



CHAPTER IV
NOVEL PROTON EXCHANGE MEMBRANE
FOR DIRECT METHANOL FUEL CELL

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Abstract

A proton exchange membrane for a direct methanol fuel cell was fabricated from sulfonated poly(aromatic imide-co-aliphatic imide) (SPI). 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid disodium salt (SDDM) was synthesized from 4,4'-diaminodiphenylmethane (DDM), using concentrated sulfuric acid and fuming sulfuric acid. Then SPI was synthesized from SDDM, DDM, hexamethylenediamine (HDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), where dimethylsulfoxide (DMSO) was used as the solvent. SPI was synthesized at various degrees of sulfonation by varying the amount of SDDM in SPI. The membrane film was fabricated by solution casting. The sulfonated position of SDDM was characterized by $^1\text{H-NMR}$ and FTIR. The chemical structure of SPI was characterized by FTIR, where the characteristic peaks of SPI occur at 1777, 1709, 1368, 1248, and 1157 cm^{-1} respectively. Thermogravimetric analysis shows that the sulfonated group of SPI decomposes at around 200 $^{\circ}\text{C}$ and the degradation of the polymer main chain occurs at 480 $^{\circ}\text{C}$. Sulfonated polyimide with the highest degree sulfonation possesses the proton conductivity of 0.003241 S/cm. The highest methanol permeability of sulfonated copolyimide is $2.7482 \times 10^{-8} \text{ cm}^2/\text{s}$ which is much lower than of Nafion[®] ($1.7400 \times 10^{-6} \text{ cm}^2/\text{s}$) by two orders of magnitude. The effects of the degree of sulfonation on the properties of the membrane were also investigated and reported here: the water uptake (WU), the dynamic mechanical analysis (DMA) and the ion exchange capacity (IEC).

Keywords: Sulfonated poly(aromatic imide-co-aliphatic imide); Direct methanol fuel cell; Proton conductivity; Methanol permeability

1. Introduction

Direct methanol fuel cells (DMFC) are proton exchange membrane fuel cells which use methanol as the fuel. The main applications of DMFC are energy sources of small vehicles such as a forklift, a tugger, consumer goods like laptop, a mobile phone, and a digital camera.

The important part of direct methanol fuel cell is the polymer electrolyte. The main application of polymer electrolyte membrane is to conduct protons. The protons from oxidized methanol migrate through this electrolyte membrane. One of the commercial proton exchange membrane is Nafion[®]. Nafion[®] possesses many advantageous properties as a proton exchange membrane. It has high proton conductivity, good mechanical and chemical properties, and also has high thermal stability. But Nafion[®] still has some weak points. The conductivity of Nafion[®] is low at a high operating temperature, high methanol crossover, and high cost.

Various sulfonated polymers were used as a proton exchange membrane. Sulfonated polyether ether ketone, poly(styrene sulfonic acid), sulfonated polysulfone have been developed as a candidate material for DMFCs.

In this work, sulfonated poly(aromatic imide-co-aliphatic imide) membranes were synthesized at various degrees of sulfonation. The polyimide membranes were synthesized from 4,4'-diaminodiphenylmethane, sulfonated 4,4'-diaminodiphenylmethane, hexamethylenediamine and 3,3',4,4'-benzophenonetetracarboxylic dianhydride using dimethylsulfoxide as a solvent. The membrane film was fabricated by casting the mixture solution on to a petri dish. The effect of the degree of sulfonation on the membrane properties was investigated. The chemical structure of SDDM and SPI were characterized by Fourier transform infrared spectrum (FTIR) and the proton nuclear magnetic resonance (¹H-NMR). Degradation temperature of SPI was analyzed by the thermogravimetry analysis (TGA). The measured membrane properties were obtained and will be reported here: the proton conductivity, the methanol permeability, the ion exchange capacity, and the water uptake.

2. Experimental

2.1 Materials

3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA; Aldrich, purity 96%), 4,4'-diaminodiphenylmethane (DDM; Aldrich, purity 97%), and hexamethylenediamine (HDA; Aldrich, purity 98%) were used as the starting monomer. Fuming sulfuric acid (Merck, 65%) and concentration sulfuric acid (Univar, 98%) were used in the sulfonation. Dimethylsulfoxide (DMSO; RCI Labscan, 99.9%) was used as a solvent and benzoic acid (Univar, purity 99.9%) was used as a catalyst in the synthesis. Triethylamine (Fluka, purity 98%) was used in the membrane synthesis. Hydrochloric acid (HCl; Univar, 37%) was used to protonate the synthesized membrane. Sodium chloride (Lab-Scan, 99.0%) and sodium hydroxide (NaOH; Univar, pellet purity 97%) were used to determine the ion exchange capacity and the degree of sulfonation. Methanol (MeOH; Lab-Scan, 99.9%) and ethanol (EtOH; Lab-Scan, 99.9%) were used in measuring the methanol permeability.

2.2 Synthesis of 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid disodium salt (SDDM)

In a round bottom flask in ice bath, 10 g of 4,4'-diaminodiphenylmethane was dissolved in 20 ml of sulfuric acid. The solution was stirred until 4,4'-diaminodiphenylmethane was completely dissolved. Fuming sulfuric acid (5 ml) was added to the solution. The solution flask was continuously stirred in an ice bath for 2 hours. The solution temperature was heated up to 80 °C for 2 hours. After that the solution was cooled down to room temperature and poured into crushed ice. Sodium hydroxide solution was added to the solution until the basic solution precipitated. The precipitate was washed with DI water. The 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid disodium salt was dried in vacuum for at least 24 hours.

2.3 Synthesis of sulfonated poly(aromatic imide-co-aliphatic imide)

The sulfonated poly(aromatic imide-co-aliphatic imide) with a molar ratio (SDDM:DDM:HDA) 1: 4: 5 was synthesized in a one-step reaction. 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid disodium salt, triethylamine, hexamethylenediamine and 4,4'-diaminodiphenylmethane were dissolved in DMSO. The solutions were mixed together in a round bottom flask with a magnetic stirrer under

nitrogen atmosphere at 70 °C. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride was added into the flask to initiate the polymerization. The benzoic acid was added as the catalyst to the reaction. The reaction was proceeded by stirring for 24 hours to obtain a polyamic acid. The sulfonated poly(aromatic imide – co – aliphatic imide) was prepared by casting in a vacuum oven at 80 °C for 24 hours, 100 °C for 24 hours, 120 °C for 16 hours and 160 °C for 18 hours, respectively. The sulfonated copolyimide membrane was protonated by immersing the membrane in 1 M HCl solution for 2 days. The membrane was washed with DI water and dried in an oven at 80 °C for 1 day.

2.4 Characterization and Testing

2.4.1 FTIR and ¹H-NMR spectroscopy

FTIR spectrometer (Thermo Nicolet, Nexus 670) was used to study the structures of 4,4'-diaminodiphenylmethane (DDM), 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid disodium salt (SDDM), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA). The spectrometer was operated in the absorption mode with 64 scans and a resolution of 4 cm⁻¹ in the wave number range 400-4000 cm⁻¹. Optical grade KBr was used as the background material. DDM, SDDM, BTDA and HDA were mixed with KBr before the measurement. FTIR-ATR was used to measure the spectra of sulfonated poly(aromatic imide-co-aliphatic imide). ZeSe was used as a background material.

¹H-NMR spectra of 4,4'-diaminodiphenylmethane-2,2'-disulfonic acid in deuterated dimethylsulfoxide (DMSO-d₆) was recorded on a Barian mercury at 400 MHz, to identify the sulfonated position of the monomer.

2.4.2 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (Parkins Elmer, Pyris Diamond TG/DTA) was used to investigate the thermal stability of the polymer membranes using the TGA technique. The membranes were dried in vacuum for 24 hours. The experiment was carried out by weighting a membrane sample of 2-4 mg and placed it in an alumina pan. The sample pan was heated under nitrogen atmosphere at a heating rate of 20 °C/min. The temperature range was 50-900 °C.

2.4.3 Ion Exchange Capacity (IEC)

Ion exchange capacity of the sulfonated polyimide membranes was measured by a titration. The membranes were cut into small pieces. Then the membranes were immersed into 1 M NaCl solution and stirred for 2 days. The solution was titrated with a 0.01N NaOH solution. Phenolphthalein was used as an indicator in the titration. Ion Exchange Capacity was calculated from following equation:

$$\text{IEC (meq/g)} = \frac{\text{Consumed NaOH (ml)} \times \text{molarity NaOH (M)}}{W_{\text{dry}} \text{ (mg)}} \quad (1)$$

where V_{NaOH} refers to the volume of sodium hydroxide solution, C_{NaOH} refers to the concentration of sodium hydroxide solution [9].

2.4.4 Degree of Sulfonation (DS)

The polymer membranes were acidified by a 0.1 M HCL solution at room temperature for 24 hours. Then the membranes were washed with DI water and dried at 80 °C for 24 hours. After that the membranes were placed in a NaCl solution for 24 hours. The degree of sulfonation of solution was determined by the titration with 0.01 M NaOH using phenolphthalein as an indicator. Degree of Sulfonation of sulfonated copolyimide was calculated by following equation:

$$\text{DS(\%)} = \frac{(V_{\text{NaOH}}(\text{ml}) \times M_{\text{NaOH}}(\text{Molar})) / 1000}{\text{Mole of polymer membrane}} \times 100 \quad (2)$$

where V_{NaOH} is the volume of NaOH consumed and M_{NaOH} is the molarity of NaOH.

2.4.5 Water Uptake

Water sorption was measured by placing several polyimide membranes into distilled water at 80 °C for 5 hours. Then the membranes were taken out, quickly wiped with a tissue paper and weighted on a microbalance. The water uptake of sulfonated copolyimide film was calculated form following equation:

$$\text{Water uptake(\%)} = \frac{W_s - W_d}{W_d} \times 100\% \quad (3)$$

where W_s and W_d refer to the weights of the wet and dry samples, respectively [27].

2.4.6 Proton Conductivity Measurement

The proton conductivity of the films was recorded on an Agilent E4980A LCR meter. The fully hydrated films was cut to 0.5 cm × 0.5 cm pieces and coated with silver. The coated film was measured at a 1V potential using the alternating current in the frequency range of 20 Hz – 2 MHz. The graphs show relationship between the radian and the impedance. The conductivity σ was calculated from the impedance as follows:

$$\sigma(\text{Scm}^{-1}) = \frac{d}{R \times A} \quad (4)$$

where σ is the proton conductivity, d is the thickness of the membrane, S is the area of the interface of membrane in contact with the electrodes, and R refers to the measured resistance of the membrane – derived from the low frequency semicircle on the complex impedance plane with the Z axis [4].

2.4.7 Methanol Permeability

The methanol permeability through the membrane was determined by a liquid permeation cell where the concentration of methanol that permeated the membrane at 30 °C and 60 °C was measured. The liquid permeation cell is composed of two components assigned as A and B. A compartment A contained methanol at 2.5 M 250 ml and a compartment B contained DI water 250 ml. The samples from the chamber B were taken and analyzed to determine methanol concentration using the gas chromatography. The methanol permeability coefficient was calculated from the following equation:

$$P (\text{cm}^2/\text{s}) = \frac{K_B V_B L}{A(C_A - C_B)} \quad (5)$$

where C_a is the methanol concentration in feed, V_b is the solution volume of the permeate, L is the thickness of the membrane, A is the effective area of membrane and K_B is the methanol concentration permeate per time of permeate (the slope of methanol concentration profile in the compartment B) [7].

2.4.8 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was performed on an EPLEXOR[®] 100N GABO qualimeter. The samples with a thickness around 0.2 mm were cut on to 1 cm × 3 cm. The dynamic frequency sweep test was taken at frequency between 1 – 100 Hz

containing 25 data points. The experiment was performed with a 1% strain level, at 30 °C and 60 °C, in the tension mode [11].

3. Results and Discussion

3.1 Characterization of sulfonated monomer

The $^1\text{H-NMR}$ spectrum of DDM is shown in figure 4.1 (a), the characteristic doublet around 6.78 ppm and 6.44 ppm can be attributed to the aromatic protons H_3 and H_2 respectively. The singlet at 4.79 ppm is assigned to the primary anime proton H_1 , and the singlet at 3.53 ppm represents the methylene proton H_4 .

The $^1\text{H-NMR}$ of SDDM is shown in the Figure 4.2 (b). The signal at 7.16 ppm (doublet), 7.12 ppm (doublet of singlet), and 6.71 ppm (doublet of doublet) are assigned to the aromatic protons H_3 , H_5 , and H_2 , respectively. The singlet at 5.55 ppm is attributed the primary anime proton, which is correlated with H_1 . The methylene proton H_4 between the phenyl groups appears at 3.82 ppm as a singlet signal.

3.2 Characterization of sulfonated poly(aromatic imide-co-aliphatic imide)

The FTIR spectra identifying functional group of sulfonated poly(aromatic imide-co-aliphatic imide) membrane is shown in figure 4.4. The spectra of copolymer with a molar ratio of SDDM: DDM: HDA = 1: 4: 5 and unsulfonated copolyimide (SDDM: DDM: HDA = 0: 5: 5) are interpreted: the band around 1777 cm^{-1} and 1709 cm^{-1} can be assigned to the C=O imide carbonyl group [1]. The band at 1662 cm^{-1} is assigned to the carbonyl group of benzophenone [24]. A band at 1368 cm^{-1} is attributed to the C-N-C stretching vibration of the imide ring [26]. The characteristic peak that represents the sulfonated of copolyimide is the SO_3 asymmetric and symmetric stretching vibration of hydrated sulfonic acids which appear at 1182 and 1019 cm^{-1} respectively [3]. These spectra show that polyamic acid was successfully converted to polyimide.

3.3 Thermogravimetric analysis

The thermogravimetric analysis of membrane is important for fuel cell membrane application. The membrane should be stable when fuel cell operates at high temperature. The thermal behavior of sulfonated copolyimide is shown in figure 4.5. Sulfonated copolyimide membrane possesses similar two steps weight losses. The decomposition occurs at around 180 to 480 °C. The first decomposition occurs between

180 - 250 °C representing the degradation of sulfonic groups. The decomposition of polymer main chain occurs at around 450 °C [2]. This sulfonated copolyimide possesses a fairly good thermal stability.

3.4 Ion exchange capacity and water uptake

The IEC of sulfonated copolyimide as determined by titrating the ion exchanged sulfonated copolyimide with sodium hydroxide is shown in table 4.1. The IEC of the membranes is controlled by the sulfonation level. A higher sulfonation level result in a higher IEC, as the ion is exchanged at the position of the sulfonic group. The hydrogens of sulfuric acid are exchanged with sodium ions as a function of the sulfonation level. The IEC of sulfonated copolyimide is in the range of 0 - 1.32 meq/g. The experimental IEC values of copolyimides are lower than the theoretical value due to incomplete acidification of the membrane. The membrane with the highest degree of sulfonation shows the highest IEC value which is 3.4 times higher than that of the Nafion[®]. The membranes were soaked in DI water at 80 °C for 5 hours and the weight differences between before and after hydration were measured as the water uptakes. The sulfonated copolyimide membranes generally show a low relative water uptake values less than 4%. The water uptake could be interpreted by the aromatic ring of copolyimide and the non side chain aliphatic part which is closely packed limiting the water uptake.

3.5 Proton conductivity

The proton conductivity was measured by a LCR meter. The membranes were hydrated by immersing in deionized water in room temperature for 24 hours before the measurement. Figure 4.7 shows the proton conductivity of sulfonated copolyimide membranes as a function of degree of sulfonation at room temperature. The conductivities of sulfonated copolyimide membranes increase significantly with increasing degree of sulfonation; as protons pass through the sulfonic channels, they increase in size. The proton conductivity value of the sulfonated copolyimides are in the range of 0.001603 – 0.003241 S/cm, the maximum value is higher than that of the sulfonated polybenzimidazoles from 3,3'-disulfonate-4,4'-dicarboxylbiphenyl which is 0.00279 S/cm [28], and also higher than that of the sulfonated polybenzimidazoles which is 0.0027 S/cm [29]. However, the conductivity values of the sulfonated

copolyimides in the present work are lower than that of the Nafion[®] (0.00683 S/cm) [14].

3.6 Methanol Permeability

The methanol permeability is the diffusion of methanol through the membrane. The concentration of methanol passing through the membrane is shown a function of time in figure 4.8 where methanol permeability was obtained from the slope. The methanol permeability of the sulfonated copolyimides was measure at 30 °C and 60 °C in a period of one week. The synthesized polymer possesses the ability to prevent methanol permeation. At 30 °C, the methanol cannot permeate through the membrane within 7 days. At 60 °C, the methanol cannot pass through the membrane in the first two days, after that the methanol slightly passes through the membrane. The methanol permeability values of sulfonated copolyimides were measured as a function of the sulfonation level and compared with that of the Nafion[®] as shown in figure 4.9. A higher sulfonation level displays higher methanol permeability. Methanol permeation is controlled by the hydrophilic channel size [4]. Methanol permeates through the hydrophilic water channel consisting of the sulfonic group [5]. The highest methanol permeability of the sulfonated copolymer is $2.7482 \times 10^{-8} \text{ cm}^2/\text{s}$ which is 63 times lower than that of Nafion[®] ($1.7400 \times 10^{-6} \text{ cm}^2/\text{s}$). The present permeability values are lower than all series of sulfonated copolyimides from the experiment of Okamoto *et al.* ($0.34 \times 10^{-2} \text{ cm}^2/\text{s} - 2.4 \times 10^{-2} \text{ cm}^2/\text{s}$) [13]. This might be caused by the stiffness of the polymer chain which is consisted of the aromatic and non branched aliphatic that are closely packed together preventing the permeation of methanol.

3.7 Dynamic mechanical analyst

The mechanical property of sulfonated copolyimide was observed by DMA using the frequency sweep and temperature sweep methods with a low amplitude strain. The frequency dependence of the storage modulus of the unsulfonated and sulfonated copolyimide membranes is in figure 4.10. The storage modulus values of the sulfonated copolyimides are in the range of 2589 – 3465 MPa for 30 °C and 2218 – 3071 MPa at 60 °C. The storage modulus value of the sulfonated copolyimides is higher than those of sulfonated poly[2,20-(p-oxydiphenylene)-5,50-bibenzimidazole] which is between 81 – 98 MPa [10]. The temperature depends on $\tan \delta$. The membrane shows a higher $\tan \delta$

indicating a higher flexibility with increasing temperature. It could be suggested that the polymer chain is stretched when heated leading to a decrease in the storage modulus at a higher temperature. The $\tan \delta$ of the membrane also does not possess a distinct Tg peak from 30 °C to 90 °C. This shows that the membrane is strong enough to operate in this temperature range and a potential candidate as a fuel cell membrane [11].

4. Conclusions

4,4'-diaminodiphenylmethane-2,2'-disulfonic acid was synthesized as monomer. Sulfonated copolyimides with different degrees of sulfonation were synthesized. The structure of SDDM was characterized by $^1\text{H-NMR}$. The chemical structure of unsulfonated and sulfonated copolyimides was confirmed by FTIR. The functional groups of imide carbonyl, imide ring and sulfonic groups appear at 1709, 1368 and 1021 cm^{-1} , respectively. Sulfonated copolyimides show high operating temperature where the first degradation of sulfonic groups occurs at around 180 °C. A higher degree of sulfonation of copolyimide results in a higher IEC. The water uptake of this sulfonated copolyimide is less than 4%. The proton conductivity of sulfonated copolyimide at room temperature depends on the proportion of SDDM. The obtained membranes possess the proton conductivities between 0.0016 and 0.0032 S cm^{-1} . The methanol permeability of sulfonated copolyimide also depends on the degree of sulfonation; the higher degree of sulfonation shows the higher methanol permeability. The highest methanol permeability of the sulfonated copolyimide is $2.7482 \times 10^{-8} \text{ cm}^2/\text{s}$ which is extremely lower than that of Nafion[®] ($1.7400 \times 10^{-6} \text{ cm}^2/\text{s}$).

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References

1. Lee CH, Park CH, and Lee YM, *J Membrane Sci* **313**: 199-206 (2008).
2. Geniesa C, Merciera R, Silliona N, Cornetb GG, and Pineric M, *Polymer* **42**: 359-373 (2001).
3. Li Q, Xu Z, and Yi C, *J Appl Polym Sci* **107**: 797-802 (2008).
4. Park HB, Lee CH, Sohn JY, and Lee YM, *J Membrane Sci* **285**: 432-443 (2006).
5. Wu D, Fu R, Xu T, Wu L, and Yang W, *J Membrane Sci* **310**: 522-530 (2008).
6. Woo Y, Oh SY, Kang YS, and Jung B, *J Membrane Sci* **220**: 31-35 (2003).
7. Zhai F, Gou X, Fang J, and Xu H, *J Membrane Sci* **296**: 102-109 (2007).
8. Zhu X, Pan H, Liang Y, and Jian X, *Eur Polym J* **44**: 3782-3789 (2008).
9. Deligöz H, Vantansever S, Koç SN, Öksüzömer F, Özgümüş S, and Gürkaynak MA, *J Appl Polym Sci* **110(2)**: 1216-1224 (2008).
10. Xu H, Chen K, Guo X, Fang J, and Yin J, *Polymer* **48**: 5556-5564 (2007).
11. Han SI, Im SS, and Kim DK, *Polymer* **44**: 7156-7173 (2003).
12. Deligöz H, Vantansever S, Koç SN, Öksüzömer F, Özgümüş S, and Gürkaynak MA, *J Appl Polym Sci* **110(2)**: 1216-1224 (2008).
13. Okamoto K, Yan Y, Yamada O, Islam MN, Honda T, Mishima T, Suto Y, Tanaka K, and Kita H, *J Membrane Sci* **258**: 115-122 (2005).
14. Matasuguchi M, and Takahashi H, *J Membrane Sci* **281**: 707-715 (2006).
15. Li N, Cui Z, Zhang S, Wei X, *J Membrane Sci* **295**: 148-158 (2007).
16. Blázquez JA, Iruin JJ, Eceolaza S, Marestin C, Mercier R, Mecerreyes D, Meguel O, Vela A, and Marcilla R, *J Power Sources* **151**: 63-68 (2005).

17. Fang J, Guo X, Harada S, Watari T, Kita H, and Okamoto K, *Macromolecules* **35**: 9022-9028 (2002).
18. Vallejo E, Pourcelly G, Gavach C, Mercier R, and Pineri M, *J Membrane Sci* **160**: 127-137 (1999).
19. Wang Z, Li X, Zhao C, Ni H, and Na H, *J Power Sources* **160**: 969–976 (2006).
20. Le X, Bai H, and Ho W, *J Membrane Sci* **279**: 570-577 (2006).
21. Lee C, Park C, and Lee Y, *J Membrane Sci* **313**: 199-206 (2008).
22. Deligöz H, and Yilmazoğlu M, *J Power Sources* **196**: 3496-3502 (2011).
23. Yin Y, Fang J, Cui Y, Tanaka K, Kita H, and Okamoto K, *Polymer* **44**: 4509-4518 (2003).
24. García MG, Marchese J, and Ochoa NA, *Int J Hydrogen Energ* **35**: 8983-8992 (2010).
25. Huang YJ, Ye YS, Yen YC, Tsai LD, and Hwang BJ, *Int J Hydrogen Energ* **36**: 15333-15343 (2011).
26. Lee CH, and Wang YZ, *Journal of Polymer Science Part A: Polymer Chemistry* 2263-2276 (2007).
27. Pan H, Zhu X, Jian X, *Electrochimica Acta* **55**: 709-714 (2010).
28. Kang S, Zhang C, Xiao G, Yan D, and Sun G, *J Membrane Sci* **334**: 91-100 (2009).
29. Qing S, Huang W, Yan D, *React Funct Polym* **66**: 219-227 (2006).

Table Caption

Table 4.1 The ion exchange capacity, water uptake and actual degree of sulfonation of sulfonated copolyimide

Figure Captions

Figure 4.1 Synthesis of the SDDM monomer.

Figure 4.2 The ^1H -NMR spectra of monomer and sulfonated monomer: (a) DDM; (b) SDDM.

Figure 4.3 Synthesis of the sulfonated copolyimide.

Figure 4.4 The FTIR spectra of unsulfonated copolyimide and sulfonated copolyimide.

Figure 4.5 The TGA curves of sulfonated copolyimides.

Figure 4.6 Ion exchange capacity and degree of sulfonation of sulfonated copolyimides.

Figure 4.7 The conductivity of sulfonated copolyimides as a function of degree of sulfonation by LCR meter.

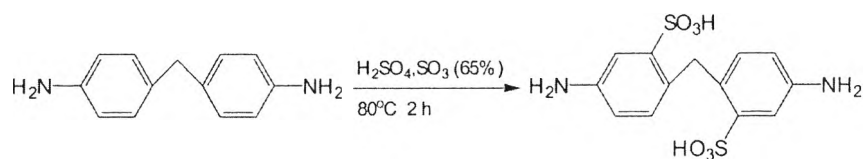
Figure 4.8 The comparison of methanol permeability of SDH 3, SDH 4 and SDH 5 at 60 °C.

Figure 4.9 Methanol permeability of sulfonated copolyimides at 60 °C.

Figure 4.10 Comparison of storage modulus (E') of sulfonated copolyimides vs. frequency at 30 °C by DMA.

Table**Table 4.1** The ion exchange capacity, water uptake and actual degree of sulfonation of sulfonated copolyimide

Sample	SDDM: DDM: HDA ratio	Calculated IEC (meq/g)	Experimental IEC (meq/g)	Water uptake (%)	Actual DS (%)
SDH 0	0: 5: 5	0	0	2.18	0
SDH 1	1: 4: 5	0.87	0.84	2.14	19.32
SDH 2	2: 3: 5	1.49	1.28	2.18	34.46
SDH 3	3: 2: 5	2.23	2.20	3.82	58.94
SDH 4	4: 1: 5	2.97	2.82	3.20	75.96
SDH 5	5: 0: 5	3.24	3.12	1.99	96.29
Nafion [®] [17]	-	-	0.91	-	

Figures**Figure 4.1** Synthesis of the SDDM monomer.

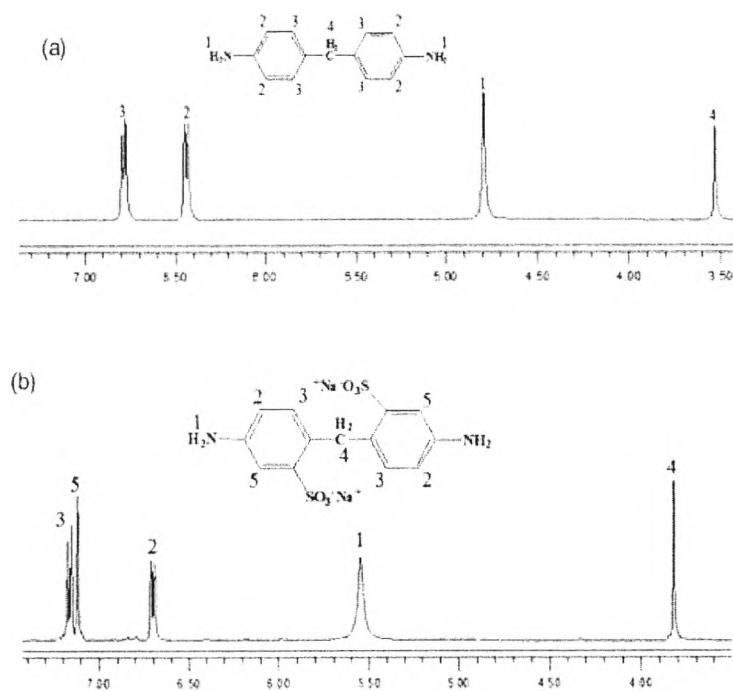


Figure 4.2 The $^1\text{H-NMR}$ spectra of monomer and sulfonated monomer: (a) DDM; (b) SDDM.

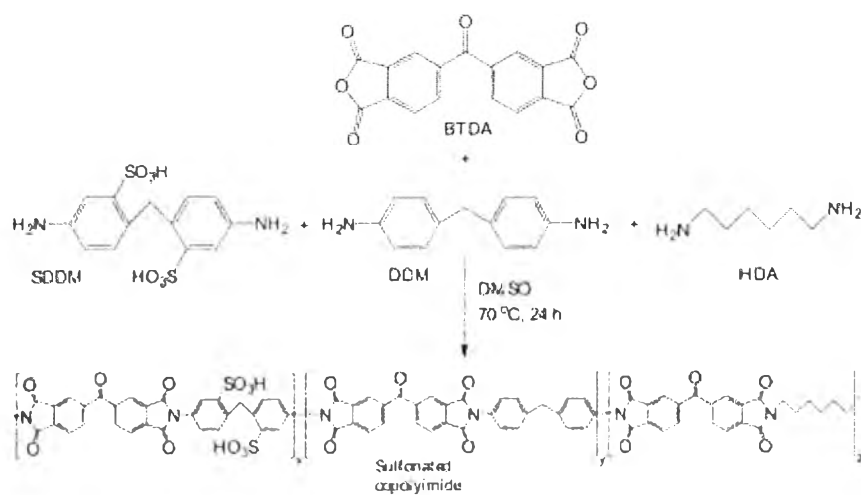


Figure 4.3 Synthesis of the sulfonated copolyimide.

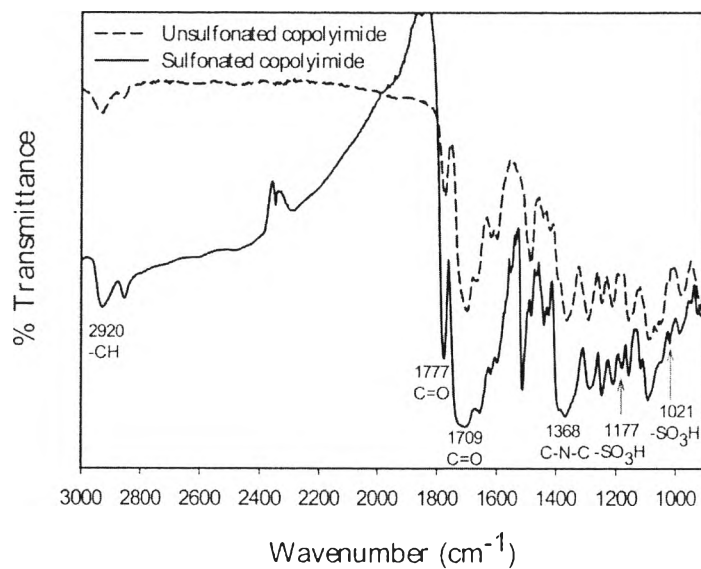


Figure 4.4 The FTIR spectra of unsulfonated copolyimide and sulfonated copolyimide.

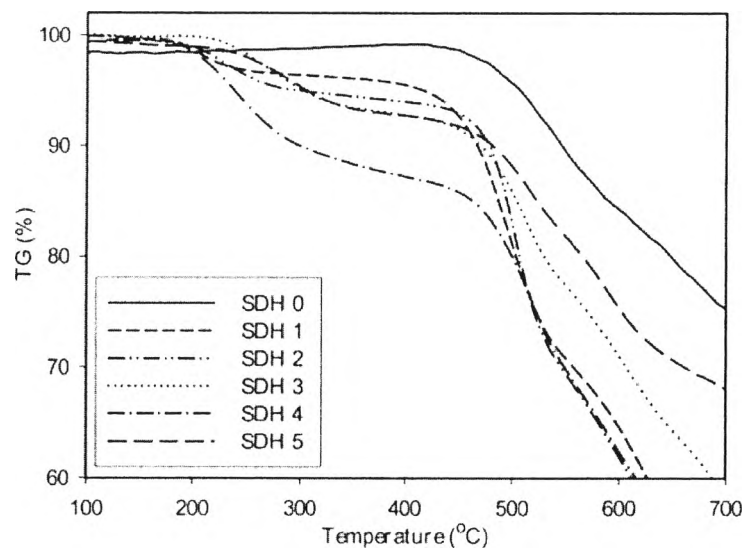


Figure 4.5 The TGA curves of sulfonated copolyimides.

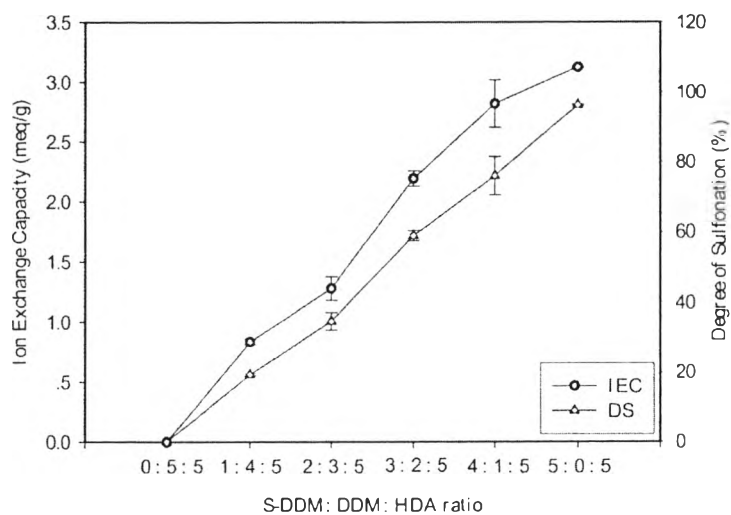


Figure 4.6 Ion exchange capacity and degree of sulfonation of sulfonated copolyimides.

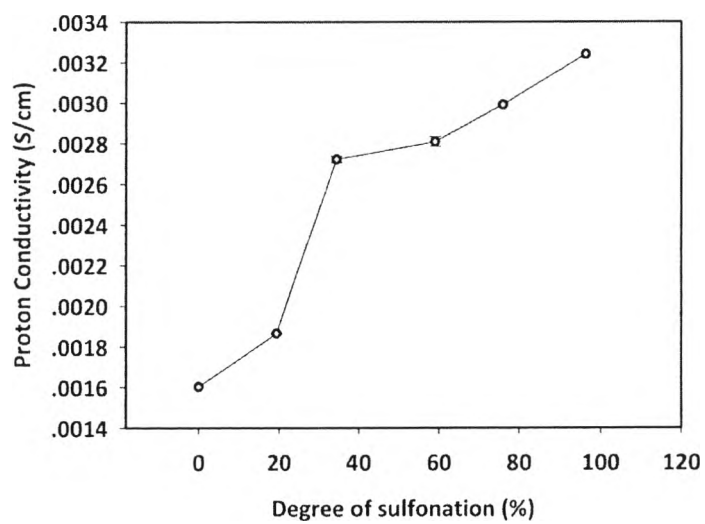


Figure 4.7 The conductivity of sulfonated copolyimides as a function of degree of sulfonation by an LCR meter.

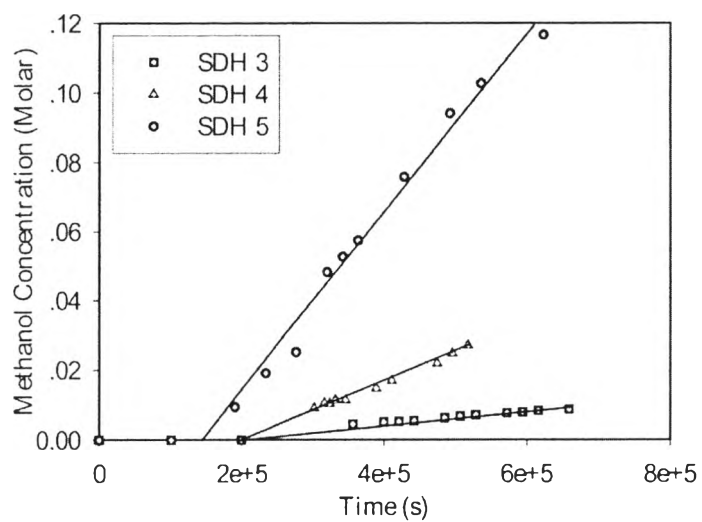


Figure 4.8 The comparison of methanol permeability of SDH 3, SDH 4, and SDH 5 at 60 °C.

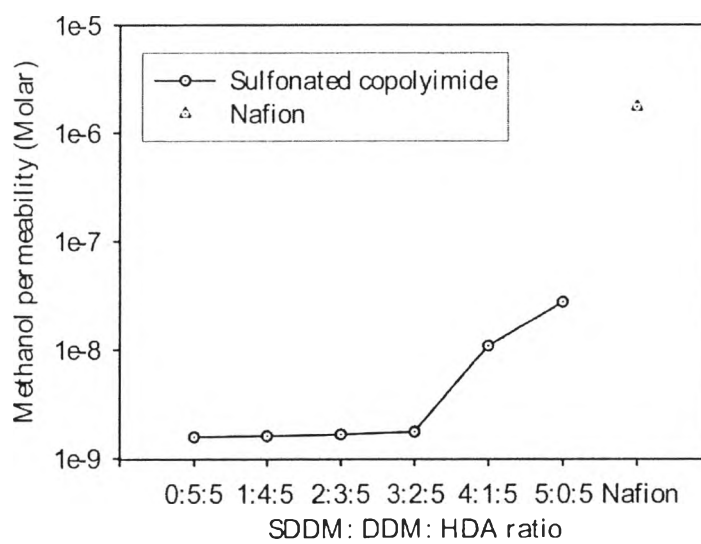


Figure 4.9 Methanol permeability of sulfonated copolyimides at 60 °C.

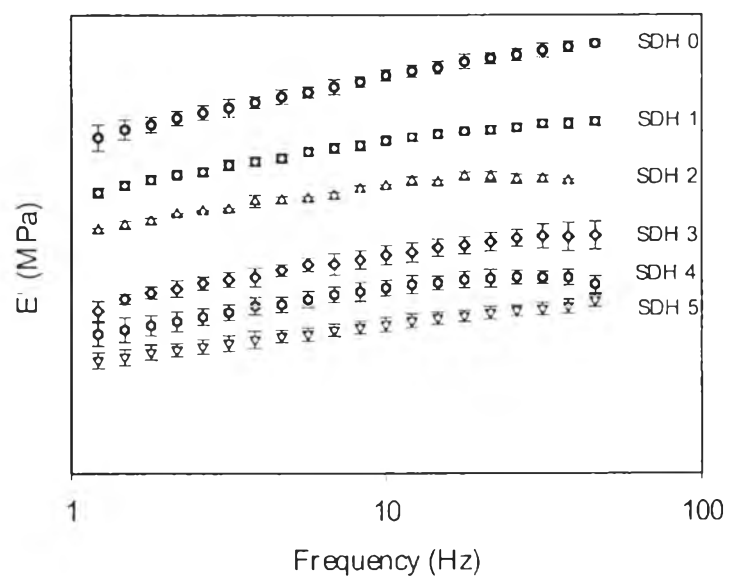


Figure 4.10 The storage modulus (E') of sulfonated copolyimides vs. frequency at 30 °C by DMA.