CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Polymeric Ligand Exchangers (PLEs)

The concept of polymeric ligand exchange was first introduced by Helfferich *et al.* (1962). The PLEs consist of a supporting polymer with transition metal cation fixed to its uncharged functional groups. Figure 2.1 (Brungryul *et al.*, 2005) shows a conceptualized illustration of the functional group of a PLE. The metal ions are firmly binded with the N atoms on the surface of supporting polymer by covalent bonding.
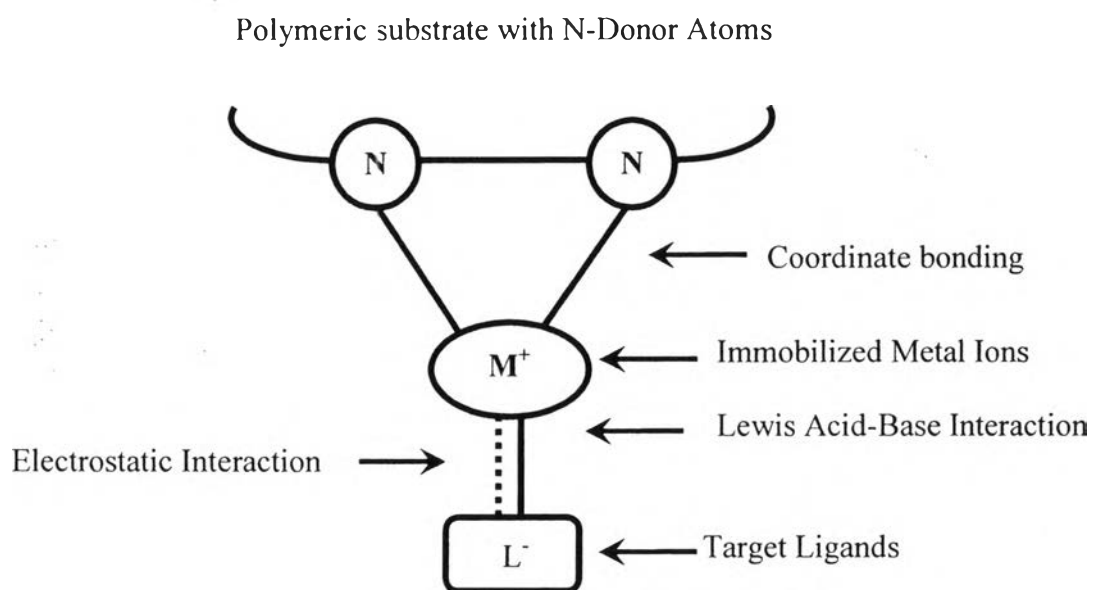
Polymeric substrate with N-Donor Atoms

Figure 2.1 Conceptualized illustration of the functional group of a PLE (Brungryul *et al.*, 2005).

The binding mechanism of PLEs is different from anion exchange, which is the popular method for anion ligands adsorption in wastewater. While the conventional anion exchange technique binds with anions through electrostatic interactions, he PLEs bind with anions via concurrent Lewis acid–base interactions and electrostatic interactions. As a result, the PLEs allow for selective adsorption of ions that are stronger ligands such as phosphate in the presence of weaker ligands.

Helfferich *et al.* (1962) prepared the PLE by loading Cu or Ni onto cation-exchange resins. They found that the PLE could adsorb only ammonia and diamine which are neutral ligands.

The early investigation mostly provided the information on uncharged ligand such as amine and ammonia derivatives (Dobbs *et al.*, 1975; Hernandaz *et al.*, 1972; Groves *et al.*, 1984). However, most of contaminant ligands are anionic ligands, namely, cyanide, selenite, sulfide, acetate, phosphate, oxalate, phthalate and phenolate. The using of polymeric cation ligand exchangers as supporting polymers is unable to absorb any anionic ligands. In 1988, Chanda *et al.* prepared a new PLE by immobilizing ferric ion onto a weak base chelating resin with di (2-picoly) amine groups (known as DOW 3N). Ferric is more desirable than other transition metals because of non-toxicity. But ferric ion is a hard cation and has a poor affinity toward DOW 3N. As a result, the amount of ferric ion loading was low which limits the adsorption capacity of arsenate. Moreover, the loaded ferric ion was almost completely stripped off the supporting polymer during regeneration. The reloading of ferric ion was required after each cycle of operation. To improve the adsorption properties, Zhao *et al.* (1995) prepared a new PLE by using a weak base chelating resin (known as DOW 2N) with 2-picolylamine group as a polymeric substrate and copper as the immobilized ion. Since, the copper ion is a stronger Lewis acid than ferric ion, according to the Irving and Williams order. Bleeding of copper ion from the PLE during the column run and regeneration was very low. Moreover, the copper loaded DOW 2N showed higher phosphate, selenite and oxalate removal capacities compared to others absorbents used in this study.

To accomplish selective removal of phosphate, Zhao *et al.* (1998) further enhanced the understanding of anionic ligand exchange mechanisms. They developed and characterized a PLE by loading copper ions onto the chelating resin (DOW 3N). DOW 3N contains one more (2-picoyl) amine group as shown in Figure 2.2. As a result, the copper capacity for DOW 3N nearly doubles that for DOW 2N (Henry *et al.*, 2004). Nitrogen donor atoms can firmly bind with copper ions in the resin phase. The positive charges and coordination site of immobilized copper still available for interacting with anions in the solutions. The metal uptake capacity is strongly affected by the amount of nitrogen donor atoms.

DOW 3N   DOW 2N

Figure 2.2 Structures of DOW 3N and DOW 2N.

2.2 Removal of Metal Ion from Wastewater

The industrial activity alters the natural flow of materials and introduces novel chemicals into the environment, especially water (Faisal and Hasnain, 2004). Heavy metal ions in wastewater can have harmful effects on the aquatic animals and directly transfer to the human by food chain. Accordingly, the presence of heavy metal ions in wastewater has become a great concern.

Heavy metal ions release to water system from many industrial effluents such as metal plating, tannery, mining, chemical manufacturing, battery manufacturing, etc.(Meena et al., 2005). A number of methods have been proposed toremove heavy metal ions from aqueous solution such as chemical precipitation, adsorption, ion-exchange, membrane separation, reverse osmosis, etc. (Namasivayam and Ranganathan, 1995).

Adsorption has been shown to be a feasible alternative method for removing heavy metals from wastewater because of most simple, economical and efficient technique (Uguzdogan et al., 2008). Several natural and synthetic hydrous solids have been investigated as adsorbent of heavy metals (Sampranpiboon et al.). The adsorbent have many types for treating wastewater such as natural waste, zeolites, limestone and chelating resin as follows.

2.2.1 <u>Removal of Heavy Metals Using Natural Waste</u>

Important problems in the industrial process are minimization of waste maximum generation of waste and energy. Therefore, many researchers have been interested in using ntural waste to treat heavy metals from solutions. Natural wastes which are available in large amount from industries or agricultural operations have advantage as low-cost adsorbent. Masri *et al.* (1974) studied the binding of metal cation by many types of bark. Bark is a by-product of the timber industry. One of advantage is it has high tannin content. The polyhydroxy polyphenol groups in tannin are the active species in the adsorption process. One problem with using bark is discoloration of the water from soluble phenols. Thus, chemical pretreatment of bark has been performed to overcome this problem (Vazquez *et al.*, 1994 and Alves *et al.*, 1993). Another waste product from timber industry is sawdust. In 1975, Sabadell and Krack investigated many wood types for adsorption of Pb, Cd, Cu and Ni. The average capacities for oak sawdust, ash shaving and cedar sawdust are 0.0982 meq/g, 0.0721 meq/g and 0.0683 meq/g, respectively. Further study, Bryant *et al.* (1992) investigated adsorption of Cr(VI) by red fir sawdust. The adsorption capacity for Cr(VI) was 10.1 mg/g. Chitin is another type of waste product from the crab meat canning industry. Chitin can be found in the exoskeletons of crabs and other arthropods and in the cell wall of some fungi (Berkeley, 1997 and Rorrer *et al.*, 1993). Masri *et al.* (1974) compared chitosan to bark, activated sludge, poly(p-aminostyrene) and other materials. Result showed that chitosan had adsorption capacity greater than 1 mmol metal/g for most metals. Moreover, chitosan showed greater adsorption capacity than poly(p-aminostyrene), the ion exchange resin. Kurita *et al.* (1979) showed that the adsorption capacity of chitosan depend on the crystallinity, affinity for water, precent deacetylation and amino group content. 50% deacetylation was the most effective for adsorption. Since, it had high solubility in water, it presented difficulty for practical use. Furthermore, another limitation of chitosan is that it is nonporous (Heisn and Rorrer, 1995).

2.2.2 Removal of Heavy Metals Using Activated carbon

Adsorptive removal of heavy metals in wastewater is usually achieved by using activated carbon or activated alumina (Faust and Aly, 1987). Activated carbon is a porous material with an extremely large surface area and intrinsic adsorption to many chemicals. However, active carbon is only able to remove around 30-40 mg/g of cadmium, zinc, and chromium in water and is nonregenerable, which is quite costly to wastewater treatment (Sun and Shi, 1998).

2.2.3 Removal of Heavy Metals Using Zeolites

Zeolite are silicate minerals, which can be produced synthetically. Leppart (1990) reported that zeolites showed strongly affinity for Pb and other heavy metals. The adsorption capacities for Cd, Cr, Hg, and Pb were 84.3 mg/g, 26.0 mg/g, 150.4mg/g, and 155.4 mg/g, respectively. Further study by Santiago *et al.* (1992) reported the use of zeolites tailored with the organic cations ethylhexadecyldimethylammonium (EHDDMA) and cetylpyridinium (CETYL). Results showed that the CETYL tailoer zeolite performed better than EHDDMA. Adsorption capacity of Cr was 0.65 mg/g zeolite with CETYL and 0.42 mg/g zeolite with EHDDMA. Dalbosco *et al.* (2005) studied the application of natural zeolite in the removal of specific toxic metals from water solutions. The results showed that the equilibrium is best described by a Freundlich isotherm. The K_f constant is related to the adsorption capacity with respect to a specific solute and obeys the order Cr > Mn > Cd > Ni. Highlty charge ions such as chromium (III) tend to have a higher affinity with the cation-exchange site on the zeolite surface than divalent cations. The benefits from using the zeolite as an ion exchange are low cost effectiveness in purifying wastewater.

2.2.4 Removal of Heavy Metals Using Limestone

Applicationof limestone for heavy metals removal has been reported by various researchers. In 1992, Aziz and Smith used limestone particle for removing manganese from water. Lab scale filtration technique was used and the results indicated than Mn solution with concentration 1 mg/L showed a good removal (above 90%). Then, Hamidi *et al.* (2007) studied, influence of limestone particle as a post-treatment method for removing heavy metals (Cd, Pb, Zn, Ni Cu and Cr) at different pH values. The results showed that limestone was capable to remove more than 90% of heavy metals from solution of 2 mg/L.

2.2.5 Removal of Heavy Metals Using Chelating Polymers

Many researchers focused on metal ions removal using chelating polymers because they are easy handling, have high adsorption capacities and high selectivity (Chen *et al.*, 2005). Zhao *et al.* (2002) prepared poly acrylamide-polyacrilic acid copolymer hydrogel (PAM-PAA) by the control hydrolysis of polyacrylamide. They found that the PAM-PAA was selective for the transition metals Cu and Cd over alkali and alkaline earth metals. Another type of chelating resin is allylthiourea. Kilic *et al.* (2005) prepared poly(acrylamide-1-allyl-2-thiourea) by a ^{60}Co γ-radiation source at various radiation dose rates and different compositions of the two monomer mixture namely, acryl amide and 1-allyl-2-thiourea. They found that gold uptake was increased by the present of high amount of 1-allyl-2-allylthiourea in the hydrogels at pH 0.5 about 940 mg/g of hydrogel. Another research, Chaisuwan *et al.* (2010) prepared polybenzoxazine aerogel as a chelating polymer to use for metal removal. The results indicated that the sorption capacity of polybenzoxazine aerogel for metals at 298 K was in the following order: $Sn^{2+} > Cu^{2+} > Fe^{2+} > Pb^{2+} > Ni^{2+} > Cd^{2+} > Cr^{2+}$. Additionally, the amount of metal ions removed depended on the amount of absorbent and sorption time. The maximum adsorption capacity of mixed-metal solutions was lower than that of single-metal solutions for all types of metals at the same conditions. Furthermore, the desorption process 40% of the Sn^{2+} could be optimally recovered when 2% (w/v) NaCl at pH 4 was used, which might be due to the ionic dissociation of NaCl and the amount of protons in acid solutions.

2.3 Benzoxazine

Polybenzoxazines are a new developed type of addition cured phenolic system. These new materials combine the flame retardance and thermal properties of phenolics. They also exhibit the mechanical performance and molecular design flexibility. In addition, they show excellent dimensional stability, low water absorption and good dielectric properties. Hence, polybenzoxazines are an attractive candidate for wide ranges of applications including a matrix of polymer composites, materials used in electronic packaging, etc.

Additionally, these materials exhibit near zero volumetric change upon curing, for some polybenzoxazines glass transition temperature is much higher than curing temperature, high char yield, no catalysts required and also no byproduct during curing.

Polybenzoxazines are formed by the ring-opening of the cyclic monomers only by heat treatment without any catalyst and without generating any by-products (Figure 2.3) (Kiskan *et al.*, 2008).
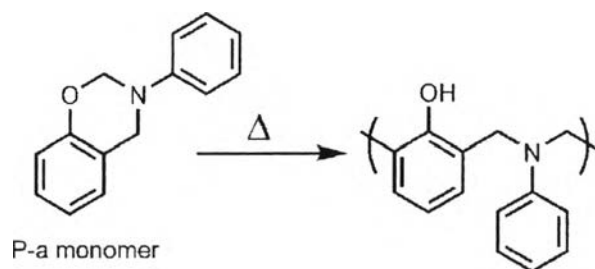

P-a monomer

Figure 2.3 Synthesis of Polybenzoxazines by the ring-opening of the cyclic monomers only by heat treatment.

2.3.1 Chemical Methodologies for Synthesis of Benzoxazine Monomer

Typically, benzoxazine monomers are synthesized by using formaldehyde mono/diphenols and various amine including aniline, allylamine, and aminophenyl propargyl ether, etc.

Holly *et al.* (1944) first reported the synthesis of benzoxazine monomers through the condensation reaction of primary amines with formaldehyde and substituted phenols. This reaction was performed in two-step method using solvent. Later, Burke *et al.* (1949) found the benzoxazine ring is in favor of reacting with the free ortho positions of a phenolic compound and form a Mannich-bridge with phenolic. In 1965, Burke *et al.* synthesized Mannich condensation via a solvent process by first amine was added to formaldehyde at low temperature (10°C) to form an N,N-dihydroxymethylamine derivative product which then reacted with the active hydrogen of the hydroxyl group and ortho position of the phenol at the higher temperature to form the oxazine ring as shown in Figure 2.4.
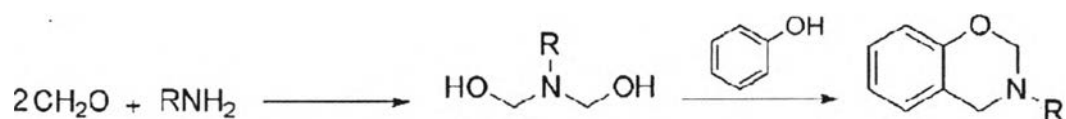

Figure 2.4 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines.

However, the curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with an average molecular weight around 1000 Da. Riess *et al.* (1985) discovered that thigh-molecular weight linear structures and also materials with good performance could not be made from this approach because of the competition between the thermal dissociation of the monomer and chain propagation reaction. Moreover, Hemvichian *et al.* (2002) reported that hydrogen bonding formation resulted in decreasing of reaction. To overcome this limitation, Ishida and coworkers (1994) have developed a new class of difunctional or multifunctional benzoxazine monomers. The precursor was synthesized using bisphenol-A, formaldehyde and metyl amine in many solvents. It was observed that the composition of the products was dependent on the polarity of the solvent and also this synthetic method consisted of a few simple steps and easily use with different phenolic structures with wide flexible design. Ishida *et al.* (1995) synthesized another precursor by using aniline instead of metyl amine and using 1,4-dioxane as a solvent resulting in pure monomer B-a and oligomer oligo-B-a as shown in Figure 2.5. From the investigation of the curing kinetics of this material

pointed out that the curing of benzoxazine precursors was an autocalyzed reaction until vitrification was occurred. This synthesis has slow reaction rate, large amount of solvent required and, in some cases, the poor solubility of the precursors are the major disadvantages associated with the solvent synthesis process. The use of an organic solvent also increases the cost of the products and causes environmental problems. Additionally, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, Ishida *et al.* (1996) developed a solventless synthesis in the melt state.

The reaction mechanism and kinetics of this solventless synthesis were proposed by Kiskan *et al.* (2008). It should be indicated that formaldehyde is not typically used because it evaporates easily causing the stoichiometry imbalanced. Instead, paraformaldehyde was used. The alternative for phenols and amines provided the flexibility in designing monomer structure for tailoring the properties of the polybenzoxazine polymer. The main advantages of the solventless synthetic method were improvement of reaction times and formation of fewer intermediates and by-products as contaminants.
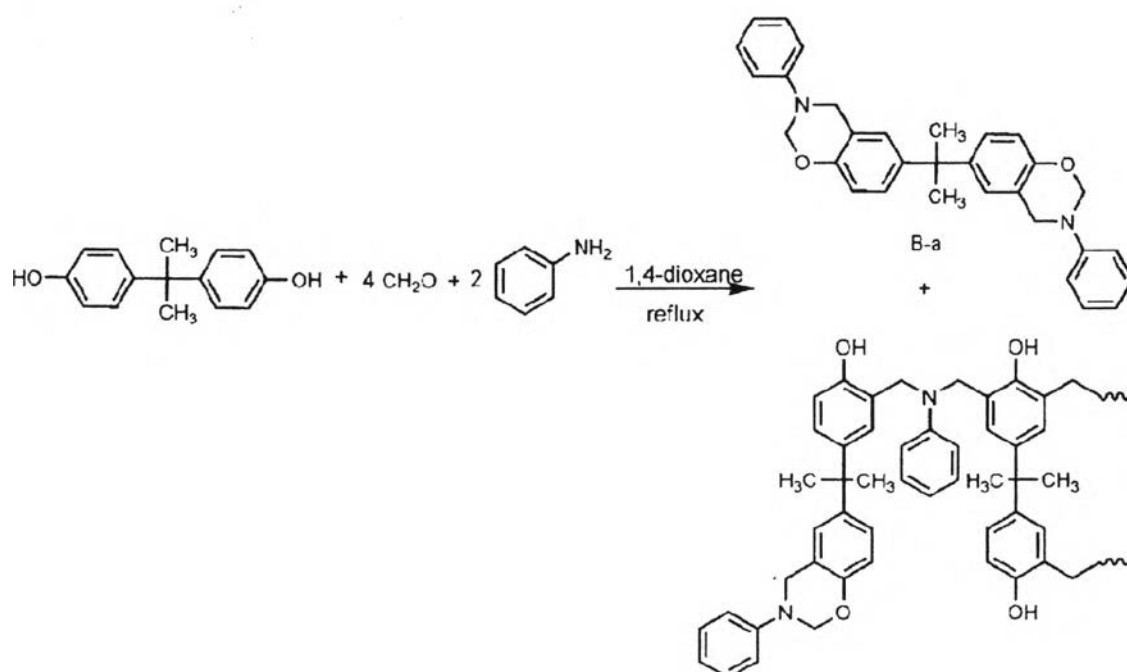

Figure 2.5 Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer.

In brief, various types of benzoxazine monomers can be synthesized using derivative phenols and amines (aliphatic or aromatic) with different substitution as starting materials in the presence of formaldehydes, by employing solution or solventless methods.

More recently, benzoxazines can be polymerized by photoinitiated cationic. These polymers were complex and related to the ring-opening process of the protonated monomer either at the oxygen or nitrogen atoms (Kiskan *et al.*, 2005). The schematic diagram of photopolymerization synthesis is shown in Figure 2.6 (Yagci *et al.*, 2009).
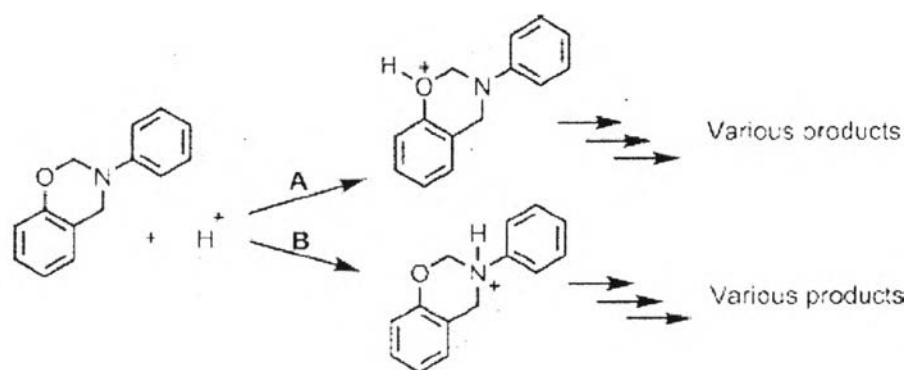

Figure 2.6 Photopolymerization of benzoxazine.

2.3.2 Improvement Properties of Polybenzoxazine

The problems with polybenzoxazine derived from monomers were their brittleness; therefore, they cannot be easily processed into thin films (Takeishi *et al.*, 2005). Low *et al.* (1999) observed that the aminomethyl, -CH$_2$-NR-CH$_2$-, group in polybenzoxazine was the weakest point of the cross-link network structure. Thermal decomposition study of the polybenzoxazines revealed that loss of amine fragment was the cause of low thermal stability.

Aiming for performance enhancement and lowering the polymerization temperature, various approaches have been investigated. One approach was the modification of monomer by introduction of another crosslinkable functional unit which was very effective for thermal properties enhancement (Kim *et al.*, 1999). Another approach, polymer alloys of polybenzoxazine with elastomers or with high performance polymers resulted in high performance and tough films (Ishida *et al.*,

1996). Third approach involving hybridization with inorganic materials such as layered clay (Agag *et al.*, 2000) and metal oxide nanoparticles (Agag *et al.*, 2004) was also successful in obtaining polybenzoxazine with improved properties. In addition, the toughness of crosslinked polybenzoxazine films from high molecular weight monomer was greatly enhanced compared with the cured films from typical low molecular weight monomers (Takeichi *et al.*, 2005).

Another shortcoming was that the crosslinking density of the polybenzoxazine networks was rather low because of intensive hydrogen bonding restricting segmental mobility and hence hindering network extension (Reiss *et al.*, 1997; Ishida *et al.*, 2001). Therefore, increasing the crosslink density of the polybenzoxazine network is expected to improve the thermal and mechanical performance. A common approach can be achieved by copolymerization through the addition of another reactive comonomer through the phenolic group, such as bisoxazoline (Kimura *et al.*, 1999), hydroxyphenylmaleimide (Agag *et al.*, 2001) or epoxy resin (Ishida *et al.*, 1996), However, these systems require higher curing temperatures than neat polybenzoxazine and sometimes the viscosities are increased because of the high melting point of some additives, which hinders the processing. Another approach is adding another polymerizable group into containing specific functionalities such as ethynyl or phenyl ethynyl (Kim *et al.*, 1999), nitrile (Brunovska and Ishida, 1999), propargyl (Agag and Takeichi, 2001), and allyl groups (Agag *et al.*, 2003) into the benzoxazine structure. These monomers give high-performance polybenzoxazines with higher glass transition temperatures (T_g) and improved decomposition temperatures in comparison with typical polybenzoxazines.

Moreover, Ishida and Ohba (2005) synthesized monofunctional benzoxazine with maleimide and aniline to develop low-viscosity benzoxazine monomers with a glass-transition temperature above 200°C. Chaisuwan *et al.* (2006) incorporated of the maleimide functionality into the monofunctional benzoxazine resulted in an increased char yield and glass-transition temperature without significantly increasing the viscosity of the monomer.

2.3.3 Preparation of High Molecular Weight Benzoxazine Precursors

Preparation of high molecular weight benzoxazine precursors would result in gel or insoluble solid because of the ring-opening polymerization of the once-formed cyclic ring. If it is possible to obtain soluble high molecular weight polybenzoxazine precursors, processing into thin films should become very easy, and application into the fields for which the low molecular weight cyclic monomer has not been used will be realized.

High molecular weight polybenzoxazine precursors have been synthesized from aromatic or aliphatic diamine and bisphenol-A with para-formaldehyde (Figure 2.7). The precursor solution was cast on a glass plate, giving transparent and self-standing precursor films, which were cured up to 240°C to give brown transparent polybenzoxazine films. The toughness of the crosslinked polybenzoxazine films from the high-molecular weight precursors was improved when compared with the cured film from the typical low molecular weight monomer. Tensile measurement of the polybenzoxazine films showed that polybenzoxazine from aromatic diamine presented the highest strength and modulus, while polybenzoxazine from longer aliphatic diamine had higher elongation at break. The glass-transition temperature of the polybenzoxazines derived from the high-molecular weight precursors were as high as 238-260°C. Additionally, these novel polybenzoxazine thermosets exhibited excellent thermal stability (Takeichi *et al.*, 2005).
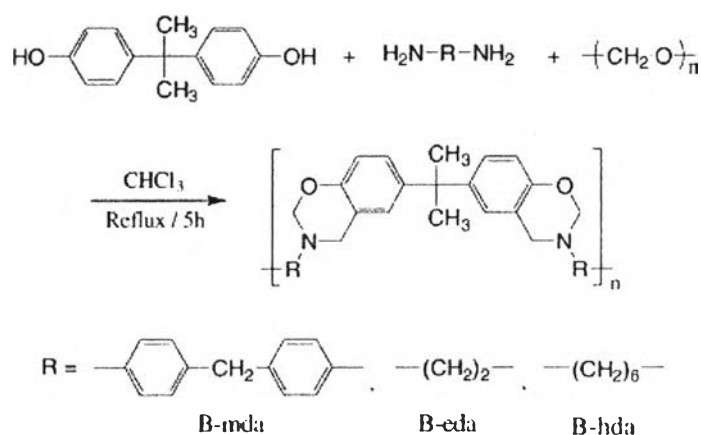

Figure 2.7 Synthesis of polybenzoxazine precursors.

Agag *et al.* (2006) prepared polybenzoxazine matrix through high molecular weight polybenzoxazine precursors. They have used AB-type aminophenols instead of amines and phenols separately (Figure 2.8). The self-standing thin films were obtained from the precursors before curing by casting the precursor solutions onto glass plates. After the thermal treatment of the AB polybenzoxazine precursor films up to 250°C, reddish-brown, transparent polybenzoxazines were achieved. Both viscoelastic analyses and TGA indicated that the thermosets derived from these novel AB precursors had excellent thermomechanical properties as well as high thermal stability. This enhancement in the thermal properties can be attributed to the increase of crosslinking density and hence suggesting that the use of AB precursors is an effective approach for obtaining a novel polybenzoxazine matrix with excellent thermomechanical properties.

$$H_2N-(CH_2)_2-\!\!\!\left\langle\!\!\!\bigcirc\!\!\!\right\rangle\!\!\!-OH \quad + \quad 2\,(CH_2O)_n$$

Reflux in $CHCl_3$

Figure 2.8 Preparation polybenzoxazine matrix by using AB-type aminophenols.

2.4 Poly(ethylene oxide) (PEO)

Poly(ethylene oxide) (PEO) is a non-ionic linear homopolymer of ethylene oxide, which is a polyether compound with many applications from industrial manufacturing to medicine. They have same chemical structure as Polyethylene glycol (PEG) but higher molecular weights. It has also been known polyoxyethylene (POE), depending on its molecular weight, and under the tradename Carbowax.

Poly(ethylene oxide) resins are made commercially by the catalytic polymerization of ethylene oxide in the presence of metallic catalyst systems. Uses of poly(ethylene oxide) include mucoadhesives, water-soluble films, rheology control agents and thickeners, and additives in pharmaceutical products (Dhawan *et al.*, 2006).

Poly(ethylene oxide) (PEO) has been widely used with/without the addition of another polymer. In electrospinning, ultrafine fibers from solutions of natural proteins with poly(ethylene oxide) were electrospun in order to improve their processability because they are very difficult to be processed into fibrous forms alone (Jin *et al.*, 2002 and Xie *et al.*, 2003).

In 2009, Nie and coworker investigated the effect of poly(ethylene oxide) (PEO) with different M_w on the viscosity of sodium alginate (SA) solution and studied physical properties of SA/PEO blended fibers. They found that increasing composition of high molecular weight PEO could improve the electrospinnability of SA aqueous solution. However, increasing composition of low molecular weight had no positive effect on the electrospinnability of SA aqueous solution. This result was explained by SA molecular chains could not form significant entanglements for the electrospinning due to its rigid and extended conformation and cannot form effective chain entanglement. The main contribution of high molecular weight PEO to improve SA electrospinnability is offering entanglement sites and enhancing the chain entanglement network of the blend system. Whereas, low molecular weight PEO the chain interaction with SA only improve the flexibility of SA chains, the chain entanglements of the blend solution is not achieved.

2.5 Electrospinning

Nano-fibres, one of the many achievements of nanotechnology are fibers with diameters that are one or two orders of magnitude smaller than that of the conventional fibers. The nano-fibers produced via electrospinning are attractive for many academic and industrial applications due to their highly porous mesh structure and their large surface to volume ratio, which are being used in filtration, protective clothing, biomedical applications and reinforced composites.

Electrospinning is an efficient, relatively simple and low cost way to produce polymer and composite fibers with diameters ranging from sub-micrometers to nanometers by applying a high voltage to a polymer solution or melt ejected from a micro-syringe pump as shown in Figure 2.9 (Doshi and Reneker, 1995; Reneker and Chun, 1996; Fong *et al.*, 1999). The polymer solution came out of the needle forming a droplet, which was attracted by the electrostatic force to form a cone known as the Taylor cone (Taylor, 1969). The cone was formed because of the surface tension of the polymer solution. As the electrostatic force overcame the surface tension, the solution was ejected in the form of fibers which were dried, electrospun in the air and accumulated at the collector plate.
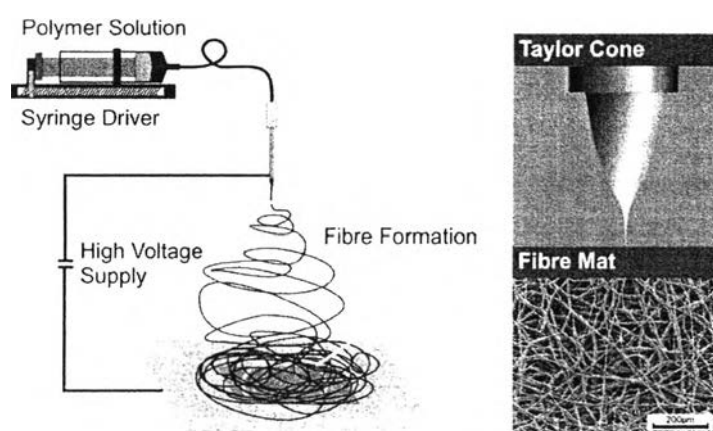

Figure 2.9 A schematic of the electrospinning process.

http://www.nanost.net/?viewthread-11586.html

To date, there are more than one hundred different polymers have been successfully electrospun into nanofibers by this technique. Many parameters can influence the transformation of polymer solutions into nanofibers through electrospinning such as the concentration of polymer solution, the applied voltage, the distance between the tip needle and the target and the needle.

In the case of viscosity was determined by solution concentration, which had an effect on jet behavior. If low concentration leads to not form fibers, the jet broke into the droplets and therefore it is called electrospraying as shown in Figure 2.10.
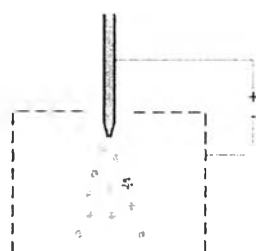

Figure 2.10 A schematic of electrospraying.

http://www.jic.ac.uk/services/metabolomics/topics/lcms/es.htm

In contrast, too high concentration and viscosity related to its cause straightforward transfer of large solution volume by gravity without electrical stretching of the jet (Dietzel *et al.*, 2001).

Koski *et al.* (2003) studied effects of polymer weight average molecular weight (M_W) and solution concentrations on the fiber structure of electrospun poly(vinyl alcohol) (PVA). PVA with molecular weights ranging from 9000 to 186,000 g/mol was dissolved in water. The PVA solution was electrospun at 30 kV, an 18-gauge stainless steel needle and the distance of 102 mm from the needle. The sample obtained on the collector was observed that for each molecular weight, the average fiber diameter was between 250 nm and 2 μm. The fiber diameter increases with M_W and concentration. At low M_W and/or concentrations, the fibers exhibited a circular cross-section. Flat fibers were observed at high M_W and concentrations.

Due to the electrospun fibers often have beads as "by products". In 1999, Fong *et al.* studied the effect of viscous solution on the bead fiber. In their experiments with the solution viscosity of 13-1835 centipoise and the applied voltage at 0.7 kV/cm were used. They recognized that higher viscosity of poly(ethylene oxide) (PEO) solution resulted in fewer beads. Moreover, they added NaCl to 3 % weight fraction PEO solution. Experimental results showed that the addition of NaCl to the PEO solution increased the net charge density, bringing more electric charges to the jet. As the charges carried by the jet increased, higher elongation forces were imposed to the jet under the electrical field, resulting in smaller bead and thinner fiber diameters. This result was agreed with Zong *et al.*, (2002) research, which electrospun biodegradable PLDA polymers.

The applied voltage was one of the important parameters, affected on the shape of the droplet at the needle tip. Li *et al.* (2007) prepared PVA via electrospinning and studied the effects of the concentration of polymer solution, spinning voltage and collecting distance between the tip to target by various concentration of PVA/water solution from 6% to 9% in mass, the applied voltage at 17.5 kV, 20 kV and 22.5 kV, and the distance between the nozzle to target from 26 cm to 38 cm. The results obtained fibers with diameter ranging from 100 nm to 1000 nm and showed that lower concentration tended to facilitate the formation of fibers with beads. With increasing solution concentration, the morphology was changed from beaded fiber to smooth and uniform fiber and the fiber diameter was increased which the same with increasing the spinning voltage. In addition, changing distance between the tip to target had not obvious effect on the morphology of fiber.

However, the work of Li *et al.* showed the changing distance between the tip to target had not obvious effect on the morphology of fiber, it was still the important parameter that has become concerned. Yang *et al.* (2006) found that longer collecting distance resulted in a larger distribution of fiber diameters.

On the other hand, in 2009 Manandhar *et al.* reported on preparation of fibers by electrospinning of levan (a polysaccharide) from distilled water. Electrospinning setup, 18 gauge (1.27 mm) of the needle was used. Three variables were investigated, the syringe pump rate of 2.29 and 3.81 cm3/h, the distance between the needle and the plate of 10 cm, 15 cm and 20 cm and the voltage of 10, 15, 20 kV. With

increasing distance between needle and collector plate, the narrow distribution of fiber diameters was observed. In the case of increasing flow rate, it observed in the decreased of fiber diameters because the Taylor cone was much bigger and gave much finer fibers. The last parameter, the voltage, higher voltage led to smaller diameter due to at low voltages, the electrostatic force was not enough to pull all the fibers to the collector plate and break the Taylor cone on the tip of the needle.

Further investigation in the effects of the diameter of needle, many researches was investigated in this parameter. In 2009, James was the initial investigator and designer of the device first investigated the electrospinning process using the polymer Poly(L-lactide-co-caprolactone) [P(LLA-CL)] in chloroform. He found that decreasing the needle diameter might have decreased the average fiber diameter.

This result was agreed with the work of Hariri and Naguib (2009), they developed novel biodegradable PLGA electrospun scaffolds for bone tissue engineering. He concluded that reduction of the needle diameter effect on reduce the fiber diameter of the electrospun fibers. A larger needle diameter led to a larger amount of polymer present at the cross sectional tip of the needle.