CHAPTER I
INTRODUCTION

1.1 Limitation of Traditional Host-Guest Compound

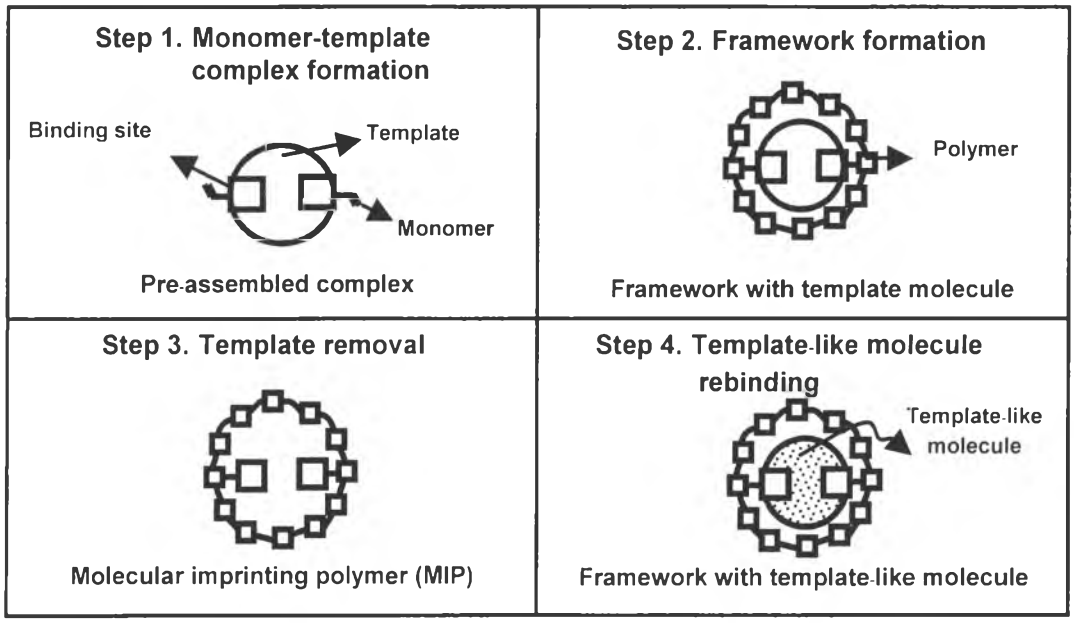
Fine separation is a fundamental process in technologies such as separation of isotopes, isomers, and ions, decontamination of waste water, and other concentration processes. Although ion exchange membranes are widely employed to separate selectively cations from anions and vice versa, the highly selective separation of different ions with the same electrical sign and same charge is still needed. To achieve high efficiency of ion exclusion system, inclusion compound is another approach to be challenged. For the past decades, inclusion compound has received much attention to develop a new compound with the understanding of molecular recognition at the molecular level.

Generally, host molecules are obtained by a molecule which consists of a cavity having a specific structure to respond guest with an effective binding site in a definite three dimensional spatial arrangement. Various ring compounds, such as, crown ether, cyclodextrin, crytrates, and calixarenes are some of those examples. However, in practical applications, inclusion compounds show some limitations, such as the stability of the compounds, high cost for preparations, and ineffective reuse procedures. Immobilization of host compound onto polymer chain has been introduced in recent years to solve the problem. Molecular imprinting is another alternative way to utilize the advantages of inclusion compound. By simply imprinting the target molecules onto polymer during polymerization, it is expected that the polymer chain will imprint the target molecules among the chain. The removing of target molecules will provide a guest cavity, while at the same time the polymer chain can act as a host. Molecular imprinting process is, therefore, considered to solve the problems in terms of simple preparation process, low cost, and effective reuse, although the high selectivity has to be sacrified.

1.2 Molecular Imprinting Polymer

Molecular imprinting is a technique to assign a specific size and structure of a particular chemical species (either molecules or ions) onto polymeric chain. Generally, the chemical species imprinted are so-called template while the polymer network obtained is molecular imprinting polymer. The strategies to imprint template into polymer network can either be non-covalent interaction or covalent bond between template and polymer. Meanwhile, the preassembled structure of template and monomer is an essential step to obtain a molecular assembly required for construction of imprinting network.

Scheme I

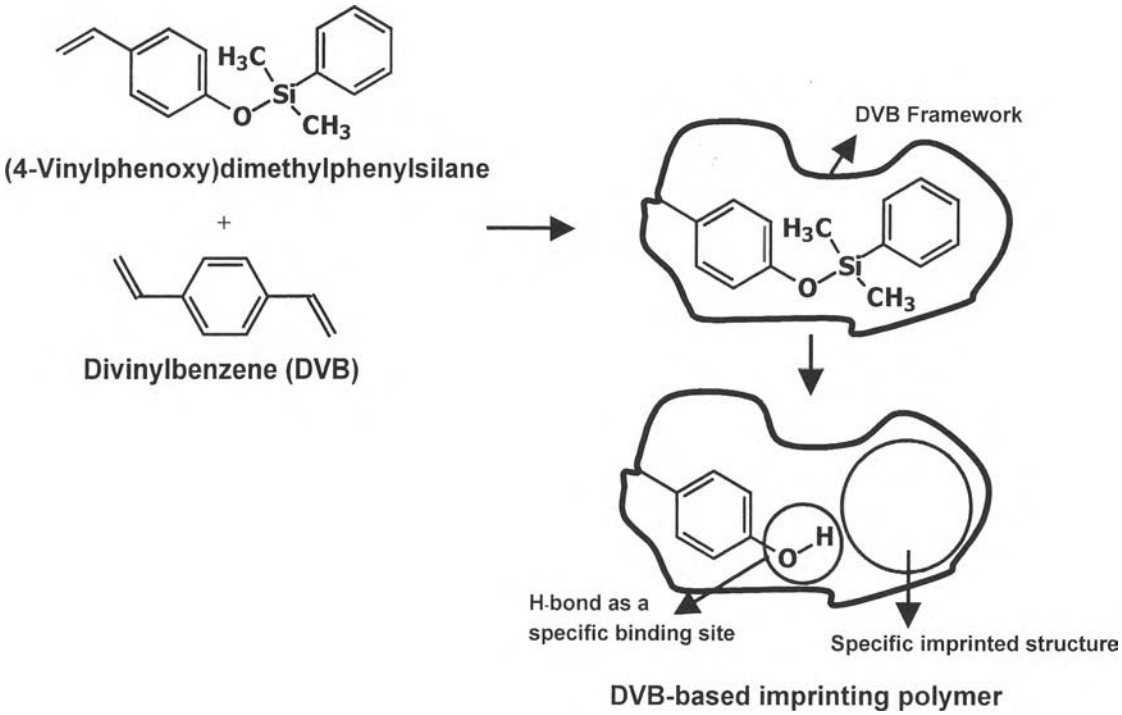


Molecular imprinting process consists of 4 steps as shown in Scheme I. In the first step, monomer, which has functional group as the binding site, forms an assembly via the binding site of template molecule using covalent or non-covalent bond to obtain preassembled complex molecule. As the polymerization proceeds, the template occupies the specific shape and size on the polymer network (Step 2). As a result, the polymer network with template molecule can be obtained. Theoretically, when the template is removed from the network (Step 3), the template imprinted will

leave a space where a selective rebinding for the specific chemical species is possible. With simple procedures but precise molecular design, imprinting polymers are highly attractive for use in applications where molecular recognition phenomena are of importance, including affinity separation, analytical chemistry (especially solid-phase extraction), sensor, and catalysis.

Recently, Kirsch et al. (2000) proposed the MIP of divinylbenzene (DVB) polymer based on phenolic group acting as a binding site for small nitrogen heterocycles, such as, pyridine and quinoline (Scheme II). MIP network with DVB provided selectivity for the templates, through hydrogen bond and the definite three dimensional structure space.

Scheme II

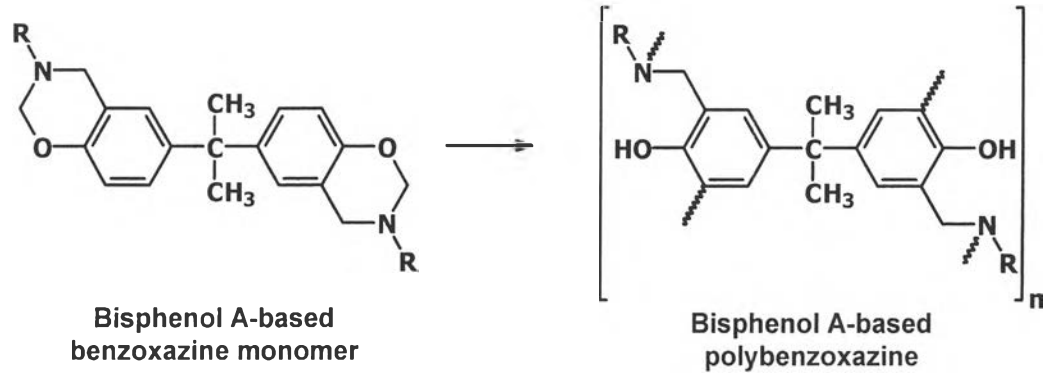


1.3 Polybenzoxazines network

Polybenzoxazine has received much interest when Ishida et al. (1994) demonstrated it as a novel phenolic resin from bisphenol A-based benzoxazine monomer (Scheme III). The key of the success in polymerizing bisphenol A-based benzoxazines can be referred to the crosslink structure generated from the two benzoxazine groups belonging to a single bisphenol ring. By varying the type of

bisphenols and biphenols, tremendous molecular designs flexibility can be achieved. Polybenzoxazines and their derivatives are superb in terms of the unique chemical and physical properties, such as no catalyst required in polymerization, near-zero shrinkage, high glass transition temperatures, high moduli, low water adsorption, good dielectric properties, and high mechanical properties.

Scheme III



Bisphenol A-based benzoxazine monomer

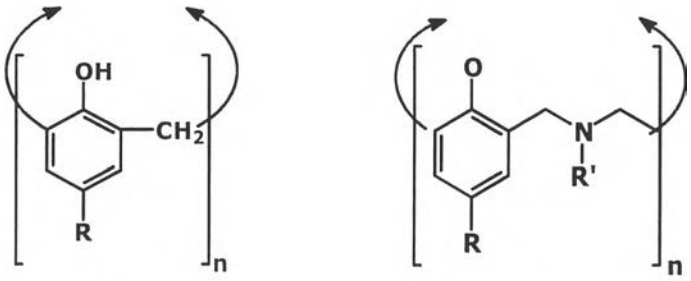
Bisphenol A-based polybenzoxazine

1.4 Polybenzoxazines: A Potential MIP

Recently, Laobuthee et al. (2001) clarified that ring opening of *p*-substituted benzoxazine provides a stable dimer with a stoichiometric reaction ratio of phenol to generate benzoxazine dimer. The reaction of benzoxazine dimer is unique, for example it gives asymmetric mono-oxazine compound, while in etherification and esterification it gives the symmetric structure of diester or diether depended on the reaction conditions. However, when we consider the structure of the open ring benzoxazine, it is interesting to note that the repeat unit of the open ring benzoxazine resembles to that of calixarenes (Scheme IV), which is possible to lead to a molecular assembly and act as a host molecule.

Siripattanasarakit (1997) reported the inclusion phenomena of bisphenol A-based oligobenzoxazine. The ion interaction ability is dependent on the polarity of the solvent and the oligomer concentration. Although the structure of oligobenzoxazine and metal ion interaction was not yet clarified, it should be noted that pseudocyclic oligobenzoxazine might have formed and entrapped ion as seen in the case reported by Yamagishi et al. (1996).

Scheme IV



(a) Calixarenes (b) Oligobenzoxazines

In the related work, Phongtamrug (1998) reported that not only bisphenol A-based oligobenzoxazine but also monophenol-based benzoxazine performed the metal ion interaction. The variation of the structures through molecular design has been carried out by Techakamolsuk(1999), Pacharaprakiti (2000), and Laobuthee (2001) for the past few years. In the meantime, Chirachanchai et al. (1999) demonstrated the stable structure of *p*-substituted benzoxazine dimer by single crystallography to find the hydrogen bonding network along molecules. The result was strongly supported by Speiss et al. (1998) when the structural analysis was done by 2D solid state NMR. This might be a key factor for being molecular assembly with metal ion interaction property.

It is one of the approaches to develop molecular recognition in the macromolecular scale of polybenzoxazines by using the molecular imprinting pathway. Thus, the present work stands on the viewpoint of combining the concept of supramolecular chemistry with the molecular design of polybenzoxazines to obtain a molecular imprinting network.

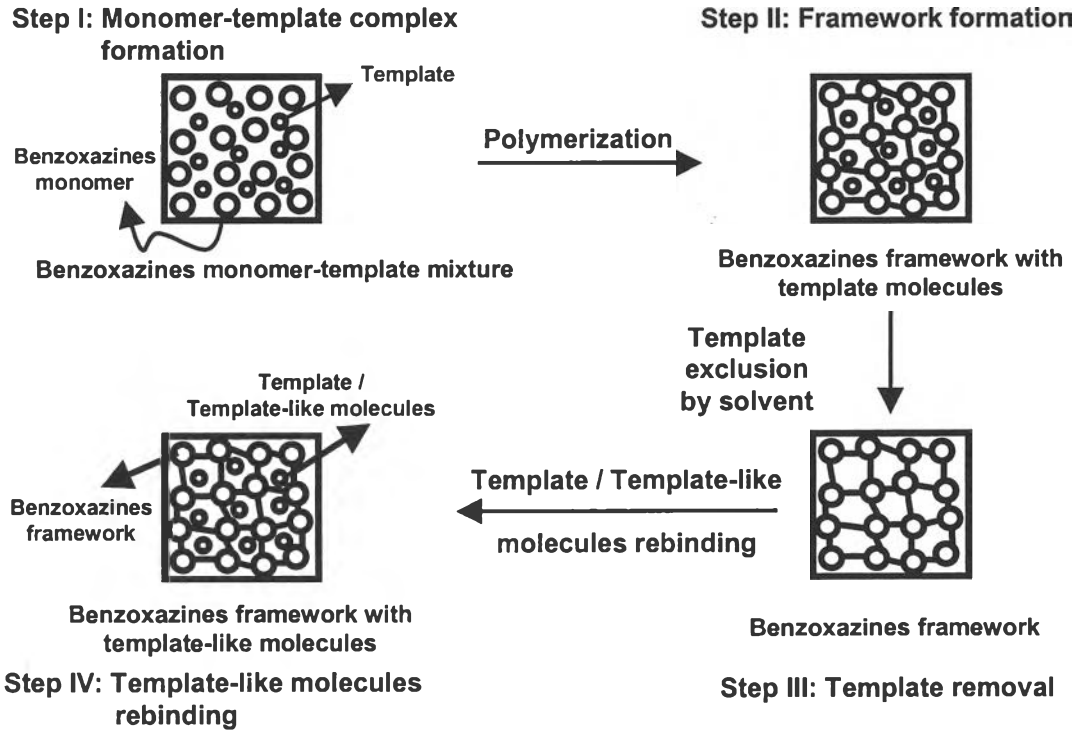
1.5 Scope of the Present Work

The present work is focused on the preparation of polybenzoxazines as molecular imprinting polymer by ring opening reaction of bifunctional benzoxazine monomer. The simple strategy to obtain the molecular imprinting polymer from the reaction of the mixture of benzoxazine monomers and template molecules is originally proposed. Through this approach, it is expected that the structure of polybenzoxazines will be controlled by the template molecules during the

polymerization. As a result, polybenzoxazines will perform the molecular recognition with template or template-like species to be a novel imprinting polymer. The present work, thus, consists of two chapters with different strategies to obtain MIP of polybenzoxazines.

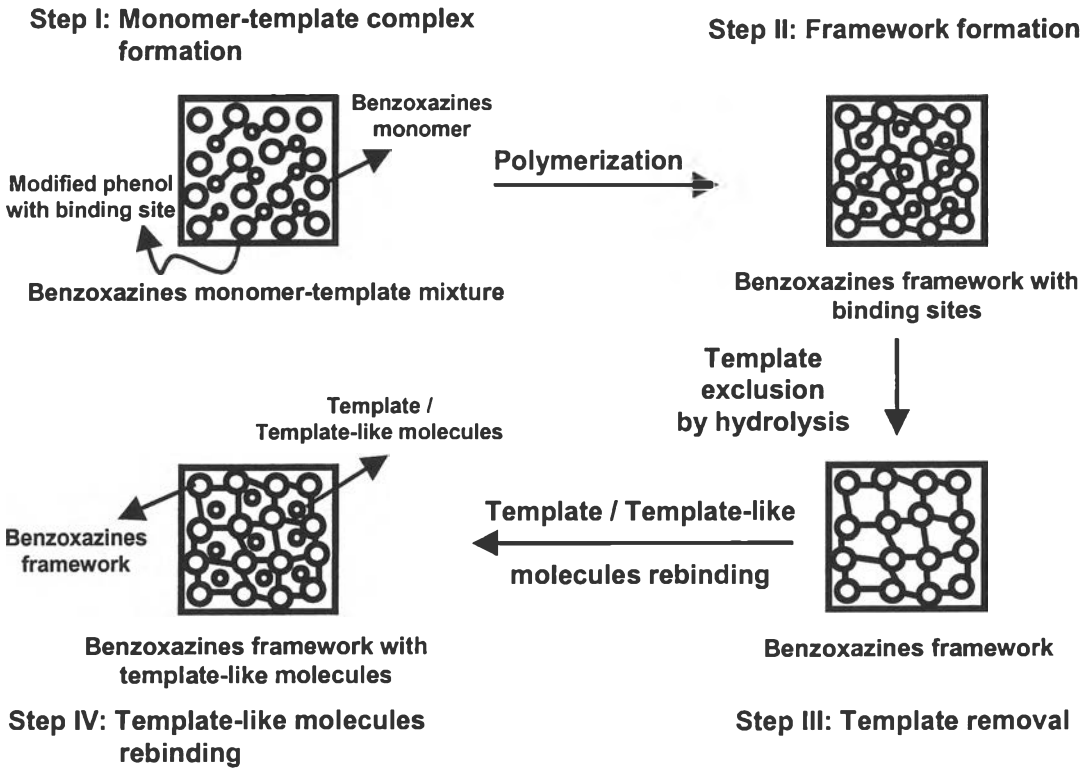
Chapter 2 (Scheme V) deals with a molecular imprinting via mixing and curing process. The template was blended with bisphenol A-based benzoxazine monomer for co-curing to obtain polybenzoxazines entrapped template. By removing the template, the polymer obtained was characterized to conclude the possibility of achieving molecular imprinting polybenzoxazines.

Scheme V



Chapter 3 (Scheme VI) deals with a molecular imprinting via covalently bonded template onto polymer chain. The polymer was designed by conjugating template onto phenol derivatives. The co-curing process of bisphenol A-based benzoxazine and phenol derivatives might give a polymer network with template. The template was removed by hydrolysis to challenge the imprinting properties of polybenzoxazines.

Scheme VI


Step I: Monomer-template complex formation
Step II: Framework formation
Benzoxazines monomer
Modified phenol with binding site
Polymerization
Benzoxazines monomer-template mixture
Benzoxazines framework with binding sites
Template exclusion by hydrolysis
Template / Template-like molecules
Benzoxazines framework
Template / Template-like molecules rebinding
Benzoxazines framework with template-like molecules
Benzoxazines framework
Step IV: Template-like molecules rebinding
Step III: Template removal