



CHAPTER III EXPERIMENTAL

3.1 Materials

All chemicals were used without further purification. Triethylenetetramine, TETA, was purchased from FACAI Group Limited, Thailand. Aniline (99%) was purchased from Panreac Quimica SA Company. Formaldehyde solution (37% by weight) and sulphuric acid (95–97% H₂SO₄ analytical grade) were purchased from Merck, Germany. Paraformaldehyde (95%) was purchased from BDH Laboratory Supplies. Bisphenol-A (commercial grade) was kindly supported by Bayer Thai Co., Ltd. Xylene (98%) was obtained from Carlo Erba Reagenti and 1,4-dioxane (reagent grade) was purchased from Labscan asia Co., Ltd., Thailand.

3.2 Instruments and Equipment

FT-IR spectra of polybenzoxazine precursor and carbon aerogel were obtained on a Nicolet Nexus 670 FT-IR spectrometer. KBr pellet technique was applied in the preparation of powder samples. TG-DTA curve was collected on a Mettler Toledo TGA/SDTA 851e instrument. The sample was loaded on the platinum pan and heated from 30° to 900°C at a heating rate of 20°C/min under N₂ flow of 50 ml/min. Scanning electron microscope (SEM, JEOL/JSM model 5200) was used to observe the surface morphology of polybenzoxazine aerogel and carbon aerogel. The specimens were coated with gold under vacuum before observation. Nuclear magnetic resonance was used to characterize the chemical structure of polybenzoxazine. ¹H-NMR spectra were recorded on a Varian Mercury 300 (300 MHz) instrument. Deuterated dimethyl sulfoxide (DMSO-d₆) was used as solvent. DSC analyses were carried out using a Perkin-Elmer DSC 7 instrument. The samples were heated from 30° to 300°C at a heating rate of 10°C/min under a N₂ atmosphere with a flow rate of 10 ml/min. N₂ adsorption-desorption isotherms were obtained at 250°C on a Quantachrome Autosorb-1. Samples were degassed at 250°C for 12 hr in avacuum furnace prior to analysis. Surface areas were calculated using the BET

equation. The testing cell for electrochemical measurements consisted of graphite sheets as current collectors, two carbon aerogel electrodes separated by microporous polyethylene membrane, and 3M H₂SO₄ as electrolyte solution. Before the measurements, the carbon aerogel electrodes were placed in 3M H₂SO₄ for 24 hr to diffuse the electrolyte into the pores of the carbon aerogel electrodes (Hwang *et al.*, 2003 and Kim *et al.*, 2005). Electrochemical characterization was succeeded with a computer-controlled potentiostat/galvanostat (Autolab PG-STAT 30 with GPES software). Cyclic voltammetry (CV) was performed between -1 V and 1 V with scanning rates of 1, 5, 20, and 50 mVs⁻¹. For galvanostatic charge/discharge measurement, the testing cell was charged with current density of 5 mA.cm⁻² up to 1 V and discharged with 5 mA.cm⁻² down to 0 V (Kim *et al.*, 2005). Electrochemical impedance spectra (EIS) were achieved using an impedance analyzer (Autolab PG-STAT 30 with FRA software) made over the frequency of 10 kHz down to 10 mHz with a sinusoidal signal of 10 mV. All of the electrochemical measurements were performed at room temperature.

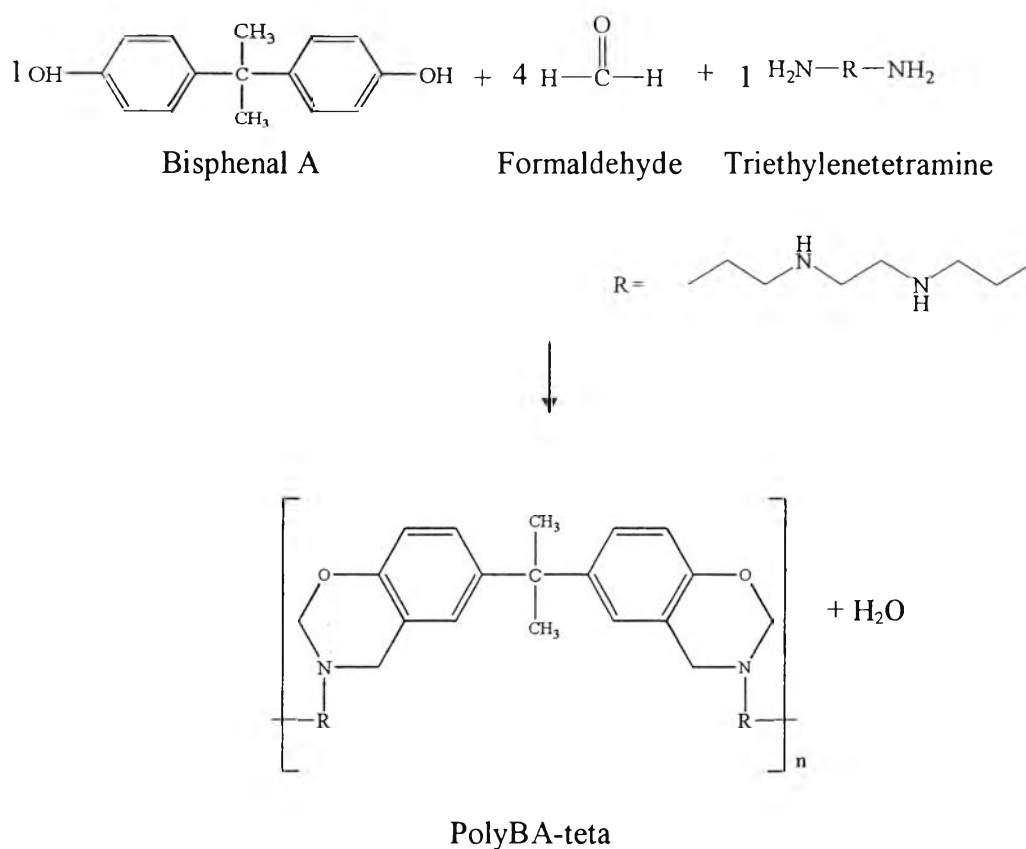
3.3 Methodology

3.3.1 Synthesis of Polybenzoxazine based Aerogels

In this research, we used two types of polybenzoxazine precursors for carbon aerogel preparation. The precursors were synthesized using two different amines, aniline and triethylenetetramine, as the reactant.

The synthesis of benzoxazine precursor (abbreviated as BA-teta), as shown in scheme 1, from bisphenol-A, formaldehyde and TETA was carried out using “quasi-solventless method”, our first recovery, unlike the traditional method requiring solvent and long reaction, as first described by Takeichi *et al.* (2005). Dioxane was used in our method to only help the mixing of all reactants to consequently produce benzoxazine precursor. The ratio of all reactants used was 1:4:1 (Scheme 3.1). The synthesis was started by firstly dissolving bisphenol A (4.52 g) in dioxane (20 ml) in a glass bottle and stirring until the clear solution was obtained. Formaldehyde solution (6.48 g) was then added to bisphenol A solution. The temperature was kept under 10°C by using an ice bath. TETA was then added

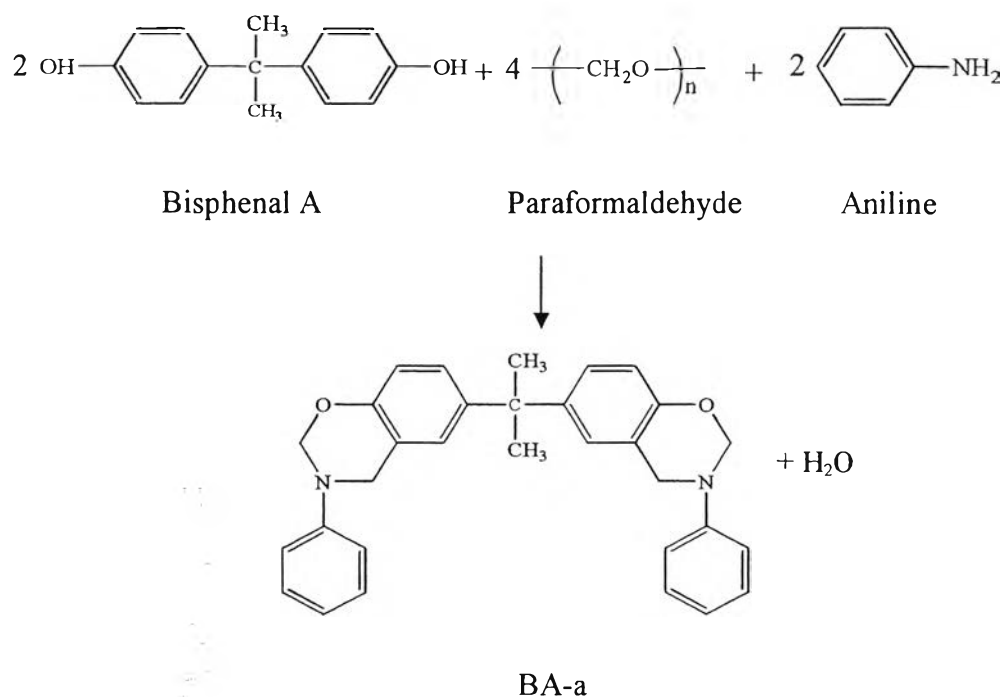
dropwise into the mixture and stirred continuously for approximately 1 hr until transparent yellow viscous liquid precursor was obtained. The precursor was placed in an oven at 80°C for 72 hr in a closed system, yielding benzoxazine aerogel. Finally, benzoxazine aerogel was cut into a disk shape and placed in an oven set the temperature at 160°, 180°C for 3 hr at each temperature, and 200°C for 2 hr in order to polymerize benzoxazine aerogel. The structural characteristics of BA-teta-based aerogel was investigated using FTIR and ¹H-NMR. The thermal properties were measured using DSC and TG/DTA. The morphology was also observed by SEM.



Scheme 3.1 Preparation of Poly BA-teta.

Another benzoxazine precursor used in this study, denoted as BA-a, was synthesized via solventless process proposed by Ishida *et al.* (1996). Bisphenol A (22.8g), aniline (18.6g), and paraformaldehyde (12g) with the mole ratio of 1:2:4

(Scheme 3.2) were mixed together and heated at 110°C for an hour until transparent light yellow viscous liquid was obtained.



Scheme 3.2 Preparation of BA-a monomer.

Benzoxazine monomer was prepared by using xylene as a solvent. The monomer concentration was 40 wt%. After that, the mixtures were moved into vials and then sealed. The temperature was gradually raised up to 130°C for 96 hr in an oven. The attained products were partially cured benzoxazine hydrogels. The hydrogels were dried at ambient temperature for 2 days to remove the xylene from their matrixes yielding organic aerogels which were then subjected to step-curing in an oven at 160°, 180°C for an hour at each temperature, and 200°C for 2 hr, respectively.

3.3.2 Preparation of Carbon Aerogel Electrodes

The fully cured organic aerogels of BA-teta and BA-a were cut into a disk shape by using diamond saw and then pyrolyzed under a nitrogen flow rate of 500 cm³/min using the following ramp cycle: 30° to 250°C in 60 min, 250° to 600°C

in 300 min, 600° to 800°C in 60 min, and holding at 800°C for 60 min. The carbon aerogel electrodes were then obtained.

3.3.3 Characterization of Carbon Aerogel Electrodes

Surface areas of the carbon aerogel electrodes were calculated from N₂ adsorption isotherm at -196°C (77K). Galvanostatic charge/discharge, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to determined electrical properties.