

Morphology and ionic conductivity of solid polymer electrolytes based on polyurethanes with various topological structures

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Polyurethanes with linear, hyperbranched and comb-crosslinked structures were synthesized and were used to prepare solid polymer electrolytes. The polymer electrolytes were characterized by means of Fourier transform Raman spectroscopy, impedance spectroscopy (IS) and atomic force microscopy (AFM). The results showed that salt concentration significantly influences the morphology and conductivity of the three kinds of polyurethane/LiClO₄ system. When the mole ratios of the ether oxygen atom to lithium ion were controlled to be 12, 4 and 4 respectively for linear, hyperbranched and comb cross-linking polyurethane, the electrolytes typically displayed micro-phase separated morphology and the ionic conductivity also reached maxima respectively at 2.2×10^{-7} S/cm, 2.8×10^{-6} S/cm and 2.8×10^{-5} S/cm at room temperature.

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1. Introduction

Since the pioneering work by Wright [1–3] on ion conductivity in poly(ethylene oxide) (PEO)/alkali metal salt complexes, the studies on solid polymer electrolytes (SPE) have attracted considerable interest because of the potential application of these materials in sensors, smart windows and high energy density batteries [4, 5]. Nonetheless, the PEO-based solid polymer electrolytes are inherently of low ionic conductivity and of poor mechanical properties while the crystallinity of PEO is high. A variety of polymers have been studied to prepare solid polymer electrolytes. The main interest has been to enhance ionic conductivity, however, morphological studies have also been carried out since in many applications the polymer electrolyte is also required to exhibit elastomeric properties in addition to high ionic conductivity. Polyurethanes are a class of important polymers, which have been widely applied due to their excellent properties. Recently, polyurethanes have been used to prepare solid polymer electrolytes because of their good chemical stability, excellent mechanical properties, and low glass transition temperature (T_g) [5–10]. The morphology of solid polyurethane electrolytes is one of the most important factors that affects their macroscopic properties. Ferry etc. have studied the phase morphology and bulk impedance of a thermoplastic polyurethane (TPU) doped with LiClO₄ [9].

In this work, we synthesized a series of polyurethanes with various topological structures to investigate the influence of morphology on ionic conductivity of solid

polymer electrolytes. The microstructure of the electrolytes and the ionic conductivity will be addressed in terms of the results of Fourier transform (FT)-Raman spectroscopy, impedance spectroscopy measurements (IS) and atomic force microscopy (AFM).

2. Experimental

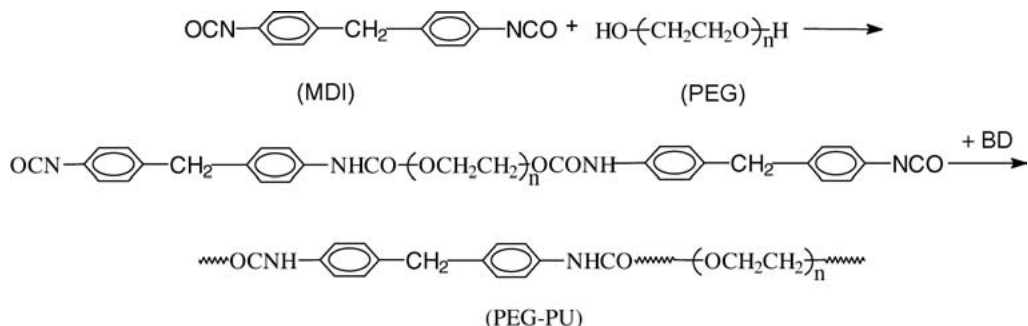
2.1. Materials and preparation of samples

Poly(ethylene glycol) (PEG), 4,4'-methylene di(phenyl methane isocyanate) (MDI) and 1,4-butanediol (BD) were purchased from Aldrich Chemical Co. USA. The PEG has a quoted molecular weight of $M_n = 1000$ and was dried in a vacuum oven at 70°C for 48 h before use. MDI was purified by reduced pressure distillation. 2-hydroxyethyl methacrylate (2-HEMA) (C. P. grade) and was supplied by Tianjin Chemical Reagent Experimental Factory, Tianjin, China. 2,2-azobisisobutyronitrile (AIBN) (A. R. grade) was recrystallized and dried at 30°C in a reduced pressure condition. Lithium perchlorate (LiClO₄) (A. R. grade) was obtained from Shanghai Chemical Reagent Factory, Shanghai, China and was dried at 120°C in a vacuum oven for 10 h before use. All other reagents were obtained from commercial source and purified by standard procedures before use.

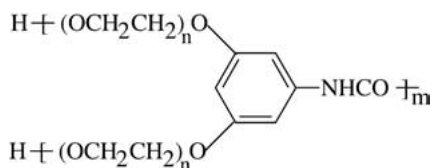
2.2. Synthesis and preparation of polyurethanes-based solid electrolytes

Linear polyurethane was synthesized by a typical two-step condensation reaction whose details were

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Scheme 1 Synthetic route to line polyurethane (LPU).

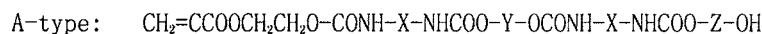


Scheme 2 Structure of hyperbranched polyurethane.

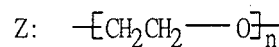
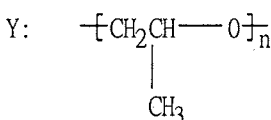
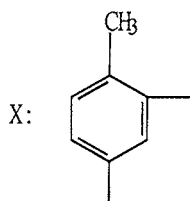
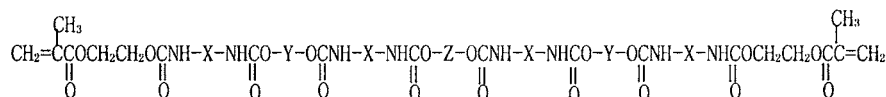
described elsewhere [11]. The reaction procedure was outlined in Scheme 1. Its molecular weight is about 4500 g/mol, the T_g is about 88°C.

The hyperbranched polyurethanes were synthesized as described in detail elsewhere [12]. Scheme 2 is the structure of hyperbranched polyurethane. Its molecular weight is about 7800 g/mol, the T_g is about 42°.

The comb-crosslinked polyurethane was synthesized by dissolving a prepolymer in dioxane (including 0.25 wt% AIBN), after eliminating oxygen, gelation at 55°C for 8 h [13]. The prepolymer was synthesized by a three-step processes. First, TDI and PPG were poured into the glass reactor under nitrogen gas. Proper dibutyltindilaurate was added under stirring. Then, HEMA was added slowly into the reactor and reacted, which introduced a reactive vinyl group to the molecular ends as polymerizable group. Finally, PEG was poured into the reactor. A- and B-type molecules were obtained. The synthesis process was described in detail elsewhere [14]. The structure of the prepolymer was shown in the Scheme 3. Its molecular weight is about 3000 g/mol, the T_g is about 60°C.



B-type :



Scheme 3 Structure of the prepolymer.

2.3. Preparation of solid polymer electrolytes

The linear polyurethane, the mixture of the linear (30 wt%) and the hyperbranched (70 wt%) polyurethanes were used as the matrix materials of the electrolytes. The matrix polymers and LiClO₄ were dissolved in propane carbonate (PC), a mutual solvent for the lithium salts and polymers and the films of polyurethane electrolytes were prepared by solution casting techniques. The linear polyurethane electrolyte sample was denoted LPU, whereas the electrolytes based on the mixture of the linear and hyperbranched polyurethanes was called LHPU.

Since the comb-crosslinked polyurethane is insoluble, the film of solid polymer electrolyte with this material was prepared by immersing it in a PC solution of lithium perchlorate and by evaporating the solvent. This sample was denoted CCPU.

2.4. Characterizations

Fourier transform Raman spectra were recorded at 25°C, at a resolution of 2 cm⁻¹, on a Bruker IFS66 spectrometer. The Raman module FRA 106 and a near infrared YAG laser with wavelength of 1064 nm were used. Atomic force microscopy (AFM) was carried out on a Nano-Scope IIIa SPM analyzer from Digital Instruments at 25°C and the tapping mode was utilized. Ionic conductivity measurements with alternating current were conducted on a Hewlett-Packard 4192A Impedance Analyzer, at 25°C, in the frequency range

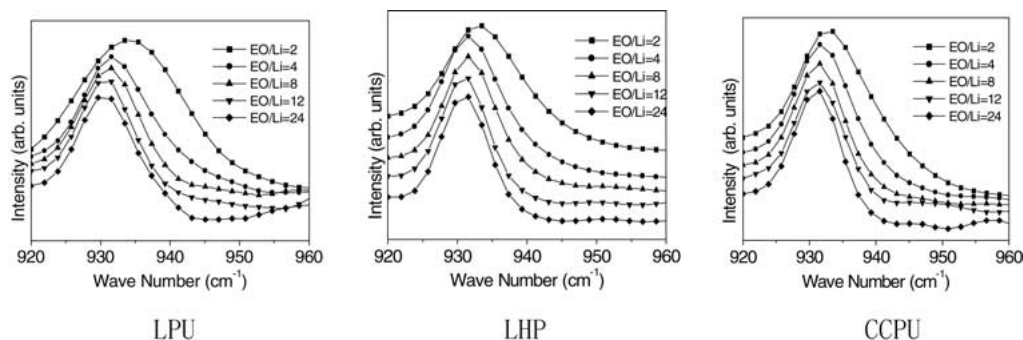


Figure 1 Raman spectra of polyurethane electrolyte at different EO/Li ratios.

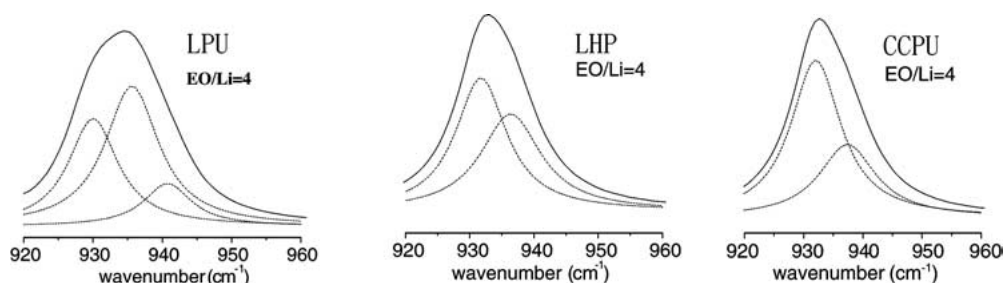


Figure 2 Raman band associated with $\text{ClO}_4^- \nu_1$ mode fitted by the sum of Lorentzian lines.

from 10 to 10^6 Hz. The films were cut into a required size (10 mm in diameter and 0.2–0.3 mm in thickness) and were sandwiched between two copper electrodes.

The ionic conductivity of the samples is calculated by

$$\sigma = (1/R)d/S$$

where σ is the ionic conductivity; S the area of the electrode; R and d are respectively the bulk resistance and the thickness of the samples.

3. Results and discussion

3.1. FT-Raman spectroscopy

Raman spectroscopy was used to study the ionic state in the solid polymer electrolyte. Fig. 1 shows Raman spectra in the range of perchlorate stretching vibration for the three kinds of polyurethane electrolyte at different ether oxygen/lithium (EO/Li) ratios. It is clearly seen that the ClO_4^- stretching band became broad and shifted to higher wavenumbers with increasing salt concentration. It is possible to study the relative proportion of free ion, ion pair and ion aggregation in the electrolytes by resolving these bands, as shown in Fig. 2. In this fitting, Lorentzian lines were used and the peak deconvolution results are summarized in Table I. The

TABLE I Peak deconvolution of the Raman band associated to the $\text{ClO}_4^- \nu_1$ mode

Sample	Peak position (cm^{-1})			Peak area (%)		
	I	II	III	I	II	III
LPU(EO/Li = 4)	930.1	935.6	940.8	35.7	50.7	13.6
LHP(EO/Li = 4)	931.8	936.4	0	53.8	46.2	0
CCPU(EO/Li = 4)	932.0	937.4	0	65.7	34.3	0

splitting of the symmetric stretching mode (ν_1 mode) for the ClO_4^- anion has been observed by several authors [15–19]. The first component at 931 cm^{-1} was ascribed to free-ions [16, 17], whereas the ion pair $\text{Li}^+ \text{ClO}_4^-$ was identified by the second band at 938 cm^{-1} [18, 19]. The appearance of new bands at higher frequencies indicates the presence of aggregates of the salts in the samples [16, 17]. From Fig. 2 and Table I, it is seen that the ν_1 mode of LPU sample can be fitted by three peaks, which correspond to free-ions, ion pair and ion aggregation, respectively, but for LHP and CCPU, there are only free ion and ion pair absorbances and no ion aggregation was detected, suggesting that both LHP and CCPU have the stronger solvent capability.

3.2. Ionic conductivity analysis

Fig. 3 shows the plots of ionic conductivity (σ) for the three PU materials, as functions of EO/Li⁺ mole ratios. It is noted that the three polyurethane-LiClO₄ systems displayed quite different relationships of ionic conductivity *versus* EO/Li⁺ mole ratios. For LPU-LiClO₄ system, the electrolyte ionic conductivity increased with increasing EO/Li⁺ mole ratio and attained the

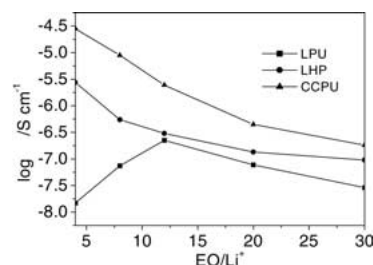


Figure 3 The effect of mole ratio of EO/Li^+ on the ionic conductivity for polyurethane/ LiClO_4 system.

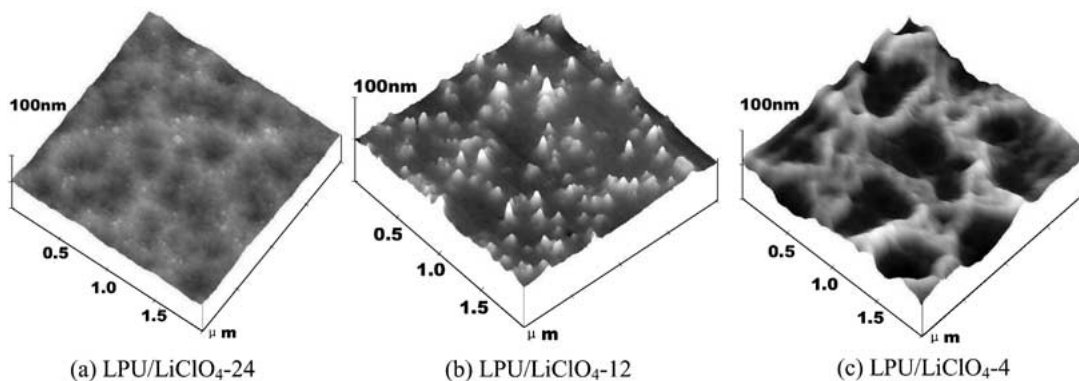


Figure 4 Three dimensional AFM images of LPU/LiClO₄ system.

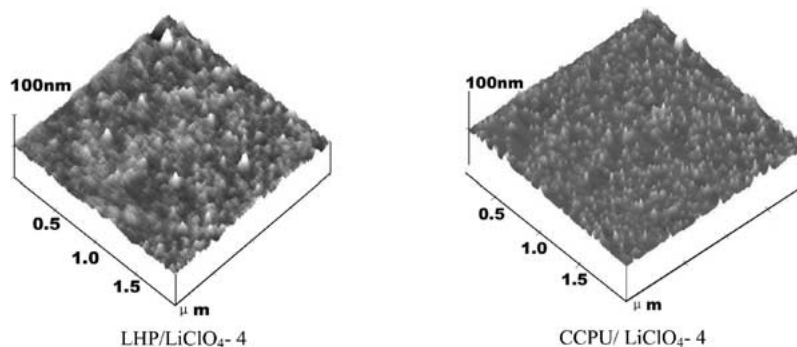


Figure 5 Three-dimensional AFM image of LHP/LiClO₄-4 sample and CCPU/LiClO₄-4 sample.

maximum of 2.2×10^{-7} S/cm when the EO/Li⁺ mole ratio was 12. However, further addition of LiClO₄ caused a decrease of the ionic conductivity, which could be interpreted by two opposite effects [20]. On the one hand, with increasing salt concentration, the number of charge carriers increases and ion pairs and ion aggregations are also formed. The former effect predominates and enhances the ionic conductivity of samples at low salt concentrations (EO/Li⁺ > 12), whereas the latter effect is dominant and decreases the ionic conductivity at higher salt concentrations. Therefore, there exists a maximum ionic conductivity for the LPU/LiClO₄ system over the whole salt concentration range investigated [5]. For LHP/LiClO₄ and CCPU/LiClO₄ systems, the ionic conductivity monotonically increased with increasing salt concentration. Their maximum ionic conductivity reached 2.8×10^{-6} S/cm and 2.8×10^{-5} S/cm, respectively, for EO/Li = 5. This observation could be ascribed to the stronger solvent ability to this salt of these two polyurethanes compared to LPU, so the maximum conductivity should emerge at a higher concentration. The results were in good agreement with those showed by the Raman spectroscopy studies.

3.3. Atomic force microscopy

AFM was utilized to study the phase-segregated morphology of polyurethane with various salt concentrations. Fig. 4 shows AFM images of LPU/LiClO₄ complexes. The AFM topographic image of LPU/LiClO₄-24 sample (the number after the polymer represents the EO/Li ratio) reveals a typical phase-segregated morphology (Fig. 4a). The bright aggregates, which might be hard-segment-rich regions

[18] are dispersed in a dark soft-segment-rich matrix. With increasing salt concentration, significant changes were observed in the surface morphology. There are two competitive tendencies between hydrogen bonding and alkali metal cation complexation with inclusion of LiClO₄ into LPU. The salt ions are capable of forming complexation with polymer chains and reduce the hydrogen bonding interactions in the hard segments of LPU, improving the compatibility between the hard and soft segments. As a consequence, the size of hard-segment-rich regions is reduced. When the EO/Li⁺ ratio reached 12, the minimum size of the hard-segment-rich region was obtained (Fig. 4b). With increasing the salt concentration, nonetheless, a different kind of aggregates appears (Fig. 4c), attributed to the precipitation of alkali metal salt. The inter-ionic electrostatic forces as well as the incompatibility between the incorporated salt and the non-polar polymer matrix induce the salt to aggregate. Indeed, ion pairs are formed when the salt content becomes higher than a critical value, leading to salt precipitation [19]. Compared with LPU, LHP and CCPU systems had the minimum size of hard-segment-rich region when EO/Li⁺ ratio reaches to 4 (shown in Fig. 5), which is related to the stronger solvent ability of LHP and CCPU to Lithium perchlorate and coincides with the Raman and conductivity results presented above.

4. Conclusions

Polyurethanes with linear, hyperbranched and comb-crosslinked structures were synthesized and used to prepare polymer electrolytes by complexation with lithium perchlorate. FT-Raman, IS, and AFM were

used to characterize the morphology and ionic conductivity of these electrolytes. The hyperbranched and comb-crosslinked polyurethanes have stronger solvation ability to the salt than the linear polyurethane; comb-crosslinked polyurethane has the strongest solvation ability. Salt concentration has significant influence on the morphology and conductivity of polyurethane. For LPU, when EO/Li⁺ is 12, the AFM image of sample reveals the typical micro-phase separated morphology. In LHP and CCPU systems, their typical micro-phase separated morphology emerged when EO/Li⁺ mole ratio is 4. At the same time they reach their maximum ionic conductivity of 2.2×10^{-7} S/cm, 2.8×10^{-6} S/cm and 2.8×10^{-5} S/cm respectively. It would be interesting to have further investigation on the relationship of morphology and conductivity in different systems and salt concentrations.

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