

# New crosslinking agent as a Lewis acid for solid polymer electrolytes

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## Abstract

Poly(ethylene glycol) borate acrylate (PEGBA) was synthesized as a new crosslinking agent for solid polymer electrolyte (SPE) based on non-woven matrix. It has not only three crosslinkable acrylate groups for higher crosslinking density, but also Lewis acid center acting as an anion receptor. The ionic conductivity of SPE containing 15 wt.% PEGBA reached  $5.5 \times 10^{-4} \text{ S cm}^{-1}$ , because the content of non-volatile plasticizer, poly(ethylene glycol) dimethyl ether (PEGDME), could be increased to 85 wt.% without leakage. In addition, its transference number and electrochemical stability were also enhanced to 0.37 and 5.2 V, respectively, due to the presence of Lewis acid center in PEGBA.

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**Keywords:** Solid polymer electrolyte; Crosslinking agent; Anion receptor; Ionic conductivity; Transference number

## 1. Introduction

Solid polymer electrolytes (SPEs) can contribute to enhancing safety of lithium secondary batteries since they exhibit no leakage during the operation of the cell. In spite of this overwhelming advantage, their low ionic conductivity especially at or below atmospheric temperature, and also high interfacial resistance are still principal barriers to their commercial application. Connected with these, there have been many attempts typically including various modification of polymer structure [1–4] or introduction of inorganic nanoparticles [5,6] into matrix polymer, however, they could not succeed in attaining the required ionic conductivity level ( $\sim 10^{-3} \text{ S cm}^{-1}$ ) for practical application. It is because they could not gain sufficient chain mobility of polymer matrix without sacrificing the mechanical strength of SPEs. In order to overcome these problems, we already suggested new SPE system based on polyethylene (PE) non-woven matrix as a mechanical supporter [7]. In that system, ionic conductivity could reach to the value higher than the order of  $10^{-4} \text{ S cm}^{-1}$  by the presence of pores in non-woven matrix which functions as an ion-conductive region. A large amount of non-volatile plasticizer could be kept in the pores with maintaining mechanical strength of SPEs. Anion receptor can also

contribute to enhancing the ionic conductivity by increasing the dissociation of Li salt [8].

In this study, new multifunctional crosslinking agent having Lewis acid center that can act as an anion receptor was synthesized and used to prepare SPEs based on PE non-woven matrix. The electrochemical properties of the SPEs such as ionic conductivities, cationic transference numbers, and electrochemical stabilities of SPEs were investigated with change of non-volatile plasticizer content and temperature.

## 2. Experimental

### 2.1. Synthesis and characterization of poly(ethylene glycol) borate acrylate (PEGBA)

Poly(ethylene glycol) borate acrylate (PEGBA) was synthesized by the dehydrocoupling reaction of poly(ethylene glycol) acrylate ( $M_n = 375$ , Aldrich) and  $\text{BH}_3$ /tetrahydrofuran complex (Aldrich) as described in Fig. 1 [9]. The mixture was heated to  $60^\circ\text{C}$  with stirring for 24 h under nitrogen atmosphere. The solvent was evaporated with a rotary evaporator at reduced pressure. The synthesized PEGBA was dried in a vacuum oven at  $40^\circ\text{C}$  for 24 h to remove residual solvent and kept in a glove box.  $^1\text{H}$  NMR spectra were obtained in  $\text{CDCl}_3$  solvent on a Bruker DSX 400 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal reference and FT-IR spectra were recorded in the transmission mode on a Bruker Tensor 27 spectrometer with

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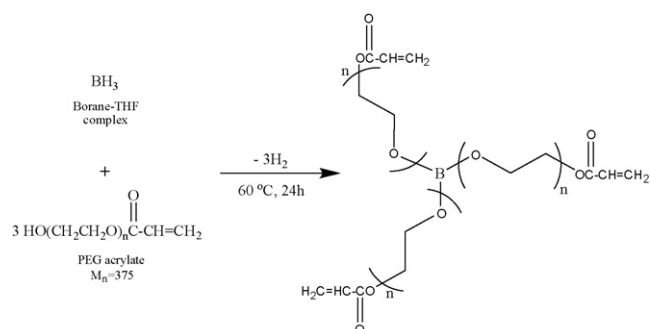


Fig. 1. Synthesis scheme of poly(ethylene glycol) borate acrylate (PEGBA) from poly(ethylene glycol) acrylate and  $\text{BH}_3/\text{THF}$  complex by the dehydrocoupling reaction.

the resolution of  $4\text{ cm}^{-1}$  in the vibrational frequency range of  $400\text{--}4000\text{ cm}^{-1}$ . The chemical structure of PEGBA was determined by  $^1\text{H NMR}$  (in  $\text{CDCl}_3$ ):  $\delta$  3.48–3.9 ( $-\text{OCH}_2\text{CH}_2$ ),  $\delta$  5.8–6.5 ( $\text{CH}_2=\text{C}$ ),  $\delta$  6.2 ( $\text{C}=\text{CHC}=\text{O}$ ) (unit: ppm).

## 2.2. Preparation of solid polymer electrolytes and their thermal properties

Polyethylene (PE) non-woven matrix with  $40\ \mu\text{m}$  thickness was used as a mechanical supporting matrix after dried in vacuum at  $80\text{ }^\circ\text{C}$  for 24 h. PEGBA as a crosslinking agent and poly(ethylene glycol) dimethyl ether (PEGDME,  $M_w = 250$ , Aldrich) as a non-volatile plasticizer were dried over  $4\ \text{\AA}$  molecular sieves prior to use.  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$  (LiTFSI, 3M) was dried in a vacuum oven at  $80\text{ }^\circ\text{C}$  for 24 h. Methyl benzoylformate (Aldrich) as a photoinitiator was used as received. All the chemicals were handled in Ar-filled glove box.

Solid polymer electrolytes were prepared by spreading an UV-curable SPE precursor solution on the PE non-woven matrix and irradiating UV ( $8\text{ mW cm}^{-2}$ ,  $365\text{ nm}$ ) for 5 min. The UV-curable SPE precursor consists of crosslinking agent (PEGBA), non-volatile plasticizer (PEGDME), Li salt (LiTFSI), and photoinitiator (methyl benzoylformate). Li salt (LiTFSI) was added into SPE precursor at a concentration of  $[\text{EO}]:[\text{Li}] = 20:1$ .

Thermal analysis of the prepared SPE was conducted by using a differential scanning calorimeter (DuPont TA 2000 DSC) to determine its glass transition temperature. Each sample was scanned at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  within an appropriate temperature range under nitrogen atmosphere.

## 2.3. Electrical measurements

The ionic conductivities of SPEs were obtained from bulk resistance of the cell consisting of stainless steel electrode/SPE/stainless steel electrode by ac complex impedance analysis using a Solartron 1455 frequency response analyzer (FRA) over the frequency range of  $10\text{ Hz--}1\text{ MHz}$ .

The transference number was determined by dc polarization/ac impedance combination method [10]. A constant polarization of  $10\text{ mV}$  was applied to the cell. The transference number of the lithium cation was calculated by the relation,  $t_{\text{Li}^+} = [I_s(\Delta V - I_0 R_0)]/I_0(\Delta V - I_s R_s)$ , where  $I_0$  and  $I_s$  are the cur-

rents at initial and steady-state,  $R_0$  and  $R_s$  are the interfacial resistances at initial and steady-state, respectively. The electrochemical stability of SPE was determined by linear sweep voltammetry experiment that is performed on a stainless steel working electrode and lithium reference electrode at a scanning rate of  $1\text{ mV s}^{-1}$ .

## 3. Result and discussion

Poly(ethylene glycol) borate acrylate (PEGBA) was newly designed as a crosslinking agent for solid polymer electrolytes (SPEs) based on non-woven matrix. SPEs based on PEGBA were expected to exhibit higher ionic conductivity at room temperature, because PEGBA can entrap sufficient amount of non-volatile plasticizer within SPE due to its three acrylate groups and it can also increase the dissociation degree of lithium salt by the presence of Lewis acid center (boron atom). In addition, Lewis acid center in PEGBA chains is expected to make stable complexes with anions to enhance the stability of anions under high oxidative voltage and temperature. With these reasons, PEGBA was designed as a good candidate of crosslinking agent for SPEs in this work.

Fig. 2 shows FT-IR spectrum of the synthesized PEGBA. When it is compared with the spectrum of the reactant, PEG acrylate, the  $-\text{OH}$  stretching peak near  $3400\text{ cm}^{-1}$  corresponding to the reactant (PEG acrylate) is not shown. In addition, carbonyl group ( $\text{C}=\text{O}$ ) near  $1750\text{ cm}^{-1}$  and carbon double bond ( $\text{C}=\text{C}$ ) near  $1650\text{ cm}^{-1}$  were well maintained. These support that PEGBA was properly synthesized.

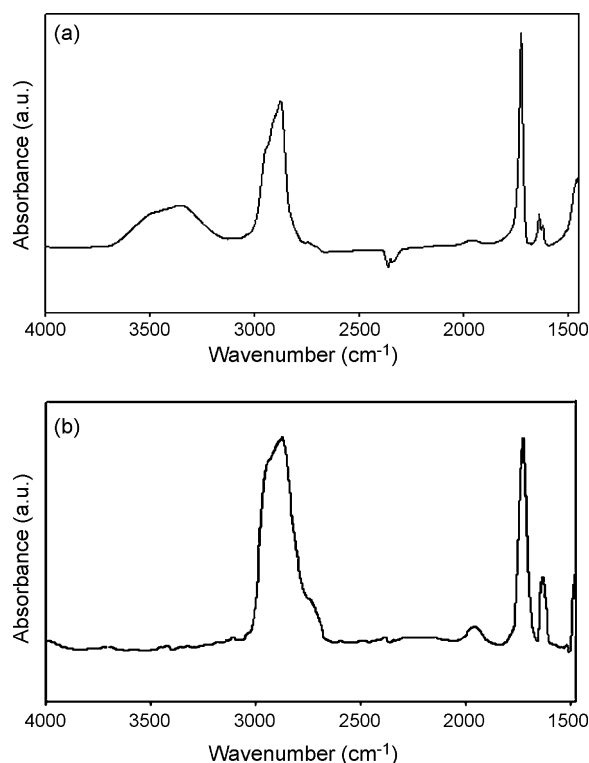


Fig. 2. FT-IR spectra of (a) poly(ethylene glycol) acrylate and (b) poly(ethylene glycol) borate acrylate (PEGBA).

Table 1

Ionic conductivities, glass transition temperatures, transference numbers, and cationic conductivities of SPEs as a function of PEGDME content

Content of PEGDME (wt.%)	$\sigma$ (S cm <sup>-1</sup> at 20 °C)	$T_g$ (°C)	$t_{Li^+}$	$\sigma_{Li^+}^a$ (S cm <sup>-1</sup> )
0	$3.6 \times 10^{-6}$	-48.4	-	-
80	$2.6 \times 10^{-4}$	-80.9	0.45	$1.2 \times 10^{-4}$
83	$3.9 \times 10^{-4}$	-82.0	0.40	$1.6 \times 10^{-4}$
85	$5.5 \times 10^{-4}$	-84.1	0.37	$2.0 \times 10^{-4}$

$$^a \sigma_{Li^+} = \sigma t_{Li^+}$$

The ionic conductivities of SPEs with different ratio of crosslinking agent (PEGBA) to non-volatile plasticizer (PEGDME) are listed in Table 1. In the case of the SPE prepared only with PEGBA, its ionic conductivity is found to be  $3.6 \times 10^{-6}$  S cm<sup>-1</sup>. This low value is caused by the limited segmental motion of the crosslinked polymer chains as is estimated by relatively high glass transition temperature of -48.4 °C compared with the case of introduction of non-volatile plasticizer. On the other hand, when PEGDME is introduced to SPE with the amount of higher than 80 wt.%, all the ionic conductivities of SPEs exceed  $10^{-4}$  S cm<sup>-1</sup> level, which is known as the minimally required level of ionic conductivity for practical application of rechargeable lithium batteries.

The ionic conductivities of SPEs are shown to increase with increase of the PEGDME content as listed in Table 1, which can be explained by the decrease of glass transition temperature. SPE with 85 wt.% PEGDME could exhibit  $5.5 \times 10^{-4}$  S cm<sup>-1</sup> at 20 °C, which is rather higher than the ionic conductivity ( $3.1 \times 10^{-4}$  S cm<sup>-1</sup>) of SPE based on poly(ethylene glycol) dimethyl acrylate (PEGDMA) reported in our previous work [7]. The above-enhanced ionic conductivity seems to be highest among the reported ones for the SPSs maintaining the required mechanical strength for practical application. This enhancement of ionic conductivity is due to the increase of non-volatile plasticizer content.

An Arrhenius plot of ionic conductivities for SPEs with 85 wt.% PEGDME is shown in Fig. 3. The measurement was conducted from -10 to 60 °C every 10 °C, and then it was cycled to -20 °C. Because all the ionic conductivities of SPE were maintained well at each temperature under thermal stress

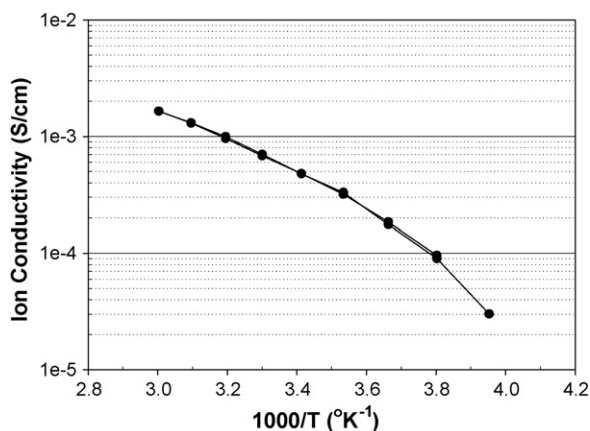


Fig. 3. Ionic conductivities of SPE with 15 wt.% PEGBA and 85 wt.% PEGDME as a function of temperature.

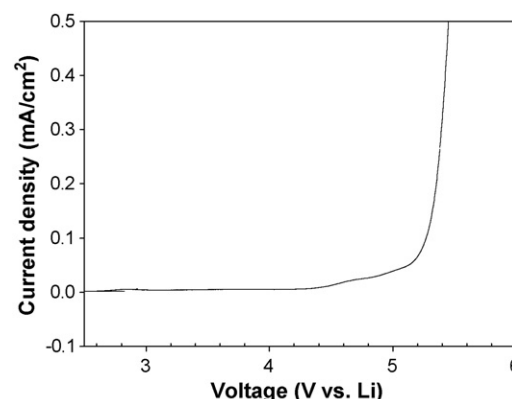


Fig. 4. Electrochemical stability of SPE with 15 wt.% PEGBA and 85 wt.% PEGDME at a scan rate of 1 mV s<sup>-1</sup>.

during the cycled heat treatment (hysteresis) between -10 and 60 °C, it is concluded that 85 wt.% PEGDME is well entrapped in crosslinked PEGBA matrix without leakage.

Transference numbers of Li cation decrease with increase of the PEGDME content as given in Table 1. It is because the relative content of Lewis acid center in SPE decreases with increase of PEGDME content. As a result, cationic conductivities, which can be calculated by multiplying ionic conductivity with transference number, increase relatively slowly than ionic conductivities with increase of the PEGDME content.

In order to evaluate the availability of Lewis acid center to interact with anions, the electrochemical stability of SPE was measured by linear sweep voltammetry. As shown in Fig. 4, it is found that SPE with 15 wt.% PEGBA and 85 wt.% PEGDME is stable up to 5.2 V, which is much higher than the SPE without Lewis acid materials [7]. This enhancement may be originated from the stabilization of anions by Lewis acid center in PEGBA.

Therefore, PEGBA is proposed to be a promising crosslinking agent for SPE due to high ionic conductivity at room temperature, transference number and electrochemical stability. More detailed analysis of the SPE based on PEGBA including its cycle performance will be performed.

#### 4. Conclusion

The solid polymer electrolyte (SPE) based on poly(ethylene glycol) borate acrylate (PEGBA) as a new crosslinking agent with high functionality and Lewis acid center has been successfully prepared. It exhibits high ionic conductivity at room temperature due to higher non-volatile plasticizer content. It also shows higher transference number and electrochemical stability compared to conventional SPE without Lewis acidic materials.

This enhancement is expected to originate from the formation of stable complexes between boron atom of PEGBA and anions.

### **Acknowledgement**

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