CHAPTER III
EXPERIMENTAL

3.1 Chemicals

Polymer Chemicals

- Bisphenol-A(Aldrich), (100% purity), 500 g
- Formaldehyde (Merck), (37%wt. in water), 1L
- Silver Nitrate (AgNO3) was purchased from Fisher Scitific, UK, 100g
- Triethylenetetramine (TETA) was purchased from FACAI Group Limited, Thailand.

Solvents

- N,N-Dimethylformamide (DMF) (Lab-Scan), 2.5 L

3.2 Measurements

3.2.1 Fourier Transform Infrared Spectroscopy (FT-IR)

A Fourier Transform Infrared Spectroscope (FT-IR), Nicolet 670, was used to identify structural characteristics of polybenzoxazine-based aerogel. Potassium bromide (KBr) pellet technique was applied in the preparation of powder samples.

3.2.2 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter (DSC), Perkin-Elmer DSC 7, was used to study the thermal behavior of partially-cured and fully-cured polybenzoxazine. The samples were heated from 30 °C to 280 °C at a heating rate of 10 °C/min under N_2 atmosphere with a flow rate of 10 ml/min.

3.2.3 Thermogravimetric/Differential Thermal Analyzer (TG-DTA)

TG-DTA curve was collected on a Perkin-Elmer Pyris Diamond TG/TGA 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 N_2 flow of 50 mL/min.

### 3.2.4 Scanning Electron Microscopy (SEM-EDX)

Surface morphology of polybanzoxazine-based aerogel was investigated by using a scanning electron microscope, Hitachi S-4800, surface morphology of polybanzoxazine-based aerogel with an accelerating voltage of 15-40 kV. Samples were coated with platinum under vacuum before observation. Furthermore, the amount of Ag^+ on the surface can be determined by EDX mode.

3.2.5 X-ray Fluorescence (XRF)

Elemental analysis of the siver inclusion polybenzoxazine, particularly investigate by Axios WD XRAF, Panalytical.

3.3 Gas Permeability Apparatus

In this study, CO_2, N_2 (Prax Air) and CH_4 (TIG) were used as testing gases for all membranes. All tested gases were of a high purity (HP) grade and used as received. The system used automatic flow meter to measure the volumetric flow rate of gas. The experiments were a conducted at room temperature under an absolute pressure of 34.59 psia. (Absolute pressure = gauge pressure 20 psig + local atmospheric pressure 14.59 psi) A schematic diagram of the system used to carry out the gas permeability experiments is shown in Figure 3.1.
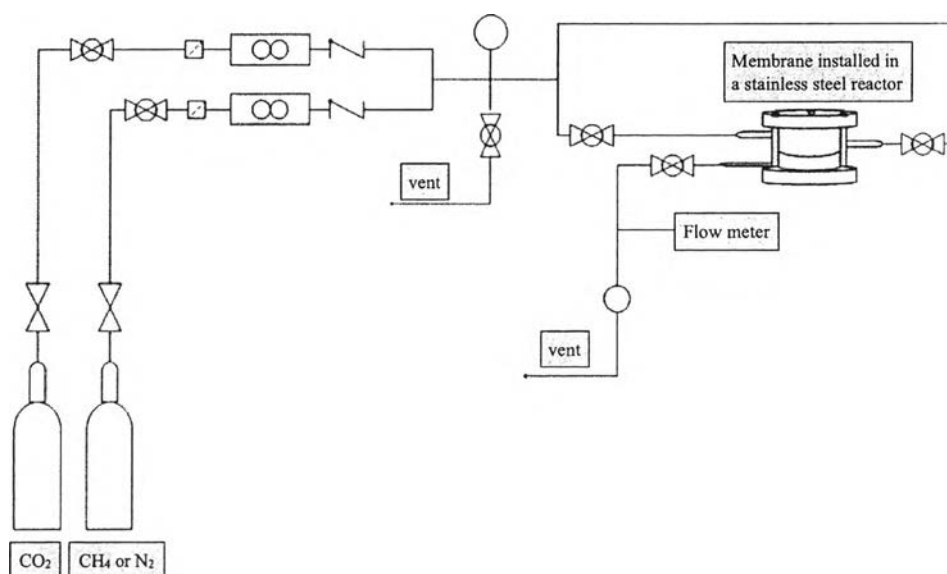
Figure 3.1 Experimental set up for the gas permeability apparatus.

3.4 Experimental

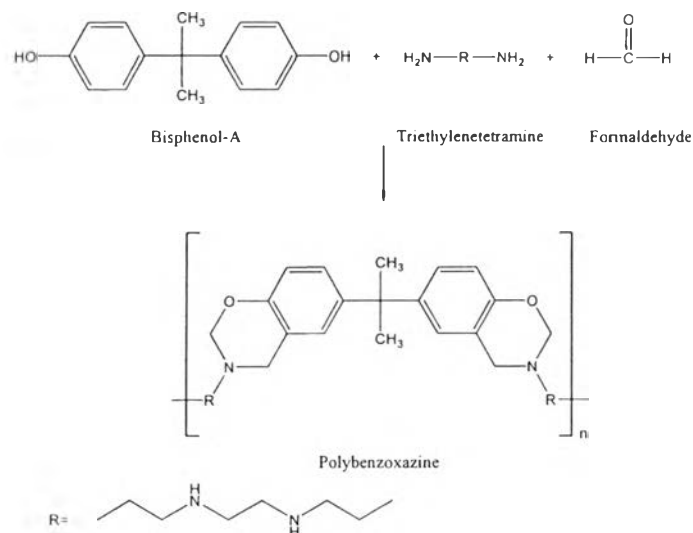### 3.4.1 Synthesis of the Benzoxazine Precursor

The benzoxazine precursor was synthesized by dissolving bisphenol-A (2.283 g) in DMF (12.978 ml), followed by adding formaldehyde (3.242 g) and TETA (1.462 g). The mixture was stirred continuously for 1 h while the reaction was cooled with an ice bath until a homogeneous yellow viscous liquid was obtained. The mole ratio of bisphenol-A: formaldehyde:diamine was 1:4:1.
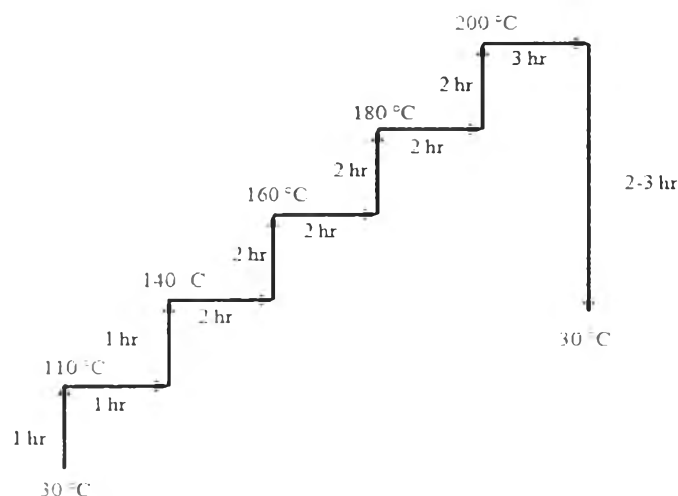
3.4.2 Preparation of Polybenzoxazine Xerogel

The benzoxazine precursor was transferred into vials and sealed before being placed in an oil bath. The samples were heated in the oil bath at 80 °C for 48 h in a closed system, followed by evaporating the solvent at ambient conditions for one day.

3.4.3 Preparation of Polybenzoxazine Xerogel Membranes

After the organic xerogel was evaporated over night. Then, it was cut by the diamond blade low speed cutter machine with the thickness 2 mm, and the rotor speed is 450 rpm. The obtained organic xerogel was then fully cured by step curing in an oven at 140°, 160°, and 180 °C for 2 h at each temperature and then at 200 °C for 3 h (as shown in Figure 3.3). The synthetic reaction is shown in Figure 3.2.

Figure 3.2 Preparation of polybenzoxazine precursor.

Figure 3.3 Schematic of a step of curing.

3.4.4 Characteristics of the Polybenzoxazine Xerogel

The structural characteristics of polybenzoxazine-based aerogel were identified by using FTIR. The morphology was observed by SEM. Moreover, the thermal property was measure using DSC. The surface area of polybenzoxazine-based aerogels were calculated from nitrogen adsorption isotherms at 77 K based on the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated with the adsorption data based on the Barret-Joyner-Halenda method (BJH).

3.4.5 Preparation of Silver-Polybenzoxazine based Xerogel

The fully cured polybenzoxazine xerogels were impregnated in aqueous $AgNO_3$ solution with different concentrations (0.5 and 1.0 mol/dm^3) and then the solution was stirred for 1 day at 60–70°C in a temperature-controlled water bath. After the reaction, polybenzoxazine xerogels with silver ion was washed with 500 mL deionized water to remove all the unreacted cations, and then was dried at 100°C overnight. The structural characteristics of silver-polybenzoxazine based xerogel were identified by using FTIR. Furthermore, the amount of Ag^+ on the surface was be determined by SEM-EDX and also the amount of Ag+ within in polybenzoxazine xerogel molecule can be determined by XRF.

3.4.6 Preparation of Polybenzoxazine and Silver-Polybenzoxazine based Xerogel Carbon

In order to prepare the carbon membranes, the polybenzoxazine membranes was carbonized in a quartz reactor. The carbonization took place in a tube furnace under nitrogen flow at 500 cm^3/min, using the following ramp cycle: 30–250 °C in 60 min, 250–600 °C in 300 min, 600–800 °C in 60 min, and holding at 800 °C for 60 min. Then the furnace was cooled to room temperature under nitrogen atmosphere.

3.4.7 Gas Permeation Measurement

The single-component gas permeation (CH_4, N_2 and CO_2) experiments of polybenzoxazine xerogel based carbon membranes were carried out at 25 °C in sequences by using a gas permeation testing unit in which the membrane was placed on a porous metal plate, then the two compartments were fixed together to prohibit the leakage. The area of the membrane in contact with the gas was 0.5024 cm^2. The pressure difference between the feed side and the permeating side (ΔP) was maintained at 20 psia. The testing gas was flowed for 1 hour in order to get equilibrium state. The equilibrium state was obtained by measuring the constant permeate rate. Once reached the steady–state, individual gas flow rate was measured using an ADM1000 universal gas flow meter, Agilent technology. The results of each sample were determined from an average of at least 3 tests. The attained data were used to calculate the gas selectivity and permeability. The ideal separation factor (Gas Selectivity, $S_{A/B}$) for component A and B is defined as the ratio of permeance of each component as shown in equation 1:

$$S_{A/B} = \frac{P_A}{P_B} \qquad (1)$$

The permeance for the permeated gas can be obtained by equation 2:

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 14.7 \times 10^6}{(A) \times (\Delta P) \times 76} \qquad (2)$$

Where; $\left(\dfrac{P}{\delta}\right)_i$ =   permeance of gas 'i' (GPU),

P   =   permeability of gas 'i' (10^{-10} cm^3 (STP) cm/cm^2 s cm Hg)

(1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cm Hg = 7.5×10^{-18} m^2 s^{-1} Pa^{-1}),

δ =   thickness of membrane (μm),

Q_i =   volumetric flow rate of gas 'i' (cm^3/sec),

A   =   membrane area (cm^2), and

ΔP =   pressure difference between the feed side and the permeating side (psia).