Synthesis and Conductivity of PEGME Branched Poly(ethylene-*alt*-maleimide) Based Solid Polymer Electrolyte

Yongku Kang,[a] Yeon-Ho Seo, and Changjin Lee

Advanced Materials Division, Korea Research Institute of Chemical Technology,
P.O. Box 107, Yusung, Taejeon 305-600, Korea
Received September 14, 1999

A thermally stable comb-like polymer electrolyte, poly(ethylene glycol) monomethyl ether (PEGME) grafted poly(ethylene-*alt*-maleimide), has been synthesized and characterized. The copolymer was thermally stable up to 250 °C and had good film forming property. The copolymer was well mixed with poly(ethylene glycol) dimethyl ether(PEGDME, $\overline{M}w$ = 400). The activation energy of ionic conduction decreased and conductivity increased with the increase of PEGDME content in the polymer electrolyte. The maximum conductivity of the resulting polymer electrolyte containing 66 wt% of PEGDME was found to be 3×10^{-4} S/cm at 30 °C. The polymer electrolyte showed electrochemical stability window of greater than 4.7 V.

Introduction

Solid polymer electrolytes, which can be used in all solid state electrochemical devices, contain functional groups that can dissolve the added salts by coordinating the cations. Poly(ethylene oxide) (PEO) based solid polymer electrolytes have been widely studied because the ethylene oxide (EO) units provide environment for the maximum solvation of metal cations.[1,2] However, the high crystallization aptitude of PEO results in the low conductivity of the salt complexes at room temperature, which limits its use in devices. Grafting low molecular weight poly(ethylene glycol) monomethyl ether (PEGME) into the side chain of polymers is a well-known method to minimize the crystallinity of PEO. PEGME has been grafted into various polymers such as poly(phosphazene),[3,4] poly(siloxane),[5,6] polyacrylate[7,8] and maleic anhydride copolymers.[9-13]

We were interested in the grafting of poly(ethylene-*alt*-maleic anhydride) since they had good film forming properties and also had highly reactive anhydride group for the easy grafting of PEGME in the side chain. It has been reported that PEGME could be readily incorporated into the maleic anhydride copolymers 1 from the reaction of PEGME with 1 (Scheme 1).[9-13] The lithium complex of the PEGME grafted copolymers 2 showed ionic conductivity of *ca.* 10^{-5} S/cm but their thermal stability was very poor due to the decomposition of the ester into the corresponding cyclic anhydride at 140 °C.[9,10]

In this paper, we describe the synthesis of a new PEGME grafted poly(ethylene-*alt*-maleimide) 7, which is expected to give better thermal properties than that of ester linked copolymer 2, its blends with poly(ethylene glycol) dimethyl ether (PEGDME) and the ion conducting properties of the lithium salt complex of the copolymer.

Results and Discussion

Synthesis of Polymer Electrolyte. The PEGME branched solid polymer electrolytes 7 were synthesized by reacting

amine terminated PEGME 5 with poly(ethylene-*alt*-maleic anhydride) (Scheme 3). The ω-amino-PEGME 5 was prepared by the reaction of PEGME-mesylate 3 with sodium azide in dimethyl acetamide (DMAC) followed by reduction of ω-azido-PEGME 4 with Zn dust in ethanol (Scheme 2). Reaction of ω-amino-PEGME with poly(ethylene-*alt*-maleic anhydride) in DMAC produced the corresponding PEG grafted amic acid containing copolymer 6. The amic acid group was converted into imide group by the addition of acetic anhydride and pyridine at 60 °C.
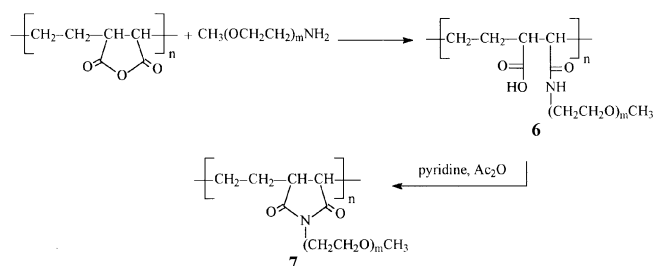
The IR spectra of the starting poly(ethylene-*alt*-maleic anhydride), amic acid containing copolymer 6 and imide containing copolymer 7 are shown in Figure 1. The peak at
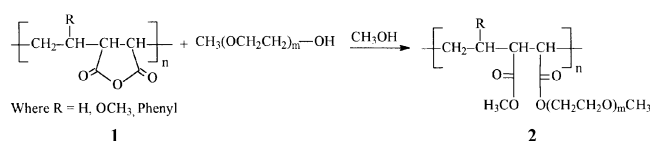
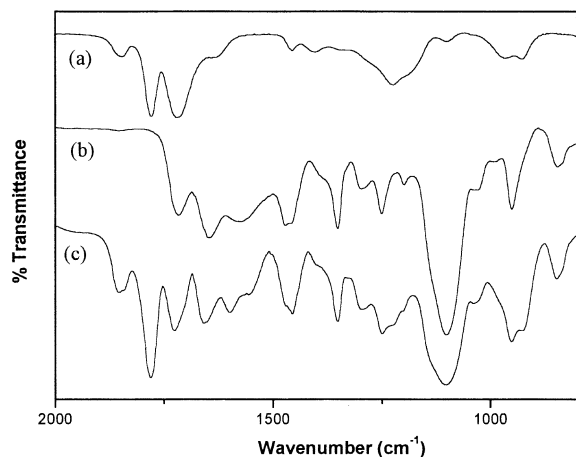**Scheme 1**
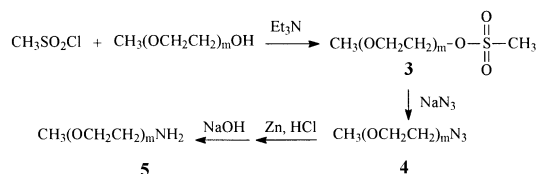
Scheme 2

Scheme 3

Figure 1. IR spectra of poly(ethylene-*alt*-maleic anhydride) (a), PEGME branched poly(ethylene-*alt*-maleamic acid) (b) and PEGME branched poly(ethylene-*alt*-maleimide) (c).

1779 and 1847 cm⁻¹ corresponding to the cyclic anhydride are disappeared and new peaks appear at 1646 and 1715 cm⁻¹ which are characteristic C–O stretching for amide and acid. After chemical imidization, these peaks are converted into the characteristic cyclic imide C–O stretching peak at 1780 and 1853 cm⁻¹. From the ¹H NMR study, it is also found that peaks at 8.15 and 12.5 ppm which correspond to the amic acid are completely disappeared after imidization.

Properties of Polymer Electrolyte. The polymer **7** was soluble in DMAC, dimethylformamide (DMF) and dimethylsulfoxide (DMSO) and a free-standing film was cast from the solution. The glass transition temperature (T_g) of **7** was found to be -35 °C and no other significant peaks such as melting or degradation were found in the temperature range from -70 °C to 250 °C in its differential scanning calorimeter (DSC) thermogram (Figure 2). Xu *et al.* reported two glass transitions for the PEGME grafted polymers; one at about -50 °C was assigned to the glass transition of the oligo(oxyethylene) side chain and the other transition in the range of 30-50 °C was assigned to the main chain of the copoly-
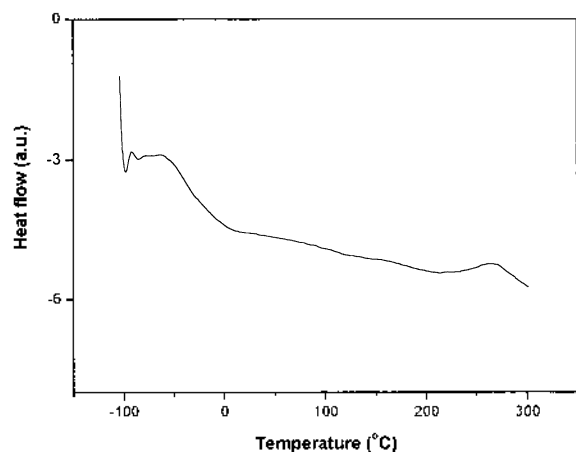
mers.[13] Although the T_g of **7** was comparable to the reported value of the T_g of side chain, we did not observe any other second glass transition corresponding to the main chain or melting for the polymer **7**.

To improve the ionic conductivity, the polymer **7** was blended with low molecular weight poly(ethylene glycol) dimethyl ether (PEGDME) ($\overline{\text{Mw}} - 400$) instead of adding polar solvent such as propylene carbonate (PC) and ethylene carbonate (EC). The addition of PEGDME resulted in as much enhancement of conductivity as the addition of polar solvent. The free-standing film could be obtained from the blend containing up to 66 wt% of the PEGDME. More than that, polymer blend became viscous gel and free-standing film could not be obtained. PEGDME and the copolymer **7** were well mixed without phase separation evidenced by the continuous decrease of T_g with the increase of PEGDME content in the DSC thermogram.

Ionic Conductivity. The conductivity of the pure polymer **7** complex with LiCF₃SO₃ was *ca.* 10⁻⁶ S/cm at 30 °C. This value is similar order of magnitude to that of the previously reported PEO-branched polymer electrolyte.³⁻¹¹ However, the conductivity of the polymer increased about two order of magnitude by the addition of PEGDME. The change of the measured conductivity and T_g as a function of the PEGDME content is shown in Figure 3. As the content of the PEGDME increases, the conductivity increases but the T_g of the PEGDME blended polymer electrolyte decreases. Similar increase of the conductivity has been reported for the PVDF-HFP polymer electrolyte plastisized with PEGDME and the maximum content of PEGDME in the PVDF-HFP polymer electrolyte film was 65 wt% and conductivity was reported to be 2×10^{-4} S/cm.¹⁴

A typical Vogel-Tamman-Fulcher (VTF) conductivity-temperature relationship was observed in the temperature range of 30 °C to 120 °C from the temperature dependence of ionic conductivity plot (Figure 4). These relationships imply that the main mechanism of ionic conduction can be explained by free volume theory. In Table 1, activation energies of ionic conduction (E_a) that were calculated from the Arrhenius plot are listed. The calculated E_a of pure polymer
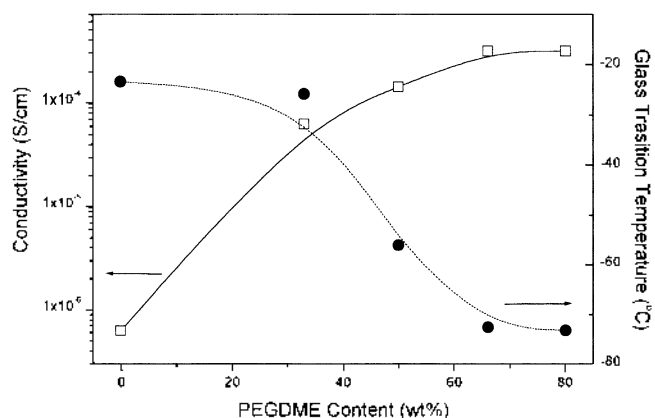

Figure 2. DSC diagram of the PEGME branched poly(ethylene-*alt*-maleimide).

Figure 3. The change of conductivity at 30 °C (□) and glass transition temperature (●) as a function of PEGDME content.
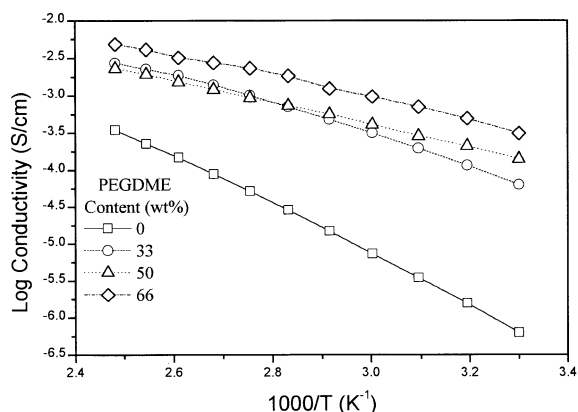
Figure 4. Temperature dependence conductivity at different PEGDME content.

Table 1. Activation energy for ionic conduction in polymer electrolytes at different PEGDME contents

PEGDME Contents (%)	0	33	50	66
Activation Energy (Kcal/mole)	14.5	8.3	6.58	6.12

was 14.7 kcal/mole and those of the PEGDME blended polymer electrolytes were in the range of 6-8 kcal/mole. The E_a of PEGDME blended polymer electrolyte was similar to that of the PEGDME plasticized PVDF-HFP polymer electrolyte.[14] Although, the ethylene oxide units in PEGDME as well as in branched PEO can form complex with lithium salt, the higher mobility of lithium ion in PEGDME than that in side chain PEO is expected because of more freedom of polymer chain movement. Thus, the E_a of ionic conduction decreased and conductivity increased with the increase of PEGDME content. This also implies that ion conduction through PEGDME is probably dominant.

Plots of isothermal conductivity as a function of ethylene oxide unit per lithium ion ([EO]/[Li]) ratio showed a typical bell shape curve with a maximum (Figure 5). As salt concentration increased at a low salt concentration region, conductivity increased due to the increase of carrier density. However, at higher salt concentration region, physical cross-linking due to ionic interaction between lithium ion and
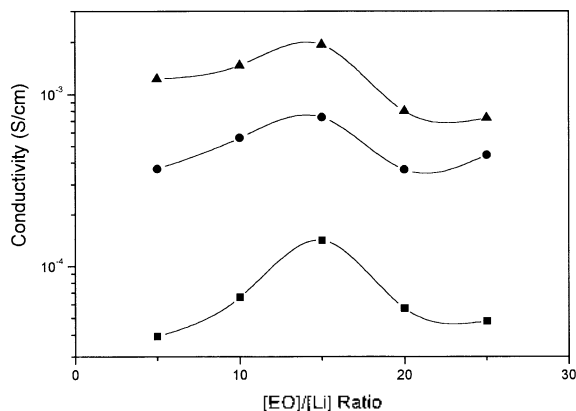

Figure 5. The change of conductivity at 30 °C (■), 80 °C (●) and 120 °C (▲) as a function of lithium salt concentration.
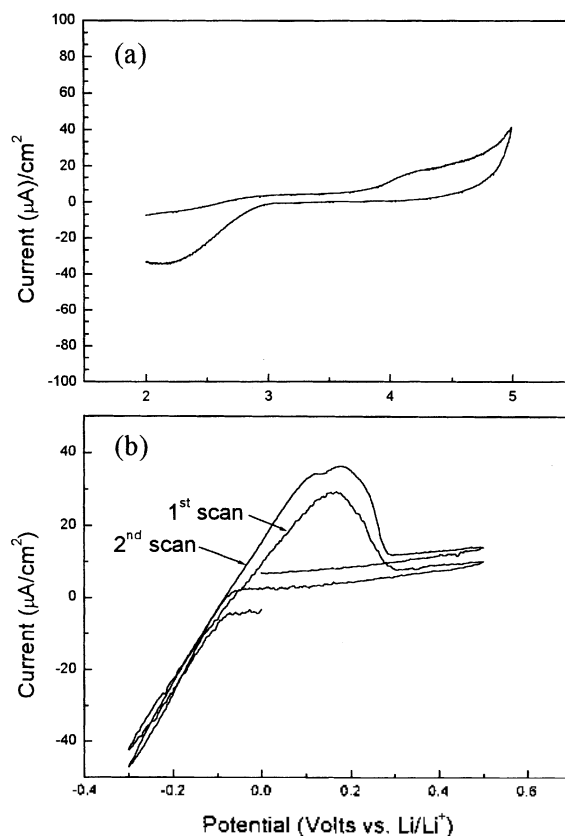

Figure 6. Cyclic voltammogram of polymer electrolyte containing 50 wt% of PEGDME at 30 °C (sweep rate = 1 mV/sec).

polymer chain causes the decrease of chain mobility which results in decrease of conductivity.[15]

Electrochemical Properties. The cyclic voltammogram of polymer electrolyte containing 50% PEGDME at 30 °C is shown in Figure 6. The irreversible anodic degradation of the polymer electrolyte started ca. 4.7 V against lithium reference electrode (Fig. 6a) and the reversible deposition/dissolution of lithium on the stainless steel electrode was observed at the potential range of -0.3 V to 0.5 V (Fig. 6b). The deposition of the lithium started ca. -0.05 V and maximum anodic peak was found to be ca. 0.15 V. Thus, the electrochemical window of the polymer electrolyte was about 4.75 V which was suitable for the lithium-polymer battery application.

In summary, a new PEGDME grafted poly(ethylene-*alt*-maleimide) has been synthesized and the polymer blend with PEGDME was examined for the polymer electrolyte. The conductivity of the resulting polymer blend complex with LiCF₃SO₃ was as high as 3×10^{-4} S/cm at 30 °C with good film forming property. The copolymer was thermally stable up to 250 °C and electrochemically stable up to 4.7V (vs. Li/Li⁺), that may be applicable to the solid lithium-polymer battery at ambient temperature.

Experimental Section

Materials. Poly(ethylene-*alt*-maleic anhydride) ($\overline{Mw}$ –

100,000, Aldrich) was used as received. Poly(ethylene glycol) monomethyl ether ($\overline{Mw}$ = 350), poly(ethylene glycol) dimethyl ether ($\overline{Mw}$ = 400, PEGDME) and LiCF₃SO₃ were purchased from Aldrich and were dried in vacuum before use.

Conductivity Measurements. The conductivity measurement was carried out using the two parallel ITO line cell. The ITO glass was etched with 0.2 N nitric acid to produce two 1-mm widths ITO lines and 1 mm gap between ITO lines. Polymer was coated to completely cover the lines with *ca* 100 μm thickness. AC complex impedance was recorded using impedance analyzer (Zahner Elektrik, model IM5d) in the frequency range of 1 Hz to 1 MHz. The temperature of the sample was controlled by using the programmable hot plate (Mettler, model FP82HT). All samples were prepared inside of the argon filled glove box.

Electrochemical Properties. The electrochemical stability of the solid polymer electrolytes was determined by means of cyclic voltammetry using EG&G model 270 potentiostat. A stainless steel plate was used as a working electrode and lithium foil was used as counter and reference electrode. The cell was assembled in the glove box and vacuum sealed using metallized polyethylene bag.

Synthesis of 3. Into a 1000 mL of three necked round bottom flask equipped with magnetic stirrer, a drying tube and a dropping funnel was placed a solution of PEGME ($\overline{Mw}$ = 350, 35 g) and triethyl amine (11.2 g) in 600 ml of dried THF. Methanesulfonyl chloride (12.60 g) was added slowly to the stirred solution over a period of 30 min at -5 °C. After the addition was over, the reaction mixture was allowed to warm up 0 °C and stirred for 2 hours. The generated triethylammonium hydrochloride salts was filtered off and the filtrate was poured into distilled water. After extraction with CH₂Cl₂, the CH₂Cl₂ layer was dried over anhydrous MgSO₄. Concentration of CH₂Cl₂ solution yielded the desired PEGME mesylate in 73% as pale yellow liquid. ¹H NMR: (CDCl₃): δ ppm 3.15 (s. CH₃SO₃; 3H), 3.45 (s. CH₃O; 3H), 3.50-3.90 (m. OCH₂CH₂O; 27H), 4.35 (t. CH₂OSO₂; 2H); ¹³C NMR (CDCl₃): δ ppm 37.55 (CH₃SO₃), 58.88 (CH₃OCH₂), 68.90 (CH₂OSO₂), 69.45 (CH₂CH₂OSO₂), 70.45 (OCH₂CH₂O), 71.81 (CH₂OCH₃).

Synthesis of 4. PEGME mesylate 3 (31.25 g) was added dropwise to the suspension of NaN₃ (7.12 g) in 400 mL of DMAC over a period of 30 min. The reaction mixture was then stirred for 16 h at 100 °C. After extraction with CH₂Cl₂ and removal of volatile, the desired azide was obtained (75%). ¹H NMR (CDCl₃) δ ppm 3.40-3.50 (m. CH₃O. CH₂N₃; 5H), 3.50-3.90 (m. OCH₂CH₂O; 27H); ¹³C NMR (CDCl₃) δ ppm 50.64 (CH₂N₃), 58.99 (CH₃OCH₂), 70.65 (CH₂CH₂O), 71.91 (CH₂CH₂N₃).

Synthesis of 5. To a solution of 4 (21.33 g) in 200 mL ethanol was added Zn dust (10.7 g) followed by dropwise addition of 16.4 mL of 10N HCl. After stirring for 7 h at 0 °C, the reaction mixture was filtered to remove the residual zinc dust. The filtrate was neutralized with NaOH and

extracted with CH₂Cl₂. The solution was concentrated under reduced pressure. The amine terminated PEGME **5** was obtained in 75% yield. ¹H NMR (CDCl₃): δ ppm 1.40 (s. CH₂NH₂; 2H), 2.90 (CH₂NH₂, t. 3H), 3.45 (s. OCH₃, 3H) 3.5-3.9 (m. OCH₂CH₂O; 27H); ¹³C NMR (CDCl₃): δ ppm 41.62 (CH₂NH₂), 58.75 (CH₃OCH₂), 70.34 (OCH₂CH₂O), 71.11 (CH₃OCH₂), 73.29 (CH₂CH₂NH₂).

Synthesis of Polymer 7. The amine **5** was added to a solution of poly(ethylene-*alt*-maleic anhydride) (2 g) in DMAC (50 mL) over 30 min. After stirring for 24 hours at 60 °C, acetic anhydride (2.65 g) and pyridine (2.06 g) were added to the reaction mixture and stirred for another 10 hr. The reaction mixture was concentrated *ca.* 5 mL using rotary evaporator and precipitated from the mixture solution of ether and methanol (9 : 1). The PEG grafted polymer was filtered and dried in vacuum oven at 80 °C for 1 day. ¹H NMR (DMSO-d₆): δ ppm 1.1-1.7 (br. CH(CO)CH(CO)-CH₂CH₂; 4H), 2.1-2.3 (br. CH(CO)CH(CO)CH₂CH₂; 2H), 3.24 (s. OCH₃; 3H), 3.4-3.8 (m. OCH₂CH₂O; 29H).

References

1. Armand, M. B. In *Polymer Electrolytes Reviews*. McCallum, J. R., Vincent, C., Eds.: Elsevier Applied Science: London. 1987; Vol. 1, p 1.
2. Gray, F. M. *Ploymer Electrolytes*: The Royal Society of Chemistry: Cambridge, 1997.
3. Blonsky, P. M.; Shiriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
4. Allcock, H. R.; Ravikiran, R.; O'Connor S. J. M. *Macromolecules* **1997**, *30*, 3184.
5. Fish, D.; Khan, I. M.; Wu, E.; Smid. J. *Br. Polym. J.* **1988**, *20*, 281.
6. Tsutsumi, H.; Yamamoto, M.; Morita, M.; Matsuda, Y.; Nakamura. T.; Asai, H. *Electrochim. Acta* **1990**, *191*, 2195.
7. Tada, H.; Kawahara, H. *J. Electrochem. Soc.* **1988**, *135*, 1728.
8. Kim, H.; Kim, E.; Rhee, S. B. *Kor. Polymer. J.* **1996**, *4*, 83.
9. Ding, L. *Polymer* **1997**, *16*, 4267.
10. Ding, L.; Shi, J.; Yang, C.; Dong, S. *Polymer J.* **1997**, *29*, 410.
11. Qi, L.; Lin, Y.; Wang, F. *Solid State Ionics* **1998**, *109*, 145.
12. Florjanczyk, Z.; Bzducha, W.; Wieczorek, W.; Zygadlo-Monikowska, E.; Krawiec, W.; Chung, S. H. *J. Phys. Chem. B* **1998**, *102*, 8409.
13. Xu, W.; Siow, S.; Gao, Z.; Lww, S. Y. *Chem. Mater.* **1998**, *10*, 1951.
14. Abraham. K. M.; Jiang. Z.; Carroll. B. *Chem. Mater.* **1997**, *9*, 1978.
15. Angell. C. A. *Solid State Ionics* **1983**, *9-10*, 3.