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가소화된 Poly(vinyl chloride)-g-Poly(oxyethylene methacrylate) 가지형 고분자 전해질막 제조 및 분석

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Preparation and Characterization of Plasticized Poly(vinyl chloride)-g-Poly(oxyethylene methacrylate) Graft Copolymer Electrolyte Membranes

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요 약: Poly(vinyl chloride)-g-poly(oxyethylene methacrylate) (PVC-g-POEM) 가지형 공중합체를 원자전달라디칼 중합을 통해 합성하여 전기변색소자의 전해질에 적용하였다. 가소화된 고분자 전해질은 가소제로서 propylene carbonate (PC)/ethylene carbonate (EC) 혼합물을 도입하여 제조하였으며, Lithium tetrafluoroborate ($LiBF_4$), lithium perchlorate ($LiClO_4$), lithium iodide (LiI) and lithium bistrifluoromethanesulfonimide (LiTFSI)를 사용하여 염의 종류에 따른 영향을 조사하였다. 광각 x-선 산란(WAXS)과 시차주사 열량법(DSC) 측정 결과 고분자 전해질의 구조와 유리전이온도(T_g)가 변하였고, 이는 POEM 내의 에테르의 산소와 리튬염 사이의 상호작용으로 인해 변했다는 것을 FT-IR 분광법을 통하여 확인하였다. 투과전자현미경(TEM) 측정 결과 PVC-g-POEM 가지형 공중합체의 미세상분리 구조가 PC/EC와 리튬염의 도입에도 변하지 않는 것을 관찰하였다. 가소화된 고분자 전해질은 poly(3-hexylthiophene) (P3HT) 전도성 고분자를 이용한 전기변색소자에 적용되었다.

Abstract: Poly(vinyl chloride)-g-poly(oxyethylene methacrylate) (PVC-g-POEM) graft copolymer was synthesized via atom transfer radical polymerization (ATRP) and used as an electrolyte for electrochromic device. Plasticized polymer electrolytes were prepared by the introduction of propylene carbonate (PC)/ethylene carbonate (EC) mixture as a plasticizer. The effect of salt was systematically investigated using lithium tetrafluoroborate ($LiBF_4$), lithium perchlorate ($LiClO_4$), lithium iodide (LiI) and lithium bistrifluoromethanesulfonimide (LiTFSI). Wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) measurements showed that the structure and glass transition temperature (T_g) of polymer electrolytes were changed due to the coordinative interactions between the ether oxygens of POEM and the lithium salts, as supported by FT-IR spectroscopy. Transmission electron microscopy (TEM) showed that the microphase-separated structure of PVC-g-POEM was not greatly disrupted by the introduction of PC/EC and lithium salt. The plasticized polymer electrolyte was applied to the electrochromic device employing poly(3-hexylthiophene) (P3HT) conducting polymer.

Keywords: *atom transfer radical polymerization, graft copolymer, electrochromic device, polymer electrolyte, conducting polymer*

1. Introduction

Recently, polymer electrolyte membranes have received much attention due to their unique properties in various areas such as lithium batteries [1], polymer electrolyte membrane fuel cells [2], facilitated transport membranes [3], dye-sensitized solar cells [4] and electrochromic devices [5]. Electrochromic devices exhibit redox states with distinct electronic absorption spectra

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and have been investigated for smart windows, glare-reduction systems, storage and sensors [6-8]. Poly(3-hexylthiophene) (P3HT) is one of the conducting polymers that have electrochromic properties and generally investigated as a thin film on electrode surfaces [9]. Liquid electrolytes can provide high ionic conductivity to electrochromic devices. However, solid polymer electrolytes are advantageous in terms of good mechanical properties, the flexible design of electrochromic device, ease of thin films formation with desirable sizes and no problems associated with the leakage or evaporation of solvent [10,11].

Poly(ethylene oxide) (PEO) is a representative polymer which is commonly used in polymer electrolytes due to its good complex formation capability with metal salt and ionic liquid. However, the ionic conductivity of PEO-based polymer electrolyte has been limited due to the high crystallinity of PEO [12]. Poly(oxyethylene methacrylate) (POEM) is a well-known amorphous PEO that possesses a high ionic conductivity but poor mechanical properties. In order to improve mechanical properties, POEM has been modified using crosslinking and copolymerization methods [13,14].

In this study, poly(vinyl chloride)-g-poly(oxyethylene methacrylate) (PVC-g-POEM) graft copolymer was synthesized via atom transfer radical polymerization (ATRP) and plasticized with propylene carbonate (PC)/ethylene carbonate (EC) mixture. The effect of salt was systematically investigated using lithium tetrafluoroborate ($LiBF_4$), lithium perchlorate ($LiClO_4$), lithium iodide (LiI) and lithium bistrifluoromethanesulfonimide (LiTFSI). Wide angle X-ray scattering (WAXS), differential scanning calorimetry (DSC), FT-IR spectroscopy and transmission electron microscopy (TEM) were used to characterize the structures and morphologies of the polymer electrolytes. The properties of electrochromic device fabricated with the plasticized polymer electrolyte and a conducting polymer, i.e. P3HT are also reported.

2. Experimental

2.1. Materials

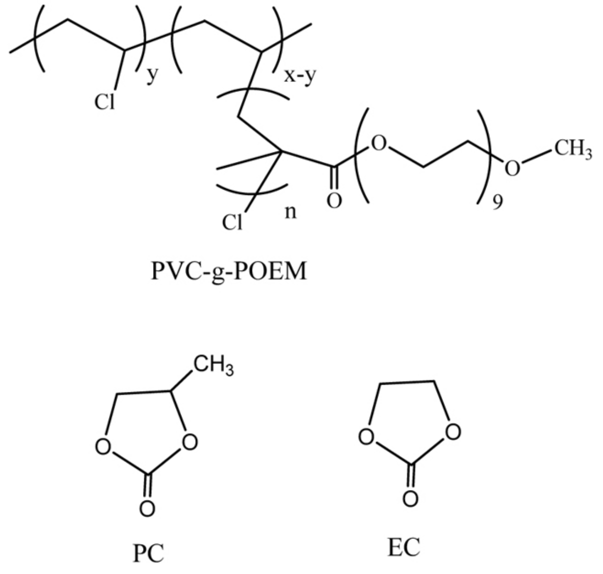
Poly(vinyl chloride) (PVC, M_w = 99,000 g/mol, M_n = 55,000 g/mol), poly(oxyethylene methacrylate) (POEM, poly(ethylene glycol) methyl ether methacrylate, M_n = 475 g/mol), lithium tetrafluoroborate ($LiBF_4$, 99.998%), lithium perchlorate ($LiClO_4$, 99.99%), lithium iodide (LiI, 99.9%), lithium bistrifluoromethanesulfonimide (LiTFSI, 99.95%), poly(3-hexylthiophene) (P3HT, regioregular), propylene carbonate (PC) and ethylene carbonate (EC) were purchased from Aldrich and used as received without further purification.

2.2. Synthesis of PVC-g-POEM Graft Copolymer

PVC-g-POEM graft copolymer was synthesized according to the previously reported method [15]. In brief, 3 g of PVC was dissolved in 40 ml of N-methyl pyrrolidone (NMP) while stirring at 60°C. Then, 18 g of POEM, 0.24 g of CuCl and 0.66 mL of HMTETA were added to the solution. The reaction flask was sealed with a rubber septum and purged with nitrogen gas for 30min. Then the flask was immersed in an oil bath for 24 h at 90°C. After passing the solution through a column with activated Al_2O_3 to remove the catalyst, it was precipitated into methanol. The polymer was purified by redissolving in THF and reprecipitating in methanol for several times. Finally, the polymer was dried in a vacuum oven overnight at room temperature.

2.3. Preparation of Polymer Electrolytes

Appropriate amount of PVC-g-POEM graft copolymer was dissolved in tetrahydrofuran (THF) to make 30 wt% polymer solution. After complete dissolution, PC and EC were added to this solution as a plasticizer with PVC-g-POEM : PC : EC = 8 : 1 : 1 weight ratio. Five kinds of lithium salt were added at 0.1 M to the as-prepared solution. These polymer electrolyte solutions were stirred for overnight to make homogeneous solutions. Then, the solutions were casted on the Teflon-coated dish and dried in a drying oven and vacuum oven successively at 40°C for 24 h.



Scheme 1. Chemical structure of PVC-g-POEM graft copolymer, PC and EC.

2.4. Fabrication of Electrochromic Device

First, P3HT was dissolved in monochloromethane and then spin-coated on the indium tin oxide (ITO) conducting glass at 1,000 rpm for 20 sec and dried at room temperature. Polymer electrolyte solutions were directly casted on the ITO glass and sandwiched with P3HT-coated ITO glass. Electrochromic device was dried at 40°C for 24 h.

2.5. Characterization

FT-IR spectra of samples were collected using Excalibur Series FTIR (DIGLAB Co.) instrument between the frequency ranges of 4,000 to 400 cm^{-1} using ATR facility. WAXS measurements were performed with a Rigaku D/max-RB apparatus (Tokyo, Japan). Data were collected from 5° to 60° at rate of 1°/min. DSC (DSC 2920, TA Instruments, INC.) was used to characterize the materials at a heating rate of 20°C/min under a N_2 environment. TEM pictures were obtained from a Philips CM30 microscope operating at 300 kV. For TEM measurements, the polymer was dissolved in THF and then a drop of these samples was placed onto a standard copper grid. Tensile evaluation was performed on universal testing machine (UTM, a LR10 KPlus Series) at a speed of 5 mm/min. Ionic conductivity was measured under a dry atmosphere using an impedance analyzer (IM6, ZAHNER, Germany) and a lab-made 2-probe conductivity cell. The impedance spectra of electrolytes were used to generate Nyquist plots, and the ionic conductivity was calculated from the plots. CHI624B (CH Instruments) potentiostat was used for source-drain voltage application and amperometric detection.

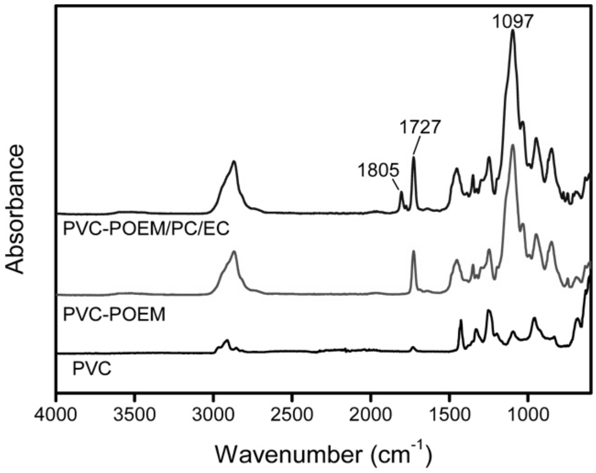


Fig. 1. FT-IR spectra of pristine PVC, PVC-g-POEM and PVC-g-POEM/PC/EC.

3. Results and Discussion

The chemical structures of PVC-g-POEM graft copolymer, PC and EC are presented in Scheme 1. Polymerization of PVC-g-POEM graft copolymer was carried out at 90°C for 24 h using CuCl and HMTETA as catalyst and ligand, respectively. The PC/EC mixture functioned as a plasticizer to increase the ionic conductivity of polymer electrolytes. Fig. 1 shows the FT-IR spectra of the pristine PVC, PVC-g-POEM and PVC-g-POEM/PC/EC. PVC-g-POEM graft copolymer exhibited absorption bands at 1,727 and 1,097 cm^{-1}, assigned to the stretching vibration of C = O and C-O-C group in POEM domain, respectively [14]. Upon the introduction of PC/EC mixture, a new absorption band at 1805 cm^{-1} appeared, attributed to the C = O bond of PC/EC. The absorption bands of C = O and C-O-C

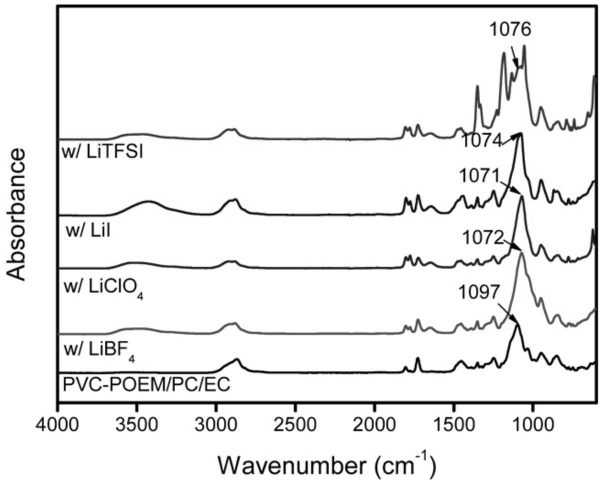


Fig. 2. FT-IR spectra of PVC-g-POEM/PC/EC electrolytes with and without Li salt.

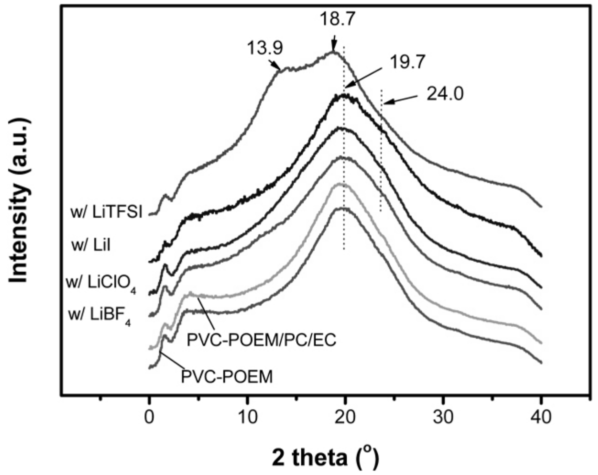


Fig. 3. WAXS patterns of PVC-g-POEM and PVC-g-POEM/PC/EC electrolytes with and without Li salt.

group in PVC-g-POEM graft copolymer were almost unchanged, indicating weak interactions between PVC-g-POEM and PC/EC.

To investigate interaction between the lithium salts and PVC-g-POEM/PC/EC, the FT-IR spectra of PVC-g-POEM/PC/EC with and without various lithium salts were measured and presented in Fig. 2. When the salts were added to the graft copolymer, the ether peak of PVC-g-POEM was shifted to a lower wavenumber, indicating the coordinative interaction between the lithium ions and the ether oxygen in POEM. In the case of PVC-g-POEM/PC/EC/$LiClO_4$, the peak shift was the largest (from 1,097 to 1,071 cm^{-1}), indicating the strongest interactions.

The changes in d-spacing and structure of polymer electrolyte were investigated using WAXS analysis. The WAXS patterns for PVC-g-POEM, PVC-g-POEM/PC/EC and PVC-g-POEM/PC/EC/LiX (X = BF_4, ClO_4, I and TFSI) electrolytes are shown in Fig. 3. The intensity of X-ray scattering was plotted against the diffraction angle (2θ). Pristine PVC-g-POEM graft copolymer showed a broad amorphous peak at 19.7° due to the lack of crystallinity. Upon the introduction of PC/EC as a plasticizer, there was no significant change in WAXS pattern, indicating negligible interaction between PVC-g-POEM and PC/EC. When lithium salts such as $LiBF_4$, $LiClO_4$ and LiI were introduced into PVC-g-POEM/PC/EC, the shape became asymmetric and an additional shoulder peak appeared at around 24°, which resulted in the decrease of d-spacing according to the Bragg's equation ($\lambda = 2d\sin\theta$). It arises from the structural contraction of polymeric chains due to coordinative interactions between lithium ions and polymer matrix. For PVC-g-POEM/PC/EC/LiTFSI electrolyte, interestingly, the main peak at 19.7° was shifted to 18.7° and a shoulder peak appeared at 13.9°. The increase of d-spacing in LiTFSI-based polymer electrolyte might be due to chain repulsion due to the large size of TFSI$^-$ anions.

DSC measurement is an effective tool to determine the glass transition temperature (T_g) of polymer. The DSC curves for pristine PVC-g-POEM, PVC-g-POEM/PC/EC and its electrolytes with four lithium salts are shown in Fig. 4. In the pristine PVC-g-POEM graft copolymer, the T_g at -58.5°C was observed, attributable to rubbery POEM side chains. However, the T_g of glassy PVC main chains was not clearly observed presumably due to high grafting degree. In the PVC-g-POEM/PC/EC system, there was no significant peak shift, indicating negligible interactions between PVC-g-POEM and PC/EC, which is consistent with FT-IR and WAXS data. Upon the introduction of lithium salt, the T_g of POEM was always increased but strongly dependent on the kind of salt. It may be due to different

Table 1. Ionic Conductivities and UTM Data of PVC-g-POEM/PC/EC/Li Salt Polymer Electrolytes

Electrolyte	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)	Conductivity (S/cm)
PVC-g-POEM	1.1	179.2	0.9	-
PVC-g-POEM/EC/PC	1.0	108.9	1.1	-
w/$LiBF_4$	3.2	117.1	35.5	3.1×10^{-5}
w/$LiClO_4$	2.0	141.0	11.2	4.1×10^{-5}
w/LiI	2.6	204.0	13.9	3.8×10^{-5}
w/LiTFSI	1.1	163.8	1.5	3.3×10^{-5}

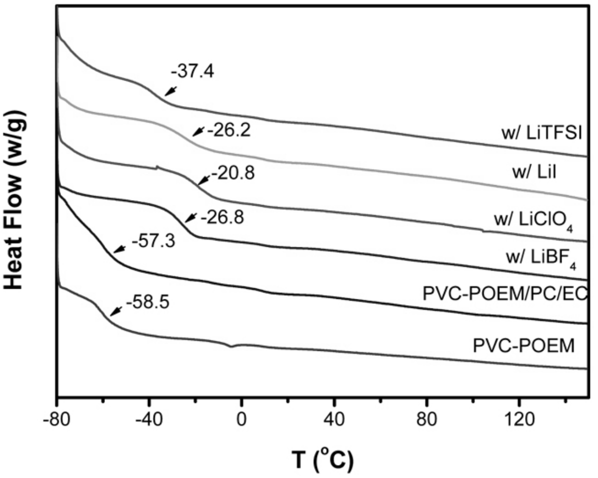


Fig. 4. DSC curves of PVC-g-POEM and PVC-g-POEM/PC/EC electrolytes with and without Li salt.

interaction strength between lithium salt and polymer matrix. The T_g of $LiClO_4$ -based electrolyte was the highest as -20.8° whereas that of LiTFSI-based electrolyte was the lowest as -37.4°. It represents that the interaction between lithium ions and polymer matrix was the strongest and weakest for $LiClO_4$ and LiTFSI-based electrolytes, respectively.

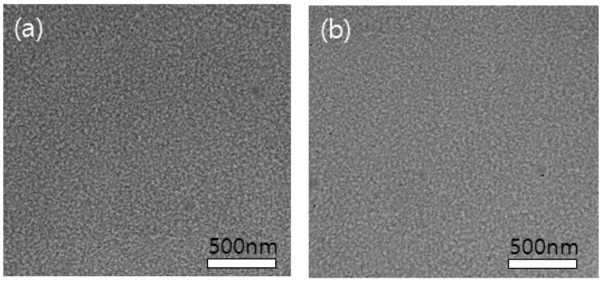


Fig. 5. TEM images of (a) PVC-g-POEM/PC/EC/LiI and (b) PVC-g-POEM/PC/EC/LiTFSI.

Fig. 5 shows the TEM images of PVC-g-POEM/PC/EC/LiI and PVC-g-POEM/PC/EC/LiTFSI electrolytes. The large difference in electron densities between PVC main chains and POEM side chains provides image contrast between two domains [17]. Bright regions represent the hydrophilic POEM domains and dark regions show hydrophobic PVC domains. The TEM images show microphase-separated morphology of plasticized PVC-g-POEM/PC/EC electrolytes. However, there was no large difference between two electrolytes and even similar to PVC-g-POEM/PC/EC without lithium salt (data not shown due to similar morphology). It might be due to the reduced electron density between PVC and POEM chains by the introduction of PC/EC plasticizer. It should be noted that the effect of salt on morphology was significant for the PVC-g-POEM electrolytes without PC/EC mixture.

The tensile strength and Young's modulus of polymer electrolyte membranes were measured using UTM at a speed of 5 mm/min as shown in Fig. 6 and summarized in Table 1. The Young's modulus and tensile strength at break of PVC-g-POEM graft copolymer were almost the same as those of plasticized PVC-g-POEM/PC/EC. However, upon the introduction of lithium salts, both Young's modulus and tensile strength at break were increased due to the interaction between the lithium salt and the ether groups in POEM chains. In the case of PVC-g-POEM/PC/EC/LiTFSI, the increase of Young's modulus was marginal, implying weak coordinative interactions.

The ionic conductivities of polymer electrolytes at 25°C are shown in Table 1. The ionic conductivities of

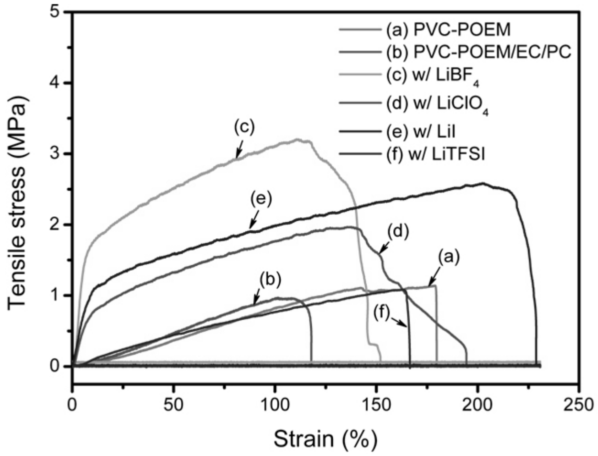


Fig. 6. UTM curves of PVC-g-POEM and PVC-g-POEM/PC/EC electrolytes with and without Li salt.

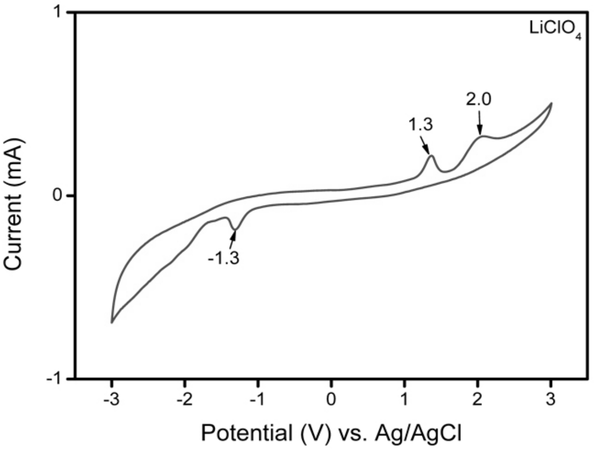


Fig. 7. Cyclic voltammograms of PVC-g-POEM/PC/EC/LiClO$_4$ electrolyte.

polymer electrolytes were affected by the anion of lithium salts. The highest conductivity (4.1 × 10^{-5} S/cm) was obtained for polymer electrolyte containing LiClO$_4$ due to strong interactions between lithium ions and polymer matrix, which makes the anions of lithium salt free and thus the conductivity is increased [18]. In the case of LiTFSI, the size of anion is too large and thus the interaction between the lithium ion and polymer matrix is weak, resulting in lower ionic conductivity.

Fig. 7 shows the voltammetric scan of PVC-g-POEM/PC/EC/LiClO$_4$ at a rate of 0.1 V/s from -3 V to 3 V. In particular, PVC-g-POEM/PC/EC/LiClO$_4$ electrolyte was chosen because it showed the highest conductivity (4.1 × 10^{-5} S/cm). The color of P3HT film was reddish purple in the neutral state. Upon electrochemical doping, the color of P3HT film changed to light blue, indication electrochemical oxidation at 1.3 and 2.0 V. Dedoping of the doped P3HT at -1.3 V changed the color from light blue to reddish purple again. From this result, the solid-state polymer electrolytes can be considered as a candidate for the flexible electrochromic devices.

4. Conclusions

Solid-state electrochromic device was constructed based on PVC-g-POEM graft copolymer. PVC-g-POEM graft copolymer was synthesized via ATRP process using PVC as a macromonomer. The plasticized polymer electrolytes were prepared by incorporation of four kinds of lithium salts. The lithium ions were complexed with the ether oxygens of POEM domain, as conformed by FT-IR spectroscopy. The WAXS and DSC results also show the coordinative interaction between the lithium ions and the oxygen atoms of POEM. All plasticized polymer electrolytes showed good mechanical properties more than 1.0 MPa and their ionic conductivities were 3.1∼4.1 × 10^{-5} S/cm at room temperature. The electrochromic device employing plasticized polymer electrolyte, i.e. PVC-g-POEM/PC/EC/LiClO$_4$ and conducting polymer, i.e. P3HT functioned well.

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