



CHAPTER II

LITERATURE REVIEW

2.1 Removal of Metal Ions from Wastewater

Heavy metal ions in wastewater can have harmful effects on the human. The aquatic animals can absorb metal ions in wastewater and directly enter to the human food chains cause health problems to the consumers. 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). The effluents from these industries need to treat by various type of method before releasing them into water environment.

Conventional technologies are available for removal of heavy metal ions such as chemical precipitation, adsorption, ion-exchange, membrane separation, reverse osmosis etc. (Namasivayam and Ranganathan, 1995).

Among these methods, the adsorption is one of most simple, economical and efficient technique (Uğuzdoğan *et al.*, 2008). This work is focused on the adsorption method. Thus, this work focuses on the adsorption technique. The adsorbent have many types for treating wastewater such as natural waste, zeolites, limestone and chelating resin as follows.

2.1.1 Removal of Heavy Metals Using Natural Waste

Important problems in the industrial process are minimization of waste maximum regeneration of wastes and energy. Therefore, many researchers have been interested in using natural waste to treat heavy metals from solutions. Natural waste 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 cations 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, 1979 and Rorrer *et al.*, 1993). However, the active specie is its deacetylated derivative or chitosan. Chitosan can be produced chemically from chitin. 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, percent 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).

2.1.2 Removal of Heavy Metals Using Zeolites

Zeolites are silicate minerals, which can be produced synthetically. Leppart (1990) reported that zeolites showed strong 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, 150.4 mg/g and 155.4 mg/g, respectively. Further studies 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 tailored zeolite performed better than EHDDMA. Adsorption capacities of Cr were 0.65 mg/g zeolite with CETYL and 0.42 mg/g zeolite with EHDDMA. Dal Bosco *et al.*, (2005) studied the application of natural zeolites 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 sorption capacity with respect to a specific solute and obeys the order Cr > Mn > Cd > Ni.

Highly charged ions such as chromium(III) tend to have a higher affinity with the cation-exchange sites on the zeolite surface than divalent cations. The benefits from using the zeolite as an ion exchange are low cost effectiveness in purifying wastewater.

2.1.3 Removal of Heavy Metals Using Limestone

Application of 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 that 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.

2.1.4 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 polyacrylamide–polyacrylic acid copolymer hydrogel (PAM-PAA) by the controlled 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, acrylamide and 1-allyl-2-thiourea. They found that gold uptake was increased by the presence of high amount of 1-allyl-2-allylthiourea in the hydrogels at pH 0.5 about 940 mg/g of dry hydrogel.

2.2 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 a transition metal cation fixed to its uncharged functional groups. Figure 2.1 shows a conceptualized illustration of the functional group of a PLE. The metal ions are firmly bonded with the N atoms on the surface of supporting polymer by covalent bonding.

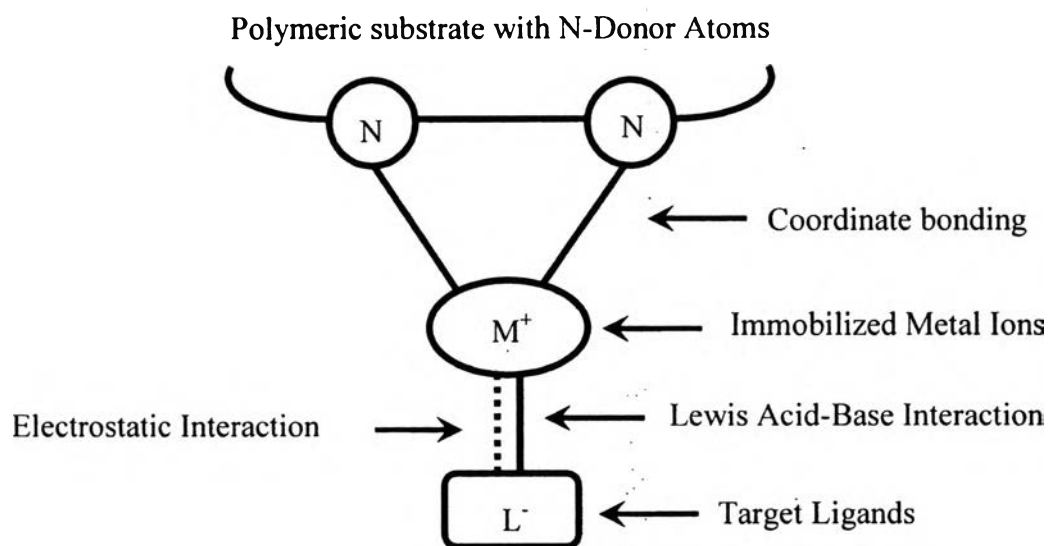


Figure 2.1 Conceptualized illustration of the functional group of a PLE (Byungrylul *et al.*, 2005).

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, the PLEs bind with anions via concurrent Lewis acid-base interactions and electrostatic interactions. As a result, the PLEs allow for a 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 XFS-4195). 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 XFS-4195. 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-picolyamine 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 improve the selectivity of phosphate removal, 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), containing one more (2-picoyl) amine group as shown in Figure 2.2. As a result, the copper capacity of DOW 3N nearly doubles that for DOW 2N (Henry *et al.*, 2004). They claimed that nitrogen donor atoms can firmly bind with copper ions in the resin phase while the positive charges and coordination site of immobilized copper were still available for interacting with anions in the solutions. They conclude that metal uptake capacity is strongly affected by the amount of nitrogen donor atoms.

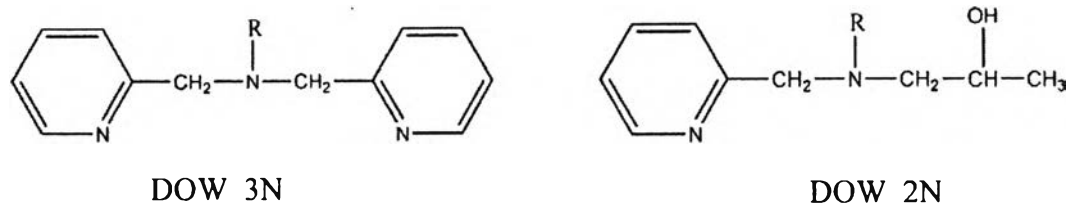


Figure 2.2 Structures of DOW 3N and DOW 2N.

2.3 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.

2.3.1 Synthesis of Benzoxazine Monomers

In general, benzoxazine monomers are synthesized by using phenol, formaldehyde, and amine as raw materials. Either solution or solventless methods can be employed. Various types of benzoxazine monomers have been synthesized by using various phenols and amines with different substituted groups. These substituted groups can provide more polymerizable sites and also affect to the curing process. Thus, polymeric materials with desired properties may be obtained by tailoring the benzoxazine monomer.

Holly *et al.* (1944) first synthesized benzoxazine monomers via the condensation reaction of primary amines with formaldehyde and substituted phenols. The procedure was performed in a solvent in two steps. In 1965, Burke *et al.* synthesized benzoxazine monomers in a solvent proceeded by adding amine to formaldehyde via Mannich condensation. At first, an N,N-dihydroxymethylamine derivative was formed at lower temperatures. Then, the N,N-dihydroxymethylamine derivative reacted with the hydrogen of the hydroxyl group and the hydrogen at the ortho position of the phenol at elevated temperature to form oxazine ring as shown in figure 2.3.

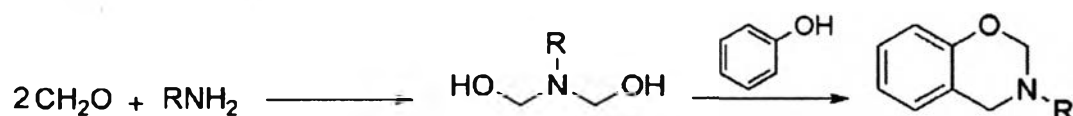


Figure 2.3 Synthesis of 3,4-dihydro-2H-1,3-benzoxazines.

The major disadvantages of this procedure are slow reaction rate, large amount of solvent required and poor solubility of the precursors (Ghosh *et al.*, 2007). To overcome these problems, Ishida *et al.* (US Pat. 5,543,516(1996)) developed a solventless method in the melt state. The mechanism and kinetics of this method were introduced by Liu *et al.* (1995). The reactants, i.e., aldehyde, amine and phenolic precursors are typically mixed together, heated to their melting temperature and kept at a certain temperature to complete the reaction. Formaldehyde is not typically used because it evaporates easily causing stoichiometric imbalance. As a result,

paraformaldehyde is preferably used. The main advantages of solventless method are less reaction time and fewer unwanted intermediates and by-products.

Curing of mono-functional benzoxazines with phenol resulted in oligomeric structures with a molecular weight around 1000 Da. Thus, the thermal dissociation of the monomer could be occurred and competed with the chain propagation reaction; therefore, high-molecular weight benzoxazines were not obtained (Riess *et al.*, 1985). To improve this limitation, Ishida *et al.* (1995) has developed a new class of difunctional or multifunctional benzoxazine monomers, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition. The precursor was synthesized by using bisphenol-A, formaldehyde and aniline in 1,4-dioxane as a solvent. The overall synthetic procedure is shown in figure 2.4. The main product was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol A. This method consists of a few simple steps and can easily provided different phenolic structures with great design flexibility. To determine the processing parameters, the cure kinetics of this material was investigated by using DSC, which indicated that the curing of benzoxazine precursors was an autocatalyzed reaction until vitrification was occurred, and diffusion began to control the curing process. The synthesis of 6,6'-(propane-2,2-diyl)bis(3-phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazine)(B-a) in high yield by the solventless method using 1,3,5 triphenyl(alkyl) hexahydro-1,3,5 triazine, paraformaldehyde and bisphenol A has been reported by Brunovaska *et al.* (1999).

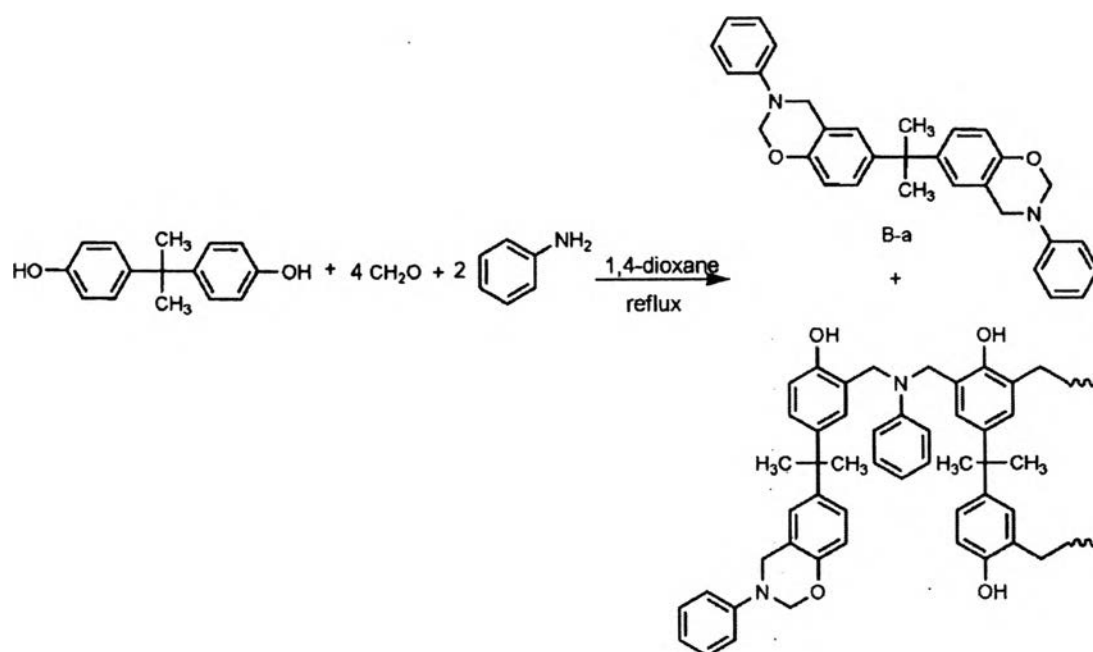


Figure 2.4 Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer.

2.3.2 Thermal Polymerization of Benzoxazines

A cross-linked network structure of polybenzoxazines can be obtained when difunctional or multifunctional benzoxazines undergo polymerization. The polymeric structures form due to curing of monofunctional and difunctional benzoxazines are shown in Figure 2.5 (Agag *et al.*, 2003).

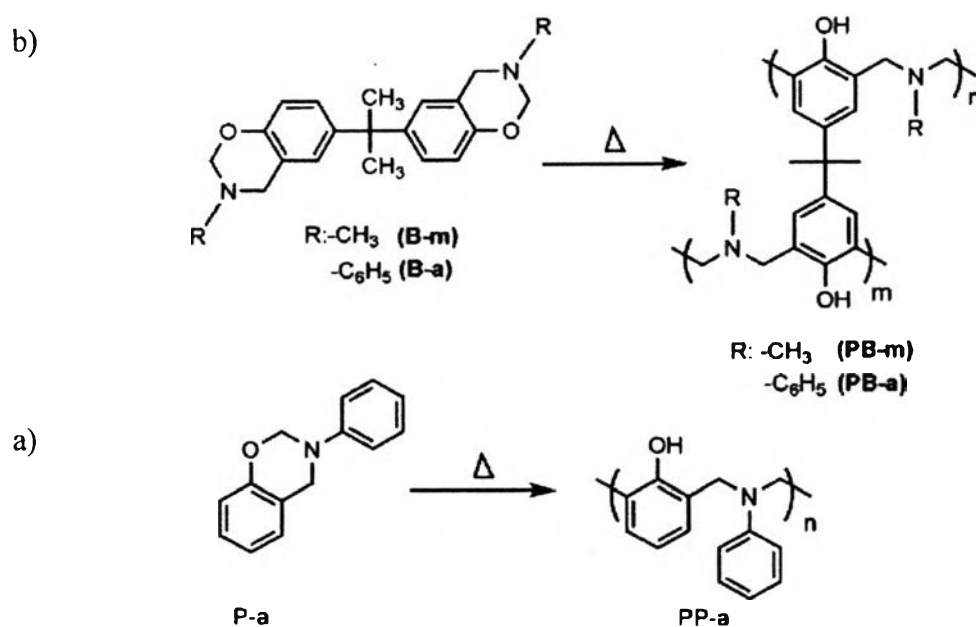


Figure 2.5 Curing of monofunctional (a) and difunctional benzoxazine (b).

It has been proposed that the ring-opening initiation of benzoxazine results in the formation of a carbocation and an iminium ion, which exist in equilibrium (Figure 2.6) (Russell *et al.*, 1998).

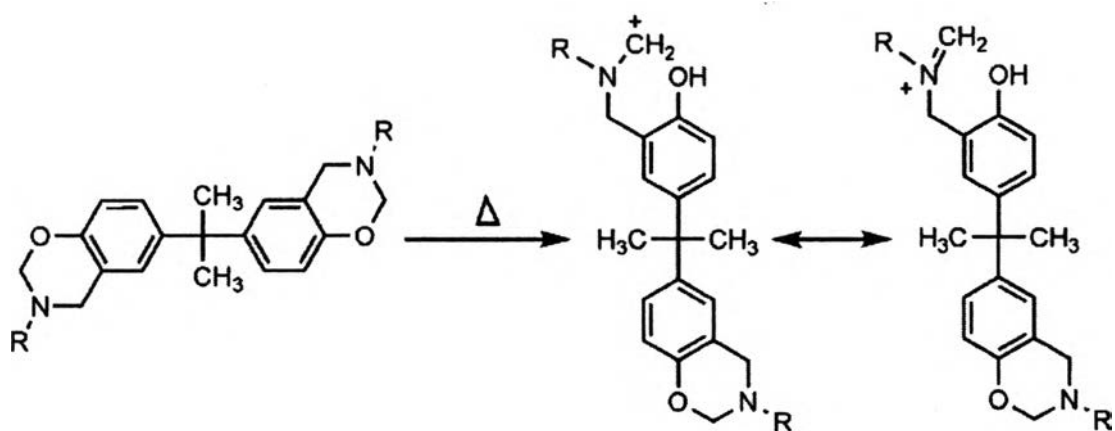


Figure 2.6 Initiation of ring-opening polymerization of benzoxazines.

Polymerization proceeds via the electrophilic substitution by the carbocation to the benzene ring. This transfer occurs preferentially at the free ortho and

para position of the phenol group. The stability of the iminium ion greatly affects the propagation rate because carbocation is responsible for propagation. Furthermore, the reactivity of the equilibrium pair depends on the basicity of the amine group. The more basic the amine, with free electron density of the nitrogen, has the capability to stabilize the more positive charge of the iminium ion. If the iminium ion is more stable, the equilibrium shifts toward it, causing lowering in propagation rate. If the iminium ion is unstable, the equilibrium will be shifted toward the carbocation, resulting in a higher propagation rate (Ghosh *et al.*, 2007).

Curing reactions at two different temperatures, below and above T_g temperature, demonstrate that the kinetics are significantly different for the two curing temperatures. Vitrification occurs sooner at higher curing-temperature than the lower curing temperature, especially below T_g as vitrification causes a large increase in the viscosity of the system as the reaction becomes largely diffusion-controlled, and greatly affect the curing kinetics (Russell *et al.*, 1998). Figure 2.7 shows the thermal polymerization of B-a through the cationic mechanism.

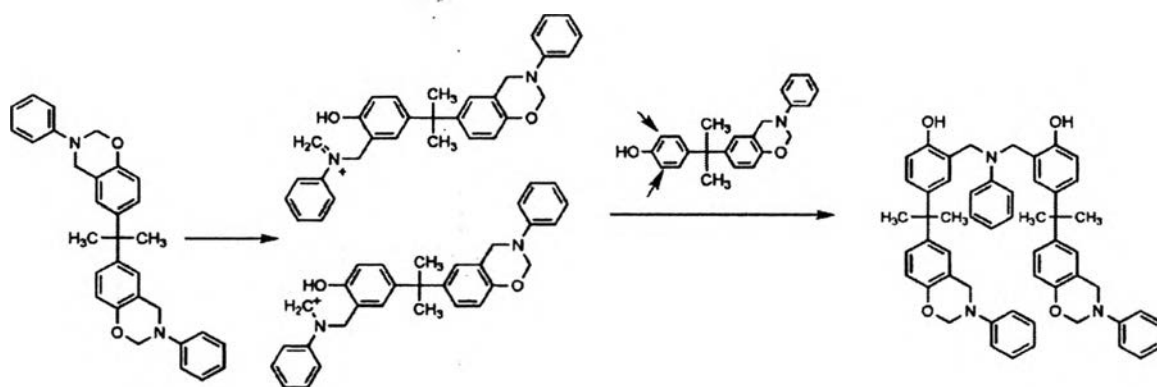


Figure 2.7 Thermal polymerization of B-a through cationic mechanism.