CHAPTER II
LITERATURE SURVEY

2.1 Inclusion compound: history and development

The history of inclusion compounds dates back to 1823 when Micheal Faraday reported the formation of the clathrate hydrate and chlorine. Other early observations include the graphite intercalation in 1841, choleic acids host-guest compound in 1885 and cyclodextrin inclusion compounds in 1891. Later milestones of the development of inclusion compounds refer to the urea adducts and phenol clathrates in 1935. However, the inclusion compounds and their phenomena were still on controversy since there is no direct evidence to clarify the host and guest molecular assemblies. The first turning point in understanding the inclusion compounds occurred in the late 1904 from the pioneer work on X-ray crystallography studied on the β-hydroquinone clathrates by Powell (1948). Pedersen (1967) made the real break through in inclusion chemistry to discover crown compounds and their inclusion phenomena in the mid-1960s. Since then, with the development of instrumentation, the understanding of inclusion compound has grown rapidly. A variety of compounds and materials having the attribute of inclusion are categorized as a chemistry of host-guest chemistry (Vogtle *et al.*, 1985). Inclusion phenomena is defined for an asset of compounds that host molecules incorporate to each other by the secondary forces to form the specific structure of the frame work fitting to the guest molecules (Scheme 2.1). Inclusion compound, inclusion phenomena, host-guest compound, and host-guest chemistry are well recognized as a supramolecular chemistry when Pedersen (1988), Cram (1988), and Lehn (1988) were awarded the 1987 Nobel Prize in chemistry (Weber, 1987).

Scheme 2.1 Concept of inclusion compound and host-guest formation

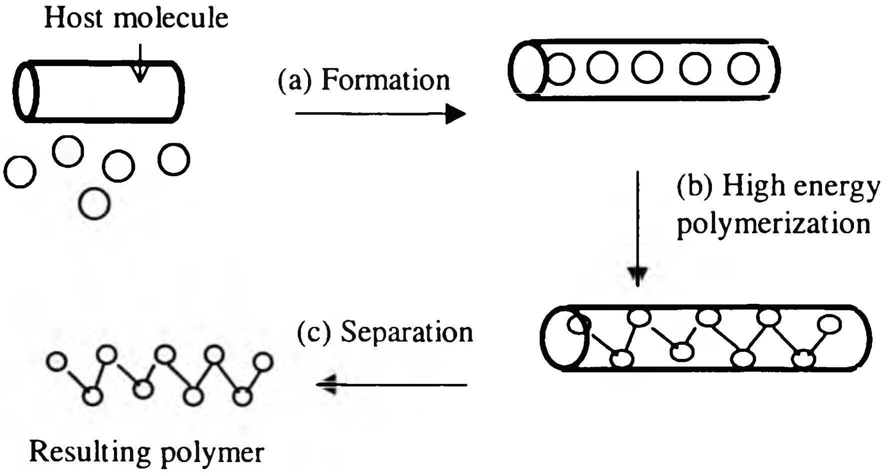
2.2 Cholic acid derivatives and its inclusion compound

The first isolation of deoxycholic acid was found by Latschinoff (1885) from ox bile. In 1972, Craven and de Titta reported the first crystal structure of deoxycholic acid with acetic acid by X-ray single crystal technique. Subsequent X-ray studies declared the crystal structure of deoxycholic acid with acetic acid as a molecular assembly. TGA and ^{1}H-NMR are the quantitative techniques to confirm host-guest ratio of inclusion compound. Since then Miyata *et al.*, 1987 have studied many inclusion compounds of bile acids and their derivatives, such as cholic acid, apocholic acid, methylcholate, etc. Many works have been conducted to clarify the host and its guest intercalation through the range of guest compounds, which now includes aliphatic, alicyclic, and aromatic hydrocarbons, alcohols, fatty acid, esters, ketones, ethers, and nitriles. Not only neutral guest that is cholic acid derivatives but also reactive species, monomer, such as butadienes, isoprene and vinyl monomers, etc, can be included (Miyata *et al.*, 1988). Thus, up to now, a considerable number of studies have extended to inclusion polymerization.

2.3 Inclusion polymerization: history and development

The synthesis of precisely controlled structure of polymer is one of the main challenges to develop polymer material at molecular level for modern scientists. Ziegler-Natta, other coordination systems, anionic, or group-transfer methods are known as an appropriate approach for the controlled structure of polymers which is achieved by using catalyst. Another effective way to control polymer structure is inclusion polymerization. In this case, host molecules have to include monomers as guests while the polymerization is carried out inside inclusion channel by high energy such as, photoradiation. Guest monomers are arranged in a controlled manner inside a channel or canal structure formed by guest. Topological constraints force the monomer to give high stereoregularity (Scheme 2.2).

Scheme 2.2 Inclusion polymerization of host-guest compound



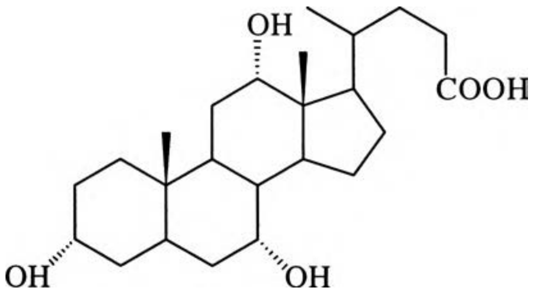
Inclusion compound formed with monomer was first reported in 1956, when Clasen achieved the inclusion polymerization starting from 2,3-dimethylbutadiene included in thiourea (Clasen, 1956). The process was initiated thermally and proceeded very slowly. A more efficient method for initiating polymerization was introduced by Brown and White in 1960, by using γ-ray, and X-ray, adopting urea and thiourea matrices (Brown *et al.*, 1960, White, 1960). With this method, in a reasonably short time, high molecular weight products were obtained. New developments in inclusion polymerization were made by the application of the transoid-trans-transoid-trans-transoid-trans isomer of perhydrotriphenylene (PHTP), introduced by

Farina in 1963. This compound was found to serve as an effective host for polymerization. In 1975, Miyata and Takemoto adopted other chiral hosts: the naturally occurring DCA and ACA. Asymmetric induction demonstrated to be exerted only ' through space ' not to chemical bonds. Other hosts, such as tris(o-phenylenedioxy) cyclotriphosphazene (TPP) and similar substituted phosphazenes, give good results when used for inclusion polymerization (Finter *et al.*, 1979 , and Allcock *et al.*, 1982). A few examples regarding to the application of β-cyclodextrins to inclusion polymerization are also discussed by Maciejewski, 1979

2.4 Cholic acid and its inclusion phenomena

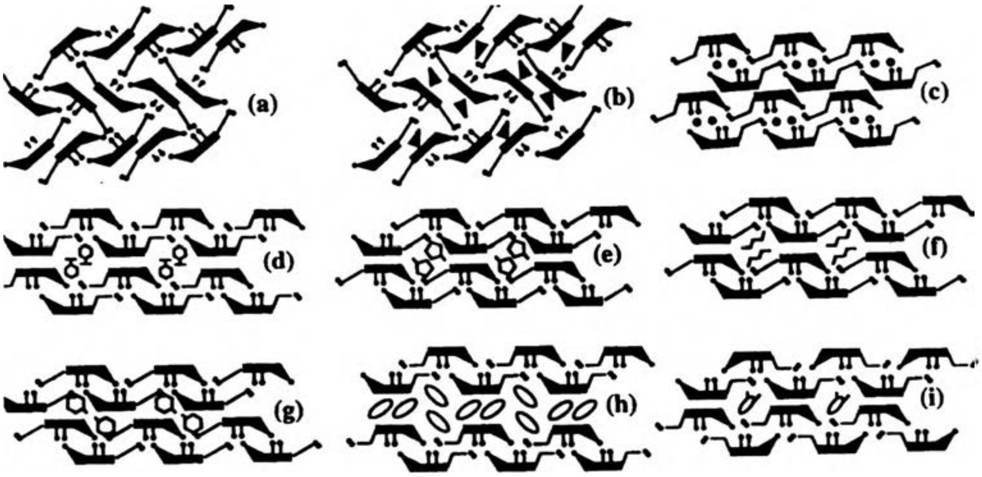
Cholic acid, as shown in scheme 2.3 for chemical structure, has been much attention in last decades.

Scheme 2.3 Chemical structure of cholic acid



Miyata *et al.* focused on the inclusion compound of cholic acid and its inclusion polymerization. The most unique point of cholic acid is the guest responsive ability. Cholic acid can change scheme, according to the guest components, whereas other hosts select only one scheme, regardless of guest. Scheme 2.4 shows schematic representation of the guest-dependent polymorphism of cholic acid that forms more than ten kinds of polymorphic crystal with various guests. Most organic guests form monoclinic crystals

($P2_1$) such as methylacrylonitrile, acetophenone, and acetyl lactone, etc. Cholic acid can form other crystal structures which are triclinic crystal (P1) in case of (c), orthorhombic ($P2_12_12_1$) in case of (g, h) and hexagonal ($P6_5$) in case of (i).



Scheme 2.4 Configurations of cholic acid in different guest molecules, (a) none; (b) methacrylonitrile ; (c) water; (d) acetophenone; (e) γ-valerolactone; (f) acetylactone; (g) 3-methylcyclohexanone; (h) Indene; (i) o-xylene (Miyata, 1996)

2.5 Cholic acid and its inclusion polymerization

Inclusion compound and inclusion phenomena of cholic acid have been received much attention in the past decade. Less studies are performed on the concept of inclusion polymerization. However, Miyata *et al.* (1988), Goonewardena *et al.* (1993) and Tsutsumi *et al.* (1990), etc. demonstrated that unique inclusion polymer obtained by using APA and DCA. With the basic idea of using inclusion channel, it is our interest to study the inclusion polymerization of CA.

2.6 Inclusion polymerization of vinyl chloride monomer (VCM) and polyvinyl chloride (PVC)

Vinyl chloride monomer (VCM) is gaseous (bp -13 °C) no color and no odor. Toxicity of VCM causes angiosarcoma, liver cancer. The major use of VCM is for production of polyvinylchloride, polyvinylidine chloride and other copolymers.

PVC is the polymer obtained from typical VCM, which receives much attention for tremendous applications for more than a half century. Conventional polymerization of VCM, i.e., radical polymerization, brings amorphous PVC with low tacticity which makes the processing of PVC require some specific conditions comparing to other ordinary polymer as polyethylene or polypropylene. Though polyvinylchloride has been utilized in a large amount, less study is focused on the controlled structure to propose as a new type of material as seen in the case of isotactic polypropylene, HDPE, and LLDPE.

Up to now, many reports have been proposed to develop PVC by means of inclusion polymerization. In 1975, Yoshi *et al.* proposed inclusion polymerization of vinyl chloride monomer. However the ratio of host-guest and the thermal stability were not clear. It was also concluded that the overall properties, such as solubility in organic solvent, crystallinity, X-ray diffraction theta angle were shown differently from the commercial PVC, however, stereoregularity was not precisely reported owing to the limited technique of broadline NMR at that period. Chatani *et al.* (1978) studied about inclusion polymerization of VCM in urea and thiourea to obtain partly syndiotactic PVC with regularity as confirmed by broad line NMR. Finter *et al.* (1979) studied in TPP with achieving mainly syndiotacticity. Silvestro also got partly syndiotactic PVC under PHTP host channel.

2.7 The unique of the present work

Vinylchloride monomer, which has the boiling point –13°C, is difficult to directly recrystallize. For inclusion polymerization, the most important step can be mentioned as a step for preparating a crystal of host and guest. Thus, the formation process of vinyl chloride monomer and host molecule can be mentioned as a main key in this present work. The interesting point of the present work can be claimed as an original idea to apply inclusion polymerization via CA channel for VCM. The success of the present work, thus, would clarify not only the possibility of CA host for inclusion polymerization but also product obtained.