

## Polystyrene-*b*-Poly(hydroxyl ethyl methacrylate) 블록 공중합체를 이용한 무가습 고분자 전해질막

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### Anhydrous Polymer Electrolyte Membranes Prepared From Polystyrene-*b*-Poly (hydroxyl ethyl methacrylate) Block Copolymer

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**요약:** 원자전달 라디칼 중합을 이용하여 polystyrene-*b*-poly (hydroxyethyl methacrylate) (PS-*b*-PHEMA) 블록 공중합체를 합성한 뒤, 블록 공중합체의 -OH 그룹과 이미다졸 디카르복실릭산 (IDA)의 -COOH 그룹과의 에스테르 반응에 의하여 가교된 전해질막을 제조하였다. 인산(H<sub>3</sub>PO<sub>4</sub>)을 도핑하여 이미다졸-인산 착체를 형성한 결과, 인산 함량이 증가함에 따라 공중합체 전해질막의 수소 이온 전도도가 계속 증가하였다. 또한 인장강도와 인장률 모두 인산 함량에 따라 증가하였다. 특히 [HEMA]:[IDA]:[H<sub>3</sub>PO<sub>4</sub>]=3:4:4의 조성을 갖는 PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> 블록 공중합체 전해질막은 100°C의 비가습 조건에서 최대 0.01 S/cm의 수소이온 전도도를 나타내었다. 열분석(TGA) 실험을 통하여 전해질막은 350°C의 고온까지 열적으로 안정함을 확인하였다.

**Abstract:** A block copolymer of polystyrene-*b*-poly (hydroxyl ethyl methacrylate), PS-*b*-PHEMA, was synthesized via atom transfer radical polymerization (ATRP) and crosslinked with 4,5-imidazole dicarboxylic acid (IDA) via esterification of the -OH groups of PHEMA in the block copolymer and the -COOH groups of IDA. Upon doping with H<sub>3</sub>PO<sub>4</sub> to form imidazole-H<sub>3</sub>PO<sub>4</sub> complexes, the proton conductivity of the membranes continuously increased as the content of H<sub>3</sub>PO<sub>4</sub> increased. In addition, both the tensile strength and the elongation at break increased with IDA content. A proton conductivity of 0.01 S/cm at 100°C was obtained for the PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membrane with [HEMA]:[IDA]:[H<sub>3</sub>PO<sub>4</sub>]=3:4:4 under anhydrous conditions. All of the PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membranes were thermally stable up to 350°C, as revealed by thermal gravimetric analysis (TGA).

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

## 1. Introduction

A fuel cell is an electrochemical device that combines hydrogen and oxygen using an electrocatalysts such as Pt to produce electricity. Fuel cell is an attractive device alternative to combustion engines for electrical power generation due to its high efficiencies and low pollution levels. Among many types of fuel cells, polymer elec-

trolyte membrane fuel cell (PEMFC) has been receiving increased attention because of its high energy efficiency, environmentally friendly nature and good flexibility in structures [1-3].

A representative polymer electrolyte membrane is perfluorosulfonic acid membranes, such as Nafion from DuPont, which are chemically inert in both the oxidizing and reducing atmospheres of the fuel cell. At ambient pressures and temperatures below 100°C, hydrated Nafion

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exhibits a high proton conductivity up to  $0.19 \text{ S cm}^{-1}$ . However, Nafion membrane contains certain drawbacks which need to be overcome, i.e. the poor performance at temperature above  $80^\circ\text{C}$  due to the loss of the water. In addition, the production cost of perfluorinated membranes is extremely high, which make it difficult for an industrialization of the PEMFC. Thus, many efforts have been dedicated to the development of high performance polymer electrolyte membranes based on a cheap material and thermal stability at high temperature [4-10].

A block copolymer consists of more than two domains with different chemical properties. Using microphase-separated structure of block copolymer, higher ionic properties as well as desirable mechanical properties were simultaneously incorporated into a material. Thus, it may allow a better control of structure and ion conducting path in polymer electrolyte membranes [11,12]. In this work, we prepared anhydrous polymer electrolyte membranes based on polystyrene-*b*-poly (hydroxyl ethyl methacrylate) (PS-*b*-PHEMA) block copolymer. The block copolymer was synthesized through atom transfer radical polymerization (ATRP) [13,14]. This block copolymer was crosslinked with 4,5-imidazole dicarboxylic acid (IDA) via the esterification of -OH groups of PHEMA and -COOH groups of IDA [15,16]. The anhydrous polymer electrolyte membranes were prepared upon doping with phosphoric acid ( $\text{H}_3\text{PO}_4$ ) to form imidazole- $\text{H}_3\text{PO}_4$  complexes. The resultant anhydrous polymer electrolyte membranes were characterized in terms of proton conductivity, mechanical and thermal properties.

## 2. Experimental

### 2.1. Materials

Styrene (99%), 2-hydroxy ethyl methacrylate (HEMA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper(I) chloride ( $\text{CuCl}$ , 99%), methyl 2-bromo-propionate (MBP), 4,5-imidazole dicarboxylic acid (IDA), phosphoric acid ( $\text{H}_3\text{PO}_4$ ) were purchased from Aldrich. Methanol, N-methyl-2-pyrrolidinone (NMP) and dimethyl sulfoxide (DMSO) were purchased from J. T. Baker. All solvents and chemicals were reagent grade and

were used as received.

### 2.2. Synthesis of PS-Br Macroinitiator

20 g of styrene, 0.296 g  $\text{CuCl}$ , 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  $110^\circ\text{C}$  oil bath for 5 h. After polymerization, the polymer product was diluted with THF. This solution was passed through an activated  $\text{Al}_2\text{O}_3$  column to remove the catalyst. The polymer was then precipitated out with methanol. The PS-Br homopolymer was then dried in a vacuum oven overnight at room temperature.

### 2.3. Synthesis of PS-*b*-PHEMA Block Copolymer

In a 250 ml flask, 6 g of PS-Br was dissolved in 10 ml of toluene. Then, 6.5 mL of HEMA, 0.089 g of  $\text{CuCl}$ , 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  $50^\circ\text{C}$  oil bath for 7 h. After polymerization, the block copolymer was diluted with THF. This solution was passed through an activated  $\text{Al}_2\text{O}_3$  column to remove the catalyst. The polymer was then precipitated out with methanol. The PS-*b*-PHEMA block copolymer was then dried in a vacuum oven overnight at room temperature.

### 2.4. Preparation of PS-*b*-PHEMA/IDA/ $\text{H}_3\text{PO}_4$ Membranes

1 g of PS-*b*-PHEMA block copolymer was dissolved in DMSO at 5 wt%. Varying amounts of IDA and  $\text{H}_3\text{PO}_4$  were added to PS-*b*-PHEMA solutions [17]. Each polymer solution was cast into a Petri dish and dried in an oven at  $80^\circ\text{C}$  for 24 h and  $100^\circ\text{C}$  for 24 h. Finally, the membranes were crosslinked at  $130^\circ\text{C}$  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 [17-19].

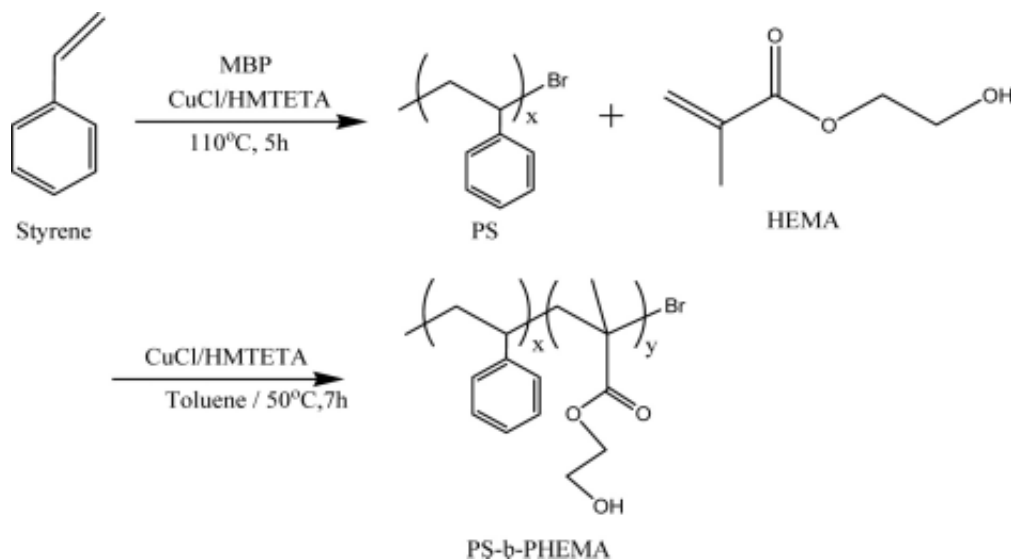


Fig. 1. Synthetic procedure for PS-b-PHEMA block copolymer via ATRP.

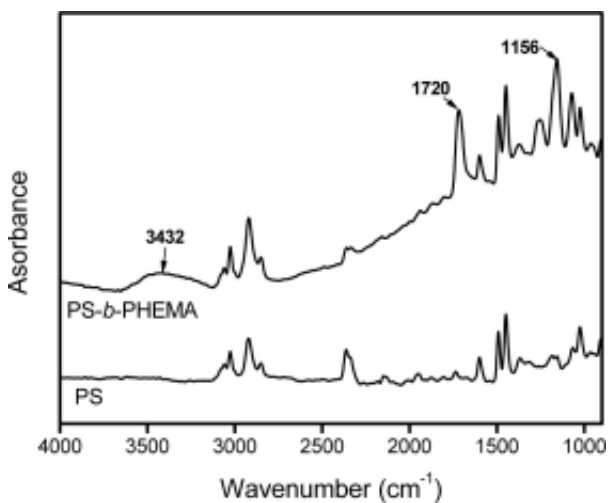


Fig. 2. FT-IR spectra of PS and PS-b-PHEMA block copolymer.

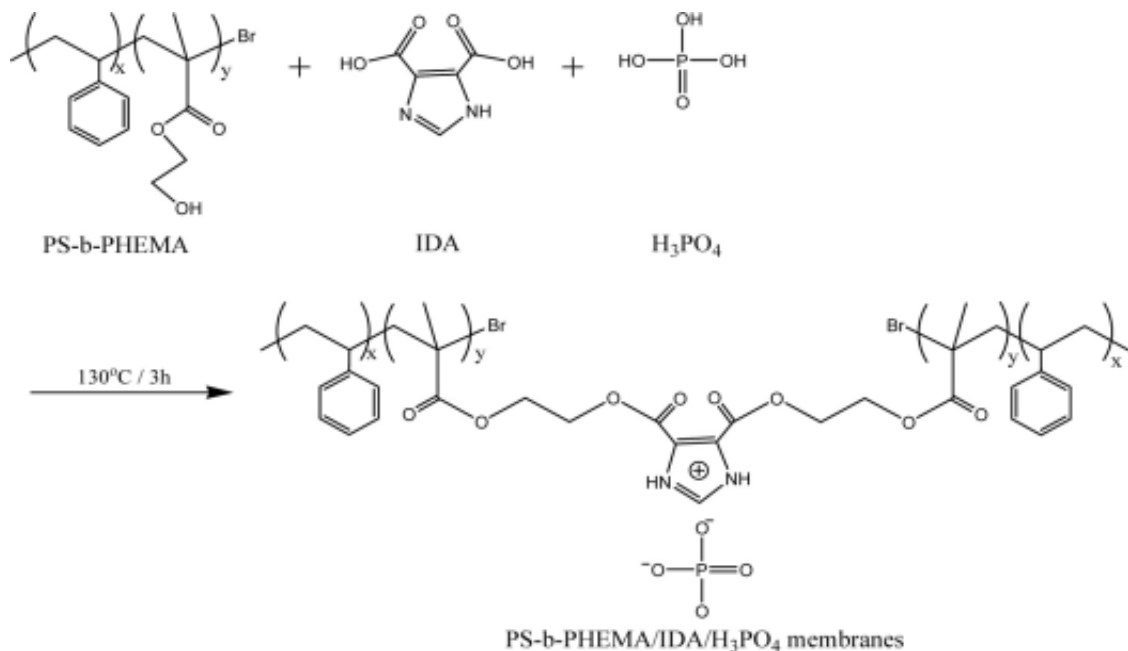
The impedances of the samples were determined using an AC impedance analyzer (IM6e, ZAHNER, Germany). The impedance analyzer was operated in galvanostatic mode with an AC current amplitude of 0.1 mA over a frequency range of 1 MHz to 1 Hz using the Nyquist method. Proton conductivity was obtained as follows:

$$\sigma = \frac{L}{RS} \quad (1)$$

where  $\sigma$  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  $\Omega$ ) and  $S$  is the surface area for ions to penetrate the electrolyte (in  $\text{cm}^2$ ). 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  $\pm 5\%$ .

## 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 400  $\text{cm}^{-1}$  in attenuated total reflection (ATR) mode. Tensile evaluation was performed with a universal testing machine (UTM, LR10KPlus Series) at a speed of 5 mm/min. All the measurements in the UTM experiment were carried out at 23°C and 50% RH. All the films were rectangular with a length of 2 cm and a width of 0.7 cm. The average thickness of the films was approximately 80  $\mu\text{m}$ . 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 per-



**Fig. 3.** Schematic procedure for the preparation of crosslinked PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membranes.

centage that occurred during the heating process. Nuclear magnetic resonance (<sup>1</sup>H-NMR) measurements were performed with 600 MHz, high resolution NMR spectrometer (AVANCE 600 MHz FT-NMR, Germany, Bruker). Gel permeation chromatography (GPC) was performed at room temperature (25°C) using a Waters 600E system equipped with Waters Styragel columns and a Waters 410 differential refractometer as a detector. Tensile evaluation was performed with a universal testing machine (UTM, LR-10KPlus Series) at a speed of 5 mm/min.

### 3. Results and Discussion

The reaction scheme for the synthesis of PS-*b*-PHEMA block copolymer via ATRP is illustrated in Fig. 1. The synthesis of copolymer involves two steps, including synthesis of PS-Br macroinitiator and synthesis of PS-*b*-PHEMA diblock copolymer. The homopolymerization of styrene in bulk was initiated by MBP/CuCl/HMTETA and carried out at 110°C for 5 h. The resultant PS-Br exhibited a molecular weight of 14,000 g/mol with a narrow molecular weight distribution (PDI = 1.3) as determined by gel permeation chromatography (GPC) [15].

The PS-Br was directly used as a macroinitiator to synthesize PS-*b*-PHEMA diblock copolymer at 50°C for 7 h with CuCl/HMTETA of copper/ligand complex. The resultant diblock copolymer showed a molecular weight of 19,000 g/mol and a polydispersity index (PDI) of 1.4. According to the <sup>1</sup>H NMR spectroscopy, the block copolymer has a composition of 56:44 wt% in PS-*b*-PHEMA [15].

The FT-IR spectra of PS macroinitiator and PS-*b*-PHEMA block copolymer synthesized by ATRP are presented in Fig. 2. The aromatic C=C stretching modes of pristine PS-Br produced four peaks at 1,601, 1,583, 1,494 and 1,451 cm<sup>-1</sup>. After block copolymerization with PHEMA, the new stretching bands appeared at 3,432, 1,720 and 1,156 cm<sup>-1</sup>, assigned to -OH, -C=O and C-O of PHEMA, respectively. This FT-IR spectroscopic result strongly supports the successful synthesis of block copolymer via ATRP.

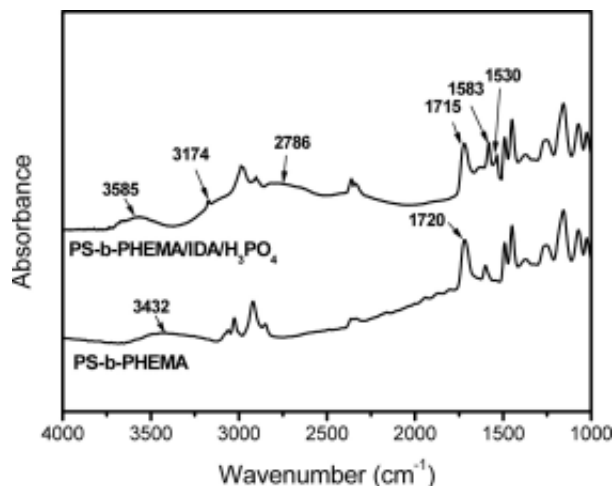
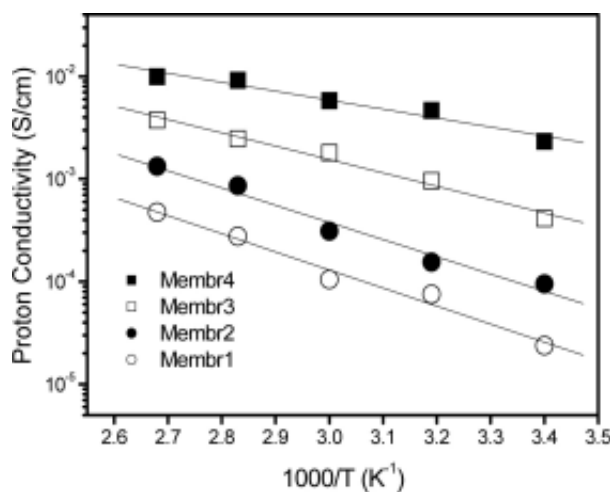
Anhydrous crosslinked membranes that deliver proton conductivity were prepared by combining PS-*b*-PHEMA block copolymer, IDA and H<sub>3</sub>PO<sub>4</sub>, as illustrated in Fig. 3. The block copolymer synthesized via ATRP was thermally crosslinked with IDA via the esterification of the -OH

**Table 1.** Composition of Crosslinked PS-b-PHEMA/IDA/ $H_3PO_4$  Membranes

	Mole ratio of added [PHEMA]:[IDA]:[ $H_3PO_4$ ]
Membr1	3 : 1 : 1
Membr2	3 : 2 : 2
Membr3	3 : 3 : 3
Membr4	3 : 4 : 4

groups of PHEMA and the  $-COOH$  groups of IDA at high temperatures such as  $130^\circ C$ . Some IDA molecules might be covalently just linked from a single polymeric chain without crosslinking but it is not easy to determine the degree of crosslinking quantitatively. Upon doping with  $H_3PO_4$ , the complexes of imidazole- $H_3PO_4$  were formed to produce anhydrous polymer electrolyte membranes. Thus, IDA plays an important role as a crosslinking agent as well as a ligand for a dopant. The membranes with four different compositions of [PHEMA]:[IDA]:[ $H_3PO_4$ ] were prepared and the mole ratio of IDA to  $H_3PO_4$  was always fixed at unity, as shown in Table 1. It should be noted that the membranes with the [PHEMA]:[IDA]:[ $H_3PO_4$ ] contents higher than 3:4:4 did not form a homogenous film.

The FT-IR spectra of PS-b-PHEMA block copolymer and PS-b-PHEMA/IDA/ $H_3PO_4$  crosslinked membrane are shown in Fig. 4. The membrane with a mole ratio of added [PHEMA]:[IDA]:[ $H_3PO_4$ ]=3:2:2 was chosen as a representative sample. The PS-b-PHEMA block copolymer exhibited a strong absorption at  $1,720\text{ cm}^{-1}$ , attributable to carbonyl ( $C=O$ ) stretching mode in PHEMA. When IDA/ $H_3PO_4$  was introduced and crosslinked thermally, the peak at  $1,720\text{ cm}^{-1}$  shifted to the wavenumber at  $1,715\text{ cm}^{-1}$ . This peak shift indicates that the PS-b-PHEMA block copolymer was crosslinked with IDA via the esterification of the  $-OH$  groups of PHEMA and the  $-COOH$  groups of IDA [15,16]. In addition, the stretching band of  $-OH$  at  $3,432\text{ cm}^{-1}$  in PS-b-PHEMA block copolymer was reduced and shifted to a higher wavenumber of  $3,585\text{ cm}^{-1}$  upon thermal crosslinking. It also supports the esterification in the membranes and the peak shift of  $-OH$  stretching is presumably due to the different hydrogen

**Fig. 4.** FT-IR spectra of PS-b-PHEMA and PS-b-PHEMA/IDA/ $H_3PO_4$  crosslinked membranes.**Fig. 5.** Temperature dependent proton conductivities of PS-b-PHEMA/IDA/ $H_3PO_4$  membranes with different mole ratios of [PHEMA]:[IDA]:[ $H_3PO_4$ ].

bonding interaction strength by doping agent of  $H_3PO_4$ . The crosslinked PS-b-PHEMA/IDA/ $H_3PO_4$  membrane also showed other absorption bands at  $3,174$  and  $2,786\text{ cm}^{-1}$ , assigned to  $-NH$  and hydrogen bonded  $-OH$  groups in the membranes [20,21]. Other characteristic peaks coming from the imidazole groups were also observed at  $1,583$  and  $1,530\text{ cm}^{-1}$  [20,21].

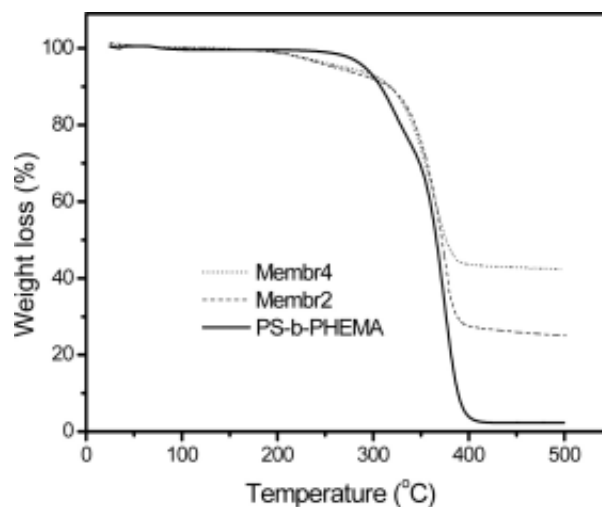
Fig. 5 shows the variation of proton conductivities of PHEMA/IDA/ $H_3PO_4$  crosslinked membranes with various compositions as a function of inverse temperature. All the membranes exhibited the increase of proton conductivity

**Table 2.** Mechanical Properties of PS-*b*-PHEMA and Cross-linked PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> Membranes

	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
PS- <i>b</i> -PHEMA	1.5	2.4	82.3
Membr1	7.6	8.8	120.5
Membr2	15.3	15.7	139.5
Membr3	21.8	25.6	150.6
Membr4	24.4	27.8	152.3

with the increasing mole ratio of IDA to PHEMA. As the concentration of IDA increases, the concentration of H<sub>3</sub>PO<sub>4</sub> also increases because the molar ratio of H<sub>3</sub>PO<sub>4</sub> to IDA was fixed at unity throughout the membranes. Therefore, the proton conductivity of PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membranes increased with the IDA concentrations. In addition, all the membranes showed the enhancement of proton conductivity as temperature was raised. The elevation 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 [20-22]. The temperature dependent proton conductivity of crosslinked PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membranes fitted well with the Arrhenius equation. The proton conductivity of PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membrane with [PHEMA]:[IDA]:[H<sub>3</sub>PO<sub>4</sub>]=3:4:4 reached 0.01 S/cm at 100°C at anhydrous conditions.

Mechanical properties of polymer electrolyte membranes would be of pivotal importance in application to membrane electrode assembly (MEA). Thus, tensile evaluation was performed on the membranes using UTM at a speed of 5 mm/min and summarized in Table 2 where tensile strength at break (MPa), elongation at break (%) and Young's modulus (MPa) are shown. All mechanical properties of the membranes were enhanced with increasing IDA/H<sub>3</sub>PO<sub>4</sub> concentrations, presumably due to both the crosslinking of the membranes and the formation of imidazole-H<sub>3</sub>PO<sub>4</sub> complexes [22]. The maximum mechanical properties of membranes were tensile strength at break of 24.4 MPa, elongation at break of 27.8%, and

**Fig. 6.** TGA data for PS-*b*-PHEMA block copolymer and PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membranes with different mole ratios of [PHEMA]:[IDA]:[H<sub>3</sub>PO<sub>4</sub>].

Young's modulus of 152.3 MPa.

Thermal properties of PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membranes were investigated using TGA. The TGA data for PS-*b*-PHEMA and PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> crosslinked membranes with different mole ratios of [PHEMA]:[IDA]:[H<sub>3</sub>PO<sub>4</sub>] are presented in Fig. 6. The small weight loss below 150°C was observed for all the membranes, attributed to the loss of water adsorbed resulting from the hygroscopic nature of membrane. In addition, all the samples including PS-*b*-PHEMA block copolymer and PS-*b*-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> crosslinked membranes were thermally stable up to 350°C. When IDA/H<sub>3</sub>PO<sub>4</sub> was introduced and crosslinked thermally, the residual amounts of membranes were increased. This result represents that the crosslinked structure of membranes and the formation of imidazole-H<sub>3</sub>PO<sub>4</sub> complexes enhance the thermal properties of polymer electrolyte membranes.

#### 4. Conclusions

Anhydrous polymer electrolyte membranes based on a block copolymer were prepared using ATRP process and thermal crosslinking reaction. PS-*b*-PHEMA block copolymer was synthesized through ATRP and thermally crosslinked with IDA via the esterification of -OH groups

of PHEMA and -COOH groups of IDA, as revealed by FT-IR spectroscopy. The anhydrous polymer electrolyte membranes were prepared upon doping with H<sub>3</sub>PO<sub>4</sub> to form imidazole-H<sub>3</sub>PO<sub>4</sub> complexes. Both the proton conductivities and mechanical properties of PS-b-PHEMA/IDA/H<sub>3</sub>PO<sub>4</sub> membranes increased with increasing contents of IDA in the membranes. A proton conductivity of 0.01 S/cm was obtained in the membranes with [HEMA]:[IDA]:[H<sub>3</sub>PO<sub>4</sub>]=3:4:4 at 100°C under anhydrous conditions. The characterization of the membranes by TGA demonstrated their good thermal stability up to 350°C.

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