

Homogeneous Synthesis and Characterization of Quaternized Cellulose Derivatives in NaOH-urea Aqueous Solutions

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Abstract: Quaternized cellulose (QC) derivatives were synthesized by reacting cellulose with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) in an aqueous solution of NaOH-urea. The chemical structures and physical properties of the obtained QC derivatives were characterized using nitrogen content analysis, Fourier transform infrared spectroscopy (FT-IR), ¹H-nuclear magnetic resonance (¹H-NMR), X-ray diffraction (XRD), and thermal gravity analysis (TGA). The FT-IR and ¹H-NMR results confirmed the successful introduction of cationic quaternary ammonium groups into the main chain of cellulose. A series of QC derivatives with the degree of substitution (DS) values ranging from 0.33 to 0.80 were derived by adjusting the molar ratio of CHPTAC to anhydroglucose unit (AGU) of cellulose, concentration of cellulose in the NaOH-urea solution, as well as reaction temperature and time. According to the DS values of the QC derivatives, the optimized synthetic conditions were as follows: 25°C reaction temperature, 3% cellulose in NaOH-urea solution, the molar ratio of etherification agent to glycosidic cellulose of 15:1, and 12 h reaction time. The TGA and XRD results revealed that the crystalline structure was destroyed during etherification, and the thermal stability of the QC derivatives was lower than that of cellulose.

Keywords: sodium hydroxide-urea aqueous solution; quaternized cellulose derivative; homogeneous synthesis

1 Introduction

Cellulose is the most abundant natural polysaccharide on earth. It has garnered significant attention due to its favorable properties, e. g. , low price, available, and excellent



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biocompatibility and biodegradability^[1-2]. Cellulose has large amounts of free hydroxyl groups in its backbone and can be derivatized into various high-value products, which will lead to new applications in the fields of high-value materials, chemicals, cosmetics, etc^[3-4]. However, the chemical functionalization of cellulose is hindered by its relatively low solubility in water and common organic solvents due to strong intra/inter-molecular hydrogen bonding as well as stiff crystallization structure^[5]. Cationic quaternized cellulose is a water-soluble cellulose derivative, which can be obtained via etherification. It has been commercially used in a variety of fields, including the paper, textile, food and chemical industries, owing to its hydrophilic, biodegradable, and antimicrobial properties^[6-8]. Nowadays, quaternized cellulose (QC) derivatives are usually prepared by the quaternization of water-soluble cellulose derivatives, e. g., hydroxyethyl cellulose^[9-10], or surface quaternization of pulp fiber or cotton linter cellulose^[11-12]. However, the reported preparation methods are often carried out in heterogeneous systems. Notably, the degree of substitution (DS) values of the obtained QC derivatives is typically in the range of 0.2 ~ 0.3, which is too low for use as a biomaterial, such as gene carrier or as a drug carrier. Meanwhile, the homogeneous distribution of quaternary ammonium substituents in the cellulose backbone is hard to control. A possible route to enhance the DS values of QC derivatives is to prepare QC in a homogeneous medium, in which the reactivity of the hydroxyl groups is greater than that in a heterogeneous system. However, the synthesis of QC derivatives via a homogeneous process has not been reported to date.

NaOH-urea aqueous solutions constitute a new and powerful non-derivatizing solvent system for cellulose, as the dissolution of cellulose can be achieved within 30 min. This system has been widely applied in non-pollution spinning and resulted in a novel type of man-made cellulosic fiber^[13-14]. Generally, the cationic quaternization of cellulose requires an alkaline environment. In the present work, an NaOH-urea aqueous solution was employed as the reaction medium. In addition to dissolving cellulose, NaOH generates the alkaline conditions needed for the quaternization reaction. Thus, QC derivatives

with high DS values were prepared using 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) as the etherifying agent. The chemical structures and physical properties of QC derivatives were determined using nitrogen content analysis, Fourier transform infrared spectroscopy (FT-IR), ¹H-nuclear magnetic resonance (¹H-NMR), X-ray diffraction (XRD), and thermal gravity analysis (TGA). The reaction conditions were optimized by evaluating the DS values of the prepared QC derivatives.

2 Experimental

2.1 Materials and reagents

α -cellulose with a particle size of 90 μm was provided by Aladdin-reagent Inc. (Shanghai, China) and was vacuum dried at 45°C for 48 h before use. 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC; 95% purity) was purchased from Ji'nan Europe Trading Co. Ltd., (Shandong, China) and was used as the cationic etherification agent as received without further purification. A dialysis bag with a cutoff molecular weight of 5000 was supplied by Sigma-Aldrich (St. Louis, MO, USA). All other reagents, e. g., sodium hydroxide, urea, potassium sulfate, and copper sulfate, were of analytical grade and were used as received without further purification.

2.2 Dissolution of cellulose in NaOH-urea aqueous solution

The cellulose/NaOH-urea solution was prepared according to a previously published method^[14]. The desired amounts of NaOH, urea, and distilled water with a weight ratio of 7:12:81 were added into a 250 mL beaker. After NaOH and urea were dissolved in the distilled water, the resulting solution was pre-cooled to -12°C in a low temperature cryotrapping instrument (DLSB, Gongyi Instrument Co. Ltd., He'nan, China). Subsequently, cellulose was added slowly under vigorous mechanical stirring. The solution was further stirred for 30 min at -12°C in order to obtain a transparent cellulose solution.

2.3 Synthesis of QC derivatives

A certain amount of CHPTAC (40 wt%, aqueous solu-

tion) was slowly injected into the prepared cellulose/NaOH-urea aqueous solution under vigorous mechanical stirring. The mixture was further stirred for the desired reaction time at room temperature. After neutralization with HCl (3 wt% solution), the reaction mixture was transferred into a dialysis bag and dialyzed against distilled water for several days until no precipitates remained in the dialysis medium after addition of AgNO_3 . During dialysis, the distilled water was refreshed every 6 h. The dialyzing solution was freeze-dried for 48 h to obtain the white QC derivatives.

2.4 Characterization of QC derivatives

The nitrogen content of the QC derivatives was determined using the Kjeldahl method with an automatic nitrogen analyzer (SKD-800, Peiou instrument company, Shanghai, China). The DS value was calculated using equation (1):

$$DS = \frac{162 \times N}{(14 - 151.5 \times N)} \quad (1)$$

where 162, 14 and 151.5 were the relative molar weight of the glucosic unit of cellulose, nitrogen, and the quaternary ammonium group, respectively; N was the nitrogen content.

The FT-IR spectra of cellulose and the QC derivatives were recorded on a Fourier transform infrared spectrometer (TENSOR27, Bruker, Germany). The QC derivatives were mixed with KBr with weight ratio of 1:100 and then the mixture was finely grounded and pressed into transparent discs. The samples were scanned over the wave numbers $400 \sim 4000 \text{ cm}^{-1}$. $^1\text{H-NMR}$ was carried out at room temperature on a 400 MHz NMR spectrometer (AV-III 400M, Bruker, Germany). The sample concentration in dimethylsulfoxide (DMSO- d_6) was 20 mg/mL. The chemical shifts were referenced by the signals of trimethylsilane (TMS). The solubility of the QC derivatives (1 wt%) in distilled water was determined at room temperature. XRD was carried out using

an X-ray diffractometer (6100 X, Rigaku, Japan). $\text{Cu-K } \alpha$ radiation was generated at 40 kV and 50 mA with the high-intensity monochromatic nickel-filtered. The XRD patterns were recorded in the range of 2θ from 5° to 60° . All samples were scanned at a speed of $4^\circ/\text{min}$, while the step size was maintained at 0.04° . The thermal stability was analyzed using thermogravimetric analysis (TGA Q500, TA, USA). An aliquot (5 ~ 10 mg) was added to an aluminum crucible and the aluminum crucible was transferred into the thermogravimetric instrument. The TGA experiments were carried out by heating the samples from room temperature to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$. All of the experiments were performed under the protection of nitrogen with a flow rate of 30 mL/min.

3 Results and discussion

3.1 Preparation of QC derivatives in NaOH-urea aqueous solution

The procedure used to synthesize the QC derivatives is illustrated in Fig. 1. NaOH-urea aqueous solution was used as the reaction medium to dissolve cellulose, and CHPTAC was employed as the etherifying agent. 2,3-epoxypropyl trimethyl ammonium chloride was formed through the cyclization of CHPTAC. Subsequently, the hydroxyl groups in the cellulose backbone attacked the epoxide and the final quaternized products were produced via alkoxylation. The added NaOH was very important. Combined with urea, NaOH provided a homogeneous medium for the cationic quaternization reaction. Meanwhile, it could also react with the hydroxyl groups

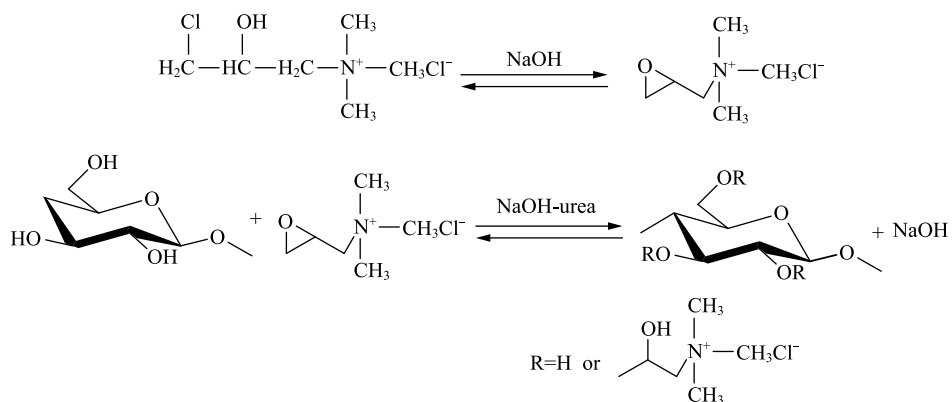


Fig. 1 The scheme for preparing QC derivatives

on cellulose to generate sodium alcoholate structures, which made the cellulose more nucleophilic. Additionally, the epoxide formation was catalyzed by NaOH, thus facilitating the cationic quaternization reaction. Notably, the cationic quaternization was the main reaction, while the hydrolysis of cellulose or the epoxide was the side reaction.

A series of QC derivatives with different nitrogen contents and DS values were prepared by changing the reaction conditions, e. g., the concentration of cellulose, molar ratio of CHPTAC to anhydroglucose unit (AGU), and reaction temperature and time^[15]. The optimum reaction conditions were determined by evaluating the effects of the reaction conditions on the DS values and nitrogen content. As shown in Table 1, the influence of the reaction conditions on the homogenous quaternization of cellulose followed the order reaction temperature > molar ratio of CHPTAC to AGU > concentration of cellulose in NaOH-urea aqueous solution = reaction time. Elevation of the reaction temperature from 25°C to 60°C led to a decrease in the DS values from 0.64 to 0.41, perhaps due to the gelation of cellulose. As the concentration of cellulose was adjusted from 2 wt% to 3 wt%, the DS values of the QC derivatives were enhanced from 0.40 to 0.54. An increase in the concentration of cellu-

lose increases the amount of hydroxyl groups in the reaction system and thus enhances the possibility of reaction with CHPTAC. However, the DS values of the QC derivatives decreased upon further increase of the concentration of cellulose from 3 wt% to 4 wt%, probably due to the precipitation of cellulose upon addition of CHPTAC. As expected, increasing the molar ratio of CHPTAC to AGU also affected the preparation of the QC derivatives. Enhancing the molar ratio of CHPTAC to AGU from 5:1 to 10:1 increased the DS values of the QC derivatives from 0.36 to 0.55. The results suggested that the hydroxyl groups in the cellulose backbone were partly substituted by CHPTAC and numerous free hydroxyl groups were still present in the cellulose backbone. Further increase of the molar ratio of CHPTAC to AGU from 10:1 to 15:1 did not affect the DS values. Therefore, molar ratio of CHPTAC to AGU > 15:1 was not beneficial for the synthesis of the QC derivatives. Moreover, prolonging the reaction time from 6 h to 12 h increased the DS values of the QC derivatives. However, when the reaction time was longer than 12 h, the DS value was nearly unchanged. Based on the above results, the DS value of the QC derivatives prepared with a reaction temperature of 25°C, 3 wt% cellulose concentration in NaOH-urea solution, molar ratio of CHPTAC to AGU as

Table 1 Conditions and results of preparing QC derivatives in NaOH-urea aqueous solution

Samples	Temperature (A)/°C	Concentration of cellulose (B)/%	Molar ratio of CHPTAC to AGU (C)	Time(D) /h	N /%	DS value	Solubility
QC-1	25	2	5:1	6	2.2	0.33	+++
QC-2	25	3	15:1	12	3.95	0.80	+++
QC-3	25	4	10:1	24	3.89	0.78	+++
QC-4	40	2	10:1	12	2.64	0.43	+++
QC-5	40	3	5:1	24	2.44	0.38	+++
QC-6	40	4	15:1	6	3.53	0.41	+++
QC-7	60	2	15:1	24	2.64	0.43	+++
QC-8	60	3	10:1	6	2.7	0.44	+++
QC-9	60	4	5:1	12	2.38	0.37	+++
DS value	A	B	C	D			
I	0.64	0.40	0.36	0.39			
II	0.41	0.54	0.55	0.53			
III	0.41	0.52	0.55	0.53			
R	0.23	0.14	0.19	0.14			

15:1, and 12 h reaction time was the highest among all the obtained samples. Another QC derivative was prepared under the above reaction conditions, and its DS value was 0.79, confirming the excellent reproducibility. Due to the introduction of hydrophilic quaternary ammonium groups, all of the QC derivatives were found to have good solubility in aqueous solutions.

3.2 Structure of QC derivatives

The structure of the QC derivatives was analyzed by FT-IR and ^1H -NMR. The FT-IR spectra of cellulose and QC derivatives (QC-1, QC-2, and QC-3) are depicted in Fig. 2. The broad peak positioned at 3372 cm^{-1} was attributed to the stretching vibration of hydroxyl groups in the glucosic units. The peaks at 2895 cm^{-1} and 1369 cm^{-1} were assigned to the stretching vibrations of $-\text{CH}_2$ and $-\text{CH}-$ groups and bending vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ groups, respectively. The band at 1059 cm^{-1} corresponded to the stretching vibration of $\text{C}-\text{O}-\text{C}$ in the glucosic units of cellulose. The peak at 1635 cm^{-1} was assigned to the stretching vibration of the absorbed moisture. Three new peaks at 1482 cm^{-1} corresponding to the vibrations of methyl groups in the ammonium moiety, a peak at 1417 cm^{-1} corresponding to the stretching vibration of $\text{C}-\text{N}$, and a peak at 907 cm^{-1} corresponding to the bending vibration of $\text{C}-\text{N}$ were observed. The comparative analysis of the FT-IR spectra of cellulose and QC derivatives indicated the successful introduction of quaternary ammonium groups into the main chain of cellulose.

The ^1H -NMR spectrum of QC-2 sample in $\text{D}_2\text{O}-d_6$ is shown in Fig. 3. The resonance peaks at 3.09 and 3.39

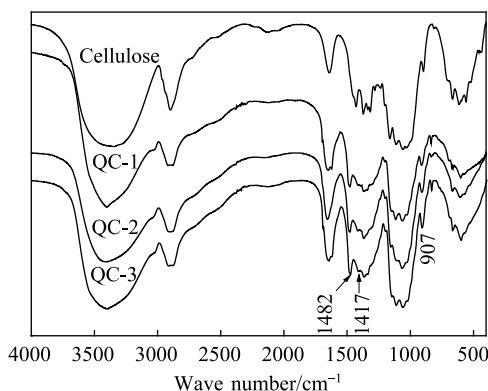


Fig. 2 The FT-IR spectra of cellulose and QC derivatives

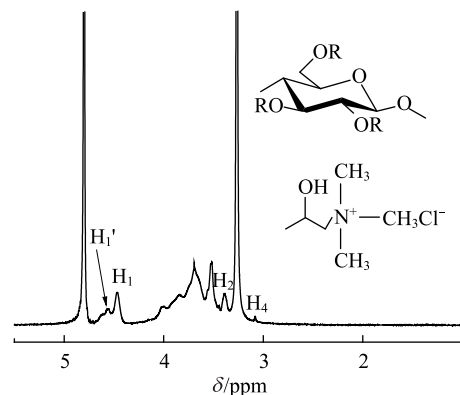


Fig. 3 The typical ^1H -NMR spectrum of QC-2 sample

ppm were ascribed to the protons at the H_4 and H_2 positions in the glucosic units of cellulose, respectively. The signals in the range of $3.44 \sim 4.15$ ppm were assigned to the protons in the H_3 , H_5 , and H_6 positions. The signals at 4.55 ppm and 4.47 ppm were assigned to the H_1 protons adjacent to C_2 with an unsubstituted hydroxyl group and substituted quaternary ammonium groups. The peak at 3.26 ppm was attributed to the methyl protons in the introduced quaternary ammonium groups $((\text{CH}_3)_3\text{N}^+)$. The peaks of methylene and methyne protons in the quaternary ammonium groups were observed at $3.44 \sim 4.01$ ppm, which overlapped with the signals of the glucosic protons on cellulose. These results suggested that the quaternary ammonium groups were successfully installed.

3.3 Thermal stability and crystallization of QC derivatives

The thermal stability of the QC derivatives was characterized using TGA. Fig. 4 and Fig. 5 depicted the TGA

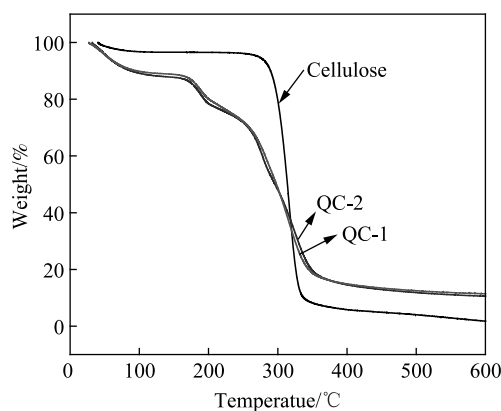


Fig. 4 The TGA curves of cellulose and QC derivatives

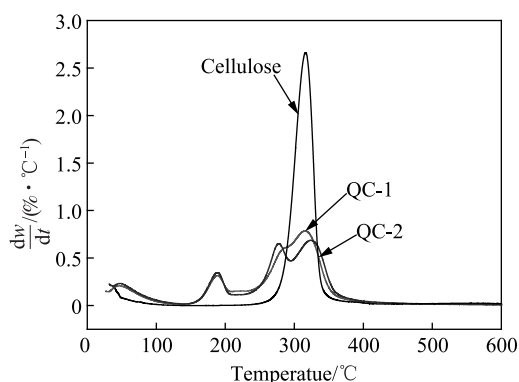


Fig.5 The DTGA curves of cellulose and QC derivatives

and differential thermogravimetric analysis (DTGA) curves of cellulose and QC derivatives (QC-1 and QC-2 samples), respectively. As shown in Fig. 4, there were two decomposition stages, which appeared at 100°C and 310°C, respectively. The former stage was mainly caused by the removal of absorbed moisture in cellulose, while the latter stage was attributed to the decomposition of the cellulose main chain. However, there was one new decomposition stage in the TGA curve of the QC derivatives, which started at 180°C. This stage was attributed to the degradation of the introduced quaternary ammonium groups. There was only one maximum weight loss temperature at 316.7°C in the DTGA curves of cellulose. Two new stages at 280°C and 190°C were also found in the DTGA curves of QC derivatives, which mainly corresponded to the scission and degradation of the quaternary ammonium groups from the cellulose backbone, respectively. Cellulose exhibited a 50% weight loss at 313.8°C, whereas the QC-1 and QC-2 samples displayed 50% weight loss at 297.9°C and 296.0°C, respectively. The initial decomposition temperature, maximum weight loss temperature, and 50% weight loss temperature of the QC derivatives were all lower than that of cellulose. The results indicated that the thermal stability of QC derivatives was reduced after the homogeneous cationic quaternization, likely owing to the disruption of inter-/intra-hydrogen bonds in the crystalline structure. Furthermore, the cellulose sample had a lower solid residue weight (9.47%) than the QC derivatives (11.09% for QC-1 sample and 10.16% for QC-2 sample). This observation could be explained by the fact that the introduction of chlorine into cellulose

during quaternization would increase the volatile substance content in the QC derivatives at 600°C.

The effects of quaternization on the crystal structure of cellulose were explored by XRD. Cellulose displayed the typical crystallization structure of cellulose type I. In the XRD pattern of cellulose, three diffraction peaks ascribed to the diffraction planes of 101, 002, and 040 were observed at 2θ of 15.37°, 22.62°, and 34.58°, respectively. For the QC derivatives, the characteristic peaks at 2θ of 15.37° and 22.62° were not observed, while the intensity of the characteristic peak at 2θ of 34.58° was reduced, indicating that the crystal structure was destroyed during the quaternization. Etherification between hydroxyl groups in cellulose and CHPTAC could interfere with the inter-/intra-hydrogen bonds between or in cellulose chains and thus influence its crystal structure. It should be noted that there still were two characteristic peaks at 2θ of 17.61° and 22.61° in the XRD patterns of the QC derivatives, confirming that the crystal structure was not disrupted completely.

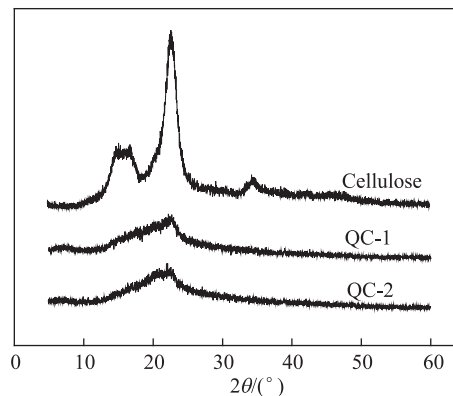


Fig.6 The XRD spectra of cellulose and QC derivatives

4 Conclusions

4.1 Quaternized cellulose (QC) derivatives were prepared through the etherification reaction between cellulose and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC). CHPTAC was used as an etherifying agent, and an aqueous solution of NaOH-urea was employed as the reaction medium. According to the degree of substitution (DS) values of the QC derivatives, the optimal conditions were as follows: 25°C reaction temperature, 3 wt% cellulose in NaOH-urea aqueous

solution, the molar ratio of CHPTAC to anhydroglucose unit (AGU) of 15:1, and 12 h reaction time.

4.2 The chemical structures of the QC derivatives were confirmed by FT-IR and $^1\text{H-NMR}$. Three new adsorption bands at 1482 cm^{-1} , 1417 cm^{-1} , and 907 cm^{-1} , corresponding to the vibrations of methyl groups in the ammonium substitutes, stretching vibrations of the C—N group, and bending vibrations of the C—N group, were observed in the FT-IR spectra of the QC derivatives. In the $^1\text{H-NMR}$ spectrum of the QC derivative (QC-2), the signal of the methyl group in the introduced ammonium substitutes appeared at 3.26 ppm. Overall, the results suggested that the cationic quaternary ammonium group was successfully grafted onto the cellulose backbone.

4.3 TGA and XRD indicated that the crystal structure and thermal stability of cellulose were destroyed after quaternization, and thus the aqueous solubility was improved.

Acknowledgments

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