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# Preparation and Characterization of Quaternized Chitosan Under Microwave Irradiation

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For the first time, N-(2-hydroxyl) propyl-3-trimethyl ammonium chitosan chloride (HTCC) was prepared through a fast, easy and efficient method with the assistance of microwave irradiation, and the quaternized chitosan was also degraded via the microwave irradiation. A comparative study was performed by using the conventional heating method to prepare HTCC. The structure and property of the quaternized chitosan obtained by these two methods were characterized by GPC, XRD, FTIR, NMR, TG and elemental analysis. It was shown that quaternized chitosan was successfully prepared within 50 min via microwave irradiation method, while a much longer time of 6–7 h was needed with the conventional heating method. The substitutions both occurred on the C2 position of chitosan with the two different methods, and their HTCC products had weight average similar molecular weight (M<sub>w</sub>), structure and thermal stability. The HTCC prepared by the microwave irradiation method had a little lower degree of substitution (DS) than those prepared via conventional heating with the same mole ratio (6:1) of the intermediate to chitosan. The degradation study showed that the M<sub>w</sub> of HTCC decreased rapidly from  $4.6 \times 10^5$  to  $1.1 \times 10^5$  in 1 h under microwave irradiation, while it only decreased from  $4.6 \times 10^5$  to  $2.1 \times 10^5$  in 1 h through conventional heating degradation. These results revealed that microwave irradiation is a more efficient and environment-friendly way to obtain the water-soluble chitosan derivatives and their degraded products.

**Keywords:** Quaternized chitosan, microwave irradiation, conventional heating, thermal stability

## 1 Introduction

Chitosan, the only alkaline polysaccharide in nature, is a copolymer of  $\beta$ -(1,4)-2-acetamido-2-deoxy-D-glucose and  $\beta$ -(1,4)-2-amino-2-deoxy-D-glucose units. It receives great attention in the field of biology and medicine owing to its good biocompatibility, biodegradability, bioadhesivity, nontoxicity and bioactivities, such as antibacterial, antitumor etc. (1–3). However, chitosan is difficult to dissolve in most organic solvents, water and alkali, only soluble in certain dilute acid and very few organic solvents, which limits its widespread applications (2).

Interestingly, the molecular structure of chitosan contains many active groups, which can be modified by a variety of chemical reactions to form water-soluble derivatives

with improved physical and chemical properties and physiological functions (1,2), and the introduction of quaternary ammonium salt on chitosan molecules is of particular interest in the chitosan derivatives research field (4–8). Compared with chitosan, quaternized chitosan is not only soluble in water, but also has an increased charge density. It has potential to be used as an absorption enhancer across intestinal epithelial due to its mucoadhesive and permeability enhancing property, and is very suitable for biomedical application, especially for the delivery of drugs, vaccines and genes (5,6,9).

Quaternized chitosan is usually prepared by a conventional heating method, which is time-consuming (6 h–3 days) (5,10,11). Compared with routine heating treatment, microwave irradiation, as a more efficient heating method due to its rapid heating and energy penetration, has been applied in many area (12,13). Currently, many microwave-based simple, fast and energy-efficient routes have been developed to synthesize soluble chitosan derivatives (11,14).

In this paper, we prepared N-(2-hydroxyl) propyl-3-trimethyl ammonium chitosan chloride (HTCC) and

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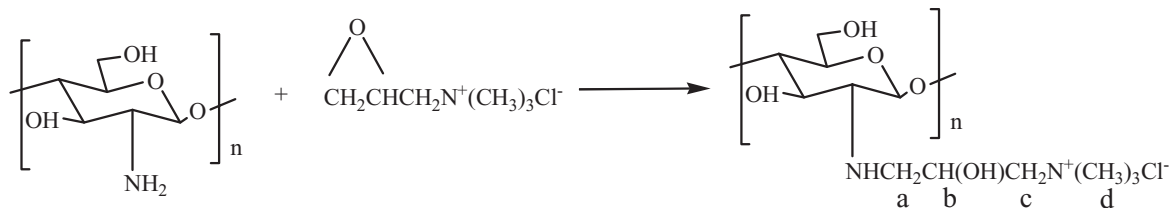


Fig. 1. The scheme of synthetic route for HTCC.

degraded it via microwave irradiation for the first time. A conventional heating method was also performed in the synthesis and degradation of quaternized chitosan for comparative studies, GPC, XRD, FTIR, NMR, TG and elemental analysis were employed to characterize the structure and property of quaternized chitosan obtained by these two methods.

## 2 Experimental

### 2.1 Materials

Chitosan (CS) from shrimp shell was obtained from Zhejiang Golden-shell Biochemical Co. Ltd. (Taizhou, China). The degree of deacetylation was 92% (determined by elemental analysis) and its weight average molecular weight was  $4.5 \times 10^5$  (determined by the GPC method). 2,3-Epoxypropyltrimethyl ammonium chloride (EPTMAC), the intermediate for preparing quaternized chitosan, was purchased from Dongying Guofeng Fine Chemical Co. Ltd. (Shandong, China). All other chemicals were of analytical grade.

### 2.2 Synthesis of Quaternized Chitosan

#### 2.2.1. Conventional Heating Method

Chitosan (2.0 g, 12.3 mmol) was dispersed in isopropyl alcohol (20.0 ml) and the solution was adjusted to pH 9. EPTMAC (7.48 g, 49.2 mmol) was dissolved in water and added to chitosan suspension at 80°C. The mole ratio of EPTMAC to amino groups of chitosan was 6. After reaction for 6 h at 80°C, the reaction mixture was precipitated by acetone, dialyzed, and finally freeze-dried at -50°C to obtain quaternized chitosan, as designed HTCC1; the reaction route is given in Figure 1.

#### 2.2.2. Microwave Irradiation Method

The preparation of quaternized chitosan via microwave irradiation was similar to the above method. The difference was that the reaction time was controlled in only 50 min in XH-100B microwave irradiation apparatus (Beijing, China). The quaternized chitosan was designed as HTCC2.

### 2.3 Degradation of Quaternized Chitosan

HTCC powder (2 g) was solved in 50 ml deionized water, a desired volume of hydroperoxide was added and then the solution was placed in the microwave irradiation or conventional heating for a predetermined time to yield HTCC with various molecular weights. The condition of microwave irradiation was as follows: microwave power was 700W, and microwave temperature was 50°C; the temperature under conventional heating was also 50°C.

### 2.4 Characterization of HTCC

FT-IR spectra were recorded in KBr pellets on a Nicolet FT-IR 8201 spectrophotometer (Madison, USA) by the transmission method.

The X-ray diffraction (XRD) experiment was performed using a D8 Advance diffractometer (Bruker, Germany) with Cu target and  $K\alpha$  radiation ( $\lambda = 0.15418$  nm) at 40 KV and 50 mA. The scanning rate was 4°/min and the scanning scope of  $2\theta$  was 5–45° in a fixed time mode at room temperature.

<sup>1</sup>H-NMR spectra were recorded on a DRX-400 spectrometer (Bruker, Germany) and chemical shifts were given by taking methanol as reference in D<sub>2</sub>O at 323 K.

Thermogravimetric analysis (TGA) was performed using a Setaram Setsys 16 TG/DTA/DSC (France) under nitrogen atmosphere of 0.15 MPa from 25–600°C at a heating rate of 10°C/min.

Weight-average molecular weights (M<sub>w</sub>) of samples were measured by Gel Permeation Chromatography (GPC) typed with 1515 Breeze (Waters, USA). The eluent was 0.2 mol/lCH<sub>3</sub>COOH-0.1 mol/lCH<sub>3</sub>COONa at a flow rate of 0.50 mL/min. All of the HTCC solutions were purified by a 0.45 μm filter and then degassed before use. The injection volume was 200 μl with a concentration of 5 mg/ml for the sample.

The degree of substitution (DS) of the quaternization group on chitosan was determined by elemental analysis and the potentiometry (15). Elemental analysis was performed via elemental analyzer typed Vario EL III (Elementar, Germany), DS was calculated by obtained C, N, and O content. Potentiometric titration of the chloride ion on HTCC was carried out with the aqueous silver nitrate, using a calomel electrode as the reference, and a silver

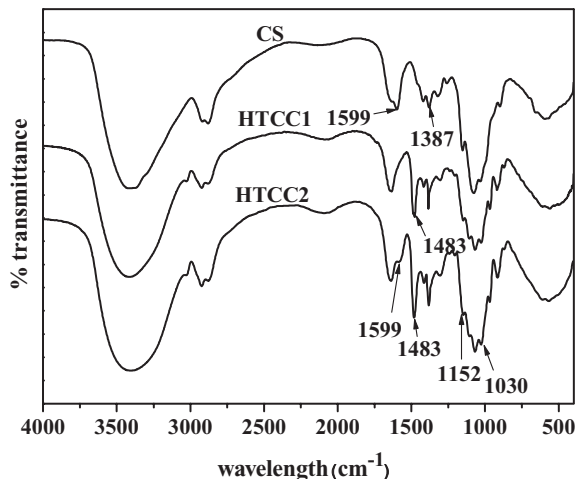


Fig. 2. FTIR spectra of chitosan and two quaternized chitosans.

electrode for the measurement. DS is calculated according to a given equation as reference 15.

### 3 Results and Discussion

#### 3.1 FTIR and NMR Spectra

FTIR spectra of chitosan and the quaternized chitosan samples obtained by two methods are shown in Figure 2. According to the spectra, the characteristic peak ( $1599\text{ cm}^{-1}$ ) ascribed to  $\text{NH}_2$  deformation vibration in chitosan was weakened in the spectrum of HTCC2 and disappeared in the spectrum of HTCC1. In the mean time there appeared a new peak positioned at  $1483\text{ cm}^{-1}$  (belonging to the methyl groups in the quaternary ammonium salt). The characteristic peaks of primary alcohol and secondary alcohol positioned between  $1152$  and  $1030\text{ cm}^{-1}$  did not change in both quaternized chitosan samples compared with original chitosan. The results proved that the chemical modification of chitosan with EPTMAC resulted in the *N*-monosubstitution on C2 position of chitosan, which coincided with the previous study (7, 8). Furthermore, the band at  $1599\text{ cm}^{-1}$  was weaker in the spectrum of HTCC2 than that of HTCC1, which reveals that the degree of the substitution of the quaternary ammonium salt on chitosan under microwave irradiation was lower than that obtained by conventional heating.

The NMR method is the most effective technique to determine the structure of chitosan derivatives (7). Figure 3 exhibits  $^1\text{H-NMR}$  spectra of the two quaternized chitosans. It is obvious that two spectra were quite similar. The most intensive signal at  $\delta = 3.14\text{ ppm}$  corresponded to the methyl protons of the quaternary ammonium salt. The peaks at  $\delta = 4.51, 2.48, 3.59, 3.71, 3.65$  and  $3.89\text{ ppm}$  were attributed to H-1, H-2, H-3, H-4, H-5 and H-6, respectively. The chemical shifts at  $2.71, 4.25$  and  $3.35\text{ ppm}$  belonged

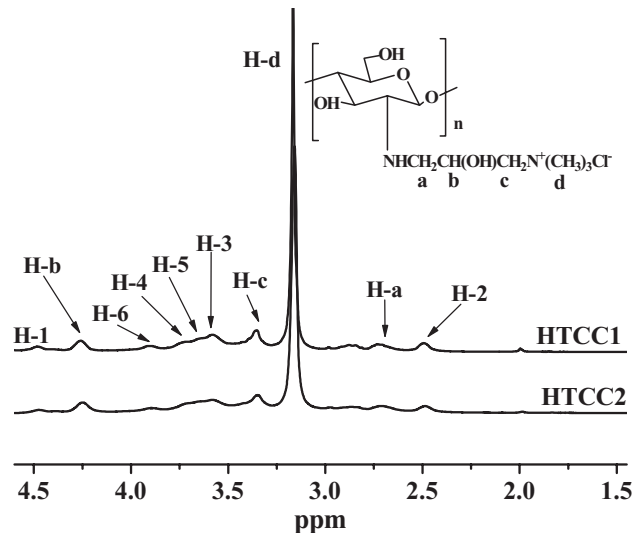


Fig. 3.  $^1\text{H-NMR}$  spectra of two quaternized chitosans.

to H-a, H-b and H-c of the substituted groups, this was in agreement with the reported studies (7, 8).

The FTIR and NMR results showed that quaternized chitosan were successfully synthesized under microwave irradiation.

#### 3.2 XRD Analysis

The X-ray diffraction patterns of chitosan and the synthesized quaternized chitosans are presented in Figure 4. Chitosan exhibits two characteristic crystalline peaks at  $2\theta = 11^\circ$  and  $20^\circ$ , while two quaternized chitosans contained only one broad diffraction peak centered at  $2\theta = 22^\circ$ , suggesting an amorphous structure, the reason may be explained that as proved by FTIR analysis, the quaternary ammonium group — 2,3-epoxypropyltrimethyl ammonium chloride was grafted onto  $\text{NH}_2$  sites on the C2

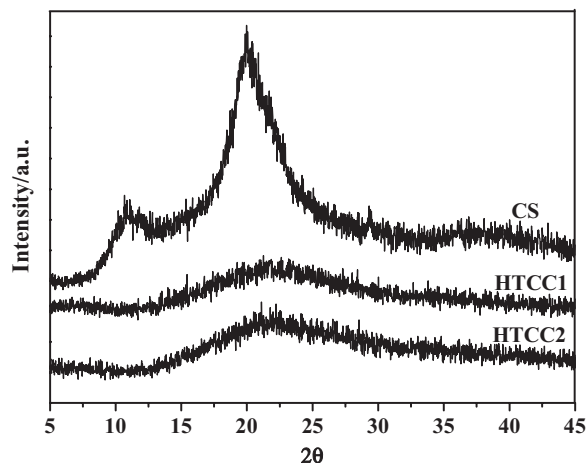


Fig. 4. XRD patterns of chitosan and two quaternized chitosans.

**Table 1.** Degree of substitution of quaternized chitosans obtained by two methods

	<i>DS determined by potentiometry (%)</i>	<i>DS determined by elemental analysis (%)</i>
Microwave irradiation method	88.5	86.7
Conventional heating method	96.1	94.8

position of pyranoid ring in chitosan, which destroyed the symmetry and regularity of chitosan chain and the intramolecular hydrogen bonding between NH<sub>2</sub> and OH, then broke the crystallization capacity significantly, so the derivative polymer was completely amorphous. The result is consistent with the previous study (16). In addition, it can be found that the broad diffraction peak of HTCC1 was a little weaker than that of HTCC2, which implies that the microwave irradiation method destroyed the crystallinity less seriously than the routine heating method. One possible reason is that the consumed time via the former was much shorter than that of the latter. Another explanation may be that the degree of substitution of the quaternary ammonium salts prepared by the former method, which derived from the FTIR analysis, was lower than that obtained by the latter one.

**3.3 DS and Mw**

It was reported that DS of the quaternary group on chitosan was affected greatly by the mole ratios of EPTMAC to chitosan (16), and the potentiometry was the most common method to obtain the DS thus far. In this work, the elemental analysis was also used to determine the DS finally. From Table 1, it can be observed that when the mole ratios of EPTMAC to chitosan were 6:1, the DS determined by two methods were not very different. Microwave irradiation can also induce high DS of the quaternary group on chitosan despite the short reaction time of 50 min, which proved the high efficiency of microwave irradiation. However, the DS obtained by microwave irradiation was a little lower than that achieved by routine heating, which confirmed the FTIR results.

From the GPC measurement we determined that the weight average molecular weight (Mw) of HTCC1 was

**Table 2.** Mw of quaternized chitosan in different degradation times via two methods

	<i>0 min</i>	<i>30 min</i>	<i>60 min</i>
Microwave irradiation method	$4.6 \times 10^5$	$3.0 \times 10^5$	$1.1 \times 10^5$
Conventional heating method	$4.6 \times 10^5$	$3.6 \times 10^5$	$2.1 \times 10^5$

**Table 3.** The content of C,N,H in quaternized chitosan before and after degradation via microwave irradiation

	<i>N</i>	<i>C</i>	<i>H</i>
Mw = 4.6	7.52	39.11	9.94
Mw = 1.1	7.35	38.62	10.28

$4.7 \times 10^5$ , while Mw of HTCC 2 was  $4.6 \times 10^5$ , there was no great difference between the two results.

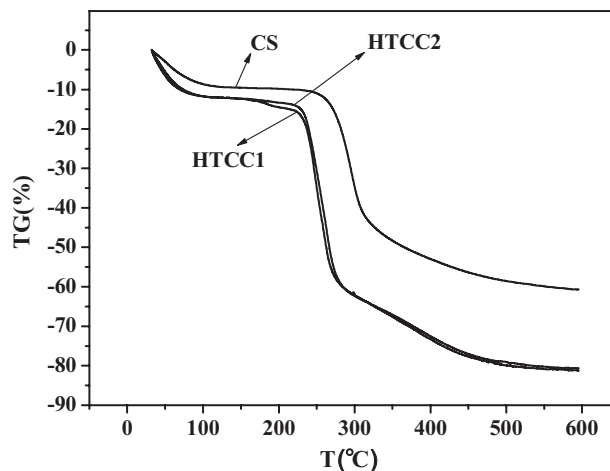
**3.4 Degradation of Quaternized Chitosan**

In order to further prove the high efficiency of microwave irradiation, the comparative degradation through two methods were studied. As shown in Table 2, the weight molecular weight of quaternized chitosan was degraded from  $4.6 \times 10^5$  to  $3.0 \times 10^5$  in 30 min and  $1.1 \times 10^5$  in 1 h under microwave irradiation, while to only  $3.6 \times 10^5$  in 30 min and  $2.1 \times 10^5$  in 1 h through the routine heating method. The result further indicated that microwave irradiation was a more efficient method than the conventional heating method.

Table 3 lists the element content in quaternized chitosan before and after degradation via microwave irradiation. Basically, the content of C, H, N between before degradation and after degradation was not different, which implied that the basic structure of quaternized chitosan did not change under efficient microwave irradiation.

**3.5 Thermogravimetric Analysis**

Figure 5 shows TG thermograms of chitosan and two quaternized chitosans. Obviously, these curves of quaternized chitosan are similar to that of chitosan, which exhibits two discrete weight losses corresponding to the loss of water and the degradation of polymer chains (17,18). T<sub>max</sub> (the



**Fig. 5.** Thermogravimetric curves of chitosan and two quaternized chitosans.

temperature when the rate of weight loss reaches a maximum) of chitosan was observed to be at 296°C, in contrast,  $T_{\max}$  of both quaternized chitosans were lower, which were observed to be at 262.77°C for HTCC1 and 260.75°C for HTCC2, respectively. The fact primarily revealed that the thermal stability of chitosan was weakened after the modification by the quaternary ammonium salt. Moreover, it can be found that the remaining weight of chitosan at 600°C was 39.4%, but those of quaternized chitosans samples were only 19.9% and 19.2%, respectively, which further indicated that the thermal stability of both quaternized chitosans were close to but a little lower than chitosan. This can be explained that the crystal of chitosan was destroyed after the substitution, which was in agreement with XRD analyses.

#### 4 Conclusions

Quaternized chitosan was successfully synthesized in only 50 min under microwave irradiation. Its Mw, structure and thermal stability were similar to those of the quaternized chitosan achieved by a conventional heating method for 6 h's reaction. The DS of quaternary group on chitosan obtained by microwave irradiation method was a little lower than that of the products obtained via a conventional heating method. The degradation study on quaternized chitosan further proved that microwave irradiation was a fast, easy and efficient method, and it can induce fast degradation without any structure change.

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