



## Ionic Conductivity of Anion Receptor Grafted Siloxane Polymers for Solid Polymer Electrolytes

Won Sil Lee<sup>a,b</sup>, Dong Wook Kim<sup>a</sup>, Changin Lee<sup>a</sup>, Seong Ihl Woo<sup>b</sup> and Yongku Kang<sup>a,†</sup>

<sup>a</sup>Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107 Yuseong, Daejeon 305-600, Korea

<sup>b</sup>Department of Chemical and Biomolecular Engineering & WCU Energy Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

### ABSTRACT:

We have prepared siloxane polymers grafted with trifluoromethane-sulfonylamide and oligoether side chains for solid polymer electrolytes with enhanced ionic conductivity. The grafted trifluoromethane sulfonylamide groups seem to be effective as an anion receiving site to enhance the ionic conductivity of the solid polymer electrolyte. The anion receptor grafted siloxane polymers showed one order of magnitude higher ionic conductivity than the siloxane polymers without anion receptor grafts. The fitting parameter A of the VTF plot which was related to the carrier density of the electrolyte increased with increasing the number of grafted anion receptor. The results of experiment indicate that the anion-complexing site of the anion receptor grafted polymer host effectively traps the anions. The anion receptor grafted polymer was found to be a promising material for lithium polymer batteries.

**Keywords** : Lithium ion polymer battery, Anion receptor, Solid polymer electrolyte, Ionic conductivity

Received December 24, 2010 : Accepted January 30, 2011

### 1. Introduction

Recent advances in the rechargeable lithium battery technology have widened the application of batteries for large capacity such as electric vehicle (EV) and energy storage.<sup>1)</sup> Safety and durability of the rechargeable lithium battery are key issues for commercialization of the large capacity battery. Solid electrolytes which contain no volatile organic solvents are promising to enhance the safety and durability. Solid polymer electrolytes and inorganic ceramic solid electrolytes are currently being studied for the solid electrolyte of lithium rechargeable batteries. Flexibility and processibility of the solid polymer electrolytes are advantages over the inorganic ceramic electrolytes.<sup>2)</sup>

Since poly (ethylene oxide) (PEO) containing alkali metal

salt was reported as a solid polymer electrolyte,<sup>3)</sup> there have been numerous studies to realize the all-solid lithium battery using PEO-based solid polymer electrolytes. However, the low ionic conductivity of the solid polymer electrolyte at ambient temperature is one of major barriers to apply on the all-solid battery operating at room temperature. There have been several efforts to enhance the ionic conductivity of the solid polymer electrolyte.<sup>2)</sup> The main reasons of low ionic conductivity of PEO-based solid polymer electrolyte are high crystallinity at ambient temperature and low dissociation of lithium salt. To decrease the crystallinity, a lot of studies have been devoted on blending,<sup>4)</sup> copolymerization,<sup>5)</sup> comb-branched polymerization,<sup>6)</sup> and cross-linked networking polymerization.<sup>7)</sup> To increase the dissociation of lithium salt in solid polymer electrolyte, anion receptors with electron deficient groups have been applied.<sup>8)</sup> Trifluoromethanesulfonyl group substituted linear or cyclic aza-ether compounds was reported to be very effective to increase the ionic conductivity.

<sup>†</sup>Corresponding author. Tel.: +82-42-860-7207

E-mail address: ykang@kriect.re.kr

ity.<sup>9,10</sup> However, low solubility and poor electrochemical stability of aza-ether compound were major drawbacks. Recently, we have reported an anion receptor based on cyclic siloxane attached with trifluoromethane-sulfonylamide at the peripherals, and the prepared anion receptor effectively enhanced the ionic conductivity without sacrificing the electrochemical stability window.<sup>11</sup>

In this work, we have designed a siloxane polymer grafted with trifluoromethane-sulfonylamide as an anion receiving site in order to avoid a possible phase separation of the oligomeric anion receptors and hence improve the solubility of the anion receptors in the electrolyte as well as to enhance ionic conductivity. The anion receptor grafted siloxane polymers have acrylates in the terminal to lead to a crosslinked solid polymer electrolyte by photo-curing. We have synthesized several siloxane polymers with a different content of anion receiving grafts and then evaluated their ionic conductivity.

## 2. Experimental

### 2.1. Materials

Poly(ethyleneglycol)dimethylether (PEGDME, average  $M_n = 250$ ), 2,4,6,8-tetramethylcyclotetrasiloxane ( $D_4H$ ), Pt(0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane complex, trifluoromethanesulfonic anhydride, 2,2'-dimethoxy-2-phenylacetophenone (DMPA, a photo initiator), and  $LiCF_3SO_3$  were purchased from Aldrich Chem. Co. Anion receptor based on cyclic siloxane ( $D_4$ -4(di-TFSA)) was prepared according to our previous work.<sup>11</sup> Triethyleneglycol monomethylether attached cyclic siloxanes ( $D_4$ -4TEGME) and acrylate-terminated disiloxane oligomer (Da) were prepared by the method of our previous work.<sup>12</sup>

### 2.2. Synthesis of the anion receptor grafted polymer

We synthesized the anion receptor grafted siloxane polymers (Da-x-10) as shown in Scheme 1. The detailed synthetic procedure is as follows.

**Da-1-10.** -In the reaction tube containing 1.39 g of  $D_4$ -4TEGME, 0.2 g of  $D_4$ -4(di-TFSA), and 0.19 g of Da, 0.04 ml of trifluoromethanesulfonic acid in 0.6 ml of anhydrous chloroform solution was added dropwise and then the mixture was stirred for 24 h at 60°C. Distilled water was added into the mixture and stirred for 1 h. The reaction mixture was poured into chloroform (~50 ml) and neutralized with 5 wt.% of sodium carbonate aqueous solution. The crude product was purified by column chromatography using ethyl acetate/n-hexane (1/1) as

an eluent to obtain *Da-1-10* (yield: 43%).

<sup>1</sup>H NMR (300 MHz,  $CDCl_3$ , ppm)  $\delta$  0.00~0.23 (s, 69H, -O-Si-**CH<sub>3</sub>**), 0.40-0.45 (m, 33H, -O-Si-**CH<sub>2</sub>**-CH<sub>2</sub>-CH<sub>2</sub>-), 1.52 (m, 33H, -O-Si-CH<sub>2</sub>-**CH<sub>2</sub>**-CH<sub>2</sub>-), 3.31-3.60 (m, 237H, -O-Si-CH<sub>2</sub>-CH<sub>2</sub>-**CH<sub>2</sub>**-), -(O**CH<sub>2</sub>CH<sub>2</sub>**)<sub>3</sub>OCH<sub>3</sub>, and -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>O**CH<sub>3</sub>**), 5.74-5.77 (m, 2H, -O-CO-CH = **CH<sub>2</sub>**), 6.01-6.10 (m, 2H, -O-CO-**CH** = CH<sub>2</sub>), 6.31~6.37 (m, 2H, -O-CO-CH = **CH<sub>2</sub>**); <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ , ppm)  $\delta$  0.00 (-O-Si-**CH<sub>3</sub>**), 13.38 (-O-Si-**CH<sub>2</sub>**-CH<sub>2</sub>-CH<sub>2</sub>-), 22.94 (-O-Si-CH<sub>2</sub>-**CH<sub>2</sub>**-CH<sub>2</sub>-), 58.94 (-O-Si-CH<sub>2</sub>-CH<sub>2</sub>-**CH<sub>2</sub>**-), 69.90-70.49 (-(**OCH<sub>2</sub>CH<sub>2</sub>**)<sub>3</sub>-O-CH<sub>3</sub>, and -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>-O-**CH<sub>3</sub>**), 115.01 (-O-CO-CH = **CH<sub>2</sub>**), 117.63 (-O-CO-**CH** = CH<sub>2</sub>), 120.08-130.40 (-N-SO<sub>2</sub>-**CF<sub>3</sub>**).

**Da-2-10.** -1.39 g of  $D_4$ -4TEGME, 0.4 g of  $D_4$ -4(di-TFSA), and 0.19 g of DA were reacted under the same procedure as Da-1-10 to obtain Da-2-10 (yield: 47%).

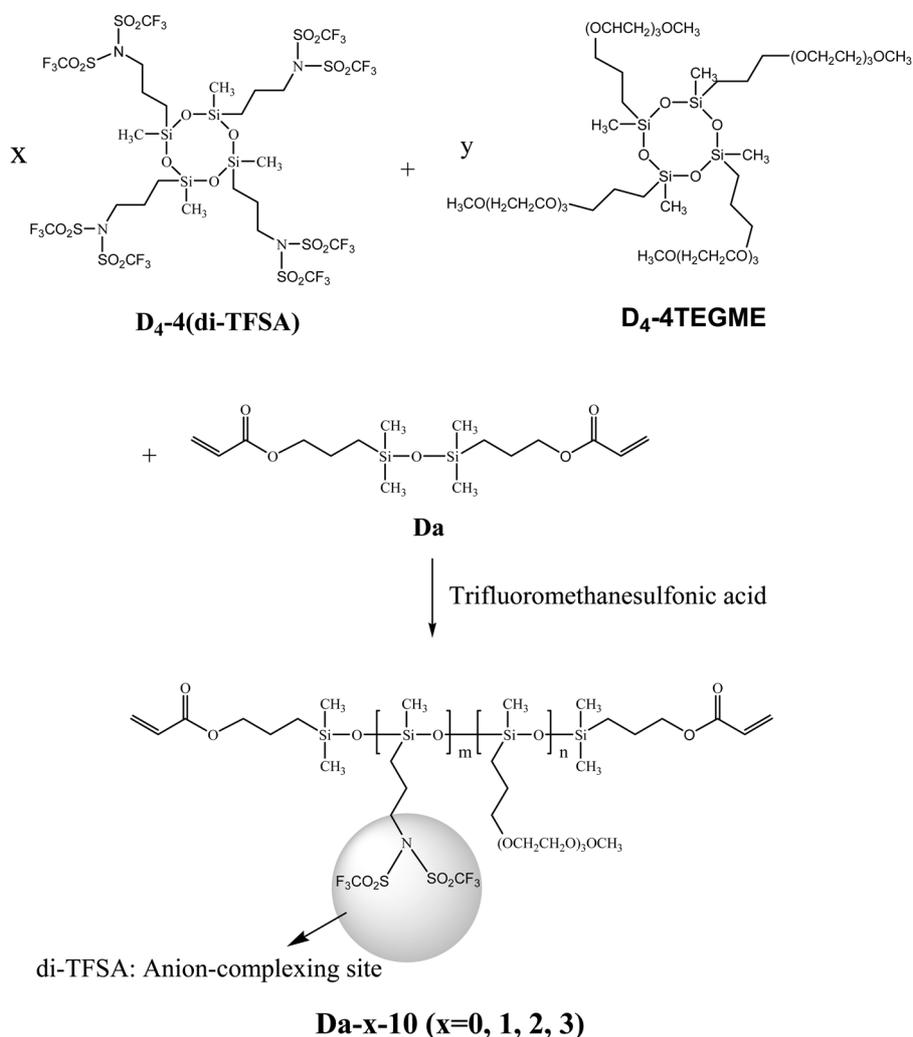
<sup>1</sup>H NMR (300 MHz,  $CDCl_3$ , ppm)  $\delta$  0.00~0.02 (s, 76H, -O-Si-**CH<sub>3</sub>**), 0.40-0.45 (m, 37H, -O-Si-**CH<sub>2</sub>**-CH<sub>2</sub>-CH<sub>2</sub>-), 1.53 (m, 34H, -O-Si-CH<sub>2</sub>-**CH<sub>2</sub>**-CH<sub>2</sub>-), 3.32-3.60 (m, 243H, -O-Si-CH<sub>2</sub>-CH<sub>2</sub>-**CH<sub>2</sub>**-), -(O**CH<sub>2</sub>CH<sub>2</sub>**)<sub>3</sub>OCH<sub>3</sub>, and -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>O**CH<sub>3</sub>**), 5.78 (m, 2H, -O-CO-CH = **CH<sub>2</sub>**), 6.06-6.14 (m, 2H, -O-CO-**CH** = CH<sub>2</sub>), 6.31 (m, 2H, -O-CO-CH = **CH<sub>2</sub>**); <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ , ppm)  $\delta$  0.00 (-O-Si-**CH<sub>3</sub>**), 13.66 (-O-Si-**CH<sub>2</sub>**-CH<sub>2</sub>-CH<sub>2</sub>-), 22.87 (-O-Si-CH<sub>2</sub>-**CH<sub>2</sub>**-CH<sub>2</sub>-), 58.86 (-O-Si-CH<sub>2</sub>-CH<sub>2</sub>-**CH<sub>2</sub>**-), 69.81-70.38 (-(**OCH<sub>2</sub>CH<sub>2</sub>**)<sub>3</sub>-O-CH<sub>3</sub>, and -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>-O-**CH<sub>3</sub>**), 114.86 (-O-CO-CH = **CH<sub>2</sub>**), 117.46 (-O-CO-**CH** = CH<sub>2</sub>), 120.04-130.36 (-N-SO<sub>2</sub>-**CF<sub>3</sub>**).

**Da-3-10.** -1.39 g of  $D_4$ -4TEGME, 0.6 g of  $D_4$ -4(di-TFSA), and 0.19 g of DA were reacted under the same procedure as Da-1-10 to obtain Da-3-10 (yield: 39%).

<sup>1</sup>H NMR (300 MHz,  $CDCl_3$ , ppm)  $\delta$  0.00~0.02 (s, 78H, -O-Si-**CH<sub>3</sub>**), 0.41-0.42 (m, 38H, -O-Si-**CH<sub>2</sub>**-CH<sub>2</sub>-CH<sub>2</sub>-), 1.52 (m, 31H, -O-Si-CH<sub>2</sub>-**CH<sub>2</sub>**-CH<sub>2</sub>-), 3.31-3.60 (m, 228H, -O-Si-CH<sub>2</sub>-CH<sub>2</sub>-**CH<sub>2</sub>**-), -(O**CH<sub>2</sub>CH<sub>2</sub>**)<sub>3</sub>OCH<sub>3</sub>, and -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>O**CH<sub>3</sub>**), 5.77 (m, 2H, -O-CO-CH = **CH<sub>2</sub>**), 6.04-6.10 (m, 2H, -O-CO-**CH** = CH<sub>2</sub>), 6.31-6.36 (m, 2H, -O-CO-CH = **CH<sub>2</sub>**); <sup>13</sup>C NMR (75 MHz,  $CDCl_3$ , ppm)  $\delta$  0.00 (-O-Si-**CH<sub>3</sub>**), 13.77 (-O-Si-**CH<sub>2</sub>**-CH<sub>2</sub>-CH<sub>2</sub>-), 22.85 (-O-Si-CH<sub>2</sub>-**CH<sub>2</sub>**-CH<sub>2</sub>-), 58.86 (-O-Si-CH<sub>2</sub>-CH<sub>2</sub>-**CH<sub>2</sub>**-), 68.97-70.40 (-(**OCH<sub>2</sub>CH<sub>2</sub>**)<sub>3</sub>-O-CH<sub>3</sub>, and -(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>-O-**CH<sub>3</sub>**), 114.90 (-O-CO-CH = **CH<sub>2</sub>**), 117.48 (-O-CO-**CH** = CH<sub>2</sub>), 120.07-130.34 (-N-SO<sub>2</sub>-**CF<sub>3</sub>**).

### 2.3. Preparation of polymer electrolyte

Precursor for the polymer electrolytes was made of the anion receptor grafted siloxane polymers (Da-x-10), a plasticizer (PEGDME), a photo initiator (DMPA), and lithium salts according to the method described previously.<sup>12</sup>



**Scheme 1.** Synthetic scheme of the anion receptor grafted siloxane polymers (Da-x-10).

The [EO]/[Li<sup>+</sup>] ratio was fixed at 20. The ratio [di-TFSA]/[Li<sup>+</sup>] was varied from 0 to 1.46 according to the content of anion receptor grafts in the siloxane polymers, where [di-TFSA] stands for a molar concentration of the anion-complexing site (di-TFSA) as shown in Scheme 1. Solid polymer electrolytes were prepared by crosslinking the precursors by UV-irradiation using a 350 nm light source for 10~30 min under the argon atmosphere.<sup>12</sup> There were seen no phase separation in the solid polymer electrolytes to result in a good self-supportive film by curing. The glass transition temperatures ( $T_g$ ) of the cured solid polymer electrolyte were measured by DSC and the values were about  $-65^\circ\text{C}$ .

#### 2.4. Ionic conductivity measurement

The conductivity measurement was carried out by coating the polymer electrolytes onto the pre-patterned ITO cell.<sup>13</sup> The thickness of the polymer layer was about 100  $\mu\text{m}$ . The ac impedance was recorded using an impedance analyzer (Zahner Elektrik, model IM6) in the frequency range of 1 Hz to 1 MHz. The temperature of the sample was controlled by means of the programmable hot plate (Mettler, model FP82HT).

#### 2.5. Instrumentation

The characterization of the synthesized compounds was examined by means of NMR and FT-IR spectroscopy

using Bruker 300 Hz spectrometer and JASCO FT-IR-610, respectively.  $T_g$  of the cured polymer electrolyte was measured by means of differential scanning calorimeter using TA Instruments universal V2.5H. The absence of low molecular impurities was confirmed by means of GPC using Younglin Instrument CTS-30.

### 3. Results and Discussion

D<sub>4</sub>-4(di-TFSA), which has trifluoromethane-sulfonylamide as an anion complexing site was recognized as an efficient anion receptor to improve the ionic conductivity in the previous our work.<sup>11)</sup> Since the anion receptor is an oligomer, there is a possible phase separation problem in the electrolyte when it is highly loaded. In this study as a continuous work, we have incorporated the anion complexing site as a graft in the polymers in order to enhance ionic conductivity as well as to avoid a possible phase separation and hence increase the solubility of the anion receptor in the electrolytes.

The cyclic siloxane anion receptors (D<sub>4</sub>-4(di-TFSA)) was reacted with the acrylate-terminated siloxane oligomer (Da) under fuming sulfuric acid or trifluoromethanesulfonic acid (Scheme 1). In our study, trifluoromethanesulfonic acid was found to be more effective for the ring opening-polymerization reaction. Cyclic siloxane with triethyleneglycolmethyl ether (D4-4TEGME) was also reacted together to introduce poly(ethylene oxide) side chains in the polymers. The feeding ratio of D<sub>4</sub>-4(di-TFSA) was varied to investigate effect of the content of the anion receiving grafts as summarized in Table 1.

The <sup>1</sup>H NMR and GPC were used to verify the synthesized siloxane polymers (Da-x-10). For example, <sup>1</sup>H NMR

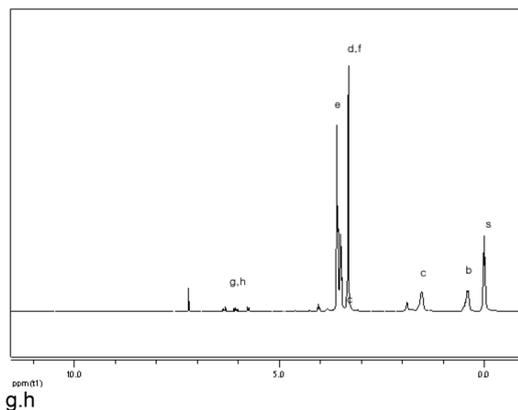
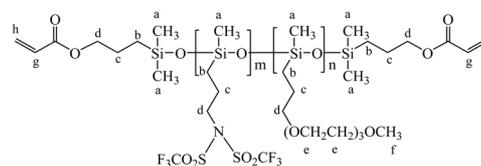


Fig. 1. <sup>1</sup>H NMR spectrum of the Da-1-10.

spectrum of Da-1-10 is shown in Fig. 1. The peak b at 0.40~0.45 ppm is due to the protons attached at the first carbons which were connected to silicon atom. And the peak e is from the protons at the carbons of the ethylene oxide side chain. The number of the repeating units of TEGME graft (n) was calculated from the integral of the peak e. And the number of the repeating units of di-TFSA graft (m) was estimated from the integral of the peaks b and e. The result of the end group analysis from <sup>1</sup>H NMR is summarized in Table 1. The average molecular weight of the siloxane polymers was also confirmed by GPC (for example, the average molecular weight of Da-1-10 was measured 4,200 by GPC and 4,300 by end group analysis in <sup>1</sup>H NMR).

We have prepared precursor solutions with the siloxane polymers (Da-x-10), lithium salts, photo-initiator, and a plasticizer. After injecting the precursor into the cell and crosslinking it by photo-irradiation, transparent polymer electrolyte films were obtained.

Fig. 2 shows ionic conductivities of the solid polymer electrolytes with and without anion receptor grafts in the siloxane polymers. The siloxane polymers containing trifluoromethane-sulfonylamide as an anion complexing sites exhibited about one order magnitude higher ionic conductivity than the polymers without anion receptors even at the low content of anion receptor. For example, Da-1-10 ([di-TFSA]/[LiCF<sub>3</sub>SO<sub>3</sub>] = 0.31) showed  $9.21 \times 10^{-5}$  S/cm at 30°C which was 4 times higher ionic conductivity

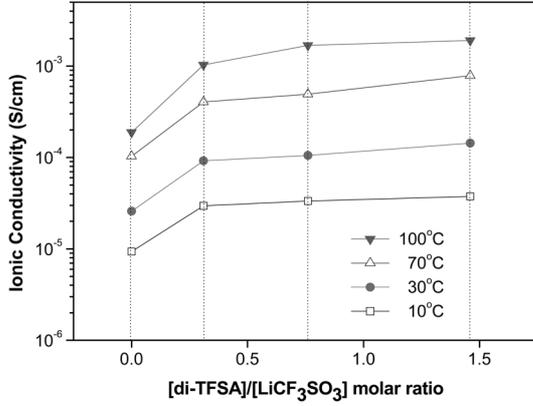
**Table 1.** Feed ratio, average number of repeating units of grafted chain, and average molecular weight of the anion receptor grafted siloxane polymers synthesized in this study

Sample code	Feed Mole ratio (x:y:z) <sup>a</sup>	Result of polymerization		
		Average number of repeating units of grafted chain <sup>b</sup>		Average molecular weight <sup>c</sup>
		m	n	
Da-0-10	0 : 10 : 4	0	14.5	4,200
Da-1-10	1 : 10 : 4	1.0	13.6	4,300
Da-2-10	2 : 10 : 4	2.1	14.2	4,900
Da-3-10	3 : 10 : 4	3.7	13.2	5,300

<sup>a</sup>x = [D<sub>4</sub>-4(di-TFSA)]; y = [D<sub>4</sub>-4TEGME]; z = [Da].

<sup>b</sup>Number of grafted chain repeating unit was estimated by end group analysis in <sup>1</sup>H NMR spectrum.

<sup>c</sup>Number average molecular weight ( $M_n$ ) was measured by GPC.

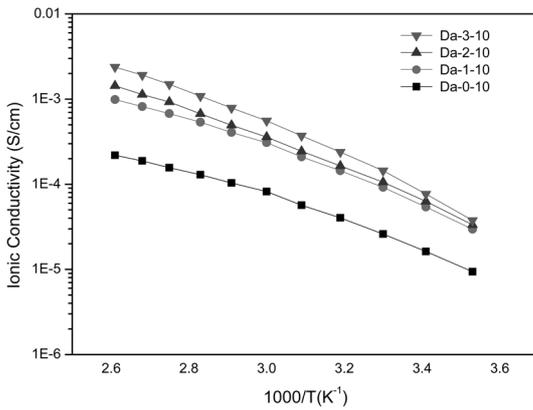


**Fig. 2.** Isothermal ionic conductivities of the polymer electrolytes at different  $[\text{di-TFSA}]/[\text{Li}^+]$  molar ratio. Host polymer, Da-x-10; Plasticizer, PEGDME 10 wt.%; Lithium salt,  $\text{LiCF}_3\text{SO}_3$ ;  $[\text{EO}]/[\text{Li}^+] = 20$ .

than Da-0-10 ( $[\text{di-TFSA}]/[\text{LiCF}_3\text{SO}_3] = 0$ ). This result indicates that anion receptor effectively traps the anions of the lithium salt and hence enhances the ionic conductivity of the electrolytes. The ionic conductivity changed little as  $[\text{di-TFSA}]/[\text{LiCF}_3\text{SO}_3]$  molar ratio was varied from 0.3 to 1.5.

The temperature dependence of the ionic conductivity with various anion receptor concentrations are shown in Fig. 3. The curves show a typical Vogel-Tammann-Fülcher (VTF) relationship (equation 1) in the temperature from 10 to 100°C.

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

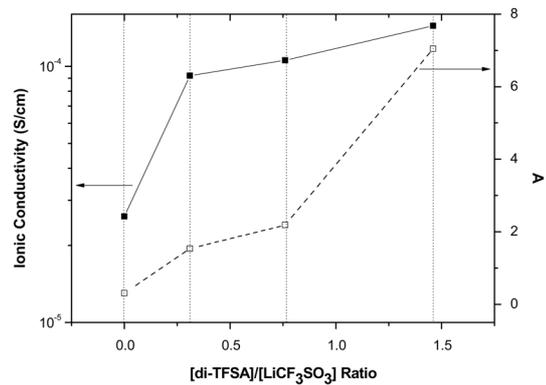


**Fig. 3.** Temperature dependence of an ionic conductivity at a different number of the repeating unit of the (di-TFSA) chain (m). PEGDME was added as a plasticizer (10 wt.%).  $\text{LiCF}_3\text{SO}_3$  was chosen as a lithium salt. The  $[\text{EO}]/[\text{Li}^+] = 20$ .

where  $A$ ,  $E_a$ ,  $R$  and  $T_0$  are fitted parameters which are related to the carrier density, pseudo activation energy, gas constant and zero configuration entropy of the polymer chain, respectively.<sup>14)</sup>

The ionic conductivity of the polymer electrolyte containing anion receptor grafted polymer showed above  $1 \times 10^{-4}$  S/cm at 30°C which is about one order of magnitude higher than that of reference polymer. All of the other reports about the polymer electrolyte which was incorporated with anion receptor showed that the ionic conductivity was below  $1 \times 10^{-4}$  S/cm at 30°C.<sup>8,10,15)</sup>

We estimated the pre-exponential factor ( $A$ ) of the VTF relationship which is proportional to the number of charge carrier density. The ionic conductivity and the pre-exponential factor ( $A$ ) of the VTF plot as a function of molar ratio of the anion receptors are shown in Fig. 4. The estimated pre-exponential factor  $A$  has increased with the  $[\text{di-TFSA}]/[\text{LiCF}_3\text{SO}_3]$  molar ratio being higher. Such increase may be explained by that the grafted anion receptor help the lithium salts dissociate. However, the activation energy ( $E_a$ ) became higher with the  $[\text{di-TFSA}]/[\text{LiCF}_3\text{SO}_3]$  molar ratio. We assumed that the increase of activation energy may be attributed to the decrease of the local segmental motion of polymer electrolyte by increase in complexing points between the polymer and the anion. Such increase in the activation energy with the  $[\text{di-TFSA}]/[\text{LiCF}_3\text{SO}_3]$  molar ratio may compensate the higher carriers density. This explain why the ionic conductivity increased at the low content of the anion receptor, but changed little when the  $[\text{di-TFSA}]/[\text{LiCF}_3\text{SO}_3]$  molar ratio was higher than 0.3.



**Fig. 4.** The change of the ionic conductivity (at 30 °C) and the  $A$  (pre-exponential factor which is proportional to the number of charge carriers) at a various molar ratio of  $[\text{di-TFSA}]/[\text{LiCF}_3\text{SO}_3]$ . Host polymer, Da-5; Plasticizer, PEGDME 10 wt.%; Lithium salt,  $\text{LiCF}_3\text{SO}_3$ ;  $[\text{EO}]/[\text{Li}^+] = 20$ .

#### 4. Conclusion

In summary, we have synthesized a siloxane polymer grafted with trifluoromethane-sulfonylamide as an anion receiving site in order to avoid a possible phase separation of the oligomeric anion receptors and hence improve the solubility of the anion receptors in the electrolyte as well as to enhance ionic conductivity. <sup>1</sup>H NMR and GPC confirmed the successful synthesis and purity of the siloxane polymer. The ionic conductivity of the polymer electrolyte containing anion receptor grafted polymer showed above  $1 \times 10^{-4}$  S/cm at 30°C which is about one order of magnitude higher than that of reference polymer without anion receptors. The ionic conductivity changed little as [di-TFSA]/[LiCF<sub>3</sub>SO<sub>3</sub>] molar ratio was varied from 0.3 to 1.5. The experimental results indicate that the anion receptor grafted polymer is a promising material to enhance the ionic conductivity for lithium polymer batteries.

#### Acknowledgements

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

#### References

1. E.J. Cairns and P. Albertus, *Annu. Rev. Chem. Biomol. Eng.*, **1**, 299 (2010).
2. J.W. Fergus, *J. Power Sources*, **195**, 4554 (2010).
3. P.V. Wright, *Br. Polym. J.*, **7**, 319 (1975); M.B. Armand, J.M. Chabagno, M.J. Duclot, *J. Fast Ion Transport in Solid*, p 131 Elsevier New York 1979.
4. H. Zhang, S. Kulkarni and S.L. Wunder, *J. Phys. Chem.*, **111**, 3583 (2007).
5. A. Ghosh and P. Kofinas, *J. Electrochem. Soc.*, **155**, A428 (2008); T. Niitani, M. Amaike, H. Nakano, K. Dokko, and K. Kanamura, *J. Electrochem. Soc.*, **156**, A577 (2009).
6. H.R. Allcock, S.E. Kuharick, C.S. Reed and M.E. Napierala, *Macromolecules*, **29**, 3384 (1996); H.R. Allcock, R. Ravikiran, S.J.M. O'Connor, *Macromolecules*, **30**, 3184 (1997); D. Fish, I.M. Khan, E. Wu and J. Smid, *Br. Polym. J.*, **20**, 281 (1988).
7. A. Nishimoto, K. Agehara, N. Furuya, T. Watanabe and M. Watanabe, *Macromolecules*, **32**, 1541 (1999); Z. Zhang, L.J. Lyons, K. Amine and R. West, *Macromolecules*, **38**, 5714 (2005); I. Y. Kang, W. Lee, D.H. Suh and C. Lee, *J. Power Sources*, **119-121**, 448 (2003); Y. Kang, J. Lee, J.-I. Lee and C. Lee, *J. Power Sources*, **165**, 92 (2007).
8. B. Xie, H.S. Lee, H. Li, X.Q. Yang, J. McBreen and L.Q. Chen, *Electrochem. Comm.*, **10**, 1195 (2008); L.F. Li, H.S. Lee, H. Li, X.Q. Yang, K.W. Nam, W.S. Yoon, J. McBreen and X.J. Huang, *J. Power Sources*, **184**, 517 (2008); H.S. Lee, Z.F. Ma, X.Q. Yang, X. Sun and J. McBreen, *J. Electrochem. Soc.*, **151**, A1429 (2004).
9. H.S. Lee, X.Q. Yang and J. McBreen, *J. Electrochem. Soc.*, **143**, 3825 (1996).
10. H.S. Lee, X.Q. Yang, C. Xiang, J. McBreen, J.H. Callahan, and L.S. Choi, *J. Electrochem. Soc.*, **146(3)**, 941 (1999).
11. W.S. Lee, S.I. Woo, D.W. Kim, C. Lee and Y. Kang, *Macromol. Res.*, **18**, 266 (2010).
12. Y. Kang, W. Lee, D.H. Suh and C. Lee, *J. Power Sources*, **119-121**, 448 (2003).
13. Y. Kang, H.J. Kim, E. Kim, B. Oh and J.H. Cho, *J. Power Sources*, **92**, 255 (2001); H.J. Kim, E. Kim, S.B. Rhee, *Korea Polym. J.*, **4**, 83 (1996); Y. Kang, H.J. Kim, E. Kim, B. Oh, J.H. Cho, *Proc. Electrochem. Soc.*, **25-99**, 534 (1999).
14. F.M. Gray, *Polymer Electrolytes*, The Royal Society of Chemistry, Cambridge, 1997.
15. S. Tabata, T. Hirakimoto, H. Tokuda, Md. A.A.H. Susan and M. Watanabe, *J. Phys. Chem. B*, **108**, 19518 (2004).