

# Synthesis and Adsorption Properties for Metal Ions of Mesocyclic Diamine-Grafted Chitosan-Crown Ether

ZHIKUAN YANG, YUTING WANG, YURONG TANG

Department of Environmental Science, Wuhan University, 430072 Wuhan Hubei, People's Republic of China

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**ABSTRACT:** A new type of grafted chitosan-crown ether was synthesized using mesocyclic diamine crown ether as the grafting agent. The C2 amino group in chitosan was protected from the reaction between benzaldehyde and chitosan to form *N*-benzylidene chitosan (CTB). After reaction with mesocyclic diamine crown ether of the epoxy propane group to give mesocyclic diamine-*N*-benzalidene chitosan (CTBA), the Schiff base was removed in a dilute ethanol hydrochloride solution to obtain chitosan-crown ether (CTDA). Its structure was confirmed by FTIR spectra analysis and X-ray diffraction analysis. Its static adsorption properties for Pb(II), Cu(II), Cd(II), and Cr(III) were studied. The experimental results showed that the grafted chitosan-crown ether has high selectivity for the adsorption of Cu(II) in the presence of Pb(II), Cu(II), and Cd(II) and its adsorption selectivity is better than that of chitosan. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1255–1260, 2000

**Key words:** grafted chitosan; mesocyclic diamine crown ether; synthesis; adsorption properties; metal ions

## INTRODUCTION

As mesocyclic diamine crown ethers have particular structures, they have specific selectivity and stability for heavy or precious metal ions,<sup>1</sup> but the solubility of mesocyclic diamine crown ethers is too great to recover after being used; therefore, their application is limited. If mesocyclic diamine crown ethers were grafted to a polymer to give polymerized crown ether, it can be predicted that these novel polymers would have a stronger complex action with metal salts and better selectivity for metal ions than have crown ethers owing to the synergistic effect of high molecular weight.<sup>2</sup>

Chitosan (CTS), which is easily derived from chitin by *N*-deacetylation, has both hydroxyl and amine groups that can be modified easily to prepare

chitosan derivatives.<sup>3–6</sup> In the present article, the C2 amino group in chitosan was protected from the reaction between benzaldehyde and chitosan to form *N*-benzylidene chitosan (CTB). Then, the chitosan–benzaldehyde–mesocyclic diamine crown ether (CTBA) was prepared by reacting CTBA and a dilute ethanol hydrochloride solution to give a novel kind of grafted chitosan-crown ether (CTDA). The present study was aimed to synthesize mesocyclic diamine-grafted chitosan-crown ether and to investigate its adsorption properties for metal ions.

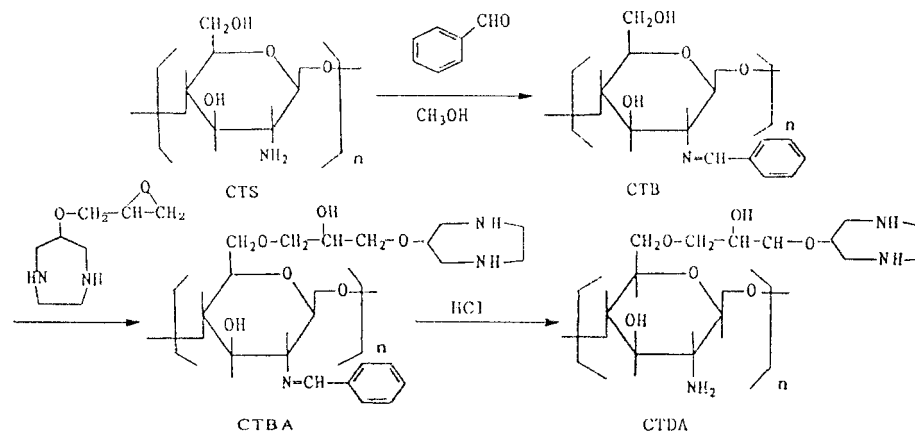
## EXPERIMENTAL

### Materials

Chitosan, whose degree of deacetylation was calculated to be 85% from the amino contents,<sup>7</sup> was prepared by *N*-deacetylation of chitin from shrimp shells. Hydroxy mesocyclic diamine crown ether

Correspondence to: Z. Yang.

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**Figure 1** Reaction scheme for the synthesis of CTDA.

was prepared according to the procedure reported previously.<sup>8</sup> Epichlorohydrin was purchased from the First Chemical Factory (Shanghai, China). Benzaldehyde was purchased from the Chemical Factory (Tianjian, China). All inorganic compounds were reagent grade and all solvents and available organic materials were commercial products used without further purification.

#### Measurements

Infrared (IR) spectra were measured on a Nicolet 5DX FTIR spectrophotometer. Wide-angle X-ray diffraction patterns were obtained with a flat-film camera using nickel-filtered  $\text{CuK}\alpha$  radiation produced by a Rigaku (D/MAX,111A) diffractometer. Metal-ion concentration was determined by a Hitachi 180-80 atomic absorption spectrophotometer.

#### Synthesis of Mesocyclic Diamine-grafted Chitosan-Crown Ether

Since chitosan has both hydroxyl and amino groups that can react with epoxide in nucleophilic substitution and opening of the epoxide ring, the most favorable nucleophilic center of chitosan is the amino group.<sup>9,10</sup> In order that the graft copolymerization of CTS can occur at the C6 position, the C2 amino group in chitosan was protected from the reaction of benzaldehyde and chitosan to form Schiff base chitosan. The basic reaction scheme is described in Figure 1.

#### Preparation of Epoxy Mesocyclic Diamine (EMDA)

Powdered 3-hydroxy-1,5-diazacyclic heptane dihydrobromic acid (3.0 g) was dissolved in 50 mL

THF and a 2-mL sodium hydroxide aqueous solution ( $5 \text{ mol dm}^{-3}$ ); then, 2 mL epichlorohydrin and 50 mL methanol was slowly added. The mixture was heated with stirring for 48 h at  $40^\circ\text{C}$  under a nitrogen atmosphere, cooled to room temperature, filtered, and washed completely with methanol ether to remove any unreacted epichlorohydrin, and dried in a vacuum system to give a light brown powder. The product was obtained at a 84% yield.

#### Preparation of *N*-Benzaldehyde Chitosan (CTB)

A mixture of chitosan (2.0 g), 40 mL acetic acid (1%), and 60 mL methanol was stirred at room temperature to become a clear and viscous solution. A mixture of 10 g benzaldehyde and 15 mL methanol was slowly added to the chitosan solution, continually stirred for 8 h, filtered, washed with methanol ethanol to remove any unreacted benzaldehyde, and dried at  $60^\circ\text{C}$  to give the Schiff base CTB.

#### Preparation of Mesocyclic Diamine-grafted Chitosan-Crown Ether (CTDA)

Powdered CTB (2.0 g) was swollen in 50 mL dichloroethane at  $40^\circ\text{C}$  for 4 h; then, 1.2 g epoxy mesocyclic diamine (EMDA), which was dissolved in 20 mL ethanol, was slowly added. The mixture was refluxed with stirring under nitrogen for 24 h, cooled, filtered, and washed with ethanol and ether to give chitosan-benzaldehyde-mesocyclic diamine crown ether (CTBA). The Schiff base was removed by reacting CTBA and a dilute ethanolic hydrochloride solution, filtered, and washed with distilled water, and the precipitate

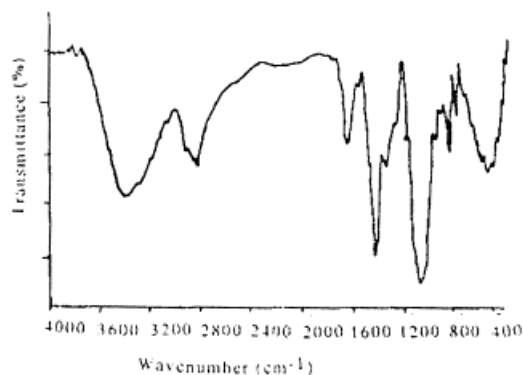


Figure 2 Infra red spectra of EMDA.

was swollen in a 1.0M NaOH aqueous solution for 10 min, filtered, washed with distilled water, and dried in a vacuum at 60°C to give CTDA in a 75% yield.

#### Determination of the Adsorption Properties for Metal Ions of CTDA

##### Ability to Absorb Metal Ions of CTDA

To 25 mL of an aqueous solution of the metal salts [ $5.0 \times 10^{-1}$  mmol,  $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ] was added 25 mg of chitosan or a chitosan-derivative sample and stirred for 8 h at room temperature; then, the mixture was centrifuged and filtered. The metal-ion concentration in the filter was determined by atomic adsorption spectrophotometry (AAS), and the quantity and efficiency of the metal ion absorbed by CTS or CTDA was calculated by the method reported previously.<sup>6</sup>

##### Adsorption Selectivity of CTDA for Metal Ions

A  $5.0 \times 10^{-1}$ -mmol solution of the desired metal ions was prepared; 25 mg CTDA was added to 25 mL of the solution and stirred for 8 h at room temperature. The equilibrated mixture was centrifuged and filtered. The metal-ion concentration in the filter was determined by an atomic adsorption spectrophotometer. The selectivity coefficient of CTDA or CTS was calculated the same way as reported.<sup>11,12</sup>

##### pH Dependence of Metal Sorption

The pH-dependent metal sorption was performed by interacting 25 mg of the CTDA sample with the metal-ion solution (25 mL  $5.0 \times 10^{-1}$  mmol).

The reaction mixture was adjusted to a different pH range. After stirring 8 h at room temperature, the metal-ion concentration in the filter was determined according to the above procedure.

## RESULTS AND DISCUSSION

### Characterization of Epoxy Mesocyclic Diamine (EMDA)

The IR spectra and mass-spectrogram of 3-epoxy-1.5-diazacyclic heptane are shown in Figures 2 and 3, respectively. Figure 2 shows the characteristic peak of the C—O—C stretch vibration that appeared at  $1080 \text{ cm}^{-1}$ , the characteristic peak of the epoxy group vibration that appeared at  $880 \text{ cm}^{-1}$ , and the characteristic peak of the C—N backbone vibration that appeared at  $1480 \text{ cm}^{-1}$ . Figure 3 shows the following:  $M/Z$  (20 eV), %, 172( $M^+$ , 48), 129[( $M - \text{C}_2\text{H}_3\text{O}$ ), 35], and 97[( $M - \text{C}_3\text{H}_7\text{O}$ ), 78]. The IR spectra and mass-spectrogram of the product correspond well with the structure of 3-epoxy-1.5-diazacyclic heptane.

### IR Spectra Analysis

Figure 4 shows the IR spectra of chitosan and the chitosan derivatives. Curves (a–d) are the IR spectra of CTS, CTB, CTBA, and CTDA. It can be seen that the characteristic peak of the aromatic C—H out-of-plane deformation appeared at 752 and  $695 \text{ cm}^{-1}$  for CTB and CTBA owing to the presence of the benzaldehyde groups. These Schiff bases used for *o*-graft copolymerization remained in the course of the reaction and effectively protected the amino group in the chitosan. After the Schiff base was removed by reacting CTBA and a dilute hydrochloride solution to form CTDA with free amino groups, the strong charac-

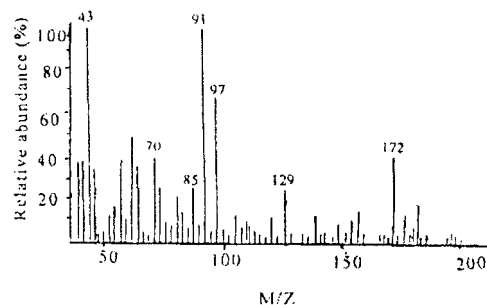
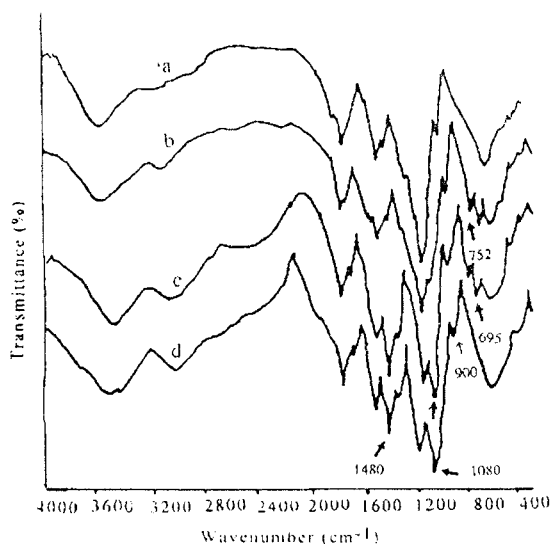


Figure 3 Mass-spectrogram of EMDA.

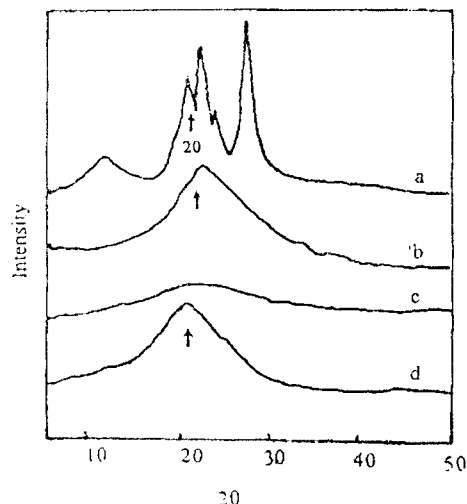


**Figure 4** IR of (a) CTS, (b) CTB, (c) CTBA, and (d) CTDA.

teristic peaks of the mesocyclic diamine vibration appeared at 1480 (C—N—C) and 1080 (C—O—C)  $\text{cm}^{-1}$  for CTDA, showing that the grafting of mesocyclic diamine and chitosan occurred. Compared with the CTBA IR spectra, the CTDA IR spectra does not have the characteristic peaks of the C=N stretch vibration near 1640  $\text{cm}^{-1}$ , which showed that the Schiff base was hydrolyzed and that benzaldehyde was removed. The intensity of the C—H stretching vibration of the methylene group in the region of near 300  $\text{cm}^{-1}$  increases for CTBA and CTDA. All these confirm the graft copolymerization of the mesocyclic diamine in the C6 position in the chitosan. The characteristic peak of  $\beta$ -D-pyranoid near 900  $\text{cm}^{-1}$  remained, showing that the graft reaction did not break up the pyranoid ring.

#### X-ray Diffraction Analysis

Figure 5 shows the wide-angle X-ray diffraction (WAXD) patterns of chitosan and the chitosan



**Figure 5** X-ray diffraction patterns of (a) CTS, (b) CTB, (c) CTBA, and (d) CTDA.

derivatives. The WAXD pattern of chitosan shows the characteristic peak at  $2\theta = 10^\circ$ ,  $20^\circ$ , and  $28^\circ$ . For CTB, the peaks at  $2\theta = 10^\circ$  and  $28^\circ$  disappeared, and the characteristic peak at  $2\theta = 20^\circ$  decreased.

For CTBA, the intensity of the characteristic peak at  $2\theta = 20^\circ$  decreased more than that of CTB. We thought that the decrease in crystallinity of the chitosan derivatives was attributed to the deformation of the strong hydrogen bond in the chitosan as the hydroxyl and amino groups were substituted by the benzylidene and the mesocyclic diamine crown ether groups. Both derivatives gave a low crystallinity, indicating that they were considerably more amorphous than was chitosan. Meanwhile, the characteristic peak of CTDA at  $2\theta = 20^\circ$  increased in the X-ray diffraction pattern. It is believed that the regenerated amino groups formed the hydrogen bond again, resulting in increase in the crystallinity.

**Table I** Relationship Between pH Values and Adsorption Capacities ( $Q$ ,  $\text{mmol g}^{-1}$ ) and Efficiencies ( $E$ , %) of CTDA (8 h)

	pH 3		pH 4		pH 5.5	
	$Q$	$E$	$Q$	$E$	$Q$	$E$
Pb(II)	0.17	20.67	0.43	52.76	0.52	64.40
Cu(II)	0.19	22.43	0.47	56.86	0.65	78.63
Cr(III)	0.08	10.76	0.26	32.17	0.34	41.42
Cd(II)	0.05	6.97	0.23	27.41	0.25	30.23

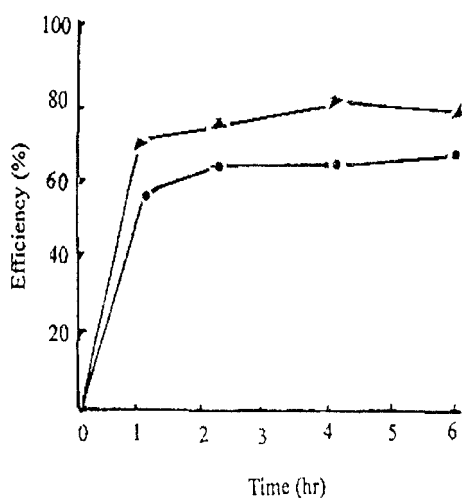
**Table II** Adsorption Selectivity of CTDA for Aqueous System Containing Pb(II), Cu(II), and Cd(II) (pH 5.5, 6 h)

	Quantity of Adsorption (mmol g <sup>-1</sup> )			Selectivity/Coefficients
	Pb(II)	CU(II)	Cd(II)	
CTS	0.21	0.24	0.11	$K_{\text{Cu(II)/Cd(II)}} = 1.14$ , $K_{\text{Cu(II)/Pb(II)}} = 2.18$
CTDA	0.14	0.47	0.02	$K_{\text{Cu(II)/Cd(II)}} = 3.36$ , $K_{\text{Cu(II)/Pb(II)}} = 23.5$

### Adsorption Properties of CTDA for Metal Ions

#### Effect of Acidity of Medium on Adsorption Property of CTDA

The adsorption experimental result of CTDA for Pb(II), Cu(II), and Cd(II) (with nitrate anions) and Cr(III) (with chloride anion) are shown in Table I. It can be seen that the adsorption capacity and efficiency for metal ions increased with the pH in the solution. The result is due mainly to the presence of amino groups ( $-\text{NH}_2$ ) and secondary amine in CTDA. The  $-\text{NH}_2$  would become  $-\text{NH}_3^+$  to cause a decreasing adsorption ability under low pH. On the other hand, the adsorption ability also would decrease because the nitrogen atoms of mesocyclic diamime do not easily form coordinate bonds with metal ions under low pH.



**Figure 6** Metal-uptake kinetics of CTDA at pH 5.0: (▲) Cu(II) and (●) Pb(II).

### Adsorption Selectivity of CTDA for Metal Ions

The experimental results of the adsorption selectivity of CTDA for Pb(II), Cu(II), and Cd(II) are shown in Table II, demonstrating that grafting may bring about remarkable changes in the adsorption properties of chitosan (CTS). Comparing several selectivity coefficients of CTDA and CTS, it can be seen that the adsorption selectivity of CTDA for Cu(II) was much higher than that of CTS, which indicated that mesocyclic diamine crown ethers might greatly increase the adsorption selectivity of chitosan for some metal ions.

### Adsorption Kinetics of CTDA

Adsorption kinetics of CTDA for Cu(II) and Pb(II) are shown in Figure 6. The results demonstrated that the adsorption of CTDA was high speed for Pb(II) and Cu(II). After 2 h, the adsorption of CTDA reached the equilibrium fundamentally. The adsorption efficiency of CTDA for Pb(II) and Cu(II) could reach 64 and 78%, respectively.

### CONCLUSIONS

CTDA was synthesized via a Schiff-base reaction between amino groups in chitosan and benzaldehyde. After reaction with EMDA and CTB, the Schiff base was removed by the chitosan derivative (CTBA) with a dilute hydrochloride ethanol solution. The adsorption capacities and efficiencies of CTDA for Cu(II) with the coexistence of Pb(II), Cu(II), and Cd(II) was greatly improved. The results demonstrated that the mesocyclic diamime can increase the adsorption ability of chitosan for some of metal ions, just as

we expected, and it can be predicted that the new type chitosan-crown ether will have wide-ranging applications for the separation and concentration of heavy metal ions.

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