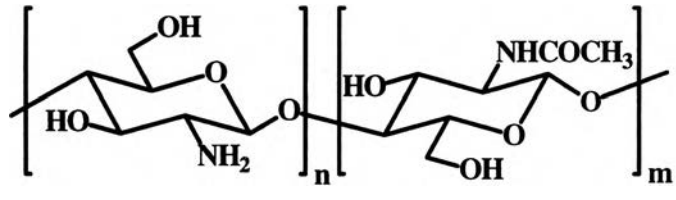
CHAPTER I
INTRODUCTION

Chitin-chitosan is a copolymer of β(1-4) D-glucosamine and β(1-4) N-acetyl D-glucosamine. The basic chemical structure of chitin-chitosan is a polysaccharide chain having two hydroxyl groups at C_3 and C_6 positions. Chitin-chitosan can be claimed to be a unique polysaccharide owing to its acetamide and amino groups at C_2 position (Scheme 1.1). Thus, chitin-chitosan is not only attractive in terms of bioactivity (Uragami *et al.*, 1988), biocompatibility (Prudden *et al.*, 1970), and biodegradability (Amano *et al.*, 1978), but also the possibility for chemical modification (Goosen, 1997).



Scheme 1.1 Chemical structure of chitin-chitosan copolymer.

For decades, chitin-chitosan and its derivatives have received much attention to develop the practical applications for biomedical, pharmacological, agricultural, and biotechnological fields. At present in our daily life, we can see products of chitosan available in the market, such as dietary foods (Ventura, 1996), cosmetics (Muzzarelli, 1983), and water treatment resins (Tsezos, 1983). The advanced applications as value-added products of chitin-chitosan are still on the expectation, owing to the advantages of the abundance and the low cost of the raw material, i.e., shrimp shell, crab shell, and squid pen.

In order to achieve novel properties, various interesting chitin-chitosan derivatives have been reported, i.e., water soluble CM-chitin (Tokura

et al., 1983), heparinoid sulfate chitosan (Tokura *et al.*, 1994), and reactive precursor tosylchitin (Nishimura *et al.*, 1991). Although the approach of chemical modification has been known well, the problem of chitin-chitosan is related to its high stability, owing to the high molecular weight, and the strong intra- and intermolecular hydrogen bonding (Hun, 1992). This generates the most common problems about the low solubility in almost all organic solvents except carboxylic acids, which are not practical in chemical reaction. In most research works, chemical reactions of chitin-chitosan are proposed in heterogeneous system (Brine *et al.*, 1991) even the reactivity is not performed well enough. In recent years, low molecular weight chitin-chitosan and/or oligochitin-chitosan are recognized as a novel material. The short chains of chitin-chitosan and oligochitin-chitosan have been reported about the good performance of bioactivity (Hirano *et al.*, 1976).

Hence, the methods to depolymerize chitin-chitosan, i.e., chemical treatment (Allan and Peyron, 1997), enzymatic hydrolysis (Aiba, 1993), and photoirradiation (Kume and Takehisa, 1984) are on the challenge. Although the chemical treatment can be easily done, a huge amount of acid and base wastes are not ideal. Enzymatic hydrolysis is an attractive way, since it can be achieved in natural system with mild condition. However, it required many steps in the enzyme preparation process. Photoirradiation is an interesting method to propose the way to apply the high radiation energy for the peaceful and useful utilization. γ-Ray irradiation is considered to be an effective way to degrade a bulk of chitin-chitosan with simple procedure (Lim *et al.*, 1998). In our previous work, we found that γ-ray irradiation of dried bulk chitosan shows the decrease in molecular weight approximately one-forth at dose of 25 kGy without any destroy of the chemical structure of chitosan. It was found that the decrease in molecular weight did not go to a satisfied level. The solubility studies indicated that chain degradation was a main reaction while chain combination (crosslinking) was a minor one.

The present work, thus, stands on the optimal condition of γ-ray irradiation on chitosan dispersed in water to achieve the effective chain degradation. The work also extends to the hydrophobic chain conjugation in order to propose the chitosan micelle, which is a unique molecular design for the aggregation. Here, the applications for chitosan micelle obtained can be expected not only for the controlled release system, but also for the excretion of lipid molecule.