



## CHAPTER II

### LITERATURE REVIEW

Flue gases, normally produced by coalbed gas consist of mixtures of methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), nitrogen ( $\text{N}_2$ ), and heavier hydrocarbons ( $>\text{C}_2$ ).  $\text{CO}_2$  and  $\text{CH}_4$  are considered to be crucial greenhouse gases that have a direct impact on the globe's atmosphere. The emission of these greenhouse gases result in not only the increasing of the world temperature and weather disaster but also considers as a hazardous to human health.

To produce high-purity energy products, gas separation technique by membrane is the attractive way since it is low capital investment, simplicity and ease of installation and operation, low maintenance requirements, low weight and space requirements, and high process flexibility.

The membrane material for natural gas separation should possess the following characteristics: (1) inherently high permselectivity for  $\text{CO}_2$  and  $\text{CH}_4$  gas pair and (2) immunity to plasticization induced by  $\text{CO}_2$ . The  $\text{CO}_2$ -induced plasticization usually results in a severe deterioration of membrane separation performance (Li et al., 2007).

#### 2.1 Gas Transport in Membranes

Membrane morphology may determine the transport mechanism and therefore affects the separation performance strongly. The membranes usually have three types of morphologies: dense, asymmetric and composite. Dense membranes are homogenous films of a single polymer layer, whereas the asymmetric membranes consist of a dense top layer supported by a porous sublayer. In composite membranes, both layers may originate from different materials (Şen *et al.*, 2007).

### 2.1.1 Solution–Diffusion Model

Mass transport behaviour through a dense, selective polymeric membrane has been thoroughly investigated experimentally and theoretically in the last 40 years. It is well known that the penetrant transports through a glassy polymer membrane is understood to proceed by a solution–diffusion mechanism, which takes place in three successive steps (Wijmans *et al.*, 1995): (1) the sorption of the penetrant in the polymer film; (2) the diffusion of the penetrant through the polymer film; and (3) the desorption at the opposite interface.

This solution–diffusion model is widely used in the gas separation applications to control the permeation of different species. The chemical potential gradient across the membrane is expressed as a concentration gradient but not a pressure gradient. A quantitative measurement of the amount of mass transported through the polymeric membrane is characterized by the permeability. According to the solution–diffusion model, the permeability is a product of a thermodynamic factor, called the solubility coefficient  $S_i$ , and a kinetic parameter, called the diffusion coefficient  $D_i$ .

$$P_i = [D_i][S_i]. \quad (2.1)$$

The ability of a membrane to separate a gaseous mixtures of  $i$  and  $j$  in a single–stage membrane process may be characterized by the ideal permselectivity,  $\alpha$ , which is defined by:

$$\alpha_{ij} = [P_i]/[P_j], \quad (2.2)$$

where  $P_i$  and  $P_j$  are the permeabilities of pure gases  $i$  and  $j$ , respectively (Ismail *et al.*, 2002). The natural gas stream is available at high pressures of a few megapascals, and can be considered to be primarily methane (CH<sub>4</sub>). CO<sub>2</sub> is a longer, slender molecule; CH<sub>4</sub> is a more compact molecule with a slightly larger cross–section. The subtle differences in the molecular dimensions of the two molecules can be exploited by allowing them to adsorb, and subsequently diffuse across membranes. From a practical point of view, it is advantageous to use a membrane

separation process in which CH<sub>4</sub> is retained on the high pressure side and CO<sub>2</sub> permeates selectively across the membrane (Krishna *et al.*, 2007).

## 2.2 Membrane Materials

### 2.2.1 Polymeric Membranes

Kim *et al.* (2001) prepared pore-filled membranes by using porous polyacrylonitrile membrane as a support and methoxy poly(ethylene glycol) acrylate (MePEGA) as a filler by UV-irradiated photografting. They achieved high CO<sub>2</sub>/N<sub>2</sub> permselectivity (32.5) with very low CO<sub>2</sub> permselectivity ( $5.65 \times 10^{-4}$  Barrer) from this pore-filled membrane at a temperature of 30 °C.

Li *et al.* (1998) fabricated poly(ethylene glycol) (PEG)/cellulose acetate (CA) blended membranes for gas permeation studies. The apparent solubility coefficients of CO<sub>2</sub> were reduced by blending PEG20000 (average molecular weight of 20,000). The blended membranes containing PEG exhibited high apparent CO<sub>2</sub> diffusivity coefficients, resulting in high permeability coefficients for CO<sub>2</sub> when compare with that of the pristine CA membrane. They claimed that the flexible main chain of PEG20000 in the amorphous domains in the blends permitted the large penetrants, CO<sub>2</sub>, and CH<sub>4</sub> to diffuse easily through the blended membranes, leading to higher permeance of CO<sub>2</sub>, and CH<sub>4</sub> relative to that of N<sub>2</sub>. Hence, the CO<sub>2</sub>/CH<sub>4</sub> selectivity decreased by blending of PEG20000 with CA.

### 2.2.2 Mixed Matrix Membranes (MMMs)

Mixed matrix membranes (MMMs) have recently emerged as a promising material for gas separation. They are obtained by embedding a filler material such as carbon or zeolites acting as molecular sieves into a polymer matrix. MMMs are expected to combine the separation properties of polymers with those of fillers to obtain membranes with better separation performances than pure polymeric membranes. A significant effort has been devoted to prepare membranes using zeolites as the filler, due to their size and shape selective properties, and glassy polymers as the polymer matrix, due to their rigidities and higher intrinsic selectivities (Şen *et al.*, 2007).

To extend the industrial applications of membrane separation technology, it is essential to synthesize and develop high-performance membrane materials. Progress has been made in the polymer-zeolite MMMs for natural gas separation, which showed a significant increase in CO<sub>2</sub>/CH<sub>4</sub> selectivity of roughly 44% at 50 wt % zeolite loading compared with that of neat polymer dense film (Li *et al.*, 2006).

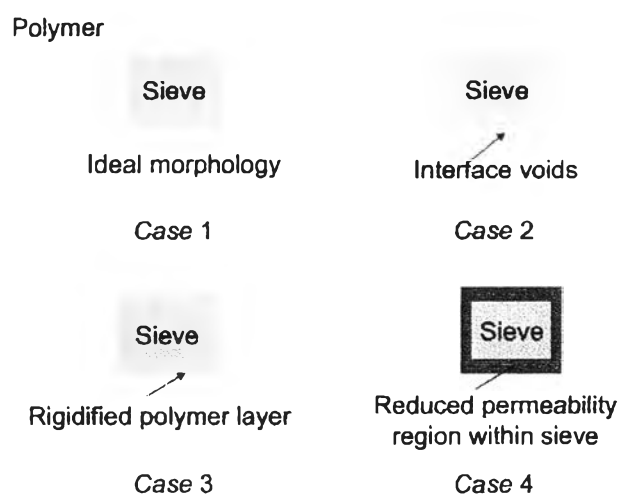
In some work, the zeolites were replaced by the carbon molecular sieves due to the excellent properties of carbon molecular sieve compared to their prices, it is very promising materials in the field of gas separation.

Vu *et al.* (2003) incorporated a carbon molecular sieve (CMS) as the disperse phase in mixed matrix membranes using two different continuous polymer matrices (Matrimid<sup>®</sup> 5218 polyimide and Ultem<sup>®</sup> 1000 polyetherimide). The CMSs were prepared by the pyrolysis of a Matrimid<sup>®</sup> polyimide precursor to the final temperature of 800° C. Mixed matrix membranes containing a high loading of CMS particles (up to 35 wt. %) dispersed within the Matrimid<sup>®</sup> 5218 polyimide and Ultem<sup>®</sup> 1000 polyetherimide polymer matrix prepared by the flat-sheet solution casting method. The results showed that the Matrimid<sup>®</sup>-CMS and Ultem<sup>®</sup>-CMS mixed matrix membranes displayed significant enhancement in CO<sub>2</sub>/CH<sub>4</sub> selectivity, about 45 and 40% respectively compared to the pure polymer.

Anson *et al.* (2004) investigated the performance of various novel mixed matrix membranes for CO<sub>2</sub>/CH<sub>4</sub> separation as a function of carbon loading. Acrylonitrile-butadiene-styrene (ABS) copolymers were used as the polymer matrix and two micro-mesoporous activated carbons (AC) were chosen as inorganic fillers. The results showed that the pure gas permeabilities and CO<sub>2</sub>/CH<sub>4</sub> selectivities of ABS-AC mixed matrix membranes were simultaneously increased with increasing activated carbon loadings in the mixed matrix membrane, compared to that of the intrinsic ABS polymeric membranes.

However, the transport properties of organic/inorganic MMMs are strongly dependent on the nanoscale morphology of the membranes. The morphology of the interface is a significantly important for the overall transport property. Case 1 represents an ideal morphology, corresponding to the ideal Maxwell model prediction. Case 2 shows the detachment of polymer chains from the zeolite

surface, causing the interface voids. Case 3 indicates that the polymer chains in direct contact with the zeolite surface can be rigidified compared to the bulk polymer chains. Case 4 displays a situation in which the surface pores of the zeolites has been partially sealed by the rigidified polymer chains.



**Figure 2.1** The schematic diagram of various nanoscale morphology of the mixed matrix structure.

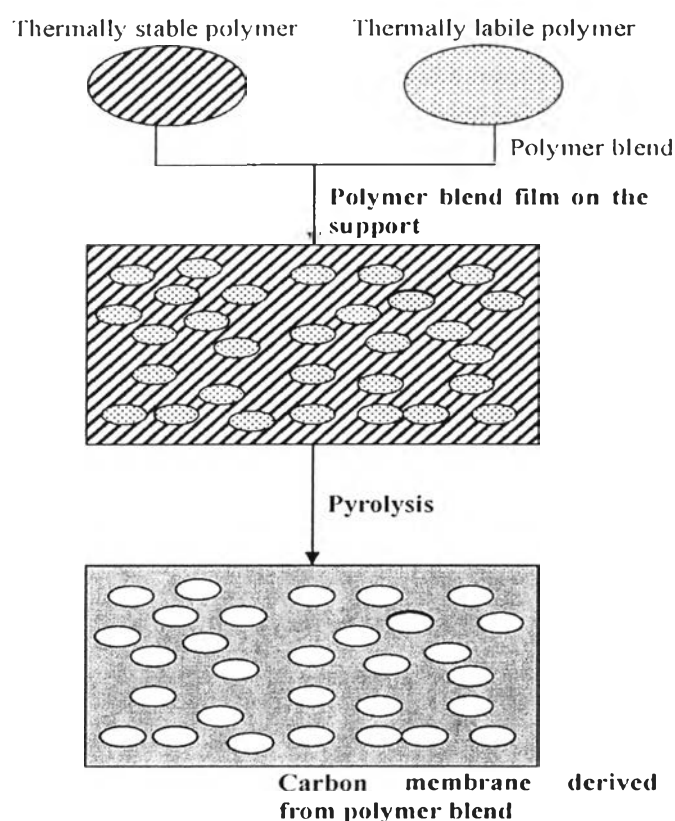
### 2.2.3 Carbon Membrane

In order to avoid the interfacial problem between mixing two phases: molecular sieve and polymeric phases. The membranes for gas separation using neat inorganic membranes, carbon membranes, have been studied.

The carbon membranes have been studied since excellence thermal, chemical stability and well-defined stable pore structure than polymeric membranes (no CO<sub>2</sub>-induced plasticization effects). It is considered to be one of the promising materials for membrane-based gas separation process because of its excellent permeation and separation properties under high pressure and temperature and also the cost of carbon membrane is inexpensive compared to other inorganic materials like zeolite.

Lee *et al.* (2007) prepared the carbon molecular sieving membranes from the polymer blend of polyphenylene oxide (PPO) and polypyrrolidone (PVP) as

thermally stable and labile polymer, respectively. The permeation results for the carbon membranes derived from the polymer blends of PPO/PVP showed that the transport of gas species was affected by the molecular sieving effect and that the permeation performances had a strong dependency upon the pyrolysis temperature and PVP molecular weight. It is considered that the introduction of the thermally labile polymer leads to control the pore structure through the permeation results for the carbon membrane derived from the PPO/PVP and that the permeation performance is affected by the molecular weight and pyrolysis temperature.



**Figure 2.2** Schematic diagram for the preparation of carbon membranes derived from a polymer blend.

In order to expand the source of raw materials and reduce the cost, many alternative materials were used to prepare carbon membranes.

Zhang and *et al.* (2006) studied on asymmetric carbon membrane. It was prepared by coating alcohol solution of novolac phenol–formaldehyde resin containing a little hexamine on a porous resin support from the same material. After

drying in air for two days at room temperature, the coated support was heated at 150 °C for 1 h in air and then carbonized at 800 °C in Ar atmosphere. The support and the membrane layer were carbonized simultaneously. The coating–pyrolysis cycle only needed one time. Pure gases of different molecular size (H<sub>2</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>) were used to test the carbon membrane permeance property. The membrane has a good selectivity for H<sub>2</sub>/N<sub>2</sub> and H<sub>2</sub>/CH<sub>4</sub> with H<sub>2</sub> permeance of  $4.05 \times 10^{-6}$  cm<sup>3</sup>cm<sup>-2</sup>s<sup>-1</sup>cmHg<sup>-1</sup>. The permeance is independent of pressure. The results indicate that the gases transport through the membrane according to molecular sieve mechanism.

#### *2.2.3.1 Advantages of Carbon Membrane Compare with Polymeric Membrane*

1. Carbon membranes display superior permeability and selectivity than polymeric membranes.
2. Carbon membranes are mechanically much stronger and can withstand higher pressure. Carbon membranes have higher elastic modulus and lower breaking elongation than the polymeric membranes.
3. The permeation properties of carbon membranes are hardly affected by the feed pressure because carbon membranes do not possess compaction and swelling problems (no CO<sub>2</sub>-induced plasticization effects). Carbon membranes will not be time dependent.
4. The activation energies required for the diffusion in the carbon membranes are smaller than those in the polymeric membranes. It means that the diffusing gas (especially with large molecule size) is much influenced by the activation energies when it diffuses in the polymeric membranes compared with carbon membranes. Therefore, the selectivity of polymeric membranes decreases remarkably if the measurement temperature increases. This situation will not happen in the carbon membranes.
5. Carbon membranes are much more stable thermally than polymeric membranes. They are suitable to be used in the separation processes with high temperature in the range of 500–900°C. On the other hand, organic polymer

membranes cannot resist very high temperature and begin to decompose or react with certain components.

6. The pore dimension and distribution of the carbon membranes can be finely adjusted by simple thermochemical treatment to meet different separation needs and objectives.

7. Carbon membranes have a superior adsorptivity for some specific gases, which can enhance its gas separation capacity and etc.

#### 2.2.4 Facilitated Transport Membrane

The facilitated transport membrane technique is one of various synthetic methods for natural gas and hydrocarbon separation where the membrane materials are incorporated with such noble metal ions as  $\text{Ag}^+$  or  $\text{Cu}^{2+}$ .  $\text{CO}_2$  and hydrocarbon gases with double bonds can react reversibly with these noble metal ions and form a  $\pi$ -bonded complex, thus obtaining a high separation performance.

Kulprathipanja *et al.* (2007) introduced a novel silver ion-exchange treatment of in order to change the physical and chemical adsorption properties of penetrants in the zeolite. Polyethersulfone (PES)-zeolite NaA mixed matrix membranes (MMMs) and PES-zeolite AgA MMMs were fabricated.  $\text{CO}_2$  permeability of PES-zeolite AgA MMMs is higher than that of PES-zeolite NaA MMMs, whereas their  $\text{CH}_4$  permeability is lower than that of PES-zeolite NaA MMMs. This trend was the result of the reversible reaction between silver ion and  $\text{CO}_2$  molecule.  $\text{CO}_2$  and  $\text{CH}_4$  permeability of PES-zeolite AgA MMMs decreased with increasing zeolite content arising from the effects of partial pore blockage of zeolite and polymer chain rigidification, whereas their  $\text{CO}_2/\text{CH}_4$  selectivity increased with an increase in zeolite loadings and the highest value reaches 59.6 at 50 wt % zeolite loading because of a combined effect of the facilitated transport mechanism of silver ion and the molecular sieving mechanism of zeolite.



### 2.3 Porous Materials

The classification of pores according to size has been discussed for many years, but in the past, the terms “micropore” and “macropore” have been applied in different ways by physical chemists and some other scientist. With an attempt to clarify this situation, the limits of size of the different categories of pores included in Table 3.1 have been proposed by the International Union of Pure and Applied Chemistry (IUPAC) (Isizaki et al.,1988 and Rouqueol et al.,1999). As indicated, the “pore size” is generally specified as the “pore width”, i.e. the available distance the two opposite walls. Obviously, pore size has a precise meaning when the geometrical shape is well defined. Nevertheless, for most purposes, the limiting size is that of the smallest dimension, and this is generally taken to represent the effective pore size. Micropores and mesopores are especially important in the context of adsorption.

**Table 2.1** Definitions about porous solids

Term	Definition
Porous solid	Solid with cavities or channels which are deeper than they are wide
Micropore	Pore of internal width less than 2 nm
Mesopore	Pore of internal width between 2 and 50 nm
Macropore	Pore of internal width greater than 50 nm
Pore size	Pore width (diameter of cylindrical pore or distance between opposite walls of slit)
Pore volume	Volume of pores determined by stated method
Surface area	Extent of total surface area determined by given method under stated conditions

According to the IUPAC classification, porous materials are regularly organized into three categories on a basis of predominant pore size as follows:

- Microporous materials ( pore size  $< 2$  nm) include amorphous silica and inorganic gel to crystalline materials, such as zeolites, aluminophosphates, gallophosphates, and related materials.

- Mesoporous materials ( $2$  nm  $\leq$  pore size  $\leq 50$  nm) include the M41S family (e.g. MCM-41, MCM-48, MCM-50, and etc.) and other non-silica materials synthesized via intercalation of layered materials, such as double hydroxides, metal (titanium, zirconium) phosphates, and clays.

- Macroporous materials (pore size  $> 50$  nm) include glass-related materials, aerogels, and xerogels.

Nowadays, micro- and mesoporous materials are generally called “nanoporous materials”. Particularly, mesoporous materials are remarkably very suitable for catalysis applications, whereas the pores of microporous materials may become easily plugged during catalyst preparation is high loading is sought

## 2.4 Polybenzoxazine

Traditional phenolic resins are widely used in many applications since they possess several desirable properties such as high mechanical strength, dimensional stability, high chemical resistance and flame retardance. However, there are some weak characteristics, for example, they are usually suffer from brittleness. Moreover, acid or base catalysts are often used for the preparation and by-products generally affect the dimensional stability by causing voids in materials.

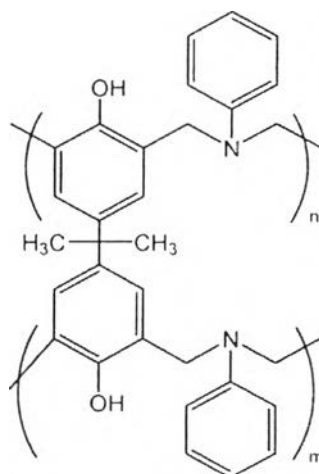
To overcome these problems, a new type of polybenzoxazines, phenolic resin, has been developed. Polybenzoxazines offer great advantages when compared with the traditional phenolic resins. Benzoxazine monomers and oligomers can be prepared from inexpensive materials which are phenols, amine, and formaldehyde, and polymerized without using strong acid or basic catalysts and without releasing any by-products.

Polybenzoxazines provide unique characteristics like near-zero volumetric change upon polymerization and low water absorption. Moreover, the molecular structure of polybenzoxazines offers great design flexibility (Ishida *et al.*, 1995). Therefore, they are widely applied in various fields such as protective

coatings for circuits in television studios and computer chips, airplane bodies, materials for airplane interiors, curing agents for other synthetic resins and varnishes which form films with good resistance to water, alkali and solvents, etc.

In addition, polybenzoxazine have been extensively used as organic precursors of carbon aerogel as they are easily available. In addition, their properties and cost are quite reasonable. Recent research on porous carbon materials prepared from phenolic-based resins by a sol-gel process have been studied. Porous materials, especially porous carbon, have been extensively studied over the past decade and have been used in various applications, such as water purification, gas separation, catalyst supports, electrode material for energy storage devices, adsorbents, molecular sieves, thermal insulation, etc.

In 2009, Lorjai and coworkers prepared carbon foam based polybenzoxazine xerogel derived from bisphenol-A, aniline, and para-formaldehyde. The polybenzoxazine structure was shown in Figure 2.3. The monomer was synthesized via a solventless method invented by Ishida H., (1996). A benzoxazine monomer was synthesized via the solventless process proposed by Ishida et al. Next, the benzoxazine solutions were prepared by using xylene as a solvent. To obtain carbon xerogels, polybenzoxazine xerogels were carbonized up to 800 °C under N<sub>2</sub>.



**Figure 2.3** Polybenzoxazine derived from bisphenol-A, aniline, and formaldehyde.

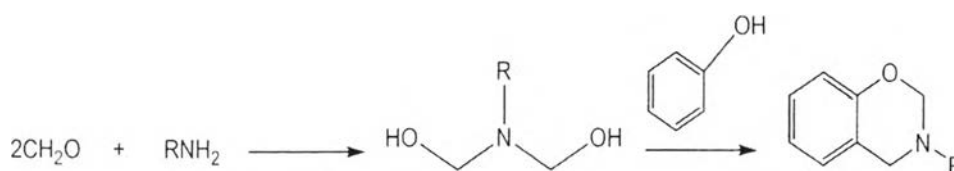
Chaisuwan et al. (2010) prepared the polybenzoxazine aerogel for removing the heavy metals from wastewater. It was synthesized by bisphenol-A, formaldehyde and triethylenetetramine. The DSC thermogram showed the exotherm peak starting at 180 °C with a maximum at 245 °C, attributed to the polybenzoxazine ring-opening polymerization. The polybenzoxazine precursor started to lose weight at 250 °C and the maximum weight loss was observed at between 250 °C and 600 °C. The polybenzoxazine aerogel consisted of different pore sizes ranging from nanopore to macropore size.

#### 2.4.1 Chemical Methodologies for Synthesis of Benzoxazine Monomers

Benzoxazine monomers are typically synthesized using phenol, formaldehyde, and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached (Ghosh *et al.*, 2007).

##### 2.4.1.1 Mono-Functional Benzoxazine Monomers

Holly and Cope (1944) first reported the polycondensation reaction of primary amine with formaldehyde and substituted phenols for the synthesis of well defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two steps. Later, Burke (1949) found that the benzoxazine ring reacted preferentially with free ortho positions of the phenolic compound and formed a Mannich bridge. The procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeded by first adding amine to formaldehyde at lower temperatures to form *N,N*-dihydroxymethylamine derivative, which then reacted with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring (Burke *et al.*, 1965).

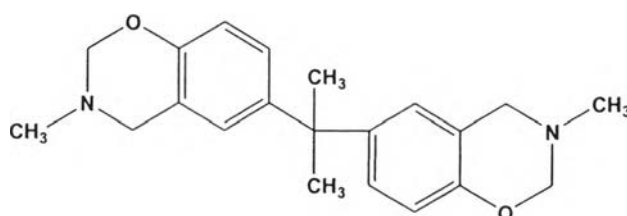


**Figure 2.4** Synthesis of 3,4-dihydro-2H-1,3-benzoxazines (Ghosh *et al.*, 2007).

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors was the disadvantages of Mannich condensation process. The use of an organic solvent also increased the cost of products and created the environmental problems. Furthermore, the solvent residue in the precursors led to problems during processing of the benzoxazine resins (Brunovska *et al.*, 1998). To overcome these shortcomings, Ishida *et al.* (1996) developed a solventless synthesis in a melt state. The reaction mechanism and kinetics of solventless synthesis were proposed by Liu (1995) in order to use this procedure to prepare a large quantity of benzoxazine monomers.

#### 2.4.1.2 Di-Functional and Multifunctional Benzoxazine Monomers

Ishida and coworkers (1994 and 2002) have developed a new class of difunctional and multifunctional benzoxazine monomers and their curing into phenolic materials with the ring opening reaction being initiated by dimers and higher oligomers in the resin composition. The precursor was synthesized using bisphenol-A, formaldehyde and methylamine in different solvents and referred to as B-m, as a reference to two of its original ingredients: bisphenol-A and methylamine. The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol-A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures.

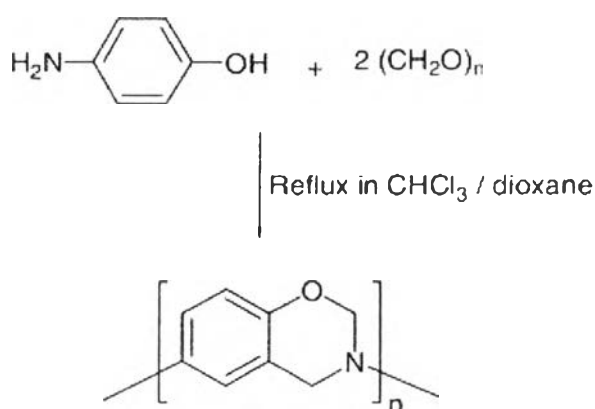


**Figure 2.5** Chemical structure of benzoxazine (B-m) monomer (Ghosh *et al.*, 2007).

### 2.4.2 Preparation of High Molecular Weight Benzoxazine Precursors

High molecular weight polybenzoxazine precursors containing cyclic benzoxazine groups in the backbone were prepared from bisphenol-A, various diamines, and paraformaldehyde. Partially ring-opened structure was observed, but the ratio of the ring-closed structure in the precursor was high enough to be used as benzoxazine precursors (Takeichi *et al.*, 2005). Takeishi *et al.* also found that after the cure of benzoxazine groups, tough film with much improve thermomechanical propertied.

Several methods were applied to prepare high molecular weight benzoxazines, namely AB-type polybenzoxazine prepolymer, based on the reaction of primary amine-containing phenols such as tryamine and *p*-aminophenol with paraformaldehyde (Agag and Takeishi, 2006). Agag and Takeishi (2006) proposed a new approach for a preparation of benzoxazine metrix through high molecular weigh benzoxazine precursors. They used AB-type aminophenol instead of amine and phenol separately and found that the precursors gave self-standing thin films when their solutions were cast in dioxane over glass plates and dried. Then, upon a gradual thermal cure up to 250°C, they afforded polybenzoxazine films. Both viscoelastic analyses and TGA have indicated that the thermosets derived from these novel AB precursors have excellent thermomechanical properties as well as high thermal stability.



**Figure 2.6** Preparation of AB-*p*-aminophenol (AB-PAP) as a benzoxazine prepolymer (Agag and Takeishi, 2006).