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The effects of anion structure of lithium salts on the properties of in-situ polymerized thermoplastic polyurethane electrolytes

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Thermoplastic polyurethane (TPU) electrolytes with lithium salts were prepared by an in-situ polymerization method. Three different lithium salts were used to study the effects of the anion structure on the properties of polyurethane electrolytes: LiCl, $LiClO_4$, $LiN(SO_2CF_3)_2$ (LiTFSI). The effects of the anion structure on monomer (PTMG) prior to polymerization and on the properties of TPU electrolytes post polymerization were investigated. The anion structure of lithium salt has a significant influence on the ionic conductivity, thermal stability and tensile property of TPU electrolytes. The TPU electrolytes with LiTFSI demonstrated a high ionic conductivity up to 10^{-5} S/cm at 300 K. The ionic conductivity of polyurethane electrolytes with lithium salts is in the order: LiCl $<$ $LiClO_4$ $<$ LiTFSI. It was found that the lithium salts with larger anions were easily dissociated in TPU and had stronger interaction with TPU, which provided more charge carriers and gave higher ionic conductivity.

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1. Introduction

Solid polymer electrolytes (SPEs) are new generation solid ionic conductive materials, which have wide potential applications in electronic devices by replacing liquid electrolytes. They have many advantages over conventional liquid electrolytes and solid inorganic electrolytes in terms of their mechanical strength, processability, no-leakage, higher energy density, flexibility for cell design and non-combustible reaction products at the electrode surface existing, etc. [1,2]. SPEs are used as solid ionic conductive component in new power devices such as dye sensitized solar cells [3], polymer electrolyte membrane full cells [4], and lithium batteries [5]. For example, in the application of thin film lithium battery, solid polymer electrolyte film is sandwiched between a lithium metal anode and a composite cathode. The entire cell assembly can be produced as a laminated thin film by using proper coating process, and then rolled or folded into its finished shape as illustrated in Fig. 1 [6]. The most attractive characteristics of the polymer electrolyte membrane in the cell are its great capacity to tolerate shock, vibration, and mechanical deformation, its exceptionally long shelf-life, its wide operating temperature range, and its shape flexibility and manufacturing integrity [7]. The application of thin film lithium batteries in high value portable electronics zero-emission vehicles, medical instruments, aerospace industry and military is starting to be realized [6]. The solid polymer electrolytes for the current battery applications are required to have high ionic conductivity ($>10^{-5}$ S/cm at ambient temperature), good thermal dimensional stability, good electrochemical stability, easy processability, etc. [8].

In the last several decades, various polymer electrolytes have been studied, but most of them exhibit low ionic conductivity at ambient temperature. PEO based electrolytes were the first generation of polymer electrolytes and have been well studied [9,10]. They demonstrate a low ionic conductivity at temperatures below T_m (60 °C). Low ionic conductivity is believed to be associated with the low ion mobility in crystal lattice. At temperatures above its T_m, the ionic conductivity of PEO electrolytes significantly increases due to the melting of the crystal phase, but this also leads to its poor dimension stability [11]. Researchers attempted to tailor the chemical structure of the polymer used in polymer electrolytes to achieve both high ionic conductivity and good thermal dimensional stability. This approach utilizes polymers with electron donors other than oxygen such as poly(ethylene succinate) [12], poly(ethylene imine) [13] and poly(alkylene sulphide) [14]; polymers with block, branch or network structures [15,16]; polymer blends [17] and polymer/filler composites [18,19].

Considering that the mobility of the ions in polymer electrolyte is associated with the flexibility of the polymer segments and that the dimensional stability of the polymeric material depends on the rigidity of polymer segments, a polymer composed of hard segments and soft segments is helpful. Recently polyurethane

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[1] Sadly, Dr Kyonsuku Min died during the preparation of this article.

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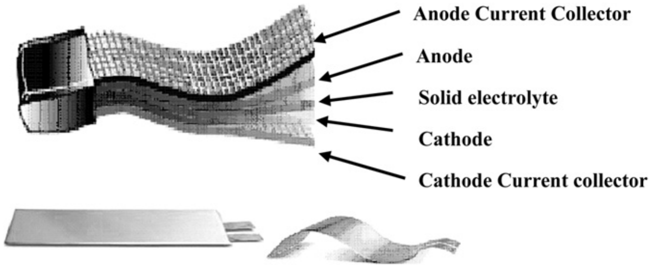

Fig. 1. Schematic diagram of basic construction of a film-like polymer electrolyte-based batteries [6].

based polymer electrolytes have attracted great attention [20–23]. The unique multiphase structure of polyether based thermoplastic polyurethane (TPU) makes it an interesting polymer matrix for polymer electrolytes. TPU is a block copolymer composed of soft segments and hard segments. The hydrogen bonding between the carbonyl group and N—H group in the hard segments leads to the formation of physically cross-linked hard domains [24]. The polyether-based soft segments act as polymer solvents to solvate the cations favoring the transportation of the ions and contribute to the conductivity of the polymer electrolyte. The hard segment is responsible for the dimensional stability acting as physical cross-link sites [25]. One great virtue of TPU is its property can span a wide range by tailoring the structure and the ratio of soft segment and hard segment [26]. Besides polymer matrix, the other important component in SPEs is salt. For the application in lithium battery, lithium salt is required in SPEs. It has been reported that the anion has significant effect on the ionic conductivity of PEO electrolytes [8]. For TPU based electrolytes, anion can affect the interactions between cation and polyurethane segments and impact on the morphology, ionic conductivity, dimensional stability, thermal stability and other properties of TPU electrolytes. So far, very few studies have been conducted on the effect of anion structure on the properties of TPU electrolytes.

As for the preparation method, most of the polymer electrolytes reported are prepared by solution cast method [27–30]. The intrinsic drawbacks of using the solution cast method to prepare polymer electrolytes are: 1) solvent residue left in the electrolyte film affects its thermal and ionic conductivity stability [8]; 2) a significant amount of solvent needs to be employed, which increases the manufacturing cost and safety risk in the mass production. The melt mixing method [31–33] and hot-pressing method [34] were also reported. In those methods, the solvation of salts in these films is poor because of the high viscosity of the polymer chain.

In this work, we proposed a novel solvent free method to prepare polyurethane electrolytes by using polymerization of the reactive monomer with the presence of lithium salts. The monomer of TPU, polyol, was mixed with salt before the reaction, then the other reactive components, isocyanate and chain extender, are added to initiate the polyurethane polymerization. The monomer functions as a common solvent to dissolve the salts and then after the polymerization it became part of the polymer. The prominent advantage of this method is that no volatile solvent used in the conventional solution cast method is needed and the ionic conductivity instability caused by the solvent residue is eliminated. Thermoplastic polyurethane electrolytes with three different lithium salts (LiCl, $LiClO_4$, and $LiN(SO_2CF_3)_2$ (LiTFSI)) were prepared by this in-situ method. The effect of anion structure of lithium salts on the ionic conductivity, thermal and tensile properties of TPU electrolytes and its mechanism was discussed. Before polymerization, the interaction between lithium salts with PTMG was characterized by Optical Microscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). After polymerization, the interaction of ions with soft segments and hard segments of TPU was studied by using FTIR and DSC. Then, the property of TPU electrolytes including ionic conductivity, tensile property and thermal stability were investigated.

2. Experimental

2.1. Material

The thermoplastic polyurethane components were formulated with a low hard segment content and high soft segment content. The polyol used was polytetramethylene oxide glycol (PTMG) with molecular weight of 2000 g/mol from Sigma-Aldrich chemical company. The chain extender, 1,4 butanediol, was purchased from ARCO and diisocynate, 4,4′ diphenylmethane diisocynate (MDI), was provided by Bayer. Three kind of lithium salts with different sized anions were used: lithium chloride LiCl, lithium percholorate $LiClO_4$, lithium bistrifluoromethanesulfonimidate $LiN(SO_2CF_3)_2$ (LITFSI). They were all from Aldrich.

2.2. Procedure

2.2.1. Preparation of TPU electrolyte via the in-situ polymerization method

In the conventional solution cast method, the pre-synthesized TPU was mixed with salt in solvent and electrolyte films were formed by vaporization of the solvent. In this work, an in-situ polymerization method with polyurethane polymerization in the presence of salt was used. TPU was formulated with equimolar quantities of PTMG and BDO. The formulation of polyurethane component in the electrolytes contains 68.26% PTMG, 6.14% BDO and 25.60% MDI by mass when the stoichiometric ratio of hydroxyl to isocyanate functionality was maintained at unity. In the experiment, 2% excess of stoichiometry of MDI was used to compensate for trace amounts of residual water in the salt, and reactants. Prior to polymerization, the liquid PTMG was mixed with lithium salts by a magnetic stirrer at 60 °C for 1 day to make sure the salts completely dissolved and then dried under a vacuum at 80 °C. No solvent was used in this method; BDO was dried under a vacuum oven first and demoistured over 3 Å molecular sieves at room temperature prior to reaction; MDI was stored under vacuum at 0 °C before usages. In the polymerization, the premixed PTMG/salt mixture was poured into aluminum pan on a hot stage, and then BDO and MDI were added at 80 °C mixed by a stirrer. The reactive mixture then was poured in a plate made of Teflon coated aluminum sheet and put into a vacuum oven for 24 h at 100 °C for curing. The lithium salt concentration in the polymer electrolytes is represented by the stoichiometry ratio of ether unit in the polymer to Li in the lithium salt, [O:Li]. The polymer electrolytes of with [O:Li] equal to 8:1, 16:1, 32:1 were prepared.

2.2.2. Characterization

Prior to the polymerization, the PTMG/salt mixtures were investigated by a Lietz Laborlux polarized optical microscope equipped with a video camera. Thermal behavior of the PTMG/salt mixture was investigated by using a Thermal Advantage 2920 differential scanning calorimeter operating in the temperature scanning mode. Samples were scanned in the range of −120 to 200 °C. All the DSC thermograms were recorded at a scan rate of 20 °C/min. In the FTIR characterization of PTMG/salt mixtures, samples were melted to liquid state and then directly coated on the KBr Plate. The plates coated with samples were scanned over the

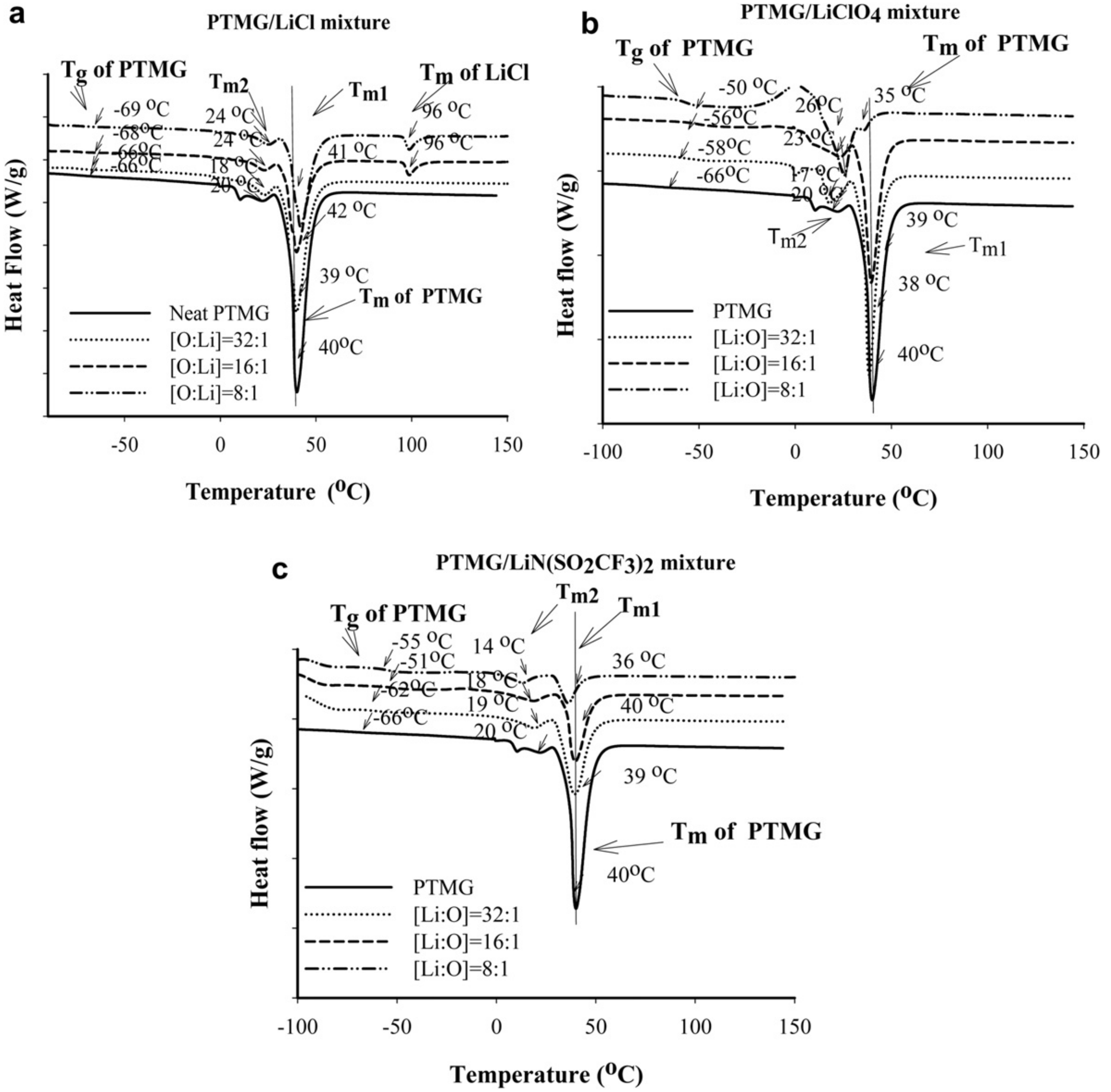

Fig. 2. DSC Thermograms of PTMG/Lithium salt mixture with various salt concentrations: (a) LiCl, (b) $LiClO_4$, (c) $LiN(SO_2CF_3)_2$ (T_{m1} is associated with well ordered crystalline structure; T_{m2} is associated with less ordered crystalline structure. The DSC thermograms presented here is the first run. T_g was obtained from the second run of DSC. T_gs from the send run were marked on the spectrum above for better illustration.).

range 4000–400 cm^{-1} by using Mattson Genesis Series FTIR. After the polymerization, FTIR and DSC were used to investigate the interaction between salt and soft segment/hard segment of polyurethane and the effect of salt on the crystallization of polyurethane.

2.2.3. Measurement of ionic conductivity

The ionic conductivities of polymer electrolytes in this study were measured by Multi-frequency LCR meter (Hewlett Packard 4274A). The electrolytes film samples were sandwiched between the stainless steel electrodes. The cell impedance was measured at various frequencies ranging from 100 Hz to 100 kHz.

2.2.4. Measurement of tensile property and thermal stability

The tensile properties of polymer electrolyte films were characterized by Instron5567 tensile tester. The gauge length was controlled to be 2 cm. The films were cut into a 5 mm × 50 mm rectangular strip samples. The crosshead speed was 20 mm/min. The thermal stability of the polyurethane electrolytes was studied by Thermal Advantage Q500 modulated thermo gravimetric analyzer (TGA).

3. Results and discussion

3.1. Characterization of PTMG/lithium salt mixtures prior to polymerization

The interaction of salt with PTMG is critical to obtain the desired ionic conductivity of TPU electrolytes prepared by this in-situ method. The ions from the dissociated salts function as charge carriers and contribute to the ionic conductivity of TPU electrolytes. The PTMG/LiCl mixture, PTMG/$LiClO_4$ mixture and PTMG/LiTFSI mixture with different salt concentrations were observed by using optical microscopy, DSC and FTIR to study the interaction between PTMG and lithium salts and the effect of the salt on the crystallization morphology of PTMG. The salt concentrations were represented by the mole ratio of ether oxygen atoms to lithium ions, [O:Li], which was controlled to be 32:1,16:1 and 8:1 ratio respectively

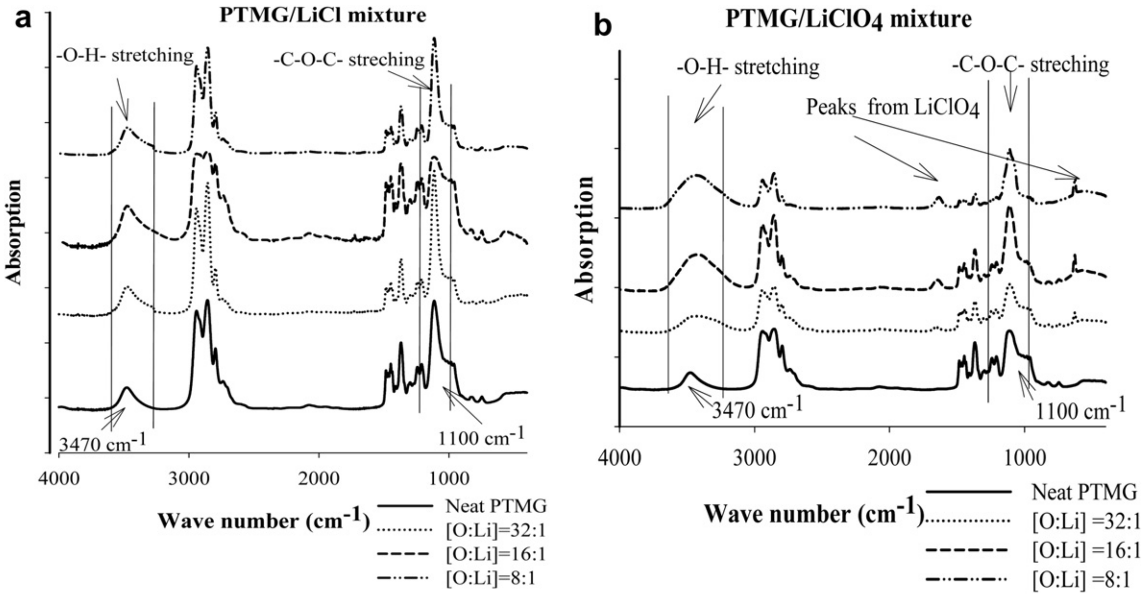

Fig. 3. FTIR spectra of PTMG/Lithium salt mixtures with various salt concentrations: (a) LiCl, (b) $LiClO_4$.

in this experiment. The higher the [O:Li] value, the lower the salt concentration.

PTMG is a semi-crystalline material with $T_m = 40\ ^\circ C$. Neat PTMG formed spherulites with a high degree of crystallinity. It was noticed that the salt type and its concentration influenced the crystalline morphology of PTMG. In cross-polarized optical microscope, it was found that the spherulite size of PTMG was significantly decreased as the concentration of $LiClO_4$ or LiTFSI increased, but the PTMG crystal size in PTMG/LiCl mixture showed little changes as the LiCl concentration increased. This is because $LiClO_4$ and LiTFSI have much stronger interaction with PTMG.

Fig. 2 shows the DSC thermogram of PTMG/salt mixtures. The neat PTMG has one strong endothermic peak around 40 °C (T_{m1}) and one weak peak around 20 °C (T_{m2}). The T_{m1} is attributed to the melting of well ordered PTMG crystal and T_{m2} is associated with the small amount of less ordered crystal structure. It was revealed that for all three lithium salts, the loading of Lithium salts had effect on the degree of crystallinity of PTMG and T_{m1}. As the lithium salts concentration increased, the peak area of T_{m1} of PTMG decreased, which indicates that the degree of crystallinity of PTMG decreased. In Fig. 2(a), a new peak around 96 °C appeared as the LiCl concentration increased. This peak was attributed to the undissolved LiCl crystal. This is due to the poor solubility of LiCl in PTMG. No peaks associated with $LiClO_4$ and LiTFSI crystal were observed in DSC spectrums of PTMG/$LiClO_4$ mixture and PTMG/LiTFSI mixture as shown in Fig. 2(b) and (c). In the study of the effect of anion size on the salt solubility in PEO electrolytes, Gray [8] pointed out that the salts comprising of large sized anions or anions with delocalized charge had low lattice energies and they required little solvation. The T_{m1} of PTMG decreased at high salt concentration like $[O:Li^+] = 8:1$ for PTMG/$LiClO_4$ mixture and PTMG/LiTFST mixture, but increased slightly for PTMG/LiCl mixtures. This indicated that lithium salts had different effects on the melting point of PTMG. T_g of PTMG increased dramatically after the addition of $LiClO_4$ or LiTFSI, but changed little as the LiCl concentration increased. At high salt concentrations, the order of T_g of PTMG/lithium salt is: PTMG/LiCl < PTMG/$LiClO_4$ < PTMG/LiTFSI. The increase of T_g was the evidence of the interaction between lithium salt and PTMG. A possible explanation was that the dissociated lithium ions or ion clusters acted as a binder to connect the different ether groups on PTMG segments, which reduced the flexibility of the PTMG segments, so raised T_g. The binder effect of ions on polymers has been reported by previous researchers on the study of polyelectrolyte and ionomer [35–37].

In the FTIR spectrums of PTMG/salts mixtures there were two prominent changes in PTMG spectrum after adding $LiClO_4$ or LiTFSI as shown in Fig. 3(b): 1) the absorption peak of ether group $-C-O-C-$ at around 1110 cm^{-1} shifted slightly to low frequency; 2) the absorption band of the hydroxyl group-OH at around 3470 cm^{-1} became broader and its peak center shifted to the lower frequency as the salt concentration increased. These changes were attributed to the coordination of Li^+ to the different functional groups of PTMG. The lithium free ions and ion clusters could interact with PTMG at two types of reactive sites on PTMG molecular chain: one was the ether oxygen and another was the hydroxyl group as illustrated in Fig. 4. However, the $-OH$ stretching region in the spectrum of PTMG/LiCl mixtures showed little change with increasing the LiCl concentration as the result of the poor solubility LiCl in PTMG as shown in Fig. 3(a). Ferry et al. [38] reported that the shifting of the absorption peak of the ether group in polyurethane electrolytes was caused by the weakening of the $C-O-C$ bond by cation coordination.

From optical microscopy, DSC and FTIR results of PTMG/lithium salt mixtures, it is concluded that 1) the lithium salts had effects on the crystalline morphology of PTMG. The crystal size, the degree of crystallinity and T_m of PTMG decreased and its T_g increased after adding $LiClO_4$ and LiTFSI. The T_g of PTMG with different lithium

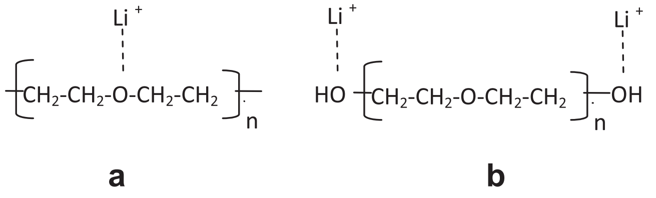

Fig. 4. Schematic representation of the interaction between lithium ion or ion cluster and oxygen atom at different sites: (a) ether group and (b) hydroxyl group (Li^+ in this scheme represents both the single lithium ions and ion clusters).

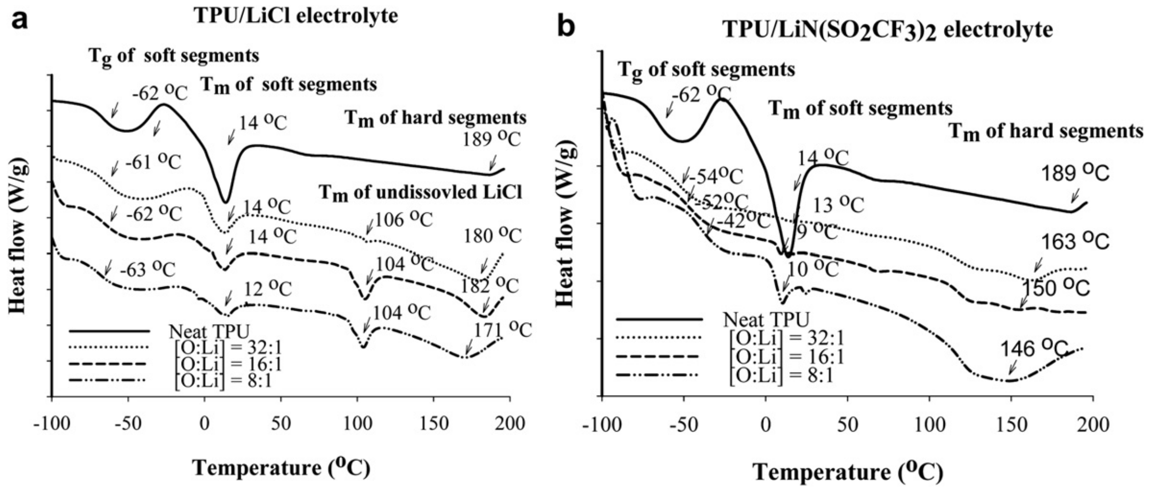

Fig. 5. DSC Thermograms of TPU electrolytes with different lithium salts: (a) LiCl, (b) $LiN(SO_2CF_3)_2$ (The DSC thermograms presented here is the first run. T_g was obtained from the second run of DSC. T_gs from the send run were marked on the spectrum above for better illustration).

salts were in the order: PTMG/LiCl < PTMG/$LiClO_4$ < PTMG/LiTFSI. Compared with the other two salts, LiCl had little effect on crystalline morphology of PTMG; 2) the Li^+ and ion cluster of lithium salt could interact with both the ether group and the hydroxyl group of PTMG. $LiClO_4$ and LiTFSI had much stronger interaction with PTMG than LiCl.

The effect of lithium salts on PTMG is associated with their anion structure. Their anion size follows the order: $Cl^- < ClO_4^- < TFSI^-$. Based on the hard/soft acid base principle [39], Li^+ is a hard base and small anions hard to polarize such as Cl^- is hard acid. The interaction occurred by matching hard acids with hard bases. $LiClO_4^-$ and $TFSI^-$ are large sized polyatomic anions with delocalized charges. They are less harder and have weaker interactions with Li^+, compared with Cl^-. When mixing LiCl crystal with PTMG melt, it is hard to separate Li^+ and ion cluster from Cl^- in the LiCl crystal. Therefore, LiCl has poor solubility in PTMG and few Li^+ ions and ion clusters were available in PTMG/LiCl mixtures to interact with PTMG. As a result, LiCl had much weaker interaction with PTMG than $LiClO_4$ and LiTFSI. This explained the variation of the effect lithium salts with different anion structures on the crystal morphology of PTMG.

3.2. *Characterization of TPU electrolytes with lithium salts after polymerization*

After polyurethane polymerization, PTMG became the soft segment of TPU. The effect of lithium salts on the crystal morphology of TPU and the interactions between lithium salts and TPU was studied by using DSC and FTIR. It is known that the DSC thermograms of TPU would reveal complicated multiple peaks associated with the co-existence of different phases composed of hard segments and soft segments. As shown in Fig. 5, the endothermic peak around 14 °C and the peaks above 110 °C were attributed to the melting of the crystalline phase of the soft segment and the order structure of the hard segments respectively. The TPU used in this study was formulated with high soft segments content, so the thermal transitions associated with hard segments were not prominent in DSC thermograms. The degree of crystallization of the soft segment in TPU electrolytes was depressed at high salt concentrations, which was consistent with the results reported by previous researchers [25,40]. A peak of undissolved LiCl crystal at around 104 °C appeared at high LiCl loading in TPU/LiCl electrolytes as shown in Fig. 5(a). The T_g of soft segment of TPU was affected by the addition of lithium salts. The soft segment T_g in TPU/$LiN(SO_2CF_3)_2$ electrolytes increased from −62 °C to −42 °C as the salt concentration increased. The observation that soft segment T_g increased with salt concentration in TPU electrolytes has been reported by Chen et al.[21]. They explained it as the formation of transient cross-links between the Li^+ ion and the ether oxygen of the soft segments which restricted the segmental motion of the soft segment. At high salt concentration, the T_g of the soft segment of TPU followed the order: TPU/LiCl electrolytes < TPU/$LiClO_4$ electrolytes < TPU/LiTFSI electrolytes. This suggested that the interaction strengths between TPU and lithium salts follow the same order.

Three important characteristic absorption regions in FTIR spectrums for study of the interactions in TPU electrolytes were examined [41,42]: (1) 3600–3100 cm^{-1} (the hydrogen bonded N–H stretching mode and the free N–H stretch); (2) 1750–1650 cm^{-1} (the carbonyl symmetric stretching vibration or amide band); and (3) 1150–1000 cm^{-1} (the C–O–C stretch for the soft segment and C(O)–O–C stretch of the hard phase. After adding of $LiN(SO_2CF_3)_2$, the following changes were observed in TPU spectrum: i) the –N–H peak at 3320 cm^{-1} shifted to high frequency, which indicated more free N–H was generated and there was less hard–hard segment hydrogen bonds left; ii) the absorption intensity ratio of the bonded –C=O at 1700 cm^{-1} to the free bonded –C=O at 1730 cm^{-1} increased slightly; iii)the peak around 1110 cm^{-1} almost became a plateau due to the overlapped peaks contributed by the Li^+ bonded ether group, free bonded ether and hydrogen bonded ether. Similar trends have been observed in the FTIR spectrum of TPU/LiCl electrolytes and TPU/$LiClO_4$. These results agreed with the results reported by other researchers [25,43,44]. Heumen et al. [41,42] pointed out that in TPU electrolytes cations interacted with both the electron-rich oxygen atoms of the soft segment and the electron-rich nitrogen atoms of the hard segment. Wen [43] explained the shifting of free –N–H peak to higher frequency after adding salts as the result of the interaction of ions with the N atoms in the –NH group.

From the DSC and FTIR results of TPU electrolytes obtained in this study, it was found that lithium salts had interaction with soft segment and hard segment of TPU and they affected the crystalline morphology of TPU. Fig. 6 illustrates the possible interactions between the lithium ions or ion clusters with the –C–O–C– of the soft segment and the N–H and C=O of the hard segments. The ions are not only in the amorphous phase and crystalline phase of soft

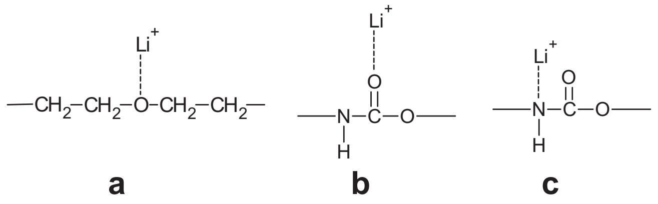

Fig. 6. Schematics of the possible interactions of lithium salt with (a) the ether group in soft segment, (b) N–H group and (c) carbonyl group in hard segment. (Li^+ represents the single lithium ions and ion clusters).

domains but also in the hard domains. These ions in different domains contributed to the ionic conductivity of TPU electrolytes.

3.3. *Ionic conductivity of polyurethane electrolytes*

The ionic conductivity of polymer electrolytes was associated with the flexibility of polymer segment and the mobility of mobile ions interacting with the polymer segments [8]. In the in-situ preparation of TPU electrolytes, PTMG as the precursor of the soft segment of TPU provided both the cation coordination sites and segment flexibility, which contributed to enhance their ionic conductivity of TPU electrolytes. The salt solvation in PTMG and the morphology of TPU electrolytes could significantly affect the ionic conductivity of the TPU electrolytes. The ionic conductivity measured in this study was the A.C. ionic conductivity, which was calculated from the bulk resistance obtained from the complex impedance plot. Bruce [45] gave a detailed review on the principle of the ionic conductivity measurement. The conductivity-temperature dependence varies from different polymer electrolytes. The typical empirically fit equations are Arrhenius law question, Vogel-Tammon-Fulcher (VTF) equation, Williams-Landel-Ferry (WLF) equation, etc. [46]. The ionic conductivity of TPU electrolytes with different lithium salts at temperatures from 27 °C up to 140 °C is shown in Fig. 7. The conductivity-temperature dependence of TPU electrolytes with lithium salts in this study fits Arrhenius law equation, $\sigma = \sigma_0 \exp(-E_a/RT)$, which describes the linear relationship of ln σ with $1/T$, where σ_0 is conductivity at the absolute temperature $T = 0$ K, E_a is the activation energy, and R is the gas constant.

The ionic conductivity of TPU electrolytes at 300 K and their activation energy are summarized in Table 1. The σ of TPU electrolytes varied with the structure of anions and the lithium salts concentration. The $\sigma_{T=300K}$ of TPU with low LiCl concentrations [O:Li] = 32:1, 16:1, was too low and it was out of the measurement limit in the measurement setup used in this study. In Table 1, as the salt concentration increased, the $\sigma_{T=300K}$ of TPU/$LiClO_4$ electrolyte increased from 2.12×10^{-9} to 2.24×10^{-7} S/cm and the one of TPU/LiTFSI electrolyte increased from 1.53×10^{-6} to 1.25×10^{-5} S/cm. TPU/LiCl electrolytes showed a low $\sigma_{T=300K}$ value of 1.51×10^{-9} S/cm even at high LiCl concentration. At equal salt concentrations, TPU/LiTFSI electrolytes demonstrated much higher ionic conductivity than TPU/$LiClO_4$ electrolytes; and TPU electrolytes with LiCl showed low ionic conductivity. Comparing Fig. 7(a) with Fig. 7(b) and (c), it was observed that as the salt concentration increased, the ln σ vs. $1/T$ curves of TPU/$LiClO_4$ electrolytes and that of TPU/LiTFSI electrolytes shifted up with much larger interval value than that of TPU electrolytes with LiCl. This indicated that the ionic conductivity of TPU electrolytes with LiCl was much less sensitive to the lithium salt concentration than TPU/$LiClO_4$ electrolytes and

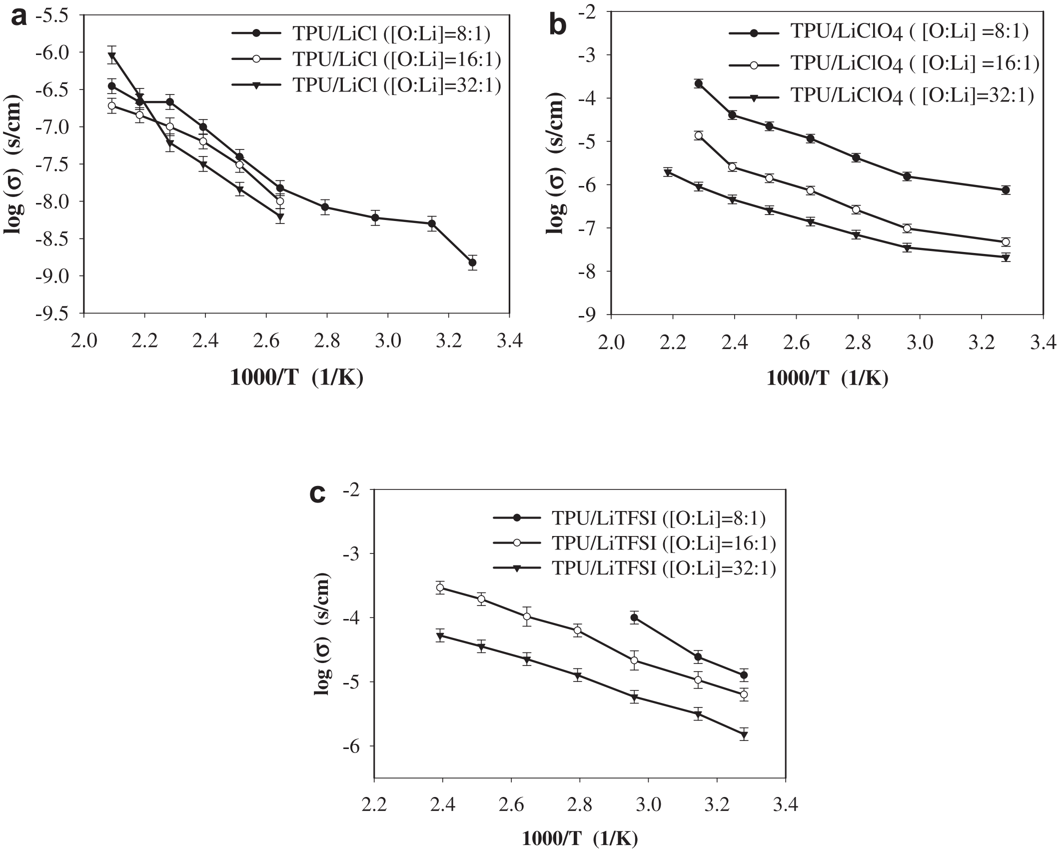

Fig. 7. Ionic conductivity of TPU electrolytes with different lithium salt at various temperatures: (a) LiCl, (b) $LiClO_4$, (c) $LiN(SO_2CF_3)_2$ (LiTFSI).

Table 1
The ionic conductivity at 300 K and the activation energies E_a of TPU electrolytes with different lithium salts.

Materials	Lithium salt concentration: [O:Li]	Conductivity at 300 K (S/cm)	E_a (eV)
TPU/LiCl	32:1	–	0.017
	16:1	–	0.019
	8:1	1.51×10^{-9}	0.032
TPU/LiClO$_4$	32:1	2.12×10^{-9}	0.015
	16:1	7.51×10^{-8}	0.020
	8:1	2.24×10^{-7}	0.020
TPU/LiTFSI	32:1	1.53×10^{-6}	0.015
	16:1	3.31×10^{-6}	0.023
	8:1	1.25×10^{-5}	0.028

TPU/LiTFSI electrolytes. This difference was associated with the anion structure of the lithium salt.

Based on the characterization studies of PTMG/lithium salt mixture and TPU electrolytes with different lithium salts, it was found that the interaction strengths between lithium salts and TPU were in the following order: LiCl $<$ LiClO$_4$ $<$ LiTFSI, which agreed with the order of the size of the anion: $Cl^- < ClO_4^- < TFSI^-$. The ionic conductivity results of TPU electrolytes showed that their σ was in the same increasing order of the anion size of lithium salts. It could be explained that the large polyatomic anions with delocalized charge had weak interactions with small Li^+, so this made lithium salts with these anions dissociate easily and more mobile ions or ion clusters were released. In solvent free polymer electrolytes, the majority of the charge carriers are single cations, anions and ion clusters. In terms of the number of charge carriers in TPU electrolytes, TPU/LiTFSI electrolytes had large amount of dissociated ion or ion clusters, so it gave high ionic conductivity. It was believed that the motion of ions was associated with motion of polymer segment and the cations could be transferred via the polymer segmental motions by making and breaking the coordination bonds between cations and polymers under electrical field [8]. LiCl had much less interaction with TPU segments than other two salts, therefore the low ionic conductivity of TPU electrolytes with LiCl was predictable.

3.4. Thermal stability and tensile property of TPU electrolytes

The thermal stability is very important for polymer electrolytes. The previous studies of PEO electrolytes revealed that the addition of inorganic salts into PEO decreased the thermal stability of neat PEO [25,47]. The 2% and 5% weight loss temperatures are summarized in Table 2. The thermal degradation temperature of TPU decreased after adding lithium salts. This finding indicated that lithium salts had strong effect on the thermal stability of TPU. The order of the thermal stability of TPU electrolytes with different lithium salts was: LiCl $>$ LiClO$_4$ $>$ LiTFSI. The neat TPU exhibited two steps of thermal degradation: the first step was attributed to the degradation of soft segments and the second step was associated with the degradation of hard segments. TPU electrolytes had three steps of thermal degradation. The extra step in their thermal degradation was attributed to the breakage of the ether bond interacting with lithium salt. In TPU electrolytes, the ether groups of soft segment were in two different environments: one without interaction with salts, and the other one interacted with salts. Because the ether bond was weakened by the interaction between ether oxygen and salts, the degradation of ether group interacting with salt occurs in the first step. Later, the degradation of ether group without interacting with salts happened in the second step. After the first two steps, the degradation of hard segments of TPU proceeded. It was observed that TPU/LiTFSI electrolytes start thermal degradation at lower temperatures than TPU electrolytes with other lithium salts. It could be explained that among the three lithium salts LiTFSI has the strongest interaction with soft segments, so the bond strength of ether groups in soft segments of TPU/LiTFSI electrolytes was influenced most.

Table 2
TGA results of TPU electrolytes with different lithium salts at [O:Li] = 16:1.

TPU electrolytes	Temperature at 2% weight loss (°C)	Temperature at 5% weight loss (°C)
Neat TPU	296	314
TPU/LiCl	248	265
TPU/LiClO$_4$	225	243
TPU/LiTFSI	210	241

Table 3
Engineering tensile properties of neat TPU and TPU electrolytes with various salt concentrations.

Materials	[O:Li]	Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
Neat TPU		12.6	19.9	1100
TPU/LiClO$_4$	32:1	8.4	6.6	482
	16:1	5.7	3.3	300
	8:1	4.2	3.6	222
TPU/LiTFSI	32:1	10.6	12.0	666
	16:1	7.1	5.7	571
	8:1	1.8	1.3	350

The important characteristics of solid polymer electrolytes over liquid electrolytes are their solid nature, flexibility and easy processability. The multi-phase hard domain–soft domain morphology of TPU made it possible that TPU electrolytes could have considerable ionic conductivity with superior dimension stability. The engineering tensile properties of neat TPU and TPU electrolytes with various salt concentrations are summarized in Table 3. It was found that the tensile properties of TPU electrolyte was affected by the addition of LiClO$_4$ or LiN(SO$_2$CF$_3$)$_2$. As the concentration of LiClO$_4$ or LiN(SO$_2$CF$_3$)$_2$ increased, their elongation at break and tensile modulus gradually decreased. This was associated with the morphology change of TPU including the level of the phase mixing caused by the interaction between lithium ions and soft or hard segments of TPU. The high modulus of TPU was mainly contributed from the existence of the hard domains and the network structure formed by physical cross-linking of the hard domains via hydrogen bonding. In TPU electrolytes, some of the hydrogen bonding was destroyed after adding lithium salts as discussed in previous sections and resulted in decreasing modules.

4. Conclusion

In this study, TPU electrolytes with lithium salts were prepared by employing an in-situ polymerization method. Three kinds of lithium salts with different anion size were used: LiCl, LiClO$_4$, and LiTFSI. In this in-situ method, lithium salts were first dissolved in monomer (PTMG), and then followed by in-situ polymerization of polyurethane. PTMG functioned as the solvent to dissolve lithium salts first and then become part of polyurethane after polymerization. The structure of the anion of lithium salts had significant influence on the morphology of PTMG and the interaction strength between lithium salts and PTMG. Li^+ interacted with both the ether oxygen group and the hydroxyl group on PTMG molecular chain. The poor solubility of LiCl in PTMG was associated with the strong interaction between Li^+ and Cl^-. The decreasing order of the interaction strength between lithium salts and PTMG were consistent with the decreasing order of the anion size.

The anion structure of lithium salts affected the ionic conductivity, thermal stability as well as the tensile property of TPU/lithium salt electrolytes. The ionic conductivity of TPU/lithium electrolytes reached up to 10^{-5} S/cm at room temperature, depending on the salt type and its concentration. At equal salt concentration, the ionic conductivity of TPU electrolytes with different lithium salts was in the order: LiCl $<$ $LiClO_4$ $<$ LiTFSI. The thermal stability of TPU with lithium salts and their tensile modules and break at elongation were in the order: LiCl $>$ $LiClO_4$ $>$ LiTFSI. The effect of the anion structure on the ionic conductivity, thermal stability and tensile property of TPU electrolytes was associated with the easiness of the cation/anion dissociation of lithium salts in TPU and the interaction strength between cations and TPU segments. The large polyatomic anions with delocalized charge like $TFSI^-$ had weak interactions with small Li^+ and it made lithium salts with these anions could be dissociated easily in TPU. The high ionic conductivity of TPU/LiTFSI electrolytes was attributed to the existence of large amounts of charge carriers and the good interaction between Li^+ and soft segments of TPU. The salt ions not only interacted with soft segment but also with hard segments, which enhanced the ionic conductivity of TPU electrolytes. The strong interaction between LiTFSI and TPU weakened the bonding strength of TPU segments. It caused TPU electrolytes with LiTFSI to degrade at lower temperature than TPU electrolytes with other lithium salts. The interaction of Li^+ with both the soft segment and the hard segment of TPU could deteriorate the hydrogen bonding between hard segments and affected the morphology of TPU. Therefore, the tensile properties of TPU electrolytes with LiTFSI were affected by increasing the LiTFSI concentration. The ionic conductivity property, thermal stability and tensile property of TPU/LiTFSI electrolytes and TPU/$LiClO_4$ indicate that they can be used as solid polymer electrolytes for lithium batteries. In the future, work involving lithium battery assembling with these TPU electrolytes needs to be conducted to further evaluate their performance.

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