New polyurethane ionomers containing phosphonate groups

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A new ionic diol, 1,2-dihydroxypropylphosphonic acid (DPPA), was synthesized from epibromohydrin and triethyl phosphite. DPPA was used subsequently as a chain extender diol in the two-step synthesis of polyurethane ionomers. Both DPPA and the polyurethane ionomers were characterized by Fourier-transform infra-red and ^{1}H and ^{31}P nuclear magnetic resonance spectroscopy. Thermal analysis by differential scanning calorimetry was performed on the ionomers.

(Keywords: ionomer; polyurethane; ionic diol)

INTRODUCTION

Polymers containing a relatively small number of ionic groups in the polymer backbone or side chains are termed ionomers. Polyurethane ionomers are a relatively new class of block copolymers that are both academically and commercially important. Consequently, growing interest has been paid to the synthesis of polyurethane ionomers[1,2].

Several methods of introducing ionic groups into polyurethanes have been reported in the past[3,4]. Most of these studies involved the initial synthesis of the polymers, which were subsequently modified by chemical methods. Another way of introducing ionic groups is to use an ionic-diol chain extender for the synthesis of polyurethane ionomers.

This paper describes the synthesis and characterization of an ionic diol containing a phosphonic acid group and its subsequent use in the synthesis of polyurethane ionomers with phosphonic acid groups pendent to the backbone.

EXPERIMENTAL

Solvents and reagents

Dimethylsulfoxide (DMSO; Aldrich) was dried over calcium hydride powder for one week, distilled under reduced pressure and stored over 3 Å molecular sieves.

N,N-Dimethylformamide (DMF; Aldrich) was dried over barium oxide powder for three days and then distilled under reduced pressure. It was stored over 3 Å molecular sieves until required.

Epibromohydrin (Aldrich) was used as supplied.

Triethyl phosphite (Aldrich) was dried over sodium for two days, then distilled under reduced pressure. It was then stored in a stoppered flask under an argon blanket.

Butane-1,4-diol (BD; BDH) was distilled under reduced pressure and stored over 3 Å molecular sieves.

4,4′-Diphenylmethane diisocyanate (MDI; Avon Tyres) was distilled under reduced pressure (1 mmHg) and stored over silica gel at −20°C.

Poly(propylene glycol) (molecular weight 1025) (PPG; BDH) was heated at 100°C in a rotary evaporator under reduced pressure for 10 h. It was then stored over 3 Å molecular sieves until required.

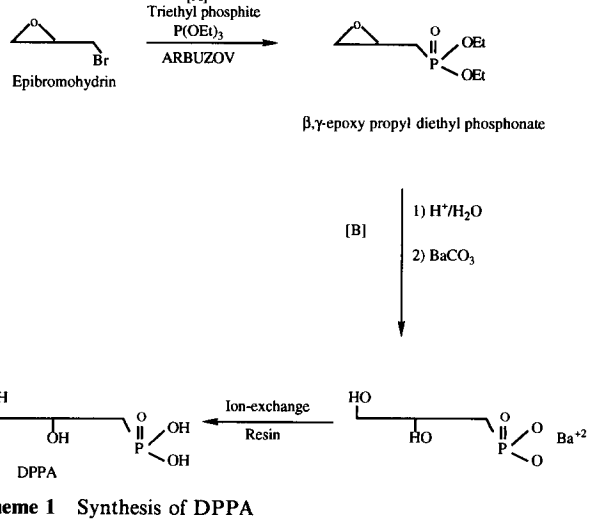
Dibutyltin dilaurate (Aldrich) was used as supplied.

Barium carbonate (Aldrich) was used as supplied.

Amberlite resin IR-120(H) was washed repeatedly with distilled water prior to use; capacity, 1.9 meq/ml.

Synthesis of 1,2-dihydroxypropylphosphonic acid (DPPA)

The reaction scheme involved in the synthesis of DPPA is shown in *Scheme 1*, and is discussed below.



Scheme 1 Synthesis of DPPA

Synthesis of β,γ-epoxypropyl diethylphosphonate. This compound was synthesized following the method of Griffin and Kundu[5].

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Freshly distilled triethyl phosphite (68.5 g, 0.5 mol) and epibromohydrin (83 g, 0.5 mol) were transferred to a 250 cm^3 three-necked flask containing an argon purge, a thermometer and a distillation column fitted with an anhydrous $CaCl_2$ guard tube. The mixture was heated slowly under an argon atmosphere to 120°C, at which point ethyl bromide began distilling over. The temperature of the reaction mixture was then maintained at 130°C for a further 4 h and finally at 158°C for another hour to ensure complete removal of ethyl bromide from the reaction mixture.

Fractional distillation of the reaction mixture, under reduced pressure, via a Vigreaux column gave as a distillate β,γ-epoxypropyl phosphonate (63 g, 65% of theoretical; b.p. 108°C at 2 mmHg).

Hydrolysis of epoxypropyl phosphonate. The successful cation-exchange resin-catalysed hydrolysis of esters of acetoacetic and malonic acids has been reported in literature[6]. The simultaneous hydration of epoxy ring and hydrolysis of ester groups was carried out by using strongly acidic Amberlite IR 120(H) resin in an aqueous medium.

Epoxypropyl phosphonate (9.7 g, 0.5 mol) was placed in a flask containing water (75 cm^3) and washed Amberlite resin IR 120(H) (7.5 ml). The contents were refluxed for 24 h with constant stirring. Following this, the mixture was cooled to room temperature and filtered.

The acid was recovered as the barium salt in the following manner. Water (50 cm^3) was added to the filtrate and then neutralized by adding $BaCO_3$. A slight excess of $BaCO_3$ was added to make the medium alkaline. The neutralized solution was filtered and then centrifuged to remove the last trace of barium carbonate. Finally, the aqueous solution was concentrated to 20 cm^3 by rotaty evaporation and left overnight to crystallize.

The crystalline product was filtered under suction and washed with alcohol. Alcohol was added to the mother liquor from the crystallization to recover a further amount of barium salt. The combined product was dried for a week in a vacuum oven at room temperature. Finally, the barium salt was purified by recrystallization from hot water and dried in the same manner. The yield of purified barium salt of 1,2-dihydroxypropylphosphonic acid was about 58%.

The free acid, 1,2-dihydroxypropylphosphonic acid, was generated from the barium salt by passing a 2% (w/v) aqueous solution down an ion-exchange column consisting of Amberlite AR-120(H) resin. The eluant, which was acidic, pink red towards methyl orange, was concentrated under reduced pressure in a rotary evaporator to a thick, viscous, non-crystallizing liquid.

Polymerization

Polyurethanes were synthesized by a two-step process. A prepolymer based on 4,4'-diphenylmethane diisocyanate (MDI) and poly(propylene glycol) (PPG) was prepared followed by chain extension with short-chain diols, 1,4-butanediol (BD) and 1,2-dihydroxypropylphosphonic acid (DPPA).

MDI and PPG were heated for 1½ h at 90°C under argon. The reaction mixture was then cooled to 70°C and 30 cm^3 DMSO was added. BD or/and DPPA, dissolved in 30 cm^3 DMSO, was then added dropwise, through a pressure-equalizing funnel, which was followed by the addition of the catalyst, dibutyltin dilaurate (0.10 g). The reaction mixture was again heated at 90°C for 7 h and finally the polymer was precipitated from water. It was then dried in a vacuum oven at 40°C for several days. The amounts of MDI, PPG, BD and DPPA taken to prepare different polymers are listed in *Table 1*. The resultant polyurethanes were designated the MPP series.

Table 1 Reactant quantities used for MPP series[a]. Molar ratios, MDI:PPG:(BD+DPPA)=3:1:2

Reactant	MPP 0%	MPP 20%	MPP 60%	MPP 100%
MDI (g)	5.000	5.000	5.000	5.000
PPG (g)	6.83	6.83	6.83	6.83
BD (g)	1.2	0.96	0.48	0.0
DPPA (g)	0	0.415	1.248	2.08

[a] 0%, 20%, 60%, 100% indicate the molar percentage of DPPA in the mixture of BD and DPPA

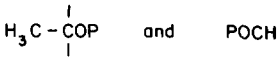
RESULTS AND DISCUSSION

^1H n.m.r.

Proton n.m.r. spectra were recorded on a Bruker WM 250 MHz spectrometer.

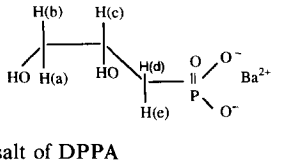
The proton spectra of epoxypropyl phosphonate and the Ba salt of DPPA were recorded in d_6-DMSO and D_2O, respectively, and are shown in *Figures 1a* and *1b* respectively. The differences are clear as the epoxide is converted to diol and the ethyl ester groups are hydrolysed.

In the spectrum shown in *Figure 1a*, the triplet at 1.2 ppm and the multiplet centred at 3.9 ppm are due to



groups, respectively. It is probable that the multiplet due to the methine proton of the epoxy ring is also merged into the multiplet at 3.9 ppm. The multiplet at 1.0 ppm is due to the $-CH_2$ group of the epoxy ring. The multiplet structure could be explained by assuming an AMX system for three ring protons (X = methine proton and A,M = methylene protons) with a very small ($\sim$0 Hz) $^3J^{AX}$ or $^3J^{MX}$. The multiplet at 1.7 ppm seems to be a double AB system, which is due to the fact that the AB system formed by the two methylene protons in the P–CH_2–CH group is doubled by the $^2J^{P-H}$. Some confirmation of this is given in the spectrum of *Figure 2c*, which shows that there exists a coupling between phosphorus and the protons of the P–CH_2–CH moiety. The singlet at 3.3 ppm is probably due to water present as impurity in d_6-DMSO. The reason for the doublet centred at 1.4 ppm, however, remains uncertain.

Figure 1b is a complex one due to the presence of the proton on the asymmetric carbon centre generated on hydration of the epoxide ring, as well as due to coupling with phosphorus. The individual hydrogen atoms are shown in the structure in *Scheme 2*. The broad singlet at 4.8 ppm is due to HOD groups. The multiplet at 3.99 ppm



Scheme 2 The Ba salt of DPPA

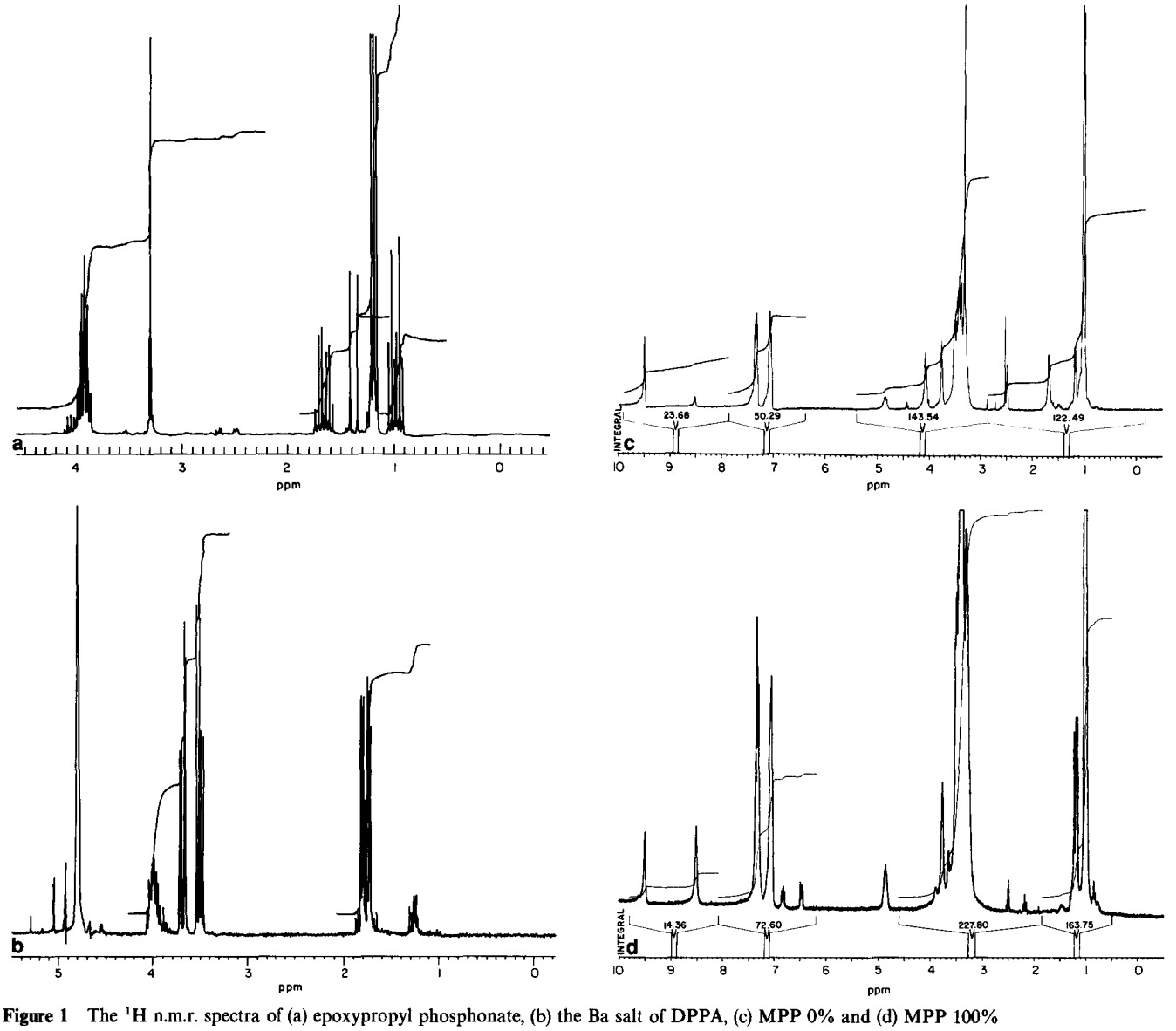


Figure 1 The ^1H n.m.r. spectra of (a) epoxypropyl phosphonate, (b) the Ba salt of DPPA, (c) MPP 0% and (d) MPP 100%

corresponds to the methine proton H(c). The double doublets of the methylene protons are due to them being diastereotopic and thus being magnetically and chemically non-equivalent. The resonances at 1.80 and 1.70 ppm are due to methylene protons H(e) and H(d), respectively, which geminally couple with each other and also couple to the P atom. The double doublets at 3.70 and 3.5 ppm are due to methylene protons H(a) and H(b), respectively, both of which geminally couple with each other and also couple to the methine proton H(c).

Figures 1c and *1d* show the proton spectra of MPP 0% and MPP 100%, respectively, recorded in d_6-DMSO. The proton n.m.r. spectra of these two polymers are fairly similar. One notable difference is the absence of peaks at 1.7 and 4.1 ppm due to BD in the spectrum of MPP 100%. In both the spectra there are peaks at 8.5 and 9.5 ppm. Chokki *et al.*[7] have indicated from a study of polyurethane model compounds involving toluene diisocyanate that peaks due to the urethane group appeared not only at 9.5 ppm but also at 8.5 ppm. Probably, the peak at 8.5 ppm shown by the present polymers is due to urethane groups but there is a possibility that urea linkages are also formed due to the presence of traces of water in one of the reactants or solvent.

The CH_3 protons of PPG groups in polyurethanes were in different chemical environments. Most CH_3 groups were in the polyol backbone while two CH_3 groups were closer to the urethane linkage. The former CH_3 proton peaks appeared at 1.0 ppm while the latter appeared at 1.2 ppm. The combined integrated area of these two peaks was thus due to the total CH_3 protons of PPG. The aromatic proton signal due to MDI protons appeared at around 7.0 to 7.5 ppm.

The molar ratio of PPG to MDI in the polyurethane could thus be calculated from the combined peak areas of the CH_3 protons from PPG to the areas due to aromatic protons from MDI. As the molecular weight of PPG was 1025, the unreacted PPG could be represented as

$$H\text{-}\left(\text{-}O\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}\right)_n OH \qquad \text{where } n = 17.4$$

Thus each MDI group in the chain had eight aromatic protons and one PPG group in the polymer chain had $3 \times 17.4 = 52.2$ methyl protons, on average.

If the total integrated absorption area in an n.m.r. spectrum of a polyurethane for CH_3 protons of PPG

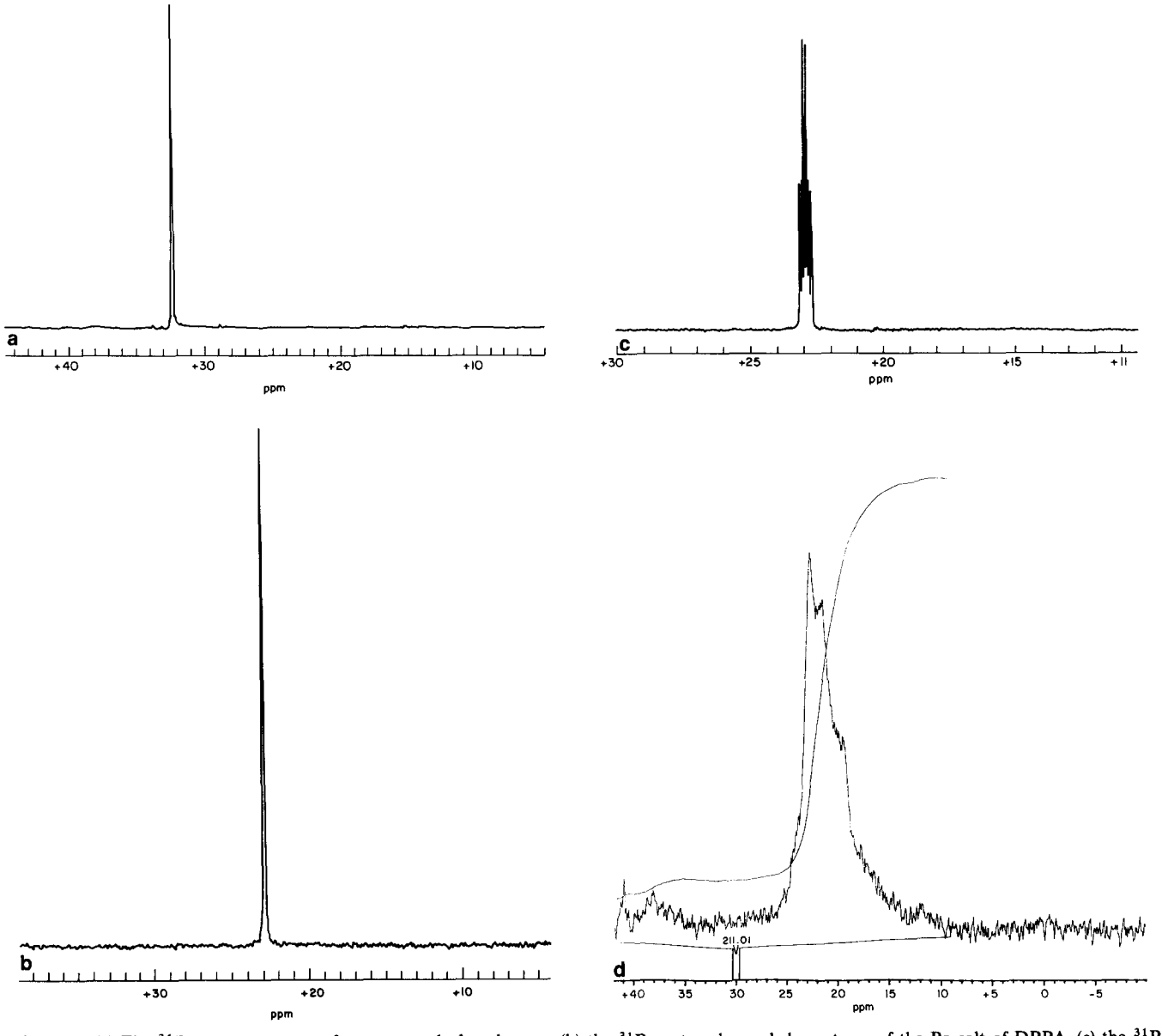


Figure 2 (a) The ^{31}P n.m.r. spectrum of epoxypropyl phosphonate, (b) the ^{31}P proton decoupled spectrum of the Ba salt of DPPA, (c) the ^{31}P proton non-decoupled spectrum of the Ba salt of DPPA and (d) the ^{31}P n.m.r. spectrum of MPP 100%

was A_1 and the corresponding integrated area for aromatic protons of MDI was A_2, then $[(A_1/52.2)/(A_2/8)]$ represents the molar ratio of PPG to MDI in the polymer. The ratios of PPG to MDI actually in the polymer and that used in the synthesis were found to be within 3.9% of each other.

^{31}P n.m.r.

^{31}P n.m.r. spectra were recorded on a Bruker WM 250 MHz spectrometer. The reference used was phosphoric acid (0 ppm).

Figures 2a, 2b, 2c and *2d* show the ^{31}P n.m.r. spectra of the phosphonate ester, the Ba salt of DPPA (both decoupled and non-decoupled) and MPP 100%. ^{31}P n.m.r. spectra of the polymers prove the successful introduction of phosphonic acid groups into the polyurethane. The phosphonate ester signal appears at +32 ppm, while the free acid appears at +23 ppm. A ^{31}P signal in the polymer also appears at around +23 ppm. The non-decoupled spectra of the Ba salt of DPPA is composed of two triplets, due to coupling of methylene and methine protons with phosphorus.

FT*i.r. analysis*

*FT*i.r. spectra were recorded in a Mattson High Resolution FTIR spectrophotometer.

The ionic diol DPPA was directly examined between two NaCl plates and the spectrum is shown in *Figure 3a*. A strong band at 3327 cm^{-1} is due to O–H stretching from the diol, and the broad nature of the band indicates the presence of hydrogen bonding. The absorption between 2800 and 3000 cm^{-1} is due to C–H stretching and the bands between 1400 and 1500 cm^{-1} are due to C–H bending vibrations[8].

The broad band between 1150 and 1225 cm^{-1} is due to the hydrogen-bonded phosphoryl (P=O) group. The presence of P–O–H leads to a broad shallow absorption between 2700 and 2500 cm^{-1}. Another band due to P–O–H group is observed at 1690 cm^{-1}. Two bands in the 950–1050 cm^{-1} region are primarily due to the P–O stretching vibration and C–O stretching vibrations[9].

The polymers were analysed directly in the form of very thin film cast from a DMF solution. The spectra of MPP 0% and MPP 100% are shown in *Figures 3b* and *3c*, respectively.

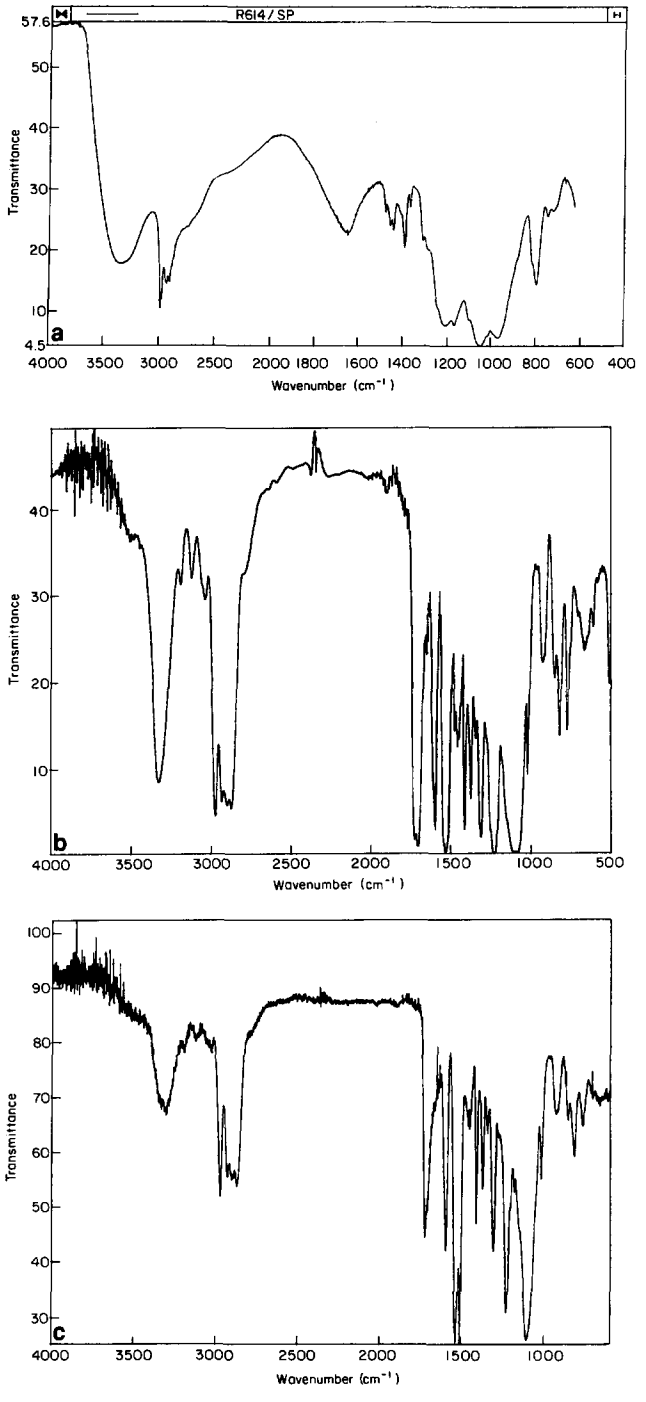


Figure 3 *F*Ti.r. spectra of (a) DPPA, (b) MPP 0% and (c) MPP 100%

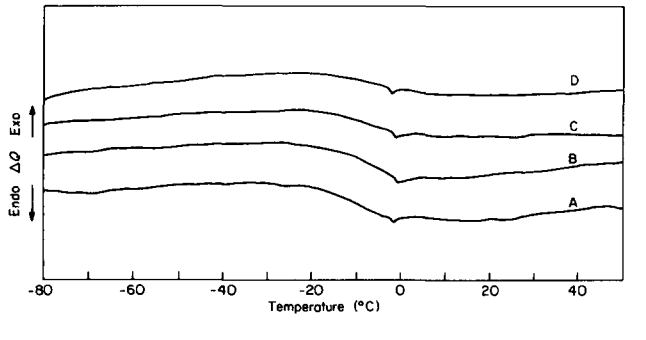


Figure 4 D.s.c. traces of the polymers: A, MPP 0%; B, MPP 20%; C, MPP 60%; and D, MPP 100%

Table 2 T_g values of different polymers

MPP 0%	10.6°C
MPP 20%	7.1°C
MPP 60%	6.5°C
MPP 100%	5.1°C

The urethane N–H stretch at 3300 cm^{-1} is relatively sharp for the non-ionic polymer. The spectrum for the ionic polymer, however, shows a broad band at this wavenumber, due to additional hydrogen bonding arising from the phosphonic acid group. The peak at 1730 cm^{-1}, due to free carbonyl, develops a shoulder at 1710 cm^{-1} for hydrogen-bonded groups[10]. This shoulder is very much prominent in the non-ionic polymer. This is probably due to the availability of phosphonic acid group (P=O) for hydrogen bonding with the urethane group.

Differential scanning calorimetry

D.s.c. studies of the polymers were performed in a Dupont 9000 Thermal Analyser. The heating rate was 10°C min^{-1}.

As the thermal behaviour of polyurethanes is dependent on their thermal history, polymers were annealed at 60°C for 72 h in a vacuum oven prior to d.s.c. studies.

D.s.c. studies were made in the temperature range −80 to 50°C, to detect any changes in the glass transition temperature of different polymers. The d.s.c. traces of different polymers are shown in *Figure 4*, and the T_g values are given in *Table 2*.

The rise in the T_g values of the polymers with the rise in the ionic content indicates a decrease in segmental motion of the soft segments. This may be due to hydrogen bonding of ether oxygens of the soft segment with the phosphonic acid groups in ionic diols.

CONCLUSION

A new ionic diol containing a phosphonate group has been synthesized. This diol has been successfully incorporated into polyurethanes containing phosphonic acid groups. The introduction of this new group influences the thermal properties of the parent polymer.

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