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A new polysiloxane based cross-linker for solid polymer electrolyte

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Abstract

A new cross-linker, poly[siloxane-(*g*-oligo(ethylene oxide)-*co*-acrylate)], was synthesized and used to prepare the solid polymer electrolytes (SPE) by in situ thermal curing method with the addition of the ion-conducting plasticizers such as low molecular weight poly(ethylene oxide)dimethyl ether (PEGDME) and poly(siloxane-*g*-ethylene oxide) (PSi-PEG). Increase of conductivity and decrease of T_g were observed as increasing the content of plasticizer. The ionic conductivity was measured to be 7.13×10^{-4} S cm^{-1} with 70 wt.% PEGDME and 4.18×10^{-5} S cm^{-1} with 70 wt.% of PSi-PEG at 30 °C. The electrochemical stability window of the resulting solid polymer electrolyte could be extended to up to 4.5 V and 5.2 V for PEGDME and PSi-PEG, respectively. Thermal stability of polymer electrolyte was greatly enhanced with siloxane based plasticizer. The degradation of SPE with PSi-PEG started at ca. 350 °C. The SPE plasticized with PSi-PEG, which has good electrochemical stability and thermal stability, could be a promising solid polymer electrolyte for lithium polymer batteries.
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Keywords: Polymer electrolytes; Lithium batteries; Ionic conductivity; Poly(siloxane-*g*-acrylate) cross-linker

1. Introduction

A solid polymer electrolyte (SPE) based on polyethylene oxide (PEO) is one of the promising electrolytes for high energy density secondary lithium batteries such as lithium sulfur batteries and lithium metal batteries [1,2]. However, ionic conductivity of the PEO based SPE at ambient temperature is relatively low compared with that of the gel-type polymer electrolyte, which is usually used in the commercial lithium ion-polymer batteries. The ionic conductivity of the SPE is strongly correlated to the segmental motion of the polymer chain and, thus, amorphous polymers with low glass transition temperature (T_g) are preferred for SPE. Oligo(ethylene oxide) grafted network polymers have been known as an efficient way to prepare amorphous polymer, and have been extensively studied for SPEs using different polymer backbones such as polyphospazene [3,4], polyacrylate [5–7] and polysiloxane [8–10].

Among them, polysiloxanes are promising because they have highly flexible backbones with a barrier to bond rotation

of only 0.8 kJ mol^{-1}, very low glass transition temperature ($T_g = -123$ °C for poly(dimethylsiloxanes)), high free volumes and thermo-oxidative stability [8,11]. Hooper et al. have reported that the double-comb type polysiloxane compounds prepared from the condensation of bis-[oligo(ethylene glycol) ether propyl] dichloro silane showed conductivity of 4.5×10^{-4} S cm^{-1} [11]. The conductivity of these polymers is very close to the conductivity of the practical use ($\sim 10^{-3}$ S cm^{-1}) but these materials may suffer from the low mechanical strength as most low T_g polymers do. To enhance the mechanical stability, cross-linking or networking of polysiloxane has been investigated [12–14]. We also reported the synthesis of a cross-linker based on the oligo(ethylene oxide) grafted polysiloxane in which the acrylate functional group was attached at the end of oligo(ethylene oxide) grafted [15]. These results indicated that the cross-linked polysiloxane SPE had good film-forming properties and improved dimensional stability. Moreover, the ionic conductivity was greatly enhanced by adding the ion conducting plasticizer, low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME) [7,15]. Although the cross-linker was very useful for preparing SPE, it required extra synthetic steps and the cross-linking density was not easily controlled.

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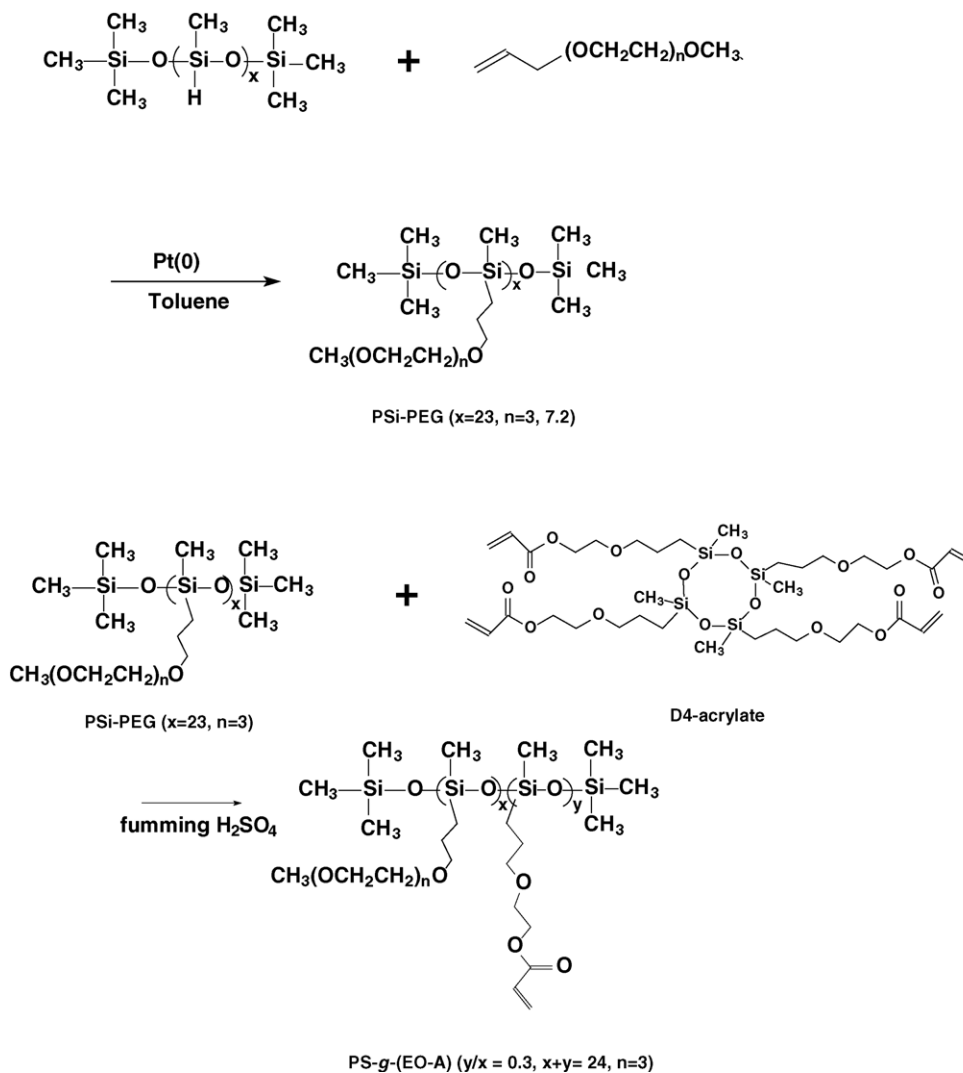
Scheme 1. Synthetic scheme of poly[siloxane-*g*-(oligo(ethylene oxide)-*co*-acrylate)] (PS-*g*-(EO-A)) cross-linker.

In this study, a new polysiloxane based cross-linker was synthesized according to the synthetic steps shown in Scheme 1. In this scheme, the content of the grafted acryl side chain can be easily controlled by adjusting the feed ratios. Ionic conductivity and electrochemical properties of the SPE were examined using different PEO based plasticizers such as PEGDME and synthesized poly(siloxane-*g*-ethylene oxide).

2. Experimental

Poly(ethylene glycol) dimethyl ether (PEGDME, $M_w = 250$, Aldrich), LiCF$_3$SO$_3$ (Aldrich), benzoyl peroxide (BPO, Aldrich) were dried in vacuum before use.

The acrylate branched polysiloxane cross-linker was synthesized by chain extension reaction using cyclic monomer (D4-acrylate) and a poly(siloxane-*g*-ethylene oxide) (PSi-PEG) as shown in Scheme 1. The mono-comb PSi-PEG ($x = 23$, $n = 3$ and $M_w = 5400$) was synthesized by hydrosilylation reaction of polymethylhydrosiloxane and tri(ethylene glycol) allyl methyl ether using the previously reported method [13,15,16]. Similarly, PSi-PEG with larger molecular weight of PEO ($x = 23$, $n = 7.2$ and $M_w = 9950$) was synthesized. The cyclic monomer (D4-acrylate) was synthesized from the hydrosilylation of 2,4,6,8-tetramethylcyclotetrasiloxane and 2-allyloxyethanol followed by the acryloylation. The cross-linkable siloxane polymer, poly[siloxane-*g*-(ethylene oxide-*co*-acrylate)] [PSi-*g*-(EO-A)], was synthesized by chain extension reaction of D4-acrylate and PSi-PEG ($x = 23$, $n = 3$ and $M_w = 5400$) with fuming sulfuric acid catalyst. The resulting cross-linker was fractionated by using THF and hexane (5/100, v/v) to remove low molecular weight siloxane oligomer and residual monomer. The absence of low molecular impurities was confirmed by means of GPC. The molecular weight of the

PSi-g-(EO-A) cross-linker was estimated to be 6900 ($x = 24$) by the end group analysis using ^{1}H NMR spectroscopy. The GPC analysis also indicated similar molecular weight. The y/x ratio was found to be 0.30 by ^{1}H NMR analysis.

The cross-linked solid polymer electrolytes were prepared by in situ radical initiated cross-linking reaction of a homogeneous solution composed of plasticizer (PEGDME or PSi-PEG), PSi-g-(EO-A) cross-linker, lithium salt (LiCF$_3$SO$_3$) and thermal radical initiator (BPO). The homogeneous solution was filled in a small gap between the desired substrates such as ITO glass, lithium and nickel. The thermal curing was carried out in a convection oven at 100 °C for 20 min under the argon atmosphere.

The T_g of the cured polymer electrolytes was determined by using a differential scanning calorinmeter (DSC) (TA Instruments, model universal V2.5H). Samples in hermetically sealed aluminum pans were stabilized at −150 °C and then elevated to 50 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. The thermal stability of SPE was examined using a thermogravimetry analysis (TGA) (TA Instruments, TGA Q 500). The temperature range is 30–700 °C at a scanning rate of 10 °C min^{-1} under nitrogen atmosphere.

The conductivity measurement was carried out by coating the polymer electrolytes onto the pre-patterned ITO cell, which has been developed by our laboratory [7,17,18]. The ac impedance of the conductivity cell was measured by using an impedance analyzer (Zahner Elekrik model IM6). A 10 mV ac amplitude was applied with a frequency sweep of from 1 Hz to 1 MHz. The temperature of the sample was controlled by means of the programmable hot plate (Mettler, model FP 82HT).

The electrochemical stability window of the SPE was determined by means of cyclic voltammetry (EG&G model 270 potentiostat) at room temperature. A nikel plate (Aldrich, 0.125 mm thick, >99.9%) was used as a working electrode and a lithium metal foil (FMC) as a counter and reference electrode. These cells were assembled by sandwiching the SPE between the two electrodes. All samples for the electrochemical measurements were prepared in argon gas filled glove box, and were sealed with a metallized polyethylene bag.

3. Results and discussion

The newly synthesized cross-linker could be blended homogeneously in any portions with plasticizer without phase separation. The dimensional stability of the thermally cured solid polymer electrolyte depended on the content of plasticizer. A self-supportive film containing up to 80 wt.% of plasticizer could be readily prepared.

The dependence of the ionic conductivity and T_g on the [EO]/[Li] ratio is shown in Fig. 1. The conductivity plot showed a typical bell-shaped curve with a maximum. The maximum conductivity was found to be at [EO]/[Li] = 20 and 10 for PEGDME and PSi-PEG, respectively. Glass transition temperatures were decreasing as increasing the [EO]/[Li] ratio. The ionic conductivity is in proportion to the number
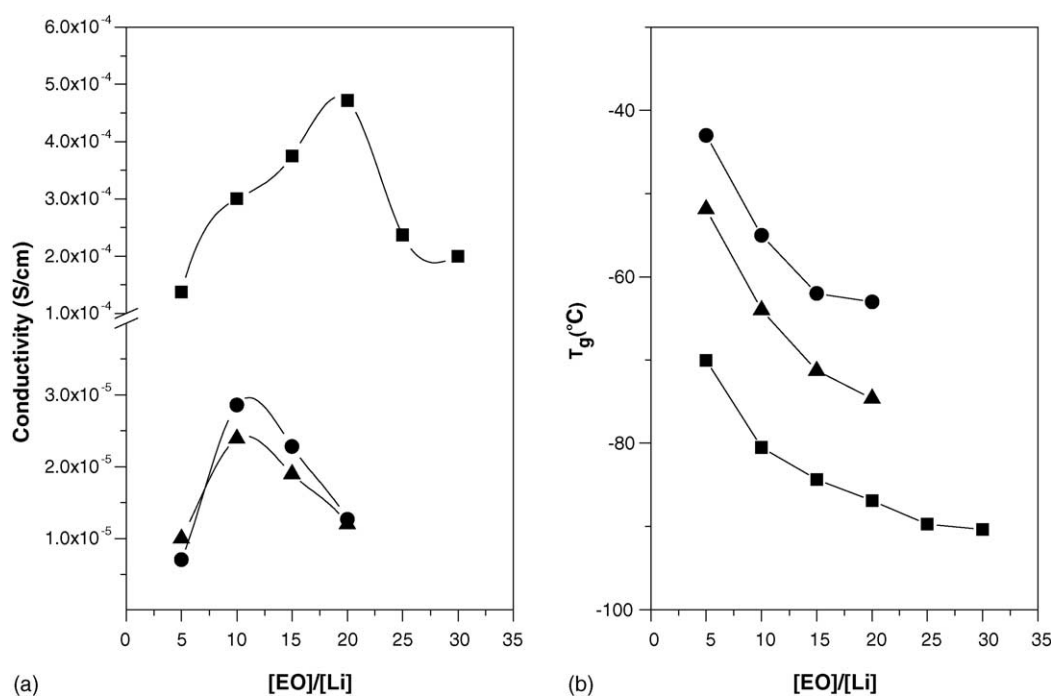

Fig. 1. Changes of ionic conductivity (a) and glass transition temperature T_g (b) as a function of [EO]/[Li] ratio: (■) PEGDME, (●) PSi-PEG ($n = 3$) and (▲) PSi-PEG ($n = 7.2$).
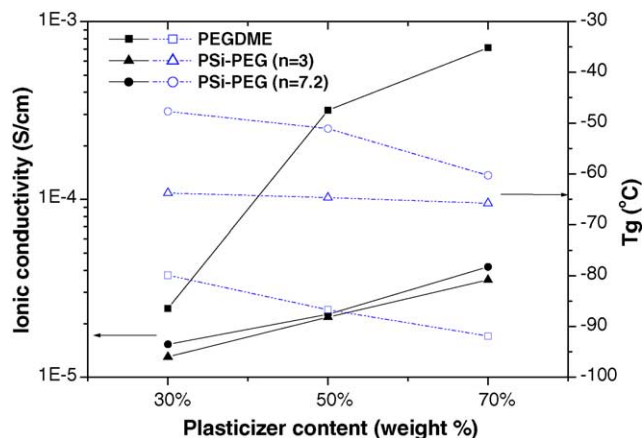
Fig. 2. Changes of ionic conductivity (closed symbol) and glass transition temperature T_g (open symbol) as a function of plasticizer contents. [EO]/[Li] was 20 for PEGDME and 10 for PSi-PEG ($n = 3$ and 7.2).
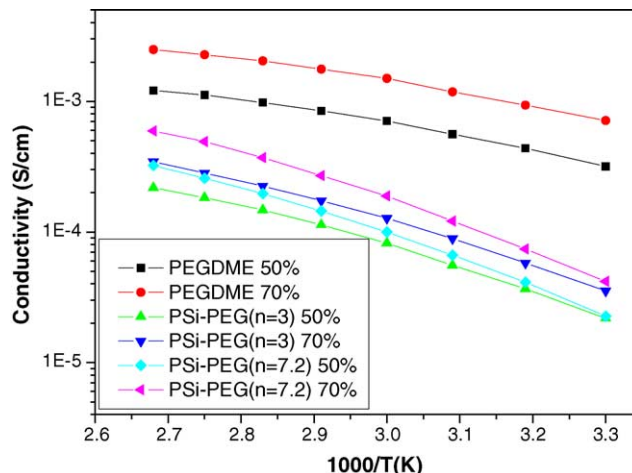

Fig. 3. Temperature dependence of ionic conductivity of solid polymer electrolytes with different contents of plasticizers. [EO]/[Li] was 20 for PEGDME and 10 for PSi-PEG ($n = 3$ and 7.2).

of the charge carriers and their mobility. The increase of T_g with increasing lithium salt concentration can be ascribed to the inter- and intra-molecular coordination of ether dipoles with the charge carriers, dissociated ions, which may act as transient cross-linking points in the polymer electrolytes. The increase in the T_g may decrease the segmental motion of the host polymer, which is directly related to the decrease of the ionic mobility [19]. In contrast, the number of charge carriers increases with increasing the salt concentration. This kind of ionic conductivity variation with the concentration of lithium salts was routinely observed for the comb-shaped [20] and cross-linked polymer electrolytes [7,17].

The conductivity of the polymer electrolyte without plasticizer was measured to be 4.5×10^{-6} S cm^{-1} at 30 °C, which was in the similar order of magnitude to that of the branched and cross-linked PEO polymer electrolytes [3–7]. When an ion-conducting plasticizer was added, the conductivity was increased (Fig. 2). From Fig. 2, it was noticed that the ionic conductivity of polymer electrolyte plasticized with PEGDME was higher than that plasticized with slioxane based polymer. This could be explained by the fact that the T_g of the solid polymer electrolyte using PEGDME as a plasticizer was much lower than that of polymer electrolyte plasticized with PSi-PEG. Using PSi-PEG ($n = 7$) as a plasticizer

instead of PSi-PEG ($n = 3$), the ionic conductivity of SPE increased slightly.

Fig. 3 shows temperature dependence of ionic conductivity of solid polymer electrolytes with various plasticizer contents. The ionic conductivity increased with increasing plasticizer contents and temperature. Arrhenius plots show a typical Vogel–Tamman–Fülcher (VTF) relationship (Eq. (1)) in the temperature range of 30–100 °C.

$$\sigma = AT^{-1/2} \exp\left(\frac{-E_a}{R(T - T_0)}\right) \tag{1}$$

where A, E_a, and T_0 are fitted parameters which are related to the change carrier density, pseudo-activation energy, and the temperature at which the segmental mobility of polymer chain, respectively. The VTF expression implies that the main mechanism of ion conduction can be related to the free volume theory [1,21]. The fitted parameter, A, E_a, and T_g, and ionic conductivity (σ) at the different contents of plasticizer are listed in Table 1. The E_a was calculated to be in the range from 6.76 kJ mol^{-1} to 9.09 kJ mol^{-1}, which was similar to the reported value of the cross-linked polysiloxane by West and co-workers [12]. The calculated E_a strongly depended

Table 1
Ionic conductivities and VTF fitting parameters for different contents and various plasticizers

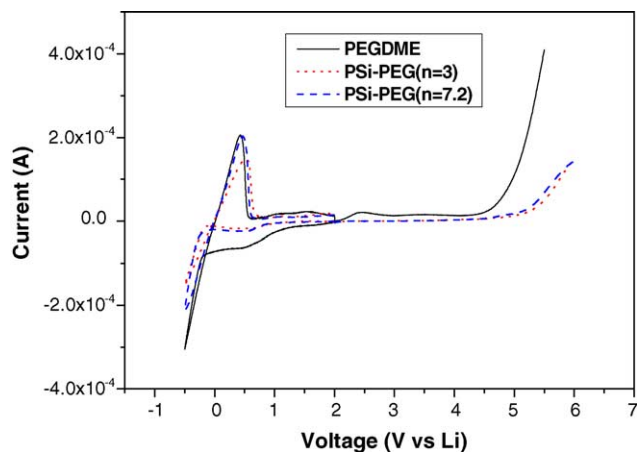| Plasticizer	Content (wt.%)	σ at 30 °C (S cm^{-1})	A (S K$^{0.5}$ cm^{-1})	E_a (kJ cm^{-1})	T_g (°C)
PEGDME	30	2.44×10^{-5}	0.10	7.10	−79.9
	50	3.17×10^{-4}	0.78	6.77	−86.7
	70	7.13×10^{-4}	1.46	6.76	−91.9
PSi-PEG, $n = 3$	30	1.30×10^{-5}	0.48	9.09	−63.8
	50	2.18×10^{-5}	0.69	8.97	−64.7
	70	3.53×10^{-5}	0.98	8.89	−65.8
PSi-PEG, $n = 7.2$	30	1.53×10^{-5}	0.37	7.64	−47.7
	50	2.26×10^{-5}	1.13	8.64	−51.1
	70	4.18×10^{-5}	2.45	8.95	−60.3

Fig. 4. Cyclic voltammograms of the SPE with various plasticizers at 30 °C. The content of plasticizer was 70 wt.%. Working electrode was nickel and sweep rate was 10 mV s^{-1}.

on the type of plasticizer. The E_a of SPE using PEGDME was smaller than that using PSi-PEG. However, E_a changed little with the content of plasticizer. The fitted A parameter, which usually correlates to the ion carrier density, increased significantly with increasing the content of plasticizer. It was also shown that the increase of ionic conductivity was well correlated with the increase of carrier density.

Fig. 4 shows the cyclic voltammograms of the polymer electrolyte sandwiched between Ni and Li metal electrode. Significant oxidative degradation of the solid polymer electrolyte started about 4.5 V for PEGDME and 5.2 V for PSi-PEG. Polymer electrolyte using PSi-PEG as a plasticizer showed wider electrochemical stability window than that using PEGDME. Reversible electrochemical plating/stripping of lithium took place in the potential range of −0.5 V to 0.5 V (versus Li/Li$^+$) on the Ni electrode.

Fig. 5 shows TGA thermograms of the solid polymer electrolyte using different plasticizers. The SPEs exhibited a small weight loss of <3% before significant weight loss,
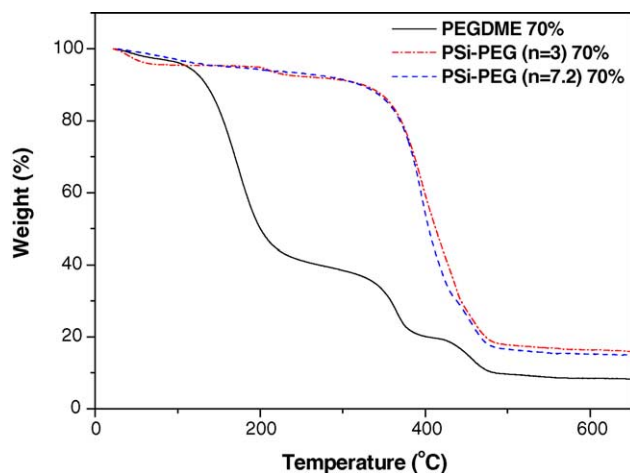
which was presumably due to the evaporation of residual moisture absorbed when the samples were loaded. Decomposition of SPE with a PEGDME started at around 120 °C. However, the thermal stability of SPE was greatly enhanced by using PSi-PEG compared with that using PEGDME. In this case, significant weight loss was not observed until 350 °C. The increase of thermal stability using siloxane based plasticizer may be explained by the strong Si−O bond of PSi-PEG compared with C−O bond of PEGDME.

The electrochemical properties and thermal stability of the resulting solid polymer electrolyte using PSi-PEG seem to be promising for the practical lithium polymer batteries.

4. Summary

A new cross-linker based on the siloxane polymers in which oligo(ethylene oxide) and acrylate functional group existed in the main chain of siloxane polymer was synthesized. The solid polymer electrolyte was prepared by thermal-curing of the synthesized PSi-*g*-(EO-A) cross-linker and plasticizer (PEGDME, PSi-PEG ($n = 3$ and 7.2)). The ionic conductivity increased but the glass transition temperature decreased as increasing the content of the plasticizer. The maximum conductivity was measured to be 7.13×10^{-4} S cm^{-1} for 70 wt.% of PEGDME and 4.18×10^{-5} S cm^{-1} for 70 wt.% of PSi-PEG at 30 °C. The cross-linked SPE with polysiloxane based plasticizer showed improved electrochemical stability window above 5.2 V and thermal stability up to 340 °C.

Acknowledgements

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Fig. 5. TGA thermograms of the solid polymer electrolytes.

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