



CHAPTER III EXPERIMENTAL

3.1 Material

All chemicals were used without further purification. Triethylenetetramine (TETA) was purchased from FACAI Group Limited, Thailand. Aniline (99%) and phenol (analytical grade) were purchased from Panreac Quimica SA Company. Formaldehyde solution (37% by weight) was 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. 1,4 - Dioxane (reagent grade) was purchased from Labscan asia Co., Ltd., Thailand. Ethylene diamine (EDA, commercial grade) was kindly supported by Thai epoxy's Company. Azodicarbonamide (AZD) used as a blowing agent was bought from A.F Supercell Co, Ltd. Titanium dioxide (TiO_2), alumina (Al_2O_3), silica (SiO_2), hexachloroplatinate (IV) hydrate, and 4-chlorophenol were purchased from Aldrich, Germany. ZSM-5 was purchased from Zeolyst International.

3.2 Instruments and Equipment

The 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 at a temperature range of 30° to 900°C, and a heating rate of 20°C/min under N_2 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. Transmission electron microscope (TEM, JEOL model JEM-2100) was used to observe the porous structure of carbon aerogel. Nuclear magnetic resonance ($^1\text{H-NMR}$) was used to characterize the chemical structure of polybenzoxazine, using a Varian Mercury 300 (300 MHz) instrument. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as a 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 Autosorb¹. Samples were degassed at 250°C for 12 hr 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. UV-VIS spectrophotometer (Shimadzu UV-2550) was used to follow the degradation of 4-chlorophenol.

3.3 Methodology

Two types of benzoxazine oligomer were prepared to be used as the organic precursors for carbon aerogel synthesis. Phenol-ethylenediamine base benzoxazine monomer (P-eda) was used as an organic precursor for carbon foam synthesis.

3.3.1. Carbon Aerogel/Foam Synthesis

3.3.1.1 *Preparation of BA-teta Derived Carbon Aerogel*

Synthesis of benzoxazine precursor using bisphenol A, formaldehyde and TETA with a mole ratio 1:4:1, as shown in Figure 4.1. Firstly, bisphenol A (4.52 g) was dissolved in dioxane (20 ml) in glass bottle and stirred until the clear solution was obtained. Formaldehyde solution (6.48 g) was then added into the bisphenol A solution. The temperature was kept under 10°C using an ice bath. Diamine (TETA) was then added drop wise into the mixture being continuously stirred for approximately 1 hr until transparent yellow viscous liquid was obtained. The benzoxazine precursor was heated in the oven at 80°C for 72 hr in a closed system. The partially cured benzoxazine hydrogels were then obtained. The organic aerogels were attained by evaporating solvent in hydrogels at ambient condition for 1 day. The obtained organic aerogel were then fully cured by step curing in an oven at 140°, 160°, and 180°C for 2 hr at each temperature and 200°C for 3 hr, respectively. Pyrolysis was performed at 800°C under nitrogen flow at 500 cm³/min, using the following temperature program: (i) ramp at 3.7°Cmin⁻¹ to 250°C; (ii) ramp at

1.17°Cmin⁻¹ to 600°C; (iii) ramp at 3.3°Cmin⁻¹ to 800°C and hold for 120 min before slowly cooling to room temperature.

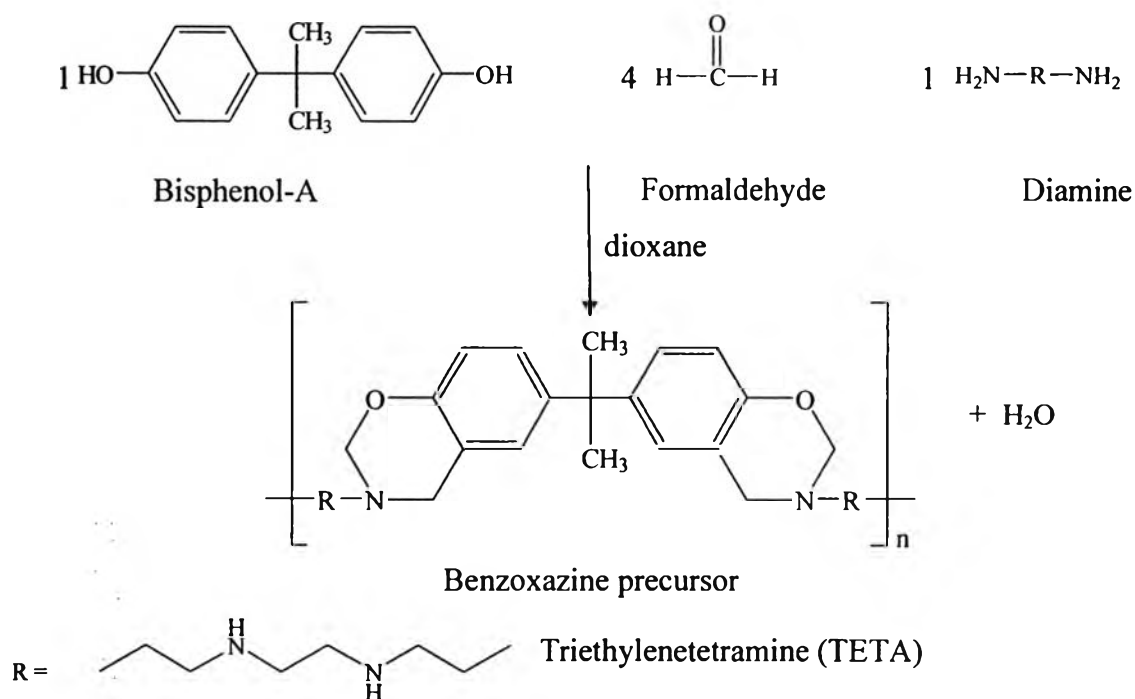


Figure 3.1 Preparation of benzoxazine precursor.

3.3.1.2 Preparation of BA-a Derived Carbon Aerogel

A benzoxazine monomer was synthesized by solventless process proposed by Ishida *et al* [11]. Bisphenol-A, aniline, and paraformaldehyde at a 1:2:4 molar ratio were mixed and heated at 110°C for 60 min until the mixture became transparent pale yellow color. The monomer was used without purification. The synthesis reaction of benzoxazine monomer is shown in Figure 4.2.

Benzoxazine monomer was prepared using 40 wt% monomer concentration in xylene solvent. The mixtures were moved into vials and sealed. The temperature was gradually raised up to 130°C for 96 hr in an oven. The products obtained at this stage 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 one hr at each temperature and 200°C for 2 hr, respectively,

to give organic aerogels. Carbon aerogels were prepared by pyrolysis of the organic aerogels in a quartz reactor. The pyrolysis took place in a furnace under nitrogen flow at $500 \text{ cm}^3/\text{min}$ using the following ramp cycle: 30° to 250°C for 60 min, 250° to 600°C for 300 min, 600° to 800°C for 60 min and held at 800°C for 60 min [14].

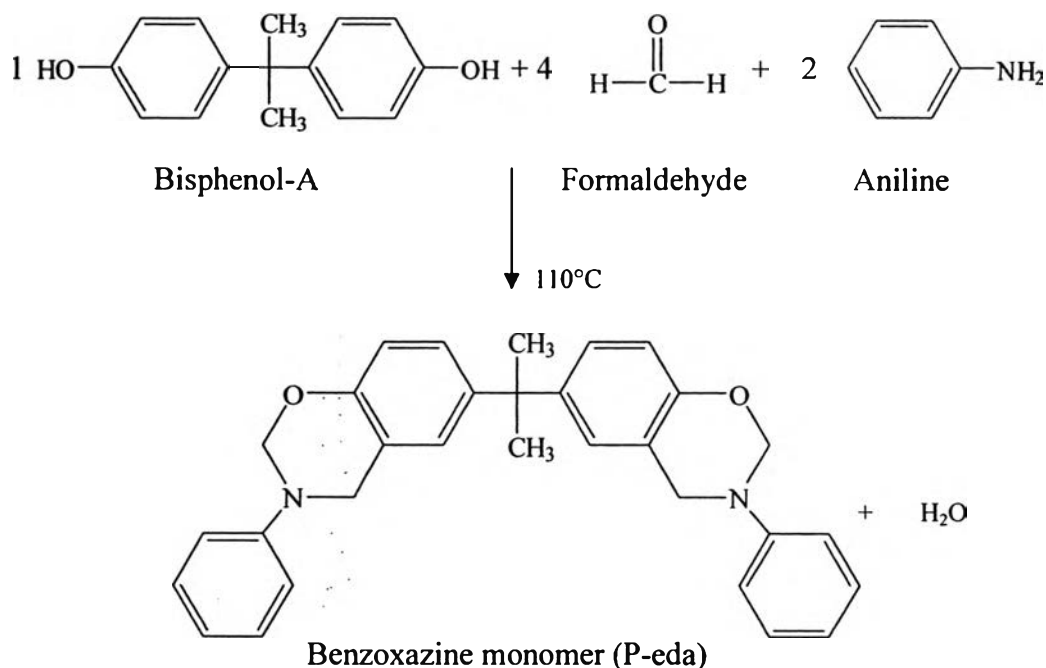


Figure 3.2 The benzoxazine monomer synthesis.

3.3.1.3 Preparation of Phenol-ethylenediamine (P-eda) Derived Carbon Foam

P-eda based polybenzoxazine was synthesized from phenol, EDA, and paraformaldehyde with a mole ratio of 2:1:4 by solventless process proposed by Ishida *et al* [11]. The mixture was stirred continuously at 110°C for approximately one hr until clear yellowish monomer was obtained. The synthesis of benzoxazine monomer is shown in Figure 4.3.

Organic foams were made from polybenzoxazine based Phenol-ethylenediamine (Poly(P-eda)) using AZD as a blowing agent. P-eda monomer was ground and mixed with 20%w/w of AZD until homogeneous. The mixtures were filled in vial and heated in an oven with a heating rate of $1^\circ\text{C}/\text{min}$ from 30° to 200°C .

Carbon foams were prepared by pyrolysis of the organic foam in a quartz reactor. The pyrolysis took place under nitrogen flow at $500 \text{ cm}^3/\text{min}$ using the following ramp cycle: 30° to 250°C for 60 min, 250° to 600°C for 300 min, 600° to 800°C for 60 min, and held at 800°C for 60 min. Then the furnace was cooled down to room temperature under nitrogen atmosphere prior to sample removal.

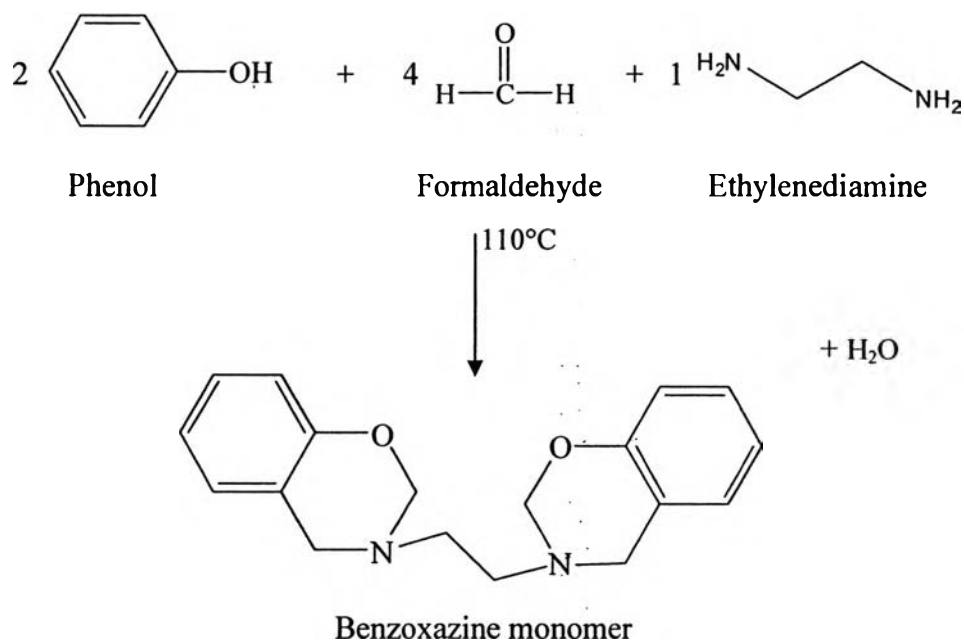


Figure 3.3 The synthesis reaction of P-eda derived benzoxazine monomer.

3.3.2. Catalyst Preparation

Pt (0.1 and 0.5 wt%) was loaded on the supports by incipient wetness impregnation, wherein a calculated amount of hydrogen hexachloroplatinate (IV) hydrate dissolved in a minimum amount of water was added dropwise before mixing with the supports. The Pt-loaded supports were then dried overnight before calcining at 450°C for 3 hr to remove the organic moieties.

3.3.3. Activity Measurements

To test performance of the prepared carbon aerogel as a catalyst support, the adsorption activity of 4-chlorophenol (4-CP) using Pt as a catalyst was investigated. The initial concentration of 4-chlorophenol (4-CP) was fixed at 40 ppm.

The experiments were carried out at 298 K. The concentration of 4-CP was analyzed as a function of time using UV-VIS spectrophotometer.