

Chemical Modification of Chitosan: Synthesis and Characterization of Chitosan-Crown Ethers

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ABSTRACT: Four novel Schiff-type chitosan (CTS)-crown ethers were synthesized through a reaction between —NH_2 in CTS or crosslinked chitosan (CCTS) and —CHO in 4'-formylbenzo-crown ethers, and four secondary-amino-type CTS-crown ethers were prepared through the reduced reaction of NaBH_4 , respectively. Their structures were characterized by elemental analysis, Fourier transform infrared (FTIR) spectra analysis, solid-state ^{13}C -NMR analysis, and X-ray diffraction (XRD) analysis. The elemental analysis results showed that the percentage of nitrogen in all CTS-crown ethers were lower than that of CTS or CCTS. From the FTIR data of CTS, CCTS, and CTS-crown ethers **I–VIII**, we saw that the characteristic peaks of C=N , N—H , and Ar appeared and that the characteristic peaks of pyranoside in the chain of CTS or CCTS were not destroyed. The XRD

spectra demonstrated that CTS-crown ethers **I–VIII** gave lower crystallinities than CTS or CCTS, which indicated that these compounds were considerably more amorphous than CTS or CCTS. In the solid-state ^{13}C -NMR spectra, all of these CTS-crown ethers had a particular peak of aromatic at 128 or 129 ppm, and the greatest difference between Schiff-type CTS-crown ethers and secondary-amino-type CTS-crown ethers was that the Schiff-type CTS-crown ethers had the particular peak of C=N , which disappeared in secondary-type CTS-crown ethers. All these facts confirmed that the structures of CTS-crown ethers **I–VIII** were as expected. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2221–2225, 2003

Key words: crosslinking; polyethers; synthesis

INTRODUCTION

Chitosan (CTS), which is easily derived from chitin by *N*-deacetylation, has recently aroused great interest as an industrial application because of its specific structures and properties. CTS has hydroxyl and amino active groups that can be used for the reactions of grafting and crosslinking, among others.^{1–12} However, CTS can be dissolved in acid media, which is one disadvantage in application; therefore, study of the modification of CTS is necessary for wide-range application.

Because crown ethers have particular molecular structures, they have good complex selectivity for many metal ions. If crown ethers are grafted to polymers, they produce polymeric crown ether compounds, which have stronger complexation with metal salts and better selectivity for metal ions than crown ethers because of the synergistic effect of high molecular weight.^{13–15}

In this article, 4'-formylbenzo-crown ethers were first synthesized and then grafted onto CTS or crosslinked chitosan (CCTS) to give four novel Schiff-base-type CTS-crown ethers, and four novel secondary-amino-type CTS-crown ethers were prepared through the reduced reaction of NaBH_4 , respectively. These CTS-crown derivatives were expected to have more wide-ranging applications in the separation and concentration of heavy or precious metal ions and to be able to be used as potential hazardous-waste-remediation materials.

EXPERIMENTAL

Materials

CTS, whose degree of deacetylation was calculated to be 80% from amino content, was prepared by *N*-deacetylation of chitin from chitin shells.^{16–17} CCTS was prepared by a method reported earlier¹⁸ and was used after passage through a 200-mesh size sieve. Dichloroethers were prepared by a method reported earlier.^{19,20} 4'-Formylbenzo-crown ethers were also prepared by a method reported earlier,^{21,22} and their structures were confirmed with Fourier transform infrared (FTIR) spectra and ^1H -NMR spectra analysis. All inorganic compounds were reagent grade, and all

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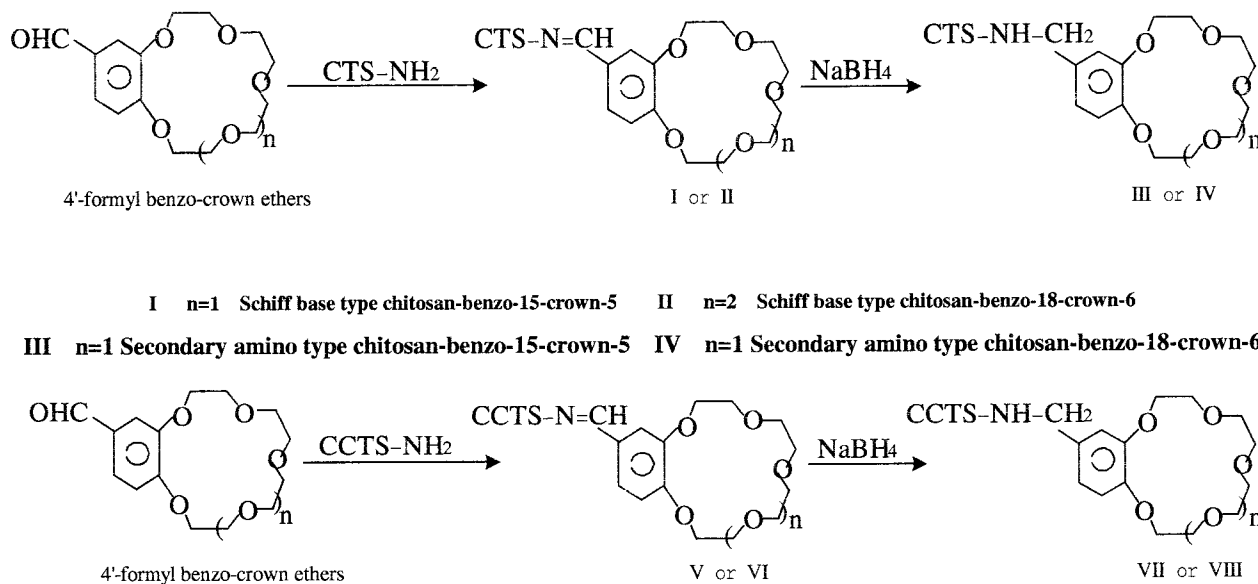


Figure 1 Reaction scheme for the synthesis of CTS-crown ethers I–VIII.

solvents and available organic materials were commercial products used without purification.

Measurements

Elemental analysis was determined with a Perkin Elmer automatic instrument (China). IR spectra were measured on a Nicolet 5DX FTIR spectrophotometer (Japan). Wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat-film camera with nickle-filtered Cu K_α radiation produced by a Rigaku (D/MAX, 111A) diffractometer (China). Solid-state ^{13}C -NMR was conducted with a Broker MSL-400 instrument (China); proton and carbon frequencies were 100 and 25 MHz, respectively.

Synthesis of chitosan-crown ethers

Figure 1 shows a schematic representation of the preparation of CTS-crown ethers I–VIII.

Synthesis of chitosan-crown ethers i and ii. Chitosan (1.0 g) was dissolved in 30 mL of 10 wt % acetic acid and diluted with an ethanol solution. 4'-Formylbenzo-crown ethers dissolved in ethanol were dropped into the previous solution over 30 min after nitrogen gas was ventilated. The mixture was refluxed with good agitation for 24 h, filtered, washed with water, and then extracted with methanol in a Soxhlet's extractor for 2 h to eliminate any unreacted 4'-formylbenzo-crown ethers. Precipitates were dried and gave CTS-crown ethers I and II (yield: I = 85%, II = 80%).

Synthesis of chitosan-crown ethers iii and iv. According to the synthesis procedure of CTS-crown ethers I or II, the colloid solution of I or II was obtained. Then, NaBH_4 (1.0 g), which was dissolved in 30 mL ethanol,

was slowly dropped into the colloid solution. The mixture was refluxed with good agitation for 12 h, filtered, washed with water, and then extracted with methanol in a Soxhlet's extractor for 4 h to eliminate any unreacted 4'-formylbenzo-crown ethers and NaBH_4 . Precipitates were dried and gave CTS-crown ethers III and IV (yield: III = 80%, IV = 78%).

Synthesis of chitosan-crown ethers v and vi. CTS-crown ethers V and VI were synthesized by the reaction of CCTS with 4'-formylbenzo-crown ethers according to the same procedure as used for the synthesis of CTS-crown ethers I and II (yield: V = 88%, VI = 81%).

Synthesis of chitosan-crown ethers vii and viii. CTS-crown ethers VII and VIII were synthesized by the reaction of CCTS with 4'-formylbenzo-crown ethers and NaBH_4 according to the same procedure as used for the synthesis of CTS-crown ethers III and IV (yield: VII = 84%, VIII = 83%).

RESULTS AND DISCUSSION

CTS-crown ethers I, II, V, and VI were gray in color and did not dissolve in organic solvents such as dimethylsulfoxide, formamide, and dimethylformamide. CTS-crown ethers III, IV, VII, and VIII were yellow in color and did not dissolve in organic solvents such as dimethylsulfoxide, formamide, and dimethylformamide. They were all rather swollen in acetic solution.

Elemental analysis

The elemental analysis results for CTS, CCTS, and all CTS-crown ethers are shown in Table I.

TABLE I
Elemental Analysis Results for CTS, CCTS,
and CTS-Crown Ethers I-VIII

Compound	N%	C%	H%	Degree of grafting ^a
CTS	6.53	37.85	6.89	
I	3.69	45.85	6.32	1.13
II	3.29	49.08	6.66	1.67
III	3.66	44.47	6.58	1.15
IV	3.28	40.91	6.61	1.67
CCTS	5.39	38.26	6.49	
V	5.36	37.43	6.52	0.30
VI	5.37	37.44	6.51	0.27
VII	5.38	37.68	6.56	0.25
VIII	5.38	38.46	6.54	0.23

^a Degree of grafting = $W_2 - W_1/W_1$, where W_1 and W_2 denote the weight of ungrafted and grafted CTS or CCTS.

As shown in Table I, the content of nitrogen in all CTS-crown ethers was lower than that in CTS or CCTS. The decrease could be attributed to the presence of the benzo-crown ether groups produced in the reaction of CTS or CCTS with 4'-formylbenzo-crown ethers.

IR spectra analysis

The IR spectra analysis results of CTS, CCTS, and all CTS-crown ethers are shown in Table II.

As shown in Table II, all CTS-crown ethers (I-VIII) had the characteristic peaks of aromatic backbone vibration at 1500–1700 cm^{-1} , and the characteristic peaks of C=N stretch vibrations in CTS-crown ethers I, II, V, and VI appeared at 1640–1650 cm^{-1} . These characteristic peaks disappeared in CTS-crown ethers III, IV, VII, and VIII because of the reduced reaction of NaBH_4 . CTS, CCTS, and CTS-crown ethers also had the characteristic peak of the pyanyl vibration at 890–900 cm^{-1} , which demonstrated that the pyranoside in CTS and CCTS was not destroyed in the process of grafting and reduction. Therefore, these evidences confirmed the introduction of benzo-crown ether groups into CTS and CCTS.

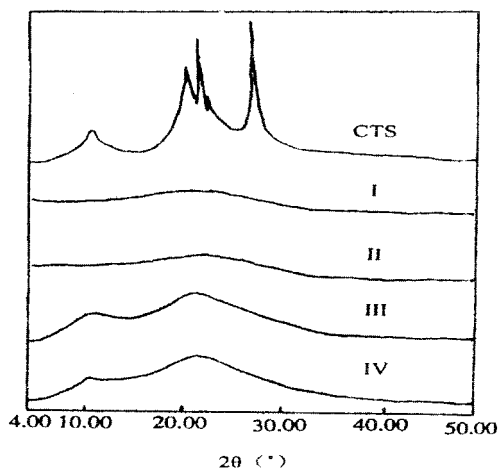


Figure 2 XRD patterns of CTS and CTS-crown ethers I-IV powders.

X-ray diffraction (XRD) analysis

Crystallinity was studied by XRD. Figure 2 shows the WAXD patterns of CTS and CTS-crown ethers I-IV. Figure 3 shows the WAXD patterns of CCTS and CTS-crown ethers V-VIII.

In Figure 2, the WAXD pattern of a CTS sample shows the characteristic peak $2\theta = 10^\circ$ due to the presence of (001) and (100) and that at $2\theta = 20^\circ$ caused by the presence of (101) and (002).²³ For CTS-crown ethers I-IV, the peak at $2\theta = 10^\circ$ and 20° disappeared or decreased. The decrease in crystallinity of CTS-crown ethers I-IV could be attributed to the deformation of the strong hydrogen bond in the CTS backbone as amino groups were substituted by the benzo-crown ether groups. These CTS-crown ethers gave low crystallinity, indicating that they were considerably more amorphous than CTS.

In Figure 3, the WAXD pattern of CCTS shows characteristic peaks at $2\theta = 10, 20, 32,$ and 46° . For CTS-crown ethers V-VIII, the peaks at $2\theta = 10, 32,$ and 46° disappeared, and the characteristic peak at $2\theta = 20^\circ$ decreased. We thought that the decrease in crystallinity of CTS-crown ethers V-VIII was attribut-

TABLE II
FTIR Data of CTS, CCTS, and CTS-crown ethers I-VIII

Compound	IR ν (cm^{-1})
CTS	3436 (OH), 3358 (NH_2), 1071, 1027 (C—O—C), 897 (pyranoside)
I	3393 (OH), 1642 (C=N), 1602, 1513 (Ar), 1270, 1044 (C—O—C), 902 (pyranoside)
II	3383 (OH), 1640 (C=N), 1600, 1515 (Ar), 1270, 1030 (C—O—C), 900 (pyranoside)
III	3342 (OH), 1565 (N—H), 1514, 1430 (Ar), 1127, 1030 (C—O—C), 939 (pyranoside)
IV	3400 (OH), 1575 (N—H), 1510, 1470 (Ar), 1265, 1066 (C—O—C), 893 (pyranoside)
CCTS	3287 (OH), 3358 (NH_2), 1070, 1030 (C—O—C), 900 (pyranoside)
V	3346 (OH), 1652 (C=N), 1600, 1510 (Ar), 1127, 1030 (C—O—C), 898 (pyranoside)
VI	3363 (OH), 1650 (C=N), 1600, 1510 (Ar), 1127, 1129 (C—O—C), 897 (pyranoside)
VII	3298 (OH), 1559 (N—H), 1561, 1457 (Ar), 1112, 1034 (C—O—C), 900 (pyranoside)
VIII	3402 (OH), 1571 (N—H), 1456, 1381 (Ar), 1111, 1069 (C—O—C), 900 (pyranoside)

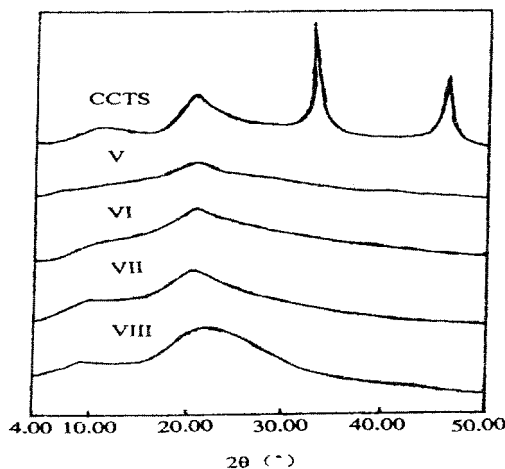


Figure 3 XRD patterns of CCTS and CTS-crown ethers V-VIII powders.

able to the deformation of hydrogen bonds in CCTS as the amino groups in CCTS were grafted by 4'-formylbenzo-crown ethers. All of these CTS-crown ethers gave a low crystallinity, indicating that they were considerably more amorphous than CCTS.

¹³C-NMR spectra analysis

The ¹³C-NMR studies of CTS, CCTS, and CTS-crown ethers I-VIII were done as solid samples because these derivatives could not easily be dissolved. Figure 4 compares the CTS spectrum with that of CTS-crown ethers I-IV, and Figure 5 compares the CCTS spectrum with that of CTS-crown ethers V-VIII.

From Figures 4 and 5, one can see that a characteristic aromatic carbon appeared at 128 or 129 ppm for all CTS-crown ethers. It was not seen in the spectra of CTS or CCTS. Changes were also noticeable for carbon

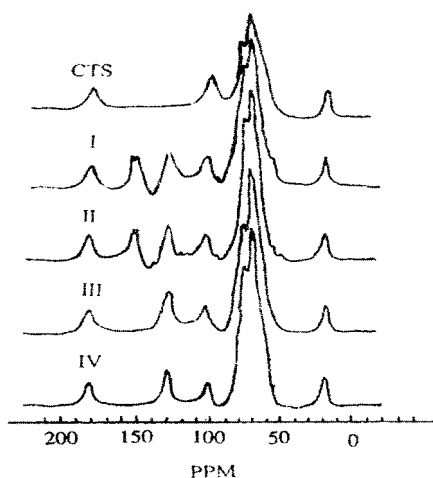


Figure 4 Solid-state ¹³C-NMR spectra of CTS and CTS-crown ethers I-IV.

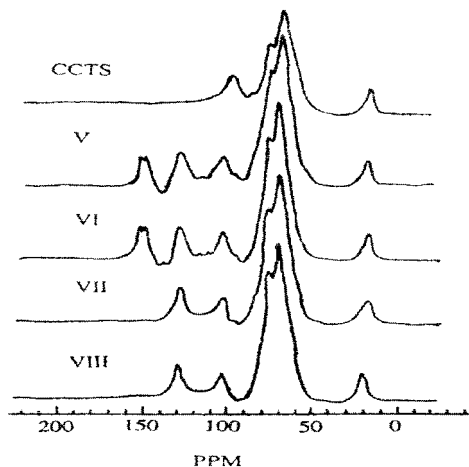


Figure 5 Solid-state ¹³C-NMR spectra of CCTS and CTS-crown ethers V-VIII.

in CH₂ groups at 59 ppm because of the presence of crown ether groups in CTS-crown ethers I-VIII.

CONCLUSIONS

Four novel Schiff-base-type CTS-crown ethers were synthesized via a Schiff-base reaction between amino groups in CTS or CCTS and 4'-formylbenzo-crown ethers, and then, four novel secondary CTS-crown ethers were prepared through a NaBH₄ reduction reaction to the colloid solution of Schiff-base CTS-crown ethers. Structures of CTS-crown ethers I-VIII were conformed with elemental analysis, FTIR analysis, XRD analysis, and solid-state ¹³C-NMR analysis. All facts illustrated that their structures were as expected.

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