Short communication

Ionic conductivity and electrochemical properties of cross-linked solid polymer electrolyte using star-shaped siloxane acrylate

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Abstract

A star-shaped siloxane acrylate with a different number of repeating units of oligo(ethylene oxide) (EO) was synthesized as a cross-linker of solid polymer electrolytes. The cross-linked solid polymer electrolytes blended with the ionic conducting plasticizers, such as low molecular weight poly(ethylene oxide)dimethyl ether (PEGDME) were prepared by the in situ thermal curing of the star-shaped siloxane acrylate. Different morphologies of the cross-linked polymer electrolytes were observed according to the number of repeating units of EO (n) in the cross-linker. A micro-phase separated solid polymer electrolyte was obtained when the n of cross-linker was 1. When the n of cross-linker was larger than 1, homogeneously blended solid polymer electrolytes were prepared. The ionic conductivity was measured to be 6.3 to $7.8 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ with 80 wt.% PEGDME at 30 °C. The ionic conductivity of the micro-phase separated solid polymer electrolyte was slightly higher than that of the homogeneously blended solid polymer electrolyte. The electrochemical stability window of the resulting solid polymer electrolyte could be extended to up to 4.8 V versus Li/Li$^+$ reference electrode.
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Keywords: Polymer electrolytes; Lithium batteries; Ionic conductivity; Siloxane cross-linker; Phase separation

1. Introduction

A solid polymer electrolyte based on polyethylene oxide (PEO) has been considered to be one of the promising electrolytes for high energy density secondary lithium batteries, such as lithium sulfur batteries and lithium metal batteries [1–3]. However, the ionic conductivity of the PEO-based solid polymer electrolyte at ambient temperature is relatively low compared with that of the gel-type electrolyte which is commonly used in the commercial lithium ion-polymer batteries. Recently, a significant enhancement of ionic conductivity has been reported for the solid polymer electrolyte blended with ion-conducting plasticizers, such as poly(ethylene glycol)dimethyl ether (PEGDME) or polysiloxane grafted oligo(ethylene oxide) [4–7]. However, they could not be applied on the commercial battery because their mechanical stability became poor by increasing the content of plasticizer. Thus, to enhance the

mechanical stability, a cross-linked network solid polymer electrolyte has been investigated [6,8,9].

The polymer electrolyte prepared by the chemical cross-linking has an improved mechanical property and thermal stability compared to that prepared by physical cross-linking [10]. The chemically cross-linked solid polymer electrolyte shows good film-forming properties and dimensional stability.

It has also been suggested that solid polymer electrolytes with ion conducting micro-domains formed by phase separation of blend and block copolymers improve ionic conductivity and mechanical properties [11–14]. Recently, it was also reported that the nano-phase separated polymer can be prepared by the polymerization-induced phase separation (PIPS) method [15]. Micro-domains have been formed in polymer electrolyte by the phase separation between polymer matrix and plasticizer complex with lithium salt during the chemical cross-linking. The micro-phase separated structure has also been observed in the poly(ethylene oxide)–polystyrene copolymer, acrylate–PVDF–HPF blend copolymers and poly(ethylene oxide methacrylate)-*b*-poly(lauryl methacrylate) block copolymer [11–13].

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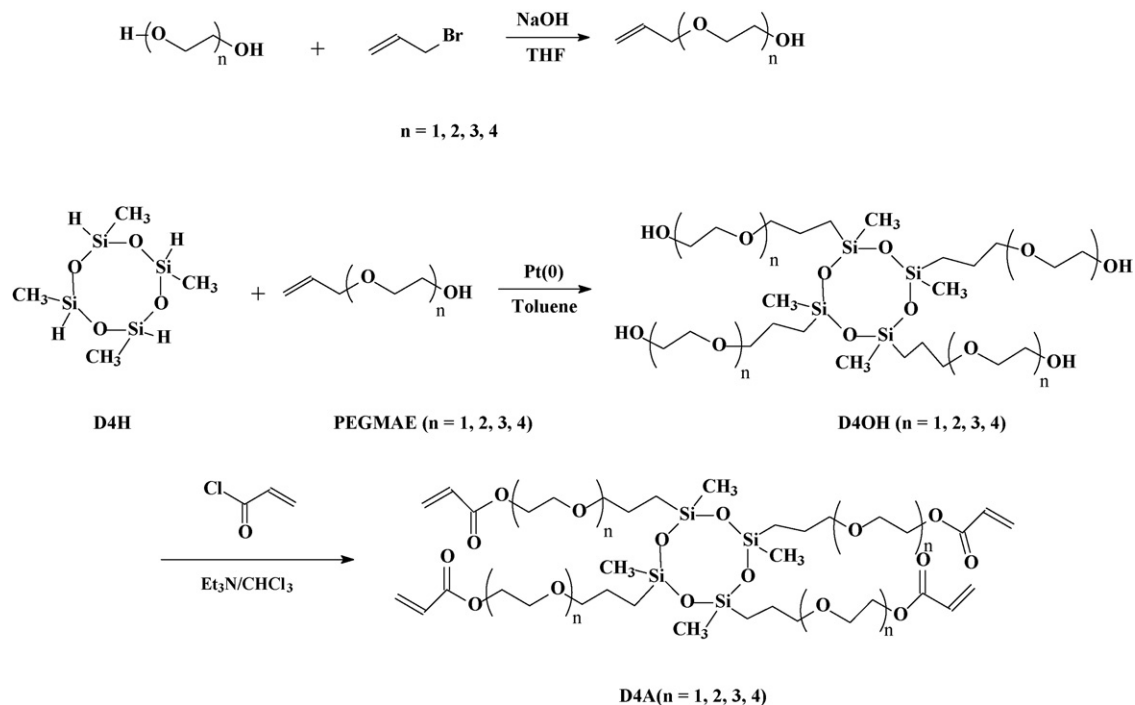
Scheme 1. Synthetic scheme of the star-shaped siloxane acrylate (D4A) cross-linker.

In this study, we synthesized a new star-shaped siloxane cross-linker with the oligo(ethylene oxide)acrylate functional group for solid polymer electrolyte and tested to prepare the cross-linked network solid polymer electrolyte. Since the non-polar siloxane usually produce phase separated morphology on the PEGDME blended polymer electrolyte, we observed a different phase separation behavior on the number of repeating units of oligo(ethylene oxide) (EO) in the cross-linker. The effect of phase separation on the ionic conductivity of the cross-linked polymer electrolyte was investigated.

2. Experimental

Poly(ethylene glycol)dimethyl ether (PEGDME, $M_w = 250$, Aldrich), $LiCF_3SO_3$ (Aldrich) and benzoyl peroxide (BPO, Aldrich) were dried in vacuum before use.

The star-shaped siloxane acrylate cross-linker (D4A) was synthesized by hydrosilylating poly(ethylene glycol)monoallyl ether (PEGMAE, $n = 1$–4) with 2,4,6,8-tetramethylcyclotetrasiloxane (D4H) and followed by acryloylation in a synthetic method similar to the one previously reported (Scheme 1) [7,16,17].

The cross-linked solid polymer electrolytes were prepared by in situ radical initiated cross-linking reaction of a homogeneous precursor solution of siloxane cross-linker (D4A), plasticizer (PEGDME), lithium salt ($LiCF_3SO_3$), and thermal radical initiator (BPO). The concentration of lithium salt was adjusted such that the EO/Li molar ratio of the polymer electrolyte was 15. The precursor solution was filled in a small gap between the desired substrates, such as ITO glass, lithium and nickel. The gap of substrate was maintained at about 100 μm by using the

polyimide tape. All samples were prepared and sealed with metallized polyethylene bag in a glove box under argon atmosphere, and they were cured in a convection oven at 100 °C for 20 min.

The morphology of solid polymer electrolyte was investigated by means of scanning electron microscopy (SEM, JEOL model SM6700F) after extracting PEGDME and Li salt with water, and the sample was dried using a freeze dryer to maintain the morphology of pores.

The T_g of the cross-linked polymer electrolyte was determined by using a differential scanning calorimeter (DSC) (TA Instruments, model universal V2.5H). Samples in hermetically sealed aluminum pans were stabilized at −150 °C, and then the temperature was elevated to 50 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

The conductivity measurement was carried out by coating polymer electrolytes onto the pre-patterned ITO cell which has been developed by our laboratory [4,18,19]. The thickness of the resulting polymer electrolyte was about 100 μm. 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 from 1 Hz to 1 MHz. The temperature of the sample was controlled within ±0.5 °C by means of a programmable hot plate (Mettler, model FP 82HT).

The electrochemical stability window of solid polymer electrolyte was determined by means of cyclic voltammetry (EG&G model 270 potentiostat) at 30 °C. A nickel plate (Aldrich, 0.125 mm thick, >99.9%) was used for a working electrode and a lithium metal foil (FMC Co.) for a counter and reference electrode. These test cells were assembled by sandwiching the solid polymer electrolyte between the two electrodes.
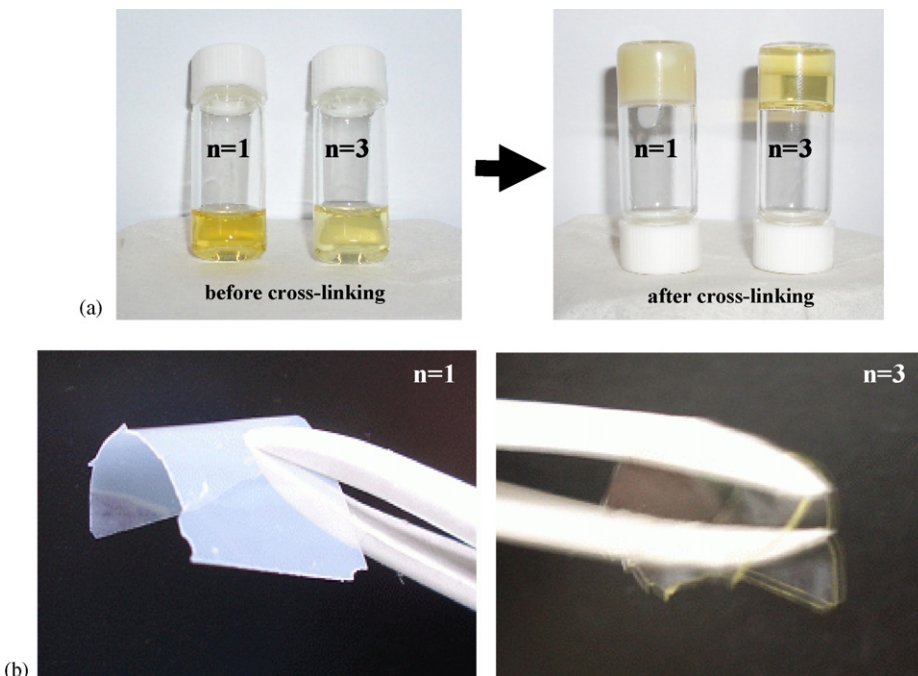
Fig. 1. Photographs of the reaction mixtures before and after cross-linking (a) and the prepared solid polymer electrolyte films (b) (cross-linker = 30 wt.%, plasticizer = 70 wt.%).

3. Results and discussion

We found that the morphology of the cross-linked polymer electrolyte depends on the number of repeating units of oligo(ethylene oxide) (n) (see Fig. 1). The resulting polymer electrolyte showed a phase separated structure when n of the cross-linker was 1. After being cross-linked in homogeneous solution, it may form a heterogeneous solid, which is known as a polymerization-induced phase separation (PIPS) mechanism [15]. This phenomenon is attributed to the phase separation of the plasticizer complexed with lithium salt and siloxane polymer during the cross-linking reaction. As a result of the phase separation, the submicron sized domains of PEGDME were formed in the polymer matrix. Fig. 2 shows the micro-porous structure of polymer electrolyte after removing the PEGDME by extracting with water. However, when the n of the cross-linker is larger than 2, the polymer electrolytes is blended homogeneously in any portion of PEGDME without phase separation. No porous structure was observed in homogeneous polymer electrolyte by the SEM (Fig. 2). The dimensional stability of the prepared solid polymer electrolyte depended on the content of plasticizer as well as the number of repeating units in the cross-linker. A self-supportive film was obtained up to 90 wt.% of plasticizer using the cross-linker ($n = 1$). On the other hand, when the content of PEGDME was larger than 80 wt.%, a stable polymer electrolyte film could not be prepared using the cross-linker ($n = 3$). The polymer electrolyte film with the cross-linker ($n = 1$) showed a superior dimensional stability than the other cross-linker ($n > 1$). The enhanced mechanical stability may be explained by the increased cross-linking density and the micro-phase separation of solid polymer electrolyte because of the relatively short repeating unit of EO in the cross-linker
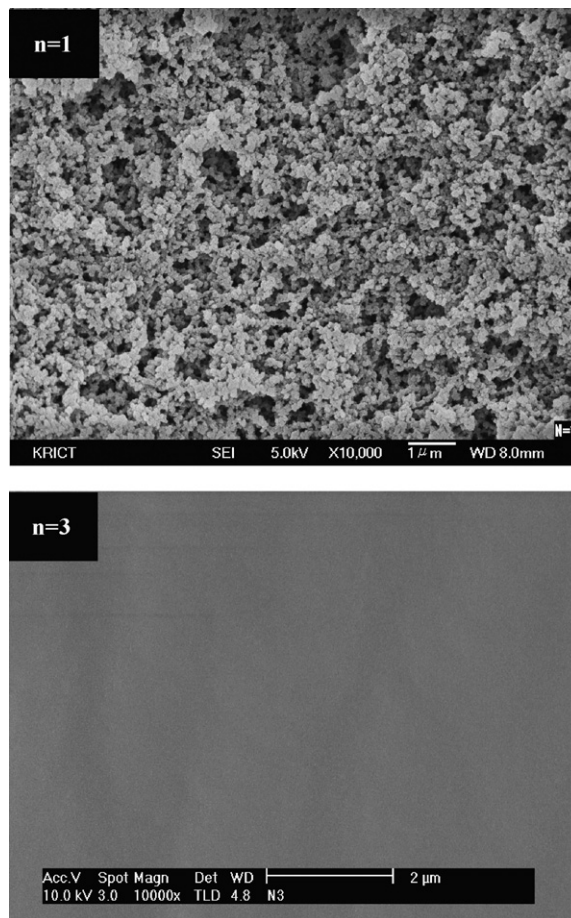

Fig. 2. SEM micrographs of cross-linked solid polymer electrolyte with a different number of repeating units of EO in cross-linker after extracting with water (plasticizer content = 70 wt.%).
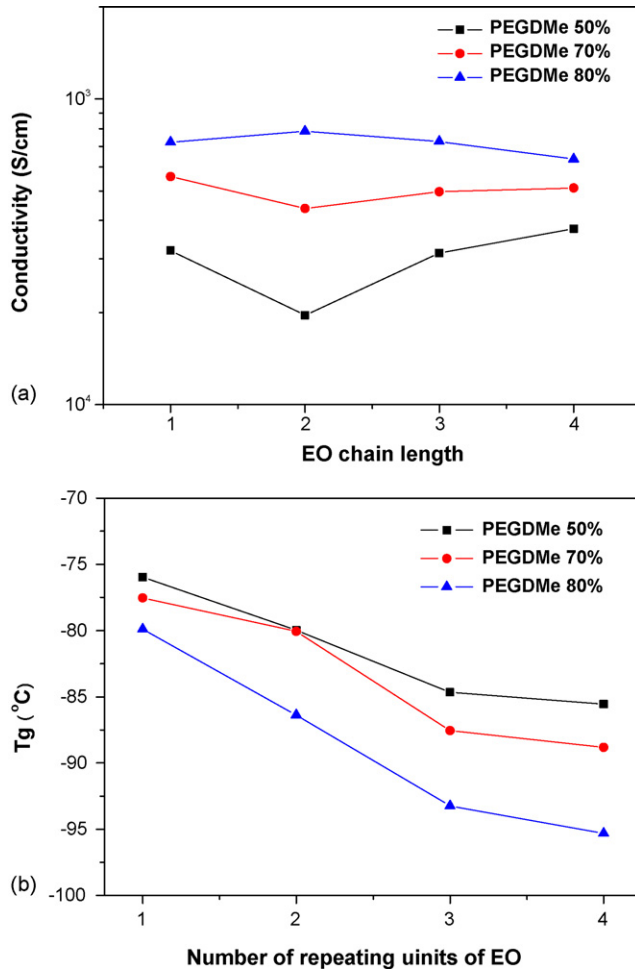
Fig. 4. Temperature dependence of ionic conductivity on the number of repeating units of EO in cross-linker (D4A 50 wt.%, PEGDME 50 wt.%, LiCF$_3$SO$_3$).

Fig. 3. Changes of ionic conductivity at 30 °C (a) and glass transition temperature T_g (b) as a function of plasticizer contents and number of repeating units of EO in cross-linker.

($n = 1$). A similar enhancement of mechanical properties of the micro-phase separated polymer electrolyte has been reported [14].

Fig. 3(a) shows the effect of plasticizer contents and the number of repeating units of EO in the cross-linker on the ionic conductivity of solid polymer electrolytes at 30 °C. The ionic conductivity of the solid polymer electrolyte plasticized with PEGDME increased with an increasing content of PEGDME up to 80 wt.%. Also, the ionic conductivity varied with the number of repeating units of EO in the cross-linker. Ionic conductivity increased with increasing number of repeating units of the cross-linker except $n = 1$ which formed phase separated solid polymer electrolyte. The increase of ionic conductivity with the increasing number of repeating units of EO (n) and PEGDME content was explained by the decrease of T_g (Fig. 3(b)). A similar increase of the ion conductivity with PEGDME content and the number of repeating units of EO has been previously reported [5,16,20]. However, the ionic conductivity of the solid polymer electrolyte containing more than 80 wt.% of plasticizer changed little with the number of repeating units of EO in the cross-linker. It was also noticed that the ionic conductivity of the solid polymer electrolyte using the cross-linker ($n = 1$) measured to
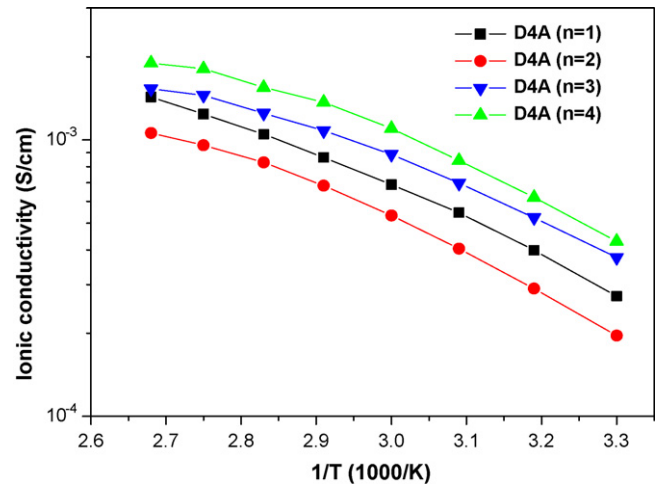
be higher than that of solid polymer electrolyte using the cross-linker ($n = 2$). This phenomenon explains how the PEGDME micro-domains in the phase separated solid polymer electrolyte act as facile ion conducting channels through which lithium ions can easily migrate.

Fig. 4 shows the temperature dependence of ionic conductivity for the solid polymer electrolyte prepared with a different number of repeating units of EO in the cross-linkers.

Conductivity–temperature (σ–T) curves are deviated from Arrhenius behavior. 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 charge carrier density, pseudo activation energy and the temperature at which the segmental mobility of polymer chain was zero, respectively. The E_a was calculated to be in the range from 4.8 to 9.0 kJ mol^{-1}, which was similar to the reported value of the cross-linked siloxane by Zhang et al. [8,9]. The E_a of SPE was decreased as the number of repeating units of EO in cross-linker increased.

Fig. 5 shows the cyclic voltammograms of the polymer electrolyte with a different number of repeating units of EO in the cross-linker. Even though the number of repeating units of EO in the cross-linker was changed, the electrochemical property of the resulting solid polymer electrolyte was not much different. A significant oxidative degradation of the solid polymer electrolyte started at about 4.8 V versus Li/Li$^+$ reference electrode. Reversible electrochemical plating/stripping of lithium took place in the potential range of −0.5 to 0.5 V (versus Li/Li$^+$) on the Ni electrode. Although the cyclic voltammetric study cannot be directly related to the long-term stability of polymer electrolytes, the resulting polymer electrolyte, which showed stable potential window up to 4.8 V as well as reversible plating/stripping of Li on the Ni electrode, may be applicable to the practical lithium polymer battery.
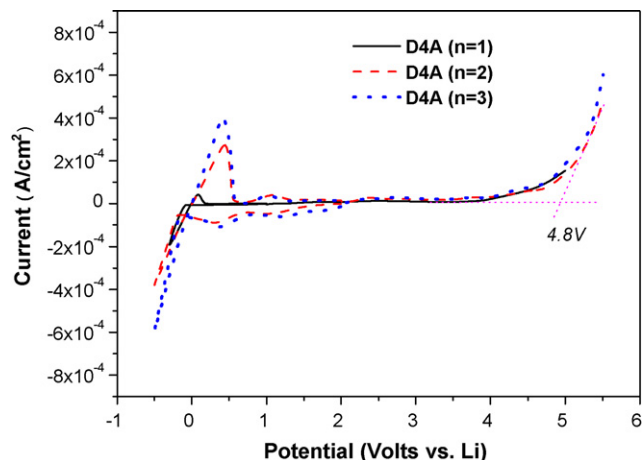
Fig. 5. Cyclic voltammogram of the solid polymer electrolyte with various number of repeating units of EO in cross-linker (PEGDME content = 70 wt.%). Working electrode was nickel and sweep rate was $10\,\mathrm{mV\,s^{-1}}$.

4. Summary

Star-shaped siloxane acrylate, a new cross-linker, was synthesized in which oligo(ethylene oxide) and acrylate functional group exist in the ring type siloxane. The cross-linked network solid polymer electrolyte blended with PEGDME was prepared by thermal-curing of the synthesized cross-linker and plasticizer (PEGDME). The cross-linked polymer electrolyte showed a different morphology with the number of repeating units of EO in the cross-linker. A micro-phase separated structure was observed in the solid polymer electrolyte using the cross-linker ($n = 1$). When n was larger than 2, however, the homogeneously blended film was obtained. The ionic conductivity of the phase separated solid polymer electrolyte ($n = 1$) was slightly higher than that of the homogeneously blended solid polymer electrolyte ($n = 2$). The ionic conductivity increased but the glass transition temperature decreased with an increase in the content of the plasticizer and the number of repeating units of EO in the cross-linker. The ionic conductivity was 6.3–$7.8 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ with 80 wt.% of PEGDME at 30 °C. The cross-linked solid polymer electrolyte, which has high ionic conductivity and stable electrochemical stability window, may be applicable to the practical lithium-polymer battery.

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