



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

Branched polyethylenimine (*b*PEI) ( $MW\ 25000\ g\ mol^{-1}$ ), 2-(chloromethyl) benzimidazole (MBz), were obtained from Aldrich Co (USA). Poly (ether ether ketone) powder was a gift from JJ-Degussa Chemical (Thailand) Ltd., Poly (acrylic acid) (PAA) was obtained from Fluka Chemical (Buchs, Switzerland). Potassium hydroxide (KOH), and dimethyl sulfoxide (DMSO) were purchased from Acros Co (Thailand). Hydrochloric acid (HCl) was bought from Labscan Co (Thailand).

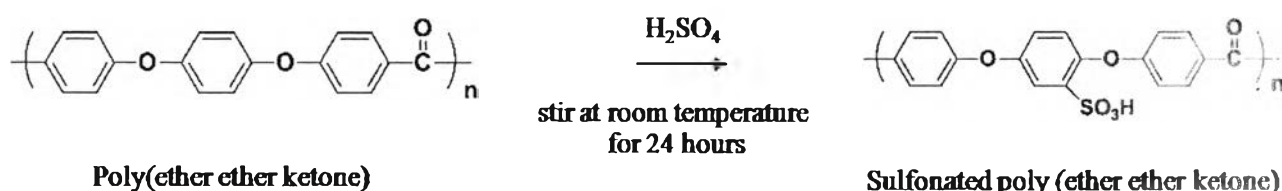
### 3.2 Instruments and Equipment

The structure characterization was carried out by using a Nicolet 6700 Fourier transform infrared (FTIR) with 32 scans with a resolution of  $2\ cm^{-1}$  and a frequency range of  $4000 - 650\ cm^{-1}$ . Proton nuclear magnetic resonance ( $^1H$ -NMR) spectra were recorded using a Bruker Avance spectrometer (Germany) operating at Larmor frequencies of 500.13 MHz. ATR-FTIR mode was used to clarify the multilayer membrane formation. Contact angle was used to investigate the surface of membrane. Thickness gauge was applied to measure the membrane thickness. The proton conductive performance of the layered-by-layered membrane was evaluated by using impedance spectroscopy and applying alternating current under the temperature range  $30\ ^\circ C$ - $170\ ^\circ C$ .

### 3.3 Experimental

#### 3.3.1 Sulfonation of Poly (ether ether ketone) (SPEEK)

PEEK was dried in a hot air oven at 70 °C overnight before dissolving in 400 ml of concentrated sulfuric acid (96%) at room temperature under strong agitation for 24 hours. The polymer solution was precipitated into an excess amount of ice-cold water. The precipitates were collected and washed several times with deionized water. The sediment was dried in an oven at 70 °C for 24 hours to obtain the yellow powder.



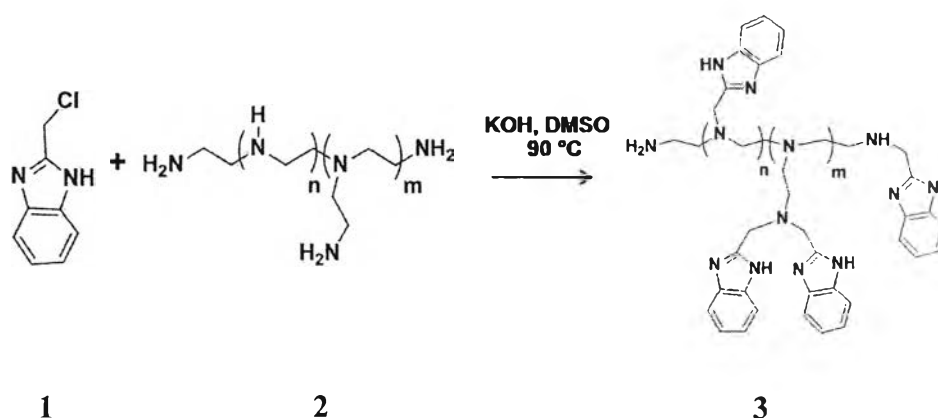
Scheme 3.1

#### 3.3.2 SPEEK Membrane

A solution of SPEEK in DMSO (5% w/w) was cast on a glass mold which was constantly heated at 80 °C for 48 hours to obtain the membrane. The membrane was immersed in H<sub>2</sub>SO<sub>4</sub> solution (1.0 M) at room temperature for 24 hours and dried in an oven at 60 °C for 24 hours.

#### 3.3.3 Preparation of Multibenzimidazole Branched Polyethylenimine (MPEI)

bPEI (2 g, 46 mmol) was dissolved in DMSO (10 ml) and KOH (0.521 g, 9.3 mmol) was further added. The solution was stirred and heated at 90 °C for 30 min and DMSO solution (20 ml) containing MBz (1.549 g, 9.3 mmol) was added dropwisely. After stirring at 90 °C under nitrogen atmosphere for 24 hours, the reaction mixture was cooled down to room temperature and neutralized with 1 M HCl. The product was dialyzed in deionized water several times followed by freeze-drying to obtain MPEI.



**Scheme 3.2**

#### 3.3.4 Preparation of Acid Polymer Solution

Poly (acrylic acid) was dissolved in methanol with concentration of 5% w/v and vigorously stirred at room temperature to obtain homogenous solution.

#### 3.3.5 Preparation of Basic Polymer Solution

MPEI was dissolved in methanol with concentration of 5% w/v and vigorously stirred at room temperature to obtain homogeneous solution.

#### 3.3.6 Layered-by-Layered Membrane Fabrication

SPEEK membrane was doped with 1M sulfuric acid ( $H_2SO_4$ ) at room temperature for 24 hours. The membrane was cut in the dimension of 3 cm  $\times$  2 cm and was alternatively immersed in both basic and acid polymer solution followed by drying at room temperature to obtain multilayer polymer membrane. The membrane obtained was kept in the desiccators to control the humidity before use.