

Synthesis and characterization of poly(ether sulfone) grafted poly(styrene sulfonic acid) for proton conducting membranes

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Abstract—Two-step synthesis of proton-conducting poly(ether sulfone) (PES) graft copolymer electrolyte membrane is proposed. Fridel Craft alkylation reaction was used to introduce chloromethyl pendant group onto the PES polymer backbone. Later on, atom transfer radical polymerization (ATRP) was applied to synthesize a series of poly(ether sulfone) grafted poly(styrene sulfonic acid) (PES-g-PSSA). Successful chloromethyl substitution and grafting of the pendant group was characterized by the ¹H-NMR and elemental analysis. Electrochemical properties such as ion exchange capacity (IEC), water uptake and proton conductivity increased with increasing PSSA contents. Thermal gravimetric analysis (TGA) showed the thermal stability of membranes up to 270 °C. Proton conductivity for maximum amount of grafting was 0.00297 S/cm.

Key words: Polymer Electrolyte Membrane, Proton Conductivity, Atom Transfer Radical Polymerization, Fuel Cell

INTRODUCTION

Solid polymer electrolyte membranes have attracted considerable attention for applications in lithium rechargeable batteries [1], dye-sensitized solar cells [2] and facilitated transport membranes [3]. Among them, many investigations have been carried out on proton-conducting polymer electrolyte membranes for applications to fuel cells over the last decade [4-9]. The most common polymer electrolyte membranes used in fuel cell applications are perfluorinated polymer membranes, e.g., DuPont's Nafion membranes. These membranes consist of a hydrophobic fluorocarbon backbone and hydrophilic sulfonic pendant side chains. These structures produce a microphase-separated morphology of membranes, and thus they exhibit excellent thermal, mechanical, and electrochemical properties. However, these membranes have the following disadvantages: (1) high cost, \$600-1,200 m⁻², (2) high cost per unit power, 300 DkW⁻¹ at 240 mWcm⁻², (3) high methanol crossover through membranes, and (4) low proton conductivity at high temperature/low humidity conditions [10]. Therefore, there has been a great deal of research in the development of alternative proton-conducting membranes to the perfluorinated membranes [11-13].

Among many engineering plastics, poly(ether sulfone) (PES) is an amorphous high performance polymer, which is characterized by excellent thermal properties, good resistance to inorganic acids and bases, and outstanding hydrolytic stability against hot water and steam sterilization. These properties have long been exploited by functionalization of the backbone with sulfonic group. In this method it is difficult to control the location of sulfonation [14]. However, it was developed to the present day well by controlling sulfonated poly(arylene ether sulfone) membranes by various groups [15-18]. For PEM materials, poly(styrene sulfonic acid) (PSSA) and its copolymers have been widely studied because of their synthetic easiness and higher conductivities, and many studies have

used PSSA in the form of random copolymers, block or graft copolymers [4,19-21].

Here we report the chloromethylation of the PES backbone by Fridel Craft alkylation reaction. Styrene sulfonic acid was grafted onto the PES through the chloromethylated group by atom transfer radical polymerization (ATRP) to prepare proton conducting PES-g-PSSA membranes. Various properties such as ion exchange capacity (IEC), water uptake, proton conductivity and thermal properties are reported.

EXPERIMENTAL

1. Materials

Polyethersulfone (PES) was purchased from BASF. 1,1,2,2-tetrachloroethane (TCE), 4-styrene sulfonic acid (SSA), copper(I) chloride (CuCl), 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA) and dimethyl sulfoxide (DMSO) were purchased from Aldrich. Stannic chloride (SnCl₄) was purchased from Fluka. Chloromethyl methyl ether (CMME) was purchased from TCI. Methanol was purchased from Samchun chemicals. All solvent and chemicals were reagent grade and used as received.

2. Synthesis of Chloromethylated Polyethersulfone (CMPES)

10 g of PES was dissolved in 140 mL TCE in a round bottom flask at 80 °C. 0.185 mL SnCl₄ and 20 mL CMME were added followed by N₂ purging. The reaction was carried out at 80 °C for 40 min. The resultant reaction mixture was precipitated into methanol. CMPES was purified by dissolving in DMSO, reprecipitating in methanol and drying under vacuum at room temperature.

3. Synthesis of PES-g-PSSA

1 g CMPES and various amount (3, 5, 7, 9 g) SSA were dissolved in 25 mL and 15 mL DMSO, respectively, in a round bottom flask, and then the two solutions were mixed. After complete dissolution, 0.2 g CuCl and 0.6 mL HMTETA were added followed by N₂ purging. The reaction mixture was stirred at room temperature until the catalyst completely homogenized. Reaction was carried out at 130 °C for 12 h. The resultant grafted product was precipi-

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tated into methanol and purified by dissolving in DMSO and reprecipitating in methanol followed by in vacuum oven overnight at room temperature.

4. Membrane Preparation

PES-g-PSSA copolymer was dissolved in DMSO and filtered with 0.45 μm membrane filter followed by casting on a preheated Petri dish. The Petri dish was kept in a vacuum oven for 24 h at 80 $^{\circ}\text{C}$ to remove solvent and soaked in distilled water to obtain free-standing film. The film was converted into proton exchange membrane by immersion in 0.5 M H_2SO_4 for 2 h, followed by immersion in boiling deionized water for 2 h. The fabricated film was then kept in deionized water.

5. Characterization

5-1. ^1H -NMR Spectroscopy

The ^1H -NMR spectrometer (Bruker, Avance-600) was used at a resonance frequency of 600 MHz. $\text{DMSO}-d_6$ and TMS were used as solvent and internal standard, respectively. Degree of chloromethylation of PES and degree of grafting of PSSA onto PES were calculated from NMR.

5-2. Elemental Analysis (EA)

Substitution degree of copolymer was calculated through the added ratio of chemical elements using EA (model: EA1110, CE Instrument, Italy). The atomic compositional percentage of carbon, hydrogen, oxygen, sulfur and nitrogen was obtained.

5-3. Ion Exchange Capacity (IEC)

IEC of the membranes was measured by the classical titration method. The membranes were soaked in a 1.0 M NaCl solution for 24 h before IEC was measured. The protons released by the exchange reaction with Na ions were titrated against a 0.01 M standardized NaOH solution with phenolphthalein as an indicator. The IEC values of the membranes were calculated with the following equation:

$$\text{IEC}(\text{mEq/g}) = \frac{X \times N_{\text{NaOH}}}{\text{Weight (polymer)}} \quad (1)$$

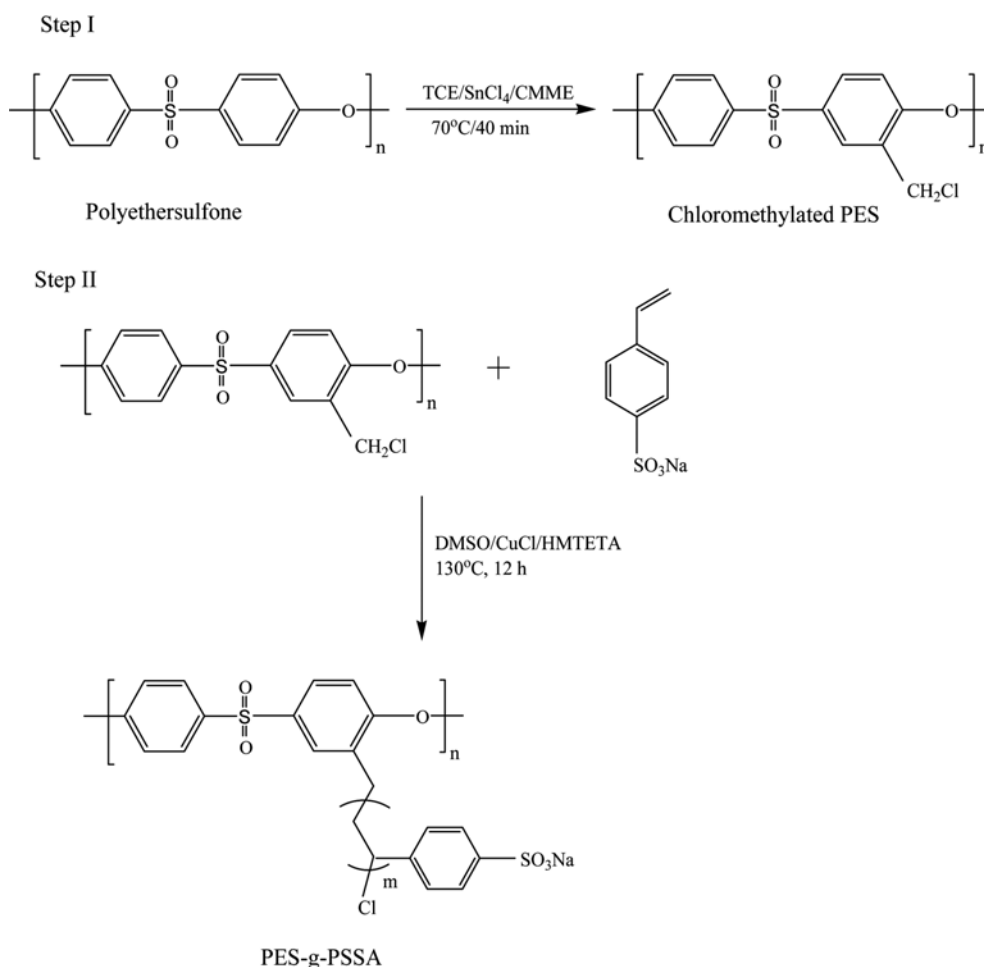
where X is the volume of NaOH consumed and N_{NaOH} is the normality of NaOH.

5-4. Water Uptake

The water uptake was determined by the weighing of a vacuum-dried membrane and a fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with absorbent paper to remove the excess of water adhering to it, and the sample was then weighed. The water uptake of the membrane was determined as follows:

$$\text{water uptake (wt\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

where W_w and W_d are the weights of wet and dried membranes,



Scheme 1. Chloro methylation of PES followed by its grafting with styrene sulfonic acid by atom transfer radical polymerization.

respectively.

5-5. Proton Conductivity

A four-point probe method was used to measure the proton conductivity of the membranes. Before the measurement of the proton conductivity, the prepared membranes were equilibrated with deionized water. Complex impedance measurements were carried out in the frequency range of 1 Hz to 8 MHz at 25 °C with a Zahner IM-6 impedance analyzer (Kronach, Germany). The impedance spectra of the membranes were used to generate Nyquist plots, and the proton conductivity was calculated from the plots [2,11].

5-6. Differential Scanning Calorimetry (DSC)

DSC measurement was carried out with a differential scanning calorimeter (TA Instrument, DSC 2010, U.S.A.) at a heating rate of 20 °C/min under nitrogen atmosphere. 50 mg samples were first dried by heating at 20 °C/min to 200 °C, quenched in liquid nitrogen reheated to 350 °C at 20 °C/min.

5-7. Thermogravimetric Analysis (TGA)

TGA was performed on TGA 1000, TA instrument in nitrogen to evaluate the thermal and thermo-oxidative stability of PES-g-PSSA copolymers. Weight loss was measured and reported as a function of temperature.

RESULTS AND DISCUSSION

1. Graft Copolymer Synthesis

Poly(ether sulfone) grafted copolymers for proton conducting membranes were synthesized in a two-step reaction, as illustrated in Scheme 1. Pendant chloromethyl group was introduced to the polymer back bone by Friedel Craft alkylation reaction by using SnCl_4 as Lewis acid and CMME as alkylating agent in TCE at 70 °C for 40 min. Chloromethylated was used as macroinitiator for grafting of styrene sulfonic acid onto PES backbone by atom transfer radical polymerization (ATRP) at 130 °C for 12 h. The beauty of ATRP is that it does not require stringent reaction conditions like anionic or cationic polymerization [22,23]. Thus, the amphiphilic graft copolymers consist of the hydrophobic PES main chain and hydrophilic sulfonic groups attached to the grafted aromatic side chains.

Successful introduction of chloromethyl group and grafting of chloromethyl polyethersulfone was characterized by $^1\text{H-NMR}$ spectroscopy and presented in Table 1. A representative $^1\text{H-NMR}$ spectrum for CMPES is presented in Fig. 1. Peaks at 2.5 and 3.5 ppm correspond to DMSO-d_6 solvent and moisture presence, respectively. Chloromethylated protons appear at 4.25 ppm [24]. Fig. 2 illustrates $^1\text{H-NMR}$ spectrum for PES-g-PSSA with 1 : 3 weight ratio of added PES : SSA amount. The para and ortho protons of the sulfonic group substituted aromatic region appeared at 6.5 and 7.5 ppm, respectively, due to deshielding effect of the sulfonic acid substituent.

Table 1. Degree of Grafting calculated from NMR

Sample	Degree of chloromethylation	Degree of grafting
PES-g-PSSA3	11.13%	7.67%
PES-g-PSSA5	11.13%	9.97%
PES-g-PSSA7	11.13%	10.33%
PES-g-PSSA9	11.13%	11.08%

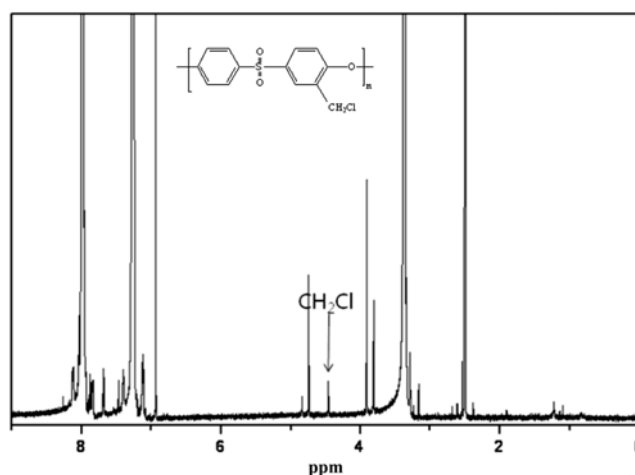


Fig. 1. $^1\text{H-NMR}$ spectra of chloromethylated PES.

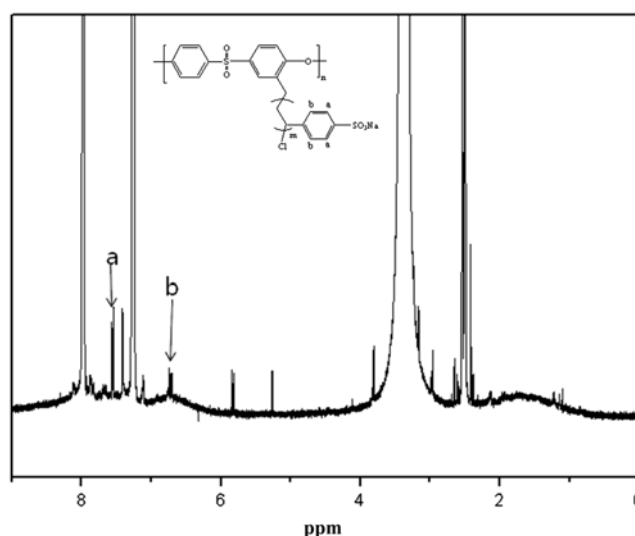


Fig. 2. $^1\text{H-NMR}$ spectra of PES-g-PSSA (1 : 3).

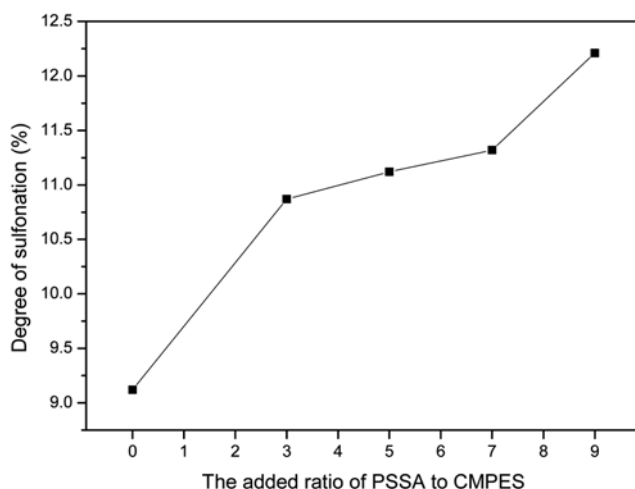


Fig. 3. Percentage of Sulfur in PES-g-PSSA series and chloromethylated PES.

2. Elemental Analysis

Substitution degree of copolymer was calculated through the added ratio of chemical elements using elemental analysis, as presented in Fig. 3. It indicates an increase in sulfur with increase in grafting percent. The maximum sulfur concentration in the membranes was 12.21% for PES-g-PSSA (1 : 9) sample.

3. Ion Exchange Capacity and Water Uptake

It has been well known that the IEC values directly depend on the content of sulfonic acid group incorporated into the polymer, and thus they are indicative of the actual ion exchange sites available for proton conduction. Generally, a high value of IEC is desirable to achieve higher proton conductivity in polymer electrolyte membranes. However, the continuous increase in the content of sulfonic acid group may result in the deterioration of mechanical properties of the membranes because of the highly hydrophilic property of the polymer. Therefore, it might be essential to optimize the amount of sulfonic acid group. The IEC of the PES graft copolymers and water uptake are presented in Fig. 4. As expected, the IEC values and water uptake increased continuously with increase in the added ratios of PSSA. PES-g PSSA (1 : 9) with maximum grafting has IEC of 0.67 meq/g, which is relatively lower than that of Nafion

117, which might be due to lower sulfonic group. Generally, higher IEC values give higher water uptake because both properties are strongly related to the amount of sulfonic acid groups. PES-g-PSSA (1 : 9) membranes with maximum PSSA grafting exhibited 37% of water uptake, which is lower than Nafion 117.

4. Proton Conductivity

Proton conductivity of the PES graft membranes was determined by using the four-probe method and compared with that of Nafion 117 in Fig. 5. As expected, the proton conductivity increased in proportion to the grafting ratios of PSSA in the membrane. As a consequence, the polymer becomes more hydrophilic and absorbs more water, which facilitates proton transport. Therefore, the sulfonation raised the conductivity of the PES, not only increasing the number of proton sites, but also through formation of water mediated pathways for proton. PES-g-PSSA (1 : 9) membranes with maximum PSSA grafting exhibited proton conductivity of 0.00297 S/cm, which is relatively lower than Nafion 117.

5. Differential Scanning Calorimetry (DSC)

The thermal behavior of the synthesized polymers was investigated by DSC analysis under nitrogen at the heating rate of 20 °C/min. The DSC curves of the PES graft copolymers are presented in Fig. 6. The important aspect to note is the experimentally determined specific heat of a vaporization of water. The heat flow for PES graft membranes was observed around 100 °C, mostly attributable to the desorption of adsorbed moisture by the hygroscopic sulfonic group. The heat flow is increased by increasing in substitution of PES. This result suggests that sulfonated PES with increasing degree of sulfonation can adsorb more water in intermolecular chain by increasing hydrophilic property.

6. Thermogravimetric Analysis (TGA)

The thermal stabilities of PES graft membrane were investigated by TGA, as shown in Fig. 7. PES membranes exhibited excellent thermal stability up to 370 °C, above which it started to decompose to around 30 wt%. The first slight weight losses for PES graft membranes were observed around 100 °C, mostly attributable to the loss of adsorbed moisture due to the hygroscopic property of the membrane. The second slight weight losses for PES membranes were observed at around 270 °C, mostly attributable to sulfonic group

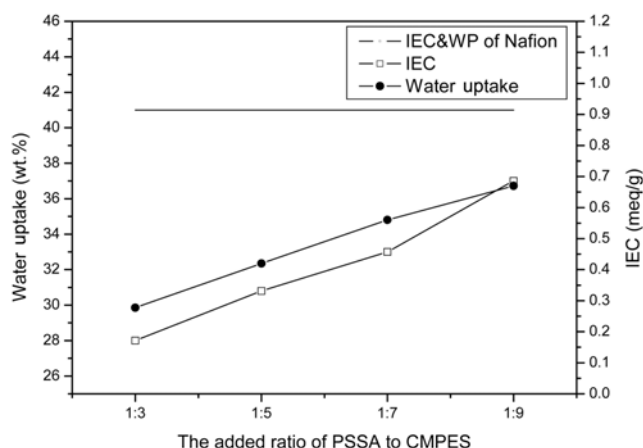


Fig. 4. IEC (meq/g) values and water uptake (wt%) of PES-g-PSSA series.

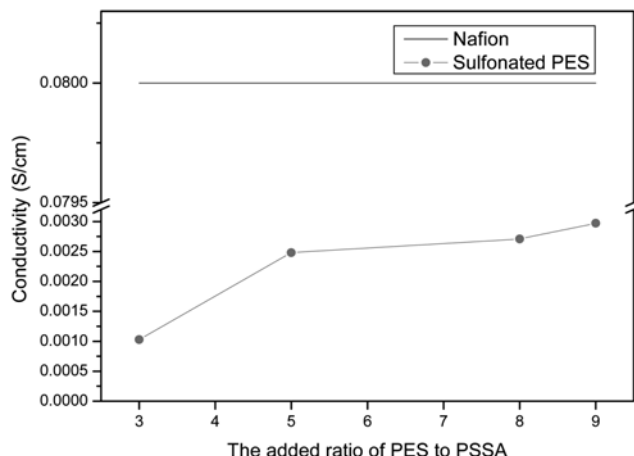


Fig. 5. Proton conductivity (S/cm) of PES-g-PSSA series.

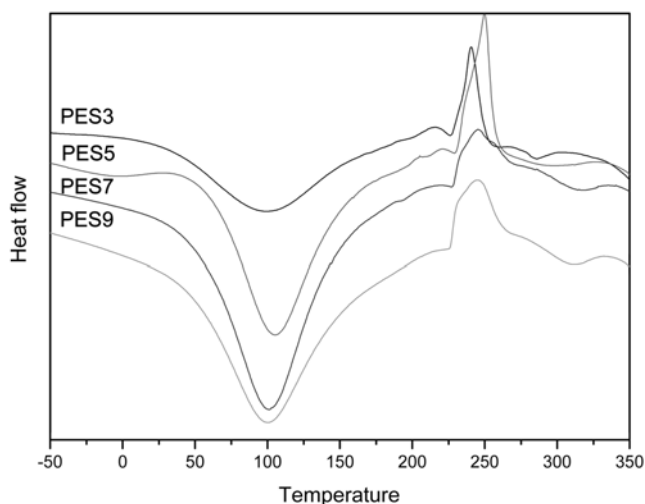


Fig. 6. DSC curves of PES-g-PSSA series.

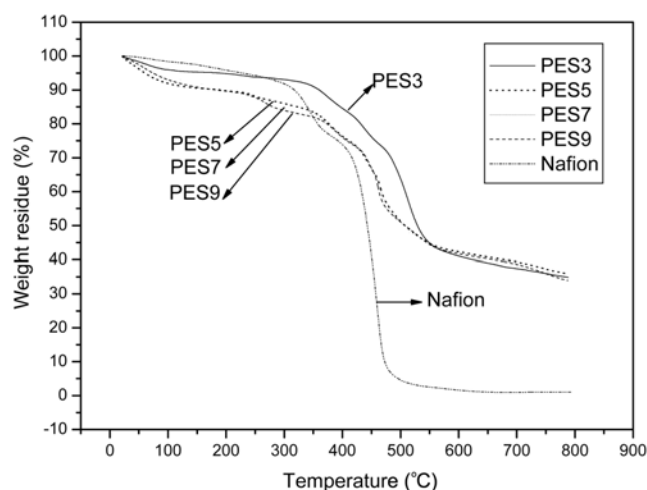


Fig. 7. TGA diagram of PES-g-PSSA series.

decomposition. The third weight loss at 370 °C relates to the degradation of the main polymer chain. But the stability of the Nafion membrane is higher than that of the sulfonated PES polymer for the second and third weight loss. However, this result suggests that the sulfonated PES membranes are thermally stable within the temperature range for PEMFC applications.

CONCLUSION

Proton-conducting PES graft copolymer electrolyte membrane was synthesized by first substitution of the polymer backbone with chloromethyl group. Secondly, chlomethylpolyethersulfone was used as macroinitiator for synthesis of PES-g-PSSA by ATRP method. Backbone substitution and grafting was confirmed by ¹H-NMR and elemental analysis. The IEC values, water uptake and proton conductivity were increased relatively with increase in grafting of PSSA in the membrane. Thermal stability was studied by TGA, which shows that different membranes were stable up to 250 °C. DSC study interprets the loss of moisture from the membranes at around 100 °C. Proton conductivity study showed 0.00297 S/cm for highest PES grafted membrane.

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