



## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Monomers

Bis-(4-chlorophenyl)-sulfon 98% ((ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SO<sub>2</sub>) was supplied by Chemical Express Co., Ltd. Divinylbenzene (DVB) was supplied by Merck. 3-Aminophenol, Maleic anhydride 99% and Bisphenol A 97% (Bis-A) were supplied by Etalma (Thailand) Co., Ltd.

#### 3.1.2 Solvents

Dimethylacetamide (DMAC), Isopropanol, N-cyclohexylpyrrolidone (CHP), methanol, ethanol, and chloroform (CHCl<sub>3</sub>) were supplied by Etalma (Thailand) Co., Ltd. Toluene (T) was supplied by Lab Scan.

#### 3.1.3 Surfactants

Sorbitan monooleate (SPAN80) and Dodecylbenzenesulfonic acid, sodium salt (DDBSS) were supplied by Sigma. Cetyltrimethylammonium [C<sub>16</sub>H<sub>31</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>] bromide (CTAB) was supplied by Fluka.

#### 3.1.4 Initiator

Potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) was supplied by Fluka.

#### 3.1.5 Catalyze

Potassium carbonate anhydrous was supplied by Fluka.

#### 3.1.6 Stabilizer

Calcium chloride dehydrate (CaCl<sub>2</sub>•2H<sub>2</sub>O) was supplied by Fluka.

#### 3.1.7 Clay Minerals

Bentonite (BN) was supplied by Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of BTN is 43 mmol/100g of clay.

#### 3.1.8 Gas

N<sub>2</sub> UHP was supplied by Etalma (Thailand) Co., Ltd.

## 3.2 Equipment

### 3.2.1 Gel Permeation Chromatography (GPC)

The number-average molecular weight of amine-terminated polysulfone oligomers were obtained by SHIMADZU GPC-RID10A, HT 6E THF Waters brand of  $7.8 \times 300$  nm column, PS standard, flow rate 1.00 mL/min.

### 3.2.2 Surface Area Analyzer (SAA)

N<sub>2</sub> adsorption-desorption isotherms were obtained at -196°C on a Quantachrome Autosorb-1. Samples were degassed at 100°C during 12 h in a vacuum furnace prior to analysis. Surface areas were calculated using the BET equation. The pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.

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

The FT-IR spectra of amine-terminated polysulfone oligomers and maleimide-terminated polysulfone oligomers were obtained using a Nicolet Nexus 670 FT-IR spectrometer in the frequency range of 4000-400 cm<sup>-1</sup> with 32 scans at a resolution of 2 cm<sup>-1</sup>. KBr pellet technique was applied in the preparation of powder samples.

### 3.2.4 <sup>1</sup>H-Nuclear magnetic resonance (<sup>1</sup>H-NMR)

The <sup>1</sup>H-NMR spectra of amine-terminated polysulfone oligomers and maleimide-terminated polysulfone oligomers were obtained using <sup>1</sup>H-Nuclear magnetic resonance at the Chemistry Department, Faculty of Science, Naresuan University.

### 3.2.5 Thermogravimetric Analysis (TGA)

Thermo-gravimetric analysis (TGA) was performed to measure the thermal stability of the poly(DVB)HIPE filled maleimide terminated PSO-oligomers. TGA of poly(DVB)HIPE filled maleimide terminated PSO-oligomers was performed using a Mettler Toledo TGA/SDTA 851e instrument. Experiment was carried out under nitrogen gas atmosphere. Sample was cut into small pieces weigh about 2–5 mg. Then the sample was loaded on the platinum pan and heated to 600°C from 40°C at a heating rate of 10°C/min. One steps degradation was observed during testing,

and the decomposition temperature was recorded corresponding to 50% decomposition of the material.

### 3.2.6 Differential Scanning Calorimetry (DSC)

Glass transition temperature of polysulfone was determined using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 250°C and cooled down at a rate of 10°C/min under a N<sub>2</sub> atmosphere with a flow rate of 10 mL/min. The sample was then reheated to 250°C at the same rate.

### 3.2.7 Scanning Electron Microscope (SEM)

Scanning electron microscopy was performed on JEOL/JSM 5200 Model to observe surface morphology of poly(DVB)HIPE filled maleimide terminated PSO-Oligomers. The specimens were coated with gold under vacuum before observation to make them electrically conductive.

### 3.2.8 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 mm/min. Samples of 25.4 mm in diameter and 25.4 mm in height were used for tested of each poly(DVB)HIPEs filled maleimide terminated PSO-oligomers. The samples were loaded until a displacement of 70 percent of the height of the examined sample was reached.

### 3.2.9 CO<sub>2</sub> Gas Adsorption

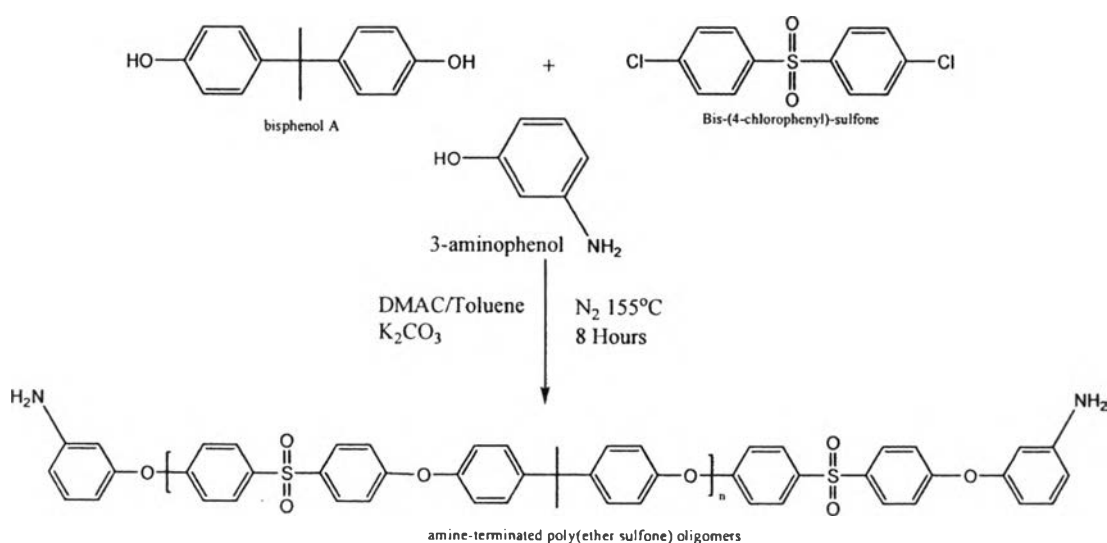
Study of CO<sub>2</sub> gas adsorption capacities of poly(DVB)HIPEs filled maleimide terminated PSO-oligomers was carried out using a pilot gasification unit at the Chemical Technology Department, Faculty of Science, Chulalongkorn University. Samples were cut into small pieces weigh about 1–2 g. Then the samples were loaded into sample tube 2×25 cm. CO<sub>2</sub> 3 mL/min and Ar 17 mL/min were flowed through the sample at room temperature. The residue of CO<sub>2</sub> was measured by a Gas Chromatography instrument, column used Shimadzu 2014, flow rate 35 mL/min.

### 3.3 Experimental Procedures

#### 3.3.1 Preparation of Maleimide terminated PSO-Oligomer.(using procedure adopted from Lyle G. D. *et al.*, 1988)

##### 3.3.1.1 Amine-terminated oligomers Synthesis

The stoichiometry of the reactants were varied according to the Carrothers equation to achieve the various molecular-weight oligomers. A four-neck roundbottomed flask were fitted with a Dean Stark trap, mechanical stirrer, thermometer and nitrogen inlet. The activated halide Bis-(4-chlorophenyl)-sulfone (57.434 g) were added to the flask followed by bisphenol A (43.388 g) and m-aminophenol (2.272 g). A total of 600 cm<sup>3</sup> of DMAC were added to the flask. Dried potassium carbonate (34 g) and toluene (150 cm<sup>3</sup>) were added next and the reaction were refluxed at 145°C. After all the water were removed from the reaction flask (~4 h), toluene were drawn from the Dean Stark trap until the temperature increased to 155°C. The reaction were allowed to proceed for 8 h, after which the solution were cooled and filtered to remove the inorganic salts, then it coagulated in an excess of rapidly stirred methanol. The polymer were purified by redissolving in chloroform and coagulating in methanol again, prior to vacuum drying at 80°C to a constant weight.( see scheme 1 )



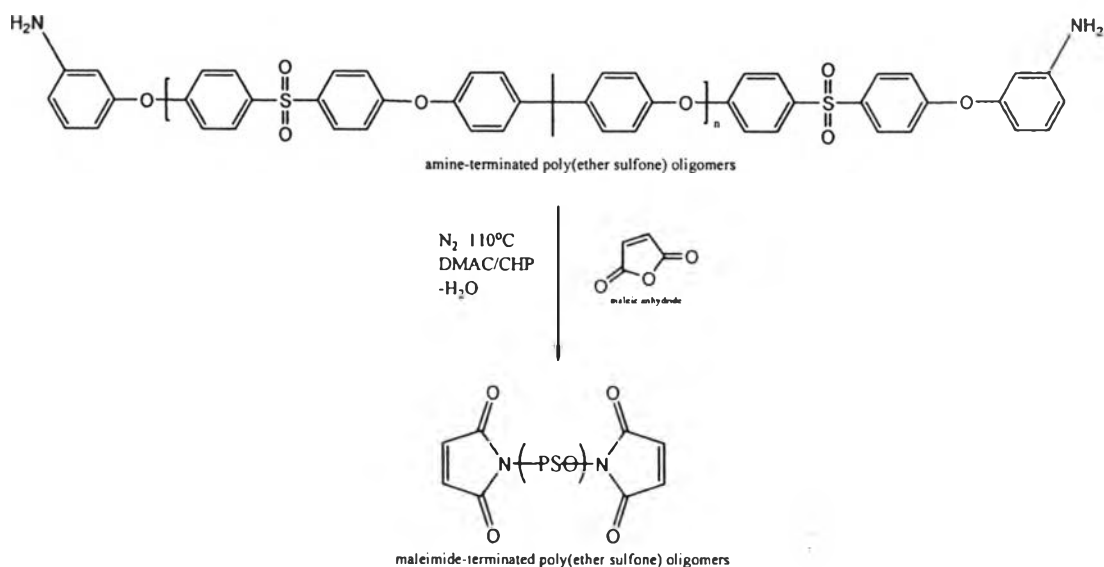
Scheme 1

### 3.3.1.2 Characterization of Amine-terminated PSO-Oligomers.

- a. Identification of Amine terminated PSO-Oligomers composition were carried out using Infrared Spectroscopy (IR)
- b. Structure of Amine terminated PSO-Oligomers were characterized by  $^1\text{H}$ - Nuclear magnetic resonance ( $^1\text{H}$ -NMR)
- c. Molecular Weight Determination by Gel Permeation Chromatography (GPC)
- d. Glass transition temperature Determination of PSO-Oligomers by Differential Scanning Calorimetry (DSC)

### 3.3.1.3 Synthesis of Maleimide-terminated oligomers

For the two-step procedure, the amine-terminated poly(ether sulfone) oligomers were determined the number-average molecular weight before imidization. For example, amine-terminated oligomers (10.804 g, MW=3485) were added to a three-neck 500 cm<sup>3</sup> roundbottomed flask equipped with a nitrogen inlet, a mechanical stirrer and a Dean Stark trap. DMAC (200 cm<sup>3</sup>) and CHP (40 cm<sup>3</sup>) were added to the flask to dissolve the polymer. Maleic anhydride (MA) (0.97g) were added and the solution were stirred for 6h. Subsequently, the nitrogen flow were increased, and the temperature were raised to 130°C and maintained at this temperature for up to 24 h. The polymer solution were coagulated at room temperature in water/methanol (30/70) and vacuum dried at 80°C to a constant weight. (see scheme 2)



Scheme 2

#### 3.3.1.4 Characterization of Maleimide terminated PSO-Oligomers.

- a. Identification of Maleimide terminated PSO-Oligomers composition was carried out by Infrared Spectroscopy (IR)
- b. Structure of Maleimide terminated PSO-Oligomers was characterized using by <sup>1</sup>H- Nuclear magnetic resonance (<sup>1</sup>H-NMR)
- c. Glass transition temperature of PSO-Oligomers was determined by Differential Scanning Calorimetry (DSC)

#### 3.3.2 Preparation of Poly(DVB)HIPE filled with Maleimide terminated PSO-Oligomers.

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 PSO-Oligomers, 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 dihydrate were added dropwise. 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°C for 24 h to polymerize (Barbetta *et al.*, 2004). After polymerization, the cellular materials were removed

from the glass bottles and washed by soxhlet for 6 h with Iso-propanol. Then the cellular materials were returned to vacuum oven to dry at 70°C for 48 h (Pakeyangkoon *et al.*, 2008).

### *3.3.2.1 Characterization of Poly(DVB)HIPE filled Maleimide-terminated PSO-Oligomers.*

a. Thermal properties characterizing: The thermal properties of poly(DVB)HIPE filled with maleimide terminated PSO-oligomers were studied using TG/DTA.

b. Morphology characterizing: morphology of poly(DVB)HIPE filled with maleimide terminated PSO-oligomers was studied using SEM.

c. Mechanical properties analysis: the mechanical properties of poly(DVB)HIPE filled with maleimide terminated PSO-oligomers were studied using LLOYD/LRX.

d. Surface area analysis: The surface area of poly(DVB)HIPE filled with maleimide terminated PSO-oligomers was analyzed using Autosorb-1.

e. Adsorption analysis: study of carbondioxide gases adsorption properties of poly(DVB)HIPE filled with maleimide terminated PSO-oligomers were carried out using a pilot gasification unit at the Faculty of Chemical Technology Chulalongkorn University.