CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

Theoretically, *p*-substituted phenol-based benzoxazine proceeds a ring opening polymerization to give a linear aza-methylene linkage phenol polymer. As seen in the case of calixarenes, by varying the reaction condition, such as reactant concentration, metal ion templates, a series of aza-methylene linkage phenol macrocyclic should also be obtained from *p*-substituted benzoxazines. However, the present work clarified two important results, which have never been reported elsewhere and contradict to the theory. The first is that, *p*-substituted phenol-based benzoxazines hardly proceed the ring opening polymerization as the known mechanism. The many reaction conditions insisted that the ring opening reaction terminates as soon as the dimers are formed as confirmed from the FTIR, NMR, EA, HPLC, and LCMS. X-ray structural analyses clarified that the intra- and intermolecular hydrogen bonds are the key factors in stabilizing the dimers and obstructing the reaction. The achievement at this part is valuable since it does not only show another rare example of "self-termination" reaction but also answers why Reiss et al. reported that the mono-substituted benzoxazines produce only tetramer at the most. The second is that even benzoxazine dimers are symmetrical, the Mannich reaction inevitably produces "asymmetric mono-oxazines", which is, again, rarely seen in organic reactions. This successful point is important in term of being a hint to generally achieve a unique asymmetrical product by simply designing the molecule with a strong intramolecular hydrogen bond to deactivate the other reactive site.

Although the unique reactivity of the *p*-substituted phenol-based dimers obstructs the polymerization, other modified dimers and the dimer based macrocyclic compounds have also been challenged. A series of benzoxazine dimer based difunctional 30-membered macrocyclic and linear oligo esters as well as ethers were originally achieved. The present work clarified that the products can be selectively obtained by simple reactions in mild condition without any specific catalysts. At this

part, the work demonstrated one of the elegant synthesis routes controlled by simple intramolecular hydrogen bonding to proceed the "self-selective" reaction.

Based on the viewpoint that the ring opening reaction of benzoxazines gives a compound with a repeat unit of aza-methylene phenol, which is resembled to that of calixarenes, the present work succeeded in originally showing that the open ring benzoxazines are a novel type of host compound. The dimer derivatives exhibited ion interaction at the concentration less than that of metal ion for 10^3 times, clarifying that the host-guest compound is formed via an assembly type. The cyclic derivatives performed stoichiometric ratios, such as 1:1 or 2:1, with metal ions as clarified either by ^{1}H NMR or UV, indicating that the host-guest compound is generated under an interaction via individual molecules.

The present work does not only give an important information about the reaction of benzoxazine molecules but also is a useful guideline to develop benzoxazines for supramolecular macromolecules in the future. The various structures of these supramolecules expected to be a novel host compounds for guest species, such as, neutral molecules, rare-earth metals, or radioactive materials.