Polymer Bulletin 21, 13–17 (1989)

Polymer Bulletin

Studies on chitin

18. Preparation of diethylaminoethyl-chitins

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SUMMARY

Chitin was aminoalkylated with N,N-diethylaminoethyl chloride in organic solvents or aqueous solutions in the presence of sodium hydroxide. The substitution reactions in organic solvents occurred under heterogeneous conditions on dispersions of powdery chitin while those using alkali chitin solutions proceeded in solution. The latter reactions were more efficient and reproducible than the former ones due to the homogeneous reaction conditions. The resulting diethylaminoethyl-chitins showed much improved solubility in contrast to the insolubility of chitin. The derivatives prepared in aqueous solutions showed especially remarkable solubility; those with substitution degrees over 0.5 were readily soluble in water and highly swelled even in various common organic solvents.

INTRODUCTION

Although chitin is a readily accessible aminopolysaccharide and, next to cellulose, the second most abundant organic resource on the earth, almost all of it has been discarded. It has, however, begun to attract a great deal of attention from various aspects quite recently in both basic and applied research fields not only as an extremely underutilized biomass resource but also as a naturally occurring specialty polymer (1).

Chitin has amino groups at the C-2 positions, which are usually acetylated, and is thus anticipated to have high possibilities in exploiting utilization as a basic polymer (2). It is, however, insoluble in ordinary organic solvents and shows only limited solubility in some special solvents including dimethylacetamide containing lithium chloride and a mixture of trichloroacetic acid and dichloroethane (3-5). This is undoubtedly responsible for the delay in its extensive studies. In order to improve the solubility and explore various sophisticated functions for possible utilization, controlled substitution on the pyranose rings appears to be promising (6). In our continuing study on the chemical modifications of chitin (7) leading to the development of novel types of materials for advanced applications, it is considered of interest to examine diethylaminoethylation in view of the high potentials of chitin as a basic polysaccharide having specific structure. The resulting derivatives are expected to be highly cationic and tractable; they will find applications in various fields as adsorbents, chelating agents, water-soluble polycations, and supports for active biological species.

EXPERIMENTAL

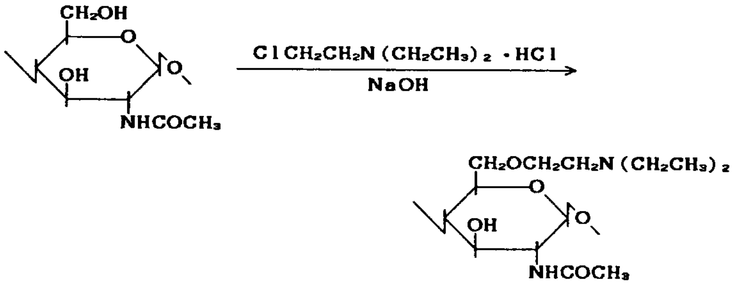
Diethylaminoethylation was carried out by treating a dispersion of powdery chitin in organic solvents with N,N-diethylaminoethyl chloride (DEAE-Cl) hydrochloride in the presence of aqueous sodium hydroxide with stirring at a given temperature. After the reaction, the product was isolated by filtration followed by washing with a mixture of acetone and methanol.

In the alternative manner, an alkali chitin solution prepared by dissolving chitin in aqueous sodium hydroxide (8) was subjected to diethylaminoethylation. After the substitution reaction at 0 °C and then at room temperature for a given time with stirring, the mixture was dialyzed and concentrated under reduced pressure. The product was N-acetylated with a mixture of acetic anhydride and pyridine (9) at 0 °C for 24 hr and isolated in acetone.

RESULTS AND DISCUSSION

N,N-Diethylaminoethylation of Chitin

Chitin is insoluble in ordinary solvents, and thus the reactions with N,N-diethylaminoethyl chloride hydrochloride were carried out on dispersions of powdery chitin in organic solvents in the presence of aqueous sodium hydroxide and also on alkali chitin solutions.



1. Reactions in organic solvents:

Powdery chitin dispersed in organic solvents was diethylaminoethylated, aqueous sodium hydroxide being used as the acid acceptor. Although the reaction of chitin with N,N-diethylaminoethyl chloride hydrochloride proceeded under heterogeneous conditions in a mixture of dioxane and aqueous sodium hydroxide solution, the chitin derivatives having diethylaminoethyl groups could be prepared fairly efficiently as shown in Table 1. Better results were, however, obtained in polar solvents such as dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO) than in dioxane probably because chitin swells in these solvents to a little extent (10). The reactions at higher temperatures generally gave higher substitution degrees.

Table 1
Diethylaminoethylation of Chitin in Organic Solvents[a]

No	Solvent	Temperature (°C)	Time (hr)	Yield (g)	Degree of substitution[b]
1	Dioxane	60	4	0.116	0.30
2	Dioxane	95	4	0.119	0.34
3	DMAc	rt	24	0.099	0.31
4	DMSO	rt	24	0.099	0.37
5	DMSO	60	4	0.057	0.77

a Chitin: 0.1 g, DEAE-Cl•HCl: 0.43 g (5-fold excess on the basis of the pyranose unit), 20% NaOH: 0.75 ml, solvent: 5 ml.
b Determined by conductometric titration.

2. Reactions in aqueous solutions:

The substitution reactions were then conducted under homogeneous conditions using alkali chitin solutions containing 1.4% of chitin and 12% of sodium hydroxide. N,N-Diethylaminoethyl chloride hydrochloride was added in the form of aqueous solution. In these reactions, however, deacetylation of chitin took place to small extents as a side reaction along with the expected substitution owing to the homogeneous reaction in aqueous alkaline solution. The free primary amino groups at the C-2 positions were thus acetylated with acetic anhydride and pyridine after dialysis of the resulting reaction mixtures.

Table 2
Diethylaminoethylation of Chitin in Aqueous Solutions[a]

No	DEAE-Cl•HCl (g)	Temperature	Time (hr)	Yield (g)	Degree of substitution[b]
6	0.43	rt	24	0.489	0.30
7	2.15	rt	24	0.596	0.56
8	4.30	rt	2	0.465	0.31
9	4.30	rt	24	0.423	0.78

a Chitin: 0.5 g in 35 ml of 12% NaOH, DEAE-Cl•HCl: a given amount (equimolar to 10-fold excess on the basis of the pyranose unit) dissolved in 10 ml of water. The reaction was carried out at 0 °C for 2 hr and then at room temperature for a given time.
b Determined by conductometric titration.

The results of substitution in aqueous solution with varying amounts of the hydrochloride are summarized in Table 2. Compared to the reactions under heterogeneous conditions, the substitutions in solution proved to proceed quite efficiently to achieve high substitution degrees and resulted in better reproducibility which makes easier the control of the extent of substitution.

Characterization of the Products

Although not marked differences were observed in the IR spectra on substitution, the absorptions at 2965 cm^{-1} due to C-H stretching and at 1000-1150 cm^{-1} due to C-O-C stretching became stronger, supporting the occurrence of substitution. The ^1H NMR spectra in deuterium oxide showed peaks at 1.05 ppm for the methyl and at 2.64 ppm for the methylene in diethylaminoethyl groups in addition to that at 2.04 ppm for the acetyl protons.

The amount of substituents introduced into chitin could be estimated by several methods. Among them conductometric titration turned out to be most appropriate, and the average extent of substitution per pyranose ring was determined reliably.

Properties of Diethylaminoethylated Chitins

The resulting derivatives were obtained as white to pale tan powdery materials. They tended to assume darker colors when prepared in polar solvents at elevated temperatures than in dioxane. The products prepared in aqueous solutions were white to off-white.

Qualitative solubilities of the diethylaminoethylated chitins were examined in excess solvents at room temperature. The affinity to solvents generally increased with an increase in the substitution degree. The derivatives prepared in organic solvents showed considerable swelling ability in water, DMSO, and dichloroacetic acid, except those with substitution degrees below 0.3 which swelled only slightly. The diethylaminoethyl-chitins prepared in aqueous solutions, on the other hand, exhibited high solubility in water and dichloroacetic acid and swelled remarkably even in common organic solvents such as benzene and alcohols in addition to polar solvents. The difference in solubility between these products prepared in different manners is interpreted reasonably in terms of the mode of substitution along the chitin backbone; the reactions in organic solvents are supposed to proceed from the particle surface leading to block-type substitution, while those in aqueous solutions result in random substitution, as in the deacetylation processes of chitin under heterogeneous and homogeneous conditions (11).

ACKNOWLEDGMENT

This research was supported in part by a grant from Science Research Promotion Fund, Japan Private School Promotion Foundation and also Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials-Design, Preparations, and Control, the Ministry of Education, Science, and Culture (#63604584).

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Accepted November 19, 1988 C