Polyurethane telechelic cationomers containing end functional 4-vinylpyridinium moieties

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Summary

Telechelic polyurethane cationomers containing end functional 4-vinylpyridinium moieties have been synthesized by the reaction of 4-vinylpyridine on 2-bromoethanol terminated polyurethane. The polyurethanes were characterized by FTIR, FTNMR and DSC studies. The introduction of ionic groups into the polyurethane shifts the T_g to lower temperatures, the shift in T_g further increases with increase in ionic groups.

Introduction

Ionomers are polymers containing small number of ionic groups (<10 mol. %) in the polymer backbone. The presence of small number of ionic groups in the hydrophobic polymer backbone leads to very interesting properties of the material. Polyurethane ionomers are a very important class of block copolymers that can be tailored according to the end user needs. Polyurethanes with ionic moieties are of interest due to the possibility to disperse them in aqueous solutions. Polyurethane ionomers have been synthesized predominantly by using an ionic diisocyanate or an ionic diol at the chain extension stage and by post modification of a preformed polyurethane. In the former case polyurethane anionomers (1-8) (with carboxylic, sulfonic and phosphoric acid groups), cationomers (9-16) and zwitterionomers (17-21) have been studied in great detail. In the latter case polyurethanes were reacted with NaH/NaOH and subsequently reacted with 1,3-propanesultone to give zwitterionomers (22-24). Further castor oil based polyurethanes have been reacted with chlorosulphonic acid to give sulfonic acid groups in the polyurethane main chain (25). All the work on polyurethane ionomers are concentrated on random ionomers. Preparation of polyurethane material with specific arrangement of ionic groups have seldomly been reported. To this effect telechelic i.e., end functional polyurethane ionomers would be of interest. When telechelic polymers are reacted with multi functional linking agents and end groups/vinyl monomers, network structures and block copolymers are obtained respectively. α,ω-Olefin telechelics have been converted to sulphonate ionomers by reacting with acetyl sulfate (26). In this paper we report the first synthesis and the characterization of polyurethane end terminated with 2-bromoethanol and the subsequent conversion of it to telechelic polyurethane cationomers containing end functional 4-vinylpyridinium moieties and their characterization. Since the polyurethane cationomers contain potential vinyl groups at their chain ends they can also be used as macromonomers.

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Experimental

Materials
Poly (tetramethylene oxide) glycol of molecular weight 1000 [PTMG$_{1000}$] (Aldrich, USA) was dried under vacuum for 2 hours at 110°C prior to use. Tolylene diisocyanate [TDI] (a mixture of 80% 2,4- and 20% 2,6- isomers), dibutyltin dilaurate [DBTDL] (Aldrich, USA) were used as received. 2-Bromoethanol and 4-vinylpyridine (Merck, India) were distilled and used. The solvents *N,N*-dimethylformamide, diethyl ether and methanol were purified by standard procedures.

Measurements
Fourier transform infrared spectra (FTIR) of the polymers were recorded as neat films (prepared by casting purified polymer in DMF over a KBr window and evaporating the solvent at room temperature under vacuum) using a Nicolet Impact 400 spectrometer. Fourier Transform Nuclear Magnetic resonance (FTNMR) were recorded on a Bruker MSLp 300 MHz spectrometer in DMSO-d$_6$. The molecular weights of the polymers were determined by using Waters Associates gel permeation chromatography (GPC) equipped with a Waters 410 RI detector, the solvent being DMF stabilized with 0.01% of LiBr. The molecular weight was calibrated using polystyrene standards. DSC studies were carried out using a Du Pont 910 differential scanning calorimeter (DSC) at a heating rate of 10°C/min under nitrogen atmosphere.
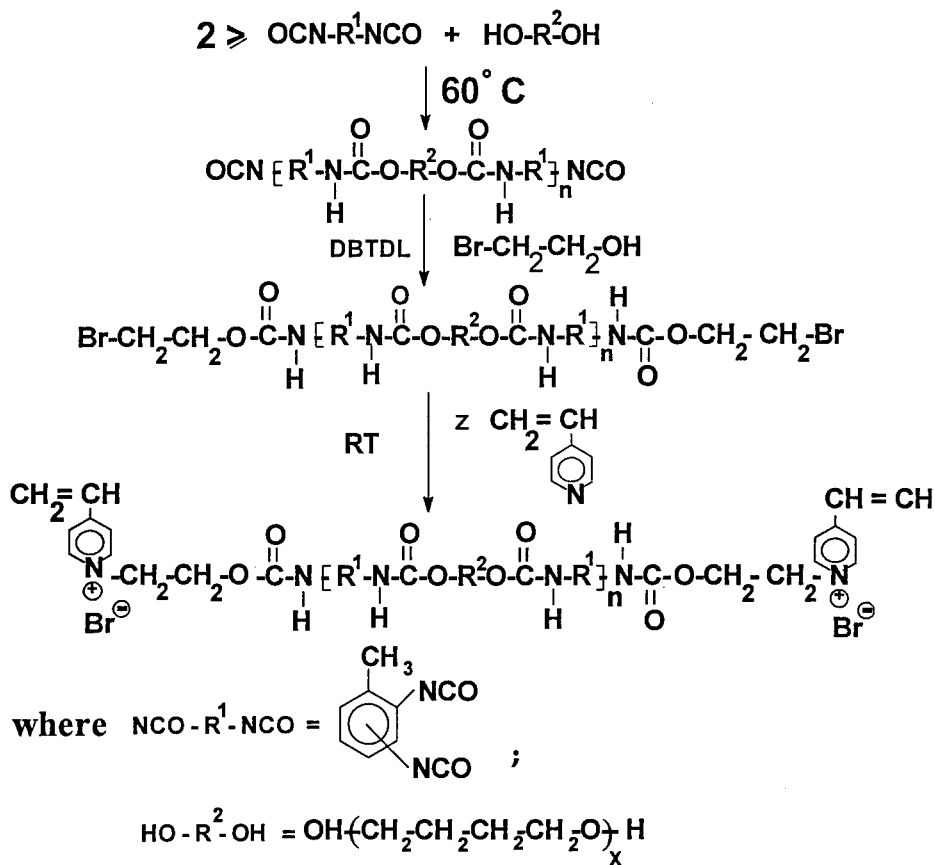
Synthesis of Polyurethanes
TDI (3.48g, 0.02mol) was added drop by drop to PTMG$_{1000}$ (10g, 0.01mol) in a 100ml three necked flask at 60°C under nitrogen atmosphere. The temperature was then increased to 70°C and the reaction was allowed to proceed till the isocyanate content reaches half the initial value (as determined by dibutylamine titration). 20ml of DMF was then added and the temperature was reduced to 60°C, 2-bromoethanol (1.24g, 0.01m) was added drop by drop. Then 0.01g of DBTDL catalyst was added, the temperature was increased to 70°C and the reaction was allowed to completion. The polyurethanes were precipitated by pouring into ten fold excess of distilled water and washed thoroughly with methanol. The polymers were dried under vacuum at 30°C for a week. Similarly polyurethane of another composition as mentioned in Table 1 was synthesized by the same procedure. The synthesis of the polyurethanes and the conversion to cationomers are schematically represented in Scheme 1.

Conversion to cationomers
The above mentioned polyurethanes were dissolved in DMF and was reacted with excess of 4-vinylpyridine, at room temperature for 60 hours. The resulting polyurethane cationomers were precipitated by pouring into ten fold excess of cold diethyl ether and dried under vacuum.

Results and discussion
The molecular weights and polydispersity of the polyurethanes and the cationomers are given in Table 1. The molecular weight of the polymers are in the expected range. The higher molecular weight of the cationomers is due to the repeated reprecipitation of the polymers in diethyl ether, in which the low molecular weight polymers were lost resulting in increased molecular weight.

$$2 \geqslant \text{OCN-R}^1\text{-NCO} + \text{HO-R}^2\text{OH}$$

$$\downarrow 60°\text{C}$$

$$\text{OCN} \left[\text{R}^1\text{-N-C-O-R}^2\text{-O-C-N-R}^1 \right]_n \text{NCO}$$

(with O double bonds on C, H on N groups)

DBTDL | Br-CH$_2$CH$_2$OH

$$\text{Br-CH}_2\text{CH}_2\text{-O-C-N} \left[\text{R}^1\text{-N-C-O-R}^2\text{O-C-N-R}^1 \right]_n \text{N-C-O-CH}_2\text{CH}_2\text{-Br}$$

RT | z CH$_2$= CH (pyridine)

$$\text{CH}_2\text{= CH} \quad \ldots \quad \text{CH = CH}$$

$$\overset{\oplus}{\text{N}}\text{-CH}_2\text{CH}_2\text{-O-C-N} \left[\text{R}^1\text{-N-C-O-R}^2\text{O-C-N-R}^1 \right]_n \text{N-C-O-CH}_2\text{CH}_2 \overset{\oplus}{\text{N}}$$

Br$^\ominus$ ... Br$^\ominus$

where

$$\text{NCO-R}^1\text{-NCO} = \text{(benzene ring with CH}_3\text{, NCO, NCO)} ;$$

$$\text{HO-R}^2\text{-OH} = \text{OH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_x \text{H}$$

SCHEME 1

Table 1 : Compositions, codes, molecular weights, molecular weight distributions and glass transition temperature of Polyurethane and their telechelic cationomers

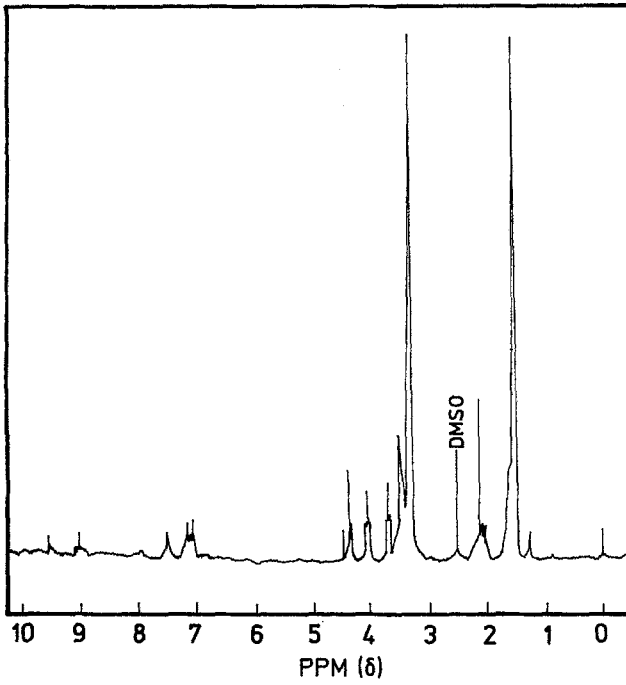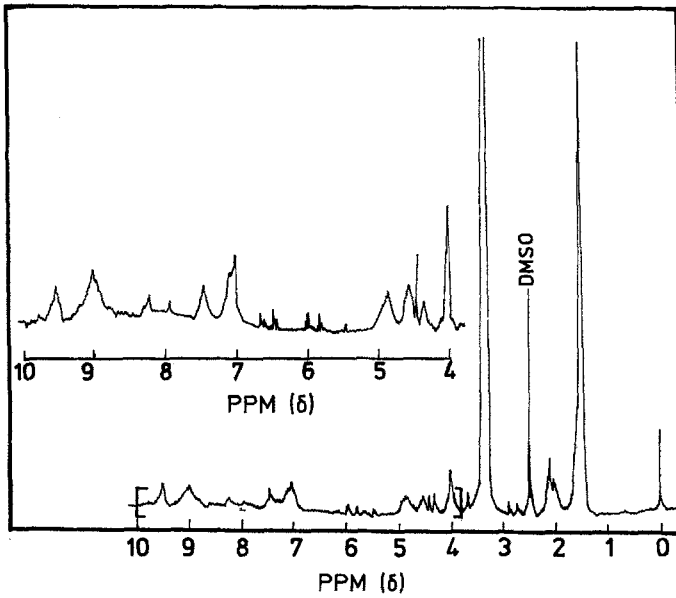| Polymer composition	Polymer code	Molecular weight		M_w/M_n	T_g (°C)
		M_n X 10^{-4}	M_w X 10^{-4}		
(a) PTMG$_{1000}$/2TDI/BrEtOH	BrPU-I	1.48	2.62	1.76	-39.0
VPy quaternized	BrPU-IVPy	1.95	4.75	2.43	-43.5
(b) PTMG$_{1000}$/3TDI/2BrEtOH	BrPU-II	0.89	1.44	1.62	-37.0
VPy quaternized	BrPU-IIVPy	1.19	2.31	1.93	-45.0

Fig. 1.   ¹H FTNMR spectrum of BrPU-II.

Fig. 2.   ¹H FTNMR spectrum of BrPU-IIVPy.

The FTIR spectra of the polyurethane and the cationomer showed characteristic peaks due to the urethane -NH at 3300 cm^{-1} and C=O stretching of the urethane linkage at 1725 cm^{-1}. The broad nature of the C=O band shows that both hydrogen bonded and non hydrogen bonded groups are present in the case of polyurethane as well as in the cationomers. The symmetric and the asymmetric stretching of the -CH$_2$- of the PTMG is observed from 3000 cm^{-1} to 2750 cm^{-1}. The aromatic C=C stretching band is seen at 1600 cm^{-1} and peak at 1540 cm^{-1} due to C-N stretching and N-H deformation. The C-O-C stretching of the polyurethane is seen as a broad peak at 1100 cm^{-1}, showing that the ether group is actively involved in hydrogen bonding. The introduction of 4-vinylpyridinium moieties in the polyurethane as end groups is accompanied by the appearance of a new peak at 1640 cm^{-1} due to the C=N stretching of the pyridine moieties. Excluding this peak, both the spectra were similar.

In the ^{1}H FTNMR spectra of BrPU-II (Fig. 1) and BrPU-IIVPy (Fig. 2) along with the aromatic protons of the polyurethanes at 7.04 to 7.48 ppm, N-H protons at 8.5 to 9.5 ppm, aliphatic CH$_2$ of the PTMG segment at 1.6 ppm, the methyl protons of TDI at 2.1 ppm, the -O-CH$_2$- protons of the PTMG segment at 3.35 ppm and the protons of the -O-CH$_2$ attached to the urethane linkage at 4.05 ppm are observed. The protons of Br-CH$_2$ appear at 3.45 ppm and Br-CH$_2$-CH$_2$ attached to urethane groups resonate at 4.37 ppm. The complete disappearance of the peak at 3.45 ppm in the case of the cationomers shows that the nucleophilic substitution of the bromine by the tertiary nitrogen of the vinyl pyridine proceeds to complete conversion. The conversion to the cationomers is accompanied by the appearance of new peaks between 4.6 and 4.8 ppm due to the new +N-CH$_2$ bond. In addition the peaks due to the protons of the double bond in vinylpyridine moieties appears between 5.7 and 6.7 ppm.

DSC studies

The T$_g$ of the polyurethanes and the cationomers are given in Table 1. The low glass transition temperatures of the polyurethanes are due to the polyol segment. The introduction of ionic groups is accompanied by a significant change in the glass transition temperature of the polyurethane especially the polyol segment. The lower glass transition temperature of the quaternized polyurethane than the bromo terminated polyurethane is due to the introduction of ionic groups which causes realignment of hydrogen bonding leading to microphase separation (7,18). The degree of phase separation depends on the amount of ionic groups present in the polymer. On comparing BrPU-I, BrPU-IVPy with BrPU-II, BrPU-IIVPy the T$_g$ of BrPU-IVPy is marginally less than of BrPU-I. This is due to the very less degree of ionic groups present in this cationomer. While comparing the T$_g$s of BrPU-II and BrPU-IIVPy, we see that the T$_g$s clearly shifts to lower temperature on introduction of higher degree of ionic groups.

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