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ABA 트리블록 공중합체를 이용한 무가습 가교형 고분자 전해질막

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Anhydrous Crosslinked Polymer Electrolyte Membranes Based On ABA Triblock Copolymer

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요 약: 원자전달 라디칼 중합을 이용하여 poly(hydroxyl ethyl acrylate)-*b*-polystyrene-*b*-poly(hydroxyl ethyl acrylate) (PHEA-b-PS-b-PHEA) 트리블록 공중합체를 합성하였다. 이렇게 합성된 PHEA-b-PS-b-PHEA 블록 공중합체의 -OH 그룹과 이미다졸 디카르복실릭산(IDA)의 -COOH 그룹과의 에스테르 반응에 의하여 가교된 전해질막을 제조하였다. 인산(H_3PO_4)을 도핑하여 이미다졸-인산 착체를 형성한 결과, 인산 함량이 증가함에 따라 고분자 전해질막의 수소 이온 전도도가 증가하였다. 특히 [HEA]:[IDA]:[H_3PO_4]=3:4:4의 조성을 갖는 PHEA-b-PS-b-PHEA/IDA/H_3PO_4 고분자 전해질막은 100°C의 비가습 조건에서 최대 0.01 S/cm의 수소이온 전도도를 나타내었다. 열분석 결과(TGA) 전해질막은 350°C의 고온까지 열적으로 안정함을 확인하여 연료전지에 적용이 가능함을 보여주었다.

Abstract: ABA type triblock copolymer of poly(hydroxyl ethyl acrylate)-*b*-polystyrene-*b*-poly(hydroxyl ethyl acrylate), *i.e.* PHEA-b-PS-b-PHEA, was synthesized throughatom transfer radical polymerization (ATRP). This block copolymer was thermally crosslinked with 4,5-imidazole dicarboxylic acid (IDA) via the esterification between the -OH groups of PHEA in block copolymer and the -COOH groups of IDA. Upon doping with H_3PO_4 to form imidazole-H_3PO_4 complexes, the proton conductivity of membranes continuously increased with increasing H_3PO_4 content. The PHEA-b-PS-b-PHEA/IDA/H_3PO_4 polymer membrane with [HEA]:[IDA]:[H_3PO_4]=3:4:4 exhibited a maximum proton conductivity of 0.01 S/cm at 100°C under anhydrous conditions. Thermal gravimetric analysis (TGA) shows that the PHEA-b-PS-b-PHEA/IDA/H_3PO_4 complex membranes were thermally stable up to 350°C, indicating their applicability in fuel cells.

Keywords: *atom transfer radical polymerization, block copolymer, crosslink, proton conductivity, anhydrous polymer electrolyte membrane*

1. Introduction

A fuel cell is an electrochemical device to produce electricity from H_2/O_2 and an attractive alternative to combustion engines for electrical power generation due to its high efficiencies and low pollution levels. Among many types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC) have undergone significant development over the past decade [1-3]. These fuel cells are now being developed and demonstrated as complete power conversion systems for stationary and transportation applications such as electric vehicles, mobile telephones, and on-site power generations.

Many efforts have been dedicated to the development of high performance polymer electrolyte membranes [4-8]. The most commonly used polymer electrolyte membrane is perfluorosulfonic acid membranes,

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such as Nafion® from DuPont. At ambient pressure and temperatures below 100°C, hydrated Nafion® shows a high proton conductivity (~ 0.1 S/cm), which allows the attainment of high power densities and efficiencies. However, it has many drawbacks which need to be overcome, *i.e.* the poor performance at temperature above 80°C due to the loss of the water. In addition, the production cost of perfluorinated membranes is extremely high, which makes it difficult for an industrialization of the PEMFC. Therefore, the highly proton conducting membrane with cheap material and thermal stability at high temperatures is necessary [9-12].

Using a micophase-separated morphology allows a better control of structure and ion conducting path in polymer membranes. Among them, block copolymers consisting of more than two domains with different chemical properties are considered to offer an effective approach for incorporating higher ionic properties into a material while retaining desirable mechanical properties of the polymer [13-15]. The advantages of a block copolymer are 1) effective controlling of the swelling of the ion conducting domains by the surrounding non-conducting domains, 2) lowering of the fuel permeability due to decreased swelling, and 3) high mechanical stability due to the inert matrix of non-conducting segments.

In this work, we report on anhydrous polymer electrolyte membranes based on poly(hydroxyl ethyl acrylate)-b-polystyrene-b-poly(hydroxyl ethyl acrylate) (PHEA-b-PS-b-PHEA) triblock copolymer. The block copolymer was synthesized through atom transfer radical polymerization (ATRP) [16,17]. This block copolymer was crosslinked with 4,5-imidazole dicarboxylic acid (IDA) via the esterification of -OH groups of PHEA and -COOH groups of IDA [18,19]. The anhydrous polymer electrolyte membranes were prepared upon doping with phosphoric acid (H_3PO_4) to form imidazole-H_3PO_4 complexes. The resultant anhydrous polymer electrolyte membranes were characterized in terms of proton conductivity and thermal properties.

2. Experimental

2.1. Materials

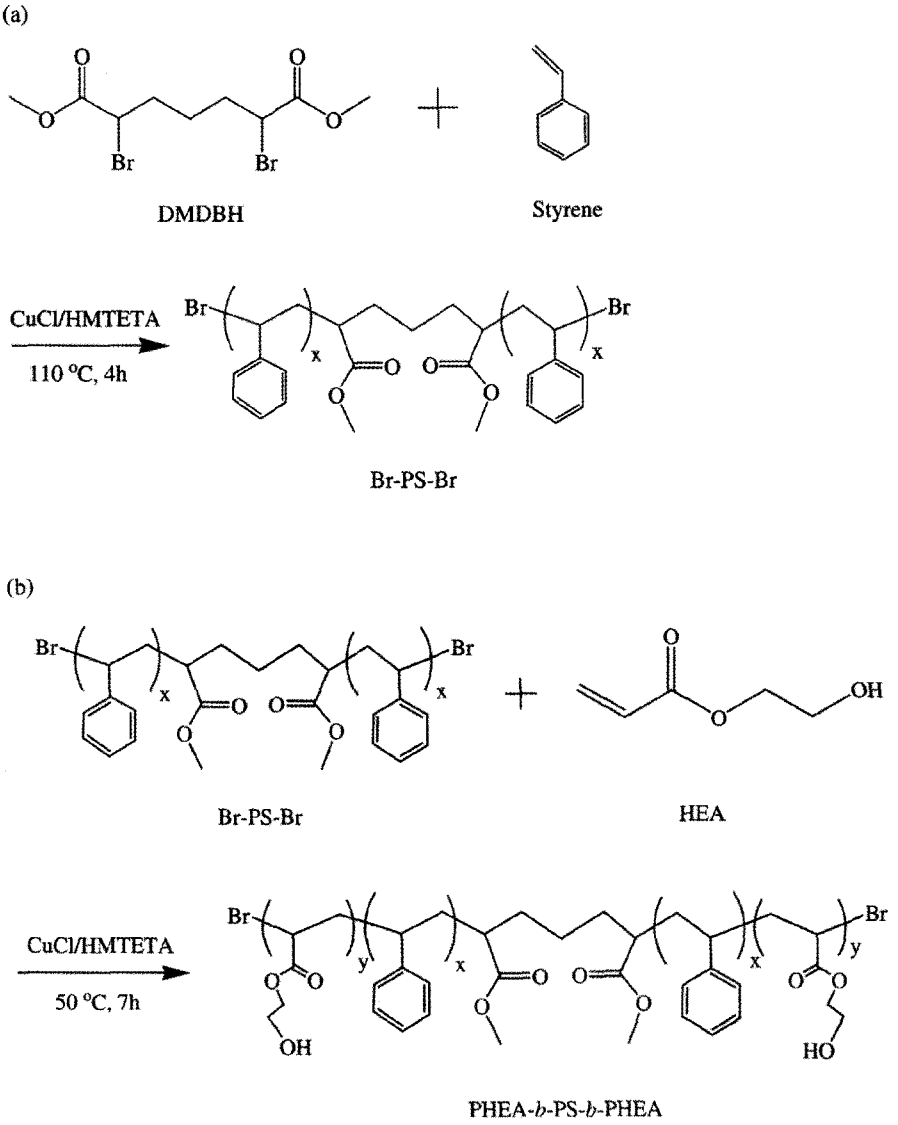
Styrene (99%), 2-hydroxy ethyl acrylate (HEA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper (I) chloride (CuCl, 99%), methyl 2-bromo-propionate (MBP), 4,5-imidazole dicarboxylic acid (IDA), phosphoric acid (H_3PO_4), and 1-methy-2-pyrrolidinone (NMP) were purchased from Aldrich. Methanol and dimethyl sulfoxide (DMSO) were purchased from J. T. Baker. All solvents and chemicals were regent grade and were used as received.

2.2. Synthesis of Br-PS-Br Macroinitiator

20 g of styrene, 0.296 g CuCl, and 1.24 mL of HMTETA were added in a 250 mL flask. This green mixture was stirred until it formed a homogeneous solution. The solution was purged with nitrogen for 30 min, and then 0.22 mL of MBP was added. The mixture was placed in a 110°C oil bath for 4 h. After polymerization, the polymer product was diluted with THF. This solution was passed through an activated Al_2O_3 column to remove the catalyst. The polymer was then precipitated out with methanol. The Br-PS-Br homopolymer was then dried in a vacuum oven overnight at room temperature.

2.3 Synthesis of PHEA-b-PS-b-PHEA Triblock Copolymer

In a 250 mL pearshaped flask, 6 g of PS-Br was dissolved in 10 mL of toluene. Then, 6.5 mL of HEA, 0.089 g of CuCl, and 0.372 mL of HMTETA were added to the solution. This green mixture was stirred until a homogeneous solution formed. The solution was purged with nitrogen for 30 min, and then placed in a 50°C oilbath for 7 h. After polymerization, the block copolymer was diluted with THF. This solution was passed through an activated Al_2O_3 column to remove the catalyst. The polymer was then precipitated out with methanol. The PHEA-b-PS-b-PHEA triblock copolymer was then dried in a vacuum oven overnight at room temperature.



Scheme 1. Synthetic procedure for PHEA-*b*-PS-*b*-PHEA triblock copolymer via ATRP.

2.4. Preparation of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 Membranes

1 g of PHEA-b-PS-b-PHEA triblockcopolymer was dissolved in DMSO at 5 wt%. Varying amounts of IDA and H_3PO_4 were added to the PHEA-b-PS-b-PHEA solutions. Each polymer solution was cast into a Petri dish and dried in an oven at 80°C for 24 h and 100°C for 24 h. Finally, the membranes were cross-linked at 130°C for 3 h.

2.5. Proton Conductivity

A four-point probe method was used to measure the proton conductivity of the membranes using a home made conductivity cell, as illustrated in our recent paper [20]. The impedances of the samples were determined using an AC impedance analyzer (IM6e, ZAHNER, Germany). The impedance analyzer was operated in galvanostatic mode with an AC current amplitude of 0.1 mA over a frequency range of 1 MHz to 1 Hz using the Nyquist method. Proton conductivity was obtained as follows:

$$\sigma = \frac{L}{Rs} \tag{1}$$

where σ is the proton conductivity (in S/cm), and L is the distance (in cm) between the electrodes used to measure the potential. R is the impedance of the electrolyte (in Ω) and S is the surface area for ions to penetrate the electrolyte (in cm^2). The impedance of each sample was measured five-times to ensure good data reproducibility. All the measurements in this experiment were carried out under anhydrous conditions (relative humidity < 20%). The average estimated error was ± 5%.

2.6. Characterization of Membranes

FT-IR spectra of materials were collected using an Excalibur Series FT-IR (DIGLAB Co.) instrument in the frequency range of 4,000 to 600 cm^{-1} in attenuated total reflection (ATR) mode. The thermal properties of membranes were determined by thermal gravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851e, Columbus, OH). TGA measurements were performed under a nitrogen atmosphere at a rate of 20°C/min. The degradation of the membranes was measured using the weight loss percentage that occurred during the heating process.

3. Results and Discussion

3.1. Synthesis of PHEA-b-PS-b-PHEA Triblock Copolymer

The reaction scheme for the synthesis of PHEA-b-PS-b-PHEA triblock copolymer via ATRP is illustrated in Scheme 1 [21]. The synthesis of copolymer involves two steps, *i.e.* synthesis of PS-Br macroinitiator (Scheme 1(a)) and synthesis of PHEA-b-PS-b-PHEA triblock copolymer (Scheme 1(b)). The homopolymerization of styrene in bulk was initiated by MBP/CuCl/HMTETA and carried out at 110°C for 4 h. The resultant Br-PS-Br macroinitiator exhibited a molecular weight of 16,000 g/mol with a narrow molecular weight distribution (PDI = 1.3) as determined by gel permeation chromatography (GPC) [22]. The Br-PS-Br was directly used as a macroinitiator to synthesize PHEA-b-PS-b-PHEA triblock copolymer at 50°C for 7 h with CuCl/HMTETA of cupper/ligand complex. The resultant triblock copolymer showed a molecular weight of 40,000 g/mol and a polydispersity index (PDI) of 1.4 [22].

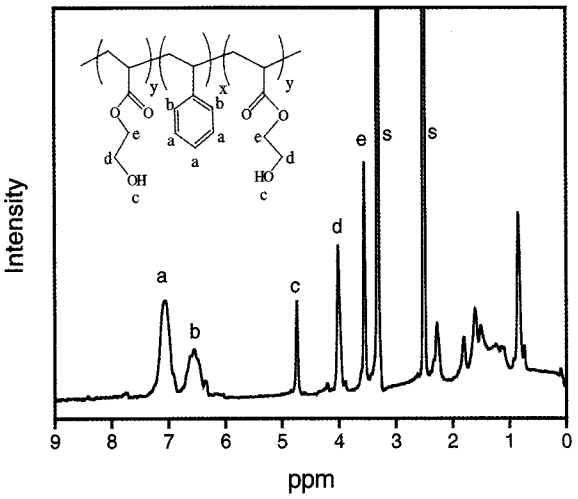
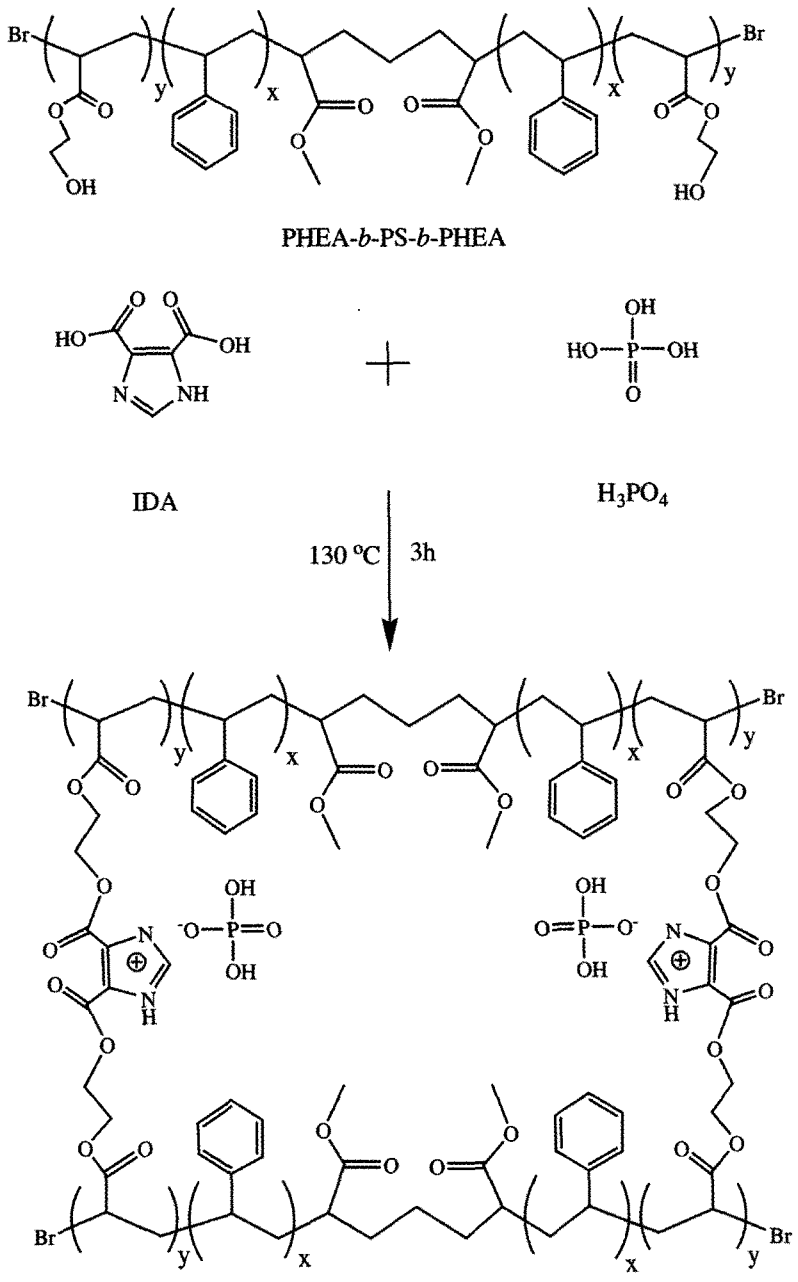


Fig. 1. ^{1}H NMR spectrum of PHEA-b-PS-b-PHEA triblock copolymer.

The triblock copolymerization of HEA from Br-PS-Br macroinitiator via ATRP was confirmed by ^{1}H NMR spectroscopy, as shown in Fig. 1. The peaks at 7.1 and 6.6 ppm are attributed to benzene groups of PS blocks. Block copolymerization of PHEA produced peaks in the region of 4.8, 4.0 and 3.6 ppm, attributable to the protons of PHEA chains [18]. Upon comparison of the integral area of the peak at 7.1 ppm (or 6.6) from PS chains with that of the peak at 4.8 ppm (or 4.0 or 3.6 ppm) from PHEA chains, the composition of PHEA-b-PS-b-PHEA triblock copolymer was calculated to be PS : PHEA = 51 : 49 wt%.

Fig. 2 shows the FT-IR spectra of Br-PS-Br macroinitiator and PHEA-b-PS-b-PHEA triblock copolymer synthesized by ATRP. The aromatic C=C stretching modes of neat PS produced four peaks at 1,601, 1,583, 1,494 and 1,451 cm^{-1} (Fig. 2(a)). Upon block copolymerization with PHEA, the new stretching bands appeared at 3,391, 1,720 and 1,167 cm^{-1}, attributable to -OH, -C=O and C-O of PHEA, respectively. This FT-IR spectroscopic result supports the successful synthesis of block copolymer by ATRP.



Scheme 2. Schematic procedure for the preparation of crosslinked PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes.

3.2. Preparation of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 Membranes

Scheme 2 illustrates the procedure for preparation of the anhydrous crosslinked membranes consisting of PHEA-b-PS-b-PHEA triblock copolymer, IDA and H_3PO_4. The triblock copolymer was thermally cross-linked with IDA via the esterification between the -OH groups of PHEA and the COOH groups of IDA at high temperatures, e.g. 130°C. Upon doping with H_3PO_4, the complexes of imidazole-H_3PO_4 were formed, producing anhydrous polymer electrolyte membranes. Four kinds of composition were used to prepare the

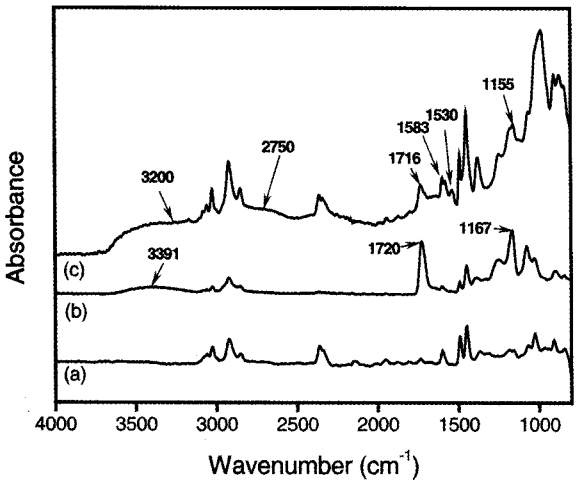


Fig. 2. FT-IR spectra of (a) Br-PS-Br, (b) PHEA-b-PS-b-PHEA triblock copolymer and (c) PHEA-b-PS-b-PHEA/IDA/H_3PO_4 crosslinked membrane.

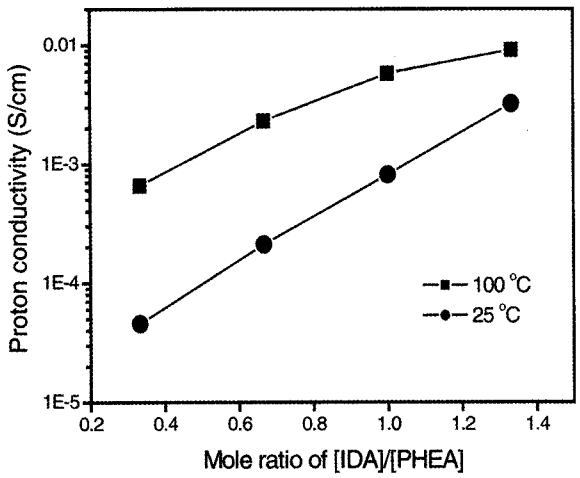


Fig. 3. Proton conductivities of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes as a function of IDA contents.

membranes, *i.e.* the mole ratio of added [PHEA] : [IDA] : [H_3PO_4] = 3:1:1, 3:2:2, 3:3:3 and 3:4:4. The mole ratio of IDA to H_3PO_4 was always fixed at unity because 1:1 mole ratio of imidazole:H_3PO_4 was reasonable [23,24].

The FT-IR spectrum of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 crosslinked membrane was also included in Fig. 2(c). The membrane sample with a mole ratio of added [PHEA] : [IDA] : [H_3PO_4] = 3:2:2 was used. The PHEA-b-PS-b-PHEA triblock copolymer exhibited strong absorption at 1,720 cm^{-1}, assigned to C=O stretching mode in PHEA. When IDA/H_3PO_4 was introduced and consequently crosslinked, the peak at 1,720 cm^{-1} shifted to the wavenumber at 1,716 cm^{-1} (Fig. 2(c)). This peak shift indicates that the PHEA-b-PS-b-PHEA triblock copolymer is crosslinked with IDA via the esterification of the -OH groups of PHEA and the -COOH groups of IDA [18,19]. The crosslinked PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membrane also exhibited absorption bands at 3,200 and 2,750 cm^{-1}, attributable to NH and hydrogen bonded OH groups in the membranes. Characteristic peaks of imidazole groups were also observed at 1,583 and 1,530 cm^{-1} [23,24].

3.3. Conductivity and Thermal Properties of Membranes

Fig. 3 shows the proton conductivity of crosslinked PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes at 25 and 100°C as a function of IDA concentration. For both temperatures, the membranes exhibited the increase of proton conductivity with the increasing mole ratio of IDA to PHEA. As the concentration of IDA increases, the concentration of H_3PO_4 also increases because the ratio of H_3PO_4 to IDA was fixed at unity for all the membranes. Therefore, the proton conductivity of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes increased with the IDA concentrations.

The effect of temperature on the proton conductivities of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes was investigated and presented in Fig. 4 as a function of inverse temperature. All the membranes showed the increase of the proton conductivities with the elevation of temperature. The increase of temperature in polymer electrolyte membranes favors both the dynamics of proton transport and the structural reorganization of polymeric chains, resulting in the increase of proton conductivity at high temperatures. The temperature dependence of proton conductivity in crosslinked PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes fits well with the Arrhenius equation. The PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membrane with [PHEA] : [IDA] : [H_3PO_4] = 3:4:4 showed the maximum conductivity of 0.01 S/cm at 100°C at anhydrous conditions, which is comparable to that of poly(2,5-benzimidazole) (PBI) membranes [25].

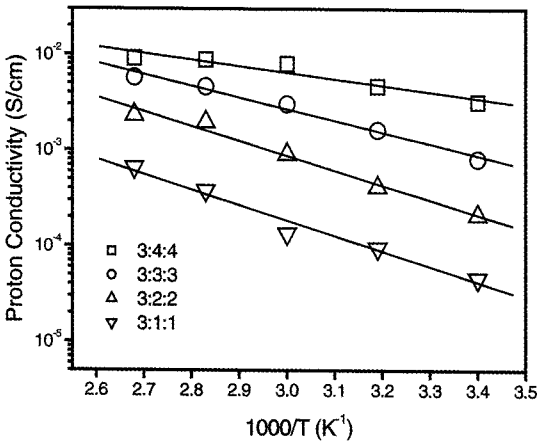


Fig. 4. Temperature dependent proton conductivities of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes with different mole ratios of [PHEA]:[IDA]:[H_3PO_4].

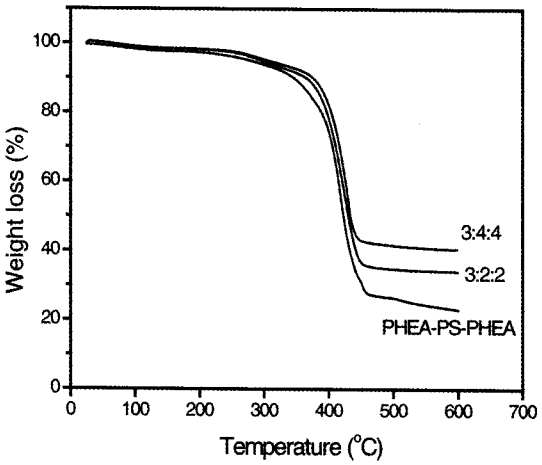


Fig. 5. TGA data for PHEA-b-PS-b-PHEA triblock copolymer and PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes with different mole ratios of [PHEA]:[IDA]:[H_3PO_4].

The thermal stabilities of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes were characterized using TGA. The TGA data for PHEA-b-PS-b-PHEA and PHEA-b-PS-b-PHEA/IDA/H_3PO_4 crosslinked membranes with 3:2:2 and 3:4:4 mole ratios of [PHEA]:[IDA]:[H_3PO_4] are presented in Fig. 5. The small weight loss observed in all the samples below 150°C is mostly due to the loss of water adsorbed because of the hygroscopic nature of the membrane. When IDA/H_3PO_4 was introduced and subsequently crosslinked, the residual amounts of membranes increased upon reaching 600°C. This result represents that the crosslinked structure of the membranes and the formation of imidazole-H_3PO_4 complexes enhance the thermal properties of the polymer electrolyte membranes. Overall, the PHEA-b-PS-b-PHEA/IDA/H_3PO_4 crosslinked membranes were thermally stable up to 350°C.

4. Conclusions

Anhydrous polymer electrolyte membranes based on a triblock copolymer were prepared using ATRP process and thermal crosslinking reaction. PHEA-b-PS-b-PHEA triblock copolymer was synthesized through ATRP and thermally crosslinked with IDA via the esterification between the -OH groups of PHEA and the COOH groups of IDA, as revealed by FT-IR spectroscopy. The anhydrous polymer electrolyte membranes were prepared by doping with H_3PO_4 to form imidazole-H_3PO_4 complexes. The proton conductivities of PHEA-b-PS-b-PHEA/IDA/H_3PO_4 membranes increased with increasing temperature and increasing contents of IDA in the membranes. A maximum proton conductivity of 0.01 S/cm at [PHEA] : [IDA] : [H_3 PO_4] = 3:4:4 was observed at 100°C under anhydrous conditions. The characterization of the membranes by TGA demonstrated their good thermal stability up to 350°C. The esterification used in the current work might be susceptible to low hydrolytic stability of membranes upon doing H_3PO_4. Thus, the development of the membranes with stronger crosslinking units is necessary, which is now in progress in our lab.

Acknowledgement

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