

## CHAPTER IV

### Development of Polybenzoxazine Membranes on $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Support for Ethanol-Water Separation via Pervaporation Technique

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#### 4.1 Abstract

Bioethanol is one of the candidates to replace fossil fuels. Currently, one way to reduce the use of fossil fuels is to utilize a mixture of gasoline/diesel with ethanol (gasohol/diesohol). Bioethanol is an alcohol produced from agricultural feedstocks by fermentation process, followed by traditional distillation to increase the purity of bioethanol. However, distillation presents some concerns regarding environment, health, and cost. Membrane technique is one of the attractive processes for ethanol-water separation, and polybenzoxazine (PBZ) membrane was evaluated for the ethanol-water separation. PBZ was successfully synthesized from bisphenol-A (BPA), formaldehyde, and two different multifunctionalamines: tetraethylene-pentamine (tepa), and diethylenetriamine (deta). Pervaporation technique was carried out to find separation performance. It was found that the optimum poly(BA-deta) and poly(BA-tepa) concentration for the preparation of the the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supporting PBZ membranes was 40 wt% and 25 wt%, respectively. The dipping cycles of poly(BA-deta) and poly(BA-tepa) was found to be 2, the membranes thickness was 12.40 and 12.34  $\mu$ m, giving the total permeation flux of 17.77 and 25.90 g/m<sup>2</sup>h, respectively. The separation factor of both membranes was higher than 10,000. The synthesized membranes had excellent separation ability at both low and high ethanol concentration (10-90%) in pervaporation process.

*Keywords:* Polybenzoxazine membrane; Ethanol-water separation; Pervaporation Performance

## 4.2 Introduction

Presently, fossil fuels become one of the most essential sources of energy in the world. As they begin to deplete, scientists look for another way to replace them. Bioethanol is one of the candidates to replace fossil fuels. Currently, one way to reduce the use of fossil fuel is to utilize gasohol. Gasohol, the mixture of gasoline and ethanol, has a number of advantages over conventional petroleum-based fuels, such as lower price, higher octane number, better anti-knocking properties, higher heat vaporization, and complete combustion, resulting in much less pollutants from emission [1]. Pervaporation is an encouraging process for separating close-boiling point mixtures, azeotropic mixtures, and for the dehydration of temperature-sensitive products [2], [3]. Pervaporation using ceramic membranes is generally economic with water contents of approximately 10 wt% and less [4].

In 1996, the cellulose acetate membrane-coated on the outer surface of a porous ceramic support by a dip-coating and rotation-drying technique for the dehydration of ethanol and isopropanol (IPA) via pervaporation. The separation factors of water were very low, in the range of 4–11 and 8–240 in the ethanol/water and the IPA/water systems, respectively [5].

In 2006, Peters and coworkers synthesized thin high flux and highly selective cross-linked poly(vinyl)alcohol (PVA)-water selective layer on the top of an  $\alpha$ - $\text{Al}_2\text{O}_3$  hollow fiber substrate combined with intermediate  $\gamma$ - $\text{Al}_2\text{O}_3$  layers in order to get a smooth surface for the ultra-thin PVA layer. In the dehydration of ethanol containing 10 wt% water at 70 °C, the membranes exhibited water flux of  $1.06 \text{ kg m}^{-2} \text{ h}^{-1}$  with a low separation factor of 40 because of the swelling problem [2]. Even the thin PVA layers were loaded with fumed silica, using 5 wt% PVA solution and 6 wt% fumed silica, and coated on porous ceramic supports, the best separation of ethanol and water via pervaporation process still resulted in a low separation factor of 50 at the pervaporation temperature of 45 °C, giving the permeation flux of  $1.69 \text{ kg/m}^2 \text{ h}$ .

In 2011, Pakkethati *et al.* synthesized PBZ membranes and studied their performance on ethanol-water separation via pervaporation process. The PBZ membranes were synthesized from bisphenol-A, formaldehyde, and three different

types of multifunctional amines, hexamethylenediamine (hda), tetraethylenepentamine (tepa), and tetraethylenetriamine (teta), which are denoted as poly (BA-hda), poly(BA-tepa), and poly(BA-teta), respectively. They found that only poly(BA-hda) provided the best total permeation flux ( $1.52 \text{ kg/m}^2\text{h}$ ) and separation factor (higher than 10,000) when using 10:90 water:ethanol. Additionally, raising the temperature of the feed solution and decreasing the membrane thickness achieved an increased permeation flux. The optimum conditions for this study were at  $70 \text{ }^\circ\text{C}$  for the feed mixtures using a  $200 \text{ }\mu\text{m}$  poly(BA-hda) membrane thickness. Both poly(BA-tepa) and poly(BA-teta) membranes swelled and were not stable [7].

In this study, due to an increase in mechanical strength of the membrane by the porous alumina support [6] and many excellent properties of PBZ [8-10], highly crosslinked poly(BA-tepa) and poly(BA-teta) membranes were, thus, studied, synthesized, and coated on porous alumina support to separate 50:50 ethanol:water mixture via pervaporation technique. Not only the separation performance, but also swelling behaviors of these highly crosslinked membranes in various concentrations of ethanol were studied.

### 4.3 Experimental

#### 4.3.1 Materials

Analytical grade 1,4-dioxane and ethanol (99.9% purity) were purchased from Labscan, Ireland. Bisphenol-A (BPA, 97% purity), tetraethylenepentamine (tepa, 85% purity), and diethylenetriamine (deta, 99% purity) were purchased from Aldrich, Germany. Formaldehyde (AR grade, 37wt% in water) was purchased from Merck, Germany. Tubular porous  $\alpha$ -alumina support, having an 11 mm O.D., a 9 mm I.D was purchased from National Metal and Materials Technology Center (MTEC), Thailand.

#### 4.3.2 Characterizations

Differential scanning calorimeter (DSC, PerkinElmerDSC7) was used to study the polymerization process of the PBZ membranes. The samples were heated from  $30^\circ$  to  $280 \text{ }^\circ\text{C}$  using a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$  under a  $\text{N}_2$  atmosphere with a flow rate of  $10 \text{ mL}/\text{min}$ . The membranes morphology and thickness were

investigated using a scanning electron microscope (SEM, JEOL model JSM-5410LV) with an accelerating voltage of 1.5 kV. Samples were coated with platinum under vacuum before observation. Gas chromatography (GC/TCD, Agilent Technologies model 6890N, G 1540N) equipped with a HP-PLOT-Q (30 m x 0.25 mm I.D.) column was used to determine the ethanol quantity in both feed and permeate. Sample of 0.5  $\mu$ L was injected under the following conditions: helium carrier gas set at 55 kPa for TCD detector, oven temperature isothermally set at 200°C, 200°C and 250 °C injector and detector temperatures, respectively [7].

### 4.3.3 Methodology

#### 4.3.3.1 *Synthesis of the PBZ Precursors*

The PBZ precursors were prepared by mixing BPA, formaldehyde, and tepa/deta at a mole ratio of 1:4:1, respectively [3]. Firstly, BPA (6.84 g, 30 mmol) was dissolved in 1,4-dioxane (15 mL) in a 50 mL glass bottle and stirred until a clear solution was obtained. A formaldehyde solution (9.73 g, 324 mmol) was then added to the BPA solution. The temperature was kept at 10 °C by using an ice bath. Multifunctional amine was then added dropwise into the mixture while continuously stirring for approximately 10 minutes until a transparent yellow viscous liquid was obtained.

#### 4.3.3.2 *Preparation of the PBZ Membranes*

A tubular porous  $\alpha$ -alumina support was cut into 6.5 cm length, cleaned by washing twice with deionized water for 15 minutes to remove dirt from the surface, and calcined in a furnace at 400 °C for 3 hours to burn off any impurities from its surface [11]. The PBZ solution to be coated on the alumina tube was prepared by using various concentrations of 5 – 40 %(w/w) PBZ prepared from 4.3.3.1. The top and bottom parts of the support tube were Teflon sealed before immersing into the PBZ-solution, followed by curing the tube in an oven at the curing temperature of each PBZ type to obtain PBZ-membrane on outer surface of the support tube.

#### 4.3.3.3 *Swelling Study*

The cured PBZ-membrane films were measured the initial weight ( $W_0$ , about 0.1 g) before immersing in the following solvents: ethanol, water, and 50:50 ethanol:water, at 70 °C (the same as pervaporation analysis condition).

The PBZ-membranes were periodically taken out, wiped dry, and weighed to obtain the mass of membrane after swelling ( $W_t$ ). The degree of swelling ( $G_s$ , eq. 4.1) of the membrane is defined as [7].

$$G_s = \frac{(W_t - W_0)}{W_0} \times 100\% \quad (4.1)$$

where  $W_0$  = the initial weight of the membrane  
 $W_t$  = the weight of the swollen membrane

#### 4.3.3.4- Pervaporation Study

A schematic of the pervaporation experiment is shown in Scheme 4.1 [12]. The tube was placed in a stainless steel module. A flow rate of 900 mL/min was used to circulate the mixture from the feed reservoir containing a 50:50 ethanol:water mixture to a permeation cell. The pervaporation temperature was fixed at 70 °C. The performance of the membrane on the alumina tube was determined by measuring % ethanol in the permeate side and calculating the permeate water flux ( $\text{kg/m}^2\text{h}$ ) and the separation factor. The quantities of ethanol and water were determined using a GC. The permeation flux ( $J$ , eq. 4.2) and the separation factor (eq. 4.3) were determined as follows:

$$J = M / At \quad (4.2)$$

where  $M$  = permeate weight (kg),  
 $A$  = effective membrane surface area ( $\text{m}^2$ ), and  
 $t$  = pervaporation time (h)

$$\alpha_{\text{water-ethanol}} = (Y_{\text{water}} / Y_{\text{ethanol}}) / (X_{\text{water}} / X_{\text{ethanol}}) \quad (4.3)$$

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

$X_{\text{ethanol}}$  = the mole fraction of ethanol in the feed.

## 4.4 Results and discussions

### 4.4.1 Curing temperature study

DSC was used to monitor the progress of ring-opening polymerization of the PBZ precursors as a cast film [13]. The precursor films were colorless and transparent. Figure 4.1a shows DSC thermograms of the poly(BA-deta) membranes before and after curing. The exotherm peak and onset were observed at 220°C and 140 °C, respectively. Poly(BA-tepa) membranes in Figure 4.1b results in the exotherm peak and onset at 260°C and 160 °C, respectively. Both PBZ results are in agreement with those obtained by Pakkatati *et al.* [7]. Scheme 4.2 shows the ring-opening polymerization reaction of poly(BA-deta) and poly(BA-tepa) precursors which clearly indicated that crosslink density increased after the heat treatment [10, 13]. These results are consistent with the DSC thermograms, giving the curing temperature of the poly(BA-deta) and poly(BA-tepa) membranes at 180° and 200 °C, respectively, when fixing the curing time at 20 minutes. The curing temperatures used for both  $\alpha\text{-Al}_2\text{O}_3$  supporting PBZ membranes were thus lower than the temperature obtained from the exotherm peaks to prevent membrane degradation because the membranes coated on the  $\alpha\text{-Al}_2\text{O}_3$  support were much thinner than the membrane films. After the heat treatment, the exotherm peaks were almost disappeared, meaning that the  $\alpha\text{-Al}_2\text{O}_3$  supporting PBZ membranes were almost cured.

### 4.4.2 Swelling Behavior

To study the synthesized membrane stability, the cured poly(BA-deta) membranes at 180 °C and poly(BA-tepa) membranes at 200 °C for 20 minutes were weighed about 0.1 g before immersing in ethanol, water, and 50:50 ethanol:water mixture. The solvent temperature was fixed at the same temperature as the pervaporation study at 70 °C. After 1, 3, 5, 7, 10, and 15 days, the membranes were taken out to determine the degrees of swelling. The obtained results are demonstrated in Figure 4.2. As increasing the polarity of the solvents from ethanol (polarity index = 5.2) to water (polarity index = 9.0), the sorption and swelling activities of the PBZ

membranes increased. As discussed by González-Velasco and coworkers [14] that the PBZ molecular structure also affected the sorption and swelling behaviors. Both poly(BA-deta) and poly(BA-tepa) are hydrophilic because they consisted of nitrogen atoms from aliphatic diamine chains and hydroxyl groups from the ring-opening polymerization, thus these membranes could form hydrogen bonding with water more than ethanol.

The poly(BA-tepa) membrane showed higher degree of swelling in water and 50:50 water:ethanol mixtures than ethanol (Figure 4.2b - 4.2c) due to longer aliphatic diamine chains, having more hydrophilic. But in ethanol, both poly(BA-deta) and poly(BA-tepa) did not swell until after 15 days, they showed very low degree of swelling (Figure 4.2a). A similar swelling behavior was also reported by Pakkatati *et al.*[7] who produced partially cured poly(BA-tepa) membranes. However, both the highly cured poly(BA-deta) and poly(BA-tepa) membranes showed a much-lower degree of swelling (0.5–5 %) and were stable after 10 days in ethanol, water, and 50:50 ethanol-water mixtures. It can be concluded that the membrane stability increased as increasing the crosslink-density [15, 16].

#### 4.4.3 Pervaporation Analysis

In this study, the ratio between ethanol-water in the feed solution was kept at 50:50, as studied by Homyen *et al.*[17] for partially cured PBZ membranes capable to resist at 70 °C. Similar to the study reported by Pakkatati *et al.*[7], an appropriate temperature for pervaporation using PBZ membrane was at 70 °C. The quantities of ethanol and water were determined using a GC for the performance of the PBZ membranes, as indicated by the permeation flux and the separation factor. The permeate was collected for a period of 1 hour and then the mass of permeate was determined gravimetrically. The flux of permeate across the membrane was determined from these mass/time data. The calculated membrane area was  $14.86 \times 10^{-4} \text{ m}^2$ .

##### 4.4.3.1 *Effect of PBZ Concentration*

The membrane thickness, an important parameter in the pervaporation process, is mainly related to the concentration of PBZ solution. In this study the concentrations of PBZ solution were varied from 5–40 wt% for poly(BA-deta) and 5–30 wt% for poly(BA-tepa) at the holding time of 30 seconds. The curing

temperatures of poly(BA-deta) and poly(BA-tepa) were at 180° and 200 °C, respectively, for 20 minutes curing time.

According to the results from Tables 4.1-4.2, it was clearly indicated that the thickness of the membrane directly affected to the separation factor and the total permeation flux. The thickness of the membrane was resulted from the concentration of the PBZ solution and the number of the dipping cycle. At the lower concentration, the higher dipping cycle number was required to increase the thickness, resulting in a decrease of the permeation flux. However, too high PBZ concentration caused the membrane too thick even though the dipping cycle number was decreased, affecting a decrease in the permeation flux. Therefore, the optimum concentration and dipping cycle number were investigated, based on the membrane performance results.

From the pervaporation results for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supporting poly(BA-deta) (Table 4.1) and poly(BA-tepa) (Table 4.2) membranes, it was found that the optimum poly(BA-deta) and poly(BA-tepa) concentrations for preparing the membranes were 40 and 25 wt%, using only 2 dipping cycles resulting in the membranes thickness of 12.40 and 12.34  $\mu$ m, the total permeation flux of 17.77 and 25.90 g/m<sup>2</sup> h, respectively, with the separation factor higher than 10,000.

#### *4.4.3.2 Physical Appearances and Morphology of the $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Support Membranes*

In the membrane preparation step, it was important to preliminarily observe the physical appearances of the membranes whether it had or had not defect before the pervaporation test. Figure 4.3 shows physical appearances of the membranes comparing to that of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support tube (Figure 4.3a). After coating with the PBZ solution for the first cycle (Figure 4.3b), the surface looks more yellow, and becomes smooth and glossy after the second dipping cycle, as shown in Figure 4.3c. The cured PBZ membrane in Figure 4.3d shows glossy orange yellow with smooth surface. The thickness of PBZ layer from SEM, generally correlating with the total permeation flux and separation factor [18] was further characterized, and the results are shown in Figure 4.4. The SEM image of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support surface in Figure 4.4a shows rough surface while the cured PBZ surface in Figure 4.4d was smooth and completely covered over the alumina support. One and two-



dipping cycle cross section images in Figure 4.4b and 4.4c, respectively, undoubtedly explain the results of the membrane thickness after curing at 180 °C for 20 minutes, as also seen the results in Tables 4.1–4.2. It was indicated that increasing the PBZ precursor concentration and the number of the dipping cycle also increased the membrane thickness.

#### 4.4.3.3 Effect of Feed Temperature

The temperature is one of the most important operating parameters in the pervaporation process, influencing three properties of (i) adsorption, (ii) diffusion, and (iii) vapor pressure in the feed during the permeation through the membranes [19]. Figure 4.5a shows the total permeation flux of the pervaporation process using the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supporting poly(BA-deta) and poly(BA-tepa) membranes as a function of operating temperature. The feed temperature was varied from 40°, 50°, 60°, and 70 °C. The feed solution was fixed at 50:50 ethanol:water. The permeation flux was increased when increasing the feed temperature. The diffusion rate was proportional to the permeation flux and increased with temperature, contributing to the elevated permeation flux, as also reported by Huang *et al.* [20]. The reason comes from the thermal motions of polymer chains, producing free volumes that provide permeating molecules to diffuse easily through the membrane. Moreover, the chain mobility increased as increasing temperature. Thus, the diffusion rate of individual permeating molecule increased, leading to high permeation fluxes at higher temperatures [21].

The activation energy of the pervaporation at the temperature range of 40 °C –70 °C through both types of the membranes was obtained from the Arrhenius eq. 4.4;

$$J = J_0 \exp(-E_p/RT), \quad (4.4)$$

where

$J_0$	= permeation rate constant,
$E_p$	= apparent activation energy for permeation flux,
$R$	= gas constant, and
$T$	= temperature (Kelvin, K)

From Figure 4.5b the apparent activation energy was a function of the permeating concentration, and calculated from the slope of the curve plotted between  $\ln J$  and  $1/T$ . The calculated apparent activation energies for the permeation flux were 16.46 and 9.85 kJ/mol, and  $R^2$  were 0.8781 and 0.9324 for the  $\alpha\text{-Al}_2\text{O}_3$  supporting poly(BA-deta) and poly(BA-tepa) membranes, respectively. These results indicated that the pervaporation through both membranes was thermally activated process and the higher temperature resulted in the more permeation flux [18]. It could be concluded that the  $\alpha\text{-Al}_2\text{O}_3$  supporting poly(BA-deta) membrane was more sensitive with temperature than the other due to its higher activation energy.

#### 4.4.3.4 Effect of Ethanol Feed Concentration on the Pervaporation Performance

The effect of ethanol feed concentration on the pervaporation performance is shown in Figure 4.6a and 4.6b. As can be seen that in the whole range of 10–90% ethanol feed concentration, both  $\alpha\text{-Al}_2\text{O}_3$  supporting poly(BA-deta) and poly(BA-tepa) membranes showed very high separation factor, more than 10,000, while the total permeation flux decreased with ethanol concentration. It could be rationalized that as higher ethanol concentration, the amount of water in the feed mixtures decreased, resulting in a decrease of the water sorption in the membranes. In addition, it can be confirmed that both  $\alpha\text{-Al}_2\text{O}_3$  supporting poly(BA-deta) and poly(BA-tepa) membranes are very stable at all feed concentrations. opposite to the results studied by Pakkatati *et al.* [7]. Who found swelling behaviors of these two membranes. Thus, the use of these membrane on the  $\alpha\text{-Al}_2\text{O}_3$  support increased the stability of the membranes.

## 4.5 Conclusions

Highly crosslink polybenzoxazine membranes were successfully synthesized from bisphenol-A, formaldehyde, and diethylenetriamine (deta)/tetraethylenepentamine (tepa). The optimum poly(BA-deta) and poly(BA-tepa) concentrations for preparation of the membranes on  $\alpha\text{-Al}_2\text{O}_3$  support were 40 and 25 wt%, respectively. The dipping cycles of both polymers were found to be 2, giving

the membranes thickness of about 12  $\mu\text{m}$ . Performance of the  $\alpha\text{-Al}_2\text{O}_3$  supporting poly(BA-deta)/poly(BA-tepa) membranes under recycle-continuous mode of 50:50 water:ethanol separation via pervaporation technique gave the total permeation flux of 17.77 and 25.90  $\text{g}/\text{m}^2\text{h}$ , respectively, with the separation factor of higher than 10,000 at the feed temperature of 70  $^\circ\text{C}$ . The synthesized membranes had excellent separation ability at both low and high ethanol concentrations (10-90%) in pervaporation process with a good stability.

#### 4.6 Acknowledgements

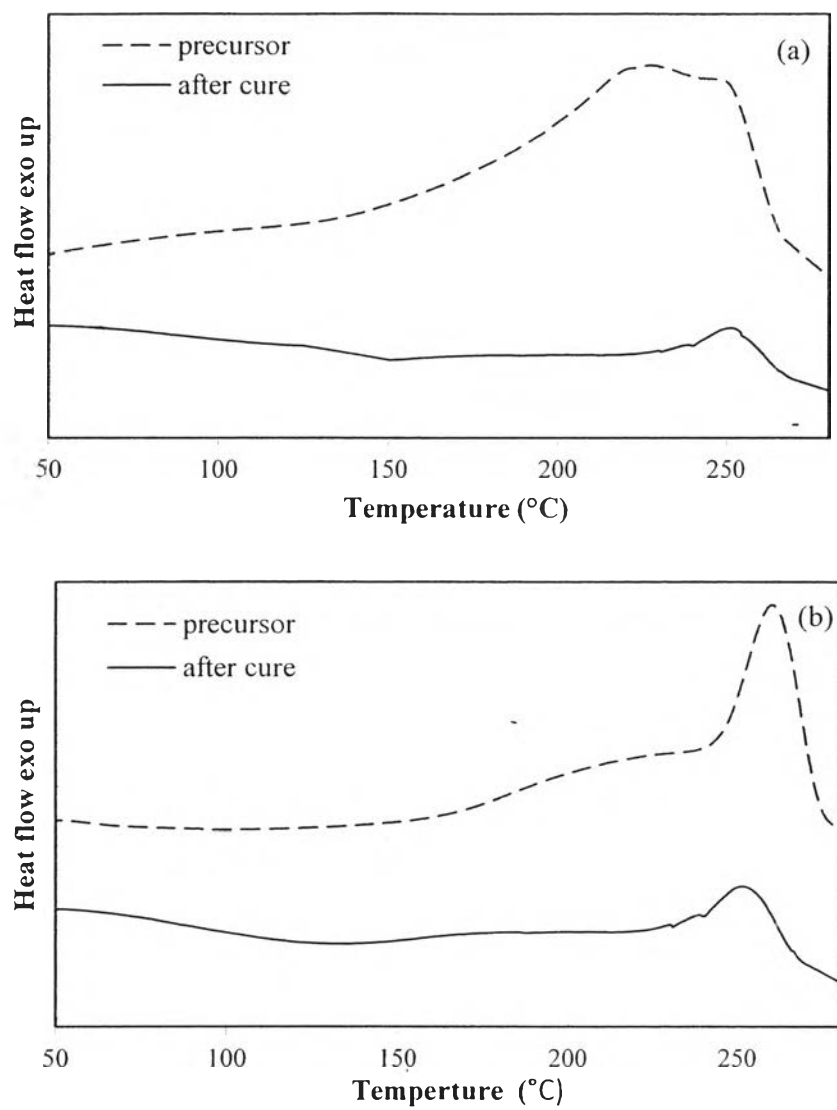
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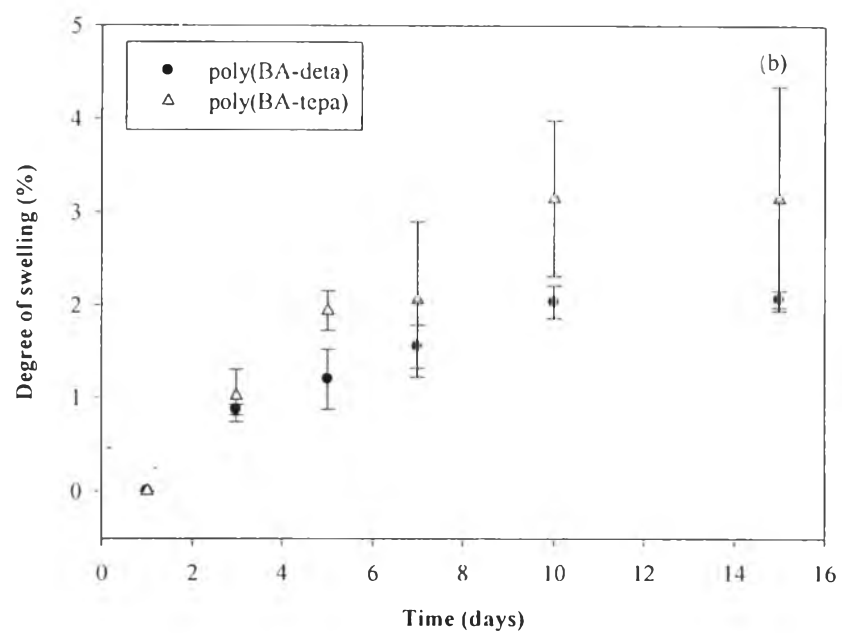
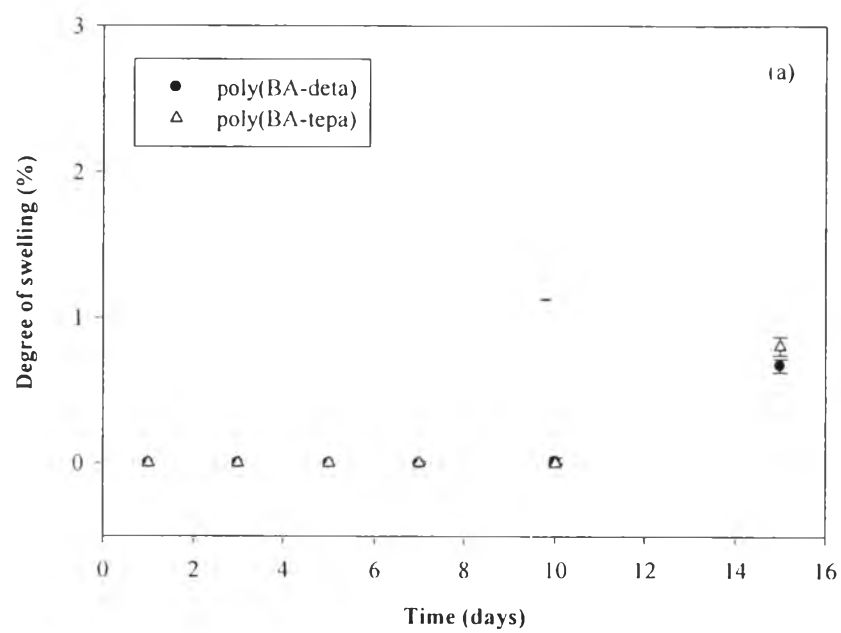
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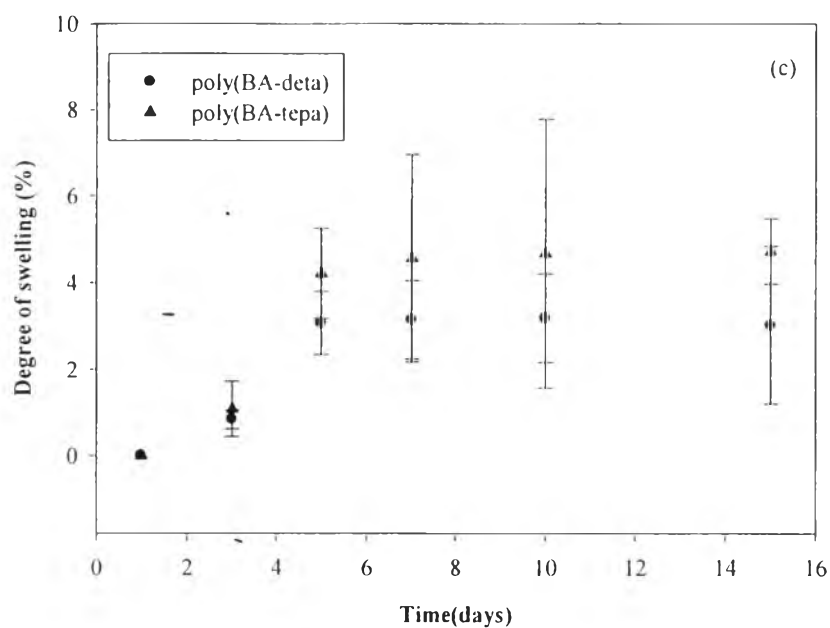
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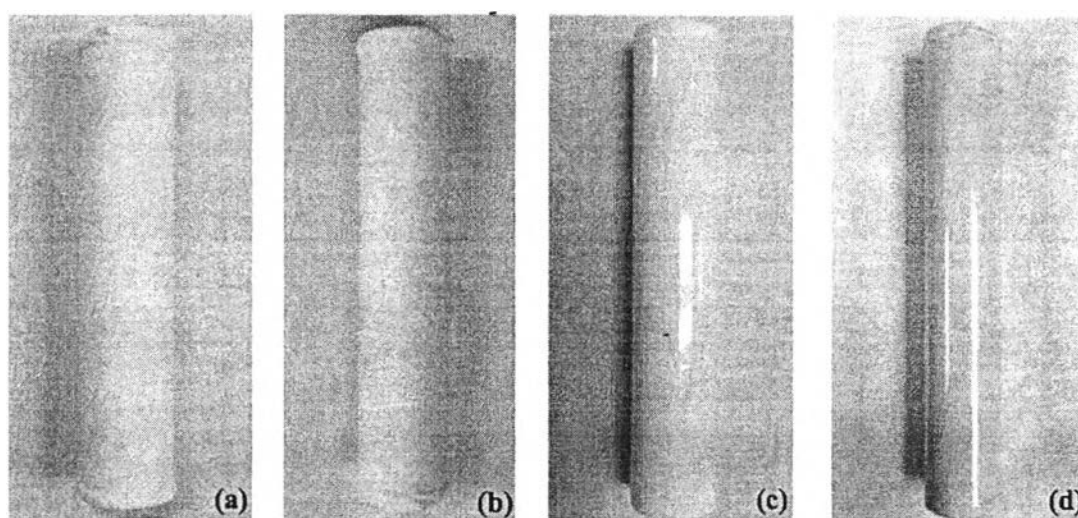


**Figure 4.1** DSC thermograms of poly(BA-deta) (a), and poly(BA-tepa) (b) before and after curing.



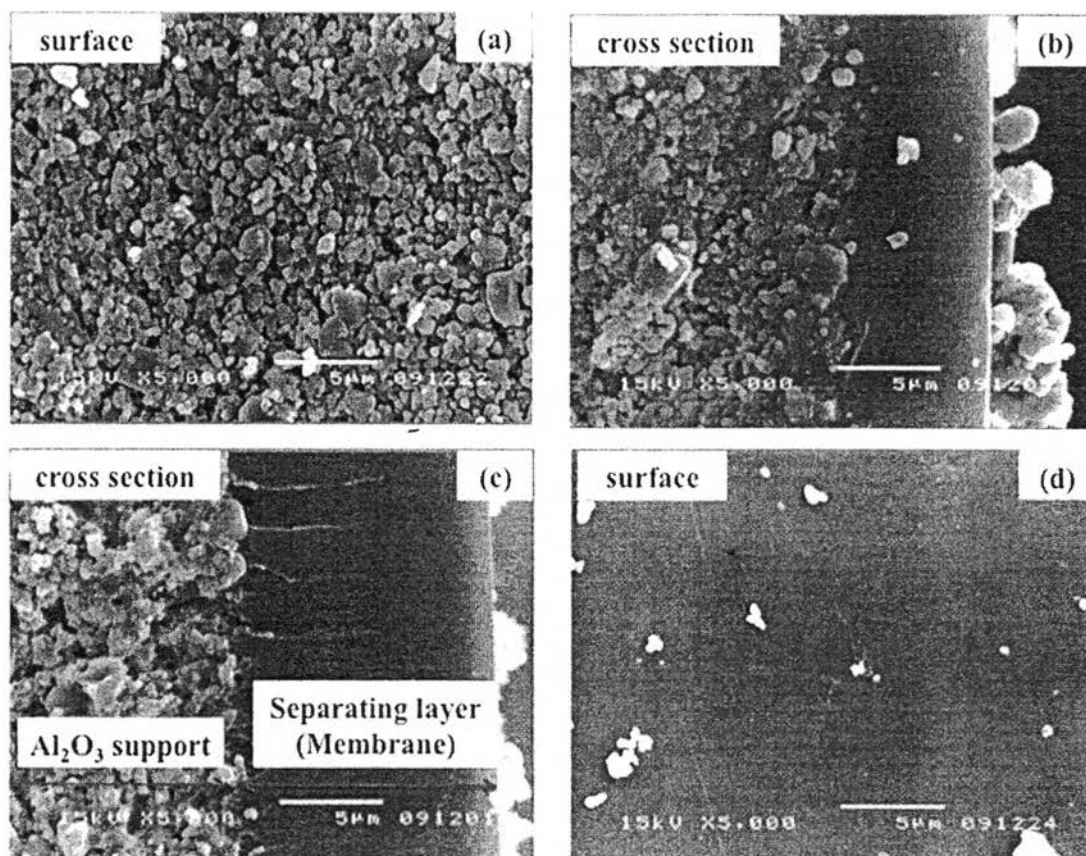


**Figure 4.2** Swelling degrees of the poly(BA-deta) and poly(BA-tepa) membranes in ethanol (a), water (b), and 50:50 ethanol-water mixtures (c) with time.

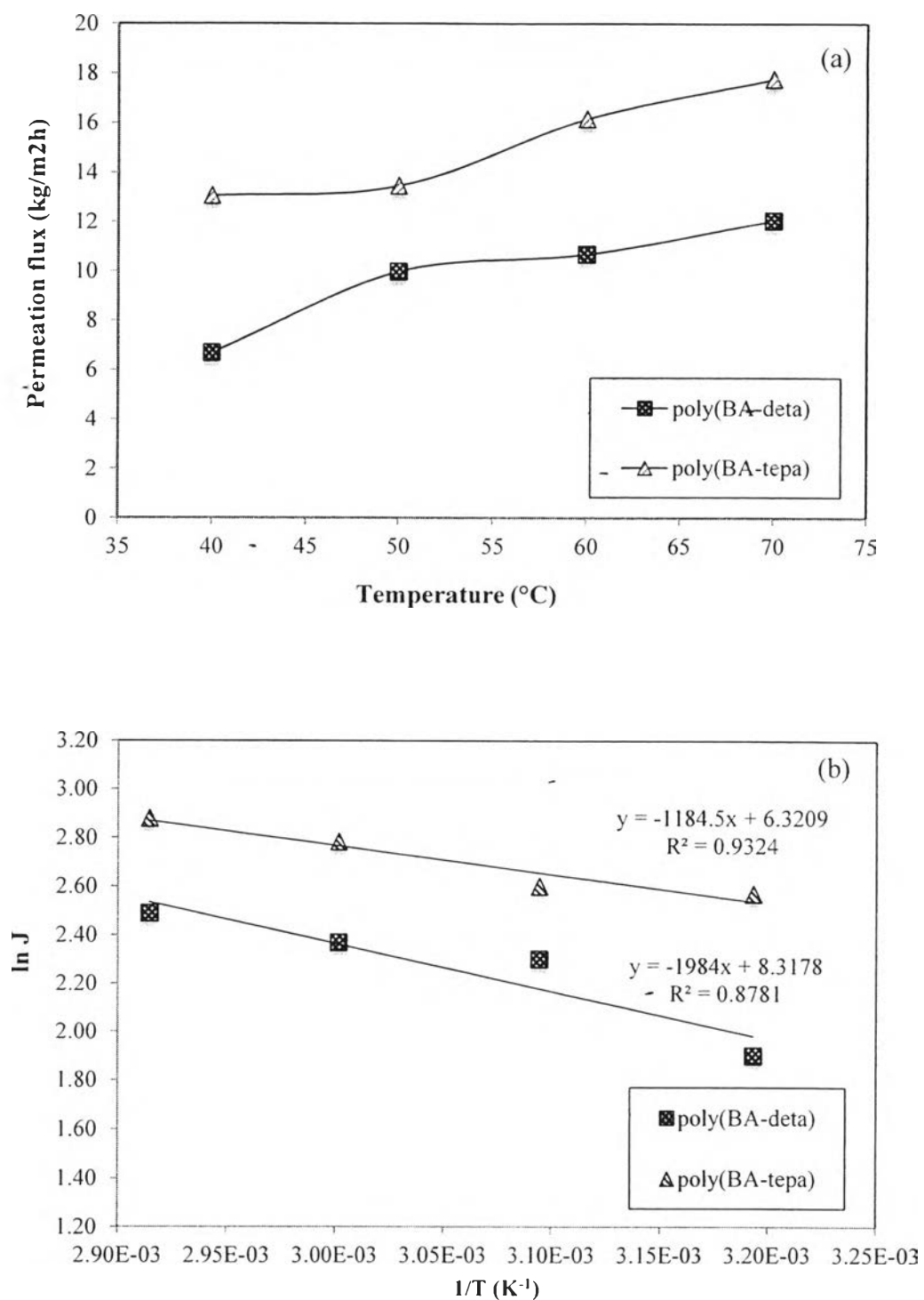


**Figure 4.3** Physical appearances of  $\alpha$ - $\text{Al}_2\text{O}_3$  support tube (a), after dipping into the PBZ solution (b), completely coated PBZ before curing (c), and the cured PBZ membrane (d).

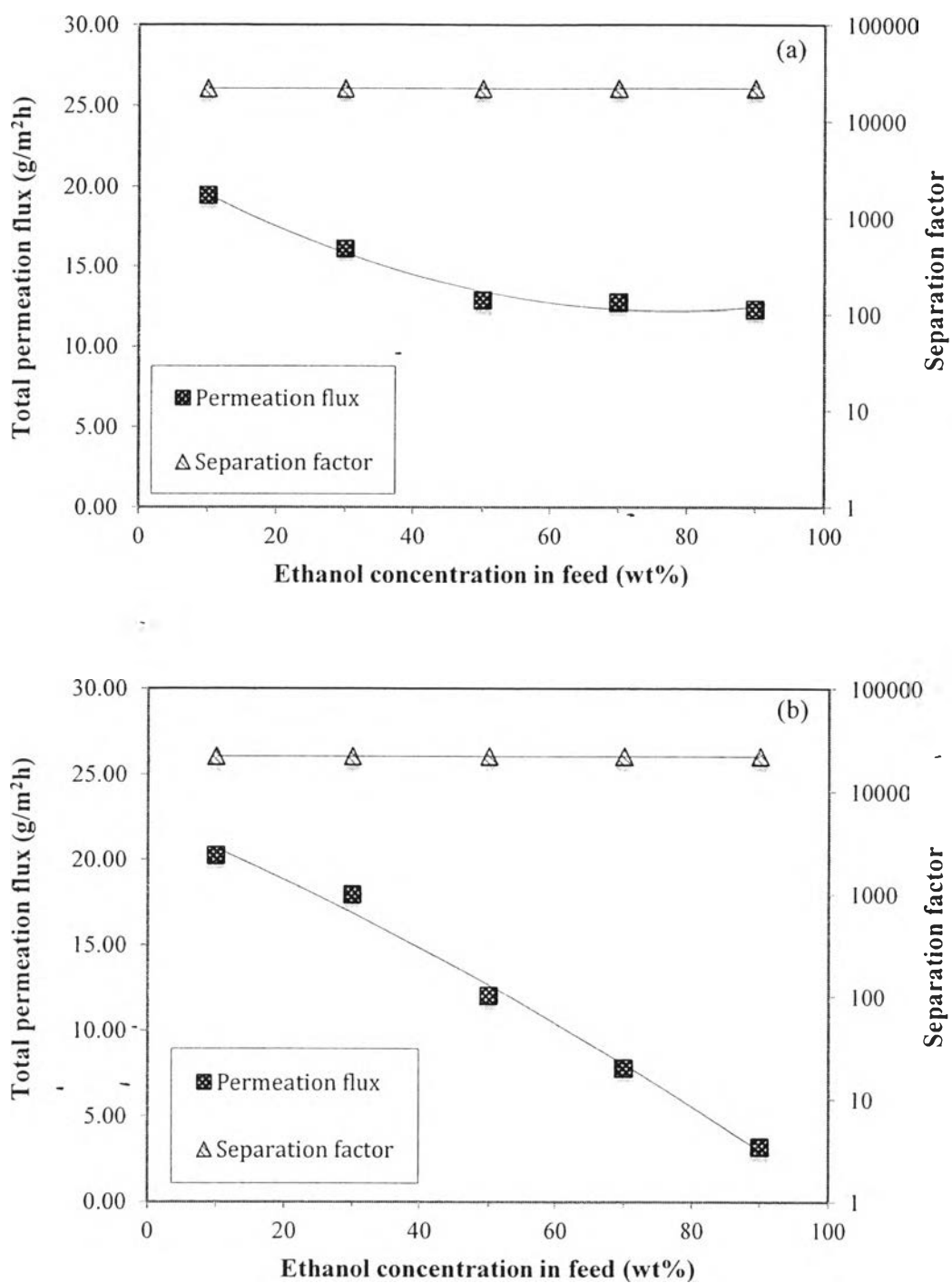




**Figure 4.4** SEM images of  $\alpha$ - $\text{Al}_2\text{O}_3$  support tube (a), and the  $\alpha$ - $\text{Al}_2\text{O}_3$  supporting poly(BA-deta) membrane with 1 dipping cycle (b), 2 dipping cycles (c), and fully crosslinking (d).



**Figure 4.5** Total permeation flux (a), and Arrhenius plot (b) of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supporting poly(BA-deta) and poly(BA-tepa) membranes in the pervaporation process as a function of the feed solution temperature.



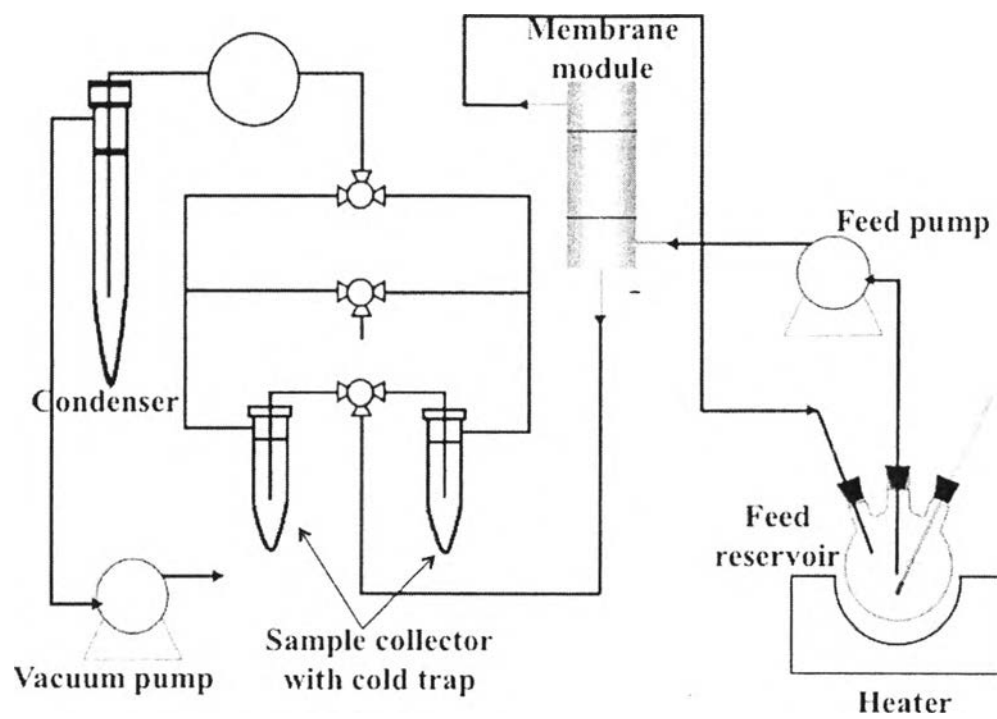
**Figure 4.6** Pervaporation performance of the membranes using various ethanol concentrations in the feed ethanol-water mixtures: (a) poly(BA-deta) and (b) poly(BA-tepa) membranes.

**Table 4.1** Separation factor and total permeation flux of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supporting poly(BA-deta) membranes from various conditions

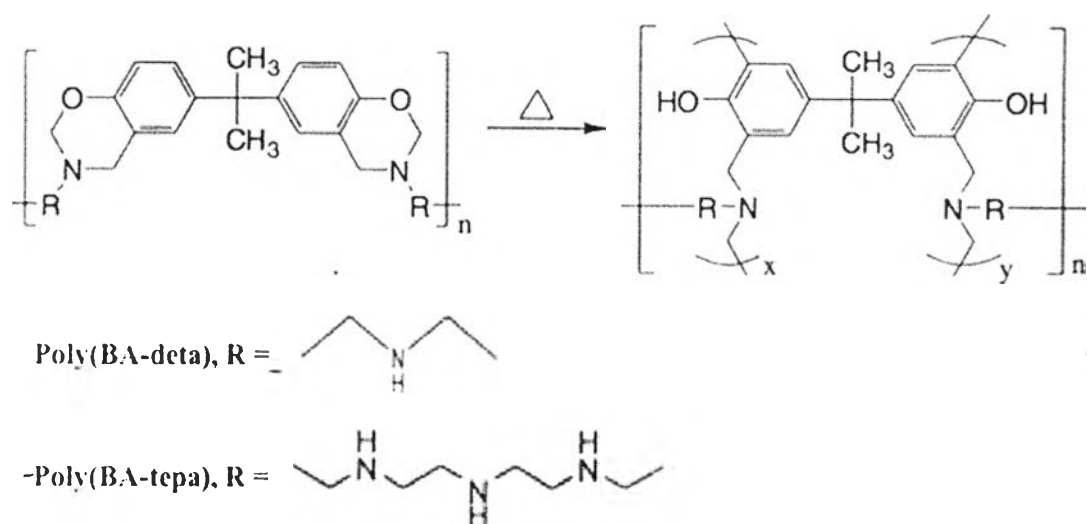
Poly(BA-deta) Concentration (wt%)	Number of dipping cycle	Separatio n factor ( $\alpha$ )	Total permeation flux (g/m <sup>2</sup> h)	Separation layer thickness ( $\mu$ m)
5	> 10	-	-	-
10	> 10	-	-	-
15	> 10	-	-	-
20	8	-	-	-
25	4	> 10,000	14.75	18.56
30	4	> 10,000	14.89	23.34
35	3	> 10,000	15.35	22.78
40	2	> 10,000	17.77	12.40

**Table 4.2** Separation factor and total permeation flux of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supporting poly(BA-tepa) membranes from various conditions

Poly(BA-tepa) Concentration (wt%)	Number of dipping cycle	Separation factor ( $\alpha$ )	Total permeation flux (g/m <sup>2</sup> h)	Separation layer thickness ( $\mu$ m)
5	> 10	-	-	-
10	> 10	-	-	-
15	8	-	-	-
20	5	1,442	13.08	5.12
25	2	> 10,000	25.90	12.34
30	2	> 10,000	7.56	22.56



**Scheme 4.1** Pervaporation apparatus.



**Scheme 4.2** Possible structures of the poly(BA-deta) and poly(BA-tepa) precursors and the cure membranes [4].