



CHAPTER III EXPERIMENTAL

3.1 Materials

Analytical grade 1,4-dioxane was purchased from Labscan, Ireland. Bisphenol-A (BPA, 97 % purity), sodium bicarbonate (NaHCO_3 , 99.5% purity), and hexa-methylenediamine (hda, 98 % purity) were purchased from Aldrich, Germany. Ethanol (99.9 % purity) was purchased from J.T. Baker; White Group, Malaysia. Formaldehyde (analytical grade, 37 %wt. in water) was purchased from Merck, Germany. Tetraethylenepentamine (tepa, 85 % purity), triethylenetetramine (teta, 85 % purity) and ethylenediamine (eda, 99 % purity) were purchased from Fluka, Switzerland. Potassium chloride (KCl) was purchased from Fisher Scientific. Zeolite (ZSM-5) powder was purchased from Zeolyst International, USA. All chemicals were used as received.

3.2 Measurements

Proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$, Varian Mercury 300) using deuterated chloroform (CDCl_3) as the solvent was used to characterize the polybenzoxazine precursors. Differential scanning calorimeter (DSC7, PerkinElmer) was used to study the polymerization process using a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under a N_2 flow. An attenuated total reflectance infrared spectrometer (ATR-IR, Thermo Nicolet Nexus 670) was used to determine the chemical structure using ZnSe 45° (flat plate) with a scanning resolution of 4 cm^{-1} . The membrane morphology was observed on a scanning electron microscope (SEM, JEOL model JSM-5410LV and Hitachi/s-4800). Thermogravimetric analyzer (TGA, PerkinElmer Pyris Diamond) was used to investigate the thermal stability of the membranes using a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ under a N_2 flow. Tensile properties of the polybenzoxazine membranes were measured using a universal testing machine (Lloyd/LRX) at a crosshead speed of $50\text{ mm}/\text{min}$. The results of each sample were determined from an average of at least 10 tests. The quantities of ethanol and water from pervaporation process were

determined using gas chromatograph (GC, Agilent GC-6890). The samples (0.5 μL) were injected under the following conditions: helium as the carrier gas at 55 kPa pressure for the thermal conductivity detector (TCD). The isothermal oven temperature was set at 200 $^{\circ}\text{C}$, while the injector and detector temperatures were set at 200 $^{\circ}$ and 250 $^{\circ}\text{C}$, respectively. Static and dynamic light scattering was analyzed by using a Stabilite Ar⁺ laser emitting vertically polarized light at $\lambda = 632.8$ nm with a power output of 15 mW. Differential refractive index (dn/dc) measurement was conducted on a Brice-Phoenix differential refractometer at three different wavelengths (436, 546, and 589 nm).

3.3 Methodology

The polybenzoxazine precursors were prepared by mixing bisphenol-A, formaldehyde, and diamine (eda, hda, tepa, or tetra) at a mole ratio of 1:1:4, respectively. Firstly, bisphenol-A (6.84 g, 30 mmol) was dissolved in 1,4-dioxane (15 mL) in a 50 mL glass bottle and was stirred until a clear solution was obtained. A formaldehyde solution (9.73 g, 324 mmol) was then added to the bisphenol-A solution. The temperature was kept under 10 $^{\circ}\text{C}$ by using an ice bath. Diamine was then added dropwise into the mixture while continuously stirring for approximately 1 h until a transparent yellow viscous liquid was obtained. When hda and eda were used, heat treatment at 100 $^{\circ}\text{C}$ was required to accelerate the reaction, implying that the hda and eda have lower reactivity than the tepa and the tetra. The benzoxazine precursors were then purified by washing with a 0.1 M NaHCO_3 solution (200 mL) before solvent removal by evaporation and drying under vacuum. The purified benzoxazine precursors were then characterized using $^1\text{H-NMR}$.

The benzoxazine precursors were cast on glass plates at room temperature using an Elcometer 3580 casting knife film applicator (from the elcometer/inspection equipment). The membranes were dried at room temperature in air for one day, followed by drying at 80 $^{\circ}\text{C}$ in an air-circulating oven for 24 h to remove excess solvent.

3.4 Characterization of Sorption and Swelling Behaviors

The polybenzoxazine membranes (approximately 25 mm x 25 mm in size, 200 μm thick, and weighting about 0.1 g) were placed in the following solvents: ethanol, water, and various mixtures of ethanol and water (20, 40, 60, and 80 % by volume of ethanol), for 8 h at room temperature to ensure the attainment of swelling equilibrium. At the specific time, the membranes were removed from the mixtures and blotted with a tissue to remove excess liquid before being weighed and replaced in the mixtures. The procedure was repeated until a constant weight for each sample was obtained. The ATR-IR was used to investigate the sorption characteristics of the polybenzoxazine membranes. The degree of swelling, G_s , is defined by the following equation:

$$G_s = \frac{W_t - W_o}{W_o} \times 100\% \quad , \quad (3.1)$$

where W_t represents the weight of the swollen membrane and W_o is the initial weight of the membrane. The results obtained from each condition were the average of 4 to 6 tested membrane samples.

3.5 Pervaporation Study

A schematic of the pervaporation experiment is shown in Figure 3.1. The membrane was placed in a stainless steel module. A flow rate of 900 mL/min was used to circulate the mixture from the feed reservoir to a permeation cell. The performance of the membranes were determined by measuring % ethanol in the permeate side using GC to calculate the permeate water flux ($\text{kg}/\text{m}^2\text{h}$) and the separation factor. The permeate flux (J , $\text{kg}/\text{m}^2\text{h}$, eq. 3.2) and the separation factor ($\alpha_{\text{water-ethanol}}$, eq. 3.3) were determined as follows:

$$J = \frac{M}{(At)} \quad , \quad (3.2)$$

where M = permeate weight (kg),
 A = effective membrane surface area (m^2), and
 T = pervaporation time (h).

$$\alpha_{\text{water/ethanol}} = (Y_{\text{water}}/Y_{\text{ethanol}})/(X_{\text{water}}/X_{\text{ethanol}}) \quad , \quad (3.3)$$

where Y_{water} = the mole fraction of water in the permeate,
 Y_{ethanol} = the mole fraction of ethanol in the permeate,
 X_{water} = the mole fraction of water in the the feed, and
 X_{ethanol} = the mole fraction of ethanol in the feed.

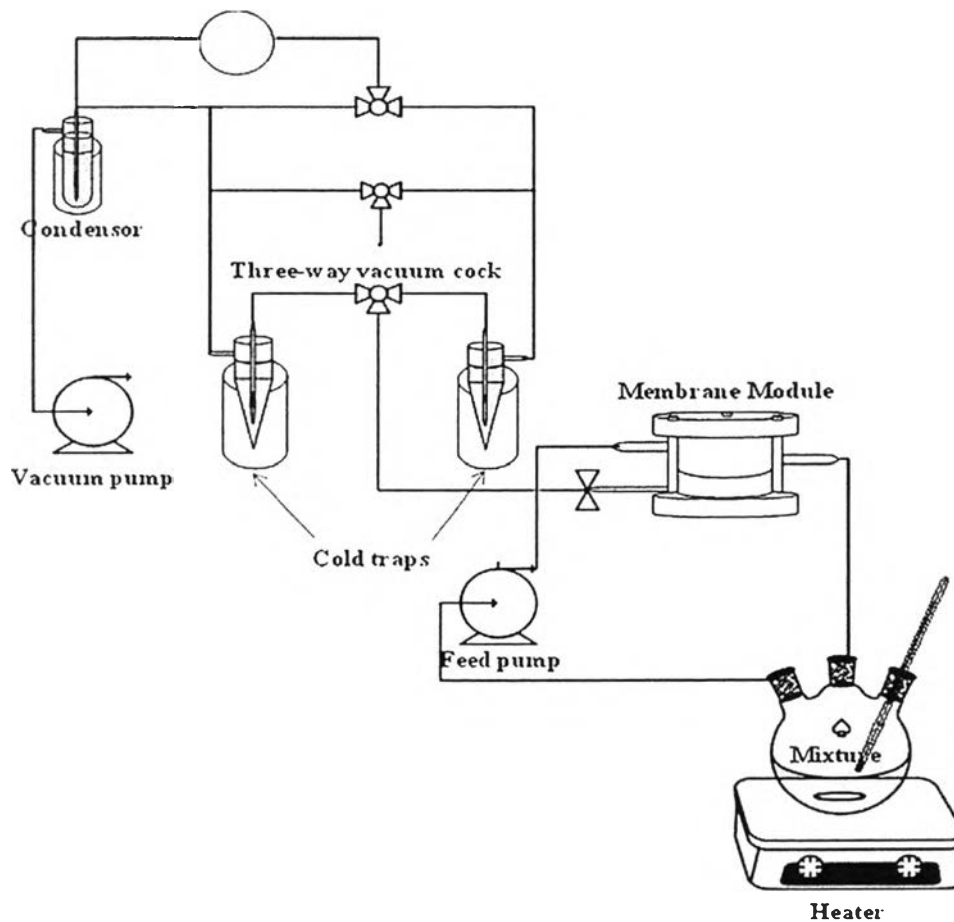


Figure 3.1 Experimental set up for the pervaporation apparatus.

3.6 Gas separation studies

CO_2 (Prax Air) and CH_4 (TIG) were used as testing gases for all membranes. All tested gases were of high purity (HP) grade and used as received. A schematic diagram of the system used to carry out the gas permeability experiments is shown in Figure 3.2 and the membrane testing unit is shown in Figure 3.3.

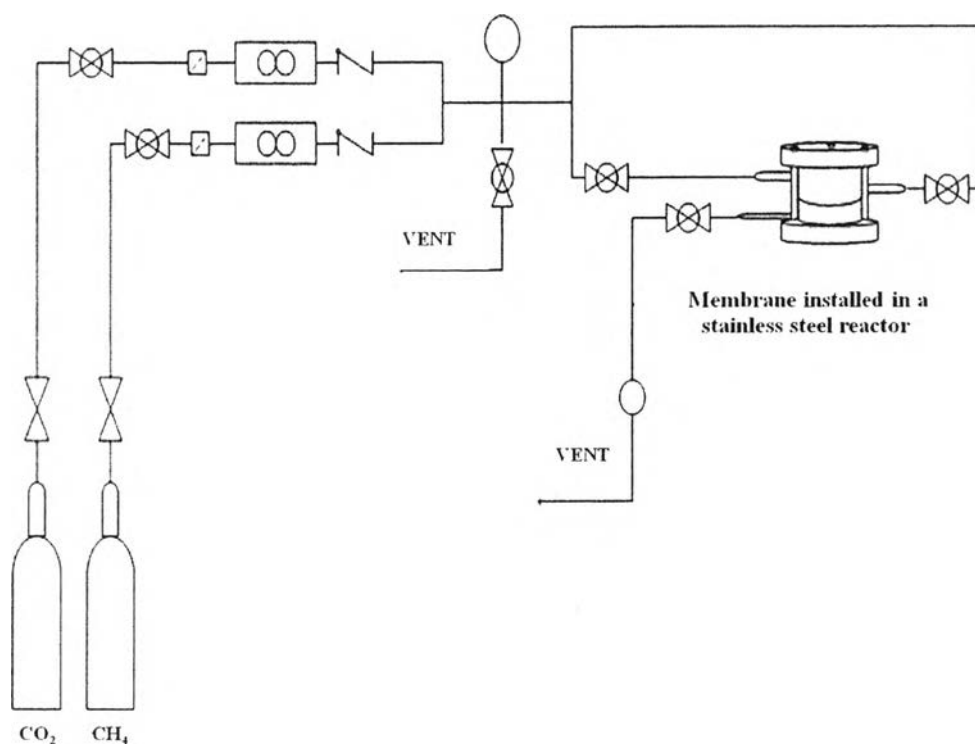


Figure 3.2 Experimental set up for a gas permeability apparatus.

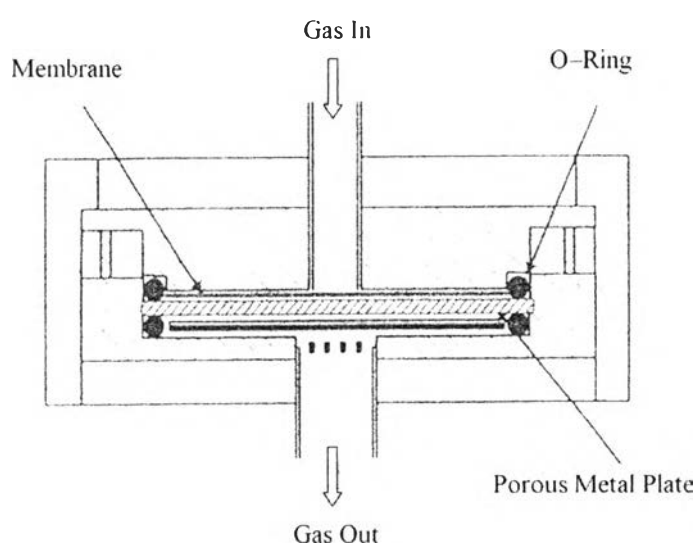


Figure 3.3 Schematic of a membrane testing unit.

3.7 Light scattering study

The benzoxazine precursors were studied molecular weight (M_w), radius of gyration (R_g), and hydrodynamic radius (R_h) using light scattering technique. The simple schematic drawing of light scattering is shown in Figure 3.4. The scattering angle of the static light scattering was increasing in 10° increments between 50° and 100° and the experiment was carried out at room temperature. Molecular weight determination using this instrument was calibrated using known molecular weight polystyrene. The solution was analyzed its differential refractive index (dn/dc) to obtain the value for the Zimm plot calculation, and the molecular weight and the radius of gyration (R_g) were calculated using eq. 3.4-3.5;

$$\frac{Kc}{\Delta R} = \frac{1}{M_w} + 2A_2c + 3A_3c^2 + \dots \quad , \quad (3.4)$$

and

$$\ln \frac{Kc}{\Delta R} = \ln \frac{1}{M_w} + \frac{q^2(R_g)^2}{3} \quad , \quad (3.5)$$

where $q = \left(\frac{4\pi n}{\lambda}\right) \sin \theta$, $K = \frac{4\pi^2 n^2 \left(\frac{dn}{dc}\right)^2}{N_A \lambda^4}$, ΔR is an excess Rayleigh ratio, q is a scattering vector, c is a concentration, K is an optical constant computed using the differential refractive index.

Dynamic light scattering was carried out using the same equipment shown in Figure 3.4 at 25°C and 90° scattering angle. The CONTIN software was used to determine R_h of polybenzoxazine in dioxane solution.

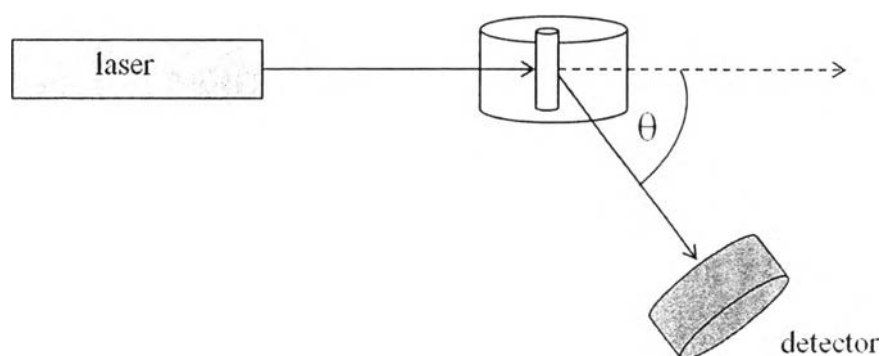


Figure 3.4 Experimental set up of light scattering.