

CHAPTER II

LITERATURE SURVEY

2.1 Phenolic Resin and Polybenzoxazine

Phenolic resin is the first synthetic polymer and widely used as a thermosetting polymer. It is derived from the condensation of phenol and formaldehyde in the presence of acid or alkaline catalyst. The inexpensive phenolic resin has played important role in construction, furniture, electrical and appliance industries owing to its specific chemical and physical properties such as high temperature resistance, flame retardance and electrical insulation. However, it shows some disadvantages, for example; strong acid or basic catalyst is required in the preparation. The weak points of the material are also known as the brittleness, limited shelf-life and volumetric shrinkage owing to the release of water by-product (Knop and Pilato, 1985; Kopf, 1985). To overcome these disadvantages, many types of phenolic resin were proposed.

Recently, Ishida et al. proposed polybenzoxazine as a novel type of phenolic material. Generally, benzoxazine can be synthesized by Mannich reaction from phenol, formaldehyde, and amine that was originally reported by Holly and Cope in 1944. Subsequently, Burke and co-workers (1949) reported that benzoxazine reacts specifically with the ortho position of phenolic compound to form a dimer with methylene-amine-methylene bridge structure. The low molecular weight benzoxazine oligomer was firstly reported by Schreiber (1973). Reiss and co-workers (1985) investigated the polymerization of mono-functional benzoxazines with and without phenol as an

initiator. The linear polymer with molecular weight lower than 4,000 was successfully prepared.

In 1994, Ning and Ishida showed a significant progress of polyfunctional benzoxazines via a thermally initiated ring-opening mechanism to obtain high molecular weight polybenzoxazines which contain both hydroxyl and tertiary amine groups in each chemical repeat unit. Ishida et al. also demonstrated that polybenzoxazine shows excellent mechanical properties which can be applied as a composite material (Ishida, 1995). In another step, Ishida and Allen (1996) investigated the mechanical, physical and rheological properties of polybenzoxazines and their copolymers with epoxy and revealed that these materials have high glass transition temperature, high moduli, low water absorption and good dielectric properties. Polyfunctional benzoxazines are applied as a thermosetting resin, which opened a wide range of advanced applications, including a flame retardant polymer.

Chirachanchai et al. (submitted) found that both benzoxazine monomer and polybenzoxazine can form inclusion compounds with metallic ions.

2.2 Chemistry of Inclusion Compound

A typical feature of inclusion compound or host-guest compound is an accommodation of a complementary guest species into a concave host framework involving the molecular recognition process such as the image of lock and key proposed by Fischer (Figure 2.1).

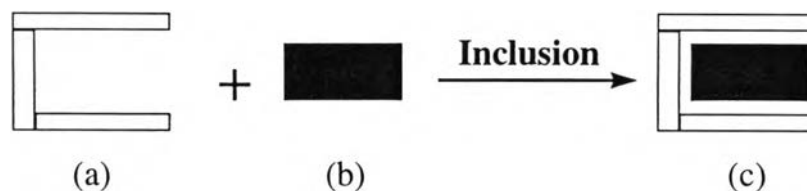


Figure 2.1 Formation of an inclusion compound (a) concave host; (b) convex guest component; (c) host-guest compound.

The best known inclusion compounds are crown-ether, cyclodextrin and calixarene. All have specific cavities on their macrocyclic rings. The structures and properties are different depending on their specific interactions which will lead to various applications.

2.3 Applications of Inclusion Compounds

Inclusion compounds exhibit a wide range of applications. For instance, it can be used in phase-transfer catalysis. Compounds included in a host take solubility properties of the host shell and thus become more soluble when trapped in polar or apolar media, depending on the nature of the host (Dehmlow, 1993). Salt-type reagents (nucleophiles, bases, etc.) including metal ions that are only poorly soluble in organic solvents may be drastically enhanced in their solubility via complexation with crown compounds or cryptands when used in solid-liquid and liquid-liquid (aqueous-organic solvent) phase-transfer catalysis systems. Increased compound solubility occupies an important place in pharmaceutical, cosmetics or food industry (Iwamoto, 1978). A good example is the sweetening agent which precipitates easily by cooling but will no longer precipitate after addition of β -cyclodextrin (Duchene and Wouessidjewe, 1992).

Inclusion compounds may be used for controlling selectivity in synthesis (Diederich, 1983). For example, cyclodextrins and cyclophane hosts can work as molecular reaction vessels via cooperative binding of reactants to perform an accelerated Diels-Alder reaction (Diederich, 1991; Murakami, 1991). Many researches claim channel complexes as a template for stereoregular inclusion polymerizations (Farina, 1984; Miyata, 1992). In addition, photoreaction of an inclusion compound, clathrate, was found to be possible for regio- and stereo-controlled products apart from solution reaction (Toda, 1991).

Furthermore, inclusion compounds can be used for shielding and stabilizing unstable species. Improved stability of included guest molecules lead to protection from environmental factors such as heat, light and oxygen. In the food industry, spices and fruit flavors included and transformed into powder by cyclodextrins exhibit good stability even under heat during industrial food processing (Duchene and Wouessidjewe, 1992). This provide the possibility to use smaller amount of those flavors to last for a longer period. Numerous dyes form stable inclusion complexes with cucurbituril host compound which leads to stabilization of such molecules (Cintas, 1994) and plays an important role in the textile industry (Buschmann et al., 1991).

2.4 Inclusion Compound for Separation and Retrieval Application

Another important field of applications is separation of chemical species that differ in shape and size. Inclusion compound offers good for high technology process on the separation and retrieval; such as separation of aromatic from mixed aromatic and aliphatic compounds, isomers or enantiomers including various types of ions. At present, there is high expectation for polymer resin which can be applied as an ion extraction material.

In 1967, Pedersen discovered cyclic polyethers (a type of crown compounds) and proved as a complex to separate the alkali metal cations. The simple crown compounds are also found to form complexes with ammonium and alkylammonium salt. Sone et al. (1989) reported that acyclic para-substituted phenol-formaldehyde oligomers form host-guest complexes with various organic compounds.

2.5 Inclusion Compound, from Calixarene to Benzoxazine

Calixarenes, the cyclic oligomers obtained by the condensation reaction of *p*-substituted phenols with formaldehyde, are well known to form host-guest complexes with various types of organic molecules and metal cations as reported by Gutsche (1989) and Bohmer (1991). The class name calixarene was chosen due to the characteristic cone- or calix-like conformation, especially of such molecules with four aromatic moieties. The cavities of adequate dimensions allow formation of complexes with certain organic molecules or with cations. Neutral complexes are selectively formed with Na^+ , Ca^{2+} or lanthanide ions when the calix[4]arene is functionalized with one, two or three carboxyl groups. *p*-Sulfonatocalix[5]arene and *p*-sulfonatocalix[6]arene, synthesized by Shinkai et al. (1988), were shown to form a selective, strong complex with the uranyl cation, UO_2^{2+} , in water. Guilbaud et al. (1993) found that calixarene derivatives can bind with neutral or anionic guests or with cations in the pseudo cavity. Furthermore, calix[4]arenes show the selectivity to entrap Li^+ over other alkali cations in acetonitrile, ketone, and ester. Carbonyl-containing calix[4]arenes were reported to selectively bind with Na^+ in methanol and extract Na^+ at water/ CH_2Cl_2 or water/ CHCl_3

interfaces. The amide derivative forms stable complexes with Eu^{3+} , Tb^{3+} and Gd^{3+} chlorides in water or in alcohols.

Moreover, Yamagishi et al. (1996) reported that not only cyclic calixarenes but also linear all-ortho phenolic oligomers, containing an ether chain to form as a pseudocyclic crown ether structure, can extract alkali and alkaline earth metal cations due to the molecular conformation.

The specific structure of the repeating unit of benzoxazine is similar to that of repeating unit of calixarene, which is one of the well-known inclusion compound (Figure 2.2).

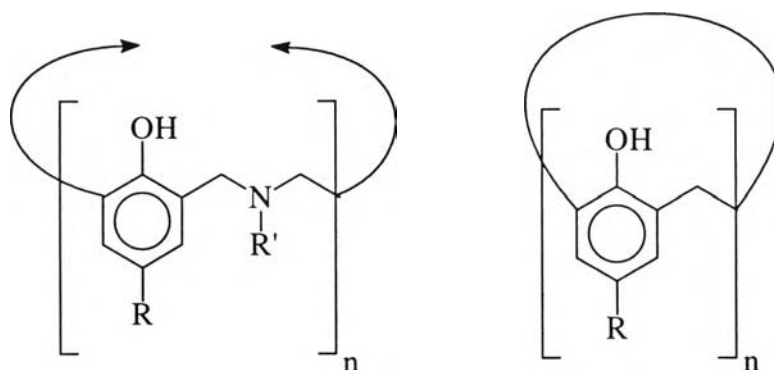


Figure 2.2 Structures of benzoxazine and calixarene.

The local structure of benzoxazine is somewhat similar to that of calixarene. It should be noted that each repeating unit has hydrophilic hydroxyl group on one side while hydrophobic benzene ring on the other, which is similar to calixarene. Here, the oxygen atom of hydroxyl group provides lone pair electrons while the tertiary amine linkage also provides lone pair electrons. Moreover, hydrophobicity of monomer unit can be controlled by varying the functional groups, R and R'. Thus, it is expected that benzoxazine might show inclusion properties as seen in the case of calixarene.

2.6 Benzoxazine as a Novel Type of Inclusion Compound

Chirachanchai et al. demonstrated that benzoxazine oligomer prepared from bisphenol-A, methylamine and formaldehyde showed ion entrapment phenomena. Ion entrapment experiments in various solvents revealed that ion extraction properties of the benzoxazine related to the Flory-Huggins' interaction parameter, χ_{ab} , of the organic solvent and benzoxazine system. The results supported that benzoxazine acts as a host compound for alkali and alkali earth ion guest.

It is also found that the benzoxazine monomer showed the ion extraction property with various types of ions. However, the ion extraction of the oligomer and monomer did not show the selectivity for ion sizes, leading to the conclusion that the inclusion phenomenon is due to a molecular assembly formation. Hence, it is the purpose of this paper to study the role of the benzoxazine structure in ion extraction property.

2.7 Scope of the Present Work

In the present work, benzoxazine monomers are selected in order to verify whether or not the molecular assembly of the benzoxazine acts as a host system. Here, three different functional groups at ortho position of phenol were utilized as a starting material for preparation of benzoxazine monomers. The obtained monomers were applied to study the ion extraction property which could be expected to see the relation between host structure and molecular assembly.