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### Crosslinked Composite Polymer Electrolyte Membranes Based On Diblock Copolymer and Phosphotungstic Acid

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**요약:** 폴리스티렌-블록-폴리히드록에틸 메타크릴레이트(PS-*b*-PHEMA), 술포석시닉산(SA), 인텟스텐산(PWA)으로 구성된 수소 이온 전도성 나노복합 고분자 전해질막을 제조하였다. 폴리히드록에틸 메타크릴레이트(PHEMA) 블록의 히드록실 그룹(-OH)와 술포석시닉산(SA)의 -COOH 그룹과의 에스테르 반응에 의하여 전해질막을 가교시켰다. 폴리헤테로산(PWA)을 도입했을 때, SO<sub>3</sub><sup>-</sup> 그룹의 신축 밴드가 1187 cm<sup>-1</sup>에서 1158 cm<sup>-1</sup>로 낮아졌으며, 이는 PWA 입자가 전해질막의 술포산 그룹과 상호작용함을 나타낸다. PWA 함량이 30 wt%가 되었을 때, 상온 전도도는 0.045에서 0.062 S/cm로 증가되었으며, 이는 PWA 입자의 고유 전도도 특성과 전해질막의 술포산기의 산도가 증가했기 때문이다. 또한 30 wt%를 함유한 복합 전해질막은 100°C에서는 최대 0.126 S/cm의 수소 이온 전도도를 나타내었다. PWA가 첨가됨에 따라 복합 전해질막의 열적특성 또한 증가하였다.

**Abstract:** Proton conductive hybrid nanocomposite polymer electrolyte membranes comprising polystyrene-*b*-poly(hydroxyethyl methacrylate) (PS-*b*-PHEMA), sulfosuccinic acid (SA) and phosphotungstic acid (PWA) were prepared by varying PWA concentrations. The PHEMA block was thermally crosslinked by SA via the esterification reaction between -OH of PHEMA and -COOH of SA. Upon the incorporation of PWA into the diblock copolymer, the symmetric stretching bands of the SO<sub>3</sub><sup>-</sup> group at 1187 cm<sup>-1</sup> shifted to a lower wavenumber at 1158 cm<sup>-1</sup>, demonstrating that the PWA particles strongly interact with the sulfonic acid groups of SA. When the concentration of PWA was increased to 30 wt%, the proton conductivity of the composite membrane at room temperature increased from 0.045 to 0.062 S/cm, presumably due to the intrinsic conductivity of the PWA particles and the enhanced acidity of the sulfonic acid in the membranes. The membrane containing 30 wt% of PWA exhibited a proton conductivity of 0.126 S/cm at 100°C. Thermal stability of the composite membranes was also enhanced by introducing PWA nanoparticles.

**Keywords:** composite membrane, heteropolyacid, polymer electrolyte membranes, block copolymer, proton conductivity

## 1. Introduction

Polymer electrolytes have been received great attention as a promising material for use in secondary batteries [1,2], dye sensitized solar cells [3] and facilitated olefin transport membranes [4]. Especially, proton con-

ductive polymer electrolyte membranes with negatively charged sulfonic acid groups (-SO<sub>3</sub><sup>-</sup>) have received particular attention for use in fuel cell applications [5-12].

The easier transportation of proton ions is one of the most crucial properties in a successful fuel cell membrane. Currently, the most commonly used polymer electrolyte membrane is a perfluorinated sulfonic acid membrane, known by its trade name Nafion. The

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widely accepted attributes of this polymer membrane are excellent thermal and mechanical properties as well as high proton conductivity, i.e.  $\sim 0.1$  S/cm at room temperature. However, high cost, low proton conductivity, and low water uptake at high temperatures have prevented the perfluorinated sulfonated membranes from being used in large scale applications.

A high proton conductivity of sulfonated polymer membranes is of pivotal importance in improving the efficiency of fuel cells. However, conventional sulfonated polymers exhibit trade-off behaviour between proton conductivity and mechanical properties. This trade-off behaviour can be controlled to some degree by adjusting the hydrophilic/hydrophobic balance properties of a membrane. Several methods have been carried out, such as crosslinking polymer membrane, grafting a selective species onto a membrane, copolymerization, and blending a hydrophilic polymer with a hydrophobic polymer [13-17].

Hybrid organic/inorganic composite membranes are being widely developed for high temperature fuel cell applications, because many of the inorganic materials are capable of operating at a much higher temperature than a pure polymer [18-21]. The incorporation of inorganic compounds, e.g. heteropolyacids into the neat polymer membranes enhances proton conductivity, water retention, and mechanical strength at high temperatures, e.g.  $> 100^\circ\text{C}$ .

In this study, we synthesized a diblock copolymer, polystyrene-*b*-poly(hydroxyethyl methacrylate) (PS-*b*-PHEMA) with 56 : 44 wt% via atom transfer radical polymerization (ATRP). The copolymer was blended with varying concentrations of phosphotungstic acid (PWA) and the PHEMA block was thermally cross-linked by sulfosuccinic acid (SA) via the esterification reaction between -OH of PHEMA and -COOH of SA. The hybrid organic/inorganic nanocomposite membranes were characterized in terms of proton conductivity, water uptake, morphological properties, and thermal properties. Particular attention was focused on the specific hydrogen bonding interactions between the PS-*b*-PHEMA diblock copolymer and the PWA nanoparticles.

## 2. Experimental

### 2.1. Materials

Styrene (99%), 2-hydroxyethyl methacrylate (HEMA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper (I) chloride (CuCl, 99%), methyl 2-bromo-propionate (MBP) and phosphotungstic acid (PWA,  $\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4]$ ) were purchased from Aldrich. The PWA was dried at  $100^\circ\text{C}$  in an air circulating oven overnight before use. The other reagents were used as received without further purification.

### 2.2. Synthesis of 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  $110^\circ\text{C}$  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 Diblock Copolymer

In a 250 mL pearshaped flask, 6 g of PS-Br was dissolved in 10 mL of toluene. Then, 6.5 mL of HEMA, 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  $50^\circ\text{C}$  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 diblock copolymer was then dried in a vacuum oven overnight at room temperature.

#### 2.4. Preparation of Crosslinked Composite Polymer Electrolyte Membranes

The nanocomposite polymer electrolyte membranes consisting of PS-*b*-PHEMA diblock copolymer, SA and PWA were prepared using solution casting method. The concentration of SA was always fixed at 20 wt% of the polymer content and the concentration of PWA was changed from 10 to 50 wt% in the total membrane content. The diblock copolymer, SA and the desired amount of PWA were dissolved in DMSO together to form a transparent solution. After complete dissolution, the polymer solutions were cast onto a glass dish. The solutions were dried in a convection oven at 80°C for 48 h, and then in a vacuum oven at 100°C for 24 h. The obtained membranes were peeled off from the dishes and then annealed at 120°C for 3 h for crosslinking reaction [16,21].

#### 2.5. Proton Conductivity

A four-point probe method was used to measure the proton conductivity of the membranes. The membranes were equilibrated with deionized water before measurement. Complex impedance measurements were carried out at 25°C between 1 Hz and 8 MHz using a ZAHNER IM-6 impedance analyzer. The impedance spectra of the membranes were used to generate Nyquist plots; the proton conductivity was calculated from these plots [22].

#### 2.6. Characterization

Nuclear magnetic resonance (<sup>1</sup>H-NMR) analysis was performed with a 600 MHz high resolution NMR spectrometer (AVANCE 600 MHz FT-NMR, Germany, Bruker). FTIR spectra of the samples were collected

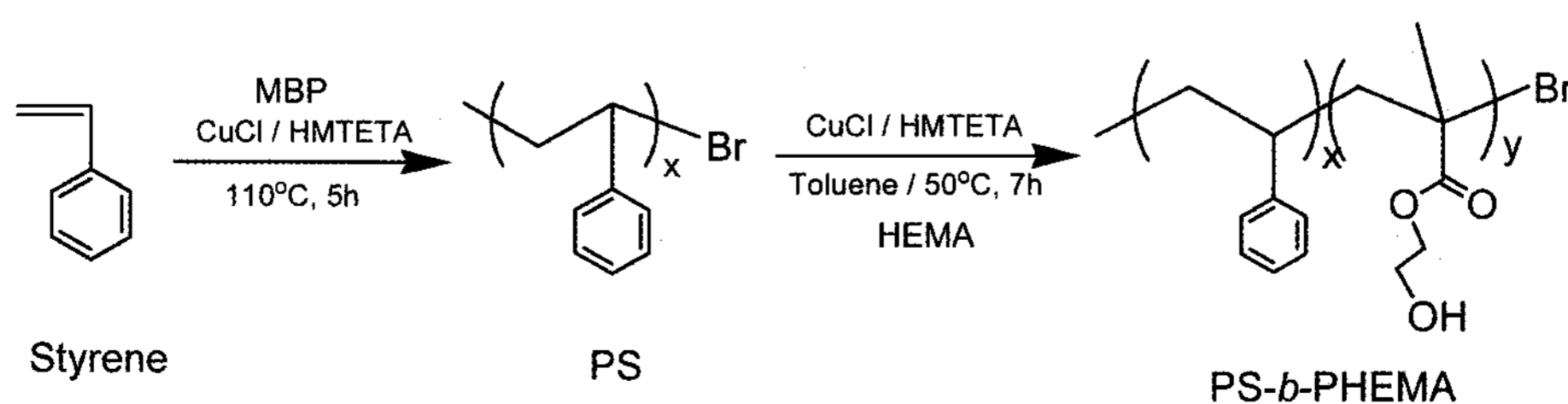
from 4000 to 400 cm<sup>-1</sup> using the ATR accessory of an Excalibur Series FTIR (DIGLAB Co.) instrument. The thermal properties of the membranes were investigated using thermal gravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851e, Columbus, OH). TGA analysis was performed from room temperature up to 600°C at a heating rate of 20°C/min. The weight loss percentage of the membrane during heating was recorded.

### 3. Results and Discussion

#### 3.1. Synthesis of Diblock Copolymer

The synthesis of PS-*b*-PHEMA diblock copolymer is schematically illustrated in Scheme 1. The synthesis of the copolymer was carried out in two steps: 1) synthesis of PS-Br macroinitiator, and 2) 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 obtained PS-Br had a molecular weight of 14,000 g/mol with a narrow molecular weight distribution (PDI = 1.3) as determined by GPC [16]. The yield of polymerization was as high as 90%. The PS-*b*-PHEMA diblock copolymer was synthesized using CuCl/HMTETA and PSBr as a macroinitiator. The resulting diblock copolymer exhibited a molecular weight of 19,000 g/mol and a narrow molecular weight distribution (PDI = 1.4).

The chemical structure and the composition of the diblock copolymer were investigated by <sup>1</sup>H NMR spectroscopy. Fig. 1 shows the <sup>1</sup>H NMR spectrum of the PS-*b*-PHEMA diblock copolymer. The both signals of (a) at 7.0 ppm and (b) at 6.6 ppm are attributed to the benzene groups of PS. The signals of (c, d, e) at



**Scheme 1.** Synthetic procedure for PS-*b*-PHEMA diblock copolymer.

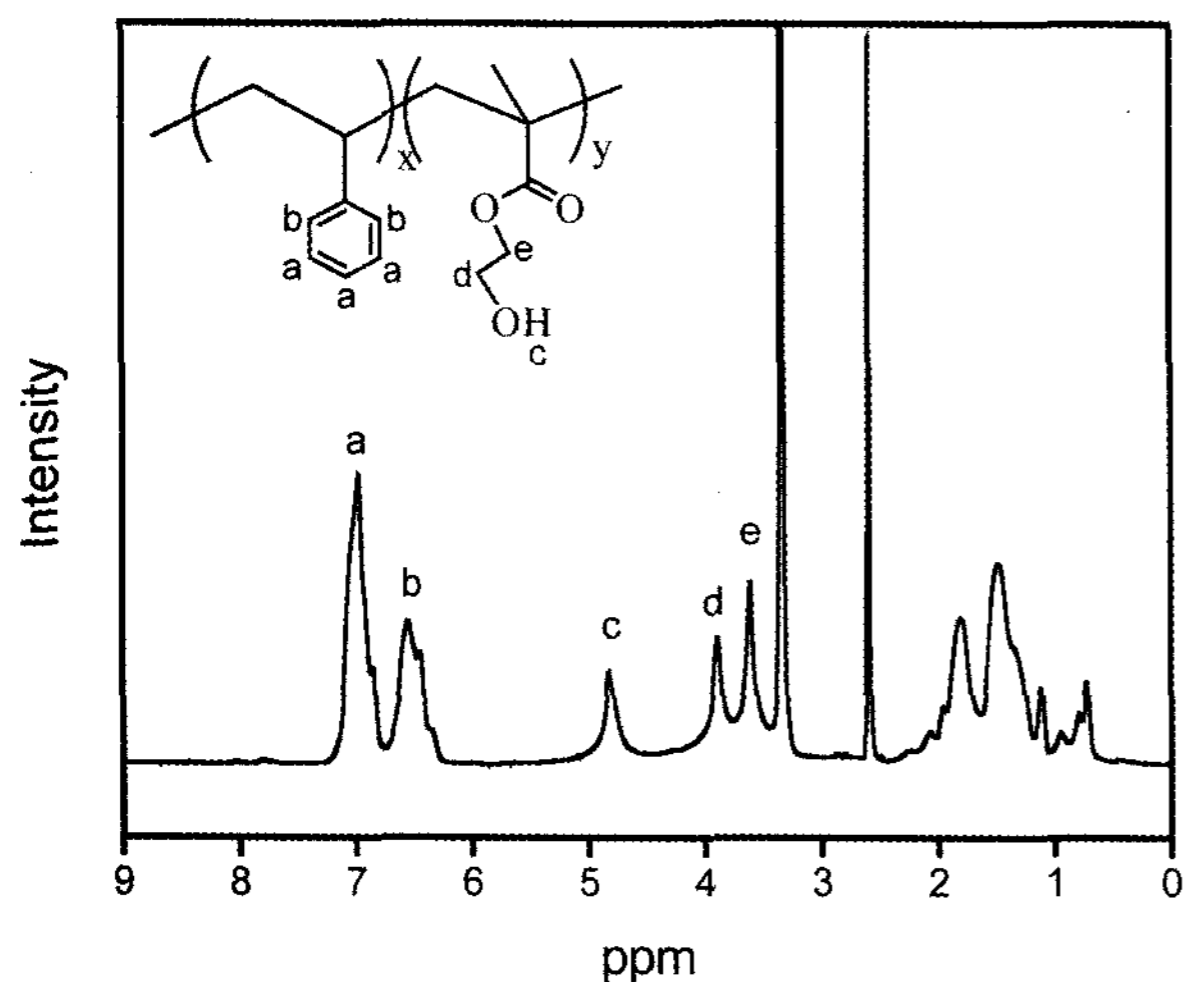
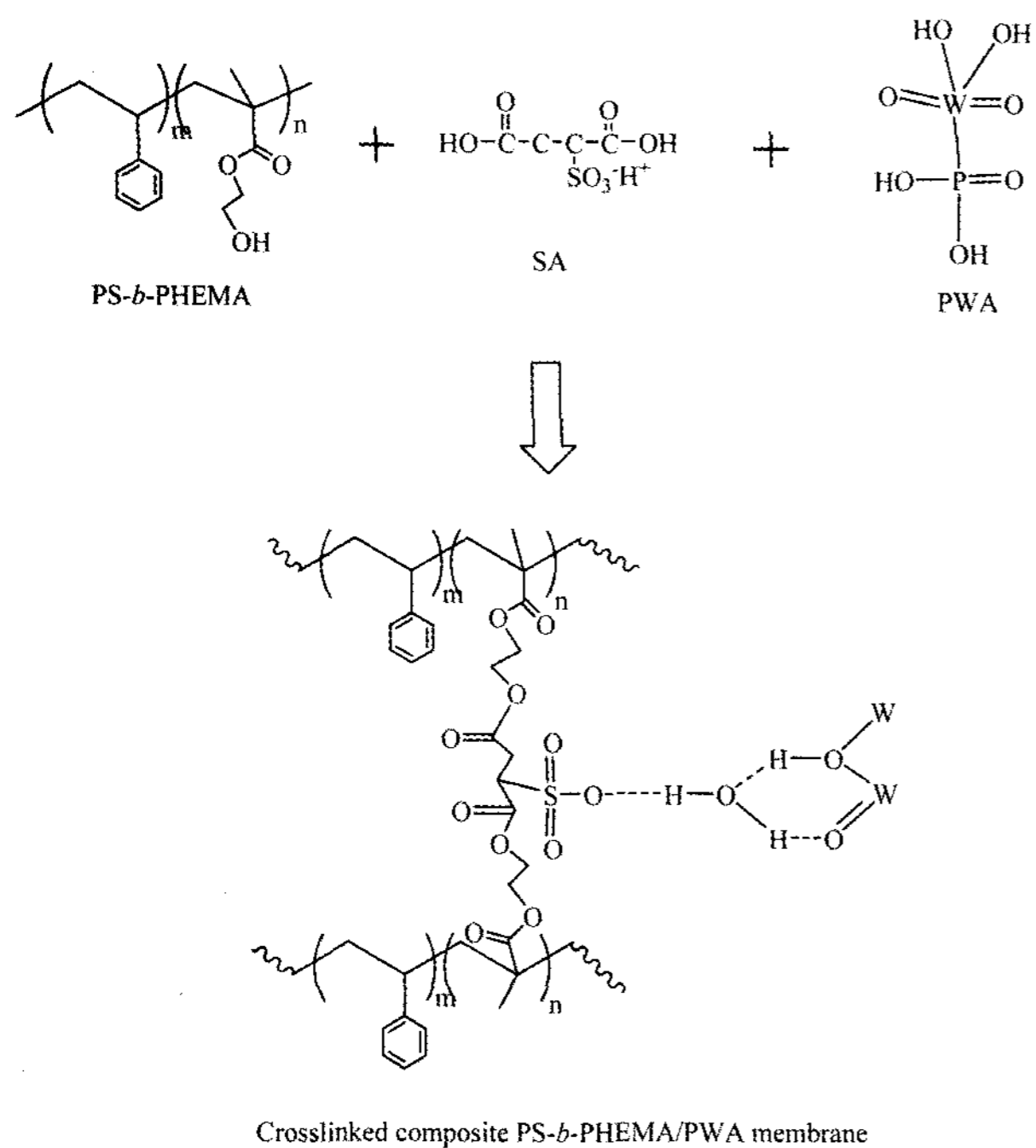


Fig. 1.  $^1\text{H}$  NMR spectrum of the PS-*b*-PHEMA diblock copolymer.



Scheme 2. Schematic structure of the composite membranes consisting of PS-*b*-PHEMA diblock copolymer, SA and PWA.

4.8, 3.9 and 3.5 ppm, respectively, result from the PHEMA block. The composition of the diblock copolymer was determined from the integral ratio of the signals originating from the PS block and the PHEMA block. The  $^1\text{H}$  NMR spectrum presents that the diblock copolymer has a composition of 56 : 44 wt% in PS-*b*-PHEMA and the synthesis via ATRP is successful.

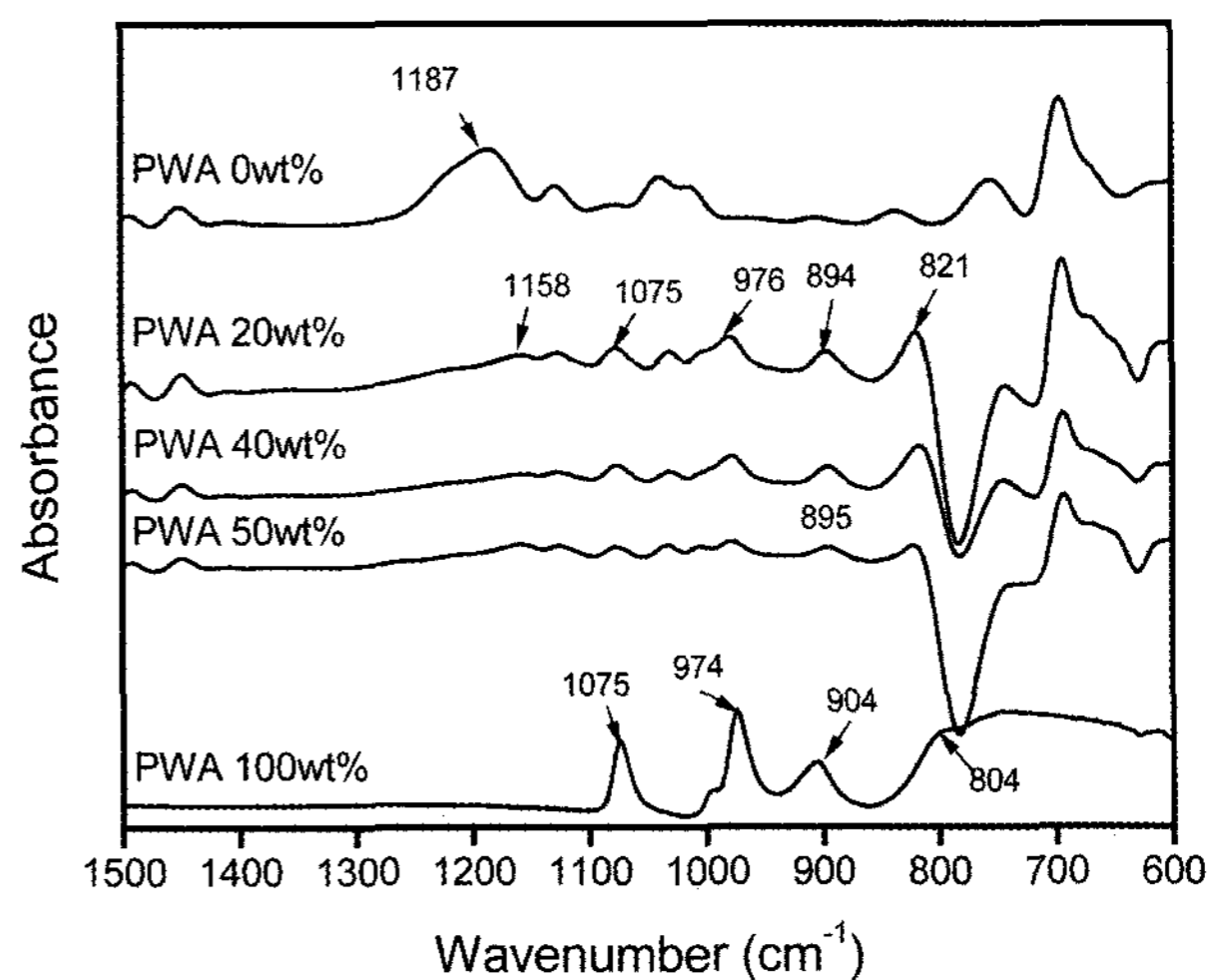


Fig. 2. FT-IR spectra of the composite polymer electrolyte membranes consisting of PS-*b*-PHEMA, SA and PWA by varying PWA concentrations.

### 3.2. Preparation of Composite Polymer Electrolyte Membranes

Scheme 2 shows the schematic diagram for the preparation of crosslinked PS-*b*-PHEMA/PWA nanocomposite polymer electrolyte membranes. The as-synthesized diblock copolymer was blended with varying concentrations of PWA and the PHEMA block was thermally crosslinked by sulfosuccinic acid (SA) via the esterification reaction between -OH of PHEMA and -COOH of SA [16]. Thus these membranes are to be the crosslinked hybrid organic/inorganic nanocomposite membranes to provide high proton conductivity and good mechanical/thermal properties.

The FTIR spectra of the composite PS-*b*-PHEMA/PWA polymer electrolyte membranes consisting of the diblock copolymer, SA and the various concentrations of PWA are presented in Fig. 2. The concentration of SA was always fixed at 20 wt% with respect to the polymer content. The symmetric stretching of  $\text{SO}_3^-$  was observed at  $1187\text{ cm}^{-1}$  due to SA groups. The stretching band shifted to a lower wavenumber of  $1158\text{ cm}^{-1}$  upon blending with PWA, representing that the sulfonic acid groups of the membranes interact with the PWA particles. The pristine PWA exhibited strong absorption bands at  $1075$ ,  $974$ ,  $904$ , and  $804\text{ cm}^{-1}$ , attributable to the stretching vibrations of P-O, W=O,

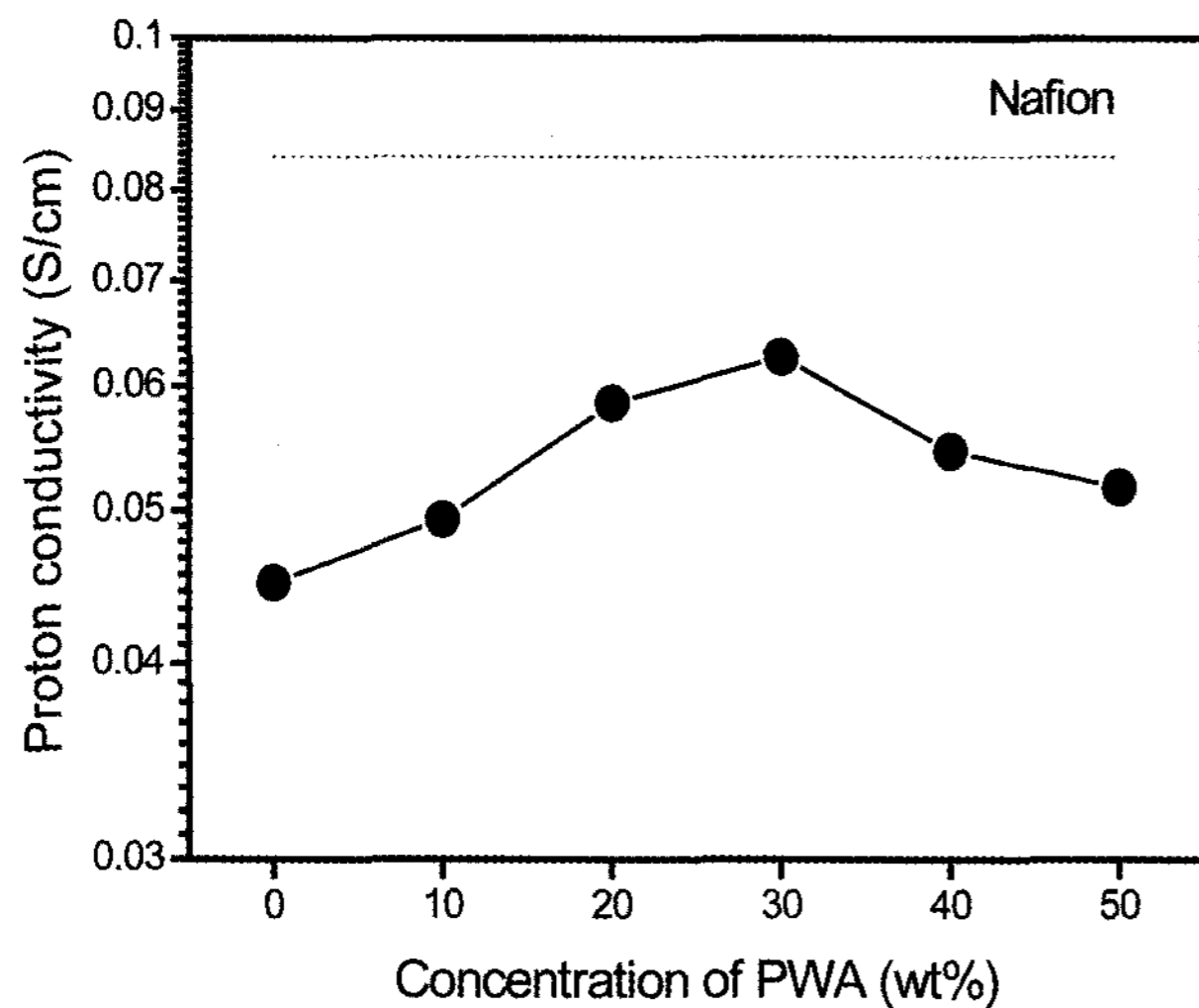


Fig. 3. Proton conductivity of the composite polymer electrolyte membranes consisting of PS-*b*-PHEMA, SA and PWA by varying PWA concentrations.

( $O_t$  is the terminal oxygen), W- $O_c$ -W (corner-shared octahedral), and W- $O_e$ -W (edge-shared octahedral), respectively [19,21]. When the diblock copolymer was combined with PWA, the stretching vibrations of P-O and W= $O_t$  were hardly changed, implying that these groups do not actively participate in the interaction of the composite polymer electrolyte membranes. On the other hand, the stretching vibrations of W- $O_c$ -W and W- $O_e$ -W shifted to 894 and 821  $cm^{-1}$ , respectively. These results show the hydrogen bonding interactions between the bridging oxygens in the PWA molecules and the sulfonic acid ( $SO_3H$ ) in the membranes.

### 3.3. Properties of Composite Polymer Electrolyte Membranes

The proton conductivity of the composite PS-*b*-PHEMA/PWA membranes was determined at room temperature using a four probe method and the results are shown in Fig. 3. The conductivity results were also compared with those obtained from Nafion 117. The crosslinked diblock copolymer membrane without PWA exhibited 0.045 S/cm of conductivity at room temperature. This good proton conductivity of membrane is mostly due to the presence of sulfonic acid groups in SA. The proton conductivity of composite membranes increased with increasing concentrations of PWA

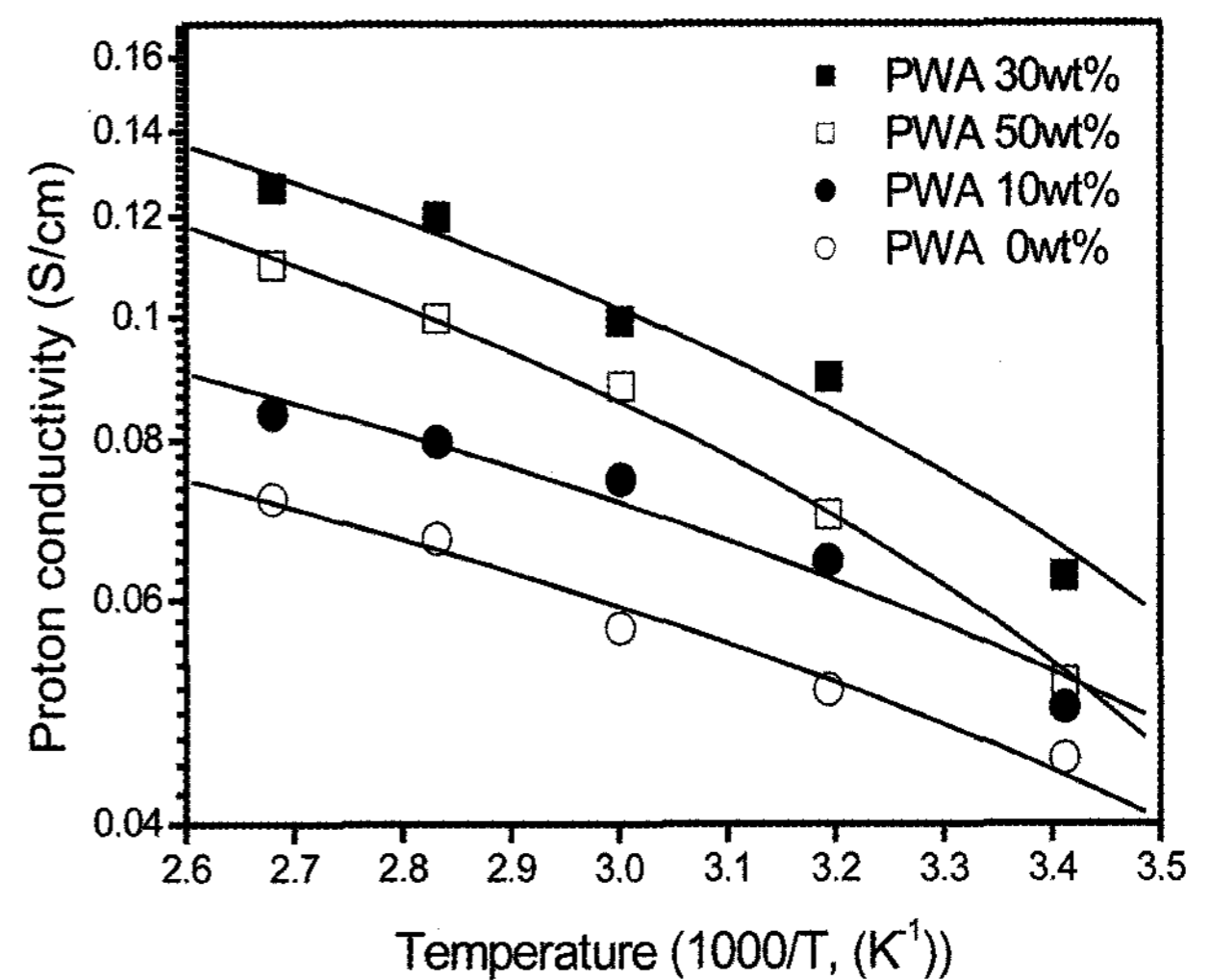
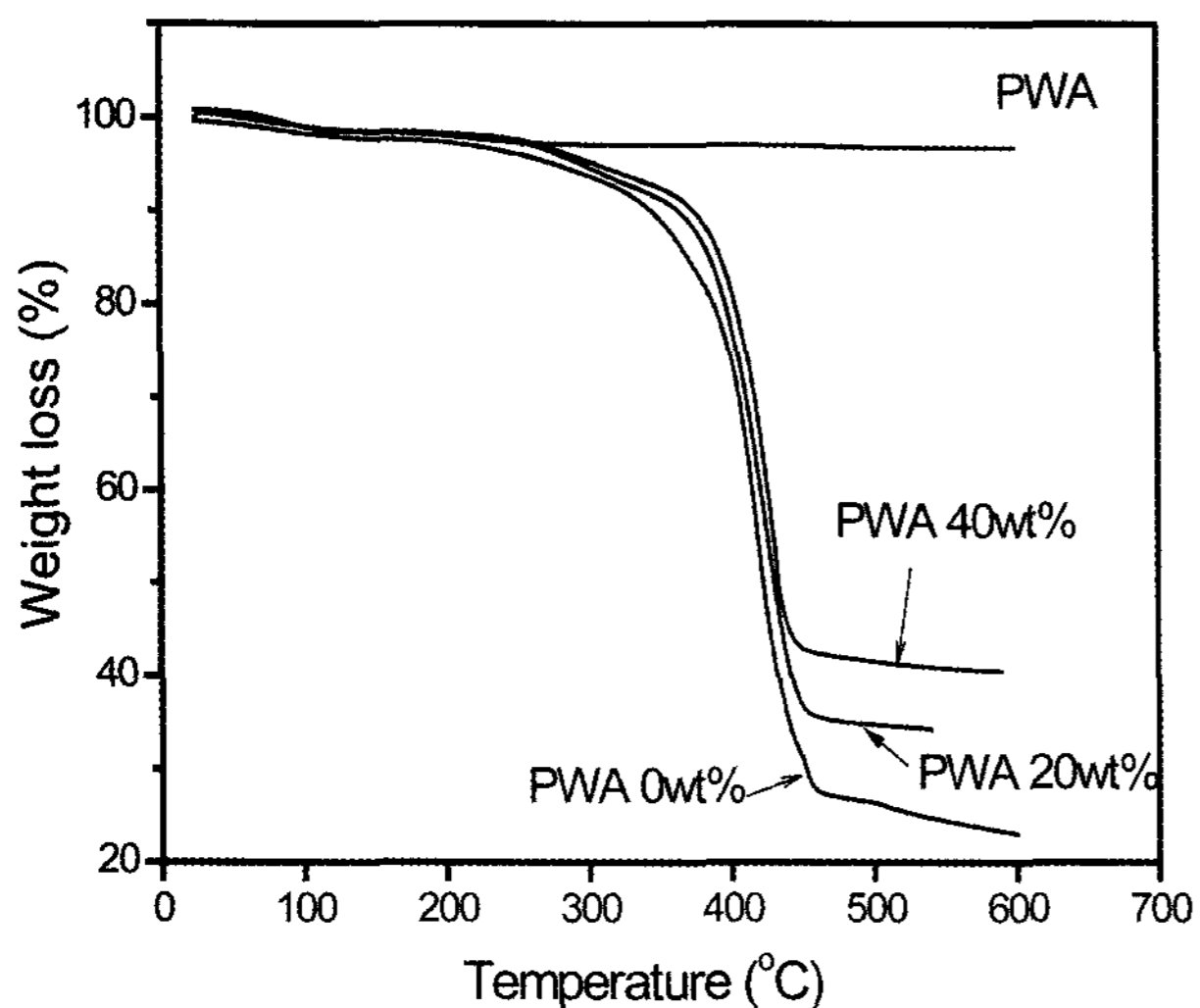


Fig. 4. Temperature dependent proton conductivity of the composite polymer electrolyte membranes consisting of PS-*b*-PHEMA, SA and PWA by varying PWA concentrations.

up to 30 wt%, after which it continuously decreased. This conductivity behavior is presumably attributed to the intrinsic conductivity of the PWA particles and the enhanced acidity of the sulfonic acid in the membrane by PWA incorporation [19,21]. A maximum proton conductivity of 0.062 S/cm was achieved at PWA concentration of 30 wt%. The decrease of proton conductivity above 30 wt% results from the loss of ionic sites ( $SO_3^-$ ) presumably due to the strong hydrogen bonding interactions between the sulfonic acids and the PWA particles [18-20].

The proton conductivities of the PS-*b*-PHEMA/PWA composite membranes were also measured as a function of temperature and provided in Fig. 4. As expected, the proton conductivities increased with the increase of temperature for all the membranes. The temperature dependency of proton conductivity can be explained by the fact that the increase of temperature favors both the dynamics of proton mobility and the structural reorientation of polymeric chains, resulting in the increased proton conductivity at high temperatures [23]. Since the amount of water molecules trapped in the polymer increases with PWA content, the conductivity is expected to increase with an increase in PWA content at the elevated temperature. The mem-



**Fig. 5.** TGA data of pure PWA and the composite polymer electrolyte membranes consisting of PS-*b*-PHEMA, SA and PWA by varying PWA concentrations.

brane containing 30 wt% of PWA exhibited a proton conductivity of 0.126 S/cm at 100°C.

The thermal stability of pure PWA and the cross-linked PS-*b*-PHEMA/PWA composite membranes with different concentrations of PWA were investigated by TGA as shown in Fig. 5. The TGA curve for the pure PWA exhibited a slight weight loss at around 120°C due to dehydration and no other significant weight loss up to 600°C. However, the PS-*b*-PHEMA/PWA composite membranes showed a two-step thermal degradation. The first slight weight loss was observed at around 100°C, probably due to the dehydration of the membranes. The second and third weight losses took place at around 250 and 400°C, presumably due to the loss of the sulfonic acid groups and the main chains, respectively. Upon introduction of PWA, the thermal stability of the membrane increased, representing that the composite membranes are more thermally stable than polymer electrolyte membranes.

#### 4. Conclusion

A diblock copolymer, i.e. PS-*b*-PHEMA with 56 : 44 wt% was synthesized via ATRP. This diblock copolymer was blended with PWA and the middle HEMA

block was thermally crosslinked by SA via the esterification reaction between -OH of PHEMA and -COOH of SA. FT-IR spectroscopy showed that the symmetric stretching bands of  $\text{SO}_3^-$  and the stretching vibrations of W-O<sub>c</sub>-W and W-O<sub>e</sub>-W in the PWA particles changed upon the blending, demonstrating that the PWA particles strongly interact with both the sulfonic acid groups in the membrane. The maximum room-temperature proton conductivity of the composite PS-*b*-PHEMA/PWA membranes was 0.062 S/cm at 30 wt% of PWA concentration. The composite polymer electrolyte membranes were thermally stable at least up to 300°C due to the strong specific interaction between the PWA particles and the sulfonic acid of membranes.

#### Acknowledgement

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