

Poly(epichlorohydrin) 가지형 공중합체 전해질막의 상호작용 및 이온 전도도

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(2010년 8월 17일 접수, 2010년 9월 8일 수정, 2010년 9월 8일 채택)

Interactions and Ionic Conductivities of Poly(epichlorohydrin) Graft Copolymer Electrolyte Membranes

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(Received August 17, 2010, Revised September 8, 2010, Accepted September 8, 2010)

요약: 원자전달 라디칼 중합을 이용하여 poly(epichlorohydrine) (PECH)를 주사슬로 한 양친성 가지형 공중합체를 합성하였다. PECH로부터 poly(methyl methacrylate) (PMMA) 및 poly(butyl methacrylate) (PBMA)의 가지형 중합이 성공적임을 ¹H NMR과 FT-IR분석을 통해 확인하였다. 합성한 가지형 공중합체에 KI나 LiI 염을 도입하였을 때, ether 신축진동 피크가 낮은 wavenumber영역으로 이동하였으며, 이는 배위결합 상호작용 때문이다. PECH-g-PBMA 복합체의 이온 전도도는 PECH-g-PMMA 복합체에 비해 항상 높게 나타났는데, 이는 고무상인 PBMA 사슬의 높은 이동성으로부터 기인한 것으로 확인되었다. 최고 이온전도도 값은 질량비 10 wt%의 KI가 도입된 PECH-g-PBMA 전해질체에서 2.7×10^{-5} S/cm 로 나타났다.

Abstract: Amphiphilic graft copolymers based on poly(epichlorohydrine) (PECH) were synthesized using atom transfer radical polymerization (ATRP). Successful graft polymerization of poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA) from PECH was confirmed by nuclear magnetic resonance (¹H NMR) and FT-IR spectroscopy. Upon the introduction of KI or LiI to the graft copolymers, the ether stretching bands were shifted to a lower wavenumber due to coordinative interactions. Ionic conductivities of PECH-g-PBMA complexes were always higher than those of PECH-g-PMMA complexes, resulting from higher mobility of rubbery PBMA chains. The maximum ionic conductivity of 2.7×10^{-5} S/cm was obtained at 10 wt% of KI for PECH-g-PBMA electrolytes.

Keywords: graft copolymer, atom transfer radical polymerization (ATRP), ionic conductivity, complex, polymer electrolyte

1. Introduction

Polymer electrolyte membranes are promising materials due to their unique properties in various electrochemical devices such as lithium batteries [1], electrochromic devices [2], polymer electrolyte membrane fuel cells [3,4], facilitated transport membranes [5], and dye-sensitized solar cells [6,7]. The main advantages of polymer electrolytes over liquid based counter-

parts are their mechanical properties, ease of fabrication of thin films with desirable sizes and their ability to form proper electrode/electrolyte contact in electrochemical devices. Polymer electrolytes are solid complexes of a solvent-free polymer and a metal salt, which are formed by dissolving salt with a low lattice energy in polar polymer host [8]. Therefore, the interaction between a metal salt and a polymer matrix directly determines the dissolution behavior of the metal salt and consequently the concentration of free ions,

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which are responsible for the ionic conductivity, mass transport properties, and nanostructural properties.

The ionic conduction of complexes based on various alkali salts dissolved in linear poly(ethylene oxide) (PEO) has been extensively investigated over the last three decades [9,10]. In general, ionic conductivity decreases with increasing mechanical strength and vice versa. It is because both ion conduction and mechanical strength of polymer electrolytes are strongly related to the mobility of polymer chains [1,11]. Thus, for practical rechargeable lithium batteries, research has been focused on developing a novel polymer material with mechanical property as well as higher conductivity. Apart from PEO, researchers also have explored the design of solid electrolytes from block or graft copolymers which are microphase-separated materials consisting of two chemically dissimilar polymers [12-18]. It is because the self-organized approach is considered to be effective in incorporating higher ionic properties into a material while retaining desirable mechanical properties of the polymer [7].

In this study, therefore, we synthesized amphiphilic graft copolymers, that is, poly(epichlorohydrin)-graft-poly(methyl methacrylate) (PECH-g-PMMA) and poly(epichlorohydrin)-graft-poly(butyl methacrylate) (PECH-g-PBMA) via atom transfer radical polymerization (ATRP) [19] and detailed the interaction between these polymer hosts and metal ions. The resultant polymer electrolyte membranes were characterized using ^1H NMR and FT-IR spectroscopy, and the ionic conductivities were also reported.

2. Experimental

2.1. Materials

Poly(epichlorohydrin) (PECH, $M_w = 700,000$ g/mol), methyl methacrylate (MMA), butyl methacrylate (BMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper(I) chloride (CuCl , 99%), lithium iodide (LiI) and potassium iodide (KI) were purchased from Aldrich and used as received without further purification.

2.2. Synthesis of Graft Copolymers

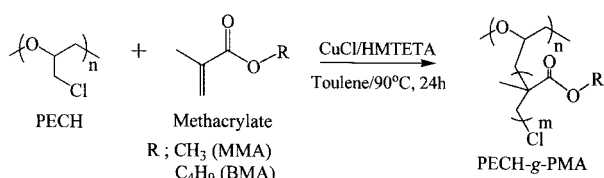
Graft copolymers of PECH-g-PMMA and PECH-g-PBMA were synthesized by ATRP technique, according to the previously reported method [19]. 1.5 g of PECH was dissolved in 30 mL of toluene with stirring for 3 h at 90°C . Six grams of MMA or BMA, 0.12 g of CuCl and 0.36 mL of HMTETA were successively added to the PECH solutions. Then the flask was sealed and purged for 30 min with nitrogen gas. The solutions were heated at 90°C in an oil bath and left under constant stirring for 24 h. After polymerization, the resultant polymer solution was diluted with tetrahydrofuran (THF). After passing the solution through a column with activated Al_2O_3 to remove the catalyst, the solution was precipitated into methanol. The polymers were purified by redissolving in THF and precipitating in methanol. The graft copolymers were obtained and dried in a vacuum oven overnight at room temperature.

2.3. Preparation of Polymer Electrolyte Films

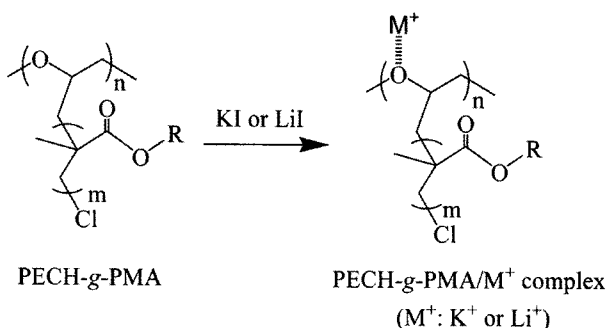
Graft copolymer (PECH-g-PMMA or PECH-g-PBMA) and KI or LiI with different concentration ratios were dissolved together in THF to make polymer solutions of 1 wt%. The solutions were cast on the dish and then dried in an inert drying oven overnight. The materials were further dried in a vacuum oven for two days to eliminate trace amounts of solvent.

2.4. Characterization

Nuclear magnetic resonance (^1H -NMR) analysis was performed with a 600 MHz high resolution NMR spectrometer (AVANCE 600 MHz FT-NMR, Germany, Bruker). FT-IR measurements were performed on a 6030 Mattson Galaxy Series FTIR spectrometer; 64-64 scans were signal-averaged at a resolution of 4 cm^{-1} . The ionic conductivity of polymer electrolyte films was measured by using an impedance analyzer (IM6e, ZAHNER, Germany) and a lab-made 4-probe conductivity cell under N_2 environment.



Scheme 1. ATRP synthesis for PECH-g-PMA graft copolymer.



Scheme 2. Coordinative interactions in PECH-g-PMA/metal salt complexes.

3. Results and Discussion

The reaction scheme for the synthesis of PECH graft copolymer via ATRP is illustrated in Scheme 1. Two kinds of methacrylate as a side chain were directly grafted from the mainchain backbone using ATRP initiated by the pendant initiating groups. PECH contains pendant chlorine atoms to act as an initiation site via ATRP and thus the graft copolymerization from PECH backbone can occur [19]. The reaction occurred in the presence of CuCl/HMTETA, catalyst/ligand complex at 90°C for 24 h. Upon the incorporation of KI or LiI into the PECH-g-PMA copolymer, K⁺ or Li⁺ ions would be predominantly coordinated to ether oxygens of PECH chains rather than PMA side chains, as illustrated in Scheme 2. It is because the interaction of metal ions with the ether oxygens is stronger than that with ester oxygens [20]. As a result, the amphiphilic PECH-g-PMA graft copolymer would molecularly self-assemble into continuous nanophase domains of PECH interweaved with hydrophilic domains of PMA brush layer, providing ion transport mechanism in the graft polymer electrolytes.

Fig. 1 shows the FT-IR spectra of pristine PECH

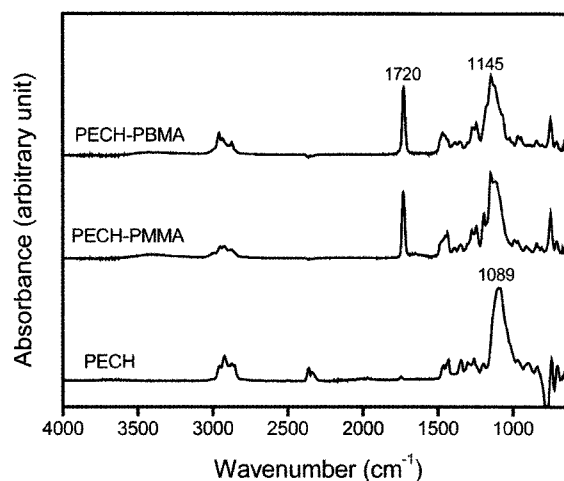


Fig. 1. FT-IR spectra of PECH homopolymer and PECH-g-PMA graft copolymers.

and PECH-g-PMA graft copolymers synthesized by ATRP. The PECH exhibited a strong ether (C-O-C) stretching band at 1,089 cm⁻¹. Upon graft copolymerization via ATRP, new strong absorption bands at 1,720 and 1,145 cm⁻¹ were additionally observed for both systems, attributable to the carbonyl (C=O) and the ether (-O-) stretching of methacrylate, respectively. These FT-IR spectroscopic results support the successful graft copolymerization of PMA side chains from PECH backbone via ATRP.

The chemical structure and the composition of graft copolymer were investigated on the basis of ¹H NMR spectroscopy. The ¹H-NMR spectra for PECH-g-PMA were presented in Fig. 2. The strong peaks at 2.5 and 3.4 ppm are due to DMSO and water, respectively. The strong peaks at around 3.6~3.7 ppm are attributed to CH₂ and CH of PECH main chains [21]. Upon grafting of PMA side chains from PECH backbone, several additional peaks appeared in the spectra. By comparing the integral area of the peak at 3.5 ppm for PMMA and 4.1 ppm for PBMA with that of the peak at 3.7 ppm (or 3.6 ppm) for PECH, the grafting ratio of PMA was determined [22]. As a result, the grafting ratio of PMMA and PBMA in the PECH-g-PMA copolymer was calculated to be 53% and 47% on a mole basis. Thus, the coordination behavior of ions and ionic conducting properties might not be significantly af-

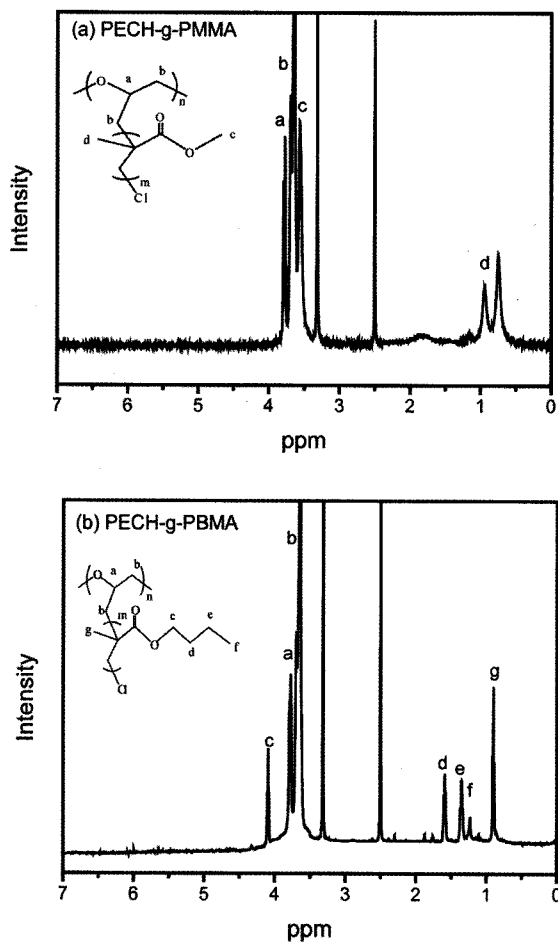


Fig. 2. ¹H NMR spectra of (a) PECH-g-PMMA and (b) PECH-g-PBMA graft copolymers.

ected by the grafting amounts.

The structural properties and coordinative interactions in graft copolymer electrolytes were characterized by FT-IR spectroscopy. The FT-IR spectra of pristine PECH-g-PMMA graft copolymer, and the PECH-g-PMMA/metal salt complexes (KI or LiI) with different salt concentrations between 600 and 2,000 cm^{-1} were presented in Fig. 3. As described above, the pristine PECH-g-PMMA copolymer exhibited the strong stretching bands at 1,720 and 1,145 cm^{-1} . Upon the introduction of salt, the ether stretching band of PECH at 1,116 cm^{-1} shifted to a lower wavenumber with increasing salt concentrations. The shift toward a lower wavenumber possibly results from the loosened C-O-C bond interaction by the coordinative interaction

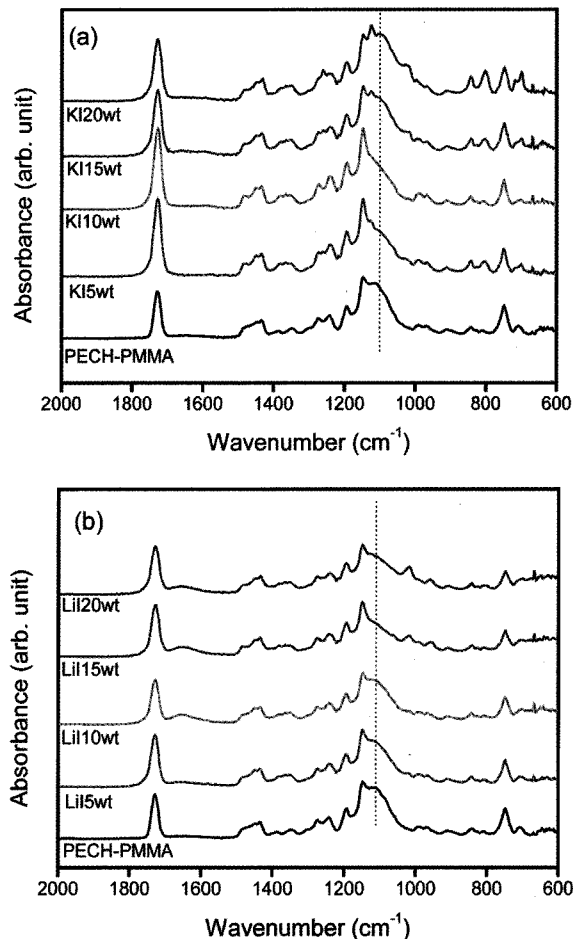


Fig. 3. FT-IR spectra of (a) PECH-g-PMMA/KI and (b) PECH-g-PMMA/LiI complexes.

between metal ions and ether oxygens. In the mean time, the carbonyl (C=O) stretching at 1,720 cm^{-1} and the ether (-O-) stretching at 1,145 cm^{-1} of PMMA domain remained almost invariant in both PECH-g-PMMA/KI and PECH-g-PMMA/LiI complexes. This is because that the interaction of metal ions with the ether oxygens of PECH domain is stronger than that with ester or ether oxygens of PMMA. Thus, most of metal ions selectively interact with the ether oxygens of PECH domain.

The ionic conductivities of PECH-g-PMA/metal salt complexes with the different salt concentrations were measured and presented in Fig. 4. The ionic conductivities increased with the increase of salt concentration up to 10 wt% at room temperature, after which

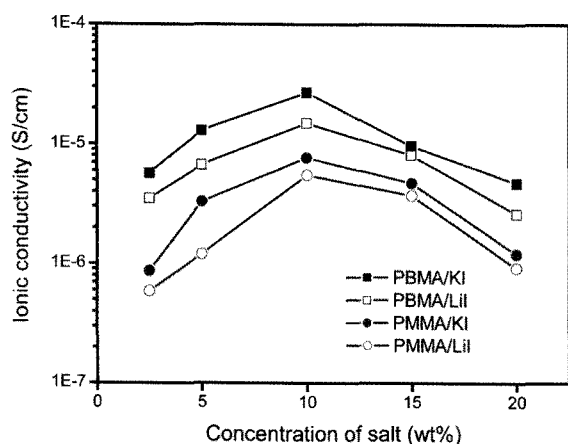


Fig. 4. Ionic conductivities of PECH-g-PMA/metal salt complexes.

they gradually decreased with increasing salt concentration. The increase of ionic conductivity in polymer electrolytes is attributable to the increased number of charge carriers, i.e. free ions. However, the decrease of conductivity at higher salt concentrations is considered to be because of the formation of ion pairs in the polymer electrolytes [23,24]. The ionic conductivities of KI salt complexes were always higher than those of LiI salt complexes in both PECH-g-PMMA and PECH-g-PBMA systems. This is because that the salt dissociation of KI is better than that of LiI in PECH-g-PMA graft copolymers. In addition, the ionic conductivities of PECH-g-PBMA complexes were always higher than those of PECH-g-PMMA complexes. It is due to the fact that the long flexible alkyl groups of PBMA increases the mobility of polymeric chains, leading to improvement of ion transport. As a result, the maximum ionic conductivity of 2.7×10^{-5} S/cm was obtained at 10 wt% of KI for PECH-g-PBMA complex films.

4. Conclusions

Graft copolymers consisting of PMA side chains and PECH backbone was successfully synthesized by ATRP using PECH as a macroinitiator. The reaction was initiated by the pendant chlorine atoms of PECH in the presence of CuCl/HMTETA complexes in tol-

uene at 90°C for 24 h. Successful graft copolymerization of PECH-g-PMMA and PECH-g-PMA was confirmed by ¹H NMR and FT-IR spectroscopy. Upon the introduction of KI or LiI salt to the graft copolymers, metal ions selectively interacted with the ether oxygens as revealed by FT-IR analysis. The ionic conductivities of KI salt complexes were higher than those of LiI complexes in both PECH-g-PMMA and PECH-g-PBMA systems due to the better dissociation of KI in graft copolymers. In addition, the ionic conductivities of PECH-g-PBMA complexes were always higher than those of PECH-g-PMMA complexes, resulting from higher mobility of rubbery PBMA chains. The ionic conductivities of graft copolymer electrolytes ranged on the order of 10^{-5} ~ 10^{-6} S/cm at room temperature and reached 2.7×10^{-5} S/cm for the PECH-g-PBMA complex containing 10 wt% of KI. These materials will be applied to electrochromic devices, which is in progress in our laboratory.

Acknowledgments

This work has been supported by the Low Observable Technology Research Center program of Defense Acquisition Program Administration and Agency for Defense Development.

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