CHAPTER III
EXPERIMENT

3.1 Materials

Bisphenol-A (BPA, $C_{15}H_{16}O_2$), 1,6-hexadiamine (hda, $C_6H_{16}N_2$), CTAB and Fumed silica (SiO_2) were purchased from Sigma-Aldrich. Formaldehyde (CH_2O, analytical grade) was purchased from Merck. 1,4–Dioxane ($C_4H_8O_2$, analytical grade), acetronitrile and sodium hydroxide (NaOH) were purchased from Labscan. Triethanolamine (TEA) was purchased from QREC. Ethylene glycol (EG) was purchased from J.T. Baker. 99.99% pure CH_4 and 99.5% pure CO_2 gas for gas permeation experiment were purchased from TIG.

3.2 Equipment

3.2.1 Elcometer 3580 casting knife film applicator

3.2.2 Fourier transform infrared spectrometer (FT–IR)

3.2.3 Proton nuclear magnetic resonance spectrometer (^{1}H NMR)

3.2.4 Attenuated total reflectance infrared spectrometer (ATR–IR)

3.2.5 Thermogravimetric analyzer (TGA)

3.2.6 Differential scanning calorimeter (DSC)

3.2.7 Scanning electron microscope (SEM)

3.2.8 X–Ray diffractometer (XRD)

3.2.9 Surface area analyzer (SAA)

3.2.10 Gas permeation tester

3.2.11 ADM 1000 Universal gas flowmeter

3.3 Methodology

3.3.1 Silatrane Synthesis

Following Wongkasemjit's synthetic method (Longloilert et al., 2011; Thanabodeekij et al., 2006), silatrane was synthesized by heating a mixture of 0.125 mol triethanolamine (TEA), 0.1 mol fumed silica and 100 ml of ethylene glycol (EG) at 200°C under nitrogen atmosphere for 10 h in oil bath. The mixture was cooled to room temperature before removing the excess EG under vacuum at 110°C for 3 h. The crude brown solid was purified by using acetonitrile and vacuum-dried overnight to obtain a fine white powder.

3.3.2 Synthesis of MCM-48

MCM-48 was synthesized by following our previous study (Longloilert et al., 2011). CTAB was dissolved in a solution containing water and 2 M NaOH. The mixtures were vigorously stirred with slight heating to dissolve surfactant. And then, silatrane precursor was added, followed by stirring for 1 h. The molar composition of the gel was $SiO_2:0.3CTAB:0.5NaOH:62H_2O$. The mixture was transferred to a Teflon-lined stainless steel autoclave and treated at 140°C for a certain time in a range of 16 h. The resulting solid product was collected by filtration and dried overnight at ambient conditions. The surfactant was removed by calcination at 550°C for 6 h to obtain mesoporous MCM-48.

3.3.3 Synthesis of MCM-41

MCM-41 synthesis was followed our previous work (Thanabodeekij et al., 2006). Silatrane precursor was added to a solution containing CTAB, NaOH and TEA. Then the water was added with vigorous stirring. The mixture was stirred for 3 h which having the formulation of $SiO_2:0.3CTAB:0.25NaOH:3.5TEA:90H_2O$. The obtained crude product was filtered and washed with water to obtain white solid, followed by drying at room temperature and calcining at 550°C for 7 h to obtain mesoporous MCM-41.

3.3.4 Synthesis of Polybenzoxazine Precursor

The polybenzoxazine precursor was synthesized using bisphenol-A (BPA, $C_{15}H_{16}O_2$), formaldehyde (CH_2O), and 1,6-hexadiamine (hda, $C_6H_{16}N_2$), with a molar ratio of 1:4:1, respectively. First, BPA was dissolved in a 1,4-dioxane in a glass bottle and stirred until the clear solution was obtained. Then formaldehyde solution was added into the BPA solution. The reaction was cooled with an ice bath before adding hda drop-wise into the mixture with continuous stirring until clear yellowish liquid was obtained. The synthesis process of polybenzoxazine precursor is shown in Figure 3.1.
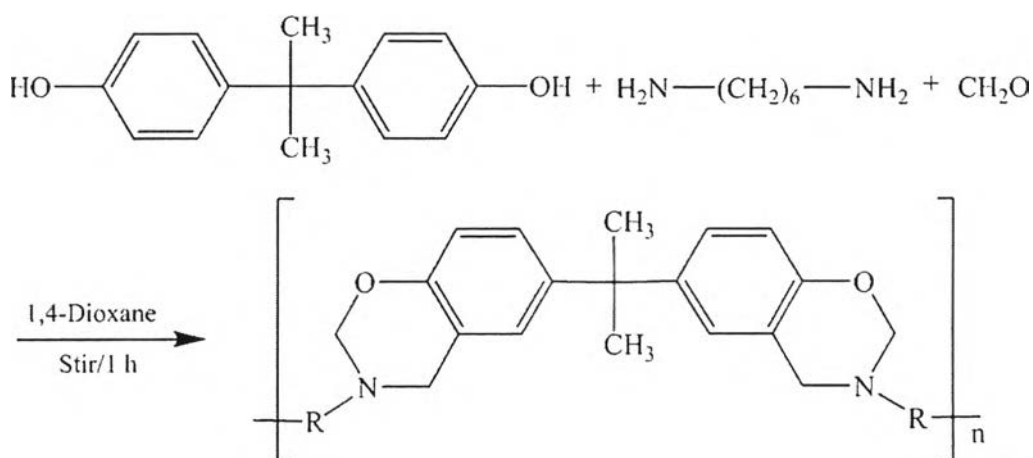
Figure 3.1 Synthesis of polybenzoxazine precursor.

3.3.5 Preparation of Polybenzoxazine Membrane

The polybenzoxazine precursor obtained from the reaction was heated and stirred continuously until viscous liquid is obtained. Then the mixture was left to cool down to room temperature before removal of any trapped air bubbles. A membrane was cast onto a glass plate which was wrapped with aluminum foil with a thickness of approximately 200 μm using Elcometer 3580 casting knife film applicator. The obtained membrane was dried at room temperature in air for one day, yielding a self-standing yellowish transparent membrane. Then the membrane was placed in an air-circulating oven at 110°C for 24 h. The thickness of the obtained membrane was around 80 μm ± 20 μm.

3.3.6 Preparation of Mixed Matrix Membranes (MMMs)

Various contents of MCM-48 were dispersed in 1,4-dioxane and stirred for 3 h. After that, the MCM-48 mixed solution was sonicated for 15 min to improve the dispersion of particles in the solution. Then MCM-48 particles were primed by adding approximately 5 wt% of the total amount of polybenzoxazine. The remaining polybenzoxazine was added in the MCM-48 solution to increase the compatibility. Then the mixture was stirred to enhance the homogeneity. The final mixture was further stirred continuously for 2 day before the casting. During this time period, the mixture was sonicated for 10 min from time to time.

3.3.7 Characterization

The structural characteristics of polybenzoxazine precursor were measured by fourier transform infrared spectroscopy (FT–IR, Thermo Nicolet Nexus 670) and proton nuclear magnetic resonance spectroscopy (^{1}H-NMR, Varian Mercury 300) using deuterated chloroform ($CDCl_3$) as the solvent. The interaction between the gas molecule and the MMMs performed by Attenuated total reflectance infrared spectroscopy (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 thermal stability of the membranes was investigated by thermogravimetric analysis (TGA, Perkin Elmer Pyris Diamond) at a heating rate of 20°C/min under a nitrogen flow. Study of the polymerization process and the glass transition temperature (Tg) of the MMMs were measured by differential scanning calorimetry (DSC7, PerkinElmer) at a heating rate of 10°C/min under a nitrogen flow. The Tg was taken from middle point of the slope transition in the DSC curve as an average value based on the second run. The membrane morphology was investigated using scanning electron microscopy (SEM, JEOL model JSM-5410LV and Hitachi/s-4800). The structural characterization of MCM-48 was performed by X–Ray diffractometry (XRD, Rigaku DMAX 2200 HV/X-ray diffractrometer) with CuK$_\alpha$ emission line ($\lambda = 0.154$ nm) over a 2θ range of 2°–8° at a voltage of 40 kV and a current of 40 mA. Nitrogen adsorption/desorption isotherms of MCM-48 were measured on surface area analysis (SAA). The specific surface area and average pore

size were determined by the Brunauer-Emmett-Teller (BET) method on a Quantasorb JR instrument (Mount Holly, NJ).

3.3.8 Gas Permeation Measurements

CH_4 and CO_2 were used as testing gases for all membranes. All tested gases were of a high purity (HP) grade and used as received. Schematic diagrams of the system to be used to carry out the gas permeability experiments and a membrane testing unit are shown in Figure 3.2.
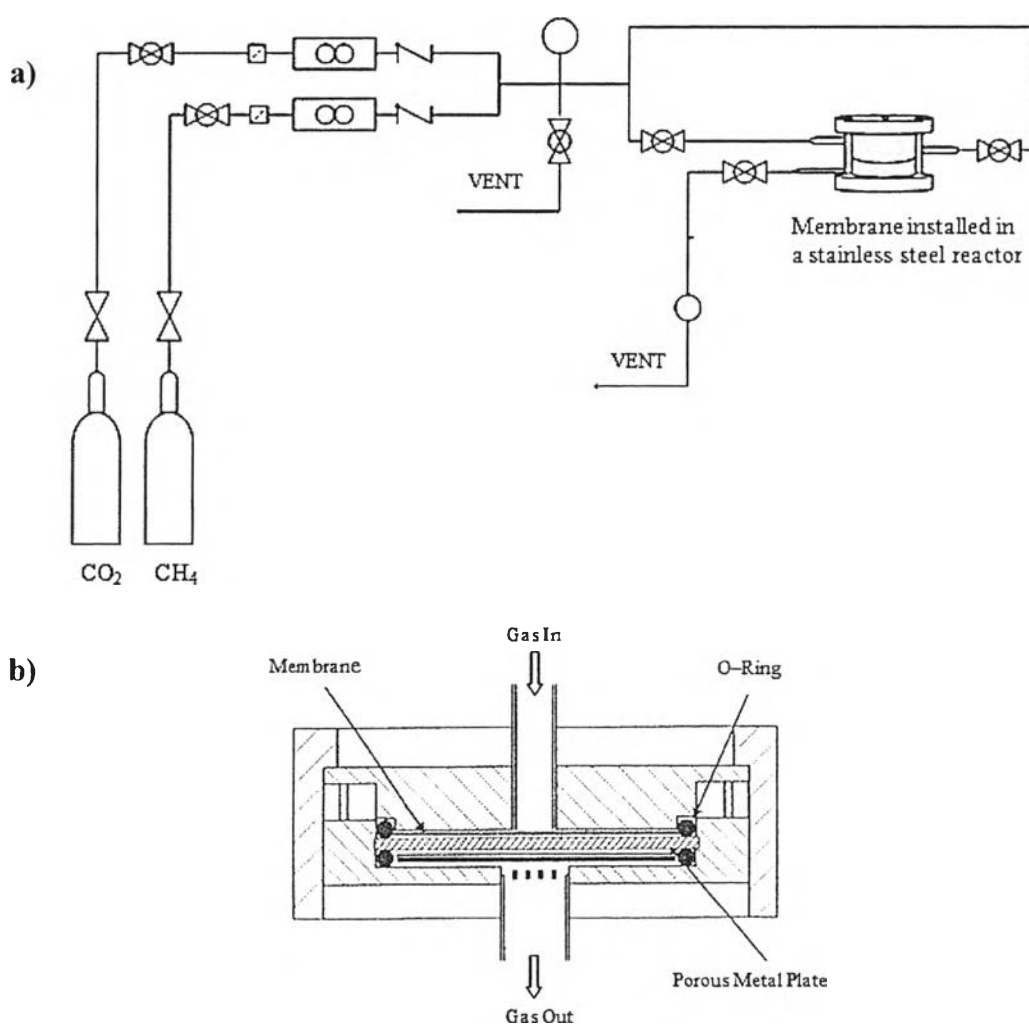
Figure 3.2 a) Experimental setup for a gas permeability apparatus and b) a membrane testing unit.

Permeabilities of the polymeric and composite membranes were measured using a constant volume varying pressure apparatus. Permeability was measured directly, including the time lag method (Kim *et al.*, 2005).

The single-component gas permeation (CH_4 and CO_2) experiments of the membranes were carried out at 25°C in sequences using a gas permeation testing unit, in which the membrane was placed on a porous metal plate. The area of the membrane in contact with the gas was 44.17 cm^2. The pressure difference across the membrane was maintained at 25 psi. After reaching the steady–state, individual gas flow rates were measured using ADM 1000 Universal gas flowmeter (Agilent Technologies). The attained data was used to calculate the gas permeability and selectivity.

The permeability coefficient for the permeated gas (equation 3.1):

$$\left(\frac{P}{\delta}\right)_i = \frac{Q_i \times 14.7 \times 10^6}{(A) \times (\Delta P) \times 76} \qquad (3.1)$$

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

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

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

δ = thickness of membrane (μm)

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

A = membrane area (cm^2)

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

The selectivity, $S_{A/B}$ for component A and B is defined as the ratio of each component, as shown in equation 3.2:

$$S_{A/B} = \frac{P_A}{P_B} \qquad (3.2)$$

The time-lag method (Bao *et al*, 2006; Rutherford and Do, 1997) allows measurements of permeability, diffusivity, and solubility simultaneously. The membrane was degassed under vacuum for between 12 and 16 h. Penetrant gas was then introduced on the upstream side at constant pressure (p_f). Depending on the rate of permeation of a given sample, variable downstream volumes may be affixed. Under these conditions, the amount of permeant per unit area permeated through the membrane, Q_t, is given by

$$\frac{LQ_t}{p_f} = DS\left(t - \frac{L^2}{6D}\right) = P\left(t - \frac{L^2}{6D}\right) \qquad (3.3)$$

where L is the thickness of membrane, D the diffusivity, t is the time, and P is the permeability, defined as the product of diffusivity and solubility. When LQ_t/p_f is plotted against time t, based on equation 3.3, the resulting curve results in an intercept of $L^2/6D$ on the t axis and has a slope of P. This intercept on the t-axis is the time lag, θ. The values of D and P lead to the value of the solubility by using S = P/D.