Synthesis and Characterization of Macrocyclic Polyamine Derivative of Chitosan

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ABSTRACT: A novel macrocyclic polyamine derivative of chitosan was synthesized by a reaction between chitosan and epoxy-activated macrocyclic polyamine. The copolymer that is obtained contains amino functional groups in its skeleton and secondary amine and more polar hydroxyl groups. Four types of analyses were used to characterize the chemical modifications of the chitosan: elemental, FTIR spectra, solid-state ^{13}C-NMR, and X-ray diffraction. The adsorption properties of the macrocyclic polyamine grafted chitosan for Ag^+, Cu^{2+}, Co^{2+}, and Cr^{3+} were also investigated. The experimental results showed that the new mac-

rocyclic polyamine derivative of chitosan has high adsorption capacity and good selectivity for Ag^+ in the presence of Ag^+, Co^{2+}, and Cr^{3+}. The selectivity coefficients were $K_{Ag^+/Co^{2+}} = 6.16$, $K_{Ag^+/Cr^{3+}} = 14.81$, and $K_{Co^{2+}/Cr^{3+}} = 2.42$, respectively. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 924–929, 2003

Key words: chitosan; azacrown ether; macrocyclic polyamine; synthesis; adsorption

INTRODUCTION

Chitosan (CTS), which is a high nitrogen content biopolymer extracted from chitin, the most abundant biopolymer in nature after cellulose, is efficient at removing metal ions from solution. CTS has both hydroxyl and amine groups that can be modified to prepare CTS derivatives.[1–6] Several processes have been proposed to modify CTS by grafting new functional groups on the polymer backbone.[7] Chemical modifications offer a wide spectrum of tools to enhance the adsorption properties of CTS 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 new functional groups improves the adsorption selectivity, as well as the sorption capacities.

Macrocyclic polyamines (azacrown ethers) are new functional compounds that have specific selectivity and stability for many heavy or precious metal ions,[8] but the solubility is too high to recover after being used. Therefore, their applications are limited. If macrocyclic polyamine were grafted onto a high molecular CTS backbone to yield CTS–azacrown ether containing the double structures and properties of CTS and macrocyclic polyamine, these novel CTS derivatives would have a wide range of applications for the

separation and concentration of heavy or precious metal ions in solution.[9] In previous studies the grafting of mesocyclic diamine on the CTS backbone was discussed for heavy metal ion adsorption.[10–12] This study was dedicated to the synthesis of new CTS derivatives on which macrocyclic polyamine is grafted through the binding on the CTS backbone of an intermediary product made by the chemical reaction of hydroxyl macrocyclic polyamine and epichlorohydrin. In this case, epichlorohydrin acts as linking spacer between the CTS and azacrown ether. The structures of new CTS derivatives were confirmed with the following analyses: elemental, IR spectra, solid-state ^{13}C-NMR, and X-ray diffraction. The adsorption properties and selectivity for Ag^+, Cu^{2+}, Co^{2+}, and Cr^{3+} were investigated.

EXPERIMENTAL

Materials

CTS was prepared by *N*-deacetylation of chitin from lobster shells. The deacetylation percentage was calculated to be 92% from the amino contents, and it was used after pressing through a 200-mesh sieve. Macrocyclic polyamine and epoxy-activated azacrown ether were prepared according to the procedure reported previously.[9,13] Other chemicals were reagent grade and were used without further purification.

Measurements

Elemental analysis was performed on a Perkin–Elmer automatic instrument; the IR spectra were measured
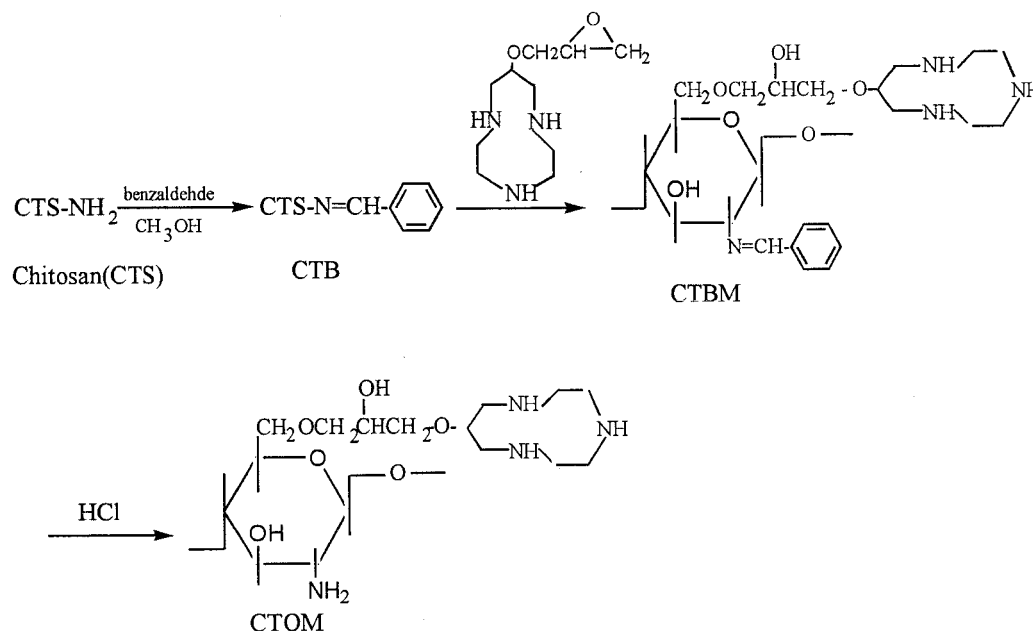
Figure 1 The reaction scheme for the synthesis of CTOM.

on a Nicolet 5DX FTIR spectrophotometer. The wide-angle X-ray diffraction (WAXD) patterns were obtained with a flat-film camera using nickel-filtered CuK_α radiation produced by a Riga (D/MAX, IIIA) diffractometer. Solid-state ^{13}C-NMR was conducted using a Bruker MSL-400 NMR spectrometer at 100 MHz. The concentrations of the metal ions were determined with a Hitachi 180-80 atomic absorption spectrophotometer.

Synthesis of macrocyclic polyamine grafting CTS

Figure 1 shows a schematic representation of the preparation of the macrocyclic polyamine CTS derivative. The CTS powder (4.5 g) was placed in a stoppered vessel containing an acetic acid solution (100 mL of 2 wt % acetic acid and diluted with 60 mL of methanol). Then 15.5 g of benzaldehyde were added dropwise into the CTS solution, which was kept at 60°C. The contents of the vessel was stirred for 12 h, filtered, washed with methanol–ethanol to remove any unreacted benzaldehyde, and dried at 60°C to obtain the Schiff base N-benzaldehyde CTS (CTB). Powdered CTB (2 g) was swelled in 25 mL of dichloroethane at room temperature for 12 h and reacted with 3.0 g of

epoxy macrocyclic polyamine. The mixture was refluxed with continuous shaking under nitrogen. After 24 h the solution was drained and the powder washed completely with ethanol and ether to give CTB-macrocyclic polyamine (CTBM). The Schiff base was suspended in 0.2M hydrochloride ethanol solution and treated at room temperature for 4 h, filtered, and washed with distilled water until the pH of the washing liquor was 7. The precipitate was treated with 0.5M NaOH solution and dried to give a light brown O-CTBM (CTOM) in an 85.4 wt % yield. The results of the elemental analysis of the CTOM sample are shown in Table I.

Metal-sorption procedure

An aqueous metal ion solution was prepared from $AgNO_3$, $Cu(NO_3)_2$, $CoCl_3 \cdot 6H_2O$, and $CrCl_3 \cdot 6H_2O$. A measure of 25 mL of an aqueous solution containing 0.5 mmol L^{-1} metal ions was placed in a glass bottle and adjusted to the desired pH with hydrochloric acid or sodium hydroxide aqueous solution (0.1 mmol L^{-1}), and then 20 mg of sorbent was added. The mixture was vibrated for 8 h for adsorption at 25°C, then the adsorbent was filtered off. The concentration

TABLE I
Elemental Analysis Results of Chitosan Derivatives

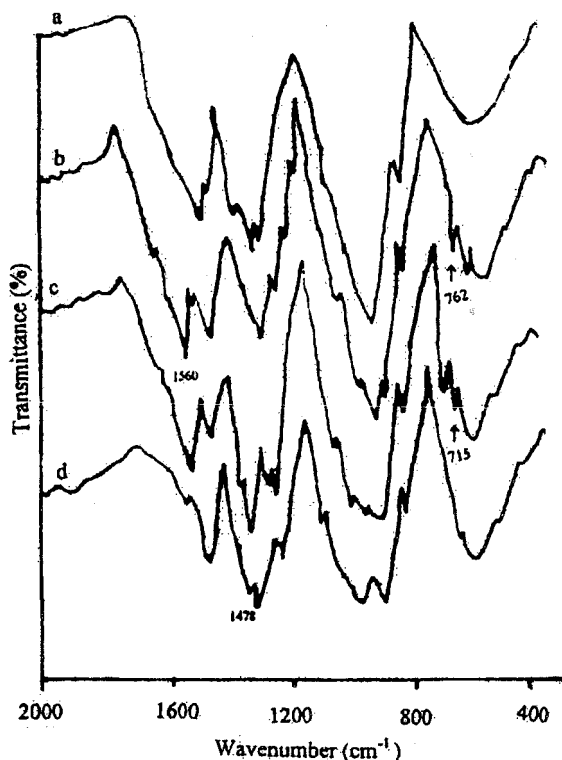| Compound	Formula	Calcd (%)			Found (%)		
		C	H	N	C	H	N
CTS	$C_6H_{11}NO_4$	44.72	7.38	8.67	39.43	6.51	6.93
CTBM	$C_{23}H_{37}N_4O_5$	61.47	8.24	12.47	57.24	7.16	10.96
CTOM	$C_{16}H_{33}N_4O_5$	53.18	9.14	15.51	50.37	8.62	14.87

Figure 2 The IR spectra of CTS (curve a), CTB (curve b), CTBM (curve c), and CTOM (curve d).

of metal ions in the filtrate and the original solution was determined by atomic absorption spectroscopy, and the quantity of metal ions adsorbed by the adsorbent was calculated as follows:

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

where Q is the adsorption capacity of the CTS derivatives (mmol metal ions/g adsorbent); V is the volume of the solution (mL); C_o and C are the concentrations of metal ions before and after adsorption (mmol L^{-1}), respectively; and W is the weight of the adsorbent (g).

The adsorption selectivity of the CTS derivative was obtained by the determination of the metal loading capacities in the presence of the desired metal ions. We added 25 mg of adsorbent to 25 mL of the solution and it was stirred for a predetermined 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 the adsorbent was calculated by a method reported previously.[14]

RESULTS AND DISCUSSION

IR spectroscopy

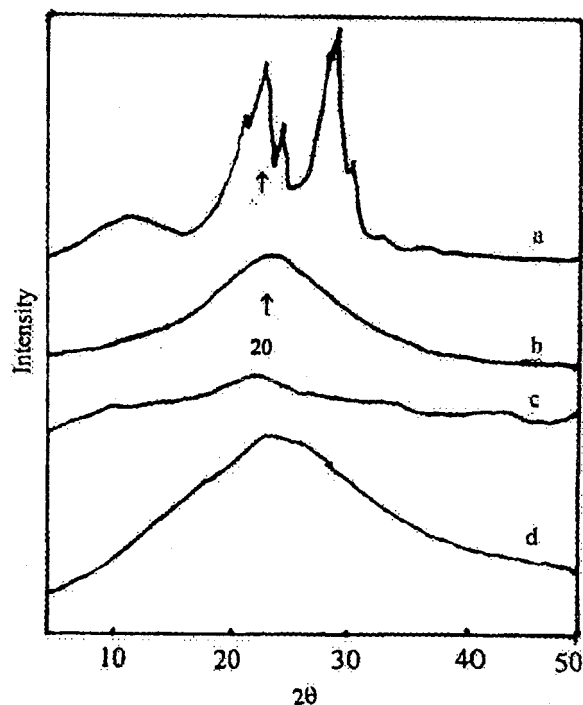IR spectroscopy is the most widely used technique for structure identification in polymers. The FTIR spectra

Figure 3 The X-ray diffraction patterns of CTS (curve a), CTB (curve b), CTBM (curve c), and CTOM (curve d).

of the resulting CTS derivatives (CTS, CTB, CTBM, and CTOM) are shown in Figure 2. Although marked differences were not observed in the IR spectra of CTS and the derivatives, the characteristic peaks of ben-
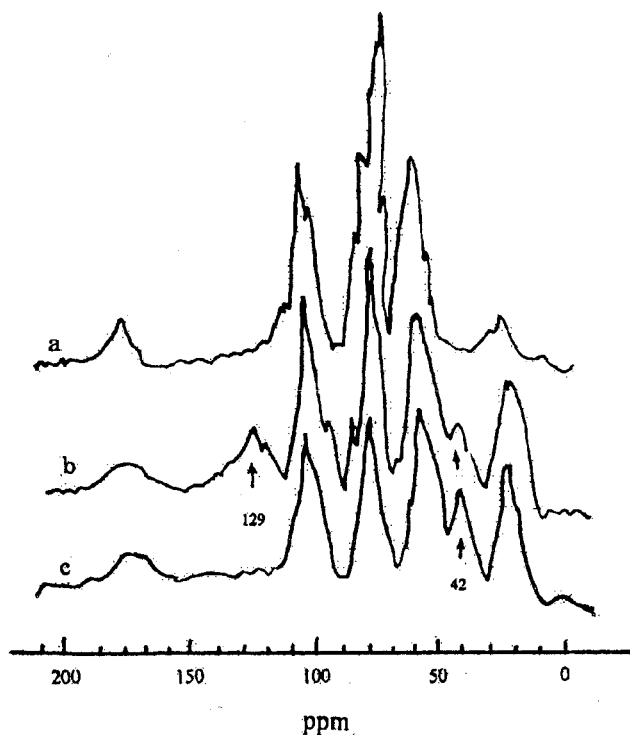

Figure 4 The ^{13}C-NMR spectra of CTS (curve a), CTBM (curve b), and CTOM (curve c).

TABLE II
Effect of pH on Metal Ion Sorption by CTOM (mg Metal Ions/g Sorbent, 12 h)

	pH 1.0	pH 2.0	pH 2.5	pH 3.5	pH 4.8	pH 5.7	pH 6.8
Ag^+	0.06	10.34	15.27	23.46	42.64	56.42	67.35
Cu^{2+}	0.03	2.17	3.25	5.47	8.42	9.70	10.25
Co^{2+}	0.07	1.38	2.63	3.06	5.31	6.24	8.36
Cr^{3+}	0.02	2.72	2.89	4.17	5.85	7.82	9.46

zene ring backbone vibration appeared at 762 and 715 cm^{-1}, because of the presence of the benzaldehyde groups of CTB and CTBM. The reaction between aldehyde groups and amine groups on benzaldehyde and CTS, respectively, involves the formation of imine linkage —C=N bonds, which are identified by a band at 1650 cm^{-1}. Note that these characteristic peaks disappear in CTOM (Fig. 2, curve d), which is caused by treating the CTBM in hydrochloride ethanol solution to remove the Schiff base. This Schiff base used for the reaction for *O*-macrocyclic polyamine remained in the course of the reaction (from CTB to CTBM) and effectively protected the amino groups in the CTS. It was seen that the new peaks at 1478 cm^{-1} corresponding to the —C—N—C group appears (Fig. 2, curves c and d). The sharp peak near 1546 cm^{-1} corresponding to the bending vibration of —NH$_2$ appeared for CTOM. This confirms the introduction of the macrocyclic polyamine in the CTS.

WAXD analysis

The WAXD patterns of the CTS and CTS derivatives are shown in Figure 3. The WAXD pattern of CTS sample shows the characteristic peak at $2\theta = 10°$, $20°$, and $28°$. For CTB the peak at $2\theta = 10°$ disappeared, and the characteristic peak at $2\theta = 20°$ decreased. The characteristic peak at $2\theta = 20°$ for CTBM decreased more than that for CTB. It was thought that the decrease was attributed to the deformation of the strong hydroxyl bond in the crude CTS sample backbone as the hydroxyl and amino groups were substituted by the benzylidene or macrocyclic polyamine groups. The CTS derivatives had a low crystallinity, indicating that they were considerably more amorphous than crude CTS.[15] Meanwhile, the characteristic peak of CTOM at $2\theta = 20°$ increased more than that of CTB. It believed that the regenerated amino groups formed

the hydrogen bond again, resulting in an increase in the crystallinity.

^{13}C-NMR analysis

Figure 4 shows the ^{13}C-NMR spectra of CTS and its derivatives. High-resolution solid-state NMR, also known as ^{13}C-NMR, has been used for the characterization of insoluble polymers.[16] The solid-state ^{13}C-NMR spectra of CTBM compared to CTS show that a characteristic aromatic carbon appeared at 129 ppm, because of the presence of benzaldehyde. Note that this is not seen in the spectra of CTS and CTOM. It also can be noted that the characteristic peak at 42 ppm corresponds to the —CH$_2$—N— group, which is from the presence of macrocyclic polymer crown ether groups in CTBM and CTOM.

Evaluation of CTOM as adsorbent for metal ions

Effect of acidity of medium

The adsorption experimental results of CTOM for Ag^+, Co^{2+}, Cu^{2+}, and Cr^{3+} at different pH values are shown Table II. It can be seen that the adsorption capacity for the metal ions increased with the pH in the medium. The pH is a major parameter, which greatly influences the maximum uptake. The results are mainly due to the presence of amino groups (—NH$_2$) and secondary amine (—NH—) in CTOM. The free amino group exists because of the following balance in aqueous solution:

$$CTS—NH_2 + H_2O \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} CTS—NH_3^+ + OH^-$$
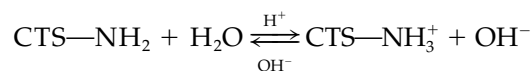
It is evident that the amino group is protophilia and becomes NH_3^+ in acid media, and competition be-

TABLE III
Adsorption Selectivity of CTOM for Aqueous System Containing Ag^+, Pb^{2+}, and Cr^{3+} (pH 5.5 Metal-Ions = 1:1, 8 h)

Compound	Quantity of Adsorption (mmol/g Sorbent)			Selectivity/Coefficient		
	Ag^+	Co^{2+}	Cr^{3+}	K_{Ag^+}/Co^{2+}	K_{Ag^+}/Cr^{3+}	$K_{Co^{2+}}/Cr^{3+}$
CTS	0.22	0.18	0.15	1.69	1.22	1.21
CTOM	0.74	0.12	0.05	6.16	14.81	2.42

TABLE IV
Desorption content of metal Ions Asorbed
by the CTS and CTOM

Adsorbent	Desorption (%)			
	Ag^+	Cu^{2+}	Co^{2+}	Cr^{3+}
CTS	84.65	94.36	96.13	93.47
CTOM	90.28	93.14	97.25	94.32

tween the protons and metal cations causes decreased adsorption ability. On the other hand, the adsorption ability would also decrease because the nitrogen atom of the macrocyclic polyamine does not easily form coordinate bonds with metal ions under low pH.[9] At higher pH the electrostatic repulsion decreases and the uptake reaches maximum adsorption.

Adsorption selectivity of CTOM

The experimental results of the adsorption selectivity of CTOM for Ag^+, Co^{2+}, and Cr^{3+} are shown in Table III. In comparing several selectivity coefficients of CTOM and CTS it could be seen that the adsorption selectivity of CTOM for Ag^+ was much higher than that of CTS in an aqueous system containing Ag^+-Co^{2+}-Cr^{3+}. It is indicated that macrocyclic polyamine might greatly increase the adsorption selectivity of CTS for some metal ions.

The interaction of the metal ions with polyamine containing nitrogen donor atoms was investigated. The results demonstrated that the metal complexes of polyamine are 1:1 (metal/ligand) with the metal ion located at the center of the cycle. The different stability orders in the case of the metal ions probably reflect different types of bonding in the ions; the binding may involve both electrostatic and covalent contributions. Generally, the metals ion whose ionic radius best matches the radius of the cavity formed by the aza-crown ether on complexation will form the most stable complex. The results indicated that macrocyclic poly-amine crown ether might greatly raise the adsorption selectivity of CTS for some metal ions.

Desorption of metal ions

After absorption, the metal ions could be quantitatively eluted off from CTOM. The CTS derivative with adsorbed metal ions was stirred in 40 mL of 0.5 mol L^{-1} hydrochloric acid for 10 h at room temperature and then filtered. The metal ions in the filtrate were determined by atomic adsorption analysis.

The desorption percentage of metal ions adsorbed by CTS and CTOM in 0.5 mol L^{-1} solution is shown in Table IV. In CTS and CTOM, a high desorption percentage of metal cations was confirmed. The amount of cation desorbed under this condition was 85–98% of the originally adsorbed cation.

Adsorption kinetics of CTOM

Simple batch kinetic experiments of the macrocyclic polyamine CTS (CTOM) for Ag^+, Cu^{2+}, Co^{2+}, and Cr^{3+} were determined. The relevant data for different metal ions are shown in Figure 5. The experimental results indicate that the metal ion adsorption of CTOM is reasonably fast. The adsorption reached equilibrium after 1.5 h.

CONCLUSION

A CTS macrocyclic polyamine azacrown ether (CTOM) was synthesized by the reaction of epoxy-
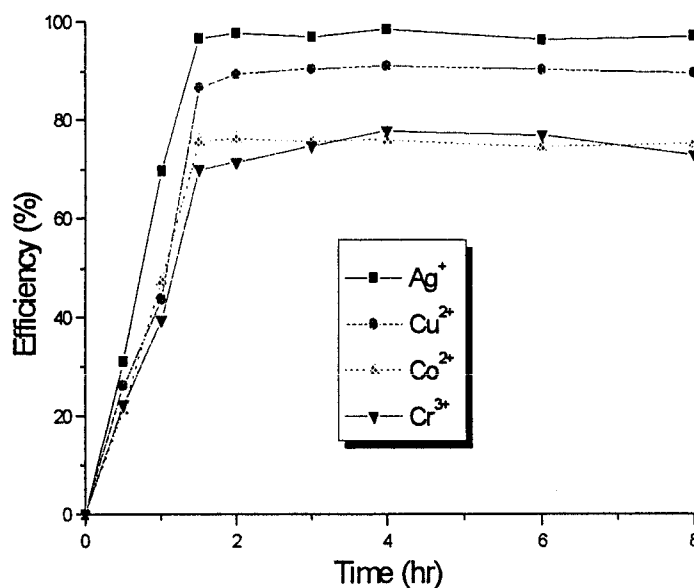
Figure 5 The metal uptake kinetics of CTOM.

activated macrocyclic polyamine with *N*-benzylidene CTS (CTB). The novel CTS derivative has high metal uptake abilities, and the selectivity property for the metal ions was improved by the incorporation of aza-crown ether groups in the CTS. The selectivity for adsorption of metal ions on CTOM was $Ag^+ > Co^{2+} > Cr^{3+}$. The experimental results demonstrated that the grafting of new functional groups onto CTS increases the sorption selectivity. As expected and predicted, the novel CTS azacrown ether will have broad applications for the separation and concentration of metal ions in environmental analyses.

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