



CHAPTER I INTRODUCTION

Chitin, 2-acetamido-2-deoxy- β -D-glucopyranose, is the second most plentiful organic resource on the earth next to cellulose obtained from the shells of crustaceans, the cuticles of insects, the cell-walls of fungi and yeasts. Acetyl group of chitin can be removed by methods such as heterogeneous alkaline hydrolysis and thermomechanicochemical technology to obtain chitosan, 2-amino-2-deoxy- β -D-glucopyranose, which shows significant property about solubility in acidic solvent. In general, chitin appears as a copolymer chain with chitosan unit.

The basic chemical structure of chitin-chitosan is a polysaccharide chain having two hydroxyl groups at C-3 and C-6 positions. The hydroxyl and amino groups of chitin-chitosan act as a crosslinkable site which can be applied to many applications such as membrane, gel, and beads. Moreover, the nitrogen atom provides lone pair electrons for metal complexation. Chitin-chitosan is a unique polysaccharide due to the nitrogen atom of acetamide and amino group at C-2 position. Chitin-chitosan is not only attractive in terms of bioactivity (Kurita *et al.*, 1997), biocompatibility (Singh *et al.*, 1994), biodegradability (Mark *et al.*, 1985) and nontoxicity (Chandy *et al.*, 1992) but also the possibility for chemical modification (Goosen, 1997). However, by considering the chemical structure, chitin-chitosan is known for its high molecular weight, and strong inter and intramolecular hydrogen bonding to limit the solubility. These become the main problem to overcome and make the chemically modified chitin-chitosan product rarely be available in the market. In order to achieve various derivatives, the breaking of crystalline structure of chitin-chitosan is the main point to be done which can be achieved by (i) the hydrophobic functionalization (Kurita *et al.*, 1991) or hydrophilic functionalization (Katsuaki *et al.*, 1981) of chitin-chitosan chain, and (ii) molecular weight reduction (Yoksan *et al.*, 2001).

At present, various chemically modified chitin-chitosan derivatives are proposed not only to improve the solubility and overcome the rigid structure but also to achieve the property that never be obtained in natural chitin-chitosan. One of the

potential value-added products is the introduction of specific functional group to achieve molecular recognition mechanism at molecular level. Generally, chitosan performs as cationic species while interacts with metal ions. A number of reports and patents deal with the use of chitosan to exclude metal ions from aqueous and organic solvents (Maruca *et al.*, 1982). The metal ion interaction and selectivity of chitin-chitosan can be improved significantly after introducing macrocyclic molecules such as crown ethers (Yang *et al.*, 1999), calixarenes, and cyclodextrins (Tanida *et al.*, 1998) onto chitosan chain. However, by considering supramolecular specific properties, it can be concluded that the ionic interaction ability is achieved mainly from the conjugated macrocyclic itself.

The present work originally proposes the molecular design and functionalization of chitosan with simple functional group as polyethylene glycol which can induce molecular recognition (Yamagishi *et al.*, 1996) onto chitosan chain to obtain a supramolecular structured chitosan generated from a linear ethylene glycol chain where the pseudocyclic cavity for ionic interaction is expected. The present work focuses on the inclusion phenomena to clarify supramolecular structure of chitosan-PEG.