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Lithium Ion Concentration Dependant Ionic Conductivity and Thermal Properties in Solid Poly(PEGMA-co-acrylonitrile) Electrolytes

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ABSTRACT :

The lithium ion concentration dependant ionic conductivity and thermal properties of poly(ethylene glycol) methyl ether methacrylate (PEGMA)/acrylonitrile-based copolymer electrolytes with $LiClO_4$ have been studied by differential scanning calorimetry (DSC), linear sweep voltammetry (LSV) and AC complex impedance measurements. In systems with 11 wt% of acrylonitrile all liquid electrolytes were obtained regardless of lithium ion concentration. Complex impedance measurements with stainless steel electrodes give ambient ionic conductivities $8.1 \times 10^{-6} \sim 1.4 \times 10^{-4}$ S cm^{-1}. On the other hand, a hard and soft films at ambient temperature were obtained in copolymer electrolyte system consists of 15 wt% acrylonitrile with 6 : 1 and 3 : 1 of [EO] : [Li] ratio, respectively. DSC measurements indicate the crystalline melting temperature of poly(PEGMA) disappeared completely after addition of $LiClO_4$ in this system due to the complex formation between ethylene oxide (EO) unit and lithium salt. As a result, free standing film with room temperature ionic conductivity of 1.7×10^{-4} S cm^{-1} and high electrochemical stability up to 5.5 V was obtained by controlling of acrylonitrile and lithium salt concentration.

Keywords : Polymer electrolyte, Copolymer, Free standing film, Ionic conductivity, Crystalline melting.

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1. Introduction

All solid polymer electrolytes (SPE) systems with high ionic conductivity and good mechanical properties is one of the most studied objectives in lithium secondary batteries due to their potential advantages based on flexibility, enhanced safety and thin film formability.[1-4] Since P. Wright introduced the alkali metal solvated polymer electrolyte in 1975,[5] SPEs are generally derived from poly(ethylene oxide) (PEO) derivatives although there are various alternatives for instance poly(propylene oxide) (PPO), poly (acrylonitrile), poly(vinylidene fluoride) and so on.[6-9] In fact, PEO is a relative inexpensive and available in an industrial scale with various structures. However, the ionic conductivity of PEO has reported as ~10^{-8} S cm^{-1} at room temperature

because of its high crystalline phase arise from regular packing of ethylene oxide (EO) unit along the polymer chain.[1] The presence of large crystalline domain also effects on a mechanical properties to reduce a chain entanglement between polymers. Therefore, a strategy is necessary to improve the low ionic conductivity and bad mechanical properties and actually numerous researches have been reported on this subject until now.[1] One of the most studied routes is incorporation of a second component to the PEO matrix to form a copolymer structures. Among the different second component described in the literature, acrylonitrile-based polymer electrolytes has many advantages, such as high ionic conductivity and good interfacial stability toward an electrode and relative good mechanical properties at room temperature.[10] However the researches of polyacrylonitrile-based electrolytes have been studied mainly on the gel system which containing liquid electrolytes and little has been reported about the all SPE system with reasonable

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mechanical properties because of its low solubility in organic solvents and a brittle bulk properties.[11-14] Undoubtedly, there are several reports about the polyacrylonitrile-based solid-type electrolytes in the literature but the results are insufficient to satisfy the demand for lithium secondary batteries with a viewpoint of ionic conductivity and all solid state.[15-16] For example, Yang et al. reported polymer electrolytes consisting of all solid polyacrylonitrile and LiClO4 but the ionic conductivity is ranged 6.5×10^{-7} S cm^{-1} at room temperature.[15] On the other hand, Chen-Yang et al. have made systematic studies on alumina containing polyacrylonitrile-based composite SPE and reported as high as 5.7×10^{-4} S cm^{-1} of ionic conductivity can be obtained at room temperature but 10 wt% of N,N-dimethyl formamide (DMF) was also incorporated into the matrix.[16]

In this paper we demonstrated preparation of poly (ethylene glycol) methyl ether methacrylate (PEGMA) and acrylonitrile-based all solid free standing polymer films by controlling the composition and lithium salt concentration. For this purpose a series of PEGMA-acrylonitrile copolymer with different composition ratio has been prepared by a solution polymerization in toluene at 65°C. The thermal properties and the temperature dependence of the ionic conductivity are discussed in detail with respect to the composition of acrylonitrile and incorporated lithium salt. Also the effect of lithium salt on the crystalline melting transition of poly(PEGMA) is investigated by differential scanning calorimetry (DSC) for explaining the enhanced ionic conductivity and physical properties.

2. Experimental

2.1. Materials

PEGMA (M_n : 1100 g mol^{-1}), acrylonitrile (98%), lithium perchlorate (LiClO4, battery grade), benzoyl peroxide (BPO, 97%), toluene (anhydride), acetonitrile (anhydride) were obtained from Sigma Aldrich Chemical Co. and used as received. Lithium metal (battery grade) was purchased from Hosen Co. and stored in an argon filled glove-box. Ethylene carbonate/diethyl carbonate (EC/DEC, 3 : 7, V/V) with lithium bis(trifluoro methanesulfonyl)imide (LiTFSI, 1 M) was supplied from Panax Etec Co. and used as received. For a usual polymer work-up, acetone and ethanol (reagent grade, Samjeon Chemical) were used without further purification.

2.2. Polymerization and preparation of polymer electrolytes

Poly(PEGMA-co-acrylonitrile) was prepared as follows.

About 16.5 g PEGMA, 10 g acrylonitrile and 50 ml toluene were placed in a glass reactor and purged with nitrogen for 30 min. The degassed reactor was then heated to 65°C and 0.1 g BPO was added at once and allowed to stir for 24 hours. The viscous solution was poured into hexane to precipitate the polymers. After 1 hour of storage in fume hood the obtained polymer was dissolved in THF and precipitated in hexane twice to remove un-reacted monomers and oligomers. The resulting polymer was filtered and dried in a vacuum oven at 40°C for 72 hours to give 19.4 g (73% yields). For the preparation of polymer electrolytes a calculated amount of LiClO4 was added into acetonitrile/THF solution of poly(PEGMA-co-acrylonitrile) at 25°C and mixed vigorously to dissolve all the reagent in an argon filled glove-box. After 2 hours of mixing the transparent solution was dried in a vacuum oven at 80°C for 72 hours.

2.3. Characterization

The composition of obtained copolymer was calculated by 1H-NMR spectra recorded on a BRUKER 300 MHz in CDCl3. To measure a molecular weight of polymer samples gel permeation chromatography (GPC, JASCO LC2000) was performed using THF as a carrier solvent with refractive index detection at 40°C. The polystyrene standard samples were used to calibrate the molecular weight and molecular weight distribution. The thermal properties are characterized by DSC (TA Instruments, Q10) over the temperature range of −30~140°C at a heating rate of 20°C min^{-1} under dry nitrogen atmosphere. The ionic conductivity of SPE was carried out by AC impedance measurements using a Solartron 1477 frequency response analyzer over a frequency range of 1 Hz to 10^6 Hz at 10 mV amplitude. Polymer electrolytes thin film was sandwiched between two stainless steel blocking electrodes and assembled into a designed symmetric cell inside an argon filled glove box. The electrochemical stability of synthesized SPE was investigated by linear sweep voltammetry (LSV) carried out using a stainless steel as working electrode and lithium metal as reference and counter electrodes at a scan rate of 1 mV s^{-1} at 25°C.

3. Results and Discussion

3.1. Synthesis of polymer electrolytes

The radical solution copolymerization of PEGMA and acrylonitrile was initiated by BPO at 65°C and carried out for 9 hours in toluene solvent as shown in Fig. 1. It should be noted that the reactivity ratio of PEGMA toward a radical
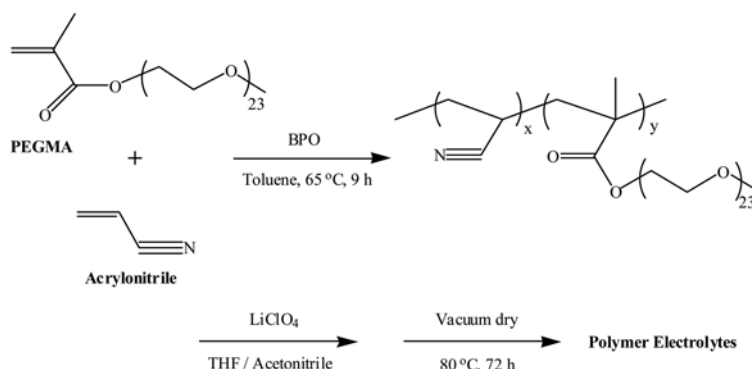
Fig. 1. Synthetic procedure for PEGMA-co-PAN polymer electrolyte.

initiator is much higher than that of acrylonitrile monomer because of the electron withdrawing CN bond is present in the latter case.[17] Therefore PEGMA-rich copolymer can possibly be formed from the solution polymerization. To verify our assumption, the composition of obtained copolymer was calculated by 1H-NMR measurement as shown in Fig. 2. Actually, the resonance peaks at 4.2~4.3 and 2.7~3.2 ppm which are corresponding to PEGMA and acrylonitrile protons, respectively, can be integrated to determine the mole ratio of synthesized copolymer product. The characterizations of PEGMA-co-acrylonitrile copolymers with respect to composition and molecular weight are summarized in Table 1. It is noticed that the compositions calculated from 1H-NMR is deviated from its feed ratio and less content of acrylonitrile than feed was observed. For example, only 15 w% of acrylonitrile have been founded in PAN2 sample after polymerization though the feed was 38 wt%, which clearly supports the low reactivity of acrylonitrile monomers in the copolymerization process. On

Table. 1. Characterization of poly(PEGMA-co-acrylonitrile) copolymers

Polymer	Composition (wt%)				Molecular weight $(g \, mol^{-1} \, GPC_b)$
	Feed		1H-NMR[a]		
	PEGMA	AN	PEGMA	AN	
PAN1	75	25	89	11	42,000
PAN2	62	38	85	15	12,000
PEO1100	100	0	100	0	45,000

[a]Measured in CDCl₃ solvent at 25°C.
[b]Determined relative to polystyrene in THF at 40°C.

the other hand, the molecular weight of resulting polymer seems somewhat low by considering the molecular weight of PEGMA. However, the real molecular weight should be higher than that of listed value in Table 1 since the linear polystyrene-equivalent is not enough to predict the real molecular weight of comb-like PEGMA-co-acrylonitrile system as suggested by Ryu et al.[18] In addition, PEGMA homopolymer designated as PEO1100 was also synthesized as control sample to investigate the effect of acrylonitrile moiety on the ionic conductivity and physical properties. Table 2 summarized the compositions and physical states for prepared SPEs in this study using PAN1 or PAN2 as parent polymer with different LiClO₄ content. Interestingly, all three PAN1-based electrolytes are liquid state, i.e. very viscous liquid, regardless of the lithium salt concentration while the PAN2-based electrolytes turned to solid products. In detail, the physical properties of PAN2-based electrolytes varied from a hard or soft film and to a sticky solid by increasing LiClO₄ content, even the reason is not clear at this point. Especially, a free standing soft transparent film (thickness: ~2 mm) was obtained as shown in Fig. 3 from the SPE5 sample which have 15 wt% of acrylonitrile and
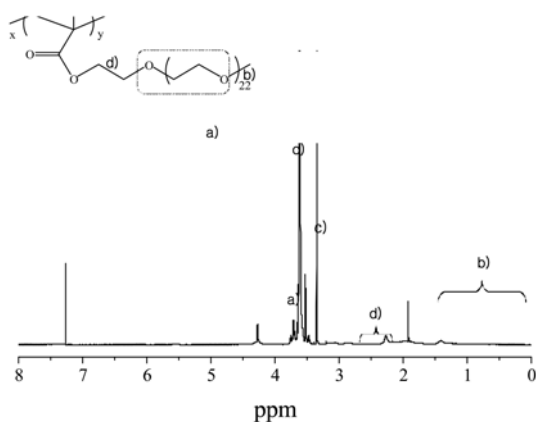

Fig. 2. 1H NMR spectrum of PEGMA-co-PAN in CDCl₃.

Table. 2. Preparation of solid polymer electrolytes by incorporation of lithium perchlorate

Sample	Parent polymer[a]	LiClO$_4$ (g)	[EO] : [Li]	Physical state at 25°C
SPE1	PAN1	0.17	12 : 1	liquid
SPE2	PAN1	0.34	6 : 1	liquid
SPE3	PAN1	0.68	3 : 1	liquid
SPE4	PAN2	0.31	6 : 1	hard film
SPE5	PAN2	0.62	3 : 1	soft film
SPE6	PAN2	1.88	1 : 1	sticky solid
SPE7	PEO1100	0.31	7 : 1	liquid

[a]One gram of each polymer was used in polymer electrolyte preparation.

3 : 1 of [EO] : [Li] ratio. Taking the liquid nature of SPE7 (homopolymer with salt) into account, the large volume percentage of PEGMA might be one of the reason of liquid physical state for PAN1-based electrolytes. In addition, it seems that the concentration of lithium salt also effect on the physical properties through the coordination complex with electron donating EO groups and/or electron withdrawing CN functions. Nevertheless, it is not easy to understand the 85 wt% of PEGMA incorporated electrolyte is a solid while the 89 wt% of the same monomer became a liquid state.

3.2. Thermal properties

The DSC curves of PAN1, PAN2 and PEO1100 homopolymer are depicted in Fig. 4. There is a sharp crystalline melting transition peak of the ethylene oxide chain in PEO1100 at around 43°C. However, this peak is decreased to 42 and 29 °C as the acrylonitrile contents are increased to 11 and 15 wt%, respectively. This result suggests that the formation of crystalline phase in PEO1100 is disturbed by the presence of acrylonitrile monomers along the polymer chain, thereby reducing the packing density. Therefore, it can be assumed that the poly(PEGMA-

Fig. 3. Photographs of free standing SPE5 sample after vacuum dry at 80°C for 72 hours.

co-acrylonitrile) is formed as a random copolymer structure rather than producing a block topology in spite of the different radical reactivity ratio between PEGMA and acrylonitrile monomer. Fig. 5 shows DCS curves of original PAN2 and LiClO$_4$ incorporated electrolytes assigned as SPE4 and SPE5. Obviously, the crystalline melting temperature of PAN2 at 29°C disappeared completely after addition of LiClO$_4$. Consequently, the close packing of crystalline EO units became unable in the presence of lithium salt by the coordination process between them. Therefore, it is clear that the crystalline domain of poly (PEGMA) is influenced strongly by the presence of acrylonitrile and the lithium salt. Actually this phenomenon is quite useful to produce an amorphous and tough polymer electrolyte with a high ionic conductivity from a crystalline PEO matrix. In addition to above, it should be noted that the glass transition temperatures of poly(PEGMA-co-
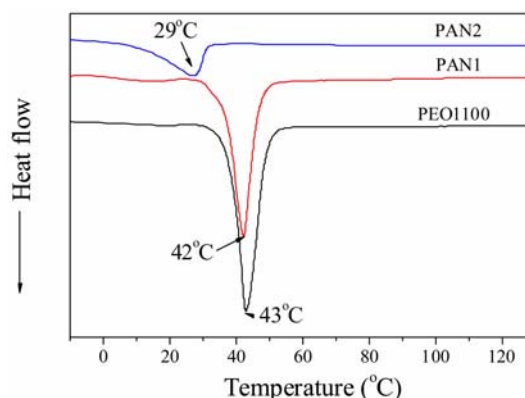
Fig. 4. DSC heating trace of polymer electrolytes as a function of acrylonitrile content.
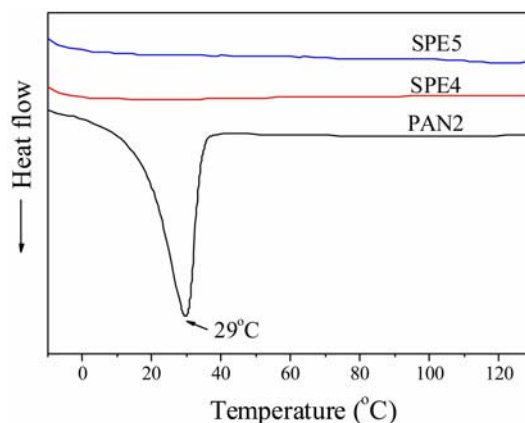
Fig. 5. DSC heating trace of polymer electrolytes before (PAN2) and after (SPE4, 5) LiClO$_4$ incorporation.

acrylonitrile) is another important factor to affect the polymer chain mobility thereby changes the ionic conductivity. However, any detectable change of heat flow was not observed in this polymer system in the temperature range from −150 to 150°C instead of crystalline melting of PEGMA at around 40°C.

3.3. Electrochemical properties

Fig. 6 shows the temperature dependence of ionic conductivity of PAN1-based polymer electrolytes namely SPE1, 2, 3 as a function of $LiClO_4$ concentration in the range between 30 and 85°C. It can be observed that the ionic conductivity is comparable when the [EO] : [Li] ratio is 12 : 1 and 6 : 1. Then the value of 1.4×10^{-4} S cm^{-1} was achieved for the sample with 3 : 1 ratio of [EO] : [Li] at 30°C. It should be noted that although the all three samples are viscous liquid state at room temperature, therefore they have no meaning as a solid polymer itself, the strong temperature dependence of ionic conductivity is observed which is consistent with a typical result of solid polymer electrolytes.[1]

The ionic conduction behaviors of PAN2-based polymer electrolytes are plotted in Fig. 7. Similar with the previous results, ionic conductivity is increased when the [EO] : [Li] ratio increases from 6 : 1 to 3 : 1 but decreased rapidly with 1 : 1 ratio. Thus, the highest ionic conductivity approaches at 1.7×10^{-4} S cm^{-1} was achieved in the solid polymer film with 3 : 1 ratio of [EO] : [Li] at 25°C. Generally, it is reported that the ionic conductivity is relative to the number of charge carriers to a certain value and then decreased gradually by forming a neutral contact ion pairs from the surplus dissociated lithium cations and counter anions. Thus, the result shows in this study is in agreement with that of researches reported previously.[19,20]
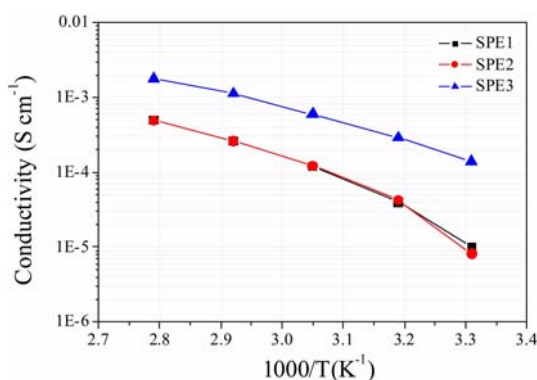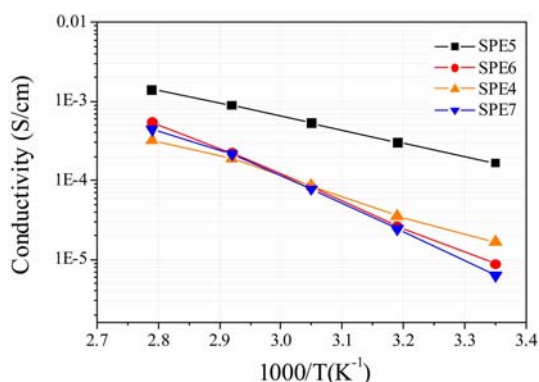

Fig. 7. Temperature dependence of ionic conductivities of the PAN2-based polymer electrolytes and control PEGMA homopolymer (SPE7).

However, the result is somewhat deviated with respect to the suggested lithium ion concentration, e.g. 9 : 1 of [EO] : [Li], for a high ionic conductivity in a general PEO-based solid polymer electrolytes. Although it is not clear at this stage, the combination effect between acrylonitrile and high molecular weight of PEGMA macronomomer might be considered as a reason for the intriguing behavior. This concept is supported by the control sample plotted as SPE7 in Fig. 7. Although the sample is a liquid state at room temperature, the lowest ionic conductivity with the value of 6.2×10^{-6} S cm^{-1} was observed. For this reason, the highest ionic conductivity was observed in the soft film type SPE5 sample rather than the sticky solid type SPE6.

The electrochemical stability of polymer electrolyte was investigated by LSV using a stainless steel working
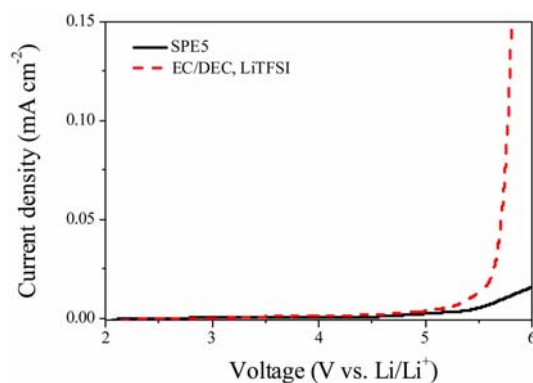

Fig. 6. Temperature dependence of ionic conductivities of the PAN1-based SPE.

Fig. 8. Linear sweep voltammetry of SPE5 using stainless steel working electrode and lithium reference & counter electrode with scan rate 1 mV s^{-1} at 25°C.

electrode and a lithium counter and reference electrodes. The results are shown in Fig. 8. As described in Introduction part, one of the important advantages of SPE is its high electrochemical stability toward a strong anodic oxidation conditions. As expected, a high electrochemical stability up to 5.5 V was obtained for SPE5 sample at 25°C. To compare with a LSV of liquid electrolyte, a reference sample consists of EC/DEC and LiTFSI salt was prepared and the test result is also plotted in Fig. 8. Consequently, a free standing solid polymer film with high ionic conductivity and good electrochemical stability was successfully prepared by incorporation of controlled acrylonitrile and $LiClO_4$ salt.

4. Conclusion

PEGMA-co-acrylonitrile based copolymer electrolytes have been prepared by solution polymerization and incorporation of appropriate amounts of $LiClO_4$ salt. The physical properties of polymer electrolytes were affected by the concentration of acrylonitrile and $LiClO_4$ salt. By controlling the compositions, free standing all solid polymer film with the highest room temperature ionic conductivity which has a value of 1.7×10^{-4} S cm^{-1} can be obtained from 15 wt% of acrylonitrile and 3 : 1 ratio of [EO] : [Li]. In addition, coordination taking place in poly(PEGMA) with lithium salt, thereby disappearing the crystalline melting transition of ethylene oxide have been confirmed from DSC studies, which can provide a good strategy to prepare an amorphous and tough film from a PEO-based polymer electrolyte.

Acknowledgement

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