

Studies on the Synthesis and Properties of Hydroxyl Azacrown Ether-Grafted Chitosan

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ABSTRACT: The chitosan hydroxyl azacrown ether was synthesized by reaction of hydroxyl azacrown ether with epoxy-activated chitosan. The C₂ amino group in chitosan was protected from the reaction between benzaldehyde and chitosan to form *N*-benzylidene chitosan. After reaction with epichlorohydrin and azacrown ether, reacting *O*-aryl mesocyclic diamine-*N*-benzylidene chitosan and dilute ethanol hydrochloride solution to obtain novel chitosan-azacrown ether bearing hydroxyl removed the Schiff base. Its structure was confirmed with elemental analysis, FTIR spectra analysis, X-ray diffraction analysis, and solid-state ¹³C NMR analysis. Its static adsorption properties for Ag(I), Cd(II), Pb(II), and Cr(III) were also investigated. The experimental results showed that the hydroxyl azacrown ether grafted chitosan has good adsorption capacity and high selectivity for Ag(I) in the coexistence of Pb(II) and Cd(II), the selectivity coefficients of hydroxyl azacrown ether chitosan were $K_{Ag(I)/Pb(II)} = 32.34$; $K_{Ag(I)/Cd(II)} = 56.12$. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1838–1843, 2001

Key words: chitosan; azacrown ether; mesocyclic diamine; graft compounds; adsorption properties; metal ions

INTRODUCTION

Hydroxyl mesocyclic diamine crown ethers are new functional compounds. Because of their particular structure, these ethers have specific selectivity and stability for many heavy or precious metal ions,¹ but the solubility is too great to recover after being used, limiting its application. If hydroxyl mesocyclic diamine crown ethers were grafted in a high-molecular-weight polymer to produce polymerized azacrown ethers containing double structures and properties of polymer and mesocyclic diamine. It can be predicated that these novel polymer would have better complex selectivity for some metal ions owing to the synergistic effect of high molecular weight.^{2,3}

Chitin is one of the most abundant organic materials that can be easily obtained in nature.

Chitosan (CTS) is a cationic polyelectrolyte that can be easily derived from chitin by *N*-deacetylation. In recent years, research on the use of chitosan has gained attention, especially for wastewater treatments.^{4–7} Chitosan has both hydroxyl and amine groups that can be modified by raw chitosan to prepare chitosan derivatives.^{8–11} Chemical modifications offer a wide spectrum of tools to enhance the adsorption properties of chitosan for metal ions. They may increase the chemical stability of the sorbent in acid media and, in particular, may decrease the solubility in most mineral and organic acids.⁷ They also increase its resistance to biochemical and microbiological degradation.¹² We have already reported on a series of chitosan azacrown ethers.^{13,14} The aim of the present study is to prepare the novel chitosan azacrown ether bear-

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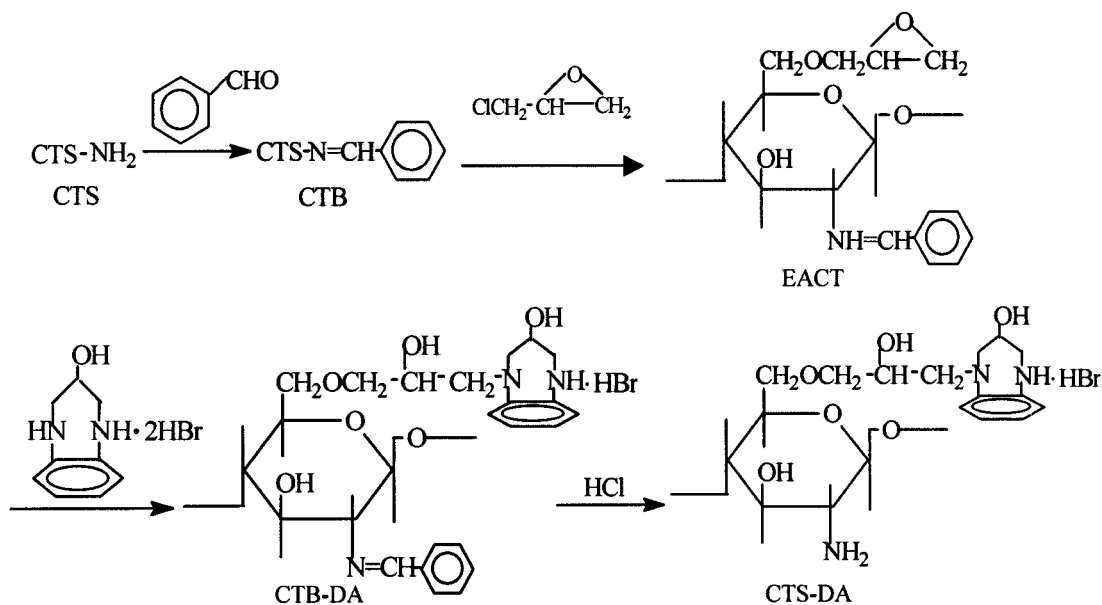


Figure 1 Reaction scheme for the synthesis of CTS-DA.

ing hydroxyl group and to investigate its properties. In this article, the C_2 amino group in chitosan was protected from the reaction between benzaldehyde and chitosan to form *N*-benzylidene chitosan (CTB), and the CTB was activated with epichlorohydrin to give epoxy chitosan-benzaldehyde (EACT). The novel chitosan azacrown ether bearing hydroxyl group (CTS-DA) was then obtained through the reaction of EACT with aryl mesocyclic diamine; the Schiff base was removed by reacting *O*-azacrown ether-*N*-benzylidene chitosan and dilute ethanol hydrochloride solution. Its structure was confirmed with elemental analysis, infrared spectra (IR) analysis, X-ray diffraction (XRD) analysis, and solid-state ^{13}C -NMR analysis. The adsorption properties and selectivity for Ag(I), Pb(II), Cd(II), and Cr(III) were also investigated.

EXPERIMENTAL

Materials

Chitosan, with a degree of deacetylation calculated to be 85% from the amino contents, was prepared by *N*-deacetylation of chitin from shrimp shells.¹⁵ Hydroxyl mesocyclic diamine crown ether was prepared according to procedure reported previously.¹⁶ Other chemicals used were analytical grade and used without any further purification.

Characterization

Elemental analysis was determined with a Perkin-Elmer automatic instrument. IR spectra were measured on a NICOLET5DX FTIR spectrophotometer; Wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat-film camera using nickel-filtered $\text{Cu K}\alpha$ radiation produced by a Rigaku (D/MAX, IIIA) diffractometer, respectively.

Preparation of Hydroxyl Azacrown Ether Chitosan

Figure 1 is a schematic representation of preparation of hydroxyl azacrown ether chitosan. Powdered chitosan (3 g) was dissolved in 100 mL of 2 wt % acetic acid and diluted with methanol. Then 12.5 g of benzaldehyde was slowly dropped into the chitosan solution. The mixture was stirred at room temperature for 8 h to obtain a transparent gel. The gel was washed with methanol several times to remove any unreacted benzaldehyde chitosan (CTB). Powdered CTB (2 g) was swollen in 25 mL aqueous sodium hydroxide solution (2 mol/L) for 4 h and was reacted with 11.15 g epichlorohydrin at room temperature for 8 h to prepare *O*-epoxy group-*N*-benzylidene chitosan (EACT). The amount of epoxy group, ~ 2.32 mmol/g EACT, was determined according to the method reported.¹⁷

Powder EACT (1.5 g) was suspended in 40 mL 1,4-dioxane aqueous solution (30%), and 1.5 g

Table I Elemental Analysis Results of Chitosan Derivatives

Compound	Formula	Calcd (%)			Found (%)		
		C	H	N	C	H	N
CTS-NH ₂	C ₆ H ₁₁ NO ₄	44.72	6.83	8.67	39.43	6.51	6.94
EACT	C ₁₆ H ₁₉ NO ₅	62.95	6.23	4.59	60.21	5.98	4.02
CTB-DA	C ₂₅ H ₃₂ N ₃ O ₆ Br	54.56	5.82	7.64	51.23	5.19	6.87
CTS-DA	C ₁₈ H ₂₆ N ₃ O ₆ Br	46.95	5.65	9.13	44.26	6.12	8.86

(14.16 mmol) sodium carbonate; then 1.62 g aryl azacrown ether bearing hydroxyl group, dissolved in 25 mL methanol, was slowly dropped into the system. The mixture was stirred under nitrogen at 50°C for 8 h. After reaction, were cooled, filtered, and washed several times with distilled water, acetone, and ether, respectively. The Schiff base was removed by reacting *O*-azacrown ether-*N*-benzylidene (CTB-DA) and a diluted ethanol hydrochloride solution (0.5 m), stirred for 4 h at room temperature, filtered, washed with distilled water. Then the precipitate was swollen in a 1.0M NaOH aqueous solution for 30 min, filtered, washed with distilled water, dried in a vacuum at 60°C to obtain hydroxyl azacrown ether chitosan (CTS-DA), in a 86.2% yield.

Determination of the Adsorption Properties for Metal Ions of CTS-DA

Aqueous metal ion solutions were prepared from AgNO₃, Cd (NO₃)₂(4H₂O), Pb(NO₃)₂, and CrCl₃(6H₂O). The chitosan or its powder derivatives (25 mg) put into a glass bottle containing 25 mL of the metal ion solution. The mixture was stirred and left a predetermined time for adsorption at 25°C; the equilibrated mixture was then centrifuged and the adsorbent was filtered off. The concentration of metal ions in the original solution and in the filtrate was determined by atomic adsorption spectroscopy (AAS), and the amount of the metal ions was calculated by the method reported previously.¹³

The pH-dependent metal sorption was performed by interacting 25mg of the chitosan powder derivative with the metal-ion solution (25 mL, 5.0 × 10⁻¹ mmol); the reaction mixture was adjusted to a different pH range with HNO₃ or HCl. After stirring at 25°C for 12 h, the adsorbent was filtered off; the adsorbed metal ion concentration in the filter was determined according to the above procedure.

Adsorption Selectivity of CTS-DA for Metal Ions

Adsorption selectivity of CTS-DA for metal ions was obtained by determination of metal ion loading capacities with the coexistence of metal ions. A 0.5 mmol L⁻¹ solution of desired metal ions was prepared; 25 mg CTS-DA was added to 25 mL of the solution and stirred for a predetermined time for adsorption. The metal-ion concentration in the original solution and the filtrate was determined by an atomic adsorption spectroscopy. The selectivity coefficient of adsorbent was calculated as follows:

$$K_{M(1)/M(2)} = \frac{Q_1}{Q_2}$$

where Q_1 and Q_2 are the adsorption capacities of adsorbency for metal $M(1)$ and $M(2)$ (mmol metal ion/g adsorbent).

RESULTS AND DISCUSSION

Elemental Analysis

The elemental analysis results of chitosan and its derivatives are shown in Table I. It can be seen that the content of nitrogen in CTS-DA was slightly higher than that in CTS-NH₂. It was thought that the increase was due to the presence of the hydroxyl azacrown ether groups produced in the reaction of epoxy active chitosan (EACT) with hydroxyl azacrown ether.

Infrared Spectra Analysis

IR spectra of the chitosan and its derivatives are shown in Figure 2. Curves a, b, c, and d are the IR spectra of the chitosan, EACT, CTB-DA, and CTS-DA, respectively. The IR spectra of the EACT and CTB-DA compared with CTS shows

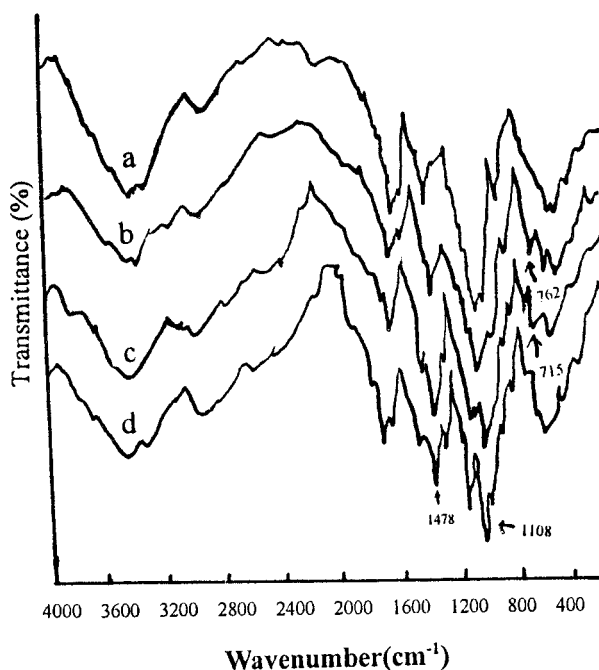


Figure 2 Infrared spectra of CTS (a), EACT (b), CTB-DA (c), and CTS-DA (d).

that the characteristic peak of the aromatic C-H out-of-plane deformation appeared at 762 cm^{-1} and 715 cm^{-1} owing to the presence of the benzaldehyde. It also can be seen that additional sharp peak at $1,478\text{ cm}^{-1}$ corresponding to the —C=N— group. Note that these characteristic peaks disappear in CTS-DA (curve *d*), caused by treating the CTB-DA in hydrochloride ethanol solution to remove the Schiff base. These Schiff base used for reaction (from CTS-NH_2 to CTB-DA) remained and effectively protected the amino groups in the chitosan. Curves *c* and *d* show that the two additional peaks at $1,478\text{ cm}^{-1}$ and $1,108\text{ cm}^{-1}$ correspond to the C—N—C and C—O—C group. The sharp peak near $1,560\text{ cm}^{-1}$ corresponding bending vibration of the free amino group (—NH_2) appeared for CTS-DA. From IR spectra of CTS-DA, we can confirm the grafting of hydroxyl azacrown ether in the C-6 position on chitosan.

X-Ray Diffraction Analysis

Figure 3 shows the WAXD pattern of chitosan and its derivatives. The WAXD pattern of the chitosan sample shows the characteristic peak at $2\theta = 10^\circ$, 20° , and 28° . Note that the peak at $2\theta = 10^\circ$ disappeared, and the characteristic peak $2\theta = 20^\circ$ decreased significantly in EACT and CTB-

DA. The decrease in crystallinity of chitosan derivatives was attributed to the deformation of the strong hydrogen bond in the crude chitosan sample backbone as the benzylidene, epoxy, and hydroxyl azacrown ether groups substituted the hydroxyl and amino groups. The chitosan derivatives gave low crystallinity, indicating that they were considerably more amorphous than crude chitosan.^{18,19} Meanwhile, the characteristic peak of CTS-DA at $2\theta = 20^\circ$ increased in the XRD pattern. The regenerated amino groups is believed to have formed the hydrogen bond again, resulting in increase in the crystallinity.

$^{13}\text{C-NMR}$ Analysis

The solid-state $^{13}\text{C-NMR}$ spectra of chitosan and chitosan derivatives are shown in Figure 4. The spectra of EACT, CTB-DA, and CTS-DA compared with CTS show that the characteristic peak of the aromatic carbon appeared at 129 ppm, because of the presence of the benzaldehyde (in EACT and CTB-DA) and aryl azacrown ether (in CTB-DA and CTS-DA). It also can be seen that the characteristic peak at 42 ppm, corresponding to the $\text{—CH}_2\text{—N—}$ group, owing to the presence of azacrown ether groups in CTB-DA and CTS-DA.

Adsorption Amounts and Selectivity of CTS-DA

The experimental results of absorption of CTS and CTS-DA for Ag(I), Pb(II), Cd(II), and Cr(III)

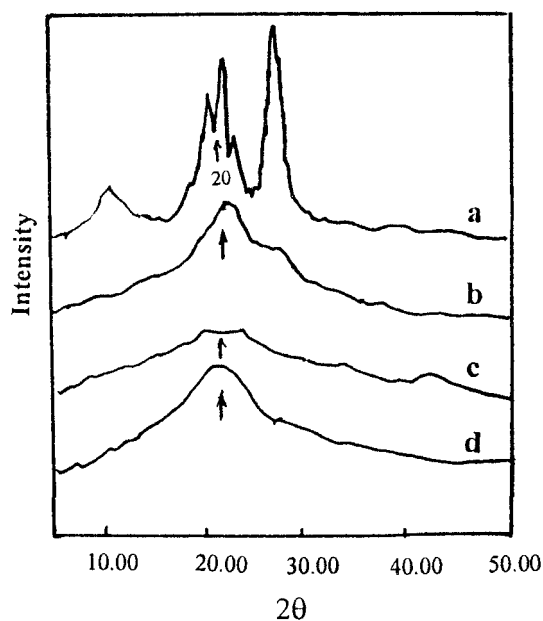


Figure 3 X-ray diffraction patterns of CTS (a), EACT (b), CTB-DA (c), and CTS-DA (d).

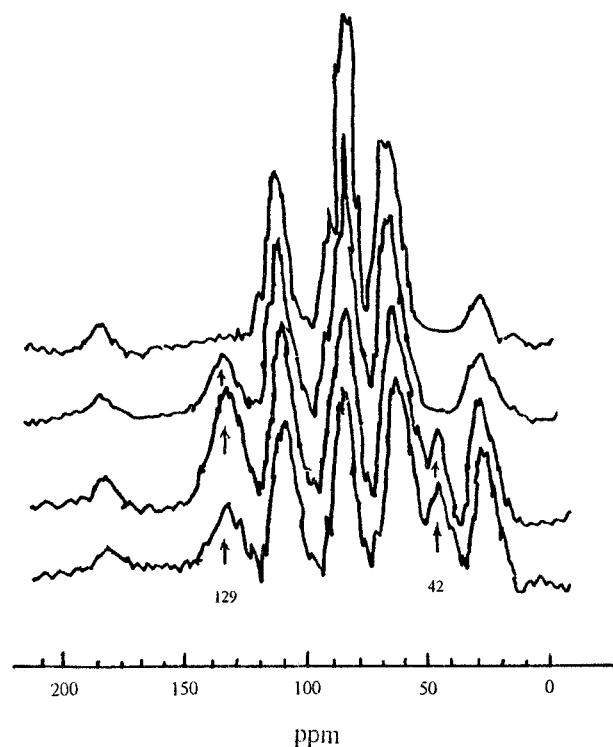


Figure 4 ^{13}C NMR spectra of CTS (a), EACT (b), CTB-DA (c), and CTS-DA (d).

are shown in Table II. It can be seen that the adsorption capacity of CTS-DA for Ag(I) was much higher than that of CTS, and that for Cd(II), Pb(II), and Cr(III) was lower. The result is due mainly to the presence of hydroxyl azacrown ether groups in CTS-DA, which demonstrates that grafting might bring about remarkable changes in the adsorption properties of chitosan.

The experimental results of the adsorption selectivity of CTS-DA for Ag(I), Cd(II), and Pb(II) are shown in Table IV. Comparing several selectivity coefficients of CTS-DA and CTS, it can be seen that the adsorption selectivity of CTS-DA for Ag(I) was much higher than that of CTS, indicating that the hydroxyl azacrown ethers might

Table II Ability of CTS-DA to Absorb Metal Ions (mmol/g, Adsorbent pH = 5.5 12 h)

	CTS	CTS-DA
Ag(I)	0.28	0.49
Cd(II)	0.17	0.01
Pb(II)	0.22	0.02
Cr(III)	0.15	0.02

Table III Effect of pH on Metal Ion Sorption by CTS-DA (mg, Metal Ion/g, Sorbent, 25°C, 12 h)

	pH Value					
	2	2.5	3.5	4.5	5.5	7.0
Ag(I)	9.84	25.34	30.87	36.35	49.82	56.16
Cd(II)	0.00	1.24	1.83	2.28	3.62	4.76
Pb(II)	1.15	1.93	4.43	6.13	8.23	10.23
Cr(III)	0.02	0.31	1.02	1.47	1.98	2.03

greatly increase the adsorption selectivity of chitosan for some heavy metal ions.

The interaction of the metal ions with mesocycles containing nitrogen donor atoms have been investigated. Generally, the metal complexes of this azacrown ether are 1:1 (metal:ligand) with the metal ion located at the center of the mesocycle. The different stability orders in the cases of the metal ions probably reflect different types of bonding in the complexes of these cations. The heavy metal ion binding may involve both electrostatic and covalent contributions.²⁰ Generally, that metal ion whose ionic radius best matches the radius of the cavity formed by the azacrown ether on complexation will form the most stable complex. The results indicated that azacrown ethers might greatly raise the adsorption selectivity of chitosan for some metal ions.

Influence of pH

The sorption performances are strongly affected by parameters such as pH, particle size, and the nature of the sorbent. Table III shows the effect of

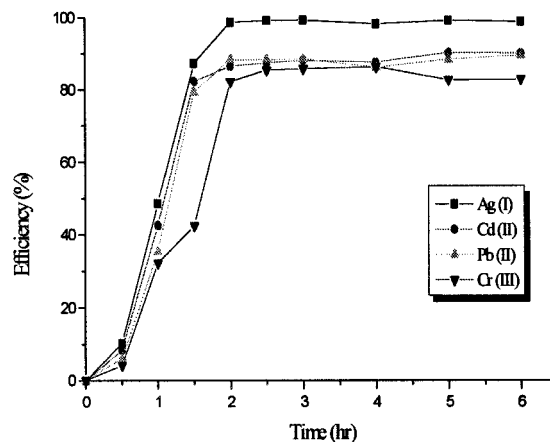


Figure 5 Metal uptake kinetics of CTS-DA.

Table IV Adsorption Selectivity of CTS-DA for Aqueous System Containing Ag(I), Cd(II), and Pb(II) (pH = 5.0, Metal Ions Ratio 1 : 1 : 1, 24 h)

Compound	Quantity of Adsorption (mmol/g, sorbent)			Selectivity/Coefficients
	Ag(I)	Cd(II)	Pb(II)	
CTS	0.21	0.14	0.20	$K_{Ag(I)/Cd(II)} = 1.51$; $K_{Ag(I)/Pb(II)} = 1.05$
CTS-DA	0.51	0.01	0.02	$K_{Ag(I)/Cd(II)} = 51.02$; $K_{Ag(I)/Pb(II)} = 21.53$

pH on metal ion sorption by chitosan hydroxyl azacrown ether (CTS-DA). It is obvious that pH is a major parameter that greatly influence the maximum uptake. The adsorption capacity for metal ion increased with pH in the solution. It is due mainly to the presence of amino group ($-NH_2$) and secondary amine groups ($-NH-$) in CTS-DA, which easily form protonation. At low pH competition between protons and metal ions causes a low uptake capacity. At higher pH, electrostatic repulsion decrease and the uptake reach a maximum. By contrast, the adsorption ability also would decrease because the nitrogen atom of azacrown ether does not easily form coordinate bonds with metal ions under low pH.

Adsorption Kinetics of CTS-DA

Simple batch kinetic experiments of the hydroxyl azacrown ether chitosan derivative for Ag(I), Cd(II), Pb(II), and Cr(III) were determined, The relevant data for different metal ions are shown in Figure 5. The experimental results appear to show that the metal ion adsorption of CTS-DA is reasonably fast. After 2 h, the adsorption reached to the equilibrium fundamentally.

CONCLUSIONS

Chitosan hydroxyl azacrown ether (CTS-DA) was synthesized by the reaction of hydroxyl azacrown ether with epoxy-activated chitosan (ETCA). The novel chitosan derivative has high metal-uptake abilities, and the selectivity property for metal ions was improved by incorporation of hydroxyl azacrown ether groups in chitosan. The selectivity for adsorption of metal ions on CTS-DA (pH 5) was $Ag(I) > (Pb(II)) > (Cd(II)) > (Cr(III))$. The experimental results demonstrated that grafting of new functional groups onto chitosan increases

sorption selectivity. The novel chitosan azacrown ether can be expected to have broad application for the separation and concentration metal ions in environmental analysis.

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