

Novel Short-chain Crosslinked Cationomeric Polyurethanes

V. Sriram* and Ganga Radhakrishnan (✉)

Advanced Centre in Polymers, Central Leather Research Institute, Adyar,
Chennai-600 020, India

Email: clrieco@md3.vsnl.net.in

* Present address of the author: AorTech Biomaterials Pty Ltd, Melbourne, Australia

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Summary

Novel PUs containing pyridinium moieties were synthesized by chain extending isocyanate endcapped prepolymers with N, N'-bis (2-hydroxyethyl) isonicotinamide. The pyridinium moieties in the PUs were chemically crosslinked using short-chain divalent quaternising agents. The polyurethane cationomers were characterized by spectral, thermal and mechanical analysis. Spectral results confirmed the quaternisation of tertiary nitrogen leading to crosslinking. Compared to conventional PUs, the crosslinked PU networks exhibited improved thermal stability. The damping value (i.e.) $\tan \delta$ for cationomers were improved over a broad temperature range when compared to conventional PU.

Introduction

Ionomers are defined as polymers containing a small number of ionic groups (<10%) in the polymer backbone. Ionomers have evinced a lot of technological and scientific interest due to the low polarity backbone combined with low ionic content. Polyurethane (PU) ionomers [1] are very important class of block copolymers that can be tailored according to end user needs. PU ionomers are prepared either by introduction of potential ionic moieties at the chain extension stage or by post-polymer modification. [2-12]. One of the ways to synthesize PU ionomers is to introduce hetero atomic sites into PU backbone and further modification of the hetero atomic sites gives PU ionomers.

Polymers having hetero atomic groups are used for specialty and high performance applications. The potential hetero atomic sites in the polymers can be further modified to improve the properties of the base polymer. Among this class of polymers, pyridines containing polyesters, polyamides and epoxy resins have been studied in detail [13-15]. Pyridine containing polymers have evinced a lot of interest due to the possibility of quaternizing the tertiary nitrogen to prepare ionic polymers [16, 17]. Sulphonated polystyrene with pyridine-based polymers has been studied in the field of ionomer blends to act as potential sites for specific inter molecular interactions [18-20]. In PUs the introduction of pyridinium moieties as chain extenders is rare

[21, 22]. Tertiary nitrogen groups have generally been introduced into PU by using N-methyldiethanolamine. To synthesize novel PUs and their modification, for the first time our group reported telechelic vinyl PU cationomers [23] by reacting bromine terminated PU with 4-vinyl pyridine.

The unique properties of PUs arise from the high degree of intermolecular hydrogen bonding. In order to further enhance the physical properties of the PU, crosslinking is usually carried out. Suitable crosslinking methods are stoving systems (heat-activated crosslinking), UV-crosslinkable systems or two-component systems. These crosslinking methods have their own disadvantages. Heat-activated systems and UV-crosslinkable systems need either an oven or UV source, which limit their use in industrial applications. A two-component system has a limited pot life after mixing and involves handling of carcinogenic crosslinkers like aziridine. These factors have limited the scope of these systems. To overcome these limitations novel short-chain crosslinking methodology is reported in this study. The advantage of this system is that it can be carried out at room temperature and more importantly the flexibility of the PUs can be tailored by varying the chain length of the dibromoalkanes. The dibromo alkanes of various chain length and even bromine terminated polymers can be used to effect crosslinking, which gives a wide scope of incorporating interesting properties to the base polymer. This article reports the novel synthesis of PU containing pyridinium moieties and subsequent conversion into crosslinked cationomers using dibromoalkanes. N, N-bis (2-hydroxyethyl) isonicotinamide (BHEIN) has been used in PU synthesis to introduce pyridinium moieties [22, 24-26] into PU backbone and they are crosslinked using dibromo butane and dibromo hexane. These synthesized cationomeric crosslinked PUs find many end-use-applications like controlling vibration and noise and as transfer coating for leathers.

Experimental

Materials

Analytical grade N, N-dimethylformamide (DMF, S.D.Fine, India) was distilled and middle portions were used after storing over type 4Å molecular sieves. Dibutyltin dilaurate (DBTDL) and a mixture of 80% 2, 4- and 20% 2, 6-tolylene diisocyanate (TDI, Aldrich, USA) were used as received. Poly (tetramethylene oxide) glycol of molecular weight 1000 (PTMG₁₀₀₀ Aldrich, USA) and Poly (propylene oxide) glycol of molecular weight 1000 (PPG₁₀₀₀, Aldrich USA) were used after drying at 105°C under reduced pressure for 4h. 1,4-dibromobutane 1.6-dibromohexane (SISCO, India) and N, N'-bis (2-hydroxyethylisonicotinamide) (BHEIN, Aldrich, USA), were used as received. All the other chemicals used were analytical grades and were used as received.

Characterization Techniques

Number average (M_n) weight average (M_w), molecular weights and Molecular Weight Distributions (M_w/M_n) were determined by gel permeation chromatography (GPC) using Waters liquid chromatograph equipped with 410 differential refractometer (RI Detector) and four μ styragel columns (10^6 Å, 10^5 Å, 10^4 Å and 10^3 Å) in series. DMF (0.01 LiBr added) was used as an eluent at a flow rate of 1.0 mL/min and the

molecular weight calibrations were done using polystyrene standards. The fourier transform infra-red (FT-IR) spectra were recorded as neat films with a Nicolet Avatar 360 IR spectrophotometer having Horizontal Attenuated Total Reflectance (HATR) accessory in the frequency range of 4000-400 cm^{-1} . Proton fourier transform nuclear magnetic resonance (^1H FT-NMR) spectra were recorded on a Bruker MSL_p 300 MHz NMR instrument using deuterated dimethyl sulfoxide as the solvent and tetramethylsilane as an internal standard. Thermogravimetric analysis (TGA) was carried out using Dupont 951 TGA instrument at a heating rate of 10°C/min under N₂ atmosphere with a gas flow of 100mL/min.

Strips (20x10x2.5mm³) of each material were examined in dynamic mechanical analyzer, DMA 2980, TA instruments, USA, in the tensile mode (tension film) over a temperature range of -100 to +100°C at a heating rate of 8°C/min, strain amplitude of 20 μm and frequency of 1Hz. The samples (3 specimens each) for stress-strain analysis were cut at geometry of 40mm x 10mm and kept for conditioning at 20 \pm 2°C and relative humidity of 65 \pm 2% for 24h before testing. The tensile testing was done using an Instron Universal Testing Machine model 4501 at an elongation rate of 50mm/min. The specimens were in conformance with ASTM D638.

Synthesis of PUs

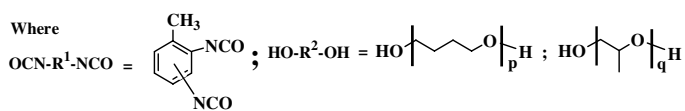
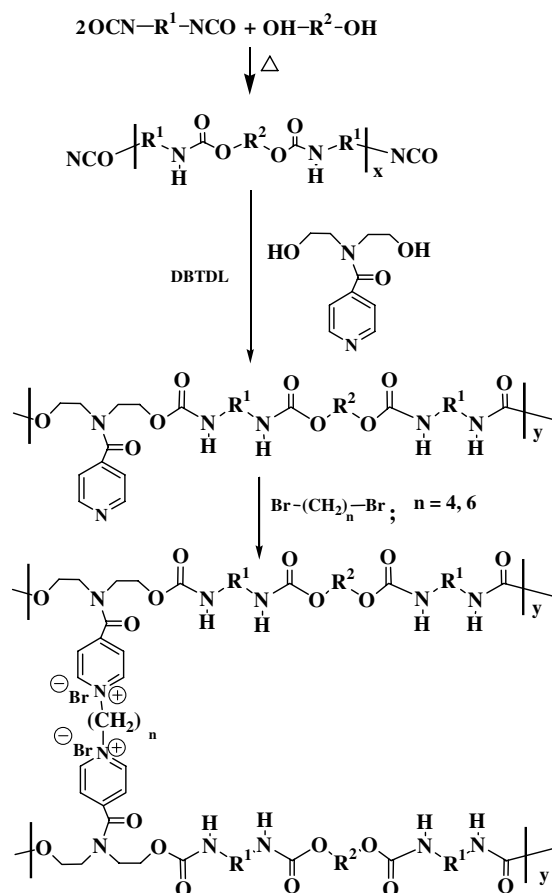
TDI (0.02 mol) was taken in a reaction flask and polyol (0.01 mol) was added drop wise with stirring. The reaction was carried under nitrogen atmosphere for 1h initially at 60°C and then at 70°C until the isocyanate content reached half of the initial value (as determined by dibutyl amine titration). The temperature was reduced to 60°C and the chain extender N, N'-bis (2-hydroxyethyl) isonicotinamide (0.01 mol) in 20 ml of DMF was added drop by drop. Then 0.01 g of DBTDL catalyst was added, the temperature was increased to 70°C and the reaction was carried out for another 3 h. The resulting PUs were precipitated into ten-fold excess of distilled water and washed thoroughly with methanol. The polymers were dried under vacuum at 80°C for one week.

Conversion to Cationomers

The synthesized PUs were dissolved in DMF and mixed with stiochiometric amount of appropriate dibromo alkanes. It was stirred for 5 min to effect uniform mixing and they were cast over silicon troughs. The solvent was evaporated at 60°C to give the crosslinked PU cationomer films, which were dried under reduced pressure (5x 10⁻²mm/Hg) at 60° C for 48hrs. The quaternised cationomers are denoted by suffix BB and BH for 1, 4-dibromobutane and 1, 6-dibromohexane respectively, as given in Table 1.

Results and Discussion

PUs containing pyridinium moieties have been synthesized and quaternised using dibromo alkanes to give chemically crosslinked PU cationomers. Schematic representation of the chemical crosslinking is shown in Scheme 1. The composition codes and molecular weights of the PUs are given in Table 1.



Scheme 1. Novel Crosslinked PU Cationomers

Table 1. Molecular weight and molecular weight distributions of PUs.

Polymer Composition	Polymer Code	Molecular weight		M_w/M_n
		$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	
a) PTMG ₁₀₀₀ /TDI/BHEIN	P ₁	4.52	6.37	1.41
1,4-dibromobutane quaternised	P ₁ BB*	-	-	-
1,6-dibromohexane quaternised	P ₁ BH*	-	-	-
b) PPG ₁₀₀₀ /TDI/BHEIN	P ₂	3.24	4.80	1.60
1,4-dibromobutane quaternised	P ₂ BB*	-	-	-
1,6-dibromohexane quaternised	P ₂ BH*	-	-	-

* Since it is crosslinked molecular weight cannot be determined

Spectral Studies

FT-IR spectra (Figure.1) of the PU and their cationomers showed characteristic peaks due to the urethane -NH at 3300 cm^{-1} and C=O stretching of urethane linkage at 1725 cm^{-1} . The broad nature of the C=O bond shows that this group is involved in hydrogen bonding. The PU cationomers show a new strong peak at 1640 cm^{-1} as reported in several references [24], which is specifically due to quaternisation of heterocyclic nitrogen. The peak is due to C=N stretching of the pyridine moieties which is influenced by the electromeric effect and undergoes a shift to lower frequency. The symmetric and the asymmetric stretching of the $-\text{CH}_2-$ of the PTMG₁₀₀₀ and PPG₁₀₀₀ are observed between 3000 cm^{-1} and 2750 cm^{-1} . The aromatic $-\text{C}=\text{C}-$ stretching band of the chain extender and diisocyanate were observed at 1600 cm^{-1} and a peak at 1540 cm^{-1} is due to C-N stretching and N-H deformation.

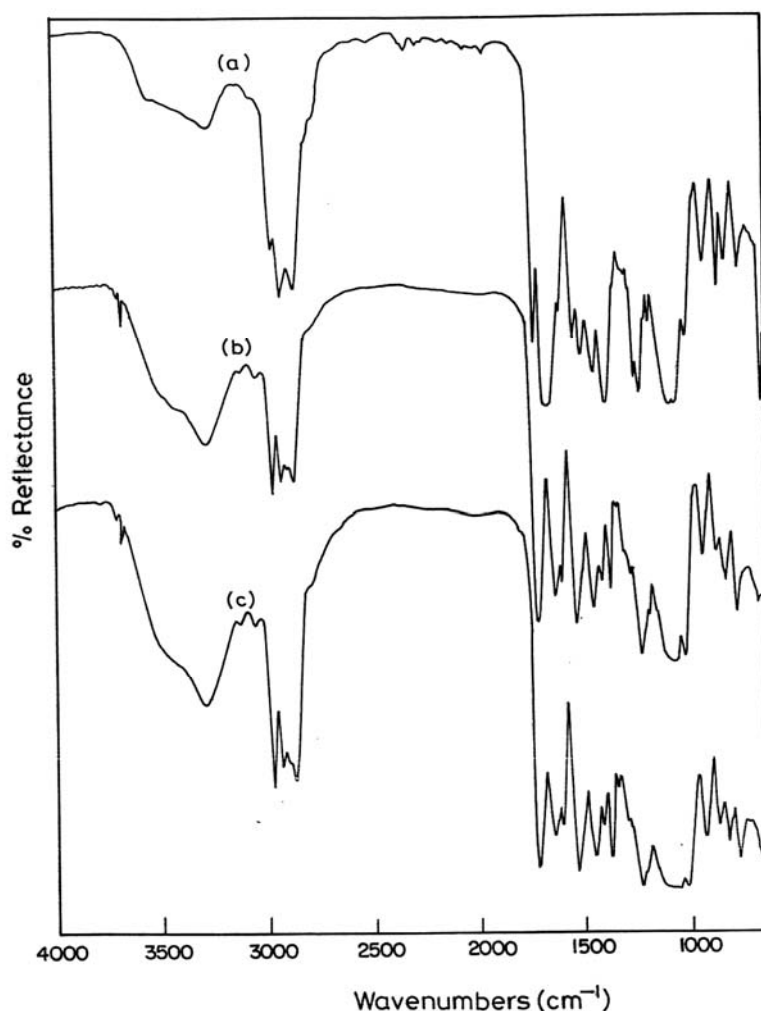


Figure 1. FT-IR spectra of (a) PU without quaternisation (P_1), (b) PU quaternised with dibromobutane ($P_1\text{BB}$) and (c) PU quaternised with dibromohexane ($P_1\text{BH}$)

The amide carbonyl bond of the chain extender is observed at 1622 cm^{-1} . In the ^1H FT-NMR spectra, the protons of Br-CH_2 appear at 3.45 ppm. The complete disappearance of the peak at 3.45 ppm in the case of cationomers shows that the tertiary nitrogen groups of BHIEN are quarternised completely. The conversion of the cationomers is accompanied by the appearance of new peaks between 4.6 and 4.8 ppm due to the new $+\text{N-CH}_2$ bond. The shifting of peak from 3.45 ppm to 4.6-4.8 ppm is due to the reason that during the quarternisation the electronic cloud at nitrogen is reduced and hence the protons in the $+\text{N-CH}_2$ group is deshielded. Since deshielding is taking place, the peak at 3.45 ppm is shifted to 4.6-4.8 ppm. Peaks due to $-\text{CH}_2-$ protons of the chain extender (attached to the amide group) resonate at 3.1, 3.7 and 4.3 ppm. The aromatic protons of the PUs resonate at 7.0 to 7.4 ppm, N-H protons at 8.5 to 9.5 ppm, aliphatic $-\text{CH}_2-$ of the PTMG segment at 1.6 ppm, the methyl protons of TDI at 2.1 ppm, the $-\text{O-CH}_2-$ protons of the PTMG segment at 3.3 ppm and the protons of the $-\text{O-CH}_2-$ attached to the urethane linkage at 4.05 ppm.

Dynamic Mechanical Properties

Table 2 shows the glass transition temperature and $\tan \delta$ values of PU and their cationomers. From the dynamical mechanical data (Table 2) it can be seen that the cationomers exhibit two maxima which may be due to low miscibility between the soft segment and ionic groups of PU leading to two phase structure. The upper transition in damping curves corresponds to plastic phase and the lower one corresponds to elastomeric phase. $\tan \delta$ is indicative of the flexibility of the polymer film. The damping value is higher for P_1BH than that of P_1BB , which indicates that P_1BH is more flexible than P_1BB . This may be due to the longer chain length of the crosslinker which render more flexibility to the crosslinked PU films. This result is in agreement with the static mechanical studies. It can also be seen that the P_1BB has a higher T_g than P_1BH . Due to the short chain, in P_1BB the polymer chains are held together tightly preventing chain mobility and thus resulting in higher T_g . Thus in conclusion it can be seen that the damping properties for cationomers is improved over a broad temperature range when compared to conventional PU.

Stress-Strain Analysis

The stress-strain analysis shows the maximum tensile strength and elongation at break of the PU and cationomers which are given in Table 2. PU consists of alternating soft and hard segments. The incompatibility of these two lead to microphase separation / two phase morphology. The hard domains in the PUs serve as multi-crosslinking

Table 2. Mechanical properties of PUs and their cationomers

Polymer Code	Max.tensile strength (MPa)	Elongation at Break (%)	T_g^1 ($^{\circ}\text{C}$)	$\tan \delta_{\text{max}1}$	T_g^2 ($^{\circ}\text{C}$)	$\tan \delta_{\text{max}2}$
P_1	2.20	167.9	-44.5	0.55	-	-
P_1BB	14.25	378.6	-46.7	0.13	57.7	0.48
P_1BH	9.54	421.0	-49.5	0.16	59.0	0.51
P_2	2.40	154.7	-39.0	0.49	-	-
P_2BB	5.69	382.0	-12.7	0.15	37.6	0.47
P_2BH	4.70	442.0	-14.0	0.17	39.4	0.49

volume elements and are responsible for the uniform distribution of stress over many chains, which in turn render good mechanical strength to these materials. The stability of these hard domains is crucial for the strength of these materials. The introduction of ionic groups in the hard segments caused an increased microphase separation. Further the quaternising agent effect crosslinking of the pyridinium moieties in the hard segment leading to hard segment cohesion which is absent in conventional PU.

The higher tensile strength and lower elongation at break of PU crosslinked with dibromobutane is due to its shortchain length leading to higher rigidity thus making chains tough and the resultant flexibility of the polymer is lower compared to dibromohexane. Higher tensile strength of PTMG based PU over PPG is due to the consolidated strain-induced crystallization of the PTMG units.

Thermal Studies

The TGA thermograms of the PTMG₁₀₀₀ based PU (P_1) and cationomers are given in Figure 2. Initial decomposition temperature was taken as the point of onset. The weight loss in the case of PUs was not observed upto 180°C. There is no appreciable weight loss upto 230°C in the case of cationomers which is higher than the P_1 implying the improved thermal stability of the crosslinked networks. The increased thermal stability can be attributed due to effective diquaternisation leading to rigidity and leading to compact structure.

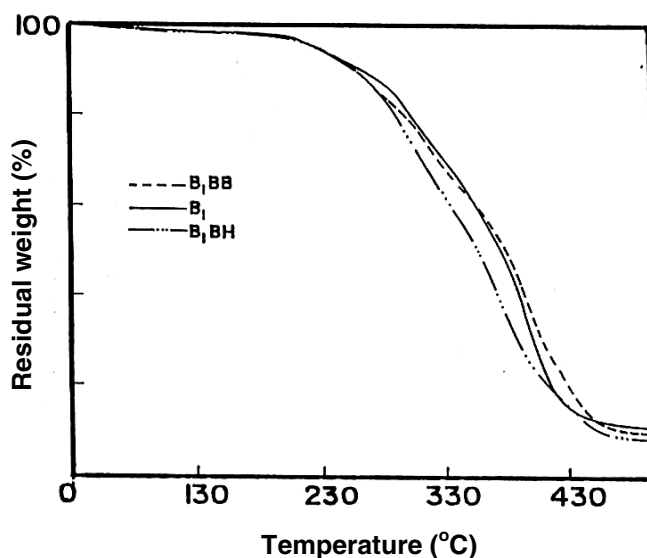


Figure 2. TGA Thermograms of PUs and their cationomers

Conclusion

The novel PU cationomers were synthesized by crosslinking the chain extended PUs with short-chain dibromoalkanes. Formation of crosslinking was confirmed by spectral studies. Thermal stability improved after crosslinking the PUs through diquaternisation. Mechanical studies showed that the tensile property and the damping

behavior were tremendously influenced by diquaternisation. The tensile strength and elongation increased upon crosslinking the PUs. The damping value is higher for P₁BH than that of P₁BB, which is consistent with the observation in the static mechanical studies.

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