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Synthesize and Characterization of Hydroxypropyl-N-octanealkyl Chitosan Ramification

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Abstract. A new type of amphiphilic ramification, hydroxypropyl-N-octanealkyl chitosan was prepared from chitosan via hydrophilic group and hydrophobic group were introduced. We could protect the amino group of chitosan via the reaction of chitosan and benzaldehyde could get Schiff base structure. Structures of the products were characterized with FT-IR, elemental analysis, themogrammetry (TG) analysis and X-ray diffraction. The degree of substitution of hydrophobic group was studied by elemental analysis. The result showed this chitosan ramification was soluble, biocompatible, biodegradable and nontoxic.

1. Introduction
Chitosan (CS) is a natural polymer which were prepared by deacetylation of chitin. In addition to cellulose, chitosan is the second richest biological resources, which were widely found in the cell walls of insects, crustaceans and fungi[1]. As a type of compatible and biodegradable material, chitosan shows good performance of biocompatible, biodegradable, nontoxic and highly antimicrobial[2]. It was widely used in chemical industry, environmental protection, cosmetics, medicine, food, agriculture and other fields[3]. As many strong hydrogen bonds between the chitosan molecules, chitosan is neither soluble in water nor soluble in ordinary organic solvents, limiting its application[4, 5].

Chitosan molecules have large of -OH and –NH₂ groups, the introduction of active groups on -OH and –NH₂ can improve its solubility. In recent years, it has been reported that chitosan can be modified by alkylation, acylation, etherification, carboxylation modification, Shiff alkali reaction modification[6-10]. But final products were mixture of chitosan derivatives, because of most of the modification did not take effective selective response. Active groups of chitosan in different positions can react. Therefore, it is necessary to selective control reaction of chitosan to obtain higher purity chitosan derivative[11].

In this study, we aimed to prepare a type of amphiphilic ramification of hydroxypropyl-N-octanealkyl chitosan(HP-N-OA-CS). The hydrophobic group and hydrophilic group were introduced to chitosan definitely. After the modification, the solubility of chitosan in water was improved greatly.

2. Experimental
2.1. Materials
Chitosan was bought from the Shanghai reagent co., China. Sodium hydroxide, acetone, isopropyl alcohol was bought from Jinan chemical Co. Ltd China. Glacial acetic acid was bought from Yantai Luyang chemical Co. Ltd, China Ethanol was bought from Zibo chemical Co. Ltd, China.
2.2. Synthesis
50ml sodium hydroxide solution (40%) and 5g chitosan were added in the flask, while kept for 3h while stirring at 120 °C. Washing to neutral twice by distilled water at 25 °C. The products were percolated and washed with ethanol twice and vacuum drying. 1g chitosan was added in the miscible liquids of 40ml 11% acetic acid and 100ml methanol solution while stirring. 6.7g benzaldehyde was added in the miscible liquids at 60 °C and this mixture was kept for 24h while stirring. The products were percolated and washed with ethanol twice at 25 °C. Benzaldehydeimine chitosan was prepared after vacuum drying at 50 °C. 1g benzaldehydeimine chitosan was added in the miscible liquids of 40ml isopropyl alcohol and 2ml 20% NaOH solution was kept for 2h while stirring, then adding 3.4g propylene oxide to the mixture at 45 °C and kept for 24h while stirring. The products were adjusted degree of pH was 6-7 at 25 °C. Products were percolated washed with ethanol. The products were prepared after vacuum drying at 50 °C. 1g hydroxypropyl-N-benzaldehydeimine chitosan (HP-N-BM-CS) was added in the miscible liquids of 40ml ethanol and 10ml 10% hydrochloric acid was kept for 15h while stirring at 30 °C. The product was filtered with acetone and washed with ethanol. Then vacuum drying at 50 °C. 1.3 g hydroxypropyl chitosan was added in the miscible liquids of 30 mL isopropyl alcohol and 4ml 20% Sodium hydroxide solution was kept for 10min while stirring at 70 °C. Then added 2.24g bromooctane in the miscible liquids and kept for 5h. The HP-N-OA-CS was percolated and washed with ethanol.

2.3. Instrumentation
Products which in KBr tablet were characterized by IR. The results were recorded on IRPrestige-21 Fourier-transform infrared spectrometer.
  - Elemental analysis of products was analyzed by Element KAI DI KD-1000 analyzer.
  - X-ray diffraction spectrometry was analyzed by an Shimadzu XRD—6100 X-Ray Diffractometer.
  - Thermogrammetry (TG) analysis analyzed by Netzsch TG 209-F3 thermogravimetric analysis.

3. Results and discussion
3.1. IR spectra analysis
The disappearance of aromatic peaks at 1501 cm⁻¹, 1581 cm⁻¹, 1600 cm⁻¹ and C=N characteristic absorption peak at 1634.5 cm⁻¹, which showed Schiff base had disappeared (Fig 1). The peaks at 3432.8 cm⁻¹ attributed to association reaction of hydroxy group and 1058.7 cm⁻¹ attributed to stretching vibration of carbonyl. Asymmetric stretching vibration of C-O-C at 1060-1150 cm⁻¹ had enhanced largely. These indicated that hydroxypropyl group had introduced to −OH. In the IR spectra of HP-N-OA-CS (c). The peaks at 2968 cm⁻¹, 1465 cm⁻¹ attributed to stretching vibration absorption of −CH₃, 1375 cm⁻¹ attributed to umbrella vibration absorption of −CH₃ and 2922 cm⁻¹ attributed to asymmetric stretching vibration of −CH₂. At the same time, the weaken of peak of amino indicated that alky group has introduced to amino.

![Fig.1 IR spectra of (a) CS, (b) HPCS, (c) HP-N-OA-CS](image-url)
3.2. Elemental analysis

We could got the content of C, H, N in product through by an Element P-E 240C analyzer and calculated the degree of substitution by the ratio of C / N. The formulas were, ① $C/N = 12 \times \frac{[6+2(1-A)]}{14}$, A was the degree of deacetylation of chitosan. ② $C/N = 12 \times \frac{[13B+6(1-B)]}{14}$, B was the degree of substitution of benzaldehydeimine. ③ $C/N = 12 \times \frac{[9C+6(1-C)]}{14}$, C was the degree of substitution of hydroxypropyl group. ④ $C/N = 12 \times \frac{[1.32 \times 3+6(1-D)+(6+8)D]}{14}$, D was the degree of substitution of octanealkyl group. We could get a group of data from estimate. The degree of deacetylation of CS was 95.7%, the degree of hydroxypropyl substitution of hydroxypropyl chitosan was 13.2%. Degree of hydrophobic substitution of HP-N-OA-CS was 31.46%.

Table 1 The data from elemental analysis of HP-N-OA-CS

| Element | CS   | (HP-N-BM-CS) | HPCS | HP-N-OA-CS |
|---------|------|--------------|------|------------|
| C (%)   | 41.0 | 57.64        | 34.99| 28.02      |
| H (%)   | 8.04 | 7.27         | 7.19 | 5.79       |
| N (%)   | 7.55 | 5.09         | 3.01 | 2.62       |

3.3. The results of X-ray diffraction

X-ray diffraction spectra of CS and its derivative were shown in Fig.2. CS had two diffraction peak at $2\theta=10^\circ$ and $20^\circ$. The reflection fell at $2\theta=20^\circ$ was assigned to perfect crystal forms, with strong hydrogen bonds between chitosan molecules. When X-ray diffraction peak of HP-N-OA-CS seemed to be a line. It indicated the original crystallinity of chitosan was destroyed.

![Fig.2 XRD spectra of (a) CS, (b) HP-N-OA-CS](image)

3.4. TG analysis

The fig.3 showed the weight of chitosan had few change at temperature of 20 to 850°C, because the original crystallinity of chitosan was very strong. The weight of Hydroxypropyl-N-benzaldehydeimine chitosan had a few decrease at 20 to 100 °C because of water it contained. The weight continued to decrease at 180 to 330 °C and 560 to 800 °C. It’s the degradation of main chain and branched chain. All these evidence affirmed that HP-N-OA-CS has low thermal stability and it’s crystallinity was damaged. The results same as X-ray diffraction.
4. Conclusion
In this study, we protected amino group of chitosan and introduced hydrophilic group to hydroxy group of chitosan. At last got the HP-N-OA-CS. And we estimated the degree of hydrophobic substitution of HP-N-OA-CS by elemental analysest. The last product was soluble, biocompatible, biodegradable and nontoxic. It had the character of polymer surfactant. In a word, the new type of amphiphilic ramification of chitosan could be widely used in many fields.

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