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SYNTHESIS AND CHARACTERIZATION OF POLYURETHANE ZWITTERIONOMERS

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ABSTRACT

Polyurethanes were synthesized using *N,N*-bis(2-hydroxy ethyl) isonicotinamide as the dihydroxy component. Simple polyurethanes were prepared with NCO/OH ratio of 1 using tolylene diisocyanate and hexamethylene diisocyanate. Chain extended polyurethanes were prepared using prepolymers based on poly (tetramethylene oxide) glycol. The polyurethanes were converted into the zwitterionomer by quaternizing the pendant nitrogen of the pyridine ring with 1,3-propane sultone. The base polyurethanes and the polyurethane ionomers were characterized by FTNMR and FTIR and thermal stabilities were analysed using thermogravimetric analyser.

INTRODUCTION

Polyurethane ionomers are a class of block copolymer in which the properties could be tailor made according to their end use. Incorporation of ionic groups into the polymer improves their final properties in certain applications. Different routes to introduce ionic groups in polyurethanes have

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been carried out of which polyurethane cationomers are prepared by reacting tertiary nitrogen or sulphur containing diols followed by quaternization of the tertiary nitrogen or the ternization of the sulphur atom (1-8). Alternatively aliphatic and aromatic diols and diamines with ionic groups are incorporated in the polymer backbone in the chain extension stage to prepare anionomers (9-12). Post polymer modification technique is also used to introduce ionic groups in to the polyurethane chain (13,14).

Pyridine based polymers are used to prepare polyurethanes, polyesters, polyamides, polyimides and epoxy resins.(15-18) These pyridine incorporated polymers have been of interest to prepare ionomers since introduction of the pyridine ring in the polymer backbone creates a reactive tertiary nitrogen that could be quaternized to form ionomers. Earlier work in this field has been done by Fouss et al., where they prepared poly vinyl pyridine ionomers and studied their solution properties (19-21). More detailed study using different quaternizing agents was done mainly using poly vinyl pyridine (22,23). Pyridine based systems have been used where the tertiary amine sites are converted into sulpho betaine derivatives (24-27). Eisenberg et al., have recently studied in detail pyridine based ionomers which were prepared by the quaternization of the pyridinium nitrogen using alkyl halides (28-30)) In our work involving the study of polyurethane ionomers using pyridinium moieties with different spacial architecture and their structure property relationships we have selected a diol with hydroxyl groups in the side chain of the aromatic ring. We report here the synthesis and characterization of polyurethane ionomers containing sulphobetaine units using N,N-bis (2-hydroxy ethyl) isonicotinamide.

EXPERIMENTAL

Materials

Poly (tetramethylene oxide) glycol (PTMG) (Aldrich) was degassed and dried at 105° C in vacuum overnight before use. N,N-bis (2-hydroxy ethyl) isonicotinamide (BHEIN), tolylene diisocyanate (TDI), hexamethylene diisocyanate (HDI), dibutyl tin dilaurate, 1,3-propane sultone (Aldrich) were used as received. The solvents dimethyl sulfoxide (DMSO), dimethyl formamide

(DMF), (SD's, India) were purified by standard distillation procedures and stored over molecular sieves until use.

Synthesis of polyurethane

PTMG 10g (0.01 mol.) was taken in a 100ml three necked flask and 3.48 g of TDI (0.02 mol.) was added slowly with stirring at 60°C under nitrogen atmosphere. The reaction was allowed for one hour and then the reaction temperature was raised and maintained at 90°C for one more hour. After the NCO content reached half the initial value as determined by dibutylamine titration, the temperature of the reaction mixture was brought down to 60°C and 5ml of DMSO was added to lower the viscosity. Then 2.1g (0.01 mol.) of N,N-bis (2-hydroxy ethyl) isonicotinamide in 10 ml hot DMSO was added slowly with stirring followed by 0.01g of the catalyst dibutyl tin dilaurate. The temperature of the reaction mixture was slowly raised to 90°C and kept for two hours. After the completion of the reaction the contents were poured into ten fold excess of double distilled water to precipitate the polymer. The polymer was filtered and dried at 30° C under vacuum.

Simple polyurethanes with NCO/OH = 1 were prepared using tolylene diisocyanate, hexamethylene diisocyanate and N,N-bis (2-hydroxy ethyl) isonicotinamide in DMSO medium. The polymers were precipitated in water, filtered and dried at 30° C under vacuum.

Conversion into zwitter-ionomers

Required amount of polyurethane was taken in 10% DMF and stoichiometric amount of 1,3-propane sultone in DMF was added and stirred for 48 hours at 35°C under nitrogen atmosphere. The ionomer was precipitated using diethyl ether, dried at 30°C under vacuum for a week. The ionomers were stored in a desiccator prior to characterization. The codes for the polymers are given in Table-1.

RESULTS AND DISCUSSION

The molecular weight distribution of the polymers were evaluated using Water's Associates Gel permeation Chromatography equipped with a 410 model RI detector. The solvent used was N,N-dimethyl formamide (DMF) with

TABLE 1

Polymer Composition	Polyurethane Code	Ionomer Code
BHEIN / TDI	BT	BT-Z
BHEIN / HDI	BH	BH-Z
PTMG1000 /2TDI/BHEIN	PBT	PBT-Z

TABLE 2

Molecular Weight distribution from GPC

Sample	$\overline{M}_n \times 10^4$	$\overline{M}_w \times 10^4$	$\overline{M}_w/\overline{M}_n$
BT	2.54	3.21	1.26
BH	2.57	3.17	1.23
PBT	5.23	6.73	1.29

a flow rate of 1ml/min. The columns used were μ -styrigel with 10^3 , 10^4 , 10^5 , and 10^6 Å pore size. The molecular weight distribution pattern of the polyurethanes as obtained from GPC are given in Table-2.

The ^1H nmr spectra of the polyurethane and the ionomer recorded with a Bruker CXP 300 MHz spectrometer in DMSO-d_6 as solvent is shown in Fig.1. The broad signal observed at 3.19 ppm due to the presence of moisture absorbed by DMSO was suppressed using an external pulse. The completion of quaternization of pyridine rings were observed from the integral value of the peak at 4.7ppm and confirmed by percentage sulphur analysis. The aromatic phenyl protons are observed as multiplets from 7-9 ppm. The urethane protons are observed at 8.34 and 9.4 ppm as a weak signal and were fixed by proton exchange technique using D_2O .

The FTIR spectra of the polyurethane and the ionomer recorded as KBr pellets with a Nicolet 20 DXB spectrometer are given in Fig.2. We observe

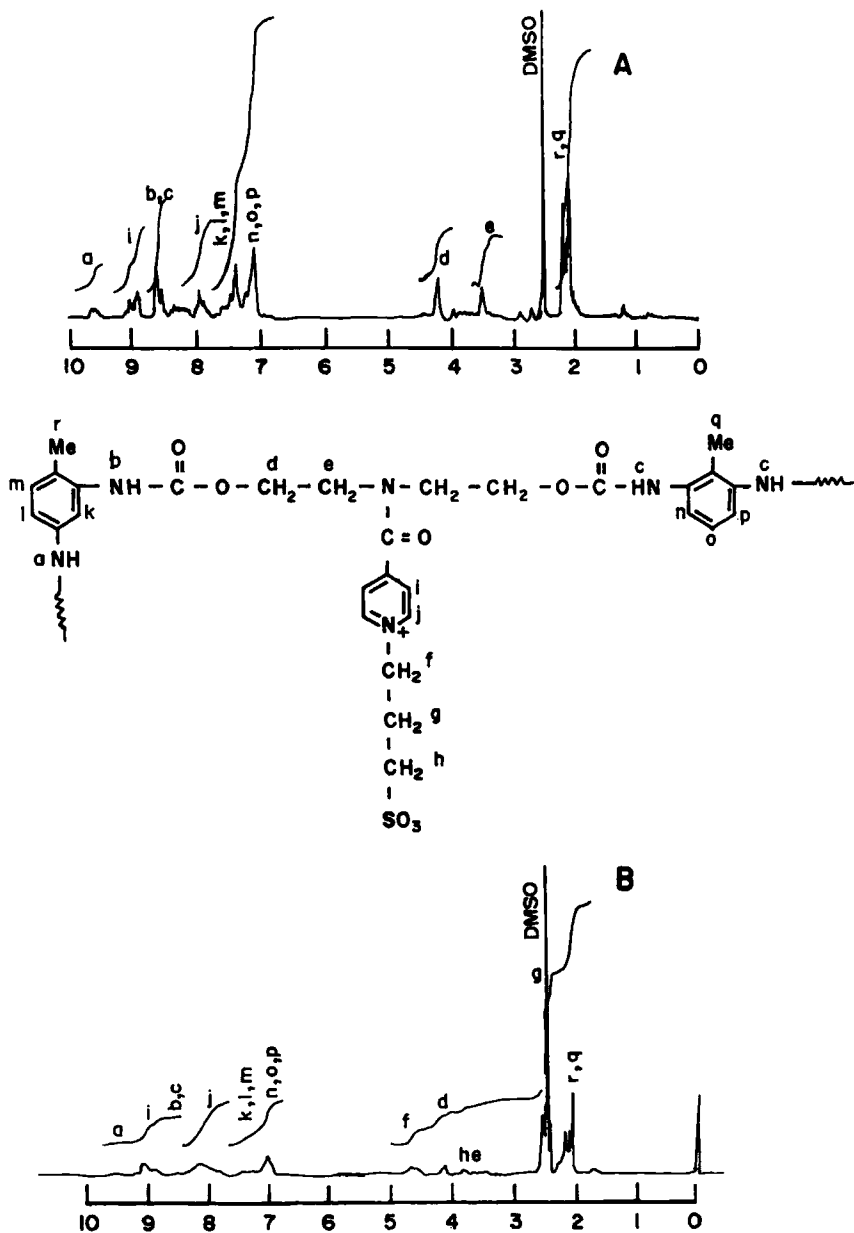


Fig. 1 FTNMR SPECTRUM OF A. Polyurethane (BT)
B. Polyurethane zwitterionomer (BT-Z)

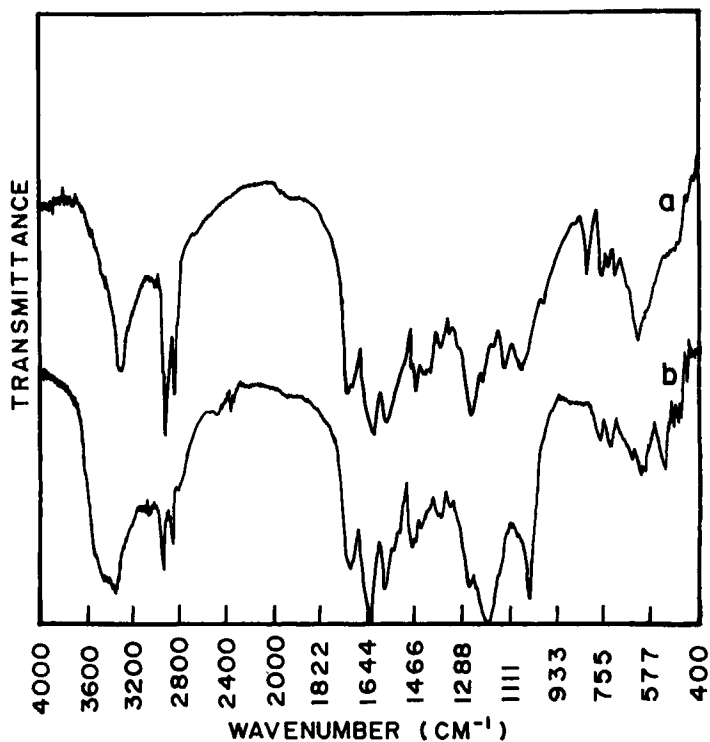


Fig. 2 FTIR spectra of (a) BH and (b) BH-Z

TABLE 3

Solubility characteristics

<u>Solvent</u>	<u>Polymer Codes</u>					
	BT	BT-Z	HT	HT-Z	PBT	PBT-Z
DMSO	++	++	++	++	++	++
DMF	++	++	++	++	++	++
THF	++	+-	++	+-	++	++
Butane-2-one	--	--	--	--	++	--
Hexane	--	--	--	--	--	--

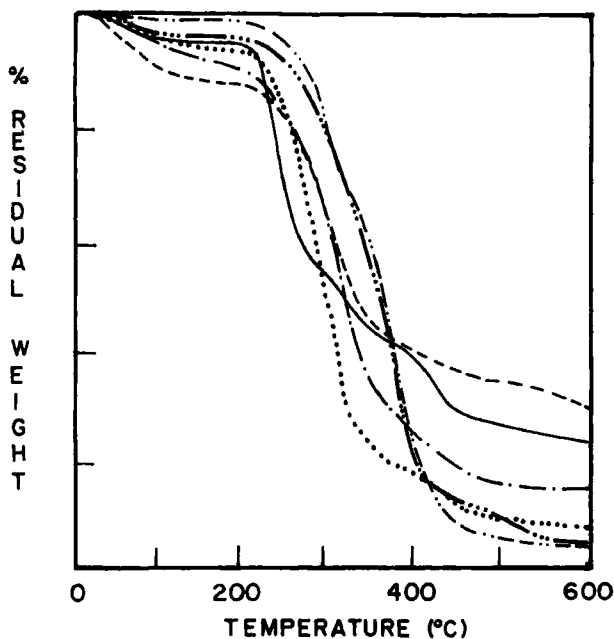


Fig. 3 TGA of (—) BT, (---) BT-Z, (.....)BH
(-·-)BH-Z, (- - -)PBT, (-·-·-)PBT-Z

splitting of carbonyl peaks, at 1720 and 1692 cm^{-1} due to the free and hydrogen bonded urethane groups. The carbonyl of the amide unit of the BHEIN is seen at 1622 cm^{-1} . The urethane NH stretching was observed around at 3318 cm^{-1} which is indicative of urethane linkage. The quaternization of the pyridinium ring is confirmed by the presence of S=O stretching at 1197 cm^{-1} .

Solubility of polyurethanes depend on the amount of hard segment in the polymer chain. Since these model 1:1 reactions were wholly based on hard segment units the solubility of these compounds are limited. As seen from the above Table-3, we observe that only high polar solvents are able to dissolve the polymers. On incorporation of polar zwitterionic groups in the polyurethane chain, solvents with high dielectric strength like DMF and DMSO are able to

solvate the ionic part well and thereby bring the whole polymer effectively into solution.

Thermogravimetric analysis

Thermogravimetric analysis of the polyurethanes and zwitterionomers carried out with a Du Pont 951 Thermogravimetric analyser in nitrogen atmosphere at a heating rate of 10 °C / min are shown in Fig.3. The multistage decomposition observed for polyurethanes is due to the combination of chemically different segments in the polymer chain. Fully aromatic polyurethane are thermally more stable than those based on HDI due to the presence of phenyl rings. Chain extended polyurethanes are thermally stable than simple ones. Initial weight loss for the zwitterionomers is due to the moisture absorbed since the compounds are hygroscopic.

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