CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

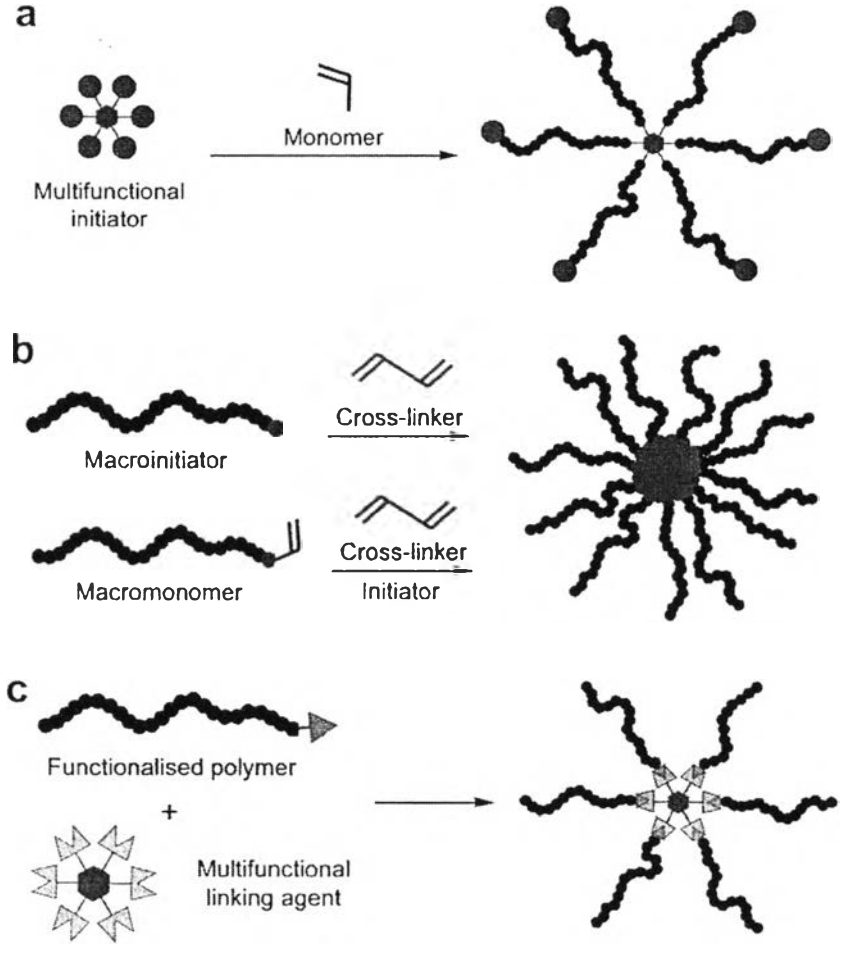
2.1 Star-shaped Molecules

Star-shaped molecules are the advanced-architecture molecular compounds which have been continuously paid attention for using as initiator, self-assembled functional membranes, and reactive-surface modifiers (Daoud *et al.*, 1982). In the past, generally, star-shaped molecules have been prepared by anionic polymerization. However, composition and functionality of the starting materials were limited for the polymerization. Instead of anionic method, the development of conventional radical polymerization had been interested to produce the star molecules with no rigorous deoxygenation process, no costly synthesis of a radical mediating agent, and no catalyst contamination in the final product (Gao *et al.*, 2007). Star-shaped molecules represent the simple model of branched structures, linking only one central branching unit per one macromolecule (Grest et al., 1996). Base on the chemical compositions of side arm, star-shaped molecules can be classified into two species: homo-arm (or regular arm) star and hetero-arm (or mikto arm) star. Homo-arm star molecules consist of symmetric structure with identical chemical composition and similar molecular weight of the linear arms (Tsitsilianis, et al., 1991). In contract, hetero-arm star molecules contain two or more arm types with different chemical composition, molecular weight (Xia, et al., 1999).

For the preparation of the star-shaped molecules, there are mainly three synthesis methods as shown in Scheme 1. The first method is core-first approach (Scheme Ia) which the controlled polymerization is conducted from either a well defined initiator or a less well defined multifunctional macromolecule (Li *et al.*, 2004). Cloutet et al. reported the synthesis of hexa-arm star polystyrene obtained via "living" cationic polymerization of styrene, using a hexafunctional initiator. The initiator was prepared by hexabenzylation of hexamethylbenzene to generate six phenylethyl chloride groups. Finally, well-defined star-shaped PS molecules were synthesized over a broad range of molar masses and experimental conditions close to engineered for the linear system (Cloutet *et al.* 1998). The second method is arm-first

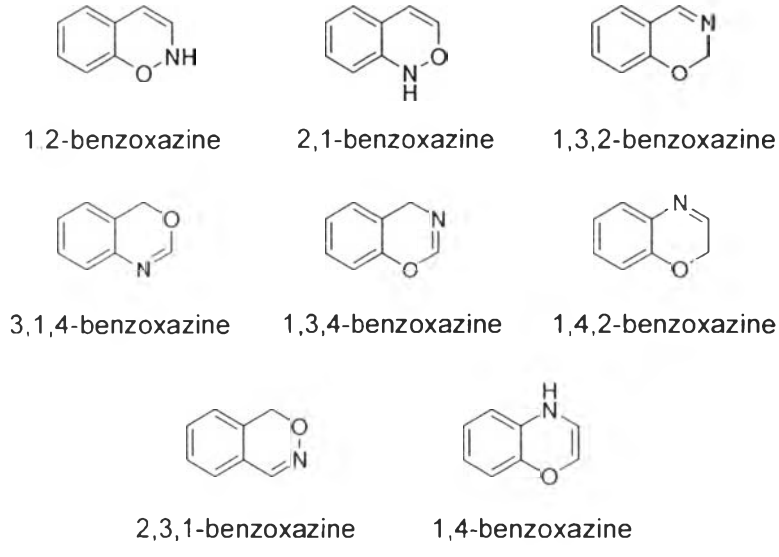
approach (Scheme Ib) which had two approaches to synthesize star-shaped molecules. One, a linear "living" chains, or macroinitiators are linked by continuing the polymerization of the mono-functional macroinitiator with a divinyl monomer forming a crosslinked core. Another is direct polymerization of macromonomers with a divinyl monomer in the presence of low molecular weight initiator (Rein *et al.*, 1993). The last method is coupling onto approach in which linear functionalized molecules are reacted with the multifunctional linking agent core molecule via coupling reaction as shows in Scheme Ic. This approach had not received as much attention due to the low efficiency of the reaction to form star-shaped structure (Kolb *et al.*, 2001).

Scheme 2.1



2.2 Benzoxazine Molecule

Scheme 2.2



Benzoxazines are heterocyclic compounds consisting of benzene and oxazine rings. There are 8 possible structures of benzoxazine with different positions of nitrogen and oxygen atoms in oxazine ring (Scheme II) (Elderfield, R. C. *et al.* 2009). In 1949, Burke has reported the preparation of benzoxazine derivatives (3,4 dihydro 1,3 2H benzoxazines) by using Mannich reaction with a single step of phenol derivatives, *p*-formaldehyde, and amine derivatives in molar ratio of 1:2:1 (Figure 2.1).

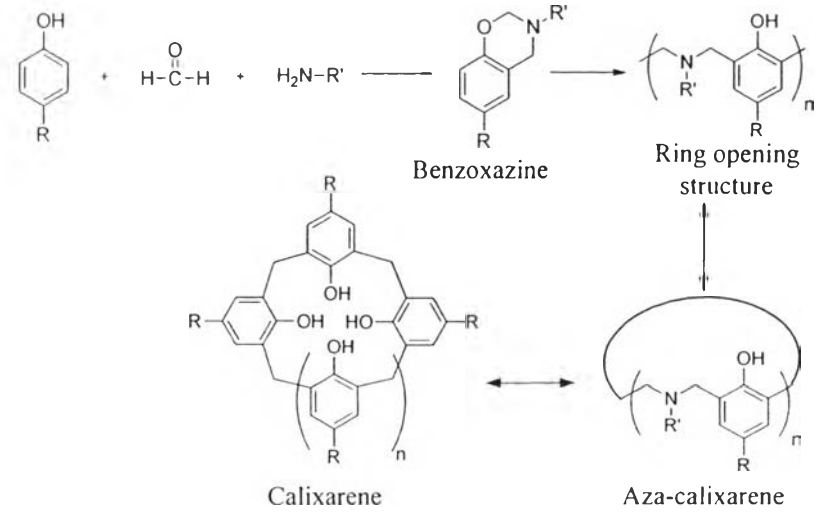
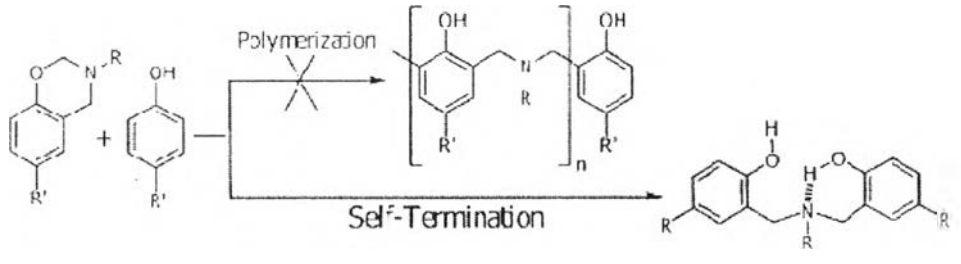


Figure 2.1. Mannich reaction of benzoxazine derivatives.

Considering the molecular chemistry, ring opening structures of benzoxazines which is derived from the unique structure of benzoxazine monomer and oligomer are similar to aza-calixarenes, derivatives of calixarene supramolacule. Calixarenes were supramolecules that have ability to trap metal ions and shown the molecular recognition so benzoxazine molecules could be supramolecules as well. Chirachanchai *et al.* 2000 proposed a unique properties of Bisphenol-A based benzoxazine monomer and its oligomer to perform host-guest phenomena with alkali and alkaline earth ions. The polymerization of benzoxazine monomers was terminated at benzoxazine dimer as a result of inter- and intra-molecular hydrogen bond formations between benzoxazine dimers as illustrated in Scheme 2.3 (Chirachanchai *et al.* 2009).

Scheme 2.3



Phongtamrug *et al.*, clarified supramolecular structure of benzoxazine dimers with copper-ion. The benzoxazine dimers exhibit themselves as host to accept guests without destroying the host framework under the double-oxygen-bridged dimeric system and perform a selective macrocyclic compounds through a simple reactions of either esterification or etherification. Rungsimanon *et al.* 2008 proposed [1+1] and [2+2] benzoxazine macrocycles derived from the reaction between *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine (benzoxazine dimer) and ditosylated compound. The benzoxazine dimers with methyl group at ortho and para positions of benzene ring and at nitrogen atom provided [1+1] dibenzo-monoazacrowns. By contrast, benzoxazine dimer without methyl group at ortho position gave [2+2] ether-linked macrocyclic benzoxazine. The molecule showed an inclusion phenomena with metal ions. For example, Laobuthee and coworkers have reported a simple, effective, and

selective approach to prepare ester-linked macrocyclic benzoxazine via esterification of terephthaloyl and benzoxazine dimer to obtain a well-defined structure product with high yield and without using expensive catalysts for multistep reactions in specific conditions.

2.3 Points of the Present Work

Base on the advantages of benzoxazine molecule and nucleophilic substitution, the present work focuses on a systematic study of star-shaped benzoxazine synthesis through a nucleophilic substitution of hydroxyl and tosyl between benzoxazine dimer and tetra-tosylated core molecule. The mechanism of nucleophilic substitution is also proposed as model case for star-shaped molecule synthesis via substitution reaction of phenolic-based arm chains and multi-tosylated core molecule.