

Synthesis of Novel Amino(alkylamino)deoxychitins and the Adsorption Behavior of Acid Dye onto the Resulting Polymers

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ABSTRACT: Novel chitin-based materials were synthesized and the adsorption behavior of typical acid dyes to the resulting polymers has been evaluated. The successful synthetic reaction was confirmed by the infrared spectroscopic measurements. By the reaction of alkalichitin with tosyl chloride, the corresponding tosylchitin was synthesized as a soluble and reactive precursor. Next, aminodeoxychitin was synthesized by the reaction of the tosylchitin with ammonia. Similarly, 2'-aminoethylamino- and 6'-aminohexylaminodeoxychitins were synthesized by reacting the tosylchitin with ethylenediamine and hexamethylenediamine, respectively. It has been confirmed that the adsorption abilities of these polymers for acid dyes

were significantly high, and also that one of the aminodeoxychitins showed a high adsorption ability for Cu²⁺ ion. On the basis of the adsorption data of acid dye on the aminodeoxychitin, the tosylchitin and the original chitin, the amino group contents at C₆ and C₂ positions were estimated. The aminodeoxychitin and aminoalkylaminodeoxychitins could be applicable to the adsorbent for anionic dyes and Cu²⁺ ion along with a precursor for further novel derivatives. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2453–2460, 2007

Key words: aminodeoxychitin; adsorption; acid dye; metal ion; tosylchitin

INTRODUCTION

Chitin, a polysaccharide of β -1,4-linked *N*-acetyl-D-glucosamine is widely distributed in nature as the skeletal material of crustaceans, insects, mushroom, and the cell walls of bacteria. Chitin is structurally similar to cellulose and has poor solubility in common solvents, such as methanol, acetone and benzene, due to its strong micelle structure. However, chitin has been chemically modified such as carboxymethylation,¹ sulfation,² and diethylaminoethylation,³ by destructing the rigid crystalline structure. Therefore, the development of novel chitin derivatives could create a wide possibility for the applications of chitin.

Tosylation of chitin has been accomplished by the condensation, because the product was expected to be useful as soluble and reactive precursors for the following chemical modification procedure under mild conditions. Kurita et al.⁴ have synthesized iodochitin and deoxychitin by the reaction of the tosyl-

chitin with sodium iodide and sodium borohydride, respectively.

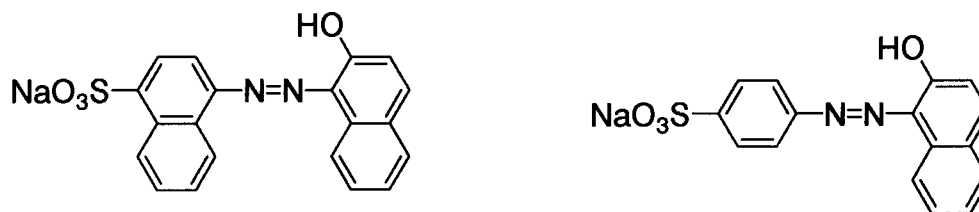
To introduce an additional functionality to chitin, in this work, we have synthesized aminodeoxychitins by the reaction of the tosylchitin with ammonia in dimethylsulfoxide at different temperatures. Similarly, 2'-aminoethylamino- and 6'-aminohexylaminodeoxychitins were synthesized by reacting the tosylchitin with ethylenediamine and hexamethylenediamine, respectively. The adsorption abilities of the resulting polymers for acid dyes were evaluated, and the adsorption of Cu²⁺ on an aminodeoxychitin was also measured.

EXPERIMENTAL

Materials and reagents

The chitin (the degree of *N*-deacetylation: 10.3%) was purchased from Nacalai Tesque, Kyoto, Japan. The chemical modification reagent, tosyl chloride (Wako Pure Chemical Industries, Osaka, Japan) was used without further purification. As the solutes, typical acid dyes (C I Acid Orange 7 and C I Acid Red 88) and a metal ion (Cu²⁺ ion) have been employed. C I Acid Orange 7 was synthesized from

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C I Acid Red 88

C I Acid Orange 7

Scheme 1 Chemical structures of acid dyes employed.

sulfanilic acid and 2-naphthol, salted out by sodium acetate, and then purified by the Robinson-Mills method.⁵ C I Acid Red 88 was used as received. They are abbreviated as Orange 7 and Red 88 in the following sections. The chemical structures of these dyes are shown in Scheme 1. Other chemicals were of reagent grade and used as received.

Synthesis of tosylchitin

A 5.0 g of chitin was stirred for 3 h in a 145 mL of 42 wt % aqueous solution of sodium hydroxide. To this a 250 g of crush ice was added and the mixture was stirred to give a clear alkali chitin solution. Then, a 71.9 g (15 mol equivalent to pyranose ring) 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 aminodeoxychitin

The synthesized tosylchitin (2.0 g) was dissolved in 200 mL of dimethylsulfoxide, and ammonia gas was bubbled into the resulting solution for 3 h at room temperature, and then for 48 h at the prescribed temperature (40, 50, 60, and 70°C). The contents were 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 diameter of about 100–300 μm. The aminodeoxychitins synthesized are abbreviated as AC40, AC50, AC60, and AC70, respectively, affixing the corresponding reaction temperature.

Synthesis of aminoalkylaminodeoxychitin

As similar to the synthesis of aminodeoxychitin described above, the tosylchitin (1.0 g) was dissolved in 100 mL of dimethylsulfoxide. Next, either ethylenediamine or hexamethylenediamine was added to the solution. Then, the mixture was stirred for 72 h at 60°C. The contents were 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 tosylchitin and the abbreviations of aminoalkylaminodeoxychitins synthesized.

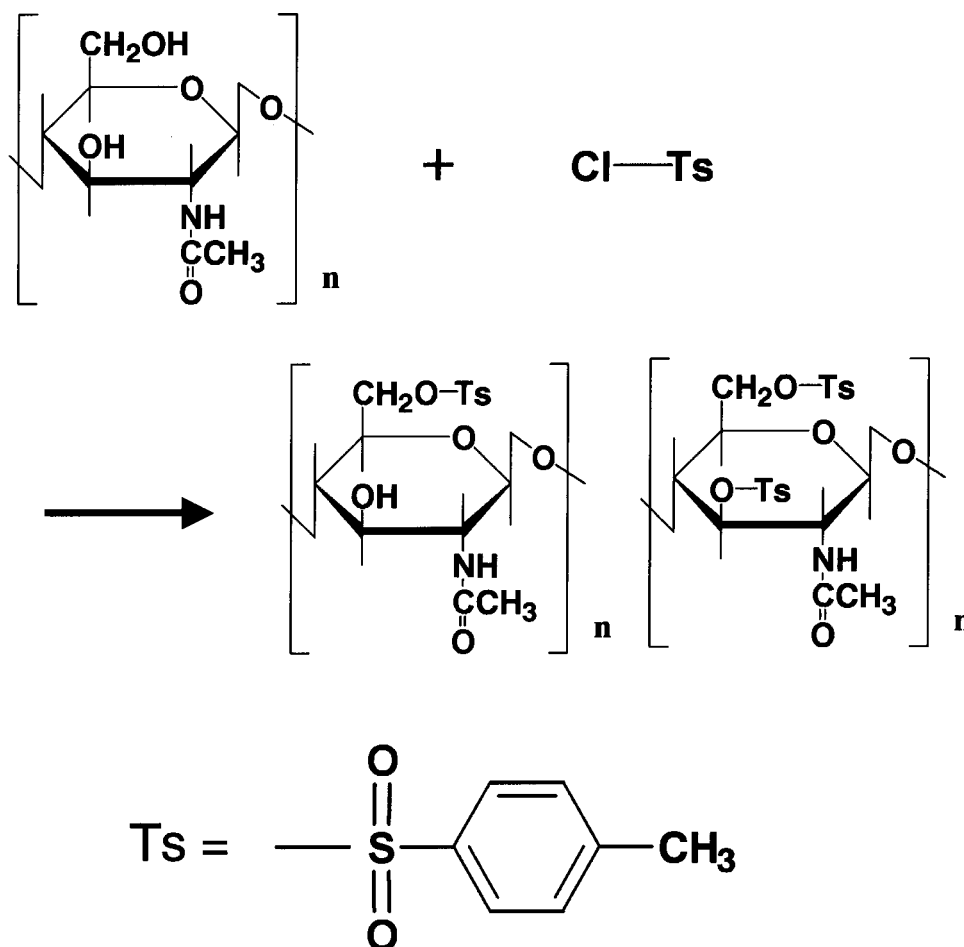
Determination of the degree of deacetylation during the tosylation and amination

Since the tosylation is performed under the strongly alkaline condition, the deacetylation of the acetyl amino group in the original chitin might be occurred to some extent during the tosylation reaction. The degree of deacetylation was determined by analyzing the adsorption of Orange 7 on the original chitin and the tosylchitin in the acetate buffer solution [0.1 mol/L, (CH₃COOH + CH₃COONa)] of pH = 4.0 for 96 h at 30°C.

Also, the deacetylation of the acetyl amino group in the tosylchitin might occur to the some extent during the amination. To confirm this, a 2.0 g of chitin was stirred in 200 mL of dimethylsulfoxide for 3 h at room temperature with ammonia gas bubbled in the suspension, and then followed by stirring for additional 48 h at 50°C with the bubbling. After the above procedures, the adsorption of Orange 7 on the treated chitin was also measured under the same conditions as previously mentioned.

Adsorption of acid dye on the aminodeoxychitin and aminoalkylaminodeoxychitins

A 1.00×10^{-2} g of the sample was added into a 100 mL of dye solution at pH 4.0, 5.0 or 6.0, where the dye



Scheme 2 Reaction scheme of chitin with tosyl chloride.

solution was prepared by 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 adsorption 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 each λ max.

Adsorption of Cu^{2+} ions on the aminodeoxychitin

The Cu^{2+} ion solutions (50 mL volume) of various concentrations were prepared, and each adsorbent of 1.00×10^{-2} g was added to the solutions. These solutions were stirred for 72 h at 30°C. The pH of Cu^{2+} ion solutions were adjusted to 6.0 using an acetate buffer solution. After the adsorption process, the solutions were centrifuged, and the supernatant liquid was analyzed by inductively coupled plasma spectroscopy (SPS 4000, Seiko Electronic Industry, Tokyo, Japan) to determine the concentrations of the unadsorbed Cu^{2+} ions. The amount of the adsorbed ions was calculated from the follow-

ing equation:

$$q = (C_0 - C_e)V/W$$

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

TABLE I
Molar Ratio of Alkylenediamines Added to Pyranose Unit of Tosylchitin and the Abbreviations of Aminoalkylaminodeoxychitins Synthesized

Alkylenediamine	Alkylenediamine/ pyranose unit	Abbreviation
Ethylenediamine	1.0	AEC-1
	2.0	AEC-2
	3.0	AEC-3
	10.0	AEC-4
Hexamethylenediamine	1.0	AHC-1
	2.0	AHC-2
	3.0	AHC-3
	10.0	AHC-4

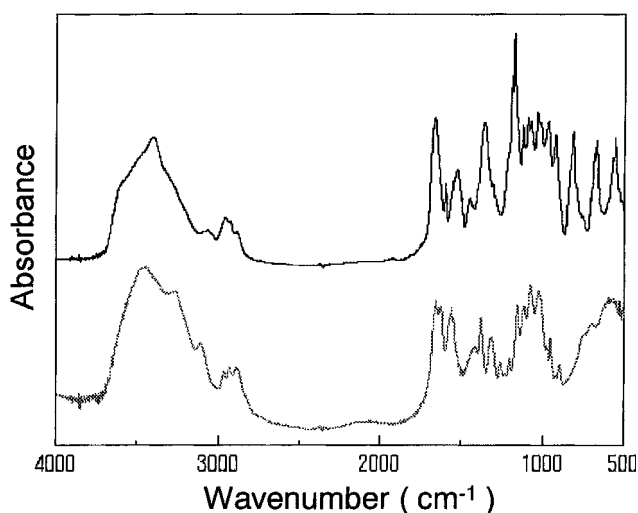


Figure 1 Infrared spectra of tosylchitin and the parent chitin. Where, an above spectrum is that of tosylchitin. A bottom spectrum is that of the parent chitin.

RESULTS AND DISCUSSION

Characterization of the tosylchitin

The formation of the tosylchitin was confirmed by the measurement of Fourier transform infrared spectroscopy (FTIR, Model 430, Jasco, Tokyo, Japan). Figure 1 shows the IR spectra of the tosylchitin and the original chitin. 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 tosylchitin. It indicates the completion of a successful reaction. The degree of substitution of the tosyl group for the hydroxyl group in the chitin 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).

Table II shows the results of the elemental analysis and the degree of substitution. The average value for the degree of substitution was calculated as 1.24. Accordingly, it is presumed that the hydroxyl groups at C_3 in addition to that at C_6 have been also substituted with the tosyl functionalities.

Characterization of aminodeoxychitins

The IR spectra of the aminodeoxychitins synthesized from the tosylchitin were measured. Figure 2 shows

TABLE II
Results of the Elemental Analysis of Tosylchitin and the Degree of Substitution

	C (%)	N (%)	C/N	Degree of substitution
Run 1	50.649	3.659	13.84	1.19
Run 2	52.076	3.598	14.48	1.29

the differential IR spectrum of the tosylchitin and an aminodeoxychitin (AC50) synthesized at 50°C . The peaks at 1175 cm^{-1} and 814 cm^{-1} based on the tosyl group disappeared, and at the same time, the peak at 1638 cm^{-1} assigned to the amino group increased in this spectra. These results demonstrated that the tosylchitin reacted with ammonia.

Degree of deacetylation during the tosylation and amination

For determination of the degree of deacetylation during the tosylation, the adsorptions of Orange 7 on the original chitin and the tosylchitin were measured in the buffer solution of $\text{pH} = 4.0$ at the temperature of 30°C . From the adsorption isotherms shown in Figure 3, it can be said that the adsorption ability of tosylchitin is higher than that of the original chitin. The increment in adsorption reflects the degree of deacetylation of acetylamino group in the original chitin during the tosylation process. Since these isotherms were of Langmuir form, we applied the Scatchard equation.⁶ A straight line was obtained by Scatchard plot, allowing the calculation of the saturation value of adsorption from the intercept on the abscissa. The values obtained are shown in Table III. The saturation value increased by 10.1% during the tosylation, representing the increase in the degree of deacetylation.

Next, to examine whether the deacetylation has occurred during the amination or not, the adsorption of Orange 7 on the ammonia-treated chitin was measured. The saturation value was determined in the same manner as mentioned above. The value obtained is shown in Table III together with those for the original chitin and the tosylchitin. The satura-

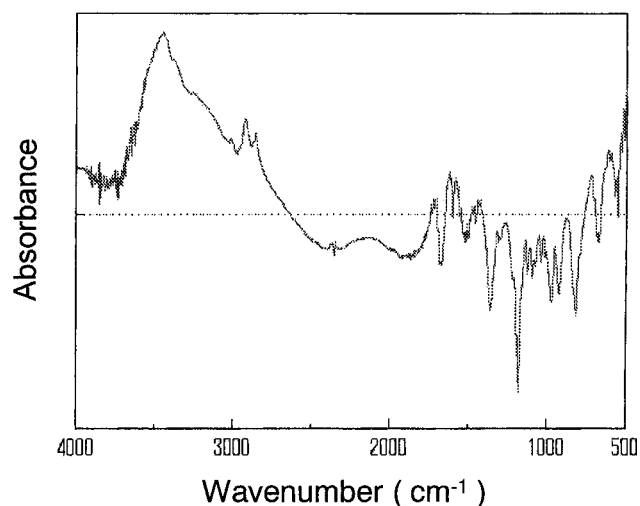


Figure 2 Differential spectrum of IR between aminodeoxychitin (AC50) and tosylchitin.

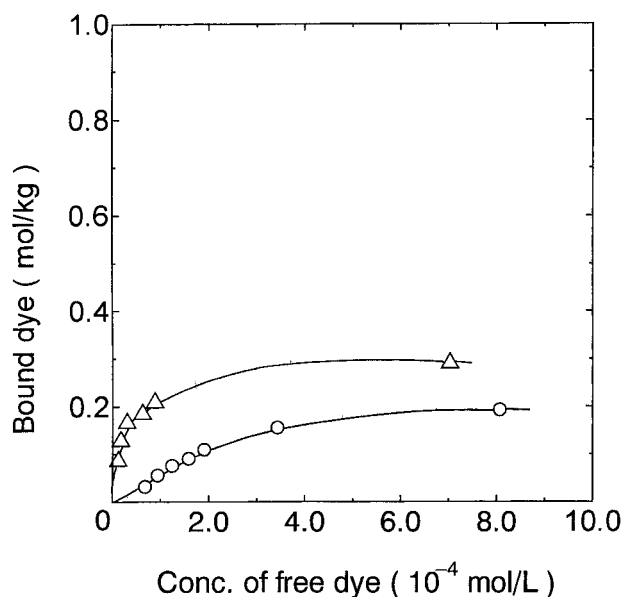


Figure 3 Adsorption isotherms of CI Acid Orange 7 by tosylchitin and the parent chitin in the buffer solution of pH 4.0 at 30°C. ○: parent chitin; △: tosylchitin.

tion value was larger by 33.9% than that for the original chitin. Therefore, it was presumed that the acetyl amino groups would be deacetylated during the amination.

Characterization of aminoalkylaminodeoxychitins

To confirm that the reaction of alkylenediamines with tosylchitin had been successfully completed, the IR spectra of the aminoalkylaminodeoxychitins were measured. Figure 4 shows the IR spectra of 2'-aminoethylaminodeoxychitin and 6'-aminohexylaminodeoxychitin together with tosylchitin and chitin. The peaks at 2928 cm^{-1} and 2859 cm^{-1} in the IR spectrum of 6'-aminohexylaminodeoxychitin were assigned to methylene group. The peak intensity at 1655 cm^{-1} assigned to the amino group increased extremely in the spectra of aminoalkylaminodeoxychitins, while the peaks at 814 cm^{-1} , 1175 cm^{-1} , and 1598 cm^{-1} based on the tosyl group disappeared. These results demonstrated that the tosylchitin was reacted with diamines.

TABLE III
Saturation Value of the Adsorption of CI Acid Orange 7 on an Original Chitin, Tosylchitin and Ammonia-Treated Chitin

Sample	Saturation value mol/kg
Original chitin	0.257
Tosylchitin	0.283
Ammonia-treated chitin	0.344

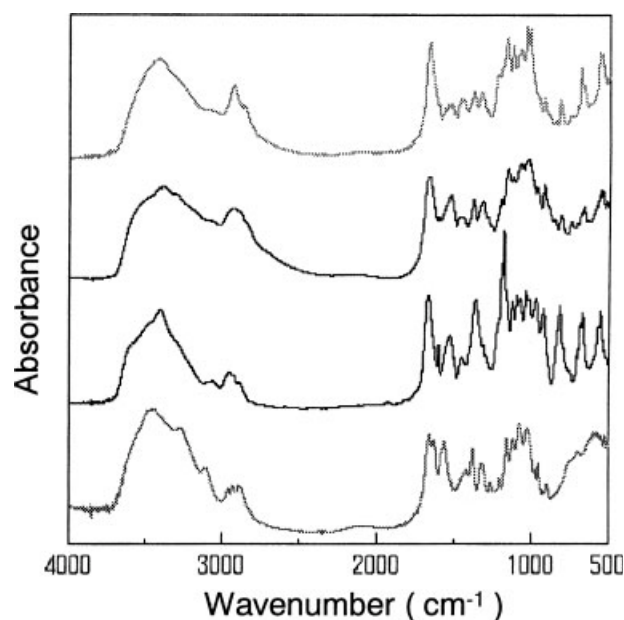


Figure 4 Infrared Spectra of 2'-aminoethylaminodeoxychitin and 6'-aminohexylaminodeoxychitin together with tosylchitin and an original chitin. Where, most above spectrum is that of 6'-aminohexylaminodeoxychitin, 2nd that of 2'-aminoethylaminodeoxychitin, 3rd that of tosylchitin. A bottom spectrum is that of an original chitin.

Adsorption of Orange 7 on aminodeoxychitin adsorbents

The adsorption behavior of Orange 7 on the amino-deoxychitins was measured in the buffer solution of pH = 4.0 at the temperature of 30°C. The corresponding adsorption isotherms are depicted in Figure 5.

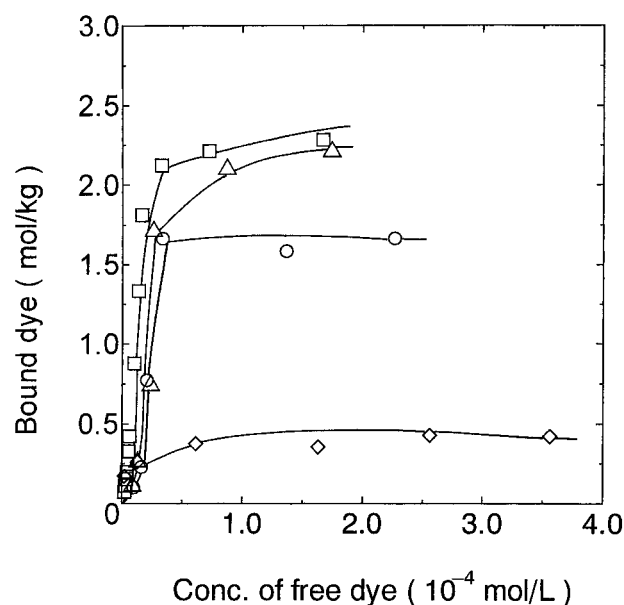


Figure 5 Adsorption isotherms of CI Acid Orange 7 by the aminodeoxychitins in the buffer solution of pH 4.0. Experimental points: ◇: 40°C; □: 50°C; △: 60°C; ○: 70°C.

TABLE IV
Saturation Value of the Adsorption of CI Acid Orange 7 on Aminodeoxychitins

Sample	Saturation value mol/kg
AC40	0.40
AC50	2.38
AC60	2.32
AC70	1.51

Applying the Scatchard equation for these adsorption behaviors, the saturation values of adsorption, as shown in Table IV, were obtained. The adsorption ability decreased as follows: AC50 > AC60 > AC70 > AC40. That is, the aminodeoxychitin synthesized at the proper temperature (at 50°C) has the largest adsorption ability. This is because both the reaction velocity and the solubility of the tosylchitin in dimethylsulfoxide are lower at the lower temperature, and also the solubility of ammonia is lower at the higher temperature. The saturation value of Orange 7 on AC50 was 9.26 times higher than that on the original chitin, suggesting the significant effect of amination.

Determination of the amino group contents at C₆ and C₂

As shown in Table IV, the saturation value of Orange 7 on AC50 is 2.38 mol/kg, where the value is the sum of amino group at C₆ and that at C₂. The amino group content at C₂ is the total of the following amino functional groups: (1) being contained in the original chitin and (2) formed by the deacetylation process during tosylation reaction, and also (3) created by the deacetylation process during the amination. The value of (1) is 0.257 mol/kg as shown in Table III. Because the value of (3) could be calculated by the subtraction of the saturation value for the parent chitin from that for an ammonia-treated chitin, it was estimated as 0.087 mol/kg. The saturation value of Orange 7 on the tosylchitin is 0.283 mol/kg as shown in Table III. However, the repeating unit of the tosylchitin is greatly different from that of the original chitin. That is, the former is larger about 1.78 times than that of the latter. Therefore, the corrected saturation value (2) is about 0.504 mol/kg.

On the basis of the above calculations, it can be concluded that the amino group content at C₆ is 1.789 mol/kg and that at C₂ is 0.591 mol/kg, along with the degree of substitution of amino group for hydroxyl group at C₆ position of 0.352.

Effect of pH on the adsorption of Orange 7 and Red 88 on aminodeoxychitin

The effects of the pH on the adsorption behavior have been examined for the adsorptions of Orange 7

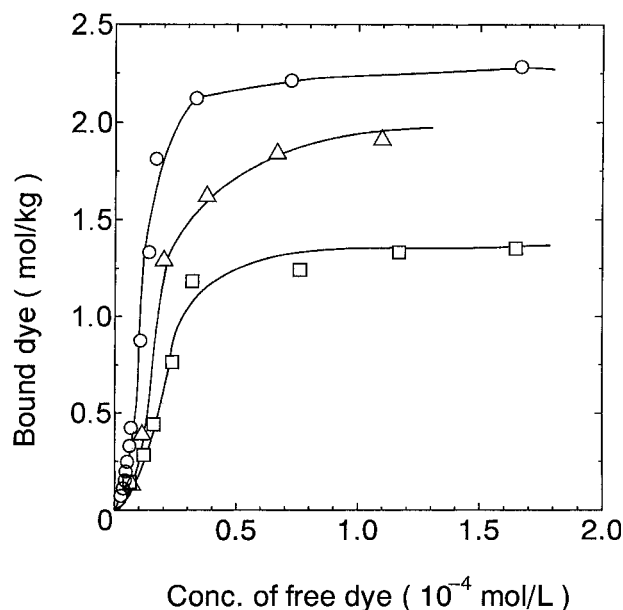


Figure 6 Adsorption isotherms of CI Acid Orange 7 by the aminodeoxychitin, AC50 in the buffer solutions of different pH values at 30°C. Experimental points: ○: pH 4.0; △: pH 5.0; □: pH 6.0.

and Red 88 onto AC50 in the buffer solution having various pH values. The measurements were carried out at 30°C for 96 h. Figures 6 and 7 show the adsorption isotherms. It can be seen a significant dependence of the amount of the bound dye on the pH value of the adsorption bath, because acid dye binds

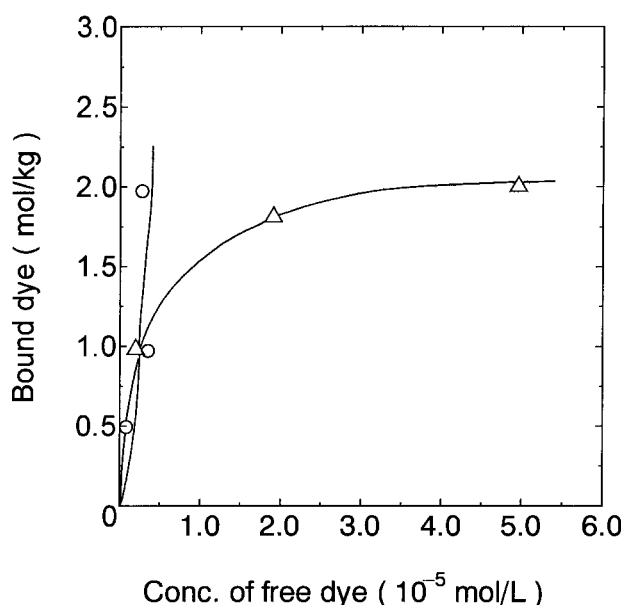


Figure 7 Adsorption isotherms of CI Acid Red 88 by the aminodeoxychitin, AC50 in the buffer solution of pH 5.0 and pH 6.0 at 30°C. Experimental points: ○: pH 5.0; △: pH 6.0.

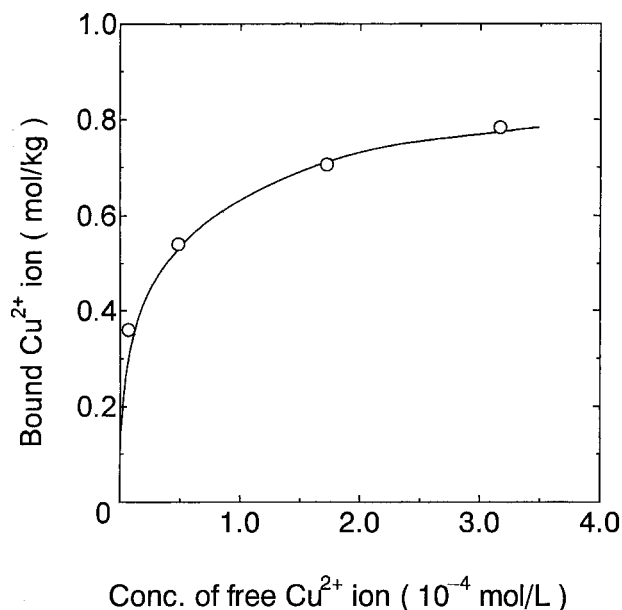


Figure 8 Adsorption isotherm of Cu^{2+} ions by the aminodeoxychitin, AC50 in an acetate buffer solution of pH 6.0 at 30°C .

to the protonated amino group⁷ in the substrate, and the amount of the protonated amino group can be increased with the drop in the pH. The affinity of Red 88 towards the substrate was higher than that of Orange 7 at the same pH value, because of its more hydrophobic character due to the presence of additional benzene ring in the structure.

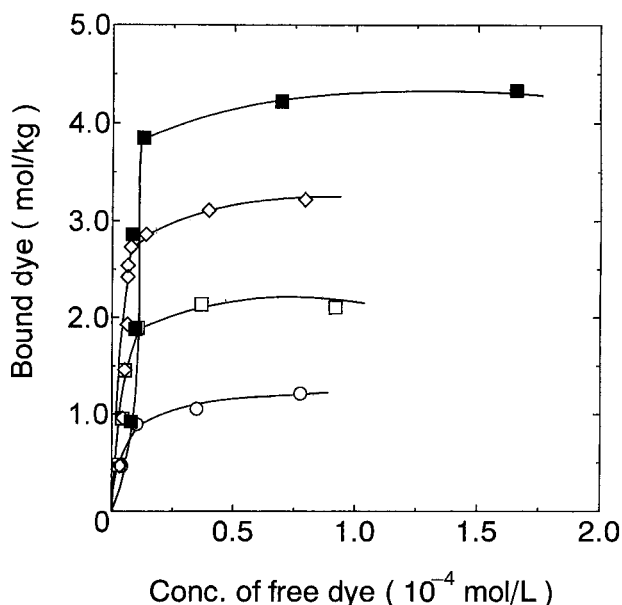


Figure 9 Adsorption isotherms of CI Acid Orange 7 by the aminoethylaminodeoxychitins in an acetate buffer solution of pH 4.0 at 30°C . Experimental points: \circ : AEC-1; \square : AEC-2; \diamond : AEC-3; \blacksquare : AEC-4.

Adsorption of Cu^{2+} ions on an aminodeoxychitin

The adsorption of Cu^{2+} ions on the aminodeoxychitin, AC50, was measured in an acetate buffer solution of pH value of 6.0 at 30°C . The adsorption isotherms are shown in Figure 8. The adsorption ability of AC50 for Cu^{2+} ion was significantly high, corresponding to that of the crosslinked chitosan.⁸ This is also the effect of amination.

Adsorption of CI Acid Orange 7 on an aminoalkylaminodeoxychitins

The adsorption behavior of Orange 7 on the aminoalkylaminodeoxychitins was measured in a buffer solution of pH value of 4.0 at the temperature of 30°C . The corresponding adsorption isotherms are depicted in Figures 9 and 10. The adsorption ability decreased as follows: AEC-4 > AEC-3 > AEC-2 > AEC-1 for AECs, and AHC-4 > AHC-3 > AHC-2 > AHC-1 for AHCs. Thus, larger the molar ratio of alkylenediamines added to the pyranose unit of the tosylated chitin, the more the adsorption amounts. Applying the Scatchard equation for the data depicted in Figures 9 and 10, the saturation values of adsorption were determined. The data are shown in Table V.

The saturation values for AEC-4 and AHC-4 were 4.36 and 3.78 mol/kg, respectively. These values are 91 and 98%, respectively, of theoretical values, where the calculation of total amino content in the substrates was made on the basis of the perfect reac-

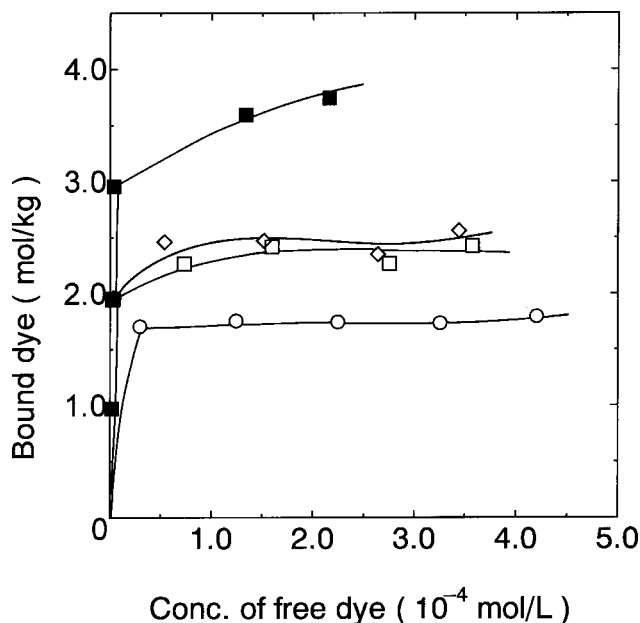


Figure 10 Adsorption isotherms of CI Acid Orange 7 by the aminoalkylaminodeoxychitins in the buffer solution of pH 4.0 at 30°C . Experimental points: \circ : AHC-1; \square : AHC-2; \diamond : AHC-3; \blacksquare : AHC-4.

TABLE V
Saturation Value of the Adsorption of CI Acid Orange 7
on Aminoalkylaminodeoxychitins

Sample	Saturation value mol/kg
AEC-1	1.37
AEC-2	2.28
AEC-3	3.27
AEC-4	4.36
AHC-1	1.78
AHC-2	2.37
AHC-3	2.50
AHC-4	3.78

tion between alkylenediamines and tosylchitin. The results suggest that the amino or aminoalkylamino groups introduced at C₆ position are very effective for the adsorption of the anionic dyes.

CONCLUSIONS

Novel chitin-based adsorbents were synthesized and the adsorption ability of the resulting polymers for acid dyes has been evaluated. First, tosylchitin as soluble and reactive precursors was synthesized by reacting alkalichitin with tosyl chloride. Next, aminodeoxychitin was synthesized by the reaction of the tosylchitin with ammonia to introduce the additional amino groups. Similarly, 2'-aminoethylaminodeoxychitin and 6'-aminohexylaminodeoxychitin were synthesized by reacting tosylchitin with ethylenediamine and hexamethylenediamine, respectively. The adsorption capacity of these polymers towards acid

dyes was significantly high, as typically found in the adsorption of the acid dyes by 2'-aminoethylaminodeoxychitins. In addition, one of the aminodeoxychitins clearly manifested a high adsorption capability towards Cu²⁺ ion. From these results, the aminodeoxychitin and aminoalkylaminodeoxychitins would be applied as the effective adsorbent towards both anionic dyes and Cu²⁺ ion, and as a precursor for further novel derivatives. Further studies on the application of aminodeoxychitin and aminoalkylaminodeoxychitins as a precursor are currently underway in our laboratory.

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