

Preparation and Characterization of Dihydroxyl Mesocyclic Diamine Derivative of Chitosan

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Received 27 May 2001; accepted 5 December 2001

ABSTRACT: The synthesis of a new dihydroxyl mesocyclic diamine grafting chitosan is presented. This derivative is formed by reaction of dihydroxyl azacrown ether with epoxy-activated chitosan. The obtained copolymer contains amino functional groups in its skeleton and the secondary amine, and more polar hydroxyl groups. Elemental analysis, fourier transform infrared analysis, as well as solid-state carbon-13 nuclear magnetic resonance analysis were used to characterize chemical modifications of the chitosan. The adsorption properties of the dihydroxyl mesocyclic diamine grafted chitosan for Ag^+ , Pb^{2+} , Cd^{2+} , and Cr^{3+} were stud-

ied. The experimented results showed that the novel chitosan derivative has good adsorption capacity and high selectivity for Ag^+ in the presence of Pb^{2+} , Cd^{2+} , and Cr^{3+} , and its adsorption selectivity is better than that of chitosan. The selectivity coefficients were $K_{\text{Ag}^+/\text{Pb}^{2+}} = 12.25$, $K_{\text{Ag}^+/\text{Cr}^{3+}} = 6.12$, and $K_{\text{Pb}^{2+}/\text{Cr}^{3+}} = 0.52$, respectively. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2677–2681, 2002

Key words: chitosan; azacrown ether; mesocyclic diamine; synthesis; adsorption

INTRODUCTION

Chitin is one of the most abundant organic materials that can be easily obtained in nature. Chitosan (CTS), which is easily derived from chitin by *N*-deacetylation, has both hydroxyl and amine groups that can be modified on the raw chitosan to prepare chitosan derivatives.^{1–4} Several processes have been proposed to modify chitosan by grafting new functional groups on the polymer backbone.^{5,6} 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, especially, decrease the solubility in most mineral and organic acids. They also increase its resistance to biochemical and microbiological degradation.⁷ Moreover, chemical grafting of a new functional group improves adsorption selectivity as well as sorption capacities.

Mesocyclic diamine (Azacrown ether) is a new functional compound. As it has a particular structure, it has had specific selectivity and stability for many heavy and/or precious metal ions,⁸ but the solubility is too great to recover after being used; therefore its application is limited. If mesocyclic diamine crown ether were grafted to high molecular weight chitosan to give polymerized crown ether containing double

structures and properties of polymer and mesocyclic diamine, it can be predicated that these novel polymers would have better complex action and ion-exchange action with metal salts and better selectivity for some metal ions. This is due to the synergistic effect of high molecular weight.⁹ We have already reported a series of azacrown ether chitosan derivatives.^{10–12} In present study, we aimed to prepare a novel chitosan mesocyclic diamine crown ether bearing the dihydroxyl group and to investigate its properties. In this research, chitosan was first reacted with epichlorohydrin to give epoxy chitosan-benzaldehyde (EACT). Then, the new chitosan derivative (CTDA) was obtained though the reaction of EACT with dihydroxyl mesocyclic diamine. Its structure was confirmed by elemental analysis, solid-state carbon-13 nuclear magnetic resonance (¹³C NMR) analysis, and infrared (IR) spectra analysis. The adsorption properties and selectivity for Ag^+ , Pb^{2+} , Cd^{2+} , and Cr^{3+} were also investigated.

EXPERIMENTAL

Material

Chitosan was prepared by *N*-deacetylation of chitin from lobster shell. The deacetylation percentage was 85% from the amino contents.¹³

Dihydroxyl mesocyclic diamine crown ether was prepared according to the procedure reported previously.¹⁴ Other chemicals were reagent grade and were used without further purification.

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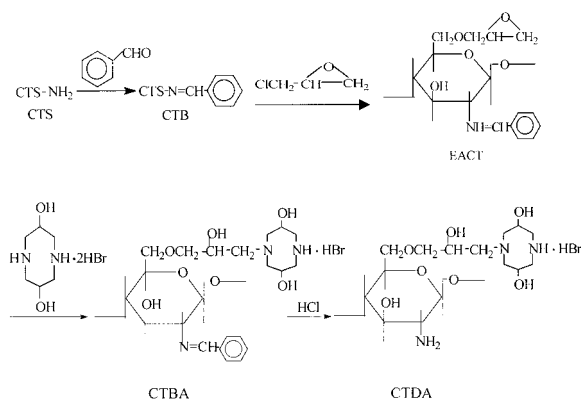


Figure 1 The reaction scheme for the synthesis of CTDA.

Preparation of dihydroxyl mesocyclic diamine grafting chitosan

Figure 1 shows a schematic representation of the preparation of the dihydroxyl mesocyclic diamine chitosan derivative. Powdered CTS-NH₂ (4.0 g) was dissolved in 100 mL of 2 wt % acetic acid and diluted with methanol. Then, 16.5 g of benzaldehyde were slowly dropped into the chitosan solution. The mixture was stirred at room temperature for 4 h to obtain *N*-benzylidene chitosan (CTB), and the CTB (2 g) was activated with epichlorohydrin (12 g) to give epoxy chitosan-benzaldehyde (EACT). The amount of epoxy group is ~2.41 mmol/g EACT, determined according to the method reported previously.¹⁵

Powdered EACT (2 g) was suspended in 50 mL of 1,4-dioxane aqueous solution (30%). Next, 1.5 g (14.16 mmol) sodium carbonate and 1.84 g of 3,7-dihydroxy-1,5-diazacyclooctane dihydrobromide, which was dissolved in 30 mL of methanol, were slowly dropped into the system. The mixture was stirred under nitrogen at 60 °C for 12 h, cooled, filtered, and washed with distilled water, acetone, and ether to obtain *O*-aza-crown ether-*N*-benzylidene chitosan (CTBA). The CTBA and a dilute ethanol hydrochloride solution were reacted, filtered, and washed with distilled water to remove the Schiff base. Then, the precipitate was swollen in a 1.2 M NaOH aqueous solution for 1 h, filtered, washed with distilled water, and dried in a vacuum at 60 °C to obtain dihydroxyl mesocyclic diamine chitosan (CTDA) in a 84.6% yield (weight percent). The results of elemental analysis of the CTDA sample are shown in Table I.

Adsorption procedure for CTDA

Aqueous metal ion solutions were prepared from AgNO₃, Pb(NO₃)₂, Cd(NO₃)₂·4H₂O, and CrCl₃·6H₂O. To 25 mL of an aqueous solution of the metal ion (0.5 mmol L⁻¹) was added 25 mg chitosan or its derivative sample, and the mixture was stirred for 10 h at room temperature. Next, the equilibrated mixture was centrifuged and filtered. The metal ion concentrations in the filter and in the original solution were determined by an atomic adsorption spectrophotometer (AAS), and the quantity of metal ion adsorbed by adsorbent was calculated as follows:

$$Q = V(C_0 - C)/W$$

where Q is the adsorption capacity of the chitosan derivatives (mmol metal ion/g adsorbent), V is the volume of solution (mL), C_0 and C are the concentration of metal ion before and after adsorption (mmol L⁻¹), respectively, and W is the weight of adsorbent (g).

Adsorption selectivity of CTDA for metal ion

The adsorption selectivity of the chitosan derivative was obtained by determination of metal loading capacities with the coexistence of the desired metal ions. A measure of 25 mL of aqueous solution containing Ag⁺, Pb²⁺, and Cr³⁺ (each ion with a concentration equal to 0.5 mmol/L⁻¹) was added to a 50-mL beaker and adjusted to the desirable pH value with HCl. Next, 25 mg of adsorbent was added to the solution, which was then stirred for predetermine time at room temperature. The equilibrated mixture was centrifuged, and then the supernatant solution was analyzed for the metal ions by an atomic adsorption spectrophotometer. 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 adsorbent for metal $M(1)$ and $M(2)$ (mmol metal ion/g adsorbent), respectively.

TABLE I
Elemental Analysis Results of Chitosan Derivatives

Compound	Formula	Calcd (%)			Found (%)		
		C	H	N	C	H	N
CTS	C ₆ H ₁₁ NO ₄	44.72	7.38	8.67	39.43	6.51	6.93
EACT	C ₁₆ H ₁₉ NO ₅	62.95	6.24	4.59	60.21	5.98	4.12
CTDA	C ₁₅ H ₂₈ N ₃ O ₇ Br	40.72	6.32	9.50	39.21	5.94	9.16

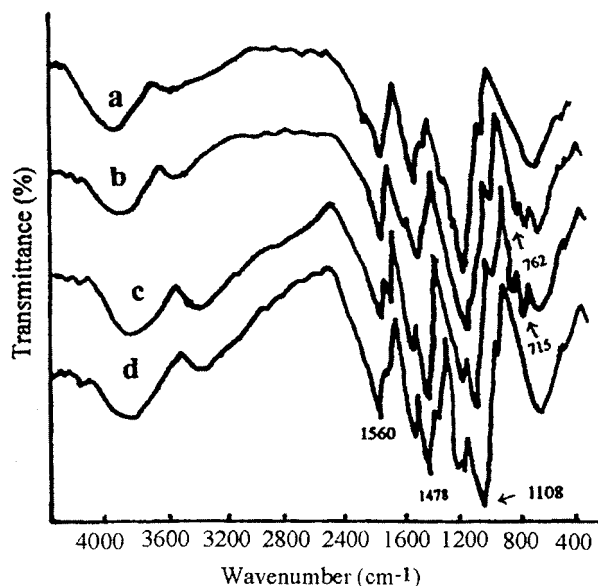


Figure 2 The infrared spectra of CTS (a), CTB (b), EACT (c), and CTDA (d).

Measurements

Elemental analysis was conducted with a Perkin-Elmer automatic instrument; FTIR spectra were measured on a Nicolet 5DX FTIR spectrophotometer. Wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat-film camera, using nickel-filtered $\text{CuK}\alpha$ radiation produced by a Riga (D/MAX, IIIA) diffractometer. Solid-state ^{13}C NMR was conducted with a BRUKER MSL-400 model NMR spectrometer at 100 MHz. Metal ion concentrations were determined by a HITACHI 180-80 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Infrared spectroscopy

Infrared (IR) spectroscopy is the most widely used technique for structure identification of polymers. The FTIR spectra of CTS and its derivatives are shown in Figure 2. Comparison of the FTIR spectra of CTB and EACT with that of CTS indicates that the characteristic peak of $-\text{C}=\text{N}$ group stretch vibration appeared at 1640 cm^{-1} and the characteristic peak of aromatic

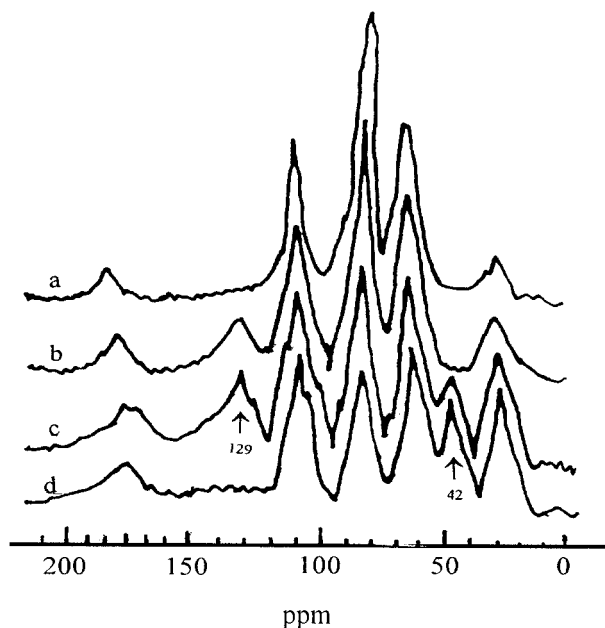


Figure 3 ^{13}C NMR spectra of CTS (a), CTB (b), EACT (c), and CTDA (d).

$-\text{C}-\text{H}$ out-of-plane deformation appeared at 762 and 715 cm^{-1} because of the presence of benzaldehyde groups. Note that these characteristic peaks disappear in CTDA (curve d) because of treatment of the CTBA with hydrochloride ethanol solution to remove the Schiff base. The Schiff base effectively protected the amino groups in the chitosan. It was also seen that the two additional peaks at 1478 and 1108 cm^{-1} corresponding to the $\text{C}-\text{N}-\text{C}$ and $\text{C}-\text{O}-\text{C}$ group appear. The sharp peak near 1560 cm^{-1} , corresponding to bending vibration of the free amino group $-\text{NH}_2$, appeared in CTDA. This result confirms the grafting of dihydroxyl mesocyclic diamine on the chitosan.

^{13}C NMR Analysis

The ^{13}C NMR spectra of chitosan and derivatives are shown in Figure 3. The high-resolution solid-state NMR, also known as ^{13}C NMR, has been used for characterization of insoluble polymers.¹⁶ The solid-state ^{13}C NMR spectra of CTB and EACT compared with CTS shows that a characteristic aromatic carbon appeared at 129 ppm because of the presence of the

TABLE II
Adsorption Selectivity of CTDA and CTS for Aqueous System Containing Ag^+ , Pb^{2+} , and Cr^{3+} ^a(pH = 5.5; 8h)

Compound	Quantity of Adsorption (mmol/g, sorbent)			Selectivity/coefficient		
	Ag^+	Pb^{2+}	Cr^{3+}	$K_{\text{Ag}^+/\text{Pb}^{2+}}$	$K_{\text{Ag}^+/\text{Cr}^{3+}}$	$K_{\text{Pb}^{2+}/\text{Cr}^{3+}}$
CTS	0.21	0.19	0.15	1.12	1.40	1.27
CTDA	0.49	0.04	0.08	12.25	6.12	0.51

^a pH = 5.5; 8 h.

TABLE III
Effect of pH on Metal Ion Sorption by CTDA (mg, Metal. Ion/g, Sorbent, 12h)

	PH=1.5	PH=2.5	PH=4.5	PH=4.0	PH=5.0	PH=6.0	PH=7.0
Ag ⁺	0.08	12.31	19.25	25.37	38.23	45.72	59.24
Cd ²⁺	0.06	2.64	4.13	8.25	10.12	11.25	12.43
Pb ²⁺	0.07	3.52	3.82	5.34	8.42	9.36	11.36
Cr ³⁺	0.01	2.63	2.94	4.58	5.34	8.13	9.45

benzaldehyde. Note that this peak is not seen in the spectra of chitosan and CTDA. Also, the characteristic peak at 42 ppm, corresponding to the —CH₂—N— group, is evident because of the presence of dihydroxyl mesocyclic diamine crown ether groups in CTDA.

Evaluation of CTDA as adsorbent for metal ions

Adsorption selectivity of CTDA

The experimental results of the adsorption selectivity of CTDA for Ag⁺, Pb²⁺, and Cr³⁺ are shown in Table II, demonstrating that grafting dihydroxyl mesocyclic diamine may bring about remarkable changes in the adsorption properties of chitosan. The interaction of the metal ions with mesocyclic diamine containing nitrogen donor atoms has 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 mesocyclic structure. The different stability orders in the case of the metal ions are likely a reflection of different types of bonding in the complexes of this cation. The heavy metal ion binding may involve both electrostatic and covalent contributions.^{17,18} Generally, that metal ion whose ionic radius best matches the radius of the cavity formed by the

mesocyclic diamine on complexation will form the most stable complex. The results indicate that the dihydroxyl azacrown ether might greatly raise the adsorption selectivity of chitosan for some metal ions.

Effect of acidity of medium

The effect of pH on metal ion sorption by dihydroxyl mesocyclic diamine grafted chitosan (CTDA) is shown in Table III. This effect is a major parameter, which greatly influences the maximum ion uptake. It can be seen that the adsorption capacity for metal ions increases with the pH of the solution. This result is due mainly to the presence of amino groups (—NH₂) and secondary amine (—NH—) in CTDA, which easily form protonation at low pH. Competition between protons and metal cations cause decreasing adsorption ability. On the other hand, the adsorption ability also would decrease because the nitrogen atom of mesocyclic diamine does not easily form coordinate bonds with metal ions at low pH.¹⁰ At higher pH, electrostatic repulsion decreases and the uptake reaches a maximum adsorption.

Adsorption kinetics of CTDA

Simple batch kinetic experiments of the dihydroxyl mesocyclic diamine chitosan (CTDA) for Ag⁺, Cd²⁺, Pb²⁺, and Cr³⁺ were determined. The relevant data for different metal ions are shown in Figure 4. The experimental results suggest that the metal ion adsorption of CTDA is reasonably fast. After 2 h, the adsorption reached equilibrium.

CONCLUSION

Chitosan dihydroxyl mesocyclic diamine (CTDA) was synthesized by the reaction of dihydroxyl 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 dihydroxyl azacrown ether groups in chitosan. The selectivity for adsorption of metal ions on CTDA was of the order Ag⁺ > Cr³⁺ > Pb²⁺. The experimental results demonstrated that the grafting of new functional groups onto chitosan increases sorption selectivity. We predict that the

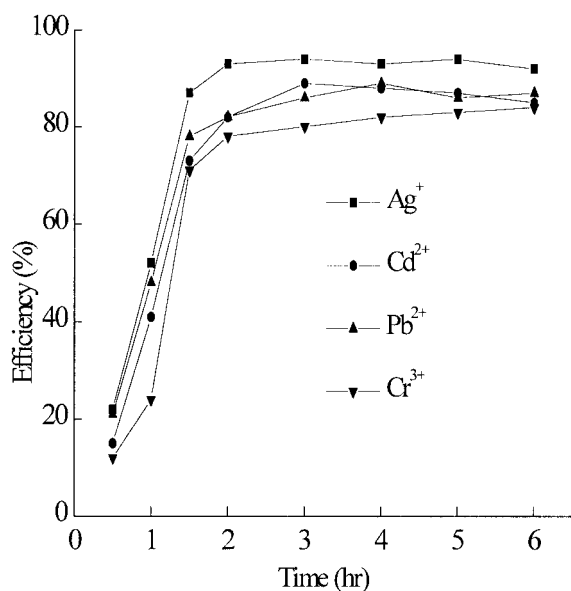


Figure 4 Metal uptake kinetics of CTDA.

novel chitosan azacrown ether would have broad application for the separation and concentration metal ions in environmental analysis.

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