



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Literature review

Holly and Cope (1944) discovered the synthesis of aromatic oxazine ring using phenol, formaldehyde, and amines through the Mannich reaction. Burke *et al.* (1965) studied the chemistry of low-molecular-weight benzoxazines while development of the polybenzoxazine was mainly presented by Ning and Ishida (1994). They studied ring-opening reaction mechanism of compounds with bifunctional benzoxazine groups in their molecular structures which form crosslinked structures characteristic of phenolic materials. Polybenzoxazine with high molecular weight was firstly prepared by them, followed by Takeichi *et al.* (2005) who synthesized high molecular weight polybenzoxazine using bisphenol-A, diamine and paraformaldehyde as starting materials and refluxed for 5 h. Agag and Takeichi (2006) found novel high-molecular-weight polybenzoxazine precursors, namely AB-type benzoxazine precursors synthesized from aminophenols and formaldehyde via the reflux process for 6 h. Precursor gave self-standing thin films when the solution was cast in dioxane over glass plate and dried. Allen and Ishida (2006) reported the physical and mechanical properties of flexible polybenzoxazine resins which the flexibility came from linear aliphatic diamine-based benzoxazine monomer. The designing of novel monomers and high molecular weight precursors, which are a promising approach to prepare any type of polybenzoxazines taking advantage of the wide selection of mono- and diamine and also mono- and bisphenols, was studied by Takeichi and Agag (2006). They also reported that polybenzoxazine have not only the advantageous properties of conventional phenolic resins, such as high thermal properties, but also other interesting advantages that are not found in the traditional phenolic resins, such as excellent dimensional stability. Allen and Ishida (2007) investigated reaction times and purification procedures of a series of linear aliphatic diamine-based benzoxazine monomers. Polymerization in dry air at an elevated

pressure allowed oxidative effects consistent with the formation of a substituted benzoquinone structure to negatively influence the polybenzoxazine properties.

Pervaporation, which is one of the most active areas in membrane research for liquid separation, demonstrates incomparable advantages in separating heat-sensitive, close-boiling, and azeotropic mixtures (Fleming H. L., 1990) because of its mild operating conditions, no emission to the environment, and no involvement of additional species into the feed stream. Feng and Huang (1997) studied on pervaporation with the following issues: mass transport in the membrane, membrane material selection, concentration polarization in the boundary layer, pressure build up in hollow fiber membranes, asymmetric and composite membranes, and the activation energy for permeation. In 1998, Hofmann *et al.* investigated molecular modeling of pervaporation separation with polymeric membranes, including poly(dimethyl siloxane) (PDMS), poly(vinyl alcohol) (PVA), and poly(methyl phenyl siloxane) (PMPHS). In the case of PDMS/water-ethanol (90:10%), the technically relevant enrichment of the permeate stream with ethanol was clearly to be anticipated from the interface behavior during the early stages of sorption and absorption of feeding molecules, while for PVA/ethanol-water (90:10%) system the technically utilized depletion of the retentate stream from water molecules was observable. Pervaporation of methanol-water and ethanol-water mixtures through a photopolymerization composite membrane has been investigated by Doguparthi (2001). Polymeric membranes, which were prepared and used in pervaporation experiment, showed good selectivity to water in both methanol-water and ethanol-water mixtures. This composite membrane exhibited good permeation and separation characteristics over the commercial membrane, GFT-PVA, which is a well-known pervaporation membrane for dehydration application. Gonzalez-Velasco *et al.* (2002) also studied pervaporation of ethanol-water mixtures through poly(1-trimethylsilyl-1-propyne) (PTMSP) membranes. The permeability of this material was related to the existence of free volume and to the hydrophobicity of the membrane surface. The separation factor reached a value of 10.7 at 10 wt% of ethanol in feed. Mohammadi *et al.* (2005) investigated separation of ethanol/water mixture through PDMS membrane using the pervaporation process and the total flux for ethanol/water mixture was observed in a range of 0.52 to 0.90 kg/m<sup>2</sup>h at 30 °C as ethanol

concentration changed from 0.3–3 wt%. Huang *et al.* (2009) also reported pervaporation of ethanol aqueous solution by polyphosphazene membranes and found that polyphosphazene with  $-\text{OCH}_2\text{CF}_3$  group had the total selectivity of 6.1 and the total flux of  $0.26 \text{ kg/m}^2\text{h}$ . Jiang L. Y. *et al.* (2009) investigated the progress of molecular design and the evolution of membrane fabrication to tailor polyimides for liquid/liquid and bioalcohols separation via pervaporation process. Polyimides are expensive materials with high production costs thus identify suitable or value-added separations to compensate or justify the use of polyimides for specific separation must be concerned. Pervaporation process for separating ethanol/water was mainly reported by using many types of polymeric membrane which usually serves the separating barrier. Because ethanol is also a significance renewable energy that can be obtained from by-products of chemical and bio-fermentation processes of agriculture products, such as corn, sugar cane, sorghum and potato etc.

Moreover, polymeric membranes are also increasing interest in the field of gas separation application (Stern S. A., 1994). Polymers are accessible in a many array of chemistries so that can be used to suit particular applications. For gas separation, the most attractive polymers are those that provide both high permeability and selectivity. However, polymer usually has been shown in term of “inverse permeability/selectivity as Rovenson (1991) suggestion. This reverse relationship is present a theoretical “upper bound” in the relationship between permeability and selectivity. Accordingly, most of the present researchers have been interested in pushing the polymer performance above the upper bound. Seo Y. *et al.* (2006) suggested a novel concept of a (universal) “organic molecular sieve” by showing that organic polymer molecules at interface between the permeable phase and the impermeable phase play the role of molecular sieves. It is not size selective like an inorganic molecular sieve but the high selectivity was given by the compatibilizer. The compatibilizer works like a molecular sieve to separate one gas molecules from the other.

Gas separation, especially natural gas in the case of removal of  $\text{CO}_2$  gas, is mostly attended by using polymeric membranes due to a number of advantages over other approaches including their low cost, high performance separation, easy of synthesis, as well as mechanical and thermal stability (Scholes C. A. *et al.*, 2009). In

1995, White *et al.* studied the properties of a polyimide gas separation membrane in natural gas stream for CO<sub>2</sub>/CH<sub>4</sub> of up to 55. They found that permeability of gas through the membrane was found to be dependent upon the carbon dioxide concentration in natural gas stream. Zhang *et al.* (1999) also examined polyimide membrane for separating CO<sub>2</sub> from CH<sub>4</sub> at 25 °C and pressure up to 0.25 MPa. Ogawa and Nakano (2000) studied the separation of CO<sub>2</sub>/CH<sub>4</sub> mixture through carbonized membrane prepared by gel modification. The permeation properties of pure CO<sub>2</sub>, pure CH<sub>4</sub>, and CO<sub>2</sub>/CH<sub>4</sub> mixture through the carbonized membranes were measured and analyzed. They found that the micropores of 0.43–0.50 nm played a very important role to create high CO<sub>2</sub>/CH<sub>4</sub> selectivity. In 2002, Xu Z. K. *et al.* investigated a series of pyromellitic dianhydride (PMDA)/oxydianiline (ODA) polyimide (PI) membranes filling with polystyrene (PS) and poly(atyrene-co-4-vinylpyridine) (PSVP)-nanoparticles for gas separation of CO<sub>2</sub> /N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub> /CH<sub>4</sub>. The gas permeability coefficients and selectivity values for PI/PS-nanocomposite membranes decrease with the increase of PS-nanoparticles in the membrane because of the increase in gas diffusion coefficients and the decrease in diffusion selectivities. Modified Matrimid 5218 membranes via chemical cross-linking with *p*-xylenediamine were studied for gas separation by Tin P. S. *et al.* (2003). The gas permeability and selectivity of pure gases He, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, as well as mixed gas of CO<sub>2</sub>/CH<sub>4</sub> were measured. The mixed gas permeability for both CO<sub>2</sub> and CH<sub>4</sub> were lower than their pure gas permeabilities at a respective partial pressure. While the mixed gas selectivity was found to be lower for untreated membranes, but higher for cross-linked membranes, when compared with the ideal selectivity of CO<sub>2</sub>/CH<sub>4</sub>.

Mixed matrix membranes (MMMs), a mixture of polymer and inorganic nanomaterial, present an interesting approach to improve the separation properties of polymeric membranes because they have properties of both organic and inorganic membranes. Pechar *et al.* (2002) reported that mixed matrix membrane (MMM) of a glassy polyimide and modified zeolites (ZSM-2) could be used as a membrane to study the permeability of He, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> gas. Additionally, high silica ZSM-5 membranes were prepared for CO<sub>2</sub> sequestration from methane reforming processes. The permeance of CO<sub>2</sub> was likely due to enhanced surface diffusion

(Bonhomme *et al.* 2003). Sen D. *et al.* (2007) investigated a blend of polycarbonate (PC), an additive of PC/*p*-nitroaniline (pNA), and incorporating zeolite 4A particles as filler, for polymeric gas separation membranes. The incorporation of zeolite 4A and small amounts of pNA into the membrane formation extremely improved the gas separation performance of the PC membranes. In 2008, Ahn J. *et al.* studied on MMMs of polysulfone (PSf), containing embedded nonporous fumed silica nanoparticles for gas separation. The performance, comprising permeability versus selectivity, of PSf/silica MMMs for O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> followed a similar slope to that of the trade-off upper bound with increasing silica content. Mirfendereski *et al.* (2008) discovered that zeolite T membranes were good choices for the separation of CO<sub>2</sub> from CH<sub>4</sub>. They studied effects of synthesis temperature, synthesis time, and feed pressure on CO<sub>2</sub>/CH<sub>4</sub> ideal selectivity and gas permeances.

## 2.2 Characterization

Light scattering is an alternative method to study the polymer solution to determine molecular weight ( $M_w$ ), radius of gyration ( $R_g$ ) and hydrodynamic radius ( $R_h$ ). Shuiqin *et al.* (1995) studied the solution properties of both unfractionated and fractionated poly(N-isopropylamide)(PNIPAM) samples in THF and water at 20 °C using light scattering (LLS) to obtain molecular weight and dynamic LLS to get translational diffusion coefficient distribution (G(D)). They found that both THF and water were fairly good solvents for PNIPAM at 20 °C and PNIPAM chain in both solvents have a flexible coil conformation. Kawaguchi S. *et al.* (1997) studied conformational properties of ethylene glycol, oligo-, and poly(ethylene oxide) ranging in weight-average molecular weight ( $M_w$ ) from 62 to  $1.1 \times 10^7$  by using static light scattering and viscometry in salt-free and 0.45 M K<sub>2</sub>SO<sub>4</sub> water and in benzene. They concluded that PEO in water behaves as a flexible polymer with a relatively large hydrodynamic diameter, compared with that in organic solvents. Static and quasielastic light scattering of poly(ethylene oxide) (PEO) in methanol at 25 °C were investigated by Vandermiers *et al.* (1998).  $M_w$ ,  $R_g$  and  $R_h$  were obtained from Zimm plots and Stokes-Einstein relation. Four PEO fractions had weight

average molecular weights of 31 500, 90 000, 230 000, and 904 000. The angular dependence of Zimm plots showed no downturn at low angle. They also reported that methanol was a good solvent for PEO. In 2001, Kawauchi T. *et al.* studied on dynamic light scattering (DLS) of poly(vinyl chloride) clusters and aggregates in tetrahydrofuran and reported that DLS was a sensitive means in characterizing gel structure and processing history for PVC films. Liu Y. *et al.* (2003) studied the flow-mode static and dynamic laser light scattering (SLS/DLS) of polymer including, polystyrene, polyethylene, polypropylene and poly(dimethylsiloxane) (PDMS), in 1,2,4-trichlorobenzene (TCB) at 150 °C. Vangeyte P. *et al.* (2004) used DLS to confirm the self-assembly of nonionic amphiphilic poly(ethylene oxide)-b-poly( $\epsilon$ -caprolactone) (PEO-b-PCL) and poly(ethylene oxide)-b-poly( $\gamma$ -methyl- $\epsilon$ -caprolactone) (PEO-b-PMCL) in a common organic solvent against water. The particle size increased when the concentration in the organic solvent was decreased. Hsiu-Li *et al.* (2005) studied light scattering and viscoelasticity of poly(vinyl alcohol)-borax aqueous solutions and gels at room temperature, and found that non-perturbing light scattering was a better technique than perturbing nature rheometer for investigating reversible crosslink gels.