



# Novel polymer electrolytes based on cationic polyurethane with different alkyl chain length



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## HIGHLIGHTS

- A series of comb-like cationic polyurethane electrolytes were synthesized.
- Alkyl quaternary ammonium salts are recognized as inherent plasticizers.
- Ionic conductivity is the charge migration between coordination sites and aggregates.
- The plasticizing effects of longer alkyl chain electrolytes are more effective.
- The systems behave like a liquid while preserving the dimensional stability.

## ARTICLE INFO

### Article history:

Received 13 August 2013  
Received in revised form  
18 October 2013  
Accepted 24 October 2013  
Available online 6 November 2013

### Keywords:

Cationic polyurethane  
Solid polymer electrolyte  
Alkyl quaternary ammonium salts  
Comb-like

## ABSTRACT

A series of comb-like cationic polyurethanes (PUs) were synthesized by quaternizing different bromoalkane ( $C_2H_5Br$ ,  $C_8H_{17}Br$ , and  $C_{14}H_{29}Br$ ) with polyurethane. Solid polymer electrolytes were prepared by complexes cationic PUs with different content of  $LiClO_4$ . All the solid polymer electrolytes had sufficient thermal stability as confirmed by TGA and exhibited a single-phase behavior evidenced by DSC results. For these electrolytes, FT-IR spectra indicated the formation of polymer–ion complexes. The ac impedance spectra show that the conductivity of the electrolytes follow the Arrhenius behavior, and ionic conductivity is associated with both the charge migration of ions between coordination sites and transmission between aggregates, as confirmed by FT-IR and SEM. Alkyl quaternary ammonium salts in the polymer backbone are recognized as inherent plasticizers, which make the electrolytes exhibit liquid-like behavior. The plasticizing effect of PU- $C_8$  and PU- $C_{14}$  electrolytes are more effective than that of PU- $C_2$  electrolyte. Maximum ionic conductivity at room temperature for PU- $C_8$  electrolytes containing 50 wt%  $LiClO_4$  reached  $1.1 \times 10^{-4} S cm^{-1}$ . This work provides a new research clue that alkyl quaternary ammonium salts could be used as inherent plasticizers and hence make the system behave like a liquid with high ionic conductivity, while preserving the dimensional stability of the solids.

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## 1. Introduction

Recently, solid polymer electrolytes (SPEs) have attracted worldwide attention and been investigated widely in lithium-ion batteries [1,2], chemical sensors, data storage and electrochemical devices [3]. Lithium-ion doped SPEs offer many advantages such as ease of manufacturing, immunity from leakage, suppression of lithium dendrite formation, elimination of volatile organic liquids and mechanical flexibility. However, the main problem in achieving the expected applications is their low ionic conductivity.

Thermoplastic polyurethane has two-phase microstructure: the soft segments and the hard segments and have been largely employed as matrix materials for polymer electrolytes [4–13]. The hard segments are interconnected throughout the soft phase parts, and act as reinforcing fillers and hence contribute to the mechanical strength of the polymer electrolytes. While the low glass transition temperature ( $T_g$ ) and hence higher segmental motion of their soft segments dissolve alkali metal without formation of ionic cluster and offer the whole system with good ionic conductivity. Because of the solvation power and complexing ability of poly(ethylene oxide) (PEO) to alkali metal ion, many studies on SPEs have dealt with polyurethane consisting of polyether-like structure with lithium salts. The transport mechanism within SPEs based on PEO and salts has been recognized that the ionic conductivity of PEO-based

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electrolytes is facilitated in the amorphous phase of PEO [14]. Various approaches have been devoted in tailing a polymer structure having a highly flexible backbone and a larger proportion of the amorphous phase. For instance, random copolymers [15,16], block copolymers [17,20], comb polymers [18] and crosslinked networks [19] have been explored and their electric properties have been investigated. Despite considerable interest in and effort devoted to SPEs, studies on the conductivity mechanism of the SPEs based on cationic polyurethane are still relatively limited.

Herein, we demonstrate for the first time the study on the properties of solid polymer electrolytes based on the cationic polyurethane. By inducing different bromoalkane ( $C_2H_5Br$ ,  $C_8H_{17}Br$ , and  $C_{14}H_{29}Br$ ) into polyurethanes, comb-like polymers with different alkyl chain length were synthesized. Solid polymer electrolytes were prepared by complexing the polymers with  $LiClO_4$ . The aim of this study is to identify the influence of the polyurethane backbone (different alkyl chain length) and the effect of the ionic salt concentration on the SPEs based on different bromoalkane quaternized polyurethane by conducting FT-IR study along with DSC, SEM and alternating current (ac) impedance measurements.

## 2. Experimental section

### 2.1. Materials

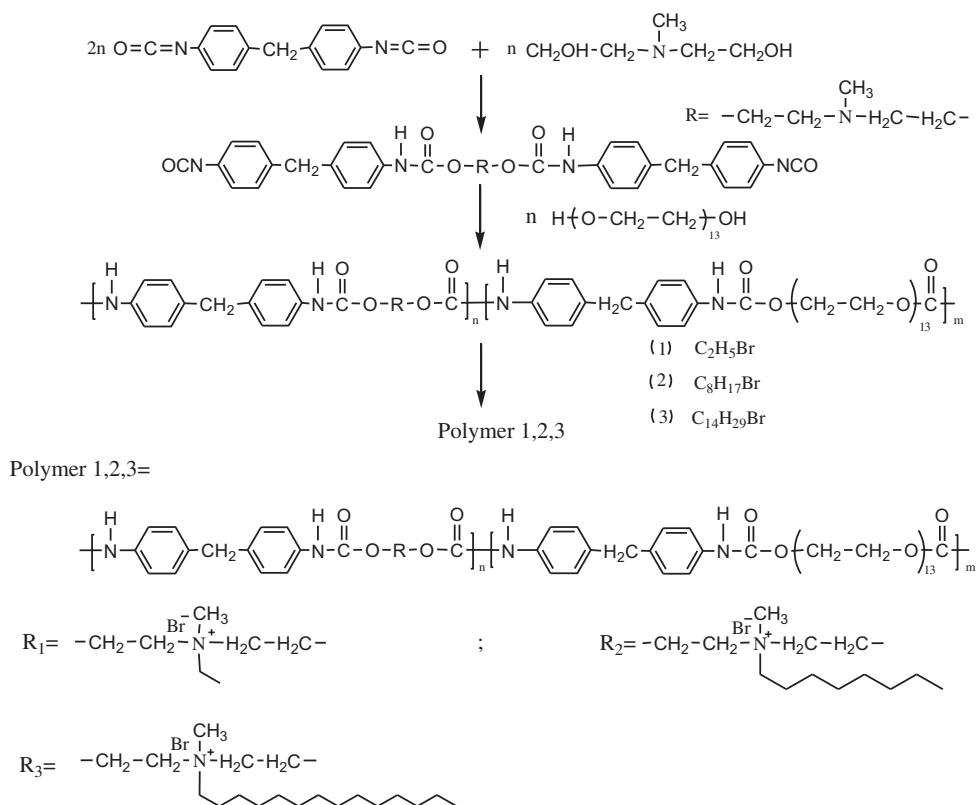
Poly(ethylene glycol) (PEG; molecular weight 600; Aladdin Industrial Inc.) was dehydrated under reduced pressure at  $90\text{ }^\circ\text{C}$  for 2 h before using. 4,4'-Methylenebis(phenyl isocyanate) (Aladdin), *N,N*-Methyldiethanolamine (MDEA, Aladdin) and  $LiClO_4$  (Aladdin) were used as received. *N,N*-Dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd) was distilled fractionally over  $CaH_2$  under reduced pressure and stored over  $4\text{ \AA}$  molecular sieves. All

the other reagents and chemicals were used without further purification.

### 2.2. Synthesis of cationic PU

All the polyurethanes were synthesized by a two-step addition process in which the prepolymer was made by reaction of excess of MDI with MDEA and then the end NCO groups were reacted with chain extender of PEG (Scheme 1). The reaction was detected by *in-situ* FTIR and the completion of prepolymer formation was confirmed by half of the intensity of NCO group. The molar ratio of MDI, MDEA, and PEG was 2:1:1. The structure of the synthesized PU is shown in Scheme 1. Appropriate amount of bromoalkane ( $C_2H_5Br$ ,  $C_8H_{17}Br$  and  $C_{14}H_{29}Br$ ) and PU were reacted in DMF solution at  $85\text{ }^\circ\text{C}$  for 30–36 h. The molar ratio of bromoalkane and DMEA was kept at 3:1. After the solution was cooled to ambient temperature, it was dropped into water. The polymer was filtered and washed with hexane to remove excessive bromoalkane, finally dried in a vacuum desiccator.  $^1H$  NMR spectra were recorded on a Bruker AVANCE II 400 spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as the internal standard. Gel permeation chromatography (GPC) was used to determine the molecular weights of polymers. GPC analysis was performed on a Wyatt DAWN HELEOS system (50 Mw GaAs,  $\lambda = 650$  nm). Polystyrene standards were used as calibration standards for GPC. The synthesized cationic polyurethanes are abbreviated to PU-C<sub>2</sub>, PU-C<sub>8</sub> and PU-C<sub>14</sub>, respectively.

PU-C<sub>2</sub> was obtained as light yellow sticky-solid. Mw = 21.35 K, Mw/Mn = 1.57 (GPC, polystyrene calibration).  $^1H$  NMR ( $d_6$ -DMSO)  $\delta$  (ppm): 0.8 ( $-CH_3$ ), 1.1–1.2 ( $-CH_2-$ ), 3.1–3.2 ( $-OCH_2-$ ), 3.3–3.5 ( $-OCH_2-$ ), 7.0–7.1 (ArH), 7.2–7.4 (ArH), 8.5–8.6 ( $-NH-$ ), 9.5–9.7 ( $-NH-$ ).



Scheme 1. Schematic representation of synthesis of cationic PUs.

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