

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Monomer

Divinylbenzene (DVB), 4-aminophenol and bis(4-chlorophenyl) sulfone were supplied by Merck. Bisphenol A 97% was supplied by Aldich. Maleic anhydride was supplied by Fluka.

#### 3.1.2 Solvents

N,N-dimethylacetamide (DMAc) 99% pure was supplied by Acros. Toluene (T) and dimethylformamide were supplied by Lab Scan. Isopropanol, methanol and ethanol were supplied by Etalma.

#### 3.1.3 Surfactants

Sorbitan monooleate (SPAN 80) and dodecylbenzenesulfonic acid sodium salt (DDBSs) were supplied by Sigma. Cetyltrimethylammonium bromide (CTAB) was supplied by Fluka.

#### 3.1.4 Initiator

Potassium persulfate ( $K_2S_2O_8$ ) was supplied by Fluka.

#### 3.1.5 Catalyst

Potassium carbonate and phosphorus pentoxide were supplied by Carlo Erba.

#### 3.1.6 Stabilizer

Calcium chloride dehydrate ( $CaCl_2 \cdot 2H_2O$ ) was supplied by Fluka.

### 3.2 Equipments

#### 3.2.1 Nuclear Magnetic Resonance (NMR)

The NMR spectra of maleimide-terminated poly(arylene ether sulfone) oligomers were obtained using  $^1H$ -NMR and  $^{13}C$ -NMR at the Chemistry Department, Faculty of Science, Naresuan University.

### 3.2.2 Fourier Transform Infrared Spectroscopy (FT-IR)

The FT-IR spectra of maleimide-terminated poly(arylene ether sulfone) oligomers were obtained using Nicolet Nexus 670 FT-IR spectrometer in the frequency range of  $4000\text{-}400\text{cm}^{-1}$  with 32 scans at the resolution of  $2\text{ cm}^{-1}$ . KBr pellet technique was applied in the preparation of powder samples.

### 3.2.3 Surface Area Analyzer (SAA)

Nitrogen adsorption-desorption isotherms were obtained at  $-196^{\circ}\text{C}$  on a Quantachrome Autosorb-1MP. Samples were degassed at  $100^{\circ}\text{C}$  in a vacuum furnace prior to analysis. Surface areas were calculated using the BET method. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using adsorption of nitrogen isotherm.

### 3.2.4 Thermalgravimetric Analysis (TGA)

Thermalgravimetric Analysis (TGA) was performed to measure the thermal stability of the PolyHIPEs. TGA of PolyHIPEs was performed using a Perkin Elmer/Pyris Diamond TG/DTA instrument. Experiments were carried out under nitrogen gas atmosphere. Samples were cut into small pieces weigh about 2–5 mg. Then the samples were loaded on the platinum pan and heated to  $800^{\circ}\text{C}$  from  $40^{\circ}\text{C}$  at a heating rate of  $10^{\circ}\text{C}/\text{min}$ . One steps degradation was observed during testing, and the decomposition temperature was recorded corresponding to 50% decomposition of the material.

### 3.2.5 Universal Testing Machine (LLOYD)

A Lloyds Universal Testing Machine (Lloyds/LRX) equipped with a 500 N load cell was used to measure mechanical properties in compression. The samples were loaded at a rate of  $1.27\text{ mm}/\text{min}$ . Samples of 25.4 mm in diameter and 25.4 mm in height were used for tested of each PolyHIPEs. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached.

### 3.2.6 Emission Scanning Electron Microscope (FE-SEM)

Field emission scanning electron microscopy was performed on Hitachi S-4800 Model to observe surface morphology of PolyHIPEs. The specimens were coated with platinum under vacuum before observation to make them electrically conductive.

### 3.2.7 CO<sub>2</sub> Gas adsorption

Study of CO<sub>2</sub> gas adsorption capacities of polyHIPEs were carried out using a pilot gasification unit at the Chemical Technology Department, Faculty of Science, Chulalongkorn University. Samples were cut into small pieces weigh about 1-2 g. Then the samples were loaded into sample tube 2×25 cm. CO<sub>2</sub> 20 ml/min and He 80 ml/min were flowed through the sample at room temperature. The residue of CO<sub>2</sub> was measured by a gas chromatography instruments, the column used Shimadzu 2014, flow rate 35 ml/min.

## 3.3 Methodology

### 3.3.1 Preparation of Maleimide-terminated poly(arylene ether sulfone)

#### 3.3.1.1 *Synthesis of 1-(4-hydroxy-phenyl)-pyrrole-2,5-dione (HPMI)*

The HPMI was synthesized according to Choi et al. In a 100 ml round bottom flask were added 30 g maleic anhydride and 30.6 g p-aminophenol and 80 ml DMF at 0 °C. A mixture of 15 g P<sub>2</sub>O<sub>5</sub> in 50 ml DMF and 8 g of concentrated H<sub>2</sub>SO<sub>4</sub> was added over 30 min to a round bottom flask while the flask was being stirred by a magnetic stirrer. Then the reaction mixture was stirred at 70°C for 3 h in an oil bath. After that the mixture was poured into 500 ml of de-ionized ice water and yellow precipitation was observed. The precipitate was dried under vacuum chamber for approximately 12 h and was purified by recrystallization in isopropanol. The product was in the form of yellow needle like crystals. (scheme 1)

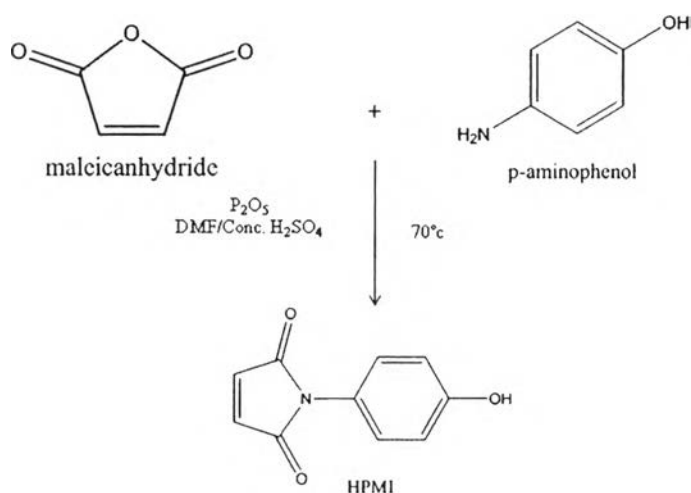
#### 3.3.1.2 *Characterization of HPMI*

Identification of HPMI composition was carried out using Fourier Transform Infrared Spectroscopy (FT-IR)

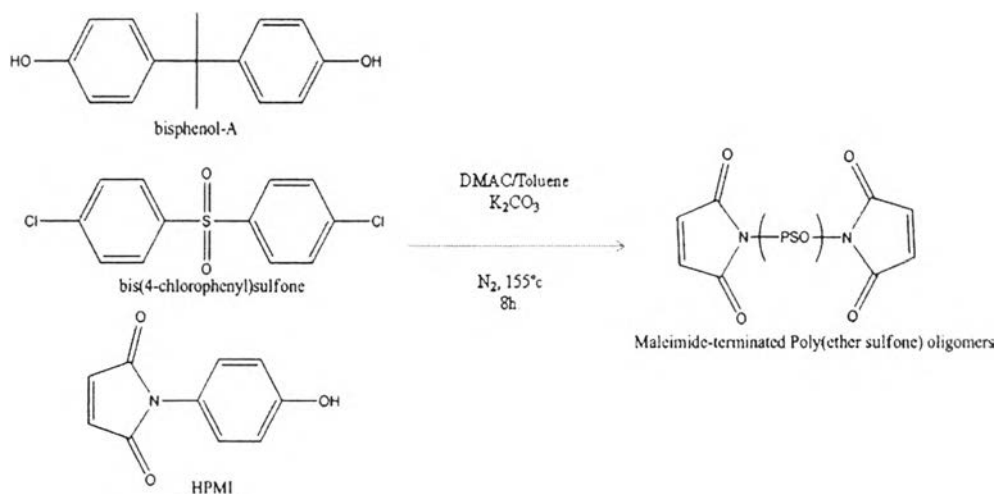
#### 3.3.1.3 *Synthesis of maleimide-terminated poly(arylene ether sulfone) oligomers*

The polymerization was carried out in a 500 ml three-necked round bottom flask which was fitted with Dean Stark trap, nitrogen inlet, and magnetic stirrer. Bis-(4-chlorophenyl)-sulfone 5.751 g was added to the reaction flask followed by bisphenol A 4.332 g and HPMI 0.4002 g, and rinsed with DMAc 65 ml to assure quantitative amount of monomers. Dried potassium carbonate 3.395 g and

toluene 18 ml were added next and the reaction was refluxed at 145°C for 4 h. After the water had been removed, toluene was drawn from the Dean Stark trap the temperature increased to 155°C. The reaction proceeded for 8 h, after the solution was cooled and filtered to remove inorganic salts, then coagulated in an excess rapid stirred methanol, prior to dried under vacuum at 60°C to constant weight. The product was in the form of light grey powder. (scheme 2)



**Scheme 1.**



**Scheme 2.**

#### 3.3.1.4 *Characterization of maleimide-terminated poly(arylene ether sulfone) oligomers*

a. Identification of composition maleimide-terminated poly(arylene ether sulfone) oligomers was carried out using Fourier Transform Infrared Spectroscopy (FT-IR).

b. Structure of maleimide-terminated poly(arylene ether sulfone) oligomers was carried out using  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ .

### 3.3.2 Preparation of PolyHIPEs containing maleimide-terminated poly(arylene ether sulfone)

#### 3.3.2.1 *Preparation of PolyHIPEs containing maleimide-terminated poly(arylene ether sulfone)*

The cellular materials were prepared by first dissolving organic phase containing 5 ml of DVB monomer, 5 ml of toluene, required amounts of maleimide-terminated poly(arylene ether sulfone), and a mixture of nonionic, anionic, and cationic surfactants: SPAN80, DDBSs, and CTAB was added to the mixture, stirred for 10 min. While 90 ml of distilled water containing 0.2 g of potassium persulfate and 1 g of calcium chloride dehydrated were added drop-wise to the reaction flask. After all the water has been added, the emulsion was further stirred for 20 min and placed in a glass bottle. The obtained emulsions were capped and put in a convection oven at  $70^\circ\text{C}$  for 24 h to polymerize. After polymerization, the cellular materials were removed from the glass bottles and washed by soxhlet extraction for 6 h with isopropyl alcohol. Then the cellular materials were returned to vacuum oven to dry at  $80^\circ\text{C}$  for 48 h.

#### 3.3.2.2 *Characterization of polyHIPEs*

Characterization of the obtained polyHIPEs were characterized using the following instruments.

a. Thermal properties characterizing of the obtained polyHIPEs were studied using TG/DTA.

b. Morphology characterizing of the obtained polyHIPEs were studied using FE-SEM.

c. Mechanical properties characterizing of the obtained polyHIPEs were studied using LLOYD.

d. Surface area analysis of the obtained polyHIPEs were analyzed using Autosorb-1MP.

e. CO<sub>2</sub> adsorption properties of the obtained polyHIPEs were carried using a pilot gasification unit at the Department of Chemical Technology, Faculty of Science, Chulalongkorn University.