CHEMISTRY LETTERS, pp. 9 - 12, 1988.

Improvement of Adsorption Capacity for Copper (II) Ion by N-Nonanoylation of Chitosan[1]

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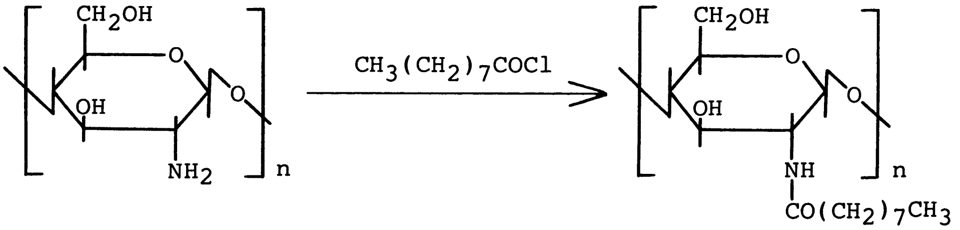
Chitosan was selectively N-nonanoylated, and the influence of the long acyl groups on the adsorption of copper (II) ion was studied. The acylation with nonanoyl chloride was achieved efficiently on a highly swelled chitosan precipitate. The adsorption capacity could be improved markedly by a small extent of acylation.

The importance of chitin as an unutilized resource is increasing owing to not only its abundance but also unique structure and properties.[2] Among some characteristic properties of this amino polysaccharide, chelating ability seems to be one of the most attractive and promising functions.[3-5] Chitosan, a deacetylated form of chitin, is especially known to be the most powerful adsorbent of natural origin.[6]

In an attempt to develop chemical modifications on polysaccharides and to elucidate the effects on the properties, controlled partial deacetylation[7] and crosslinking[8] of chitin were shown to be quite effective to bring about improved adsorption capacities, much higher than that of chitosan. This suggests the possibility of similar effects through the introduction of relatively long substituents into the polysaccharide backbones without crosslinking. Selective and effective introduction of nonanoyl groups, $CH_3(CH_2)_7CO-$, to the amino groups of chitosan by the acylation with the corresponding acyl chloride and also the influence of the N-nonanoyl groups on the adsorption behavior have therefore been examined.

Nonanoylation of chitosan (degree of deacetylation: 88%) was carried out on a highly swelled precipitate under almost homogeneous conditions to enable



random substitution along the backbone for effective destruction of the tight arrangement of the rigid polysaccharide molecules leading to increased hydrophilicity and easy accessibility of coordinating groups, primarily amino groups. A chitosan solution in a mixture of 10% aqueous acetic acid and methanol was poured into pyridine, and the acyl chloride was added to the mixture. The reaction efficiency was, however, very low owing to some side reactions with protic components in the solvent.

The contents of the protic components were then reduced by repeatedly replacing most of the supernatant by fresh pyridine after centrifugation; this improved the N-acylation efficiency highly, making possible the smooth reaction with the acyl chloride. The reaction with nonanoyl chloride was conducted at 0 °C initially to enhance the reaction selectivity toward the amino groups of chitosan against hydroxyl groups of various components. The reaction mixture was allowed to warm to room temperature, and after 3 h, the product was isolated in acetone/water (7:1). It was then treated with 1 mol dm^{-3} methanolic potassium hydroxide at room temperature for 24 h to ensure the regeneration of the amino groups lost by the salt formation of the unreacted groups with acetic acid. This alkaline treatment is also effective to cleave ester groups formed by the reaction at the hydroxyl groups, probably a very small amount if any judging from the IR spectra, but caused no reduction in the N-acylation degree. The products were obtained as white or off-white solids. The results shown in Table 1 indicate the N-acylation of chitosan to proceed quite efficiently, although acyl chlorides are generally too reactive and unstable compared to acid anhydrides for the acylation of this kind of polysaccharides. Reproducible and fairly selective acylation thus proved to be effected with acyl chlorides and useful for modifications if carried out under these mild conditions in a highly swelled state in pyridine. The resulting derivatives with low substitution degrees were still soluble in aqueous acetic acid like chitosan, whereas those with degrees above around 0.30 were insoluble. They showed strong amide I and

Table 1. Nonanoylation of Chitosan

Chitosan/ g	Nonanoyl chloride/ml	$-COCl/-NH_2$[a)]	Yield/ g	Degree of substitution[b)]	
				Acetyl	Nonanoyl
0.400	0.38	1	0.291	0.12	0.05
0.401	0.77	2	0.294	0.12	0.10
0.400	3.85	10	0.417	0.12	0.29
0.400	7.70	20	0.467	0.12	0.40

a) Molar ratio.

b) Determined by IR spectroscopy[9)] for the acetyl group and by C/N ratio of elemental analysis for the nonanoyl group.

II bands at 1650 and 1550 cm^{-1} and C-H stretching bands at 2850 and 2900 cm^{-1} in the IR spectra.

Adsorption behavior of the resulting nonanoylated chitosans was examined using copper (II) ion. A 50 mg sample (100-200 mesh) of the derivative was treated with 25 ml of 5.00×10^{-4} mol dm^{-3} aqueous copper (II) chloride solution at room temperature for 72 h. The amount of copper (II) ion left in solution was determined by UV spectroscopy using sodium diethyldithiocarbamate.[8)] The influence of the extent of nonanoylation on the adsorption is illustrated in Fig. 1. As anticipated, the adsorption capacity was improved makedly by the acylation from a collection percentage of chitosan of 75% to that of a derivative of as high as 98%. It is noteworthy that the maximum was observed at a

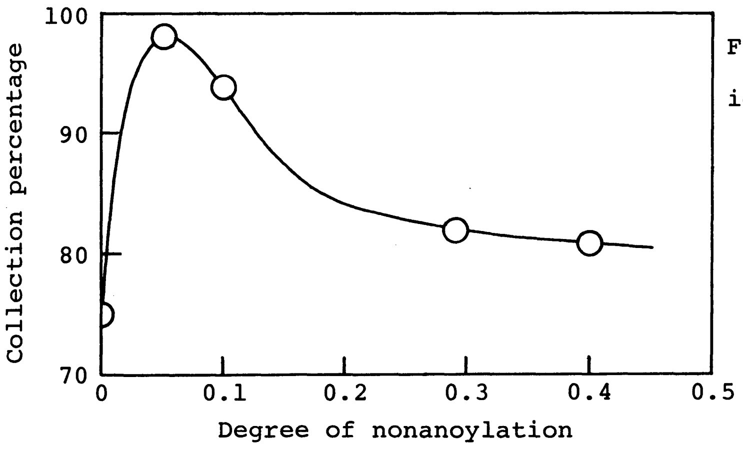


Fig. 1. Adsorption of copper (II) ion by nonanoylated chitosans.

relatively low degree of nonanoylation, as in the case of the crosslinking. The capacity then decreased with an increase in the substitution degree. This adsorption profile is quite similar to those of the crosslinked derivatives,[8)] and the increase and decrease in the capacity are most likely attributable to the interference with the tight arrangement of the rigid polysaccharide molecules and the increased hydrophobicity, respectively.

Consequently, controlled N-acylation of chitosan with nonanoyl chloride was established to introduce relatively long groups efficiently under mild conditions, and a low extent of nonanoylation was confirmed to increase the adsorption capacity remarkably. A balance between the destruction of the molecular arrangement and the hydrophobicity brought about by chemical modifications has turned out quite important.

This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials -Design, Preparations, and Control-, the Ministry of Education, Science and Culture, #62604600.

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(Received August 14, 1987)