

CHAPTER I

INTRODUCTION

Macrocycles such as crown ethers (Cram, D.J. and Cram, J.M., 1983), calixarenes (Vicens and Boehmer, 1991), and cyclodextrins (Bender and Komiyama, 1978) have received much attention due to their unique properties. One of the most important properties of macrocyclic compounds is inclusion phenomena of metal ions or guest molecules into its cavity. By employing the host-guest property, macrocyclic compounds have been applied for various applications such as catalysts, indicators and sensors. Trippe *et al.* (2002) synthesized bis(pyrrolo)tetrathiafulvalene macrocycles which exhibited high binding affinities for Pb^{2+} and Ba^{2+} in order to induce optical or redox properties.

Macrocyclic compound can be obtained by macrocyclization under the dilute system (Dietrich, 2004). There are many reports on the preparation of macrocyclic compound and their unique properties such as molecular recognition, host-guest system. For example, Nagahata *et al.* (2003) reported the synthesis of macrocyclic ethylene isophthalate dimer by reacting ethylene glycol diacetate with isophthalic acid dimethyl ester using sodium ethoxide as a catalyst. Yuan *et al.* (2004) proposed the one-step macrocyclization of cyclic hexa(aramides) by treating diacid chloride with 4,6-dimethoxy-1,3-phenylenediamine. In the most cases, in general, the preparation of macrocyclic compound is multi-steps especially purification steps, and giving a low-yield product.

The reaction efficiency becomes more severe if one considers a polymer chain linked with macrocycles, so-called macrocyclic polymer. Macrocyclic polymer is polymers containing macrocycles, such as crown ethers, as side chain or main chain that show metal and molecular recognition abilities. Habaue *et al.* (2002) synthesized macrocyclic polymer by anionic polymerization of macrocyclic vinyl monomer. In those case, the preparation of macrocyclic vinylmonomer deals with a problem of low-yield product (22%) which are the limitation in polymerization.

In the recent years, our group has succeeded in preparing a series of benzoxazine-based macrocyclic esters (Laobuthee *et al.*, 2002) and macrocyclic ethers (Chirachanchai *et al.*, 2003) with simple and effective preparation, high-yield prod-

uct (up to 80%), and flexible molecular-design. In those cases, by simple esterification of *N,N*-bis(2-hydroxyalkylbenzyl)alkylamine with terephthaloyl chloride, [2+2] macrocyclic can be obtained. It brings us a challenge to design a novel benzoxazine-based macrocyclic containing propargyl moieties for further development to challenge a novel macrocyclic polymer.

Up to this point, the benzoxazine-based macrocyclic has been focused on only in academic research. It comes to our question that how to design and synthesize the benzoxazine-based macrocyclic by further applying simple and effective reaction of benzoxazine chemistry. We also extend the works to show the macrocyclization condition to obtain the benzoxazine-based macrocyclic.