction intermediates in nujol.

Gel permeation chromatography, g.p.c.

G.p.c. measurements were carried out by the Polymer Supply and Characterisation Centre, RAPRA, Shawbury, Shrewsbury, using THF as solvent.

Nuclear magnetic resonance, n.m.r.

The spectra were recorded using a Varian E360A (60 MHz) n.m.r. spectrometer, with fully deuterated DMSO as solvent.

Equilibrium water sorption measurements

These measurements were carried out by immersing preweighed samples of polymer film in distilled water maintained in a water bath at 25°C; a method similar to that described by Illinger and Schneider[12].

Differential thermal analysis, d.t.a.

The DuPont Thermal Analyser 990 with a d.s.c. cell attachment was used for measuring the glass transition temperature (T_g) of the polyurethanes. The measurements were performed at a heating rate of 10°C/min and the T_g's were located by the method described by Kinshore[13].

RESULTS AND DISCUSSION

Van der Does *et al.*[14] have recently investigated the reactions of CSI with polyisoprene followed by hydrolysis with methanolic potassium hydroxide solution. Following microanalysis of their isolated products, two main types of reaction were postulated, in agreement with previous work by Graf[15] and others[16]. However, other side reactions occurred, and it was also found that not more than 75% of the olefinic double bonds reacted, even with excess CSI, possible due to steric effects[14]. By analogy with previous work, two main products, designated (I) and (II), (*Figure 1*), are expected to be formed following addition of CSI to the unsaturated dibenzoate, DB. The ratio in which structures such as (I) and (II) are formed is expected to be dependent on the structure of the olefin and not on the nature of the solvent or the reaction temperature[17]. Usually structures such as (I) predominate (about 70%)[17].

The microanalytical results for the *N*-sulphonyl derivatives (BOS) do not agree with the calculated values of (I) and (II) (identical compositions) and could not be explained simply by the presence of unreacted dibenzoate in the mixture. Other non-volatile products, with a relatively high percentage of sulphur and low percentage of chlorine appear to have formed in addition to (I) and (II), probably resulting from unknown secondary reactions.

These non-volatile side-products on hydrolysis do not appear to have regenerated -OH groups, since the calculated microanalytical values for the ionomers PUM and PUN are in good agreement with experimental values, assuming that BOH(III) and BOH(IV) are formed in a molar ratio of 70:30 and that only these latter products react to form the final polyurethane ionomers.

The infra-red spectra of the dibenzoate (DB), the CSI addition product (BOS), and the ionic diols (BOH) are shown in *Figure* 2 (*a*), (*b*) and (*c*), respectively. The strong absorption band at 1800 cm^{-1} shown in *Figure* 2 (*b*) is due to the carbonyl groups of β-lactam-*N*-sulphonyl chloride while the band at 1730 cm^{-1} is due to the carbonyl groups of the ester of the dibenzoate and the β-γ-unsaturated carbonamide-*N*-sulphonyl chloride. The absorptions at 1175 cm^{-1} and 1405 cm^{-1} are characteristic of $-SO_2Cl$ groups.

The infra-red spectrum of the hydrolysed product, i.e. ionic diol (BOH), does not show the absorption band 1800 cm^{-1} which is characteristic of the β-lactam-*N*- sulphonyl chloride. The absorptions at 3400 cm^{-1} and 1565 cm^{-1} correspond to the hydroxyl group and carboxylate ions respectively, Infra-red and n.m.r. spectra of polyurethane ionomer (PUM) are shown in *Figures 3* and *4*, respectively. *Table* 1 shows the glass-transition temperatures, T_g, and number-average molecular weights of the polyurethanes, $\bar{M}_n$.

The introduction of ionic groups in the polyurethanes results in an increase in their glass transition temperatures. Similar results were reported by Fitzgerald *et al.*[18] who found an increase of 11°C in the T_g of polystyrene when it was copolymerized with 10% of methacrylic acid salt. Noshay *et al.*[19] have related this increase with the resulting increased intermolecular association through the polar ionic sites, and also to the increased molecular bulkiness. The introduction of ionic groups often also results in the formation of ionic domains which act as physical crosslinks and reinforce the residual hydrogen bonds leading to an increase in the glass transition temperature. The dependence of T_g on the ionic content of a polymer may be explained in terms of volume shrinkage due to the formation of crosslinks. The effect of the nature of the counterions on T_g is not clearly understood although cation valency is expected to have some effect on T_g.

G.p.c. results show that all the polyurethanes have comparable number-average molecular weights and molecular weight distributions. Consequently the higher T_g values for the ionic polyurethanes could not be due to molecular weight differences.

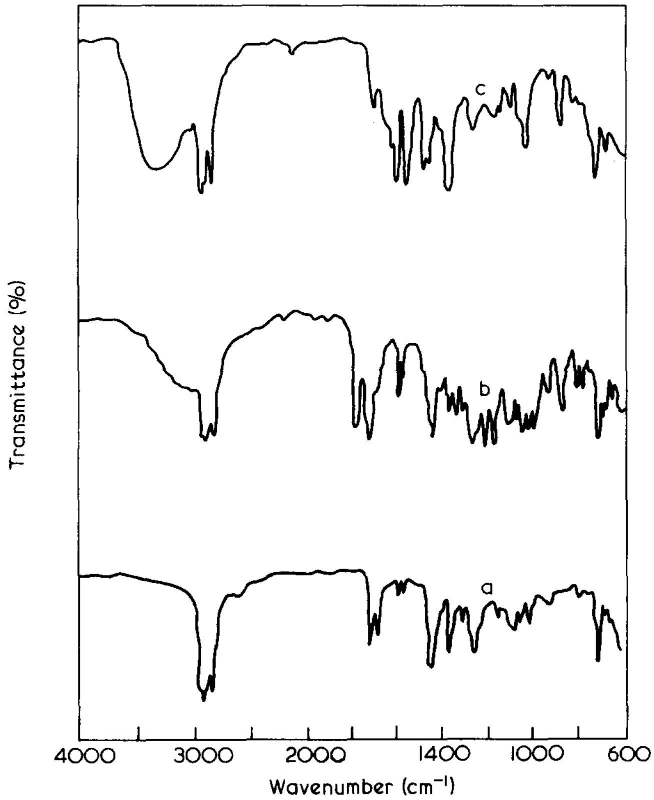


Figure 2 Infra-red spectra of intermediates. (a) *cis*-2-butene-1,4-dibenzoate (DB); (b) CSI addition product (BOS); (c) ionic diols (BOH)

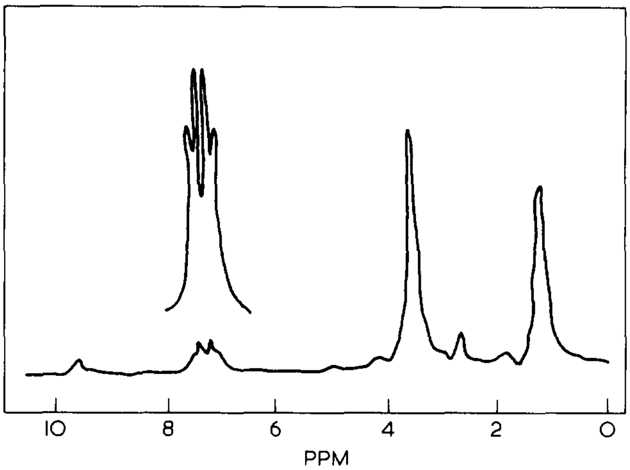


Figure 4 N.m.r. of polyurethane ionomer (PUM)

Table 1 Glass transition temperatures, T_g, and molecular weights, $\bar{M}_n$, of polyurethanes

Sample code	T_g (K)	$\bar{M}_n \times 10^{-4}$
PUA	236	3.06
PUM	249	3.20
SHE/2	248	3.00
SHE/3	248	3.02

SHE/2 and SHE/3 are polyurethane ionomers in which some of the $-\overset{+}{N}(But)_4$ groups were replaced by Na^+ and K^+ respectively

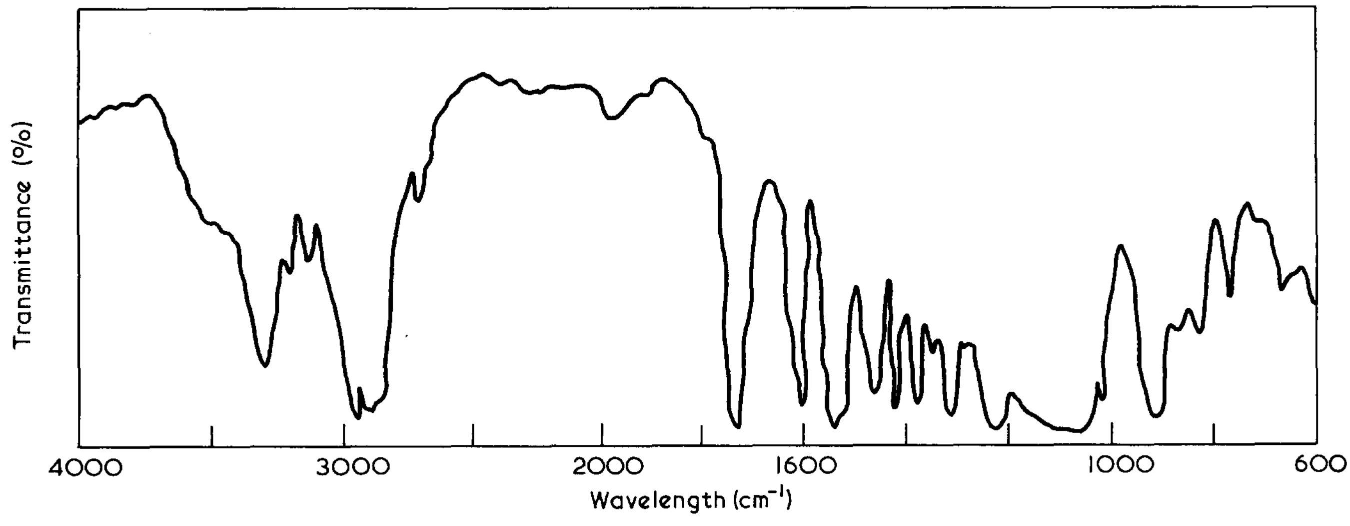


Figure 3 Infra-red spectra of polyurethane ionomer (PUM)

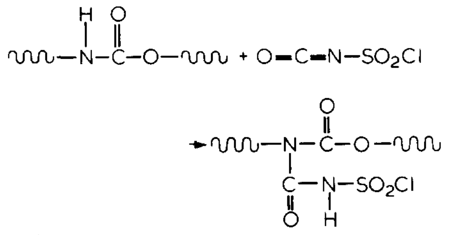
Table 2 Equilibrium % water sorption at 25°C for polyurethanes

Sample code	Equilibrium water sorption % (w/w)
PUA	2.84
PUM	8.09
SHE/2	16.72

The values of equilibrium water sorption at 25°C for the polyurethanes are shown in *Table* 2.

The polyurethane, PUA, based on poly(propylene glycol) has a low equilibrium water sorption value due to the hydrophobic nature of the soft block. However, the introduction of ionic groups in this polyurethane results in an increase in its equilibrium water sorption, *Table* 2. Eisenberg *et al.*[20] and others[21] have reported similar observations on the dependence of equilibrium water-uptake values on the percentage of ionic groups and on the nature of the counterions.

Attempts were also made to synthesize the β-lactam derivatives from the unsaturated polyurethanes by reacting them directly with CSI. However, the infra-red spectrum and microanalytical results showed that, instead of the lactam formation, CSI reacts with the labile hydrogen on the polyurethane in preference to the double bond in the polymer. Such reactions of CSI with primary and secondary amines, amides of carboxylic and sylphonic acids, imides and lactams have been previously reported[22]. A reaction such as that shown in equation (1) may be involved:



$$\sim\!\sim\!\sim-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\sim\!\sim\!\sim + O{=}C{=}N-SO_2Cl \rightarrow \sim\!\sim\!\sim-\underset{\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}-SO_2Cl}{\underset{|}{N}}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\sim\!\sim\!\sim \qquad (1)$$

One other difficulty involved in the reaction of the unsaturated polyurethanes with CSI is the limited choice of solvents. The polyurethanes with high hard block content were soluble only in solvents such as dimethylsulphoxide and *N,N*-dimethyl formamide. Both these solvents react vigorously with CSI[23], thus preventing the formation of the β-lactam derivative of these polyurethanes.

Further studies are continuing with regard to the morphology, mechanical properties and biocompatability of these polymers. Results will be reported in subsequent papers.

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