CHAPTER III
EXPERIMENTAL

3.1 Materials

1. 1,4-Dioxane (Lab-Scan), AR grade, 2.5 L
2. Bisphenol-A (Aldrich), (97% purity), 2 kg
3. Distilled Water
4. Ethanol (J.T. Baker; White Group), (99.9% purity), 2.5 L
5. Formaldehyde (Merck), (37%wt. in water), 1 L
6. Tetraethylenepentamine, TEPA (Fluka), (85% purity), 1 L
7. Triethylenetetramine, TETA (Facai), (95-98% purity), 1 L
8. 1,6-Hexadiamine (Aldrich), (98% purity), 100 g

3.2 Instruments

1. Perkin Elmer/DSC7 Differential Scanning Calorimeter (DSC)
2. Nicolet/Nexus 670 Attenuated Total Reflectance Infrared Spectrometer (ATR-IR)
3. Agilent/GC-6890 Gas Chromatography (GC)
4. JNM-A500/Fourier Transform Nuclear Magnetic Resonance Spectrometer (FT-NMR)
5. JEOL/JSM 5200 Scanning Electron Microscopy (SEM)
6. Perkin Elmer/Thermogravimetric Analyzer (TGA)
7. Air-circulating Oven
8. Pervaporation Apparatus Unit

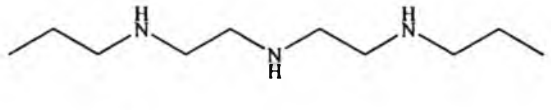
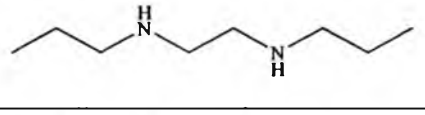
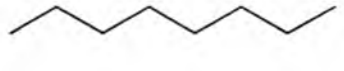
3.3 Methodology

3.3.1 Synthesis of Polybenzoxazine Precursors

Polybenzoxazine precursors were prepared using bisphenol-A, formaldehyde, and three types of diamines, whose structures are shown in Table 3.1,

with a mole ratio of 1:1:4, respectively. Firstly, bisphenol-A (6.84 g, 30 mmol) was dissolved in 15 ml of 1,4-dioxane in a 50 ml glass bottle and stirred until obtaining a clear solution. Formaldehyde solution (9.73 g, 324 mmol) was then added to bisphenol-A solution. The temperature was kept under 10 °C by using an ice bath. Diamine was then added dropwise into the mixture with continuously stirring for approximately 1 hour. Transparent yellow viscous liquid was obtained. However, when hda was used as the reactant, the mixture needed heat treatment, 100 °C, to drive the reaction go with stirring continuously until transparent yellowish viscous liquid was obtained, implying that hda has lower reactivity than those of TEPA and TETA. Benzoxazine precursors were then purified by washing with 200 ml of 0.1 M $NaHCO_3$ solution before removing solvent by evaporation and drying under vacuum. The purified benzoxazine precursors were then characterized using ^{1}H-NMR.

Table 3.1 The chemical structure of diamines

Diamine	Chemical structure
Tetraethylenepentamine (TEPA)	
Triethylenetetramine (TETA)	
hexamethylenediamine (hda)	

3.3.2 Preparation of Polybenzoxazine Membranes

Polybenzoxazine precursors obtained from the reactions were cast on a glass plate at room temperature with the thickness of approximately 300 μm using Elcometer 3580 casting knife film applicator (from elcometer/inspection equipment). The membranes were dried at room temperature in air for one day, yielding the yellow transparent membranes. The membranes were then further dried at 80 °C in

an air-circulating oven for 24 hours to remove excess solvent. Figure 3.1 depicts the synthesis of polybenzoxzine membranes.

Figure 3.1 depicts the chemical structure of polybenzoxzine membranes. The obtained polybenzoxazine membranes were characterized by Differential Scanning Calorimeter (DSC), Attenuated Total Reflectance Infrared Spectrometer (ATR-IR), Scanning Electron Microscopy (SEM) and Thermogravimetric Analyzer (TGA).

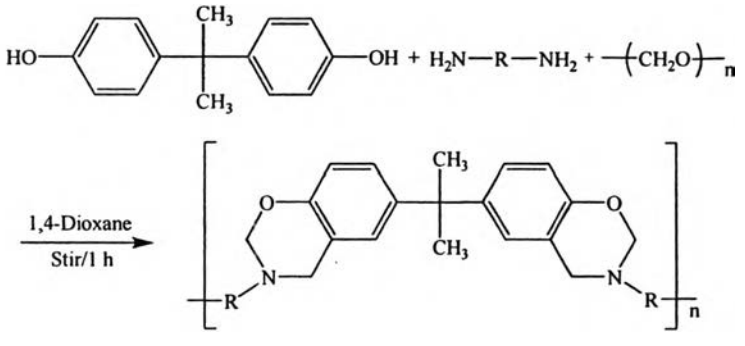


Figure 3.1 The structure of polybenzoxazine membranes.

3.3.3 Characterization of Polybenzoxazine Precursors

3.3.3.1 Proton Nuclear Magnetic Resonance (^{1}H-NMR)

^{1}H-NMR spectras were recorded on a Varian Mercury 300 (300 MHz) instrument. To identify chemical composition in the range of 1-5 ppm. The prepared polybenzoxazine precursors were dissolved in deuterated chloroform ($CDCl_3$) for 24 hours prior to used.

3.3.4 Polybenzoxazine Membranes Characterizations

3.3.4.1 Differential Scanning Calorimeter (DSC)

To study the polybenzoxazine polymerization, Differential Scanning Calorimeter (DSC7, Perkin-Elmer) with heating rate of 10°C/min under N_2 flow was used. The data was recorded from 25 to 300°C.

3.3.4.2 Attenuated Total Reflectance Infrared Spectrometer (ATR-IR)

Attenuated total reflectance infrared spectra of films were obtained from a Thermo Nicolet Nexus 670 by using ZnSe 45° (flat plate) with scans at a scanning resolution of 4 cm^{-1}.

3.3.4.3 Scanning Electron Microscopy (SEM)

The morphology was investigated using SEM (JEOL model JSM-5410LV). This technique was done at a faculty of Dentist, Chulalongkorn University.

3.3.4.4 Thermogravimetric Analyzer (TGA)

Thermogravimetric analysis was carried out by using a Perkin-Elmer Pyris Diamond with heating rate of 20°C/min under a N_2 flow. The thermogravimetric data was recorded from 25 to 800 °C.

3.3.5 Pervaporation System

A schematic diagram of pervaporation experiment is shown in Figure 3.2. The membrane was equipped in a stainless steel module. The feed was maintained at 70 °C in the cell. The mixture of ethanol and water (1:9) was used as the feed solution. The flow rate of 900 ml/min was used to circulate the mixture from the feed reservoir to a permeation cell. This condition was similar to the work done by Hsueh *et al.*, carrying out the experiment using different of the ethanol/ water ratios.

A Teflon gasket was also applied on the membrane to avoid leaking. The capacity of the upper cell compartment is approximately 100 ml while the area of the membrane in contact with the liquid is 22.1 cm^2. A water bath on a hot plate was used to control the feed solution temperature. The mixture was stirred continuously during the experiments. Vacuum was applied to the permeate side of the membrane, and the permeate vapour was condensed and collected in a cold trap immersed in liquid nitrogen.

The performances of the membranes were determined by measuring % ethanol in the permeate side to calculate the permeate water flux (kg/m^2hr) and the separation factor of the ethanol/water mixture. The quantities of ethanol and water were determined using gas chromatography (GC) on an Agilent

GC-6890. Samples of 0.5 μL were injected under the following conditions: the carrier gas was helium and the pressure was set at 55 kPa for TCD. The isothermal oven temperature was set at 200 °C while the injector and detector temperatures were set at 200 °C and 250 °C, respectively.

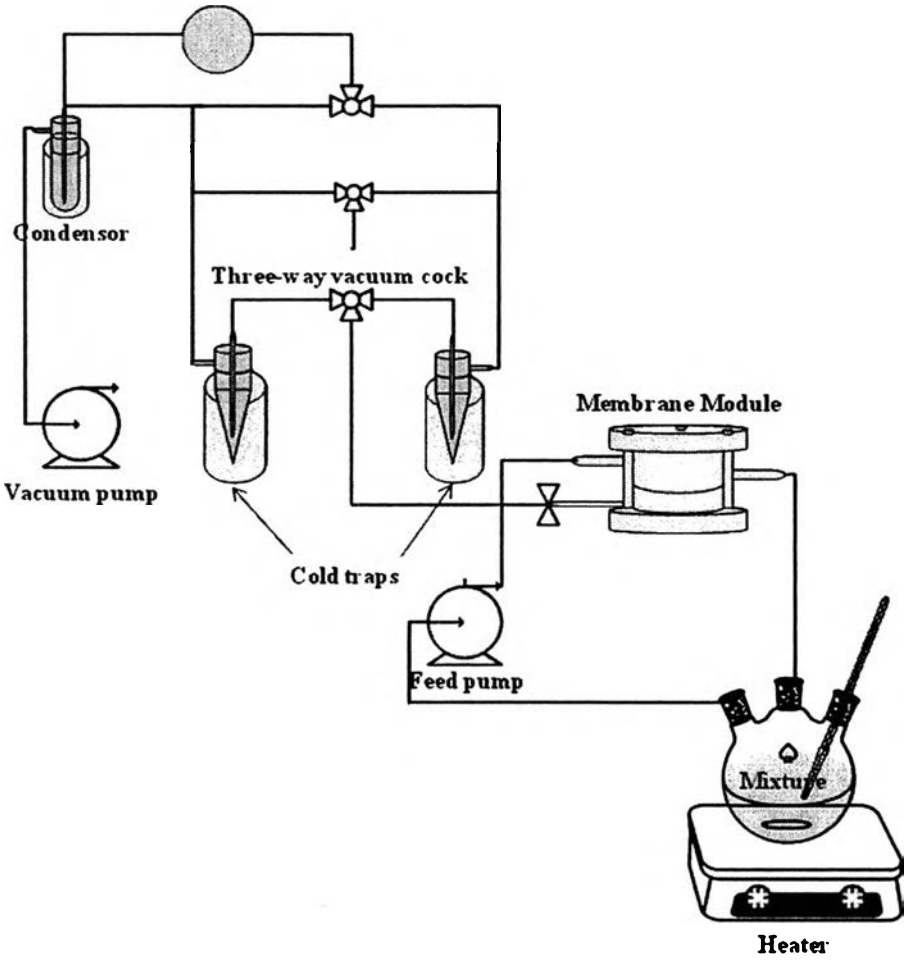


Figure 3.2 Experimental set up for the pervaporation apparatus.

3.3.6 Pervaporation Analysis

The permeate water flux (kg/m^{2}hr) and the separation factor of the ethanol/water mixture (88:12 % by volume) are determine using the quantities of ethanol and water obtained from GC, as follows;

3.3.6.1 Permeate Water Flux (J, kg/m^{2}hr)

The J can be calculated from equation 3.1:

$$J = M/At \quad (3.1)$$

where M = permeate weight (kg)

A = effective membrane surface area (m^2)

t = pervaporation time (hr)

3.3.6.2 Separartion Factor ($\alpha_{water/ethanol}$)

The $\alpha_{water/ethanol}$ was calculated from equation 3.2:

$$\alpha_{water/ethanol} = (Y_{water}/Y_{ethanol})/(X_{water}/X_{ethanol}) \quad (3.2)$$

where Y_{water} = the weight fraction of water in the permeate

$Y_{ethanol}$ = the weight fraction of ethanol in the permeate

X_{water} = the weight fraction of water in the the feed

$X_{ethanol}$ = the weight fraction of ethanol in the feed