



CHAPTER III METHODOLOGY

3.1 Materials

3.1.1 Chemicals

- 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (Aldrich, purity 96%)
- 4,4'-Diaminodiphenylmethane (Aldrich, purity 97%)
- Hexamethylenediamine (Aldrich, purity 98%)
- Fuming sulfuric acid (Merck, 65%)
- Concentration sulfuric acid (Univar, 98%)
- Benzoic acid (Univar, purity 99.9%)
- Triethylamine (Fluka, purity 98%)
- Hydrochloric acid (Univar, 37%)
- Sodium chloride (Lab-Scan, 99.0%)
- Sodium hydroxide (Univar, pellet purity 97%)
- Methanol (Lab-Scan, 99.9%)
- Ethanol (Lab-Scan, 99.9%)

3.1.2 Solvent

- Dimethylsulfoxide (RCI Labscan, 99.9%)

3.1.3 Gas

- Nitrogen gas (N₂; High purity, 99.99%)

3.2 Equipment

3.2.1 Analytical Instruments

- Fourier transform infrared spectrometer (FTIR; Thermo Nicolet, Nexus 670)
- Nuclear magnetic resonance (NMR)
- Thermogravimetric analysis (PerkinElmer, Pyris Diamond TG/DTA)
- Gas chromatography (GC; Pr2100)
- LCR meter (Agilent E4980A)
- Dynamic mechanical analysis (DMA; EPLEXOR[®] 100N GABO qualimeter)

3.2.2 Glassware and Apparatus

- One-neck round bottom flask
- Two-neck round bottom flask
- Magnetic bar
- Oil bath
- Stand, clamp and clamp holder
- Hot-plate/Stirrer (Yellowline, MSH B)
- Thermostat and controller (Maxtech, MC-2438)
- Oven (Memmert, U50)
- Liquid permeation cell

3.3 Experimental Method

3.3.1 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 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 (Zhu *et al.*, 2008).

3.3.2 Synthesis of Sulfonated Poly(aromatic imide-co-aliphatic imide)

The sulfonated poly(aromatic imide-co-aliphatic imide) with molar ratio (SDDM:DDM:HDA) 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 polymerize. The benzoic acid was added as a catalyst to the reaction. The reaction was continued by stirring for 24 hours to obtain polyamic acid. The sulfonated poly(aromatic imide – co – aliphatic imide) was prepared by casting in 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 (Lee and Wang, 2007).

3.4 Characterizations and Measurement

3.4.1 ¹H-Nuclear Magnetic Resonance (¹H-NMR)

¹H-NMR, the monomers and polymer membranes were dissolved in deuterated dimethyl sulfoxide (DMSO-d₆). The internal standard was tetramethylsilane (Zhai *et al.*, 2007).

3.4.2 Fourier Transform Infrared (FTIR)

Sulfonated 4,4'-Diaminodiphenylmethane and poly(aromatic imide-co-aliphatic imide) were characterized by FTIR (Thermo Nicolet, Nexus 670). The FTIR spectra were measured in the transmission mode. The homogenous membrane was measured in the wave number range 400-4000 cm^{-1} . The number of scan of each sample was 64 and a resolution was 4 cm^{-1} (Woo *et al.*, 2003).

3.4.3 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (PerkinElmer, 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 membranes of 2-5 mg were placed in an alumina pan and heated at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere. The temperature range was 50-900 $^{\circ}\text{C}$ (Zhu *et al.*, 2008).

3.4.4 Ion Exchange Capacity (IEC)

The Ion exchange capacity (IEC) indicates the number of milliequivalents of ion in 1 g of dry sample. The IEC was determined by acidified by 0.1 M hydrochloric solution at room temperature for 24 hours. Then the membranes was washed with deionization water and dried at 80 $^{\circ}\text{C}$ for 24 hours. After that the membranes was placed in a sodium chloride solution for 48 hours. The degree of sulfonation of solution was determined by the titration with 0.01 M sodium hydroxide using phenolphthalein as an indicator. The IEC was calculated from the following equation:

$$\text{IEC (meq/g)} = \frac{\text{Consumed NaOH (ml)} \times \text{molarity NaOH (M)}}{W_{\text{dry}} \text{ (mg)}} \quad (3.1)$$

where W_{dry} refers to the weight of dry sample (Deligöz *et al.*, 2008).

3.4.5 Degree of Sulfonation (DS)

The degree of sulfonation represents the numbers of sulfonic groups in the sulfonated membrane was calculated from the same experimental of IEC by the following equation:

$$DS(\%) = \frac{(V_{NaOH} \times M_{NaOH}) / 1000}{\text{Mole of polymer membrane}} \times 100 \quad (3.2)$$

where V_{NaOH} and M_{NaOH} refer to the used volume and molecular weight of sodium hydroxide respectively.

3.4.6 Water Uptake (WU)

Water sorption was measured by drying the membranes at 80 °C for 24 hours. The membranes were weighted on a microbalance and placed them into distilled water at 80 °C for 5 hours. Then the membranes were taken out, quickly wiped with a tissue paper and then weighted again. The water uptake was calculated from following formula. The measurements were repeated three times to obtain the average water uptake value

$$\text{Water uptake} = \frac{W_s - W_d}{W_d} \times 100\% \quad (3.3)$$

where W_s and W_d refer to the weights of the wet and dry samples, respectively (Deligöz *et al.*, 2008).

3.4.7 Proton Conductivity Measurement

The proton conductivity of the membrane was recorded on an Agilent E4980A LCR meter. The fully hydrated membranes were cut to 0.5 cm × 0.5 cm pieces and coated with silver. The coated membranes were 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 follow:

$$\sigma(\text{Scm}^{-1}) = \frac{d}{SR} \quad (3.4)$$

where σ = the proton conductivity

d = the thickness of the membrane

S = the area of the inter face between the membrane and the electrode

R = 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 (Park *et al.*, 2006).

3.4.8 Methanol Permeability

The methanol permeability through the membrane was determined by a liquid permeation cell and the concentration of methanol that permeated the membrane at 60 °C. The liquid permeation cell is composed of 2 chambers assigned as A and B. The chamber A contained 2.5 M of methanol, the chamber B initially contained DI water where the sample membrane was placed in the between. The sample from the chamber B was analyzed to determine methanol concentration using the gas chromatography. The methanol permeability coefficient was calculated from the following equation:

$$P = \frac{C_b V_b L}{A C_a t} \quad (3.5)$$

where P = the methanol permeability

C_a = the methanol concentration in feed

C_b = the methanol concentration permeated

V_b = the solution volume of the permeate

L = the thickness of the membrane

A = the effective area of membrane

t = the time of the permeation (Zhai *et al.*, 2007).

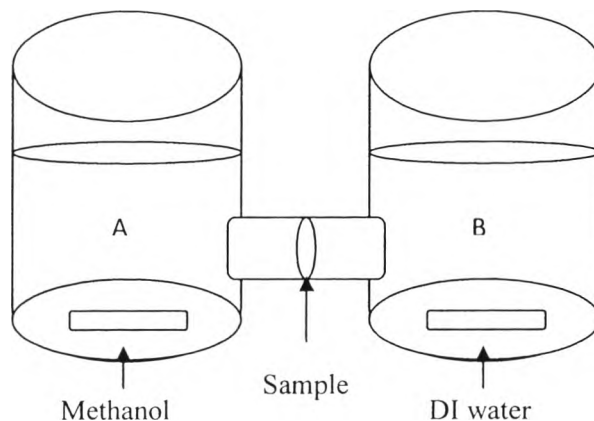


Figure 3.1 Schematic diagram of methanol permeability measurement.

3.4.9 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis was performed on a 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 1% strain level, at 30 °C and 60 °C, in the tension mode (Han *et al.*, 2003 and Xu *et al.*, 2003).