Polyurethane ionomers containing phosphate groups

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(Received 28 October 1992; revised 31 March 1993)

A new ionic diol, the monosodium salt of β-glycerophosphoric acid, was synthesized. The commercially available disodium salt was first converted to the β-glycerophosphoric acid which was then neutralized with the requisite amount of sodium hydroxide to yield the monosodium salt of the acid. The monosodium salt was soluble in DMSO, in contrast to the disodium salt, which was found to be insoluble in almost all solvents with the exception of water. The monosodium salt of glycerophosphoric acid (GPA-Na) was used subsequently as a chain extender diol in the two-step synthesis of polyurethane ionomers using also butane-1,4-diol, polypropylene glycol and diphenylmethane-4,4'-diisocyanate. The reaction was catalysed by using a trace of dibutyl tin dilaurate. Both the ionic diol and the polyurethane ionomers were characterized using *FT*i.r., ^{1}H n.m.r. and ^{31}P n.m.r. Differential scanning calorimetry was also performed using these polymers.

(Keywords: ionomer; polyurethane; ionic diol)

INTRODUCTION

The modification and control of polymer properties through the use of ionic functional groups have received a considerable amount of attention in recent years. It is now well established that the introduction of relatively small amounts of ionic groups into a polymer can significantly modify the mechanical and thermal behaviour of the resulting material. Such polymers are known as ionomers and a comprehensive review of the ionomer literature can be found in recent monographs[1,2] and a review article[3]. Polyurethanes are a class of highly versatile polymers and their range of use can be further broadened by the introduction of ionic groups into their structures. Consequently, growing attention has been paid to the synthesis of polyurethane ionomers[4,5].

A convenient way of introducing ionic groups to the polyurethane is to use an ionic diol chain-extender in the synthesis of polyurethane ionomers. This method has already been successfully used in this laboratory to synthesize polyurethane ionomers[6,7].

This paper describes the synthesis and characterization of an ionic diol with a phosphate side group and the subsequent use in the synthesis of polyurethane ionomers with phosphate groups.

EXPERIMENTAL

Solvents and reagents

Dimethyl sulfoxide (DMSO, Aldrich), was dried over calcium hydride for 1 week and then distilled under reduced pressure and stored over 3 Å molecular sieves. *N,N*-dimethyl formamide (DMF, Aldrich), was dried over barium oxide for 3 days and then distilled under reduced pressure and finally stored over 3 Å molecular sieves. Butane-1,4-diol (BD, BDH), was distilled under reduced pressure and stored over 3 Å molecular sieves. Polypropylene glycol 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. Diphenyl methane-4,4'-diisocyanate (MDI, Avon Tyres) was distilled under reduced pressure (1 mmHg) and stored over silica gel at −20°C. β-glycerol phosphate disodium salt (GPA-Na_2, Fluka), was used as supplied and stored at +4°C. Amberlite resin, IR-120(H), was washed repeatedly with distilled water prior to use (capacity 1.9 meq cm^{-3}). Dibutyl tin dilaurate (Aldrich) and sodium hydroxide pellets (BDH), were used as supplied.

The scheme of synthesis is shown in *Scheme 1*. A 3% (w/v) aqueous solution of the disodium salt of β-glycerophosphoric acid (GPA-Na_2) was passed through an ion-exchange column of the strongly acidic resin, Amberlite IR-120(H), at the rate of 2 cm^3 min^{-1}. The feed solution was strongly alkaline (pH = 9) and the eluent was strongly acidic (pink-red to methyl orange). The eluent was rotary evaporated at 33°C under high vacuum. The colourless viscous liquid thus obtained was β-glycerophosphoric acid, GPA.

The aqueous solution of the acid was neutralized to form the monosodium salt by adding the required amount of standard NaOH solution. The resulting solution was rotary evaporated to a thick paste which was then extracted with the minimum amount of DMSO. The monosodium salt was then precipitated by adding an excess of ethanol. This precipitate was filtered under suction, washed with ether and dried in a vacuum oven at 40°C for several days to remove the last trace of ethanol. The white hygroscopic solid was then stored in a desiccator over silica gel.

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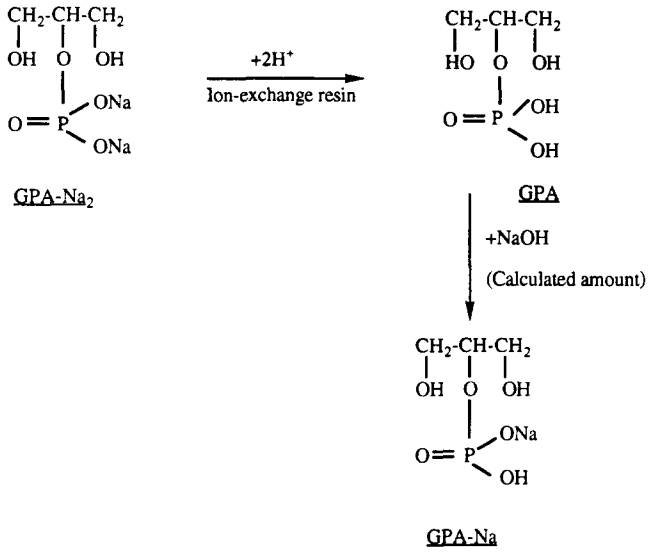
0032-3861/93/204319-06

Table 1 Reactant quantities used for the MPBS series

Reactant	MPBS0	MPBS20	MPBS40	MPBS60	MPBS80	MPBS100
MDI	1.00	100	1.00	1.00	1.00	1.00
PPG	1.366	1.366	1.366	1.36	1.366	1.366
BD	0.24	0.192	0.144	0.096	0.048	0
GPA-Na	0	0.104	0.2064	0.3096	0.412	0.516

Amounts are given in grams
Molar ratios: MDI:PPG:(BD + GPA-Na) = 3:1:2



Scheme 1 Synthesis of the monosodium salt of β-glycerophosphoric acid

Polymerization

The polyurethanes were synthesized by a two-step process. A prepolymer based on 4,4′-diphenyl methane diisocyanate (MDI) and polypropylene glycol (PPG) was first prepared followed by chain extension with short-chain diols, 1,4-butane diol (BD) and/or the monosodium salt of β-glycerophosphoric acid (GPA-Na).

MDI and PPG were heated for 1.5 h at 90°C under argon. Next, 15 cm^3 DMSO was slowly added. The reaction mixture was cooled to 80°C and BD and/or GPA-Na dissolved in 5 cm^3 DMSO was added dropwise through a pressure-equalizing funnel. This was followed by addition of the catalyst, dibutyl tin dilaurate (two drops). The reaction mixture was then heated again at 90°C for 15 h and finally the polymer was precipitated either from water (< 50 mol% ionic diol in the hard segment) or ether (> 50 mol% ionic diol in the hard segment). It was then dried in a vacuum oven at 40°C for several days. The amounts of MDI, PPG, BD and GPA-Na taken to prepare different polymers are listed in *Table 1*. The resultant polyurethanes were designated the MPBS series, and the numbers in each compound name indicate the mole percentage of GPA-Na in the reactant mixture of BD and GPA-Na, i.e. MPBS20 has 20% GPA-Na.

RESULTS AND DISCUSSION

^1H nuclear magnetic resonance

Proton n.m.r. spectra were recorded on a Bruker WM 250 MHz spectrometer. The proton spectrum of GPA was recorded in D_6-DMSO and is shown in *Figure 1a*. Three principal peaks were observed: a doublet at 3.5 ppm was due to two methylene protons, a multiplet at 4.0 ppm was due to to the central methine proton and a singlet at 5.4 ppm was due to the hydroxyl protons.

Figures 1b and *c* show the ^1H n.m.r. spectra of the polyurethanes MPBS0 and MPBS100, respectively, recorded in D_6-DMSO. The ^1H n.m.r. spectra of these polymers are fairly similar. One notable difference is the absence of peaks at 1.7 ppm and 4.1 ppm, due to BD, in the spectrum of the ionomer. Another difference is observed in the shape of the urethane $-O-\overset{\overset{O}{\|}}{C}NH-$ peak at 9.5 ppm. The urethane peak of the ionomer, *Figure 1c*, develops another small peak at a slightly higher value than 9.5 which may be due to deshielding of the urethane proton by ionic groups. Also, in *Figure 1b*, there is a small ^1H n.m.r. peak at 8.5 ppm. Chokki *et al.*[8] have indicated from a study of polyurethane model compounds, involving toluene diisocyanate, that peaks due to the urethane group appear not only at 9.5 ppm but also at 8.5 ppm. The peak at 8.5 ppm shown in the present polymers is probably 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 rather broad peak at 9.00 ppm shown in *Figure 1c* is probably due to the proton of the –OH group of the phosphate.

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 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

$$H\text{-}\left[O\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_2\right]_n\text{-}OH \quad \text{where } n = 17.4$$

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 a n.m.r. spectrum of a polyurethane for CH_3 protons of PPG was A_1 and the corresponding integrated area value for

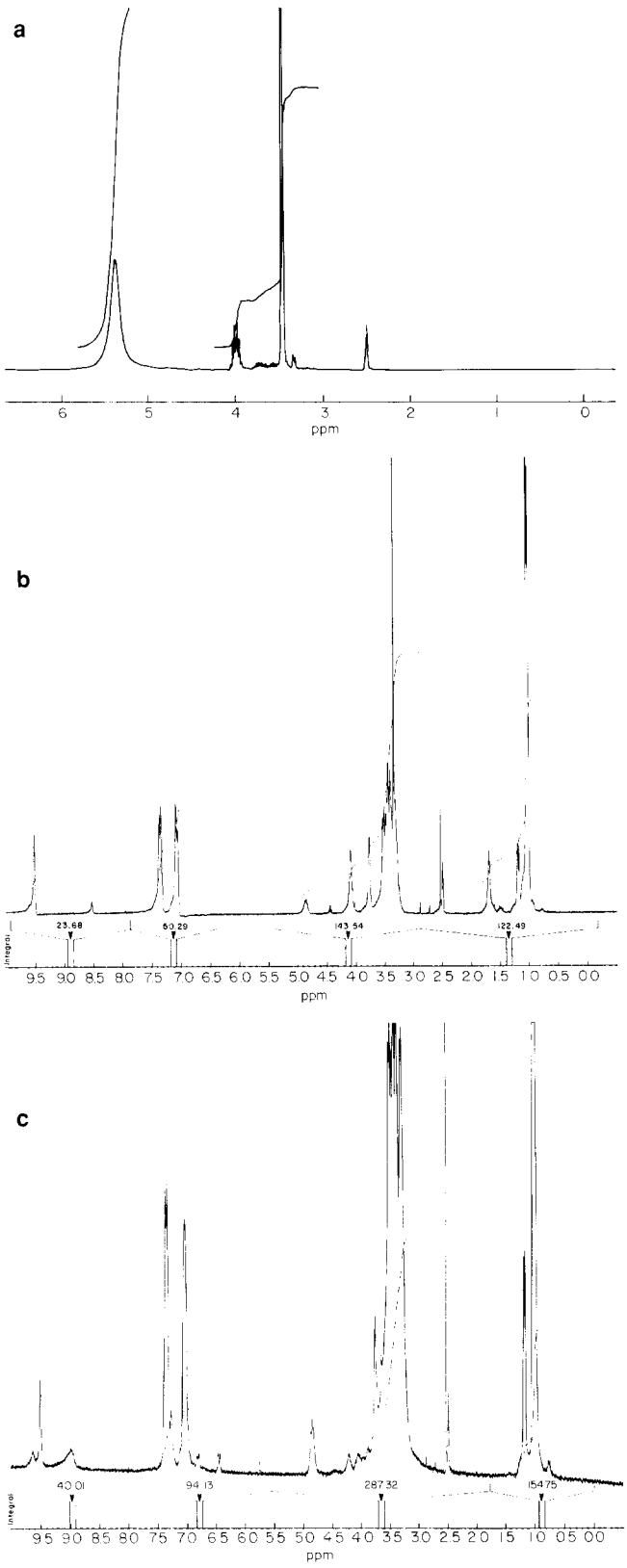


Figure 1 ^{1}H n.m.r. spectra of (a) GPA, (b) MPBS0 and (c) MPBS100

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 molar ratio of PPG to MDI actually in the polymer and that used in the synthesis were found to be in good agreement, as shown in *Table 2*.

^{31}P nuclear magnetic resonance

^{31}P n.m.r. spectra were recorded using a Bruker WM 250 MHz spectrometer. The reference used was phosphoric acid. All the spectra were recorded in D_6-DMSO.

Figures 2a and *b* show the decoupled and non-decoupled ^{31}P n.m.r. spectra of GPA-Na. *Figure 2c* shows the ^{31}P non-decoupled spectra of MPBS100. Whereas the decoupled spectrum of GPA-Na is a sharp singlet at +2 ppm, the non-decoupled spectrum is a triplet centred at +2 ppm[9]. The triplet nature of the non-decoupled spectrum may be due to coupling with the methine proton and the acidic proton, respectively. However, the triplet peak is well developed in the polymer but not in the monomer. This indicates the rise in the P–H coupling constant in the polymers compared with the monomer, but a suitable explanation of this phenomenon needs further work.

FT*i.r. analysis*

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

The ionic diol GPA was examined between two NaCl plates and the spectrum is shown in *Figure 3a*. A strong band at 3325 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.

The P=O group is detected by the presence of a medium to strong i.r. band[10] with a frequency between 1087 and 1314 cm^{-1}. A medium strength absorption is observed at 1249 cm^{-1}. The $\begin{matrix} >P\text{–}OH \\ \| \\ O \end{matrix}$ group is normally characterized[10] by bands in the regions 1600–1740 cm^{-1} and 917–1040 cm^{-1}. The spectrum of the diol shows the presence of bands at 1725 cm^{-1} and 1020 cm^{-1}.

The polymers were analysed directly in the form of very thin films cast from the polyurethanes in DMF solution. The spectra of MPBS0 and MPBS100 are shown in *Figures 3b* and *c*, respectively.

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 ionic groups. The peak at 1730 cm^{-1} due to free carbonyl develops a shoulder at 1710 cm^{-1} due to hydrogen-bonded groups[11]. This shoulder is much more prominent in the non-ionic polymer than in the ionic polyurethane. This probably due to the availability of ionic groups for hydrogen bonding within the urethane groups.

Differential scanning calorimetry

D.s.c. studies of the polymers were performed using a Du Pont 9000 Thermal Analyser. The d.s.c. studies were carried out in the temperature ranges −80 to +50°C and 35 to 380°C. The heating rate was 10°C min^{-1}.

Table 2 Comparison of the (PPG/MDI) molar ratios calculated from ^{1}H n.m.r. of the polymers and that used in synthesis, for MPBS0 and MPBS100 polyurethanes

Polymer designation	Molar ratio of PPG/MDI in the polyurethanes (calculated from n.m.r. spectra)	Molar ratio of PPG/MDI used in the synthesis
MPBS0	0.32	0.33
MPBS100	0.32	0.33

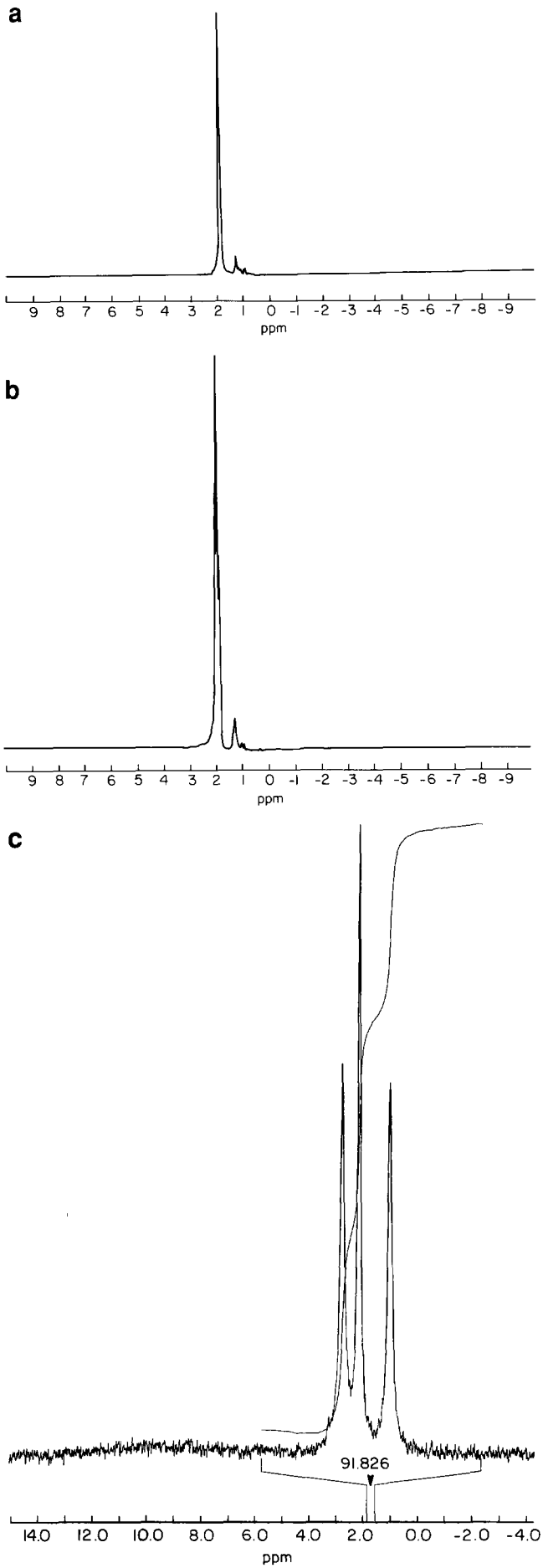


Figure 2 (a) ^{31}P decoupled spectrum of GPA-Na; (b) ^{31}P non-decoupled spectrum of GPA-NA; (c) ^{31}P non-decoupled spectrum of MPBS100

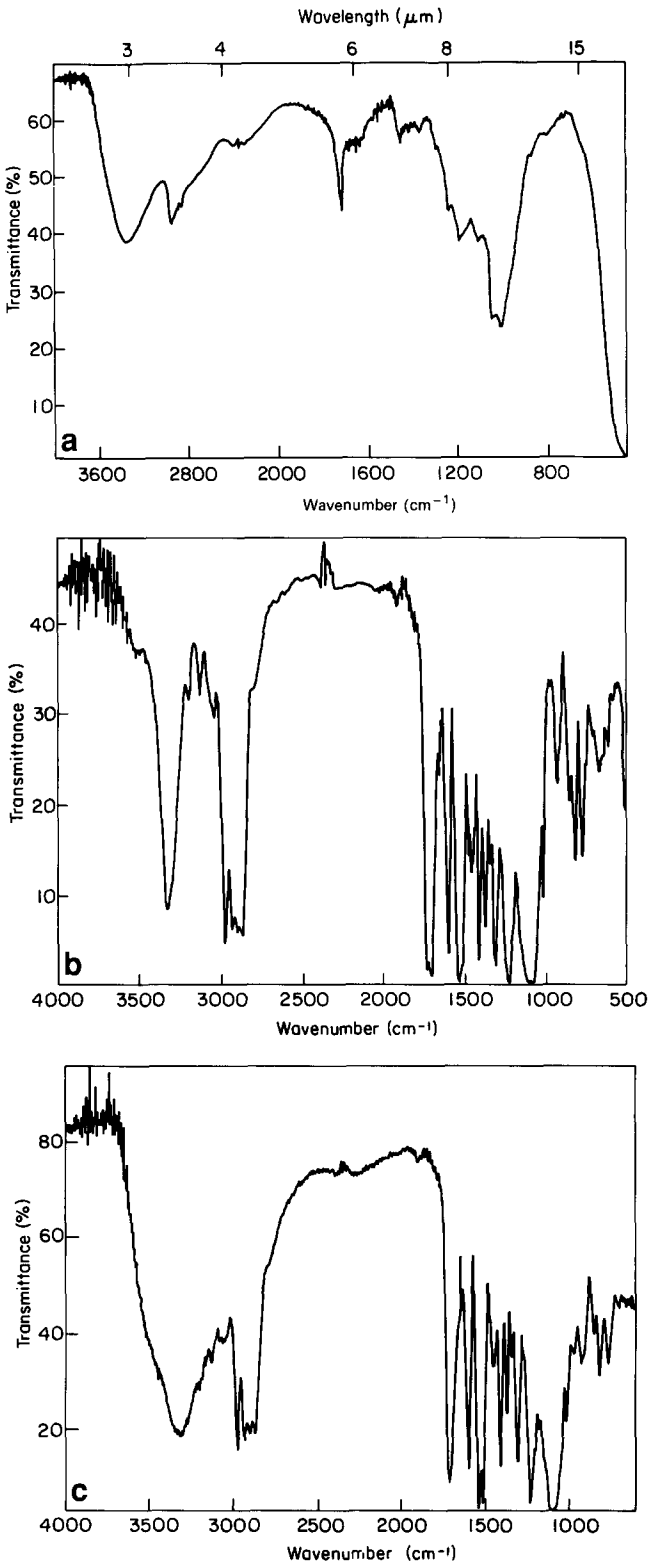


Figure 3 *FT*i.r. spectra of (a) GPA, (b) MPBS0 and (c) MPBS100

As the thermal behaviour of any polyurethane is strongly dependent on its previous thermal history, all the samples were first annealed at 60°C for 72 h in a vacuum oven prior to the d.s.c. studies. These studies were performed in the low-temperature region basically to detect the glass transition temperature of the soft PPG segments in the polyurethanes.

Using the d.s.c. traces, the values of T_g for the soft segments are shown in *Table 3*. In each case, the T_g values were assumed to be the midpoint of the steepest portion

Table 3 Glass transition temperatures (T_g) of soft segments

Sample	T_g (°C)
MPBS0	−10.6
MPBS20	−4.3
MPBS40	−3.4
MPBS60	−4.1
MPBS80	−5.8
MPBS100	−6.7

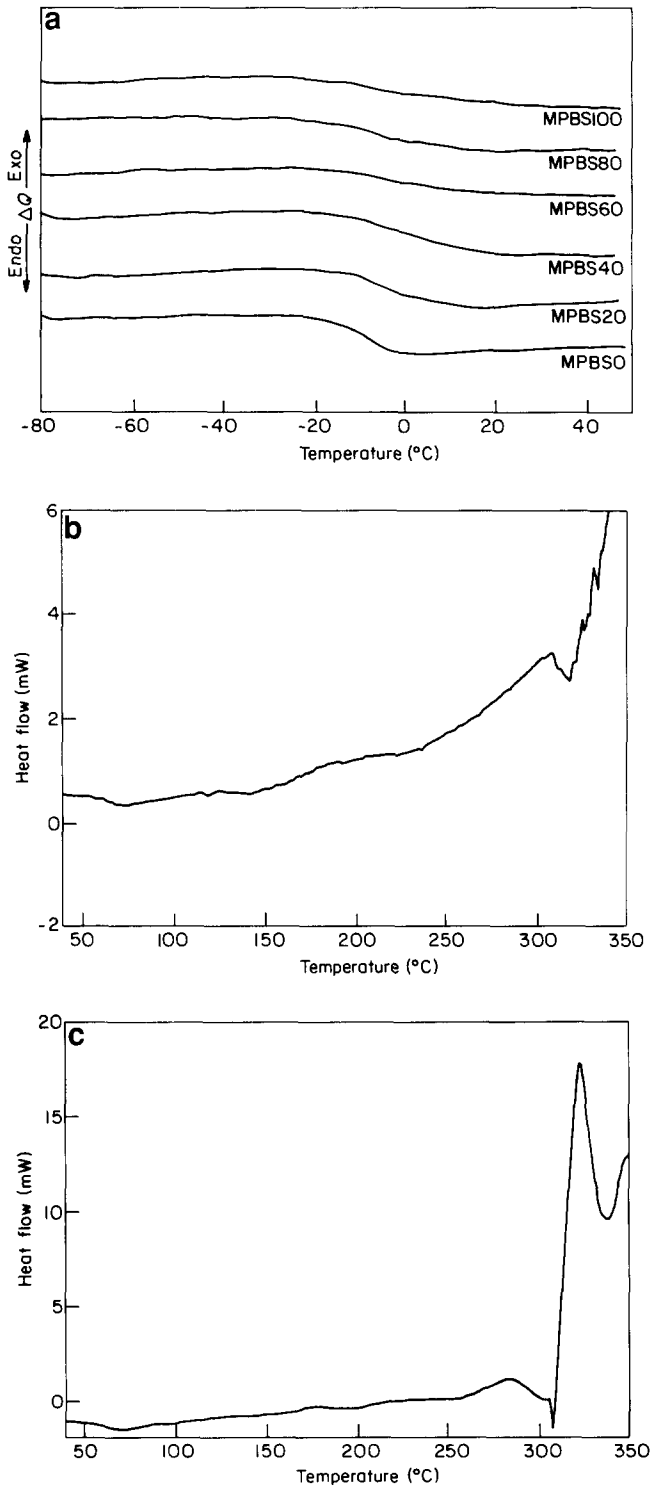


Figure 4 (a) D.s.c. traces of the MPBS series polymers in the low-temperature region (−80 to +50°C); (b) d.s.c. trace of MPBS0 in the high-temperature region (35–380°C); (c) d.s.c. trace of MPBS100 from 35 to 380°C

of the trace of the endothermic change, *Figure 4*. In all instances, the T_g values of the PPG segments in the polyurethanes were higher than the T_g values of pure free PPG (about −63°C and dependent on molecular weight). There appears to be an initial increase of soft segment T_g with increase in ionic content (MPBS0–MPBS40) but thereafter, at higher ionic contents, the soft segment T_g decreases (MPBS40–MPBS100).

The explanation of these results probably depends on the fact that increased ionic content in the hard blocks increases phase separation and ionic aggregation, lowering T_g, whereas interaction between the Na^+ ions and the polyether segments raises T_g. All these effects would broaden the T_g region.

The second set of d.s.c. studies was done in the high-temperature region, 35–380°C. According to Seymour and Cooper[12], the d.s.c. endotherms in the regions of 80°C and 150–170°C are due to disordering of hard segments with relatively short-range order. A third well developed endothermic peak at around 200°C appears in those polyurethanes having relatively well ordered microcrystalline aromatic polyurethane segments. The appearance of the third peak is dependent on the length of the hard segment: the longer the hard segment, the more prominent is this peak.

Figures 4b and *c* show the d.s.c. traces of MPBS0 and MPBS100 in the high-temperature region. In both traces, two endothermic transitions are detected in the regions 80–100°C and 150–170°C. However, the third endothermic change at around 200–250°C is very broad, which is due to the lack of a high degree of long-range order. The hard segment to soft segment ratio is only approximately 1:1 in the polymers. Thus the hard-segment lengths will not be sufficient to give rise to long-range order.

A further rise in temperature degrades the polymer. For MPBS0 this decomposition peak is observed at 318°C whereas for MPBS100, peaks are observed at both 310 and 340°C. The peak at 340°C is particularly well developed. Further work is needed to explain the existence of these two peaks.

CONCLUSION

A new ionic diol has been synthesized and has been successfully used as a chain extender diol in the synthesis of polyurethane ionomers. The new polyurethanes have been characterized using ^1H and ^{31}P n.m.r., *FT*i.r. and d.s.c.

ACKNOWLEDGEMENT

The authors thank the Government of Assam (India) for the financial support given to D. K. K.

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