CHAPTER III
EXPERIMENTAL

3.1 Materials

1. 1,4-Dioxane (Lab-Scan), AR grade, 2.5 L
2. Bisphenol-A, (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. 1,6-Hexadiamine (Aldrich), (98% purity), 100 g
7. Ethylenediamine (Fluka), (99%purity), 1L

3.2 Instruments

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

3.3 Methodology

3.3.1 Synthesis of Polybenzoxazine Precursors

Polybenzoxazine precursors were prepared by using Bisphenol-A, formaldehyde anddiamine with mole ratio of 1:4:1, respectively. The diamine such as 1,6-Hexadiamine and Ethylenediamine were used to obtained Poly (BA-hda) and

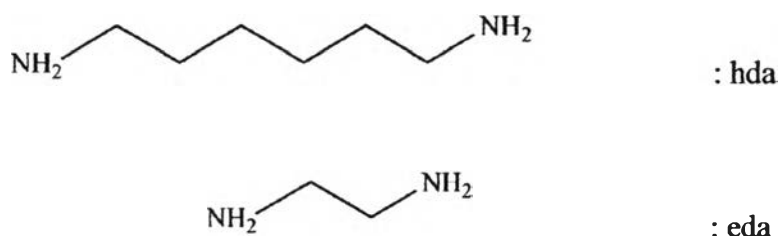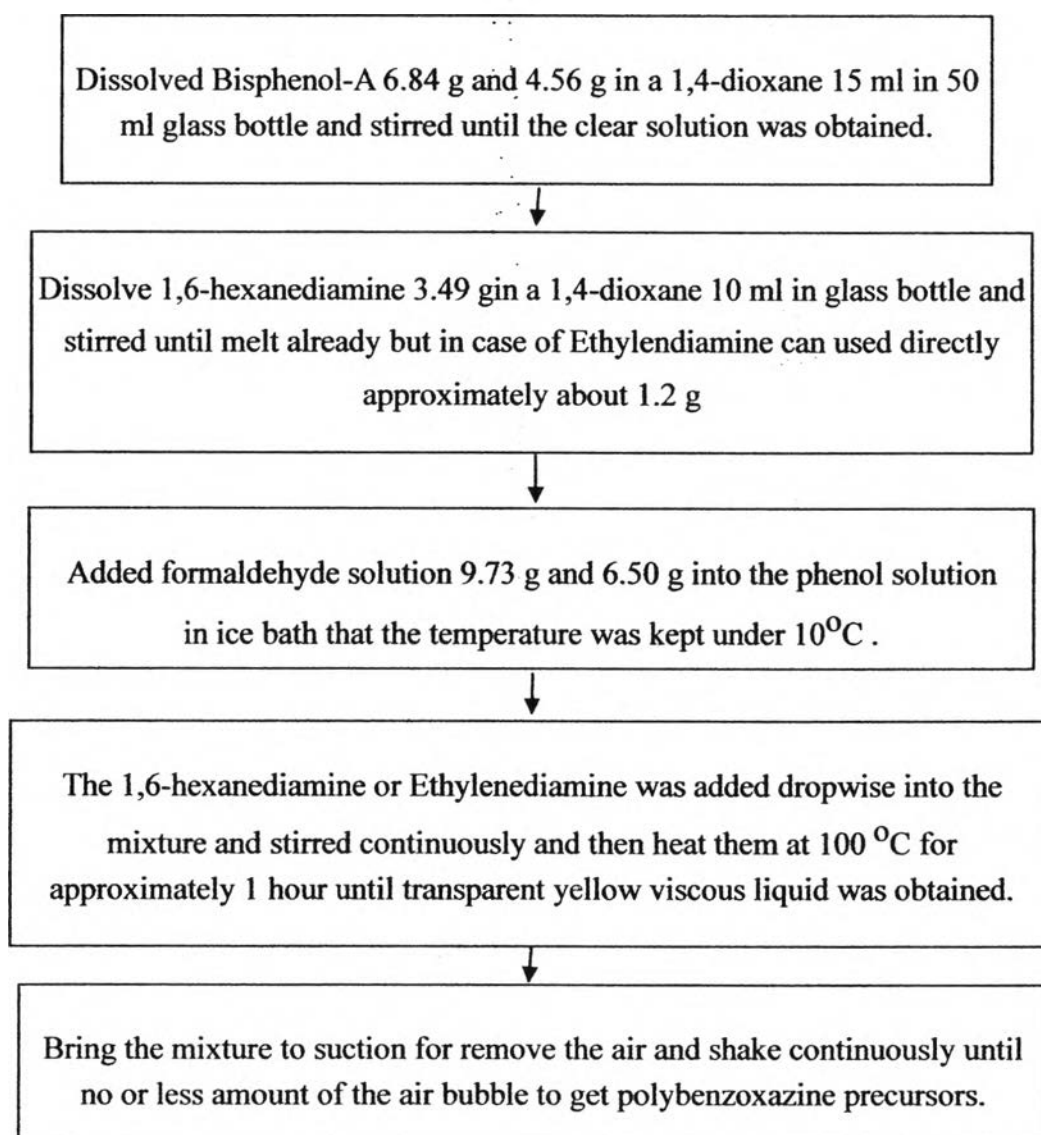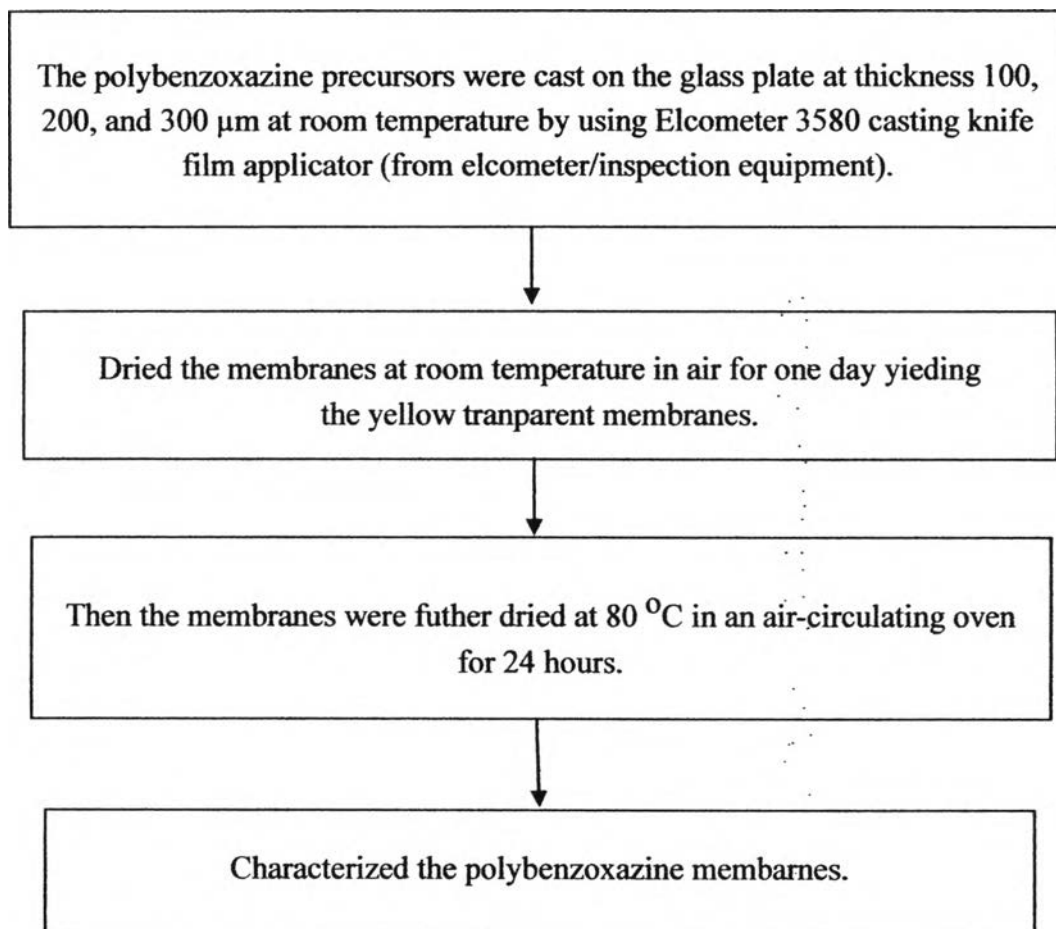Poly (BA-eda), respectively. The structure of two diamine types used in synthesis are shown in Fig. 3.1

: hda

: eda

Fig. 3.1 The chemical structure of 1,6-hexanediamine (hda) and Ethylenediamine (eda)

Dissolved Bisphenol-A 6.84 g and 4.56 g in a 1,4-dioxane 15 ml in 50 ml glass bottle and stirred until the clear solution was obtained.

Dissolve 1,6-hexanediamine 3.49 g in a 1,4-dioxane 10 ml in glass bottle and stirred until melt already but in case of Ethylendiamine can used directly approximately about 1.2 g

Added formaldehyde solution 9.73 g and 6.50 g into the phenol solution in ice bath that the temperature was kept under $10^{\circ}C$.

The 1,6-hexanediamine or Ethylenediamine was added dropwise into the mixture and stirred continuously and then heat them at $100\ ^{\circ}C$ for approximately 1 hour until transparent yellow viscous liquid was obtained.

Bring the mixture to suction for remove the air and shake continuously until no or less amount of the air bubble to get polybenzoxazine precursors.

3.3.2 Preparation of Polybenzoxazine Membranes

The polybenzoxazine precursors were cast on the glass plate at thickness 100, 200, and 300 μm at room temperature by using Elcometer 3580 casting knife film applicator (from elcometer/inspection equipment).

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Dried the membranes at room temperature in air for one day yieding the yellow tranparent membranes.

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Then the membranes were futher dried at 80 °C in an air-circulating oven for 24 hours.

↓

Characterized the polybenzoxazine membarnes.

3.3.3 Characterization of Polybenzoxazine Precursor

3.3.3.1 Proton Nuclear Magnetic Resonance (^1H NMR)

^1H 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 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}.

3.3.4.2 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.

3.3.4.3 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 the system used to carry out the pervaporation experiments is shown in Fig. 3.2. The membrane is supported on a stainless steel disc. The feed was maintained at 40, 50, 60 and 70°C in the cell. The membrane thickness was used at 100, 200 and 300 μm. Moreover, the mixtures of ethanol/ water solution with ratio of ethanol also studied at 5, 10, 15 and 20 as the feed solution. The flow rate of 900 ml/min was used to circulate the mixtures from the feed reservoir to a permeation cell.

A Teflon gasket was applied on the membrane. After the membrane was placed in the chamber, then the two compartments were fixed together to prohibit the leakage. The capacity of the upper cell compartment is approximately 100 ml, while the area of the membrane in contact with the liquid is 22.07 cm^2. A hot plate was used to control the feed solution temperature. The mixtures were stirred continuously during the experiments. The outlet joint from the lower compartment was connected to a trap cooled by liquid nitrogen. A vacuum with a pressure of 0 mmHg was

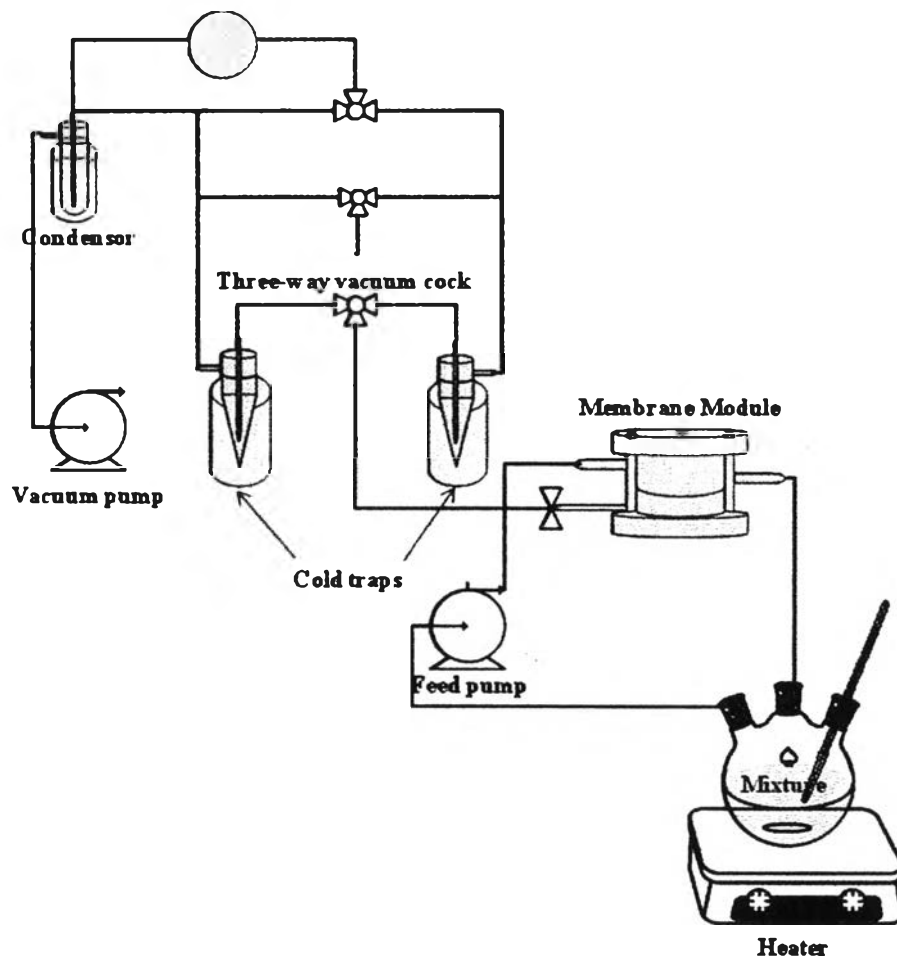maintained for all runs using a vacuum pump.

Figure 3.2 Experimental set up for the pervaporation apparatus.

3.3.6 Pervaporation Analysis

The separation performances of two polybenzoxazine membranes (BA-hda and BA-eda membrane) were determined by measuring percentage of ethanol and water in permeate side by using Gas Chromatography. After, the total water flux (kg/m²hr) and separation factor of ethanol-water at various conditions were determined. Thetotal water flux (kg/m²hr) and separation factor is shown in eq. (3.1) and (3.2).

3.3.6.1 Total water flux (J, kg/m²hr)

Total water flux (J) can be calculated from the following equation 3.1:

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

where
M = permeate weight (kg)

A = effective membrane sueface area (m²)

t = pervaporation time (hr)

3.3. 6.2 Separartion Factor ($\alpha_{water/ethanol}$)

The separation factor ($\alpha_{water/ethanol}$) was calculated from equation 3.2:

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

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

3.3 6.3 Gas Chromatography (GC)

The composition of the feed solutions, permeates and solutions adsorbed in the membrane were measured by gas chromatography on an Agilent GC-6890. A ZEBRON-WAX (30 m x 0.25 mm I.D.). Samples of 0.5 μL were injected under the following conditions: the carrier gas was helium and set at 55 kPa for TCD were maintained. The isothermal oven temperature was set at 200 °C, while the injector and detector temperatures were set at 200 °C and 250 °C, respectively.