

Synthesis of Novel Amino(alkylamino)deoxychitosans and Those Thiol-Derivatives and the Chemisorption Behaviors of an Acid Dye and Hg^{2+} Ion onto the Resulting Polymers

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ABSTRACT: Introducing an additional functionality to chitosan, novel chitosan-based materials were synthesized. The reactions of tosylchitosan with ammonia, ethylenediamine, and hexamethylenediamine have been studied, and the chemisorption behavior of a typical acid dye (CI Acid Orange 7) onto the resulting polymers has been evaluated. Thiol groups were introduced to the above chitosan derivatives having additional amino group at the C₆ position, and the chemisorption behavior of Hg^{2+} ion onto the resulting polymers was measured and compared with that of *N*-thioacetylchitosan. The successful synthetic reaction was demonstrated by the infrared spectroscopic measurements. It has been confirmed that the abilities of the chito-

san derivatives with additional amino groups to the chemisorption of an acid dye were significantly high, and that the saturation value of the chemisorption amount of CI Acid Orange 7 toward one of 2'-aminoethylaminodeoxychitosans was significantly high as 6.16 mol/kg. The results also showed that the saturation amounts of Hg^{2+} ion chemisorption were larger with the increase in the thiol group content of the chitosan derivatives with the thiol groups. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1895–1902, 2007

Key words: aminodeoxychitosan; chemisorption; acid dye; Hg^{2+} ion; tosylchitosan

INTRODUCTION

Chitin is widely distributed in nature as a component of the exoskeletons of crustaceans and insects. However, it is insoluble in common organic solvents such as benzene or methanol, and the resulting intractability has limited the utilization. Kurita et al. found that solubilization can be achieved by a random introduction of an appropriate amount of acetyl groups¹ or by an introduction of bulky groups such as phthaloyl group.² They also reported a high reactivity of tosylated chitin, enabling further modification under mild conditions.³

To introduce an additional functionality to chitin, in our previous work,⁴ we have synthesized aminodeoxychitins by the reaction of the tosylchitin with ammonia in dimethylsulfoxide at different temperatures. Similarly, 2'-aminoethylamino- and 6'-amino-hexylaminodeoxychitins have been synthesized by reacting the tosylchitin with ethylenediamine and hexamethylenediamine, respectively. It has been con-

firmed that the chemisorption abilities of these chitin-based adsorbents, designed for the chemisorption of acid dyes, were significantly high, and also that an aminodeoxychitin showed a high chemisorption ability for Cu^{2+} ion.

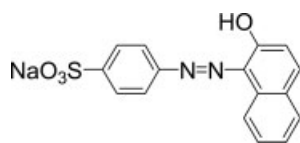
In this study, novel chitosan-based materials have been synthesized by the reaction of the tosylchitosan with ammonia, ethylenediamine, or hexamethylenediamine. Then, the chemisorption abilities of the adsorbents to an acid dye have been evaluated. Furthermore, we have synthesized the corresponding thiol-derivatives from these chitosan derivatives having additional amino groups therein, and evaluated the chemisorption abilities of the resulting polymers to Hg^{2+} ion.

EXPERIMENTAL

Materials and reagents

Chitosan (Daichitosan 100D, the degree of *N*-deacetylation: 94.0%) was supplied from Dainichiseika Color and Chemicals, Tokyo, Japan. Chemicals for the modification reactions, tosyl chloride, ethylenediamine, and hexamethylenediamine (Wako Pure

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Scheme 1 Chemical structure of CI Acid Orange 7 employed.

Chemical Industries, Osaka, Japan) were used without further purification. As the solutes, a typical acid dye (C I Acid Orange 7) and a metal ion (Hg^{2+} ion) have been employed. C I Acid Orange 7 was synthesized from sulfanilic acid and 2-naphthol, salted out by sodium acetate, and then purified by the Robinson-Mills method.⁵ It is abbreviated as Orange 7 in the following sections. The chemical structure of this dye is shown in Scheme 1. Other chemicals were of reagent grade and used as received.

Synthesis of tosylchitosan

A 5.0 g of chitosan was stirred for 3 h in a 145 mL of 42 wt % aqueous solution of sodium hydroxide. To this mixture, a 250 g of crushed ice was added and the mixture was stirred to give a clear alkali chitosan solution. Then, a 87.4 g (15 mol equivalent to pyranose ring of chitosan) of tosyl chloride dissolved in 150 mL of chloroform was added with vigorous stirring for 1 h at 0°C and the mixture was stirred for 3 h at room temperature. Next, it was poured into a large amount of deionized water with stirring and the precipitate was filtrated through a sintered glass filter, washed sequentially with methanol and ether, and finally dried *in vacuo*. The reaction route is presented in Scheme 2.

Synthesis of aminodeoxychitosan

The synthesized tosylchitosan (2.0 g) was dissolved in 200 mL of dimethyl sulfoxide, and ammonia gas was bubbled into the resulting solution for 3 h at room temperature, and then the solution was stirred for 48 h at 50°C without bubbling. The content was poured into 400 mL of acetone. The precipitate was filtrated through a sintered glass filter, washed with acetone, and finally dried *in vacuo*. The solid was used after grinding to powders with a mean diame-

ter of about 100–300 μm . This reaction route is presented in Scheme 3.

Synthesis of aminoalkylaminodeoxychitosan

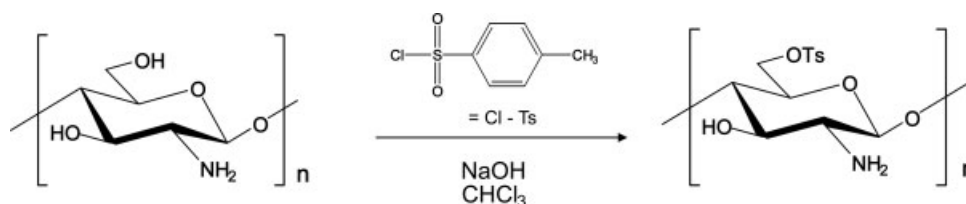
As similar to the synthesis of aminodeoxychitosan described earlier, the tosylchitosan (1.0 g) was dissolved in 100 mL of dimethyl sulfoxide. Next, either ethylenediamine or hexamethylenediamine was added to the solution. Then, the mixture was stirred for 72 h at 60°C. The content was poured into 500 mL of acetone, and the precipitate was filtrated through a sintered glass filter, washed sequentially with acetone, ethanol, and diethyl ether, and finally dried *in vacuo*. Table I shows molar ratio of alkylendiamine added to pyranose unit of the tosylchitosan and the abbreviations of aminoalkylaminodeoxychitosan synthesized.

Synthesis of S-benzyloxycarbonylmercaptoacetic acid (Z-mercaptoacetic acid)

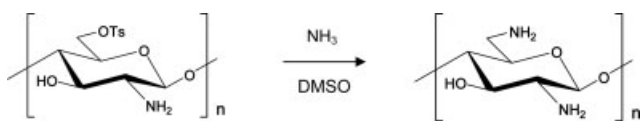
A 5.1 g of mercaptoacetic acid was dissolved in 48 mL of aqueous sodium hydroxide of 2 mol/L, and then benzoyloxycarbonyl chloride (4.75 g) and 6 mL of aqueous sodium hydroxide of 2 mol/L were added to the solution. Next, the mixture was stirred for 1 h at 0°C. The content was entered into a separatory funnel for washing with diethyl ether. The water layer was separated and adjusted to the pH value of 2 with dilute hydrochloric acid. The precipitate was filtrated off, washed with hexane–benzene mixture, and then dried *in vacuo*.

Synthesis of N-mercaptoacetylchitosan

A 1.0 g of chitosan was dissolved in 30 mL of 10% acetic acid and diluted with 30 mL of methanol. To the solution, a 4.1 g of Z-mercaptoacetic acid and 3.8 g of *N,N'*-dicyclohexylcarbodiimide (DCC) in 100 mL of tetrahydrofuran (THF) were added and stirred for 16 h at room temperature. Then, 100 mL of 5 wt % aqueous sodium hydrogen carbonate solution was added. After stirring for 3 h, the precipitate was filtrated, washed with deionized water until it was neutral, followed by ethanol and acetone, and finally dried *in vacuo*. A 1.0 g of the product was



Scheme 2 Synthesis scheme of tosylchitosan.



Scheme 3 Synthesis scheme of aminodeoxychitosan.

swelled in 20 mL of methanol. To this, a 0.93 mL of acetic anhydride was added. Then, the mixture was stirred for 16 h at room temperature. The content was poured into 67 mL of ice-cold water, and the precipitate was filtrated, washed with methanol and diethyl ether, and dried *in vacuo*. A 1.0 g of the product was swelled in 20 mL of methanol. To this, a 0.5 g of sodium methoxide was added. Then, the mixture was stirred for 16 h at room temperature under nitrogen atmosphere. The resulting precipitate was filtrated off, washed with methanol and diethyl ether, and dried *in vacuo*. These reaction routes are presented in Scheme 4.

Introduction of thiol groups into 2'-aminoethylaminodeoxychitosan and 6'-aminoethylaminodeoxychitosan

A 0.3 g of 2'-aminoethylaminodeoxychitosan (AEC-6) or 6'-aminoethylaminodeoxychitosan (AHC-5) synthesized earlier was swelled in 18 mL of 10 vol % acetic acid. Then, the thiol groups were introduced into both C₆ and C₂ positions of AEC-6 or AHC-5 by the same operations as described in the synthesis of *N*-mercaptoacetylchitosan.

Introduction of thiol groups into *O*- and *N*-positions in chitosan via tosylchitosan

A 2.0 g of tosylchitosan was swelled in 73 mL of dimethyl sulfoxide. To this, 2.16 g of potassium thioacetate was added, and then stirred for 16 h at 80°C under an atmosphere of nitrogen. The content was poured into 182 mL of methanol and the precipitate was filtrated off, washed with methanol and diethyl ether, and dried finally *in vacuo*. A 0.5 g of the product was swelled in 30 mL of dimethyl sulfoxide. To this, 1.53 g of *Z*-mercaptoacetic acid and 1.39 g of DCC in 50 mL of THF were added, and stirred for 16 h at room temperature. The content was poured into 100 mL of THF. The precipitate was filtrated, washed sequentially with THF, ethanol and acetone, and dried *in vacuo*. A 0.4 g of the product was swelled in 8 mL of methanol. To this, 2.45 g of acetic anhydride was added and stirred for 16 h at room temperature. The content was poured in 26.8 mL of ice-cold water. The precipitate was filtrated, washed sequentially with water, methanol, and diethyl ether, and dried *in vacuo*. A 0.3 g of the product was swelled in 6 mL of methanol. To this, 0.3 g of sodium methoxide was added to hydrolyze by the

same operations as those in the synthesis of 2'-thioacetylaminodeoxy-*N*-thioacetylchitosan to give *O*-thioldeoxy-*N*-thioacetylchitosan. The contents of thiol group in the several chitosan derivatives synthesized earlier were determined by Ellman's method.⁶

Chemisorption of acid dye on the aminodeoxychitosan and aminoalkylaminodeoxychitosans

A 1.00×10^{-2} g of the sample was added to a 100 mL of dye (CI Acid Orange 7) solution at pH 4.0, where the dye solution was prepared using the acetate buffer solution of 0.1 mol/L, and the mixture was continued to be stirred at 30°C until the equilibrium was established. After the chemisorption process, a part of the solution was poured into the test tube and centrifuged for 30 min. The dye concentration of the supernatant liquid was determined by colorimetry measurements at λ max.

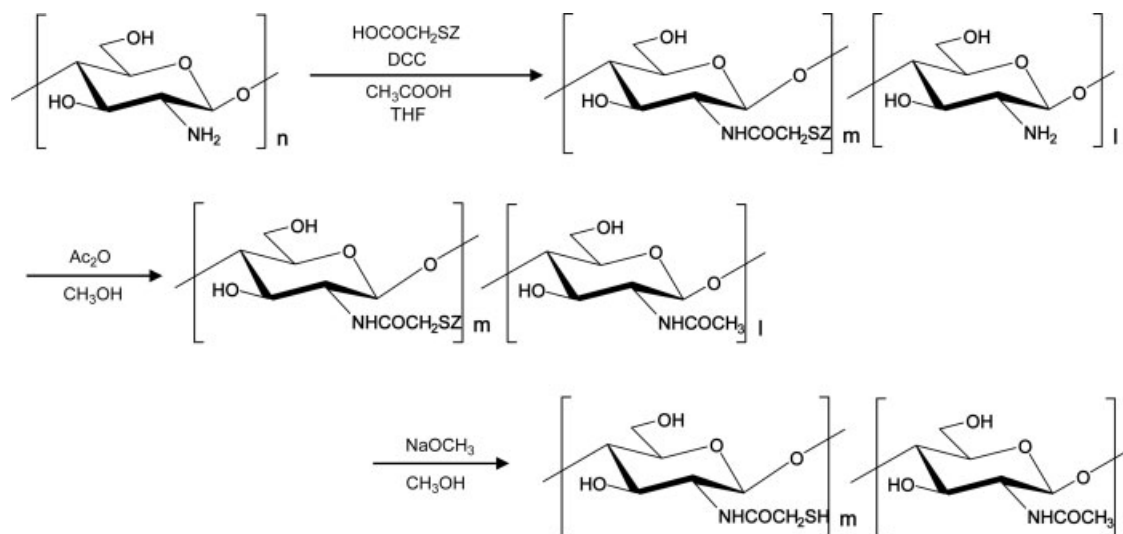
Chemisorption of Hg²⁺ ions on the chitosan derivatives having thiol groups

The Hg²⁺ ion solutions (50-mL volume each) of various concentrations were prepared, and each adsorbent of 1.00×10^{-2} g was added to the solutions. These solutions were stirred for 48 h at 30°C. The pH of the Hg²⁺ ion solutions were adjusted to 6.0 using an acetate buffer solution. After the chemisorption process, the solutions were centrifuged, and the supernatant liquid was analyzed by Mercury Analyzer (SP-3D, Japan Instruments, Tokyo, Japan) to determine the concentrations of the unadsorbed Hg²⁺ ions. The amount of the adsorbed ions was calculated from the following equation:

$$q = (C_0 - C_e) \frac{V}{W}$$

TABLE I
Molar Ratio of Alkylenediamines Added to Pyranose Unit of Tosylchitosan and the Abbreviations of Aminoalkylaminodeoxychitosans Synthesized

Alkylenediamine	Alkylenediamine/ Pyranose Unit	Abbreviation
Ethylenediamine	1.0	AEC-1
	2.0	AEC-2
	3.0	AEC-3
	10.0	AEC-4
	20.0	AEC-5
	30.0	AEC-6
Hexamethylenediamine	1.0	AHC-1
	2.0	AHC-2
	3.0	AHC-3
	10.0	AHC-4
	20.0	AHC-5
	30.0	AHC-6



Scheme 4 Synthesis scheme of *N*-thioacetylchitosan.

where q is the amount of Hg^{2+} ion adsorbed on the substrate, C_0 is the initial Hg^{2+} ion concentration, C_e is the Hg^{2+} ion concentration at equilibrium, V is the volume of Hg^{2+} ion solution, and W is the weight of the dry sample.

RESULTS AND DISCUSSION

Characterization of the tosylchitosan

The formation of the tosylchitosan was confirmed by the measurement of Fourier transform infrared spectroscopy (FTIR, Model 430, Jasco, Tokyo, Japan). Figure 1 shows the IR spectra of the tosylchitosan and the original chitosan. The new peaks at 1175 cm^{-1} and 814 cm^{-1} , assigned to $-\text{SO}_2-$ and benzene ring, respectively, were found in the IR spectrum of the tosylchitosan. It indicates the completion of a successful reaction. The degree of substitution of the tosyl group for the hydroxyl group in the chitosan was determined from the C/N ratio, where C and N represent the carbon and nitrogen contents, respectively, in a sample measured with a Yanako CHN Corder MT-5 (Yanagimoto Seisakusyo, Tokyo, Japan).

The average value for the degree of substitution was calculated as 1.06.

Characterization of the chitosan derivatives having introduced additional amino groups

The IR spectra of the aminodeoxychitosan and aminoalkylaminodeoxychitosans synthesized from the tosylchitosan were measured. Figure 2 shows the spectra of an aminodeoxychitosan, 2'-aminoethylaminodeoxychitosan, and 6'-aminoethylaminodeoxychitosan. The peaks at 1175 cm^{-1} and 814 cm^{-1} based

on the tosyl group disappeared in any spectrum, and at the same time, the peak at 1638 cm^{-1} that could be assigned to the amino group increased in these spectra. These results demonstrated that the tosylchitosan successfully reacted with ammonia, ethylenediamine, and hexamethylenediamine, respectively.

Characterization of the *Z*-mercaptoacetic acid

Figure 3 shows the IR spectrum of the *Z*-mercaptoacetic acid. In this spectrum, the peaks at 695 and 742 cm^{-1} based on the phenyl group, at 1157 cm^{-1} assigned to C—O and at 1698 and 1725 cm^{-1} assigned to the carbonyl group, respectively, are found,⁷ indicating the successful reaction of mercaptoacetic acid with benzoyloxycarbonyl chloride.

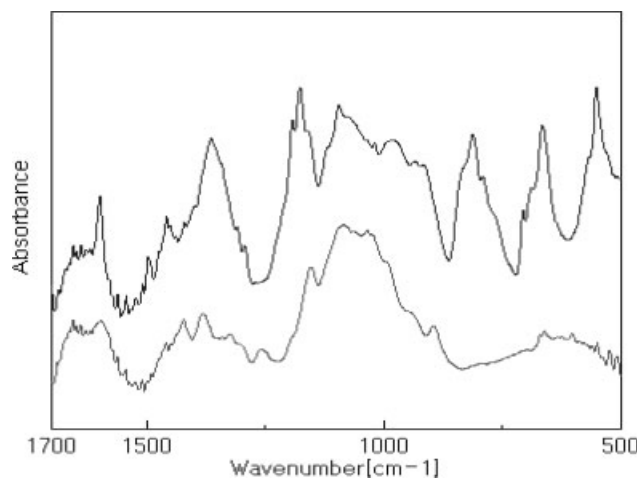


Figure 1 Infrared spectra of tosylchitosan and the parent chitosan. Where an above spectrum is that of tosylchitosan. A bottom spectrum is that of the parent chitosan.

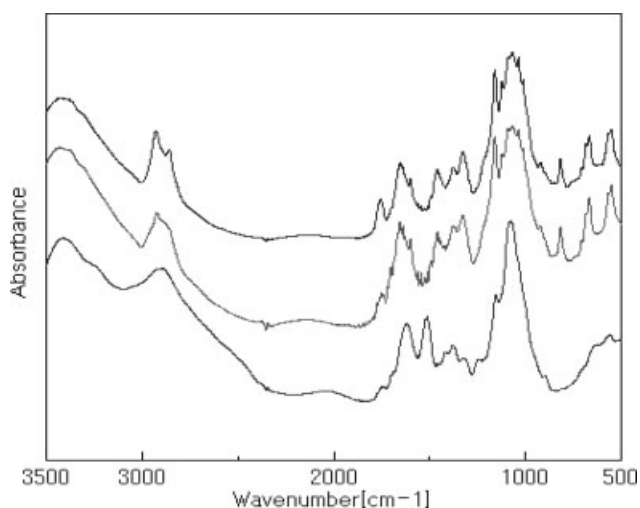


Figure 2 Infrared spectra of 2'-aminoethylaminodeoxychitosan, 6'-aminohexylaminodeoxychitosan and O-aminodeoxychitosan. Where most above spectrum is that of 6'-aminohexylaminodeoxychitosan, the middle spectrum is that of 2'-aminoethylaminodeoxychitosan, and the bottom spectrum is that of O-aminodeoxychitosan.

Characterization of the chitosan derivatives with thiol groups therein

The introduction of thiol groups with the amino groups in chitosan as the reaction site was also confirmed. Figure 4 shows the IR spectra of *N*-thioacetylchitosan, 2'-thioacetylaminohexylamino-*N*-thioacetylchitosan, and 6'-thioacetylaminohexylamino-*N*-thioacetylchitosan. In these IR spectra, the characteristic peaks at 1640 and 1550 cm^{-1} assigned to Amide I and Amide II, respectively, were appeared. The strong peaks at 2859 and 2928 cm^{-1} based on the methylene group were also appeared in the IR spectrum of 6'-thioacetylaminohexylamino-*N*-thioacetylchitosan. This evidence supported the formation of these products.

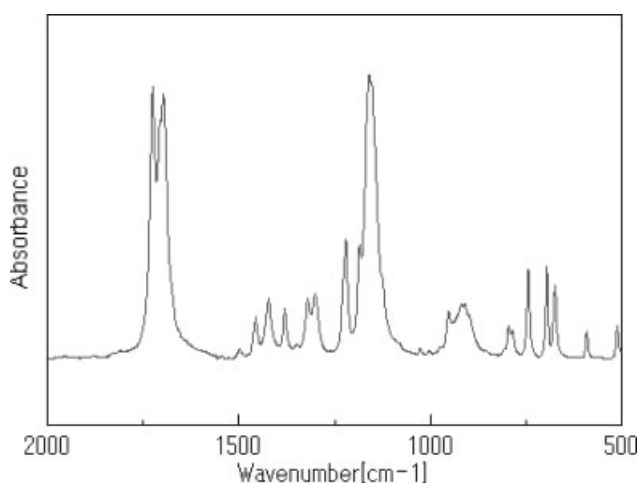


Figure 3 Infrared spectrum of Z-mercaptoacetic acid.

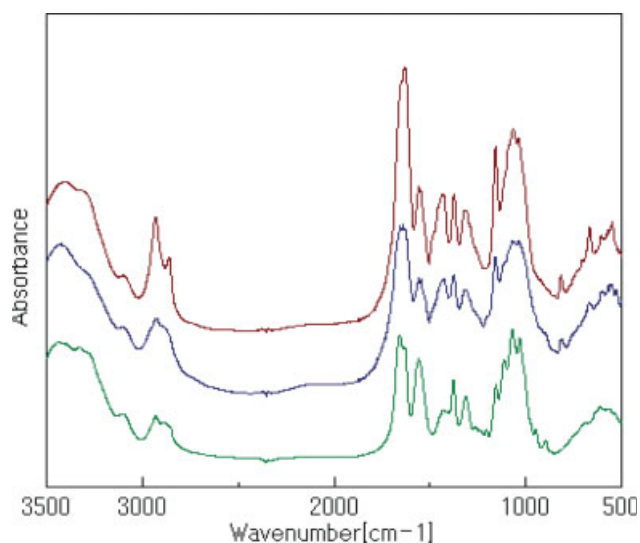


Figure 4 Infrared spectra of the chitosan derivatives introduced the thiol group(s). Where most above spectrum is that of 6'-thioacetylaminohexylamino-*N*-thioacetylchitosan, the middle spectrum is that of 2'-thioacetylaminohexylamino-*N*-thioacetylchitosan, the bottom spectrum is that of *N*-thioacetylchitosan. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 is the IR spectrum of the chitosan derivative introduced thiol group via the tosylchitosan. In this spectrum, the peaks at 1640 and 1550 cm^{-1} assigned to Amide I and Amide II, respectively, could be observed, and also the peak at 2570 cm^{-1} based on the thiol group are found, indicating the satisfactory formation of O-thioldeoxy-*N*-thioacetylchitosan.

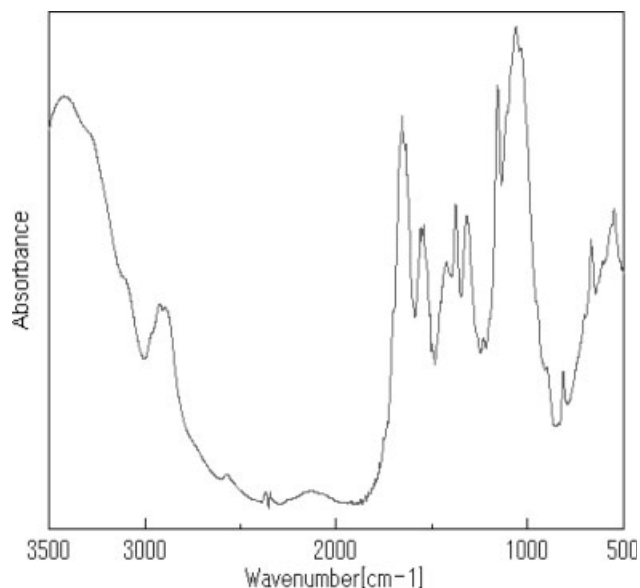


Figure 5 Infrared spectrum of O-thioldeoxy-*N*-thioacetylchitosan.

TABLE II
Thiol Group Content of the Chitosan Derivatives
Determined by Ellman's Method

Chitosan Derivatives	Content of thiol group (mol/kg)
<i>N</i> -thioacetylchitosan	2.28
2'-Thioacetylaminoethylamino- <i>N</i> -thioacetylchitosan	2.75
6'-Thioacetylaminohexylamino- <i>N</i> -thioacetylchitosan	3.09
<i>O</i> -thioldeoxy- <i>N</i> -thioacetylchitosan	4.07

The thiol group contents of the chitosan derivatives determined by Ellman's method are shown in Table II together with that of *N*-thioacetylchitosan. From this table, it was found that the thiol group content could be increased by the introduction of additional amino groups to chitosan.

Chemisorption of Orange 7 on the chitosan derivatives having additional amino group

The chemisorption behavior of Orange 7 to the chitosan derivatives, having introduced additional amino group therein, was measured in the buffer solution of pH = 4.0 at the temperature of 30°C. The corresponding adsorption isotherms of Orange 7 toward *O*-aminodeoxychitosan, 2'-aminoethylaminodeoxychitosans, and 6'-aminohexylaminodeoxychitosans are depicted in Figures 6–8. Since these isotherms were of Langmuir form, we applied the Scatchard equation⁸ [$r/C = Kn - Kr$, where r (mol/kg) is the dye uptake, C (mol/L) is the free dye concentration, K is

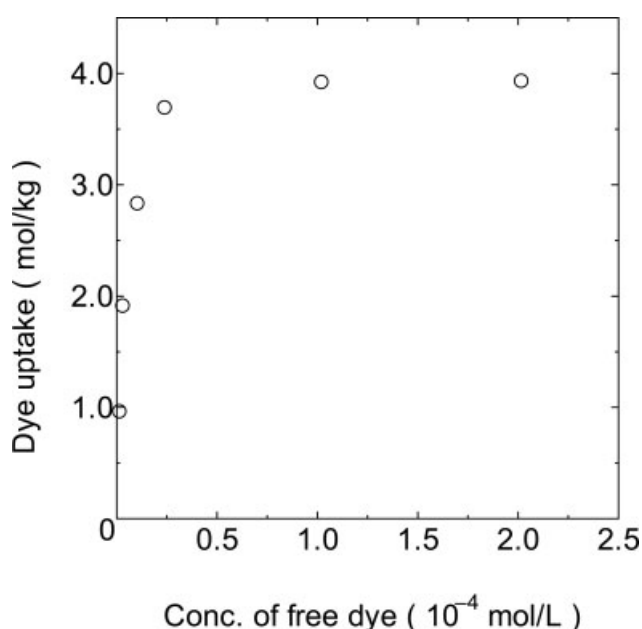


Figure 6 Adsorption isotherm of CI Acid Orange 7 by *O*-aminodeoxychitosan in the acetate buffer solution of pH 4.0 at 30°C.

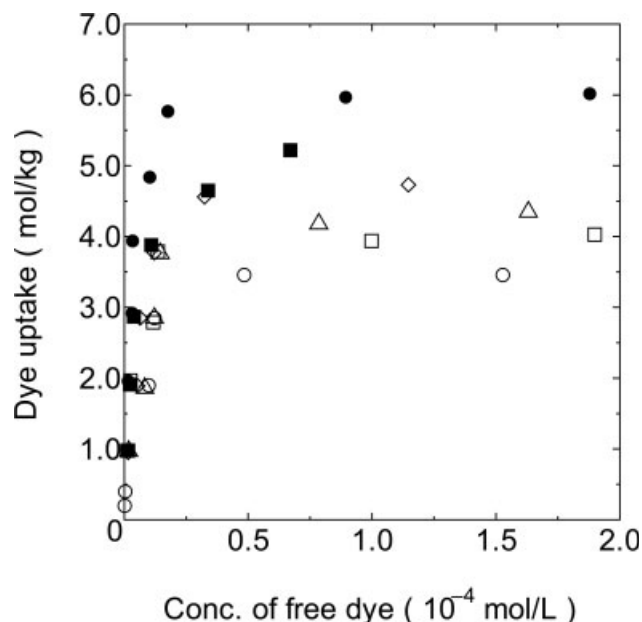


Figure 7 Adsorption isotherms of CI Acid Orange 7 by the 2'-aminoethylaminodeoxychitosans in the acetate buffer solution of pH 4.0 at 30°C. ○: AEC-1; □: AEC-2; △: AEC-3; ◇: AEC-4; ■: AEC-5; ●: AEC-6.

the binding constant, and n (mol/kg) is the saturation amount of chemisorption.] A straight line was obtained by Scatchard plot (r/C against r), allowing the calculation of K value and n value from the slope of the straight line and intercept on the abscissa. A typical example of Scatchard plot is shown in Figure 9.

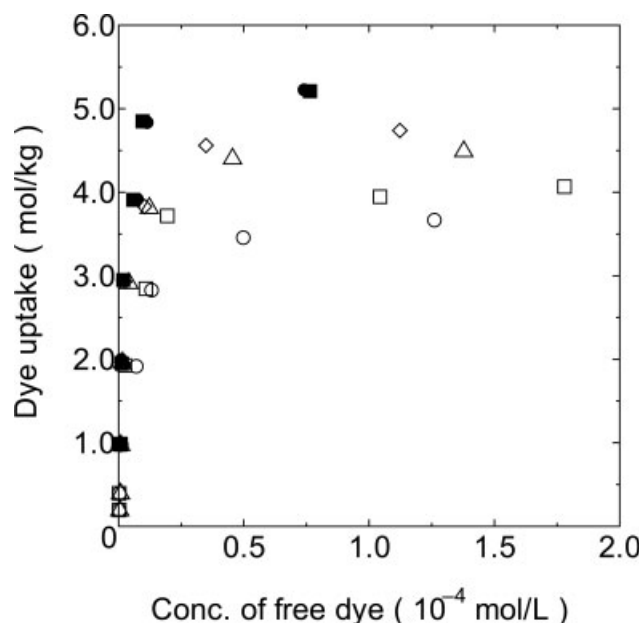


Figure 8 Adsorption isotherms of CI Acid Orange 7 by the 6'-aminohexylaminodeoxychitosans in the acetate buffer solution of pH 4.0 at 30°C. ○: AHC-1; □: AHC-2; △: AHC-3; ◇: AHC-4; ■: AHC-5; ●: AHC-6.

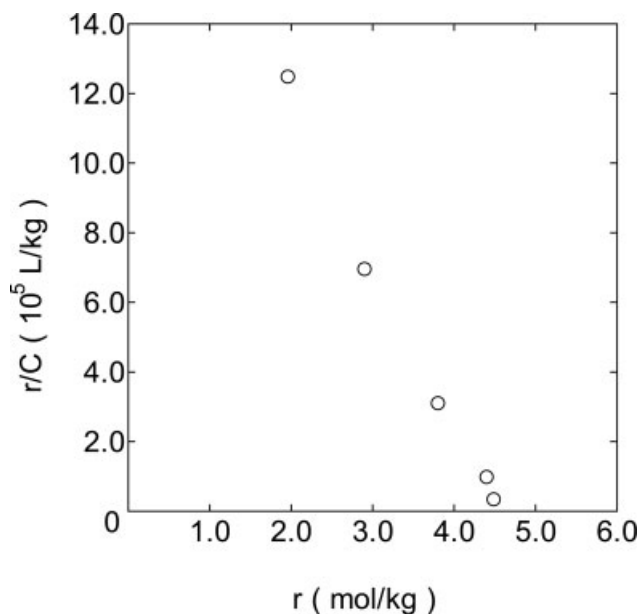


Figure 9 Scatchard plot for the data of the chemisorption of CI Acid Orange 7 onto the 6'-aminoethylaminodeoxychitosan, AHC-3. In the vertical line, r is the dye uptake (mol/kg) and C is the free dye concentration (mol/L).

The saturation value of chemisorption (n) onto the *O*-aminodeoxychitosan was 4.06 mol/kg, and the value was greatly larger than that toward amino-deoxychitin (2.38 mol/kg).⁴

Next, the saturation amounts of chemisorption onto 2'-aminoethylaminodeoxychitosans and 6'-aminoethylaminodeoxychitosans are summarized in Table III. The saturation amount of the dye adsorption was increased as the amount of ethylenediamine increased. The maximum saturation value (6.16 mol/kg) of the dye adsorption was obtained in the chemisorption of Orange 7 toward AEC-6. In the 6'-aminoethylaminodeoxychitosans, the maximum saturation value (5.42 mol/kg) of the dye chemisorption was obtained in the adsorption of Orange 7 toward AHC-5. These values exceeded the maximum saturation amount (4.36 mol/kg) in the chemisorption of the same dye toward 2'-aminoethylaminodeoxychi-

TABLE III
Saturation Amount of Adsorption of CI Acid Orange 7 on 2'-Aminoethylaminodeoxychitosans and 6'-Aminoethylaminodeoxychitosans

Adsorbent	Saturation amount (mol/kg)	Adsorbent	Saturation amount (mol/kg)
AEC-1	3.68	AHC-1	3.70
AEC-2	4.01	AHC-2	4.09
AEC-3	4.37	AHC-3	4.54
AEC-4	5.13	AHC-4	4.81
AEC-5	5.29	AHC-5	5.42
AEC-6	6.16	AHC-6	5.28

TABLE IV
First Binding Constant k_1 and Gibbs Free Energy Change ΔG of Adsorption of CI Acid Orange 7 onto 6'-Aminoethylaminodeoxychitosans

Adsorbent	First binding constant ($k_1 \times 10^6$)	ΔG (kcal/mol)
AHC-1	0.998	-8.32
AHC-2	1.271	-8.46
AHC-3	2.115	-8.77
AHC-4	2.426	-8.85
AHC-5	2.546	-8.88
AHC-6	2.682	-8.91

tin.⁴ However, these values corresponded 64 and 73%, respectively, for those values assumed that all the tosylchitosan reacted perfectly with alkylendiamine. The proportions are considerably lower, compared to those (91–98%) in the dye adsorption toward the corresponding chitin derivatives. It is probably because a limited access of the dye molecules to the substrate owing to the compact structure or the some dyes binds to only one amino group in the repeat unit of aminoalkylaminodeoxychitosan.

To facilitate a quantitative comparison of the chemisorption ability, we evaluated the first binding constant $k_1 (=Kn)$. Also, the Gibbs free energy change (ΔG) of adsorption was determined from the following equation.⁹

$$\Delta G = -RT \ln k_1$$

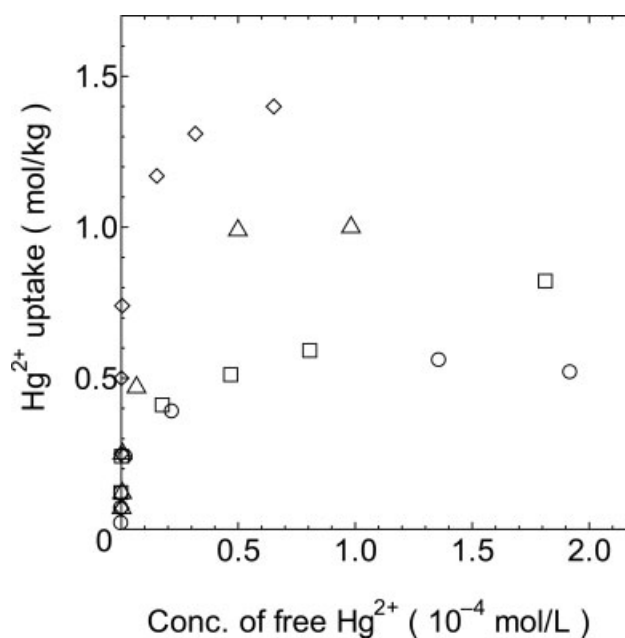


Figure 10 Adsorption isotherms of Hg^{2+} ions by the chitosan derivatives with the thiol group(s) in an acetate buffer solution of pH 6.0 at 30°C. \circ : *N*-thioacetylchitosan; \square : 2'-thioacetylaminodeoxychitosan; Δ : 6'-thioacetylaminodeoxychitosan; \diamond : *O*-thioldeoxy-*N*-thioacetylchitosan.

TABLE V
Maximum Amount of Chemisorption of Hg²⁺ on the Chitosan Derivatives with the Thiol Group(s)

Chitosan derivative	Maximum amount of chemisorption (mol/kg)
<i>N</i> -thioacetylchitosan	0.56
2'-Thioacetylaminoethylamino- <i>N</i> -thioacetylchitosan	0.82
6'-Thioacetylaminohexylamino- <i>N</i> -thioacetylchitosan	1.00
<i>O</i> -thioldeoxy- <i>N</i> -thioacetylchitosan	1.40

The k_1 value and ΔG value for the chemisorption of Orange 7 onto 2'-aminoethylaminodeoxychitosans were from 6.78×10^5 to 1.46×10^6 and from -8.08 to -8.55 kcal/mol, respectively. Those values for the chemisorption onto 6'-aminohexylaminodeoxychitosans are depicted in Table IV.

The k_1 value and the absolute value of ΔG for the chemisorption of Orange 7 onto these substrates are extremely larger than those in the chemisorption of Methy Orange by crosslinked polyethyleneimine.¹⁰ This suggests that novel amino(alkyl)aminodeoxychitosans synthesized are excellent adsorbents for anionic dyes.

Chemisorption of Hg²⁺ ions on the chitosan derivatives with the thiol groups

The chemisorption of Hg²⁺ ions on the chitosan derivatives with the thiol group was measured in an acetate buffer solution (pH = 6.0) at 30°C. The adsorption isotherms are shown in Figure 10. Table V shows the maximum value of Hg²⁺ ion adsorption at the highest free Hg²⁺ ion concentration examined for each substrate. The adsorption ability of these polymers to Hg²⁺ ion was higher as the thiol group content was increased. The largest value among these maximum amounts was 1.40 mol/kg in the chemisorption toward the *O*-thioldeoxy-*N*-thioacetylchitosan. This value exceeds to the reference value (0.41 mol/kg) obtained in the chemisorption of Hg²⁺ ion toward the macrocyclic tetra-amine derivative of chitosan.¹¹

CONCLUSIONS

Novel chitosan-based adsorbents with additional amino groups were synthesized by the reaction of tosylchitosan with ammonia, ethylenediamine, and hexamethylenediamine, and the chemisorption behaviors of the resulting polymers for an acid dye have been studied. The chitosan derivatives with the thiol groups were further synthesized from the chitosan derivatives obtained earlier. The chemisorption abilities of these substrates to Hg²⁺ ion were also evaluated. The experimental results demonstrated that the chitosan derivatives with additional amino groups have a high adsorption ability for an acid dye, and that of the chitosan derivatives with the thiol groups toward Hg²⁺ ion was considerably high. From these results, the chitosan derivatives with additional amino groups would be applied as the effective adsorbent toward anionic dyes, and as a precursor for further novel derivatives. For example, the chitosan derivatives with the thiol groups have an application for the removal of Hg²⁺ ions in environmental analyses.

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