CHAPTER IV

SYNTHESIS AND CHARACTERIZATION OF SULFONATED POLY(AROMATIC IMIDE-*CO*-ALIPHATIC IMIDE) (S-coPI) MEMBRANE FOR DIRECT METHANOL FUEL CELL

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Abstract

A novel polymer electrolyte membrane (PEM) was based on the sulfonated poly(aromatic imide-*co*-aliphatic imide) (S-coPI) was synthesized by the poly condensation of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride(BPTDA) with 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenyl methane-2,2′-disulfonic acid disodium salt (S-DDM), and adipic acid dihydrazide (ADH). ADH helped to increase the flexibility of the backbone structure due to its aliphatic structure. The sulfonation degree of S-coPI was controlled by varying the mole ratio of DDM, S-DDM and ADH. The S-DDM containing two sulfonated groups was confirmed by ^{1}H-NMR. S-coPI membranes were characterized by FTIR to confirm the characteristic peaks of the sulfonated group at 1298, 1159, 1098, and 1065 cm^{-1}. TGA was used to investigate the thermal stability of S-coPI, it underwent a 2 steps degradation process, one at 320 °C which represented the decomposition of the sulfonated group and one at 560 °C which represented the polymer backbone degradation. The S-coPI-3, with the highest sulfonation degree, had the proton conductivity about $1.16×10^{-2}$ S cm^{-1}. The methanol permeability of the S-coPI films is in the range of $3.864×10^{-8}$ - $6.521×10^{-8}$ cm^2/s which is lower than that of Nafion117 about 26 - 40 times.

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Introduction

Fuel cells are alternative energy sources which replace the traditional fossil energy of the future. The most important reasons are: fuel cells are environmental friendly, and they are available in a wide size range, from a portable electronic device to an electric vehicle. One of the most popular fuel cell is the direct methanol fuel cell (DMFC) because of its high energy efficiency and the operating system is of the simplest design. The polymer electrolyte membrane required should have the following properties: high proton conductivity; chemical and thermal stabilities; mechanical property; and low cost. DMFC consists of an anode where methanol is fed and catalyzed to proton and electron; and another one is a cathode in which oxygen (usually air) is fed, which combine with a proton that passes through the polymer membrane from the anode and an electron which passes through an external circuit that generate electric power to a connected device [1].

The main problems of DMFC are: 1) the crossover of methanol over the membrane from the anode to the cathode which leads to the poisoning of the catalyst (reduce electrical efficiency [2] of fuel cell); and 2) the drying of the polymer electrolyte at high temperature, resulting in the loss of proton conductivity from the evaporation of water. Furthermore, an electrolyte membrane may degrade at a higher temperature. The degradation problem has been worked out by some researchers, however a new problem occurs in the film casting step as polymers cannot dissolve in common organic solvents.

Several techniques have been developed to solve these problems such as blending with other polymers, loading some particles into the membrane, and etc. Some of the most common methods for dealing with these problems are to modify the polymer structure which is used as the electrolyte membrane. Several monomers

and polymers have been selected to be modified and synthesized with different functional groups containing in the main chains and/or existing at pendant groups. Aromatic polymers have already been well-known for high temperature stability. Polyimide has been commercially available possessing good mechanical, thermal, and oxidative stabilities [3]. A problem occurs in the processing, namely the insolubility [4] in common organic solvents due to the rigidity of backbone, the strong hydrogen bonding in aromatic polyimide, and the charge transfer complex formation in aromatic polyimide [5]. One way to improve solubility of the polymer membrane is to introduce a sulfonated group to the polymer structure; a sulfonated group not only improves solubility but also increases the proton conductivity because increasing the number of sulfonated groups increases the proton hopping area [6].

The objective of this research is synthesize and characterize a sulfonated poly(aromatic imide-*co*-aliphatic imide) (S-coPI) membrane which contains a flexible backbone structure, and to study proton conductivity, thermal, mechanical properties, and methanol permeability of S-coPI cast films.

Experimental

Materials

3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPTDA; Aldrich, 96%), 4,4'-diaminodiphenylmethane (DDM; Aldrich, 97%), and adipic acid dihydrazide (ADH; Fluka, 97%) were used as the starting monomers. Fuming sulfuric acid (SO_3; Merck, 65%), concentration sulfuric acid (H_2SO_4; Univar, 98%), and sodium hydroxide (NaOH; Univar, pellet 97%) were used in sulfonation step. Hydrochloric acid (HCl; Univar, 37%), sodium chloride (NaCl; Lab-Scan, 99%), and 1M sodium hydroxide (Fisher Scientific) were used to determine the sulfonation degree and the ion exchange capacity. Methanol (Lab-Scan, 99.9%) and ethanol (Lab-Scan, 99.9%) were used in the determination of the methanol permeability. Dimethylsulfoxide (DMSO; RCI Labscan, 99.9%) and dimethylformamide (DMF; RCI Labscan, 99.8%) were used as solvents. Benzoic acid (Univar, 99.9 %) and triethylamine (Et_3N; Fluka, 98%) were used in the synthesis step. Acetone (Burdick & Jackson, 99.9%) was used to precipitate the polymer.

Sulfonation of 4,4'-Diaminodiphenylmethane-2,2'-Disulfonic Acid Disodium Salt (S-DDM)

10 g (50.45 mmol) of 4,4'-diaminodiphenylmethane was dissolved in 20 ml of 98% sulfuric acid to a 100 ml three-necked round bottom flask with a mechanical stirring device. The solution was submerged in an ice bath until completely dissolved. Then 10 ml of 65% fuming sulfuric acid was added and stirring was continued for 2 h, after which it was heated to 80 °C and stirred for another 2 h. The solution was slowly poured into a crush ice and the product was precipitated by adding a sodium hydroxide solution until obtaining basic solution. The precipitate was filtered, washed with deionized water, and dried at room temperature in vacuum for 24 h [7]. The scheme of the sulfonation was shown in the Figure 1.

Preparation of Sulfonated Poly(Aromatic Imide-co-Aliphatic Imide)

S-DDM, DDM, and ADH at various mole ratios were dissolved first in dimethylsulfoxide; the degree of sulfonation was controlled by changing the molar ratio of S-DDM and DDM. For example, to synthesis of S-coPI-1 with molar ratio of 1:3:6, it was proceeded as follow; 0.374 g (0.931 mmol) of S-DDM and 0.554 g (2.793 mmol) of DDM were dissolved in DMSO and then 0.26ml (1.86 mmol) of triethylamine was added, after that 0.973g (5.586 mmol) of ADH was added to the solution, 3.00 g (9.31 mmol) of BPTDA in dimethylsulfoxide solution was added later, and lastly 0.25 g (2.05 mmol)of benzoic acid was added. The reactions were carried under a nitrogen atmosphere for 24 h to get a sulfonated polyamic acid. After that, the solution was heated to 90 °C for 4 h. After the solution was cooled, the precipitate in acetone was vigorously stirred to get a yellow powder. The precipitate was dried at room temperature under vacuum for 24 h. The powder was dissolved in DMF and casted onto a glass plate, then dried at 80 °C under vacuum for 24 h and 160 °C, and under vacuum for 24 h [8] to get sulfonated poly(aromatic imide-*co*-aliphatic imide) membrane. The scheme of the synthesis is shown in the Figure 2.

Characterizations and Testing

FT-IR and ^{1}H-NMR Spectroscopy

S-DDM and S-coPI powders were first characterized for the functional groups by a FT-IR spectrometer (Thermo Nicolet, Nexus 670), in the absorption mode with 64 scans and a resolution of 4 cm^{-1}, and in a wavenumber range of 4000 - 400 cm^{-1}. Optical grade KBr was used as the background material and the powders were mixed with the dried KBr before measurements. The ^{1}H-NMR spectra of S-DDM in deuterated dimethylsulfoxide (DMSO-d_6) were recorded on a Varian mercury 400 MHz instrument to confirm the positions and the number of sulfonated groups on the monomer.

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (PerkinElmer, Pyris Diamond TG/DTA) was performed to determine the thermal stability of the polymer membrane [4]. The experiment was carried out by weighting a film sample of 2 - 4 mg and placed in an alumina pan, and then heated it under nitrogen atmosphere with the heating rate of 10 °C/min in the temperature range of 50 - 800°C. All the samples were dried at 100 °C for 24 h before measurement.

Tensile Test

The mechanical properties of the polymer films were measured using a universal testing machine (Lloyd, model SMT2-500N) at the gauge length 30.0 mm, at the speed of 10 mm/min, and at room temperature. At least five measurements were taken for each polymer sample. The membranes about 160 - 200 μm in thickness were cut in to 1cm × 5cm pieces and soaked in a deionized water for 2 days before testing.

X-Ray Diffraction (XRD)

The Wide angle X-ray diffraction microscope (Bruker AXS, model D8 Advance) was used to study crystallinity of Non S-coPI and S-coPI. The S-coPI-3 was used as a sample of S-coPI. The Cu K-alpha radiation source was operated at 40

kV / 30mA. K-beta filter was used to eliminate the interference peak. A divergence slit and scattering slit 0.5 deg together with 0.3 mm of receiving slit are set on the instrument. The film was placed into a sample holder and the measurement was continuously run. The data were recorded by monitoring the diffraction appeared in the 2θ range from 5 to 90 with a scan speed of 5 deg/min and a scan step of 0.02 deg.

Water Uptake and Moisture Absorption

The polymer membranes were dried in an oven at 100 °C for 24 h. The dried membranes were weighed (W_d). Then the polymers were soaked in de-ionized water at room temperature for 2 days. They were removed from the water, quickly dry-wiped with an absorbent paper to remove any surface moisture, and then weighed immediately to determine their wet masses (W_w). The measurements were repeated three times to obtain the average water uptake value. The water uptake was calculated by the following formula [9] (1):

$$\text{Water uptake}(\%) = \frac{(W_w - W_d) \times 100}{W_d} \tag{1}$$

The moisture absorption was determined in the same method of water uptake but after the membranes were dried, the membranes were placed at room at room temperature for 2 days before weighted (W_m) again. The moisture absorption was calculated by the following formula (2):

$$\text{Moisture absorption}(\%) = \frac{(W_m - W_d) \times 100}{W_d} \tag{2}$$

Degree of Sulfonation (DS)

Polymer membranes were acidified with an excess 0.1 M HCl solution at room temperature for 24 h. Then, they were washed and dried at 80 °C for 24 h. The membranes were immersed in 50 ml of 1 M NaCl for 24h. The solution was titrated by 0.01 M NaOH using phenolphthalein as an indicator. The titrations were repeated two times and the DS value was obtained with formula (3).

$$DS(\%) = \frac{(V_{NaOH} \times M_{NaOH})/1000}{Mole\ of\ polymer\ membrane} \times 100 \tag{3}$$

V_{NaOH} is the volume of sodium hydroxide solution, M_{NaOH} is the concentration of sodium hydroxide solution.

Ion Exchange Capacity (IEC)

The membrane samples (0.25-0.30 g) in acid form were immersed in 50 ml of 1 M NaCl solution at room temperature for 24 h to allow the H^+ ions to be replaced by Na^+ ions. Then, the H^+ ions were titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The titrations were repeated two times for the average IEC value. The IEC was calculated from the titration result using the equation (4):

$$IEC \ (meq./g) = \frac{V_{NaOH} \times M_{NaOH}}{W_d} \tag{4}$$

where V_{NaOH} is the volume of sodium hydroxide solution, M_{NaOH} is the concentration of sodium hydroxide solution, and W_d is the weight of dried membrane.

Proton Conductivity

Proton conductivity of the films was measured by an Agilent E4980A LCR meter in terms of the impedance data. The fully hydrated films [10] were cut into 0.5×0.5 cm and painted with silver paints on both side of the films. The films were measured at a potential of 1 V and an alternating current frequency range of 20 Hz - 2 MHz. A graph was plotted between the radian and the impedance data. The conductivity σ of the samples was calculated from the impedance data by the following equation (5):

$$\sigma (S \ cm^{-1}) = \frac{d}{SR} \tag{5}$$

where σ is the proton conductivity, d is the thickness of the membrane, S is the area of the interface between the membrane and the electrode, and R is the measured resistance of the membrane — derived from the intersection of the low frequency semi-circle on the complex impedance plane with the Z' axis.

Methanol Permeability

The methanol permeability of the membranes was determined by using the two compartments diffusion cell technique. One compartment (V_A = 250 ml) was

filled with a solution of 2.5 M methanol. The other compartment (V_B = 250 ml) was filled with deionized water. The membrane was clamped between the two compartments. The solutions in the two compartments were magnetically stirred during the permeation experiments. Methanol passed through the membrane due to the methanol concentration difference between the compartment A and the compartment B. The methanol permeation [11] in the compartment B as a function of time is given by equation (6):

$$P\ (cm^2/s) = \frac{k_B \times V_B \times L}{A \times (C_A - C_B)} \tag{6}$$

where P is the methanol permeability, C_A is the methanol concentrations in the compartment A, C_B is the methanol concentrations in the compartment B, A is the area of a membrane, L is the thickness of a membrane, V_B is the volume of the solution in the compartment B, and k_B is the slope of methanol concentration profile in the compartment B. The methanol concentrations were measured by using a PR2100 gas chromatography fitted with a Thermal Conductivity Detector (TCD); 2.5M ethanol was used as the internal standard. The selectivity (Φ) was also calculated by the equation (7):

$$\Phi = \sigma/P \tag{7}$$

The selectivity is an effective parameter evaluating the membrane performance in DMFC system. The higher selectivity is the better performance the membrane [12].

Results and Discussion

Sulfonated Monomer

The ^{1}H-NMR of S-DDM peak is shown in the Figure 3. The signal at 7.16 ppm (doublet), 7.12 ppm (doublet of singlet) and 6.71 ppm (doublet of doublet) are attributed to the aromatic protons H_3, H_5 and H_2, respectively. The signal at 5.55 ppm (singlet) is assigned to the primary anime proton, correlated with H_1. The signal at 3.82 ppm (singlet) is assigned to the methylene proton H_4 between the phenyl groups.

Fourier Transform Infrared (FT-IR)

The FT-IR peak of S-coPI is shown in Figure 4; the bands at 1740 and 1665 cm^{-1} which can be attributed to the C=O asymmetric and the symmetric stretching of the carbonyl group of the imido ring, respectively. The band at 1386 cm^{-1} is attributed to the C–N–C stretching of the imide ring [13]. The S=O bond of the sulfonic group can be observed at around 1298 and 1159 cm^{-1}. The bands at 1098 and 1065 cm^{-1} are assigned to the S–O of sulfonated group [14]. The peak intensity at 1298 cm^{-1} increases with increasing sulfonation degree.

Thermogravimetric Analysis (TGA)

The thermal property of S-coPI membranes was investigated by TGA and is shown in Figure 5. The weight loss at about 320 °C is assigned to the decomposition of the sulfonated group, and the weight loss due to degradation of backbone structure appears at about 560 °C.

Tensile Test

Young's modulus of the membrane increases which increasing degree of sulfonation; Non S-coPI, S-coPI-1, S-coPI-2, and S-coPI-3 have the Young's modulus about 651.00 ± 53.84, 829.58 ± 27.84, 980.01 ± 68.88, and 1065 ± 47.86 MPa, respectively.

X-Ray Diffraction (XRD)

The crystalline structure of Non S-coPI and S-coPI were characterized by wide-angle X-ray diffractions as shown in Figure 6. The five main peaks of Non S-coPI are found at 2θ of 26.64°, 20.84°, 50.14°, 59.94°, and 68.14°. For the S-coPI, the diffraction data represent an amorphous structure with only board peaks at 2θ about 24.7° and 43.5° since the sulfonated group obstructs the chain packing of the polymer chain which reduces the crystallinity.

Degree of Sulfonation (DS) and Ion Exchange Capacity (IEC)

The degree of sulfonation of the polymer membranes are controlled by varying monomers feed ratio, but the actual degree of sulfonation is lower than

expected about 10 - 15 % because of some monomers did not react. The ion exchange capacity of each S-coPI membranes is tabulated in the Table 1.

Water Uptake and Moisture Absorption

The water uptake data of the S-coPI membranes are shown in Figure 7 The water uptake increases with increasing degree of sulfonation since the sulfonated group induces water into the membrane. The water uptake of the S-coPI membranes are lower than that of Nafion117 due to a tighter chain configuration and the formation of agglomerated ionic water clusters [8] based on two main reasons. First, the main chain structure of the S-coPI is composed of rigid aromatic group, whereas the Nafion117 is composed of the linear fluorinated chain where it contains a long grafted ionic group which enhances the membrane flexibility [8, 15]. Secondly, the crosslinking bonds between the S-coPI chains generates a built-in network structure, thus the water uptake is much lower than that of Nafion117 [8]. The water absorption of non S-coPI is higher than S-coPI-1 due to the loose chain packing of non S-coPI and thus with a higher free volume. The moisture absorption of the S-coPI membranes is about a half of the water absorption as no chain expansion occurs in the moisture absorption test.

Proton Conductivity

The proton conductivity of S-coPI membranes is shown in Figure 8 and in Table 2. The proton conductivity increases with increasing degree of sulfonation from 5.07×10^{-10} S cm^{-1} for Non S-coPI to 1.16×10^{-2} S cm^{-1} for S-coPI-3, because an increase in the number of the sulfonated groups increases the proton hopping area.

Methanol Permeability

Table 2 lists the methanol permeability and the membrane selectivity [16] of the S-coPI membranes. The proton conductivity data of Nafion117 reported in literature are also listed in this table. All the S-coPI membranes are of lower methanol permeability than that of Nafion117 and the selectivity of S-coPI-3 is higher than Nafion117 about 6 times, so the S-coPI-3 is of higher performance than Nafion117 with respect to the DMFC membrane.

Conclusions

In this study, S-DDM was successfully sulfonated by using the 98% sulfuric acid and the 65% fuming sulfuric acid. 2 sulfonated groups were contained in the S-DDM monomer; the positions of the sulfonated groups were confirmed by ^{1}H-NMR. The S-coPI membrane was synthesized by the polycondensation method using the thermal imidization to obtain the imide structure; the four monomers at various mole ratios of S-DDM were used to control the amount of sulfonated group. The characteristic peaks of the sulfonated group are at 1298, 1159, 1098, and 1065 cm^{-1} as confirmed by FTIR. TGA shows the thermal stability of S-coPI; it has two structure decompositions at 320 °C and 560 °C. The DS of the membranes from titration is lower than the expected DS about 10-15%. The crystallinity of the S-coPI membrane decreases with increasing DS due to the effect of the sulfonated group which disrupts the polymer chain packing. The proton conductivity of the membranes increases with increasing sulfonated groups in the polymer chain; the highest proton conductivity is 1.16×10^{-2} S cm^{-1} for S-coPI-3 at the highest S-DDM feed ratio. The S-coPI membranes are of lower methanol permeability than that of Nafion117 and the membrane selectivity of S-coPI-3 is 2.89×10^5 S s cm^{-3}, a higher value than that of Nafion117 about 6 times.

Acknowledgements

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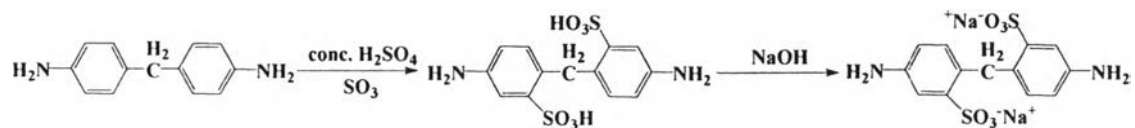[17] **Li, T., Zhong, G., Fu, R., and Yang, Y.** (2010) J. Membr. Sci. 354, 189-197.
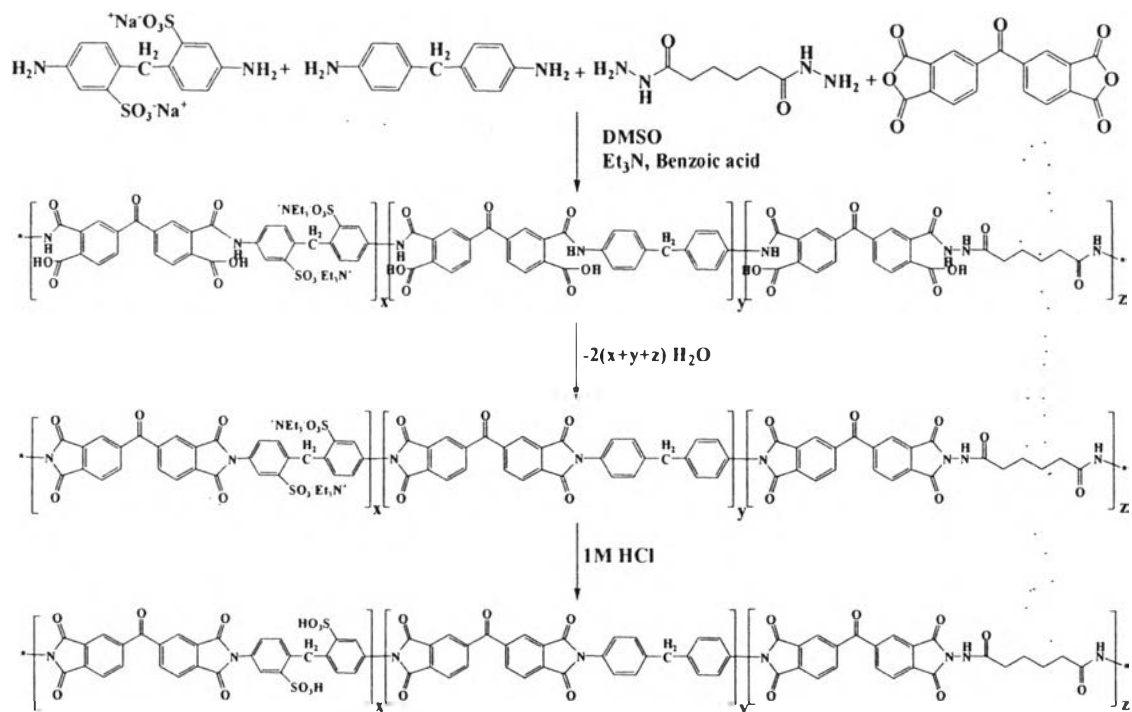
Figure 1 The scheme for sulfonation of DDM.
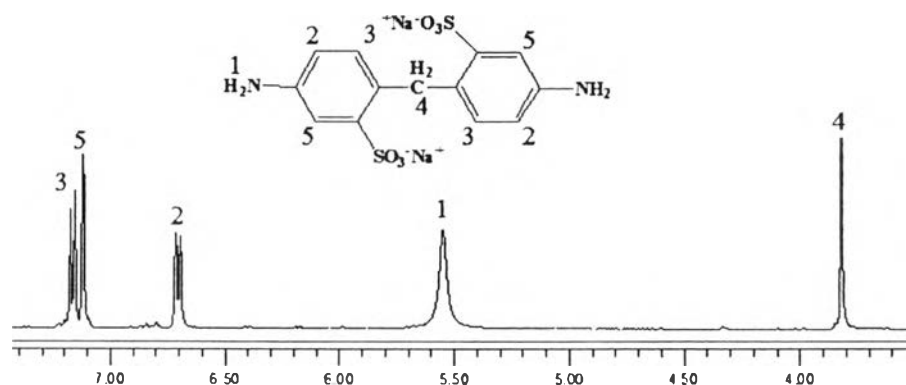

Figure 2 The scheme for S-coPI synthesis.

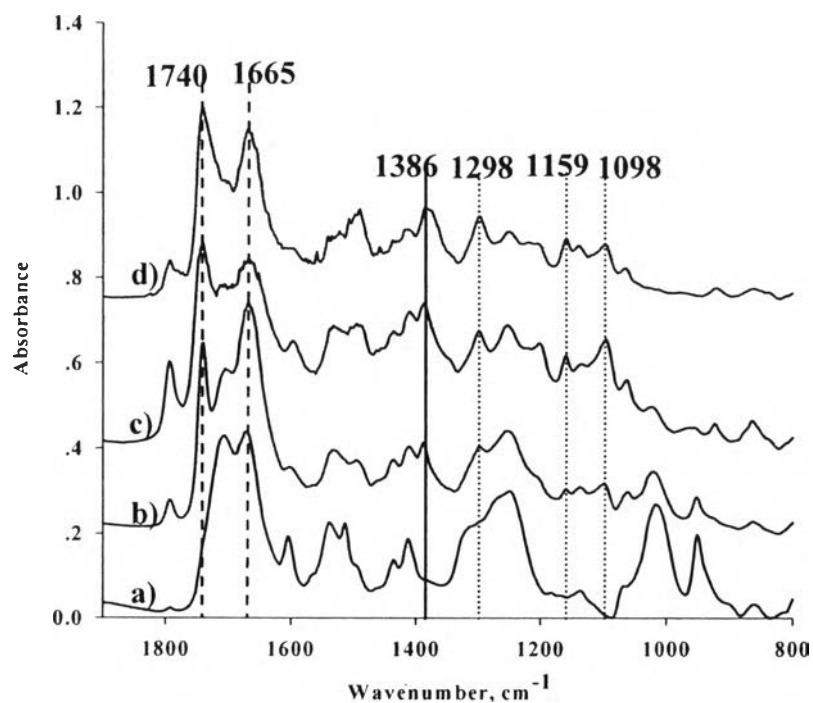**Figure 3** The ^{1}H-NMR spectrum of S-DDM.

Figure 4 FT-IR spectra of: a) Non S-coPI; b) S-coPI-1; c) S-coPI-2; d) S-coPI-3.
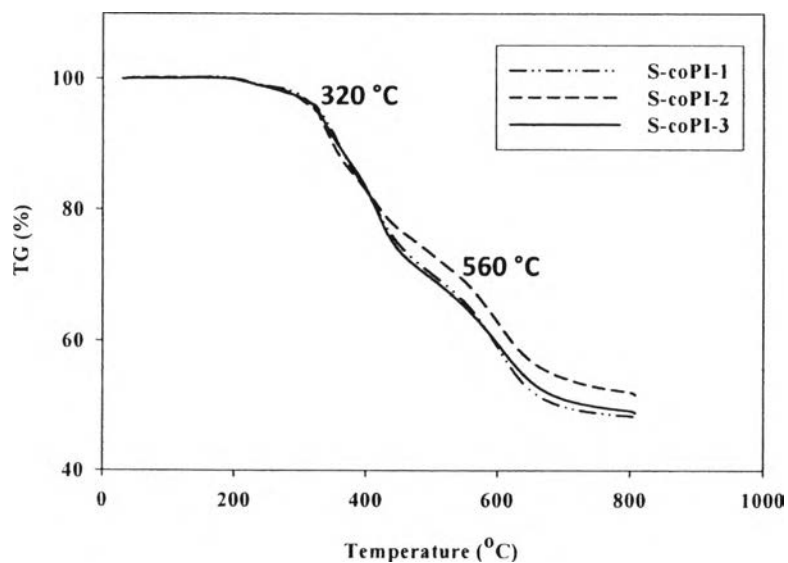

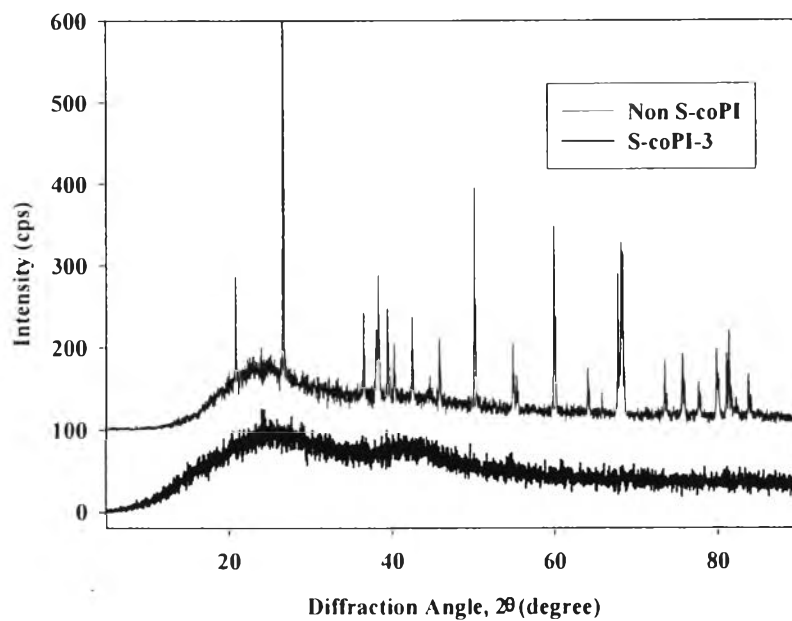**Figure 5** The thermogravimetric analysis curves of S-coPI membranes.

Figure 6 XRD diffraction patterns of the Non S-coPI and S-coPI-3 films.
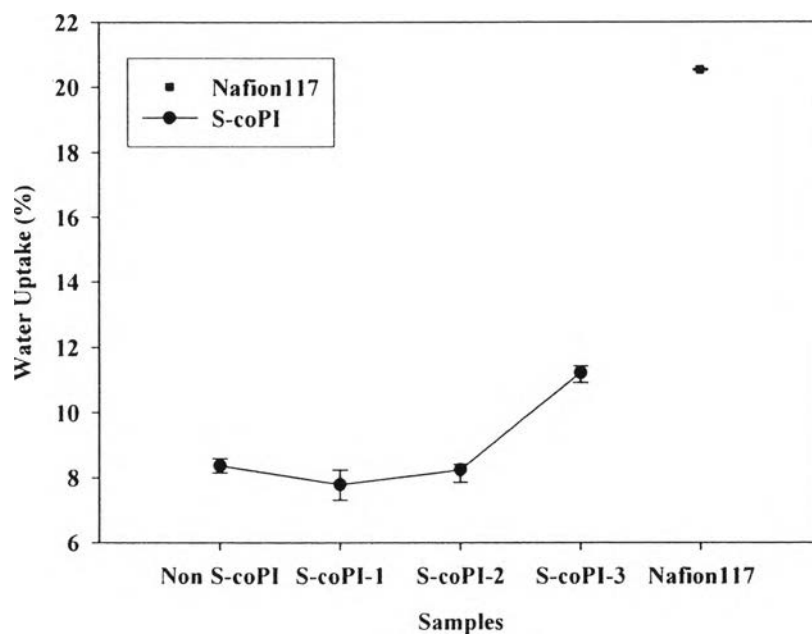

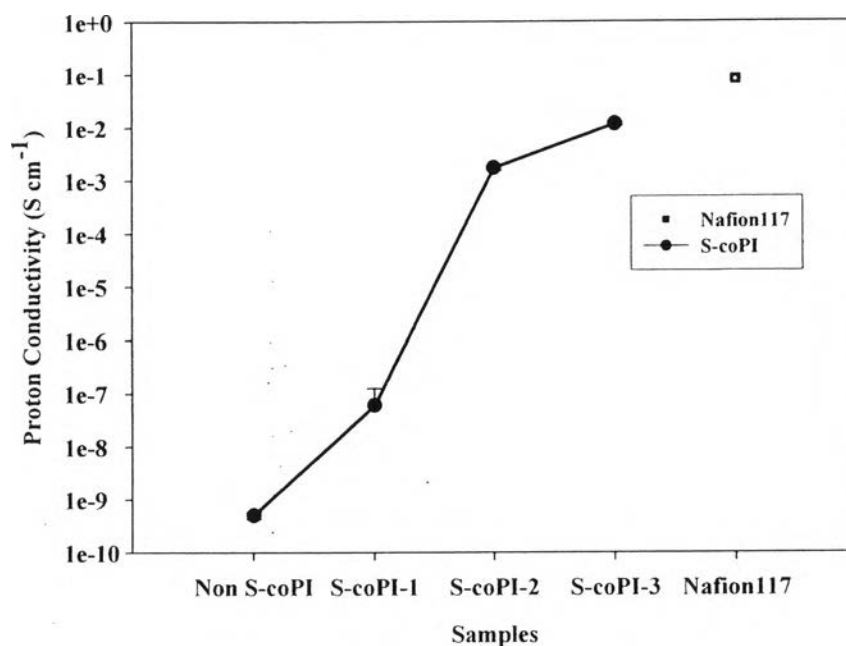**Figure 7** Water uptake of S-coPI and Nafion117 films.

Figure 8 The proton conductivity of the S-coPI and Nafion117 films.

Table 1 The degree of sulfonation with difference monomer feed ratio by titration method

Sample	Monomer feed ratio (mol) S-DDM : DDM : ADH	Expected DS (%)	Actual DS (%) from titration	IEC (meq./g)
Non S-coPI	0 : 4 : 6	0	0	0
S-coPI-1	1 : 3 : 6	20	18.450 ± 1.287	0.380 ± 0.026
S-coPI-2	2 : 2 : 6	40	34.530 ± 0.042	0.689 ± 0.001
S-coPI-3	4 : 0 : 6	80	65.585 ± 0.417	1.230 ± 0.008

Table 2 Proton conductivity, methanol permeability, and selectivity of S-coPI membranes and Nafion117

Sample	Proton Conductivity, σ (S cm^{-1})	MeOH Permeability, P (cm^2/s)	Selectivity, $\Phi = \sigma/P$ (S s cm^{-3})
Non S-coPI	5.07×10^{-10}	3.864×10^{-8}	1.31×10^{-2}
S-coPI-1	6.01×10^{-8}	5.854×10^{-8}	1.03
S-coPI-2	1.73×10^{-3}	6.521×10^{-8}	2.65×10^{4}
S-coPI-3	1.16×10^{-2}	4.019×10^{-8}	2.89×10^{5}
Nafion117	8.00×10^{-2}*	1.744×10^{-6}	4.59×10^{4}

* Ref. [17].