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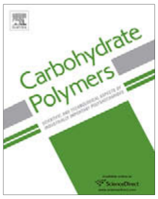

Short communication

# Chemical modification of chitosan under high-intensity ultrasound and properties of chitosan derivatives

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ABSTRACT

Chitosan (CTS), a biocompatible, biodegradable, nontoxic polymer, shows poor affinity for organic solvents. A novel chitosan derivative carrying the *p*-acetamidobenzoylate group was synthesized by the acylation reaction of chitosan with *p*-acetamidobenzoylate chloride in an acetic acid system under high-intensity ultrasound. The maximum substitution degree of the derivative was 0.42. The structure of the *p*-acetamidobenzoylate chitosan was characterized by FT-IR spectrometry, UV spectrometry and elemental analysis. The UV results showed that the derivative had good ultraviolet absorption at 273 nm. The solubility of the derivative was higher than that of chitosan. Taking advantage of the known capacity of solubility and ultraviolet absorption, the new derivative opens new possibilities for use as a sunscreen.

## 1. Introduction

Chitosan [poly (β-(1, 4)-2-amino-2-deoxy-D-glucose)] is a hydrophilic, biocompatible and biodegradable polysaccharide prepared by *N*-deacetylation of chitin, which is the main structural component of crab and lobster testae (Vasnev, Tarasov, Markova, Vinogradova, & Garkusha, 2006). Chitin is the most important natural polysaccharide after cellulose (Jose, Edward, & Eder, 2005). However, in contrast to cellulose, the systematic investigation of chitin and chitosan and their practical applications have begun relatively recently. As a natural renewable resource, chitosan possesses unique properties such as biocompatibility, biodegradability, non-toxicity and excellent film-forming ability, and has important applications in the biomedical, agriculture, functional food, wastewater purification, environmental protection, biotechnology and cosmetics domains (Marguerite, 2006; Ravi Kumar, 2000; Kima et al., 2006).

Although chitosan should be useful for even more numerous applications, its use is severely limited sever limitations because it is insoluble in neutral or alkaline media owing to its compact crystalline structure Cravotto, Tagliapietra, Robaldo, & Trotta, 2005). Various chitosan derivatives have been designed to improve its solubility. So reactivity is an important requisite to make possible versatile molecular designs leading to novel functional materials. Chitosan and many of its derivatives have chelating ability towards transition metal ions and some have special ability to absorb ultraviolet radiation. For instance, chitosans carrying phosphonic groups might chelate calcium ions (Heras, Rodriguez, Ramos, & Agullo, 2001), and 3,4,5-trimethoxy benzoylate chitosan might have good ultraviolet absorption (Chen, Duo, Luo, & Tan, 2004).

In this paper, we reported an efficient method for the improvement of the solubility of chitosan in neutral aqueous media by a mild and convenient acylation reaction, on the basis of which the ultraviolet absorption was investigated (Scheme 1).

## 2. Experimental

### 2.1. Materials

Chitosan ($1.0 \times 10^5$ molecular weight, 97% deacetylation) was purchased from Qingdao Haihui Bioengineering Co., Ltd. (Qingdao, China). Paraaminobenzoic acid was obtained from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Thionyl chloride was purchased from Tianjin Biaozhun Technology Co., Ltd. (Tianjin, China). Acetic anhydride was provided by Chengdu Top Chemical Reagents Plant (Chengdu, China). All other reagents were analytic grade.

### 2.2. Preparation of p-acetamidobenzoic acid

Paraaminobenzoic acid (10 g, 0.073 mol) was dissolved in water under plain magnetic stirring at 60 °C. Then acetic anhydride (10 ml, 0.106 mol) was rapidly added to the system under intense stirring for 30 min. After cooling to room temperature, the precipitate was collected on a filter and dried under vacuum at 60 °C.

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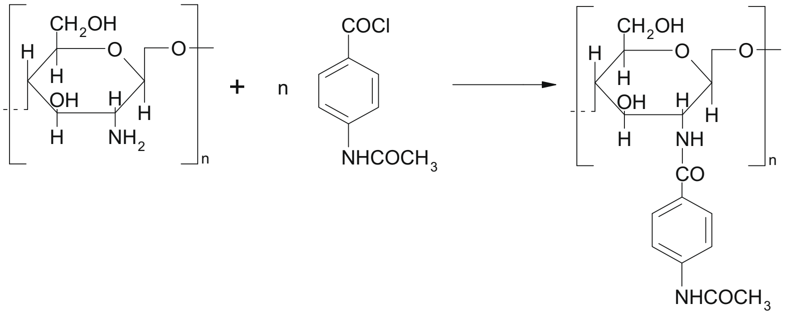


**Scheme 1.** Synthesis of *p*-acetamidobenzoylate chitosan.

### 2.3. Synthesis of p-acetamidobenzoylate chitosan

The solution of *p*-acetamidobenzoic acid (1 g, 0.006 mol) in ether (30 ml) was prepared in a three-necked flask and thionyl chloride was simultaneously added under stirring at 30 °C for 15 min. Then chitosan (0.5 g, 0.0031 mol) dissolved in acetic acid was added in *p*-acetamidobenzoyl chloride solution under high-intensity ultrasound (18 kHz, 200 W) for 1 h at 25 °C. The product was precipitated into 50 ml acetone, filtered off and dipped in a mixture of ethanol and ether (1:1 v/v) for 24 h. The precipitate was collected by filtration and dried in vacuum at 50 °C for 6 h.

The same reaction was carried out under plain stirring at 25 °C.

### 2.4. Characterization of p-acetamidobenzoylate chitosan

#### 2.4.1. Solubility test

Chitosan (0.1 g) and its derivative (0.1 g) were placed in 10 ml water and 10 ml organic solvents, respectively.

#### 2.4.2. IR spectroscopy

The IR spectra of the compounds were measured in the 4000–500 $cm^{-1}$ regions using a Nicolet Avatar 360 FT-IR spectrometer with KBr pellets.

#### 2.4.3. UV spectroscopy

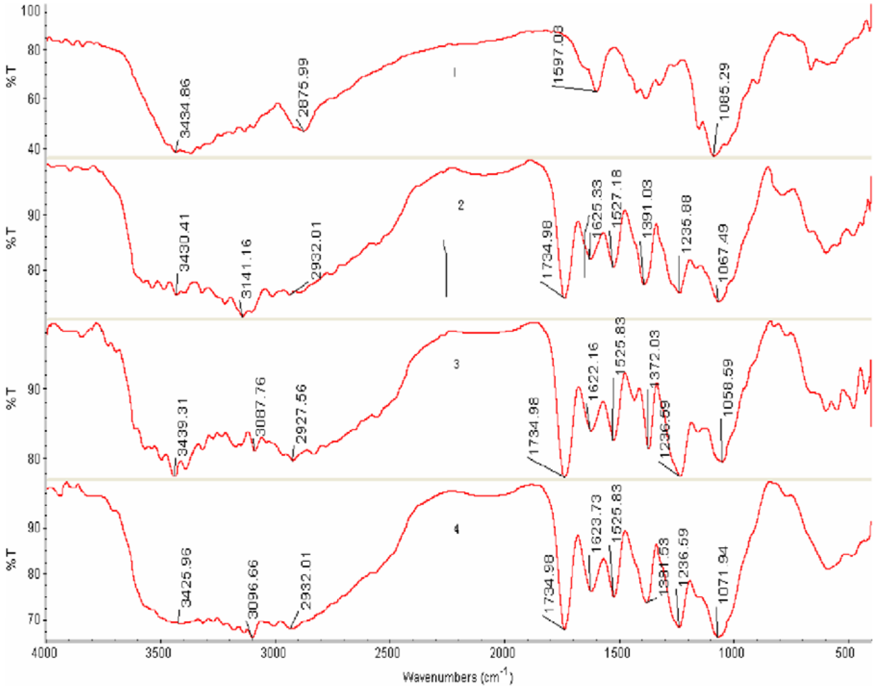
UV absorption spectra were obtained using a Shimadzu UV-2550 spectrophotometer in the range of 200–400 nm.

#### 2.4.4. Calculation of substitution degrees

The substitution degree (SD) was determined based on the elemental analysis data.

## 3. Results and discussion

Fig. 1 shows the IR spectrum of the starting chitosan and *p*-acetamidobenzoylate chitosan in different quantity ratios. As can be seen, the spectrum of chitosan presents the following bands: axial stretching of the OH group at 3434.86 $cm^{-1}$, an amide I band at 1598.03 $cm^{-1}$, and $CH_3$ symmetrical angular deformation at 1385.60 $cm^{-1}$, in addition to the other characteristic polysaccharide bands at 1152.30 and 1085.29 $cm^{-1}$ (Batista, Pintoa, Gomes, & Gomes, 2006). In comparison with the chitosan IR spectrum, the *p*-acetamidobenzoylate chitosan spectra display a new absorption peak at 1734.98 $cm^{-1}$, corresponding to the C=O stretching mode of the carboxyl-functionalized substituents.



1 : chitosan ; 2 : quantity ratio=1:1 ; 3 : quantity ratio=1:2 ; 4 : quantity ratio=1:4.

**Fig. 1.** FT-IR spectra of chitosan and its derivatives in different quantity ratios.

**Table 1**
Synthesis conditions of *p*-acetamidobenzoylate chitosan with different degrees of substitution under high-intensity ultrasound (Jiangtao Wang).

| Sample number | Chitosan: *p*-acetamido-benzoic acid quality ratio | Reaction time (h) | Reaction temperature (°C) | SD |
|---|---|---|---|---|
| 1 | 1:1 | 1 | 25 | 0.08 |
| 2 | 1:2 | 1 | 25 | 0.23 |
| 3 | 1:4 | 1 | 25 | 0.16 |
| 4 | 1:2 | 1.5 | 25 | 0.28 |
| 5 | 1:2 | 2 | 25 | 0.23 |
| 6 | 1:2 | 2.5 | 25 | 0.19 |
| 7 | 1:2 | 1 | 15 | 0.16 |
| 8 | 1:2 | 1 | 35 | 0.13 |
| 9 | 1:2 | 1 | 5 | 0.10 |
| 10[a] | 1:2 | 1.5 | 25 | 0.42 |

[a] Chitosan solution in 10 ml acetic acid and 10 ml dimethylacetamide.

**Table 2**
Synthesis conditions of *p*-acetamidobenzoylate chitosan with different degrees of substitution under plain stirring (Jiangtao Wang).

| Sample | Chitosan/*p*-acetamido-benzoic acid quantity ratio | Reaction time (h) | Reaction temperature (°C) | SD |
|---|---|---|---|---|
| 1 | 1:2 | 3 | 25 | 0.08 |
| 2 | 1:2 | 4 | 25 | 0.10 |
| 3 | 1:2 | 5 | 25 | 0.16 |
| 4 | 1:2 | 6 | 25 | 0.15 |

Table 1 demonstrates the synthesis conditions of *p*-acetamidobenzoylate chitosan with different degrees of substitution (SD) under high-intensity ultrasound. SD can be widely varied from 0.06 to 0.42. The results in Table 1 confirm that a higher temperature or a prolonged time was not effective to further improve the SD. The SD reached 0.42 under optimal conditions.

Table 2 shows that attempt to raise the SD by carrying out the reaction under plain stirring were not successful. The SD was only 0.16 under plain stirring in comparison to 0.42 under high-intensity ultrasound.

Acetic acid solution has no obvious absorption peaks from 200 nm to 400 nm. So chitosan solution (0.1 g/L) and its derivative solutions (0.1 g/L) were prepared in the acetic acid solution (1 g/L) (Chen et al., 2004; Dong et al., 2005). Fig. 2 shows the UV spectra of the *p*-acetamidobenzoylate chitosan and chitosan solution. The UV spectrum of the *p*-acetamidobenzoylate chitosan solution has an absorption peak at 273 nm, while the chitosan solution (0.1 g/L) has no absorption peaks from 220 nm to 400 nm. Certainly, according to the solubility test, the chitosan derivative shows excellent solubility with respect to chitosan, especially in water.

## 4. Conclusion

The peculiarities of chemical modification of chitosan have been studied and shown. The SD of *p*-acetamidobenzoylate chitosan reached 0.42 under optimal conditions. The chemical identity of the *p*-acetamidobenzoylate chitosan was assessed by FT-IR, UV spectrometry. It was demonstrated that it has the expected molecular structure of *p*-acetamidobenzoylate chitosan. The product is soluble in water, glycol and dimethylacetamide. It undoubtedly widens the scope of application of chitosan-based materials.

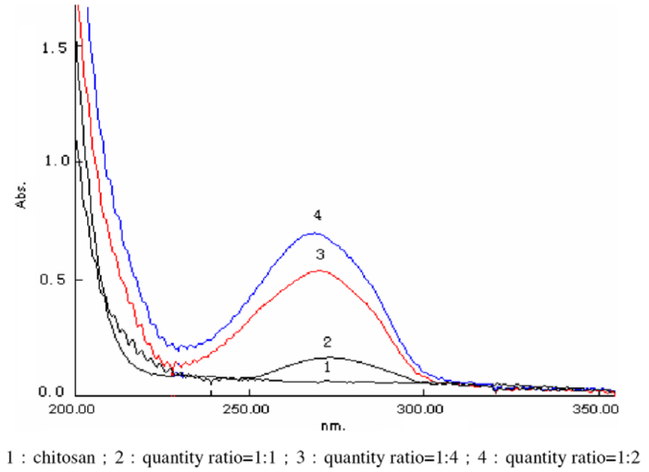


**Fig. 2.** UV spectra of the *p*-acetamidobenzoylate chitosan and chitosan.

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