Solid Polymer Electrolyte Based on Peg-Co-Ppg-Pu/Liclo 4

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With a view to enhancing the ionic conductivity via the control of chain mobility of solid polymer electrolyte (SPE) based on poly(ether urethane) (PEU), polyurethane (PU) matrix containing polyethylene glycol (PEG) and polypropylene glycol (PPG) randomly distributed within matrix was synthesized from the simultaneous polymerization of PEG-PU and PPG-PU prepolymers. The efficacy of PEG-co-PPG-PU complexed with LiClO₄ salt as a SPE is discussed and compared with that of PEG-PU/LiClO₄.

Keywords: glass transition temperature; ionic conductivity; random copolymerization

INTRODUCTION

Many studies on solid polymer electrolyte (SPE) systems of polymer/salt complex-type have attracted considerable interest because of their potential application in sensors, smart windows, electronic devices and high-energy-density batteries [1–5]. Most of the works related to ionic-conducting polymer matrices were focused on PEO and modified PEO [6–8]. According to the conventional ionic-transport mechanism based on

PEO-type electrolytes, the ionic-conducting polymer can be viewed as a solvent for alkali metal salts in the polymer matrix, where the salt dissociates into free ions under the coordinating effects of neighboring polymer segments containing polar ether oxygen groups. The segments can rearrange their position and configuration and thus change the location of ions [9,10]. Ionic conduction is achieved through a coupling between the ionic transport and polymer segmental motion taking place in the amorphous phase of a polymer matrix [11]. On the other hand, the SPEs based on poly(ether urethane) (PEU) consisting of hard and soft segments have also attracted much interest due to their superior mechanical properties [12–14]. However, their ionic conductivity at room temperature is still low for the practical applications ($\sim 10^{-6}$ S/cm). In PEUs, hard segments determine the inter-chain interaction and act as a supporting structure to sustain the polymer electrolyte whereas soft segments function as a pathway to transmit the ionic diffusion and chain motion.

In this work, we report the efficacy of PEG-co-PPG-PU/LiClO$_4$, where PEG and PPG are randomly distributed within PU matrix, as a SPE made from a 1:1 mixture of polyethylene glycol (PEG) and polypropylene glycol (PPG) as the soft segment with a view to suppressing the crystallinity of PU matrix, and hence enhancing the ionic conductivity of the resulting SPE.

EXPERIMENTAL

Materials

Poly (ethylene glycol) (PEG; number-average molecular weight (M_n) = 1000; Aldrich Chemical Co.) and poly (propylene glycol) (PPG; $M_n = 2000$; Aldrich Chemical Co.) were dried at 65°C in a vacuum oven for 48 h before use. 4,4′-diphenylmethane diisocyanate (MDI; Aldrich Chemical) was purified by vacuum distillation. 1,4-butanediol (BD; Aldrich Chemical) was dried by refluxing over CaH$_2$ for 4 h to remove the trace water and then was distilled under vacuum. The solvent N,N-dimethylformamide (DMF; Junsei Chemical Co. Ltd.) was dried and distilled before use. The lithium perchlorate (LiClO$_4$) complexed to PEU was Aldrich product, and dried under vacuum at 120°C, 24 h prior to their use.

Preparation of Poly(ether urethane) (PEG-co-PPG-PU)

A poly(ether urethane) (PEG-co-PPG-PU) material (PEG: PPG: MDI: BD = 1:1:4:2 in mole ratio) used as the polymer matrix for solid electrolyte was synthesized by the typical two-step condensation reaction. PEG and PPG were reacted with MDI to make pre-polymer, respectively. PEG-PU
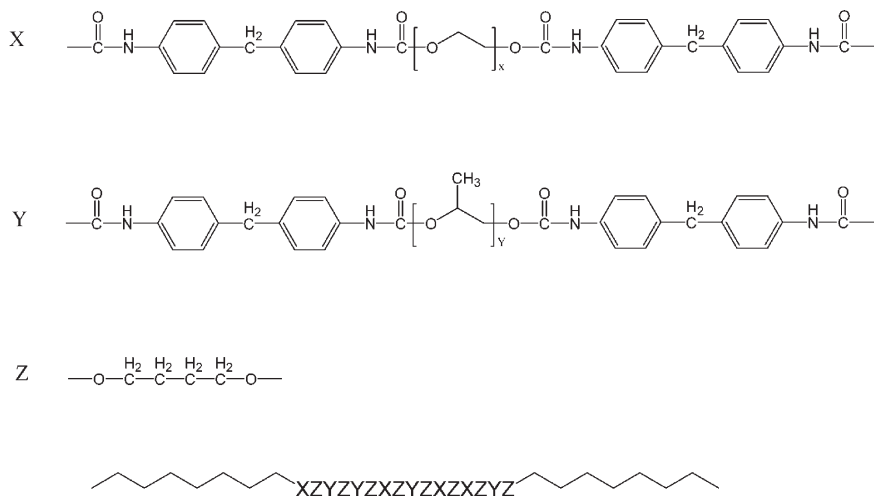
SCHEME 1 Chemical structure of PEG-co-PPG-PU: (X) MDI/PEG/MDI; (Y) MDI/PPG/MDI; (Z) 1,4-Butanediol.

and PPG-PU were simultaneously added to the reactor that was charged under a nitrogen gas atmosphere to form the PEG-co-PPG-PU via the random copolymerization of two components. The temperature was kept at 50°C initially. After proper mixing (150 $\sim$ 200 rpm), 0.15 wt% dibutyltin diaurate was added into the reactor to catalyze the reaction and then the temperature was raised to 70°C. One-step reaction was stirred for 90 min. Then, BD was added dropwise and stirred for an additional hour. The viscosity of the reaction system was found to increase in this step. To ensure a complete reaction, the polymer solution was stirred at 80°C for 3 h and precipitated into a large amount of distilled methyl alcohol. After filtration, the material obtained was dried in a vacuum-drying oven at 60°C for 48 h. The structure of polymer matrix thus prepared is outlined in Scheme 1.

Preparation of the Complex Samples

Films of PEG-co-PPG-PU/LiClO$_4$ complex electrolytes were prepared by the solution-cast technique. The samples with different salt contents, expressed as the molar ratio of ether oxygen to alkali metal cation [O]/[Li$^+$], were prepared by an appropriate amount of PU and LiClO$_4$ being dissolved in DMF and then poured onto a Teflon plate. After the solvent evaporated at 60°C in an oven for 24 h, the films were transferred to a vacuum oven and further dried 60°C for 24 h to remove the residual solvent. The formation of the bubbles could be avoided if the polymer solution in

the hot crucible was vacuum-dried prior to making the film. PEG-co-PPG-PU/LiClO$_4$ complex films with diameter 15 mm and thickness $0.25 \sim 0.35$ mm were finally obtained.

Characterization

The formation of complexes between PEU chain and salt was confirmed by IR spectra with Bruker IFS66 FT-IR spectrometer at a resolution of 2 cm^{-1} [15]. Differential scanning calorimetry (DSC) measurements were performed on a Perkin – Elmer Pyris 1 DSC system. Samples of approximately 10 mg were hermetically sealed in aluminium pans in a nitrogen-filled glove-box. The pans were heated to 120°C and then quickly quenched with liquid nitrogen to −100°C. The pans were placed in the DSC apparatus and heated up to 100°C with a heating rate of 10°C min^{-1}. This second heating was used to determine the glass transition temperatures (T_g). It was defined as the intercept of the extrapolated baseline with the extrapolated slope of the heat capacity in the transient state. Ionic conductivity of the polymer electrolyte was evaluated by a Hewlett-Packard 4192A AC impedance analyzer in the frequency range $10 \sim 10^6$ Hz. The sample films were sandwiched between symmetrical cells containing blocking stainless steel (SS) electrodes. The ionic conductivity of the samples was calculated by using the following equation:

$$\sigma = (1/R_B)d/S \tag{1}$$

where σ is the ionic conductivity, d is the thickness of the sample, S is the area of the SS electrode and R_B is the bulk resistance of the sample determined from the complex impedance plot for polymer electrolyte/blocking electrode cell [16]. Cyclic voltammetry measurements of the lithium plating-stripping process on SS in a cell using the above SPE samples were performed with a Hewlett-Packard 4192 A AC impedance analyzer operating at a 20 mV s^{-1} scan rate in the potential range of −1 to 4 V against lithium.

RESULTS AND DISCUSSION

The glass transition temperature reflects the segmental mobility in the amorphous region of the polymer chain, largely responsible for the ionic transport within the SPE. The DSC was used to determine the T_g of the resulting SPEs. Figure 1 and Table I show the DSC thermograms of PEG-co-PPG-PU/LiClO$_4$ complex electrolytes at different salt concentrations. It is observed that the T_g increases with increasing salt concentration until the [O]/[Li$^+$] reaches 16 for the PEG-co-PPG-PU/LiClO$_4$ complexes,
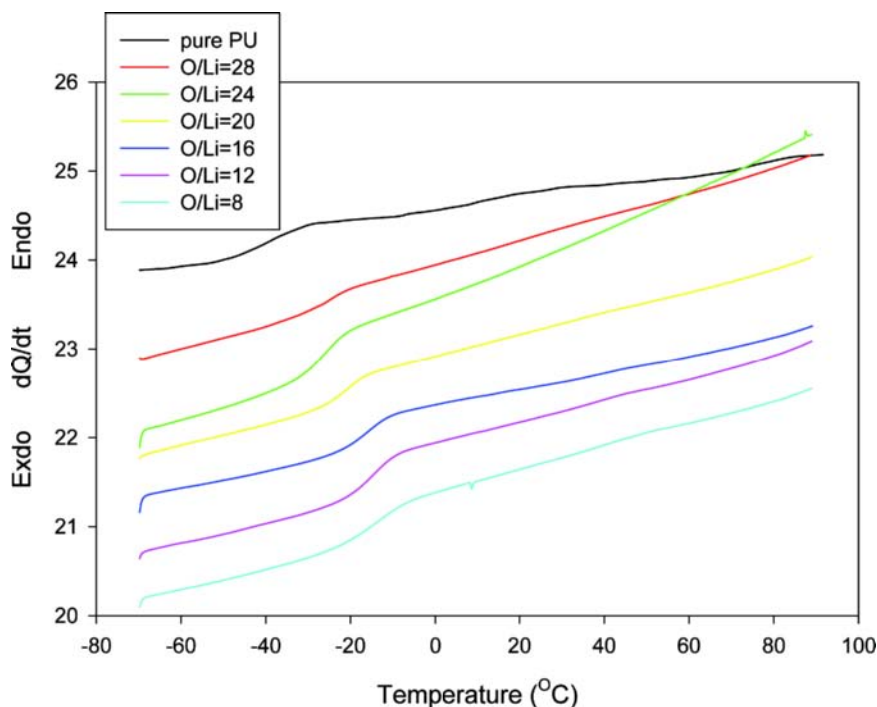
FIGURE 1 DSC thermograms of PEG-co-PPG-PU/LiClO$_4$ complexes at different [O]/[Li$^+$] ratios.

probably due to the transient crosslink formation between salt and polymer chain. However, a further increase in salt content beyond [O]/[Li$^+$] = 16 decreases the T$_g$, probably due to the destruction of the transient network

TABLE I DSC T$_g$ and Specific Heat Difference (ΔC_p) at the Transition Interval as a Function of [O]/[Li$^+$] for PEG-co-PPG-PU/LiClO$_4$ Complex Samples

[O]/[Li$^+$]	Onset(K)	Endpoint(K)	T$_g$[a]	ΔC_p(kJ/mol)
Pure PU	225.2	238.5	231.9	0.32
28	234.6	245.6	240.1	0.28
24	239.1	250.6	244.8	0.51
20	241.2	254.1	247.6	0.35
16	255.7	262.4	259.1	0.24
12	252.1	260.7	256.4	0.22
8	248.6	260.8	254.7	0.30

[a] The DSC T$_g$ was taken as the midpoint at the transition interval.

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caused by the ionic aggregates at higher salt contents [17]. The polymer matrix must posess the moderate chain flexibility, and hence lower glass transition temperature for the elevated ionic conductivity. On the other hand, the T_g values of the PEG-co-PPG-PU/LiClO$_4$ SPEs are found to be much lower than those of the PEG-PU/ LiClO$_4$ SPEs reported in our previous article [17]. The decrease of T_g in the present samples could be interpreted by assuming that by a random introduction of PEG and PPG as the soft segment within PEU matrix, the ordered crystallization region of polymer chain was destroyed because of disordered rearrangement of chains and the bonds of the cations with the carbonyl groups located in the hard segment of PEU. Therefore, it is expected that the SPE obtained from a random copolymerization of PEG and PPG may exhibit a relatively good ionic conductivity.

The ionic conductivity of all polymer electrolytes was determined by means of the impedance spectroscopy using stainless steel as blocking electrodes [17]. From the Z′ vs Z″ (Cole-Cole) plots as shown in Figure 2, ionic conductivity (σ) values were calculated at room temperature from the intercept of the curve with real axis with the aid of Eq. (1), whose results are represented in Table II.
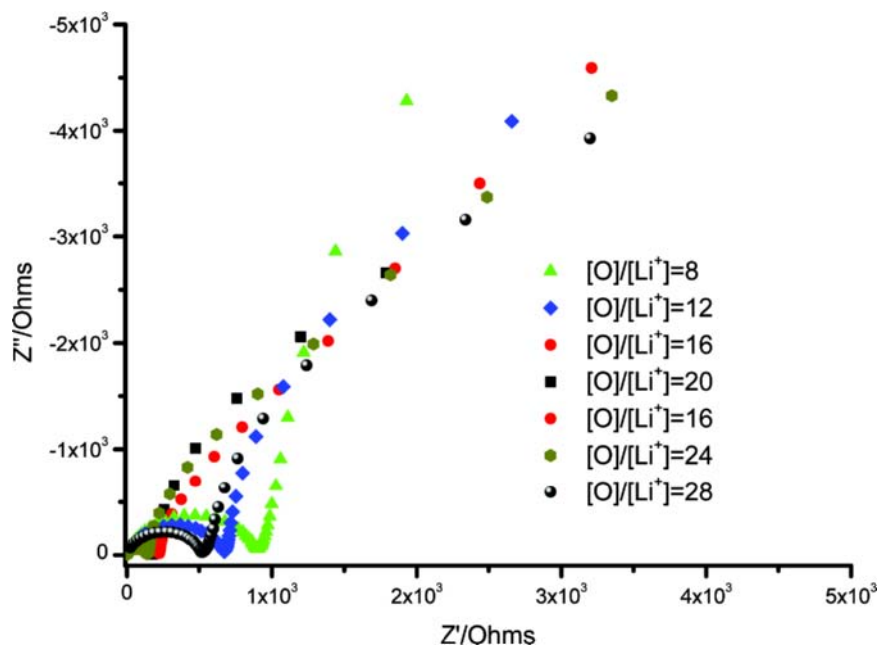

**FIGURE 2** The impedance spectra of PEG-co-PPG-PU/LiClO$_4$ SPE films at different [O]/[Li$^+$] ratios.

TABLE II The Values of Ionic Conductivity (σ) Calculated from Equation (1) for PEG-co-PPG-PU/ LiClO₄ SPE Films at Different [O]/[Li⁺] Ratios

[O]/[Li⁺]	$d(10^{-2}$ cm)	$S(\text{cm}^2)$	$R_B(10^2\Omega)$	$6(10^{-4}S\sigma\text{Cm}^{-1})$
8	3.30	2.064	9.500	0.1683
12	4.81	2.071	6.750	0.3445
16	4.32	2.070	2.240	0.9310
20	4.40	2.061	1.770	1.2061
24	3.01	2.072	1.410	1.0300
28	3.80	2.063	4.120	0.5860

Figure 3(a) and (b) show the ionic conductivity curves at different salt concentrations from [O]/[Li⁺] = 8 to 28 for homopolymer and copolymer complexes, respectively. In SPEs, the dependence of σ on salt concentration usually reveals a maximum due two opposing combined effects: the increased number of carrier ions dissociated and decreased segmental mobility caused by the addition of salt [5,17]. Hence, the PEG-PU/LiClO₄ system exhibited the maximum conductivity at [O]/[Li⁺] = 16 with the value $\sigma = 2.43 \times 10^{-6}$ S/cm whereas the PEG-co-PPG-PU/LiClO₄ system had the maximum conductivity at [O]/[Li⁺] = 20 with $\sigma = 1.2 \times 10^{-4}$ S/cm. And at all salt concentrations covered, the ionic conductivity of copolymer complexes proved to be much higher than those of homopolymer complexes. By a similar reasoning to the case of T_g, the larger difference in σ between two types of complexes could be explained as follows. That is, the current SPE is based on PEG and PPG randomly distributed within the PEU matrix as the soft segment, where the random occurrence of pendant methyl groups of PPG serves to disrupt the chain
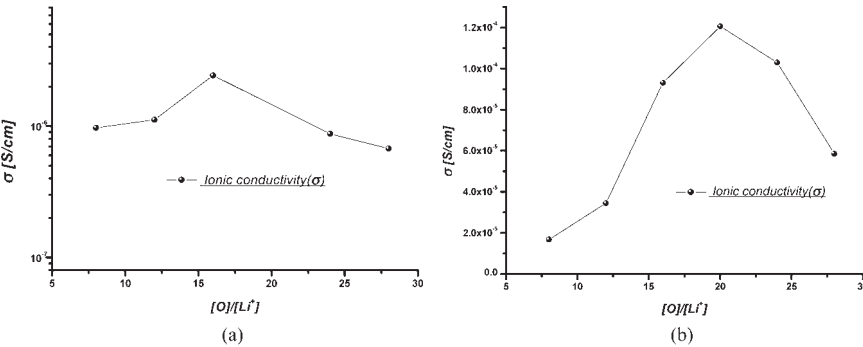
FIGURE 3 Ionic conductivity (σ) of (a) PEG-PU/LiClO₄ and (b) PEG-co-PPG-PU/LiClO₄ complexes at different [O]/[Li⁺] ratios.

(a)   (b)
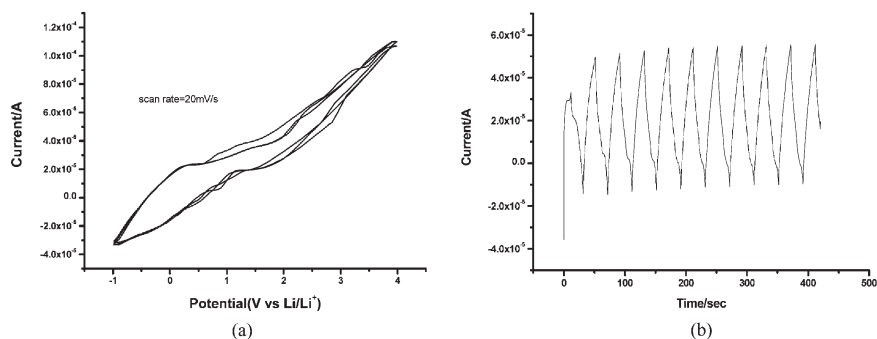
FIGURE 4 Cyclic voltammograms for [O]/[Li] = 20 copolymer SPE sample
expressed as (a) current vs. potential and (b) current vs. time.

symmetry sufficiently to diminish the extent of crystallinity, and hence to
increase chain mobility, leading to the greatly increased ionic conductivity.
Accordingly, a random introduction of PEG and PPG as the soft segment
within PEU matrix appears to bring about more active motion of segments
coordinated with the added Li^+ ions, responsible for much enhanced
ionic mobility. Finally, to investigate the electrochemical characteristics
of the current SPEs cyclic voltammograms were obtained at a scan rate
of $20\,mV\,s^{-1}$ against lithium at room temperature. The results for
$[O]/[Li^+] = 20$ copolymer SPE sample are displayed in Figure 4(a) and
(b) as current vs potential and current vs time plots, respectively. Voltam-
mograms show peaks associated to the oxidation on the anodic site and
that for the reduction on the cathodic site. As shown in Figure 4(a), the
irreversible oxidation at $4\,V$ *vs.* Li/Li^+ in the anodic scan. Consequently,
it was confirmed that the Li salt exhibits an electrochemical potential
window up to $4\,V$ in our SPE. In addition, referring to the electro-
chemical responses against the repeated cycling test (Figure 4(b)), we
can see that all samples exhibit nearly constant profiles, except for finite
differences between the first cycle and the following ones.

CONCLUSION

With a view to suppressing the crystalinity of matrix polymer, and hence
enhancing the ionic conductivity of the resulting SPE based on PEG-
co-PPG-PU matrix with the random introduction of PEG and PPG as soft
segments was synthesized from the simultaneous polymerization of the
PEG-PU and PPG-PU prepolymers in the present study. The efficacy of
PEG-co-PPG-PU/$LiClO_4$ complex electrolyte as a SPE was investigated

by using the AC impedance analyzer, DSC, and cyclic voltammeter. The dependences of T_g and ionic conductivity (σ) on salt concentration exhibited the maximum values at certain salt contents due two oppsing effects, i.e., increased number of charge carriers and decreased chain mobility with increasing salt content. At all salt contents covered, the copolymer complex PEG-co-PPG-PU/LiClO₄ had the lower T_g's and much higher conductivity than homopolymer complex PEG-PU/LiClO₄, probably due the increase in chain mobility caused by the crystalinity-suppressing ability of PPG soft segment.

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