Preparation and Evaluation of Two Kinds of Solid Polymer Electrolytes Made from Crosslinked Poly(ether urethane) Elastomers Consisting of a Comb-Like and a Hyperbranched Polyether

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ABSTRACT: Two novel polyethers, one comb-like and another hyperbranched, were synthesized by the cationic ring-opening polymerization of 3-(methoxy(triethylenoxy)) methyl- and 3-(hydroxy-(triethylenoxy))methyl-3′-methyl-oxetane, respectively. The former reacted with a multifunctional isocyanate and the latter with a difunctional isocyanate to give rise to the corresponding crosslinked poly(ether urethane) elastomers, PCEU and PHEU. Accordingly, two kinds of solid polymer electrolytes (SPEs) were prepared from these two elastomers *in situ* in the presence of lithium salt trifluoromethanesulfonimide. It was found that the PCEU-based SPEs shows a higher ionic conductivity than that PHEU-based ones due to its more mobile pendent chains and appropriate crosslinking density in the polymeric network. The maximum ionic conductivities of 1.4×10^{-5} S/cm at 30°C and 3.5×10^{-4} S/cm at 80°C were attained at the molar ratio of O/Li = 7.5. The DSC measurements clearly demonstrated that PCEU indeed possesses the more flexible chain motion ability than PHEU. The electrochemical stability window of PCEU, which is 1.7–4.0 V was measured by cyclic voltammogram. Additionally, the significantly high decomposition temperature as evidenced by TGA analyses endowed these SPEs a good safe performance. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1955–1961, 2008

Key words: comb-like polyether; hyperbranched polyether; crosslinked poly(ether urethane) elastomer; solid polymer electrolyte; ionic conductivity

INTRODUCTION

Since it was first disclosed by Wright and Armand in 1970s,[1–3] solid polymer electrolytes (SPEs) have been expected to be capable of applying in solid-state lithium ion batteries because they can potentially get rid of battery leakage and negate the need for a separator to impart those batteries a high safety and reliability. However, for a long time a relatively lower ionic conductivity of about 10^{-7} S/cm at ambient temperature has impeded the progress in conventional PEO-LiX-based SPEs due to the high crystallinity tendency and poor chain motion performance of the polymer matrices. It still remains a challenge to develop polymer-LiX-based electrolytes with an acceptable ionic conductivity, about 10^{-3} S/cm at ambient temperature for practical applications.

In the recent years, hyperbranched polymers have attracted immense attention for their unique molecular structure and their ease of preparation when compared with dentrimers. Hawker[4] firstly reported a class of hyperbranched polymer electrolytes made from the self-condensation of a typical AB_2 monomer 3,5-dihydroxybenzoic acid (DHA) into which the oligomer chain of poly(ethylene glycol) (PEG) was incorporated. Later, also by using the DHA and PEG oligomer, Itoh[5,6] and Tang[7] synthesized and evaluated hyperbranched polyester- and polyurethane-based polymer electrolytes, respectively. The amorphous nature of the resulting hyperbranched structures led to these materials potential SPE candidates used in lithium ionic batteries. As is well known, lowering the glass transition temperature (T_g) of polymer matrices as low as possible offers one effective approach to improve the ionic conductivity. However, for these hyperbranched polymers, it is nearly unlikely to reduce their T_g further due to the inherently poor chain motion performance of the enchained aromatic moieties in DHA.

Meanwhile, poly(ether urethane)s (PEUs)[8–10] have been also exploited as SPE matrices. The soft segments in the PEUs can dissolve Li+ cations, and at

the same time the hard segments as reinforcing fillers can greatly improve the mechanical properties of the resulting polymer electrolytes. In general, the ionic conductivity of the PEU-based SPEs can reach the magnitude of about 10^{-5} S/cm.[11–18] Because the soft segments in these PEU matrices usually possess a linear and regular structure, such as PEO, poly (propylene glycol) and poly(tetramethylene glycol), they inevitably also experience a partial crystallization in bulky state as in the PEO-LiX-based systems, which is regarded as one of the main obstacles that prevents the improvement of the ionic conductivity of PEU-based SPEs further.

As an alternative, two polyethers, one comb-like and another hyperbranched, were chosen as the soft segments of the crosslinked PEU elastomers in the present study. The former, poly(3-(methoxy(triethylenoxy))methyl-3′-methyloxetane) (PMTMO), showing a relatively lower T_g, about $-52°C$, was prepared via the cationic ring-opening polymerization (CROP) in our previous account.[19,20] The latter, poly(3-(hydroxy (triethylenoxy))methyl-3′-methyloxetane) (PHTMO), has been just synthesized in our laboratory.[21] Subsequently, two novel crosslinked PEU-based SPEs, PCEU and PHEU, were fabricated in situ in the presence of the lithium trifluoromethanesulfonimide (LiTFSI) salt. In fact, PCEU was formed from the crosslinking reaction of a linear comb-like polydiol with multifunctional isocyanates LM-100, arising from the diverse hydrolysis of hexamethylene diisocyanate (HDI). PHEU was prepared from the reaction between HDI and a multifunctional hyperbranched polyol. It was anticipated that these two PEU-based polymer electrolytes will benefit the ionic conductivity improvement owing to their comb-like or hyperbranched structures as well the absence of rigid aromatic moieties in the polymer backbones. Additionally, although the same oligomer PEG chains was incorporated into PMTMO and PHTMO, for the former this oligomer was grafted as a pendant group whereas in the latter it was bound into the main chains. As a result, this unique difference would exhibit a significant influence on the ion conductivity of the resulting SPEs.

EXPERIMENT

Materials and measurement

LiTFSI was available from Aldrich, USA and used as received. All other solvents and reagents were of analytical grade as used in our previous work.[19–21] LM-100 was kindly provided by Liming Institute of Chemical Industries, Province Henan, China, and used without further treatment. The isocyanate content of LM-100 is 18.9%.

FTIR spectra were measured with Shimadzu IR Prestige-21. ^{1}H NMR spectra were recorded on Bruker ARX 400 using $CDCl_3$ as solvent containing TMS as internal standard. Elemental analysis was carried on Vario EL III. Netzsch PC-200 was used for analysis of the thermal behavior of the polymers at a heating rate of 10°C/min. The polymer samples were heated from -100 to $100°C$ in stainless steel pans. The results of the second run were used for glass transition temperature investigation. Thermogravimetric analysis (TGA) was conducted with TA 2000 thermogravimeter under N_2 atmosphere at a heating rate of 20°C/min. Gel permeation chromatograph (GPC) analysis was made on Waters 2414 at 35°C using THF as eluent. From the GPC results, the molecule weight was determined as calibrated with polystyrene standards.

Synthesis of comb-like polyether

Synthesis of the comb-like polyether, PMTMO, was described in our previous work.[19,20] The number average molecular weight (M_n) was determined to be 4500 g/mol by means of GPC analysis.

PMTMO, FTIR/cm^{-1}: 3317 (O—H), 2903 (CH_2), 1069 (C—O—C); ^{1}H NMR/ppm: $\delta = 0.90$ (CH_3 in side chain), 3.19 (C—CH_2—O in main chain), 3.30 (C—CH_2—O in side chain), 3.38 (OCH_3 in side chain), 3.55–3.57 (O—CH_2CH_2—O, the middle ethyloxy group in side chain), 3.61–3.66 (O—CH_2CH_2—O, the rest two ethyloxy groups in side chain).

Synthesis of hyperbranched polyether

Preparation and characterization of the hyperbranched polyether, PHTMO, was separately reported.[21] A brief description was as follows. The solvent CH_2Cl_2 was first added to a dry round flask under N_2 atmosphere. After 3-(hydroxy(triethylenoxy))methyl-3′-methyloxetane (HTMO) was added, initiator $BF_3 \cdot Et_2O$ was introduced at room temperature into the flask. The CROP continued for 72 h, and then was terminated by adding a mixture of methanol and water. The resultant hyperbrached polyether was purified by precipitation into hexane three times, and dried in vicuo.

PHTMO, FTIR/cm^{-1}: 3434 (O—H), 2876 (CH_2), 1112 (C—O—C); ^{1}H NMR/ppm: $\delta = 0.89$–0.92 (3H, CH_3), 3.14–3.29 (6H, CH_2 next to the quarternary carbon), 3.45–3.76 (12H, CH_2 in triethylene glycol units), and 5.24 (1H, OH). M_n of PHTMO was measured to be 4300 g/mol by GPC analysis.

Preparation of PEU polymer electrolyte

Firstly, the prepolymer was mixed with LiTFSI during a drying process. After adding the corresponding
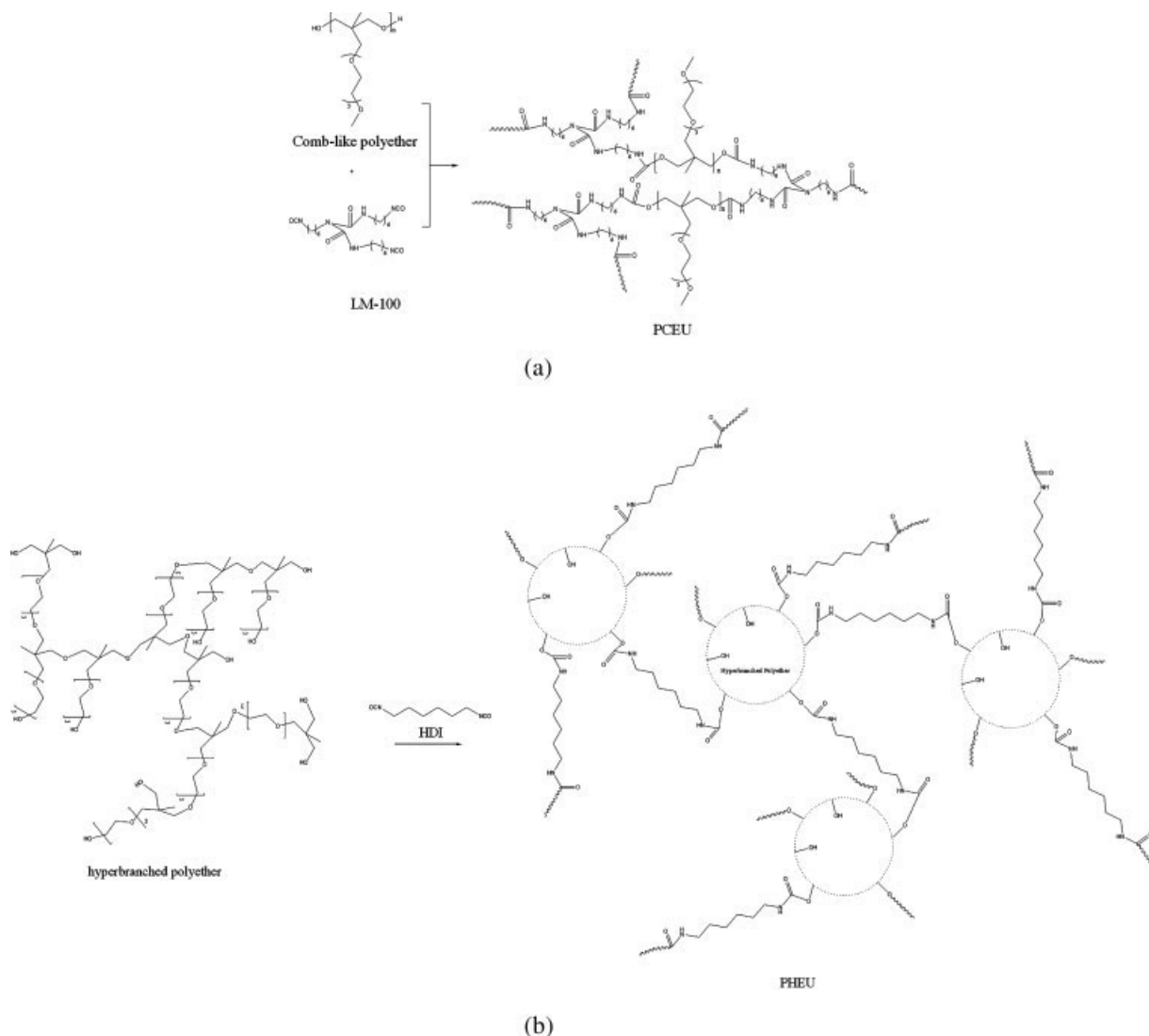
Scheme 1 Preparation protocols of the crosslinked PCEU (a) and PHEU (b).

isocyanate, the resulting mixture was stirred and heated at 70°C for half an hour under N₂ atmosphere. Then, it was poured onto a PTFE plate and placed in the oven at 70°C under N₂ atmosphere to undergo the crosslinking reaction for at least 24 h to give rise to a free-standing PEU-based polymer electrolyte film.

Ionic conductivity and cyclic voltammogram measurement

The ionic conductivity of these two PEU-based polymer electrolytes was measured via AC impedance analysis with an electrochemical cell consisting of the resulting PEU polymer electrolyte film sandwiched between two blocks of stainless steel. The AC impedance analysis was performed using CHI 660A Electrochemistry Station made in Chen Hua Instrument Company, Shanghai, China. The measurements were carried out from 30 to 80°C with an interval of 10°C.

The cyclic voltammogram measurement was performed using a two-electrode cell, where the polymer electrolyte was sandwiched between the lithium and aluminum foils. And the cell was assembled in the MBRAUN glove box filled with argon. The measurement was carried out on the CHI660A electrochemical station from open circuit voltage to 5 V, and the sweeping rate is 5 mV/s.

RESULTS AND DISCUSSION

Preparation of PEU

The synthetic pathways of the comb-like and hyperbranched polyether, PMTMO and PHTMO, were described elsewhere,[19,21] respectively. And the preparation strategy for the crosslinked PEU elastomers, PCEU and PHEU, is outlined in Scheme 1. The crosslinking reactions of a difunctional comb-like polydiol PMTMO with a multifunctional isocyanate

LM-100 and a hyperbranched polyol PHTMO with a diisocyanate HDI were carried out under the condition of [NCO]/[OH] = 1.0. LM-100 is a mixture of bi, tri, and even higher functional uret derivatives made from the hydrolysis of HDI whose number average functionality is determined to be 3.6. PHTMO has the number average hydroxyl functionality of about 10 calculated from the ^{1}H NMR spectrum.[21] It was found that both the comb-like and the hyperbranched polyether can be directly crosslinked with the corresponding isocyanate at 70°C in the absence of any curing catalyst, which is benign to the following evaluation on the ionic conductivity of PEU-based polymer electrolytes.

Ftir analysis

The FTIR spectra of PCEU and PHEU without doping with LiTFSI are shown in Figure 1. Compared with the starting isocyanates, the absorbance peak disappeared at about 2270 cm^{-1} ascribed to —NCO group indicated the occurrence of the crosslinking reaction between the isocyanates and polyethers. In addition, these two PEU elastomers were characterized further by the following three peaks. The peaks at about 3360 and 1690 cm^{-1} imply the N—H group and carbonyl group stretching vibration, respectively, both resulted from the reaction of the terminal hydroxyl groups of the polyethers with the isocyanates. The peak assigned to the ether bond of the soft segments emerges at about 1110 cm^{-1}. Moreover, these two spectra were found to resemble each other very much because either PCEU or PHEU is composed of the similar polyether and isocyanate.

Ionic conductivity measurement

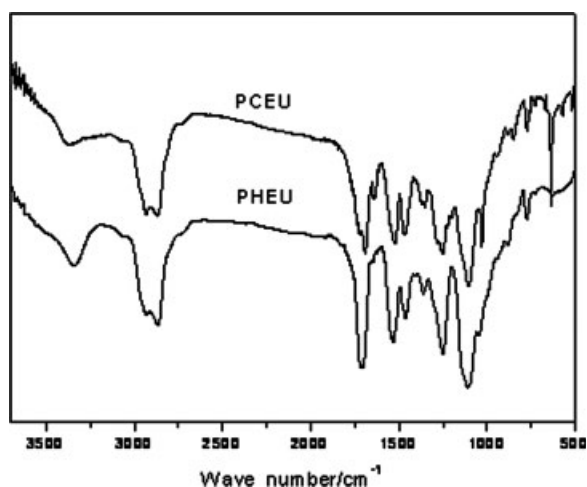According to our previous result,[22] a polymer electrolyte doped with LiTFSI generally yields a higher ionic conductivity compared with the other commonly used lithium salts, such as LiClO$_4$, LiBF$_4$, LiPF$_6$, and so on. Consequently, only LiTFSI was used and tested in the current work. Figure 2 shows the typical AC impedance plot of PCEU doped with LiTFSI, where the value of the point of intersection between the plot and x axis represents the value of the bulk resistance of SPE. Thus, the ionic conductivity of the corresponding PEU-based polymer electrolytes can be calculated according to the following equation.[23]

$$\sigma = \frac{l}{(R_b \times A)} \tag{1}$$

where R_b is the bulk resistance of polymer electrolyte, l is the film thickness, and A is surface area of electrode.

The Arrhenius plots of the ionic conductivity of both PCEU and PHEU are depicted in Figure 3, where the amount of LiTFSI added was kept at the molar ratio of O : Li = 15. The ionic conductivity of the former reached 5.8×10^{-6} S/cm at 30°C and

Figure 2 Typical AC impedance of PCEU at 80°C.

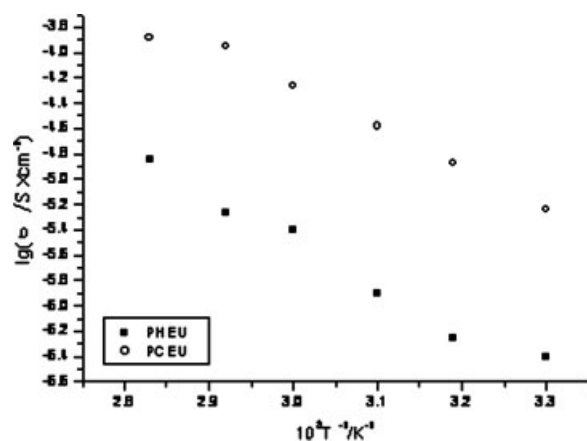**Figure 1** IR spectra of the crosslinked PEU elastomers.

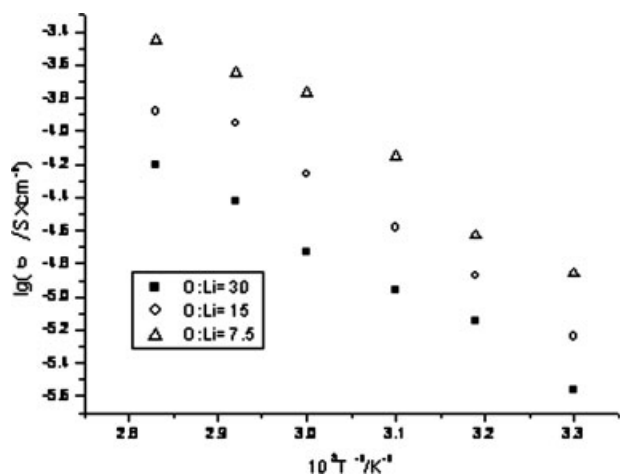**Figure 3** Arrhenius plots of ionic conductivity of PCEU and PHEU.

Figure 4 Ionic conductivity of PCEU with varying lithium salt concentration.

1.4×10^{-4} S/cm at 80°C, whereas that of the latter attained 4.0×10^{-7} S/cm at 30°C and 1.6×10^{-5} S/cm at 80°C, respectively. As documented, the ionic conductivity of SPEs is usually determined by two factors, i.e., the concentration of lithium salt and the chain motion performance of the polymer matrix. Since the concentration of LiTFSI was kept constant here, the ionic conductivity was exclusively determined by the polymer chain motion performance. It appeared that the chain motion ability of PHEU is much poorer than that of PCEU, which can be well explained by taking account the DSC measurement results in the following section. Moreover, the impact of the lithium salt concentration on the ionic conductivity of PCEU was investigated. As shown in Figure 4, a maximum ionic conductivity of 1.4×10^{-5} S/cm at 30°C and 3.5×10^{-4} S/cm at 80°C were obtained at O : Li = 7.5, respectively.
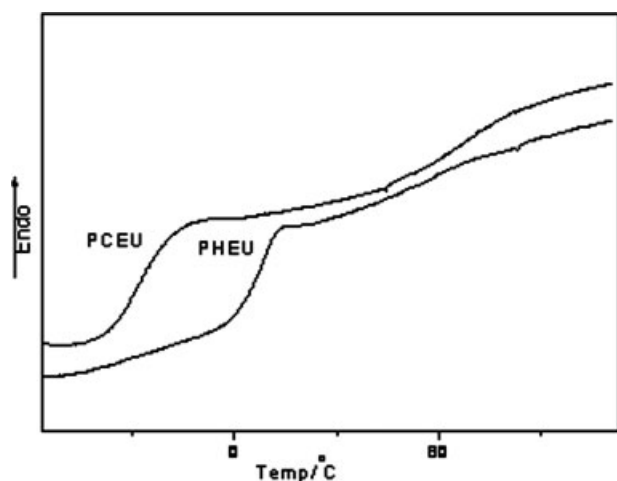

Figure 5 DSC curves of pure PCEU and PHEU.

DSC measurement

Figure 5 shows the DSC curves of both pure PCEU and PHEU, and their glass transition temperatures are summarized in Table I. Two glass transition temperatures related to the soft segment and hard segment motion were clearly visible in these curves. The T_{gs} is associated with the transition of the soft segments from glassy state to rubbery state.[8,17] However, the T_{gh} is difficult to be precisely determined as the corresponding heat transition of the hard segments is not very obvious. During the ionic transporting processes, the Li$^+$ ion moves along with the moving of the soft segments through the continual formation and crack of the transient crosslinkages between the Li$^+$ ion and ether oxygen atoms of the soft segments. In general, the lower T_{gs} of the polymer chain is, the higher is the ionic conductivity. As a result, the lower T_{gs} of PCEU endows this kind of SPEs a higher ionic conductive ability.

Although triethylene glycol ether (TME) segment as a lithium ion complexing group was incorporated into both the comb-like and hyperbranched polyether, it was grafted as a pendent chain in the former whereas it was bound into the main chain in the latter. Obviously, TME appended as the side chain has a better motion performance than in the main chains, leading to PCEU holding the lower T_{gs} than PHEU. On the other hand, the crosslinking density of the PEU elastomers also significantly affects the ionic conductivity, which is directly related to the number average functionality of the starting polyethers or isocyanates. A higher functionality will yield a higher crosslinking density. As the number average functionality of LM-100 is much lower than PHTMO, the resulting PHEU certainly had a very higher crosslinking density and a higher T_{gs} than PCEU to limit the motion ability of polymer chains.

The DSC curves of PCEU doped with varying lithium salt concentration are shown in Figure 6, and the results are summarized in Table I. The T_{gs} increased with the increasing of the concentration of the lithium salt due to the increasing transient crosslinkages between Li$^+$ ions and ether oxygen atoms of the soft segments. This clearly implied that the ionic conductivity cannot be further enhanced by persistently increasing the concentration of lithium salt. Additionally, the heat transition of T_{hs} becomes

TABLE I
T_g of PCEU and PHEU

| Name	O : Li	T_{gs} (°C)	T_{gh} (°C)
PCEU	–	−37.3	–
	30	−22.8	–
	15	−23.7	–
	7.5	−16.8	48.9
PHEU	–	13.7	–
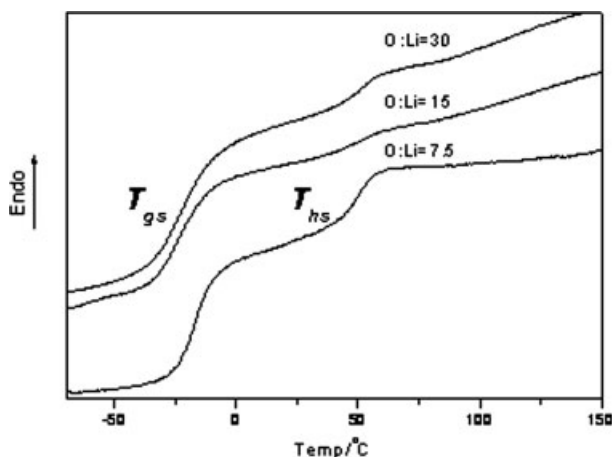
Figure 6 DSC curves of PCEU with varying lithium salt concentration.

more obvious in the DSC curve with increasing the lithium salt content. This is most likely due to that the doped lithium ions seize the more soft segments from the hard domains through coordination with the ether oxygen atoms of the soft segments to extend the phase separation between soft and hard blocks of the crosslinked PEU elastomers.

Cyclic voltammogram measurement

As PCEU has the higher ion conductivity, its electrochemical stability window is measured by cyclic voltammogram (CV). The CV's first three potential cycles for the Li/PCEU/Al cell at room temperature is given in Figure 7, and the sweep rate was kept at 5 mV/s. In the first cycle, the scanning started from its open circuit voltage (1.7 V). The current rose abruptly at about 4.0 V, which indicates the occurring of oxidation in Al electrode, and it rapidly decreased to current baseline in the reversed scanning. Furthermore, in the subsequent tow cycles, the
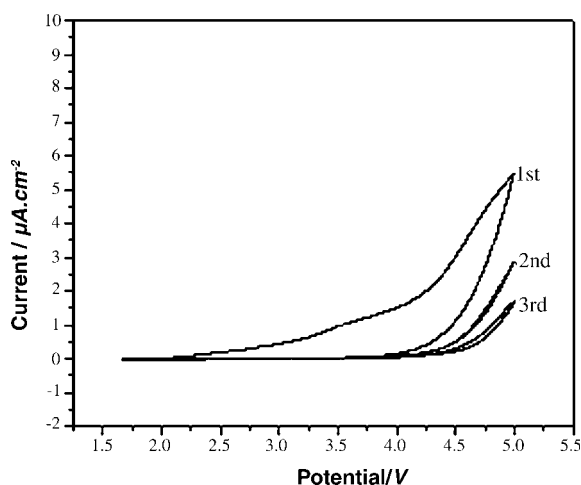
oxidation potential moved to the high value and the current kept at the very lower value compared with the first cycle. So it can be concluded that the electrochemical stability window of PCEU should be 1.7–4.0 V.

Thermal stability

The thermal decomposition processes of the resultant PCEU-based SPEs are shown in Figure 8. It can be noted that all the samples start to lose weight at around 350°C, and the weight lose completes over 450°C. This means that the decomposition temperature of this kind of SPEs as-prepared is substantially higher than liquid electrolytes currently used in lithium ion batteries. Compared with those liquid counterparts, the weight-losing process of these SPEs is gradual and slow. Accordingly, if used in lithium ion batteries, they are certainly more thermostable than the liquid electrolytes.[24]

In addition, it was found here that the weight-losing curves of the PEU-based SPEs move to the lower temperature range when doped with LiTFSI at a higher molar ratio of O : Li = 30. This observation was probably due to the weakening of the C—O bond in the polymer backbones, caused by the interaction of Li^+ ions with ether oxygen atoms.[25] However, the curves would reverse to move to the higher temperature range even over that of the pure PEU matrix when the lithium salt concentration continues to increase to the molar ratio of O : Li = 7.5. This was maybe attributed to that the interaction between Li^+ ions and ether oxygen atoms of the soft segments becomes increasingly stronger.[26,27] Thence, two opposite interactions, one involving the decreasing of the bond strength of C—O bond and the other concerning the increasing stronger of the interaction between Li^+ ion and ether oxygen atoms of the soft segments, were evidenced by gradually adding the

Figure 7 Cyclic voltammogram of the PCEU.
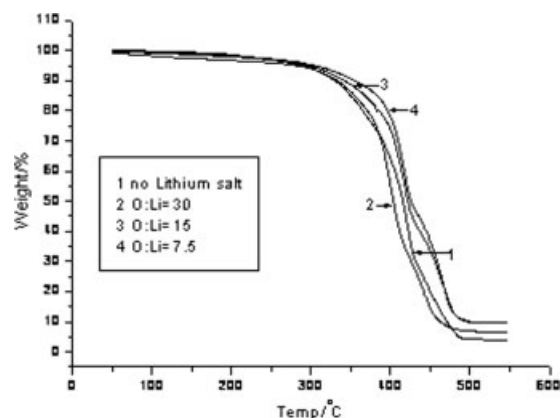
Figure 8 TGA curves of PCEU-based solid polymer electrolytes.

lithium salt. When the former predominated in the PEU-based SPE, the TGA curve would move to low temperature range and *vice versa*.

CONCLUSIONS

Two kinds of SPEs were prepared by doping two novel crosslinked poly(ether urethane) elastomers, PCEU and PHEU with lithium salt LiTFSI. The ionic conductive performance was evaluated by measuring the AC impedance of the PEU-based SPEs. PCEU showed a maximum ionic conductivity of 1.4×10^{-5} S/cm at 30°C and 3.5×10^{-4} S/cm at 80°C when doped at the molar ratio of O : Li = 7.5. The electrochemical stability window of PCEU was founded to be 1.7–4.0 V. The good safe performance of PCEU-based SPEs was also demonstrated by TGA measurement. Hence, it showed highly promising as candidate for SPEs in rechargeable lithium ion batteries.

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