

실란을 반응을 통한 가교된 내구성있는 이온성 액체 고분자 합성 및 평가

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Synthesis and Evaluation of Durable Cross-linked Poly(ionic liquid) via Silanol Reaction

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초록: 최근에 이온성 액체의 합리적인 물성으로 인해 많은 관심을 받고 있다. 자유 라디칼 중합공정과 친핵성 치환 반응을 이용하여 내구성 있는 3-클로로프로필-트리에톡시실란으로 부분 4차화된 폴리비닐에틸이마다졸륨(C-QPVEm)을 제조하였으며, 이를 열처리를 통하여 가교하였다. 고분자의 물성을 향상시키기 위해 가교 가능한 프로필 에톡시실란을 도입하였다. 합성된 QPVEm을 수소 핵자기 공명 분석과 적외선 분광분석을 이용하여 화학적 구조를 확인하였으며, 순환 전류 전압법을 이용하여 열처리로 가교된 C-QPVEm의 전기화학적 안정성이 향상됨을 확인하였다.

Abstract: Ionic liquids (ILs) have attracted a lot of interest because of their favorable properties. Durable cross-linked partially quaternized poly(1-vinyl-3-ethylimidazolium) with 3-chloropropyl-triethoxysilane (C-QPVEm) was fabricated via free radical polymerization and nucleophilic substitution reaction followed by thermal treatment. A cross-linkable propyl-triethoxysilane group was covalently incorporated into the polymer matrix to enhance the properties of the PVEm. The chemical structures of the synthesized pristine and cross-linked QPVEm were confirmed by ¹H NMR and FTIR spectra. The electrochemical stability of the C-QPVEm was determined by the CV technique, and found to be significantly improved due to the cross-linked networks in the polymer matrix.

Keywords: ionic liquid, free radical polymerization, quaternization, cross-linking, electrochemical device.

Introduction

Recently, electrochemical devices have attracted a lot of scientific interest because the need for energy storage systems is expanding beyond portable electronic devices to electric transportation.¹ The current growth in the electric vehicle market is mostly being driven by concerns over global warming. Future energy storage systems for electric transportation and large unit energy storage systems require further evolution towards higher energy density and power density, as well as longer cycling stability.^{2,3} To date, most of energy storage studies have focused on designing new electrode materials and electrolytes

that will remain stable in harsh conditions, while only a few research groups have reported on polymeric binder so far.⁴ Unlike other key components in the energy storage system, an efficient polymeric binder is important to maintain both the electrical and mechanical properties of electrodes. It effectively glues together all of the powdered components, including electrochemically active materials and conductive additives on the current collector. Commercially, polyvinylidene fluoride (PVDF) has been widely used for electrode binder due to electrochemical stability however PVDF binder have the disadvantages such as insulating character and a large amount of electrolyte swelling, which frequently occurred serious decline for performance of electrochemical devices. Thus, the development of new polymeric binder affected on the overall behavior of the electrode system is highly important to the capacitance and the cycling stability of energy storage system.

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In recent year, the monomers of ionic liquids (ILs) have attracted widespread interest application as an electrolyte due to their practical properties, including being chemically stable with electrochemical stability, their non-volatility, and high ionic conductivity.⁵⁻¹⁰ In the last decade, polymerized ionic liquid moieties have also been reported as solid polymer electrolytes for wide applications.¹¹⁻¹³ To our knowledge, only in a few of recent paper for poly(ionic liquid) form have been examined as a binder for electrochemical devices.^{4,10,14}

To improve the properties of polymer, many effective methods have been developed such as blending with other polymers,^{15,16} cross-linking^{17,18} and forming composites with inorganic materials. Among these various methods, cross-linking was frequently preferred since it is a simple and efficient method of enhance the physicochemical durability of polymer.

In this paper, we report a direct route to prepare a cross-linked QPVEm by free radical polymerization and quaterinization followed by thermal treatment. By using functional moiety containing ethoxysilane as a cross-linking agent, C-QPVEm has exhibits improved electrochemical properties for application of energy devices.

Experimental

Materials. 1-Vinylimidazole (Alfa Aesar, 98%) (Vm), ethyl bromide (Sigma-Aldrich, 99%), (3-chloropropyl) triethoxysilane (Sigma-Aldrich, 95%) (CPTES), azobisisobutyronitrile (AIBN) (Sigma-Aldrich, 98%), diethyl ether (Duksan, Extra pure grade), tetrahydrofuran (THF) (Duksan, extra pure grade) were used without any further purification.

Synthesis of Poly(1-vinyl-3-ethylimidazolium) (PVEm). 1-vinyl-3-ethylimidazolium, Br⁻ (VEm) was synthesized by nucleophilic substitution reaction of Vm and ethyl bromide. This synthesis was conducted based on the mole ratio of 0.05:0.057. Firstly, Vm (5 g, 0.05 mol), ethyl bromide (7.3267 g, 0.06 mol) and MeOH (100 mL) were added into a round bottom flask and reacted at 40 °C for 48 h with a magnetic stirrer. After the reaction, the mixed solution was precipitated in diethyl ether (1 L). Finally, the collected VEm was dried in a vacuum oven overnight at 40 °C. PVEm was synthesized by the free radical polymerization of VEm and Vm. This synthesis was conducted based on the mole ratio of 5:5, 6:4 and 7:3. Firstly, each ratio of VEm and Vm were added with D.I. water into a round bottom flask, and then AIBN was added as an initiator. After de-gassing the flask, inside was filled with nitrogen and reacted at 65 °C for 48 h with a magnetic stirrer.

After 48 h, the mixed solution was precipitated in THF (1 L). Finally, the collected PVEm was dried in vacuum oven overnight at 40 °C. The prepared PVEm samples were designated to PVEm (5:5), PVEm (6:4) and PVEm (7:3), respectively.

Quaterinization of Poly(1-vinyl-3-ethylimidazolium) with (3-Chloropropyl) Triethoxysilane. The quaterinization of poly(1-vinyl-3-ethylimidazolium) (PVEm) was conducted in excess conditions of (3-chloropropyl) triethoxysilane. PVEm, CPTES and EtOH (100 mL) into a round bottom flask. After blocking the entrance to the flask, the contents were reacted at 40 °C for 48 h on the magnetic stirrer. After 48 h, the mixed solution was precipitated in the diethyl ether (1 L). Finally collected QPVEm was dried in vacuum oven overnight at 40 °C as shown in Figure 1. The prepared QPVEm films were put into a vacuum oven at 80, 100, 120, 140 and 160 °C for 1 h, respectively, to conduct thermal cross-linking.

Characterization. The gel content of the cross-linked QPVEm (C-QPVEm) was determined by a solvent extraction and evaluated using the following eq. (1):¹⁹

$$\text{Gel content(\%)} = M_2/M_1 \times 100 \quad (1)$$

where M_1 and M_2 are the weights of the cross-linked QPVEm before and after the solvent extraction, respectively. The thermal treatment ranged from 80 to 160 °C. The chemical structures of the pristine and cross-linked QPVEm (C-QPVEm) were characterized using, FTIR and ¹H NMR spectroscopy. Electrochemical stability was measured in a three-electrode system by cyclic voltammetry technique. Carbon black, Pt mesh, Ag/AgCl, and 1 M H₂SO₄ were used as the working electrode, counter electrode, reference electrode, and electrolyte, respectively. To measure their electrochemical properties, carbon black was mixed with commercial PVDF and C-QPVEm as a binder (10 wt%), and then the mixture was pasted onto a stainless steel electrode (1 cm × 1 cm) and dried at 150 °C for 20 min in an oven. The cyclic voltammetry was carried out at different scan rates ranging at 2, 5, 10, 20, 50 and 100 mV/s.

Results and Discussion

The schematic illustration of the experimental method is shown in the Figure 1. Firstly, 1-vinylimidazole and ethyl bromide are synthesized at 40 °C for 48 h. When 1-vinyl-3-ethylimidazolium, Br⁻ (VEm) was formed, the synthesized VEm and 1-vinylimidazole were subjected to free radical

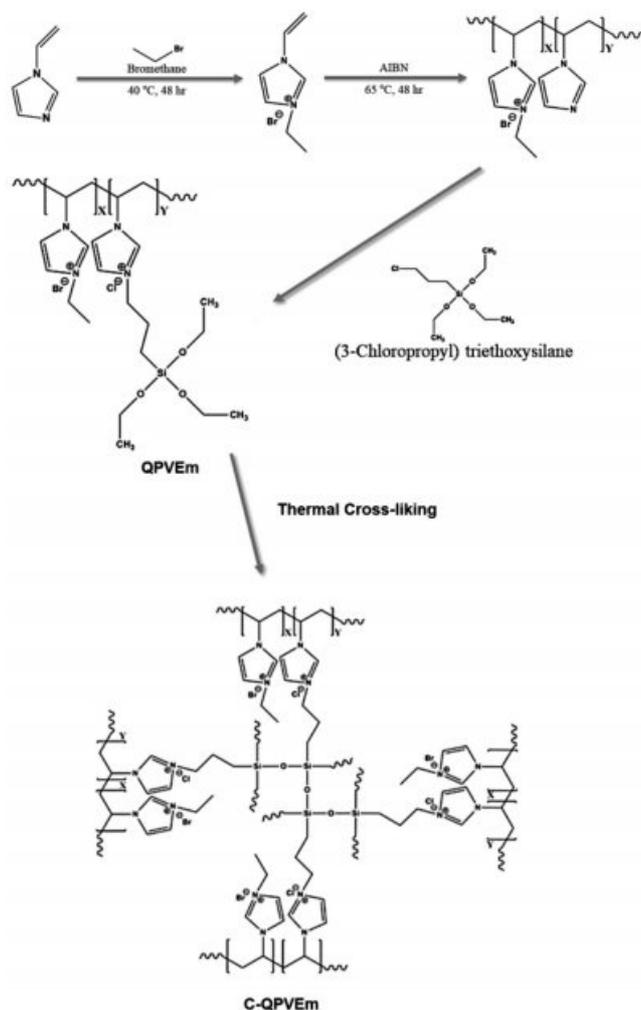


Figure 1. Reaction scheme for the synthesis of cross-linked QPVEm (C-QPVEm).

polymerization at 65 °C for 48 h by using the AIBN. (3-Chloropropyl)triethoxysilane was added to the polymer, which was thus quaternized and the synthesis was carried out at 40 °C for 48 h. In order to confirm the cross-linking rate depending on the ratio of silane, polymerization was carried out by controlling the ratio of Vm and VEm.

The samples obtained from these processes were made into films and cross-linked at different temperatures (80, 100, 120, 140, and 160 °C, respectively) for 1 h.

We performed ¹H NMR analysis at each step to confirm the correct polymer was being synthesized. The structure of the initial monomer was determined by ¹H NMR spectrum before synthesis. As shown in Figure 2(A), the NMR spectrum of VEm showed 8 specific peaks at 1.4, 4.2, 5.4, 6, 7.3, 8, 8.2 and 9.6 ppm, respectively except for the peak of the solvent.^{20,21}

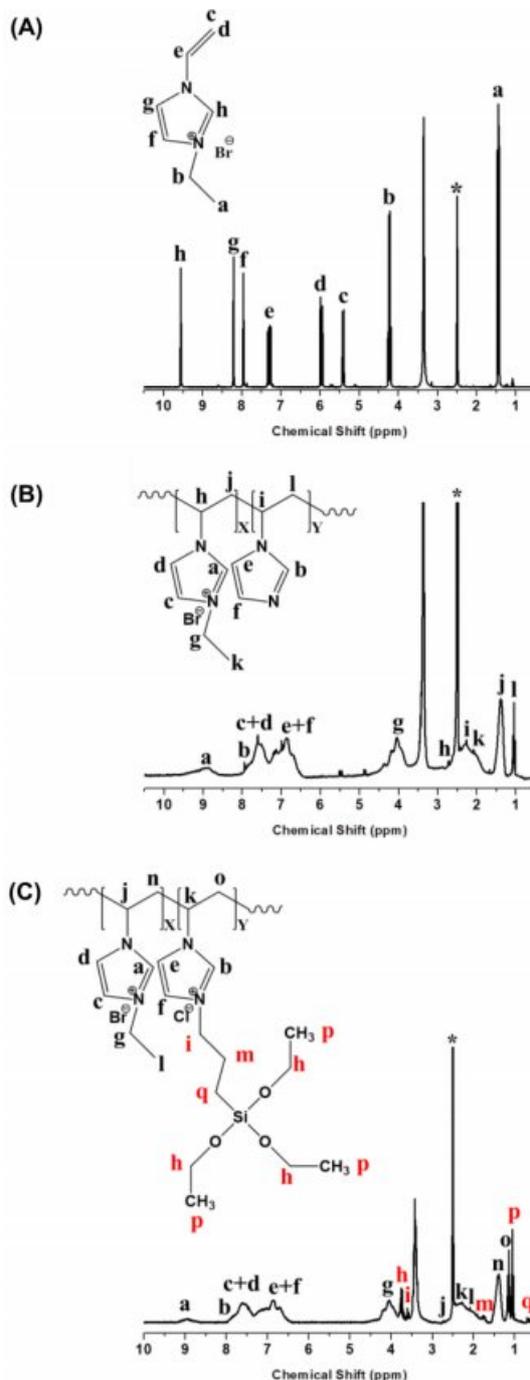


Figure 2. ¹H NMR spectra of (A) VEm; (B) PVEm; (C) QPVEm (5:5).

In Figure 2(B), the NMR spectrum of PVEm shows specific peaks containing VEm and Vm and it can be seen that the peaks become relatively broad as the monomer becomes a polymer. Finally, there are also peaks (red mark) of the CPTEs in the polymer backbone after quaternization, which indicates

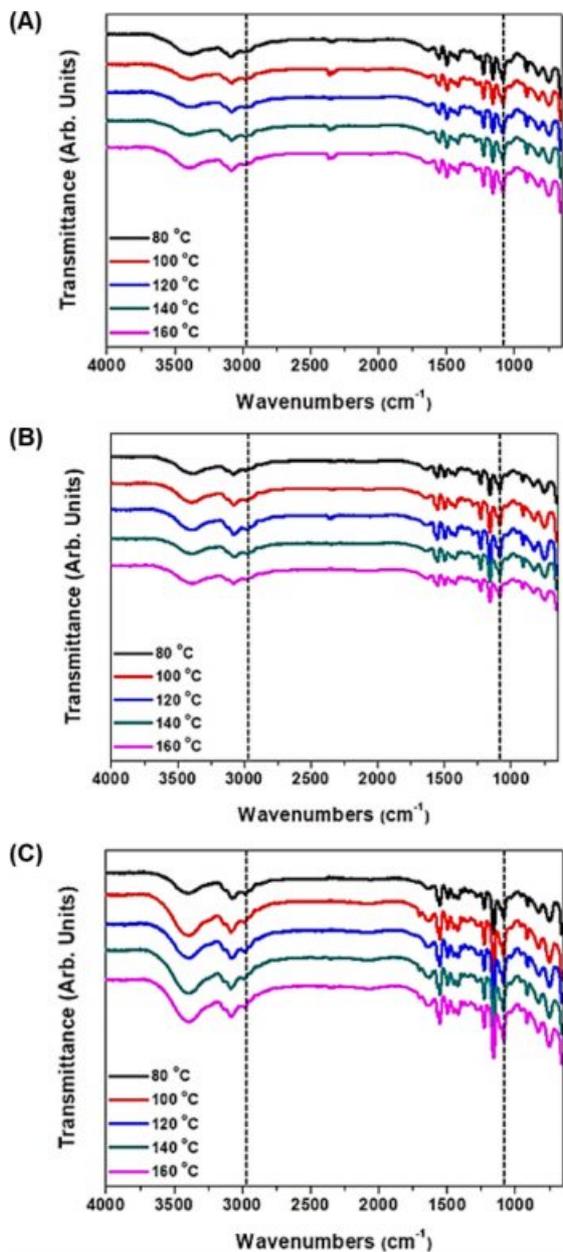


Figure 3. FTIR spectrum of (A) QPVEm (5:5); (B) QPVEm (6:4); (C) QPVEm (7:3) with increasing thermal treatment temperature.

that the synthesis of QPVEm was successfully carried out.

The chemical changes in QPVEm were confirmed by FTIR spectroscopy for each temperature in the thermal treatment, and the results are shown in Figure 3. The characteristic peaks of pristine QPVEm appeared at 3066 cm^{-1} for the C-H stretch in the imidazole ring, 2974 cm^{-1} for the C-H stretch in CH_3 , and 1643 cm^{-1} for the C=C stretch, 1550 cm^{-1} for the C-C and C-N stretch in the imidazole ring, 1423 cm^{-1} for the C-H bending

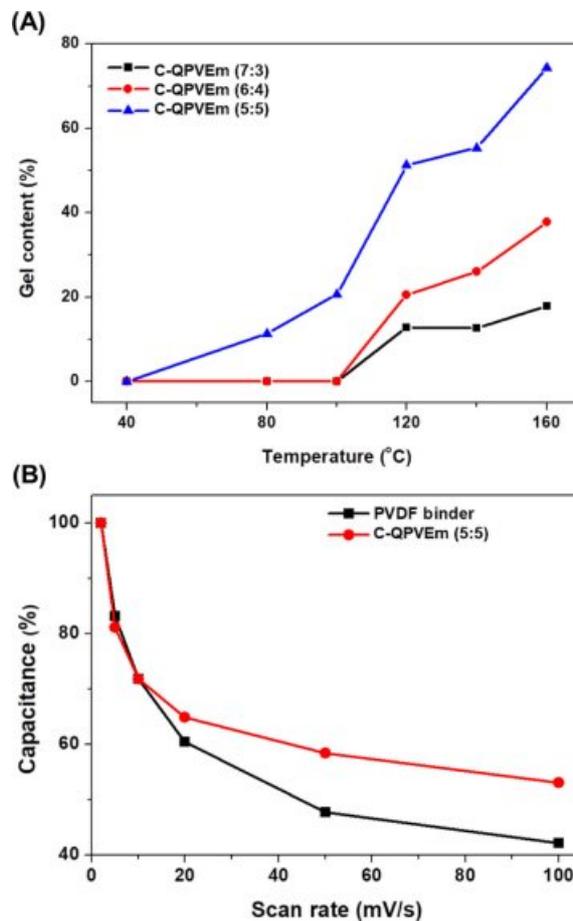


Figure 4. Gel contents of (A) C-QPVEm with increasing thermal treatment temperature; (B) electrochemical stability of C-QPVEm at 2, 5, 10, 20, 50 and 100 mV/s scan rates.

in the backbone, 1178 cm^{-1} for the C-H bending in the imidazole ring and 1084 cm^{-1} for the ether group in CPTES.^{14,22,23} After the thermal treatment, the peak intensity of the C-H groups at 2974 cm^{-1} decreased with increasing temperature.

It can be inferred that Si-O-C decomposed. However, there was no change in the Si-O-C peak (1084 cm^{-1}), indicating that Si-O-C is changed to Si-O-Si and the resultant condensation between Si-OH occurred the cross-linking reaction with the neighboring QPVEm chains as shown in Figure 1.²⁴

The C-QPVEm was prepared by thermal-induced cross-linking. It is well known that the thermal treatment of ethoxysilane group leads to the formation of insoluble cross-linked networks (Si-O-Si) in the polymer matrix. The gel content as a function of temperature is shown in Figure 4(A). The results confirm that the gel content significantly increased with increasing ratio of quaternized Vm in the PVEm matrix and thermal treatment temperature up to $160\text{ }^{\circ}\text{C}$.

To confirm its potential for application in an electrochemical device, the stability of C-QPVEm was determined by the CV technique at different scan rate.

According to increasing scan rate, the C-QPVEm (5:5) in harsh electrochemical conditions exhibited superior stability compared with commercial PVDF, as shown in Figure 4(B). At initial slow scan rate, C-QPVEm and PVDF exhibited the similar capacitance however C-QPVEm exhibited higher capacitance over 20 mV/s than PVDF. It was implied that the C-QPVEm glued more tightly active materials on current collector and well conducted the electrolyte ions to active materials.

Conclusions

In summary, C-QPVEm was successfully prepared through free radical polymerization and quaternization followed by thermal treatment. The chemical structures of the C-QPVEm were confirmed by ¹H NMR and FTIR. The high gel contents and superior electrochemical stability of the C-QPVEm were largely confirmed by solvent extraction and CV technique. The prepared C-QPVEm in this study has potential application as electrolytes and electrode binders of electrochemical devices, with improved properties.

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