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Facile Preparation of Water-Soluble Chitin from Chitosan

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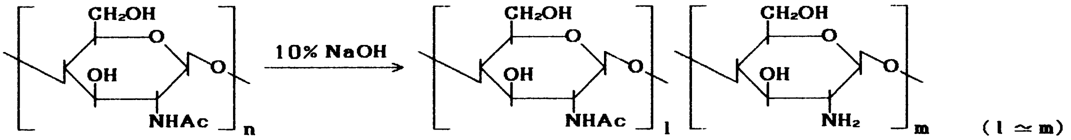
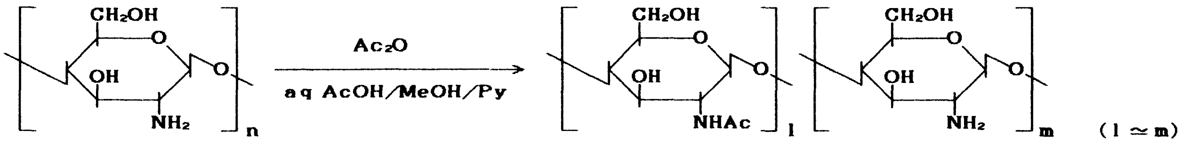
A simple and efficient procedure for the preparation of water-soluble chitin was developed by controlled partial N-acetylation of chitosan. Acetylated chitosans with about 50% substitution prepared in a highly swelled state exhibited high water-solubility, and the procedure proved much superior to the conventional one.

Although chitin is attracting a great deal of attention because of its high potentials, its utilization has scarcely been exploited yet due primarily to the intractable nature. The insolubility in solvents except some special ones such as hexafluoro-2-propanol,1) dimethylacetamide/lithium chloride,2) and trichloroacetic acid/dichloroethane3) has undoubtedly delayed the basic and utilization studies.

During the course of alkaline deacetylation in solution, chitins with about 50% deacetylation were found to become soluble in water.4) The solubility is strongly dependent on the deacetylation degree, and the samples with over 60% and under 40% deacetylation show only poor or even no solubility. Moreover, those prepared under heterogeneous conditions are insoluble regardless of the deacetylation extent.5) This suggests the importance of random distribution of a definite amount of acetyl groups for solubilization. The water-solubility is significant in that it made possible efficient modification reactions6) and also helped develop various utilizations.7) The preparation of water-soluble chitin, however, requires large quantities of solvents and long time in some stages including neutralization of the mixture and removal of the resulting salt. This causes much trouble especially in large scale production. If the solubility arises from the randomly distributed acetyl groups at half the number of amino groups, it may possibly be prepared by controlled partial N-acetylation of chitosan. This approach is much simpler and less costly. Elucidation of the influence of substituents on solubility behavior is also of importance to get a clue to solubilization of rigid polymers.



The acetylation reaction should be carried out under homogeneous or almost homogeneous conditions to achieve random substitution. A solution of chitosan from shrimp shell chitin (deacetylation degree: 90%) in 10% aqueous acetic acid/methanol was first subjected to acetylation. The mixture, however, tended to form a gel and was not suitable for the purpose. A highly swelled chitosan precipitate prepared



by pouring the chitosan solution into pyridine was thus treated with acetic anhydride to avoid gel formation (method A). During the reaction at room temperature for 5 h , the precipitate remained swelled with a slight extent of coagulation. About 50% acetylation was observed with 20 to 25-fold excess acetic anhydride.

In order to further improve the desirable highly swelled state to allow random substitution during the reaction, the acetylation was then conducted by pouring the chitosan solution into a mixture of acetic anhydride and pyridine (method B). In this way, the appearance of the precipitate changed little, ensuring almost homogeneous reaction conditions. With 2 to 25-fold excess acetic anhydride, 30-90% of amino groups were acetylated reproducibly. For 50% acetylation, 6 to 7-fold excess reagent was sufficient. The sample, prepared with 0.3 g of chitosan, 8 ml of 10% aqueous acetic acid, 8 ml of methanol, 100 ml of pyridine, and 0.93 ml (6-fold excess) of acetic anhydride, had a degree of acetylation of 49%.

The N-acetylated chitosans obtained here showed identical IR spectra with those of the corresponding deacetylated chitins. The samples exhibited high hydrophilicity. Those with about 50% acetylation showed water-solubility as expected and remained in solution even on alkalization. The characteristics of 50%-N-acetylated samples were evaluated quantitatively in terms of solubility and turbidity. The soluble proportions in aqueous acetic acid were 67 and 92% for the samples obtained by methods A and B, respectively. The filtrates of these mixtures were then made alkaline to pH 8.9, and the absorbances at 600 nm were determined at 0.025% concentration as turbidities. They were 3.5x10^{-2} and 0.9x10^{-2}, respectively. The latter value is comparable to that (1.1x10^{-2}) of the conventional water-soluble chitin, indicating method B to be more efficient than method A not only in the progress of acetylation but also in random substitution along the backbone.

High quality water-soluble chitin is thus confirmed to be prepared conveniently by this alternative method. It is much simpler and more efficient than the conventional one, especially in that they involve no neutralization process, and consequently has remarkable advantages for the preparation even in large scales.

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