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((Diethylamino)ethyl)chitins: Preparation and Properties of Novel Aminated Chitin Derivatives[1]

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ABSTRACT: Procedures for (diethylamino)ethylation of chitin with (diethylamino)ethyl chloride have been established. ((Diethylamino)ethyl)chitins (DEAE-chitins) were prepared in dispersion in organic solvents with a small amount of aqueous sodium hydroxide. Among the solvents examined, dimethyl sulfoxide was confirmed to be most suitable, and degrees of substitution above 1.2 were achieved. The substitution reactions in solution in aqueous sodium hydroxide also proceeded smoothly, and DEAE-chitins with substitution degrees above 1.4 were obtained. Addition of a phase-transfer catalyst to the aqueous solution enhanced the reaction efficiency considerably. The resulting DEAE-chitins exhibited highly improved affinity to water and organic solvents, and these properties were dependent on both the mode of preparation and substitution extent. The derivatives prepared in aqueous solution showed much better solubility and swelling; they were readily water soluble and swelled remarkably in common solvents such as benzene and alcohols. The separation behavior of these DEAE-chitins for organic dyes was studied, and those with high substitution degrees proved useful as adsorbents and separating materials.

Introduction

Much attention is currently being paid to chitin as an important biomass resource. It is produced in a huge amount annually in nature, but remains an almost unutilized resource. Recent rapid progress in chitin chemistry is revealing a high potential for developing new advanced materials on the basis of specific structure. Many efforts have been focused on exploration of various modes of chemical modifications to open the way to utilization.[2]

Introduction of additional amino groups into chitin is considered especially interesting because of the resulting strong cationic character due to the presence of the original and introduced amino groups. The utility of aminated polysaccharides such as ((diethylamino)ethyl)cellulose (DEAE-cellulose) and DEAE-Sephadex is well appreciated, and they have found many applications, especially for separation of biological components such as proteins and nucleic acids due to their high selectivity in adsorption.[3] Chitin itself is an amino polysaccharide and shows specific affinity for some proteins such as lectins,[4] and thus ((diethylamino)ethyl)chitin (DEAE-chitin) may possibly be another polycation useful in various fields as gels for effective bioseparation, supports for enzymes, chelating agents, ion exchangers, and water-soluble polycations for cosmetics and water treatment. (Diethylamino)ethylation of chitin has, however, attracted little attention thus far, and we have examined various factors influencing the reaction and established efficient preparative procedures. Some characteristic properties of the resulting DEAE-chitins are also discussed.

Experimental Section

General Procedures. Chitin was isolated from shrimp shells by the method reported before[5] and pulverized to 100-mesh pass. The degree of deacetylation was 0.10 as determined by conductometric titration. β-(Diethylamino)ethyl chloride hydrochloride was recrystallized from dioxane/ethanol (9:1). IR spectra were recorded on a JASCO IRA-1. NMR spectra were taken with a JEOL JNM-GX270, and chemical shifts are referenced to sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS). The degree of substitution was measured by conductometric titration with a Toa CM-40S conductivity meter. Absorption spectra were obtained with a JASCO Ubest-30. X-ray diffraction patterns were obtained with a Rigaku RAD-IA using nickel-filtered Cu Kα radiation. Elemental analyses were performed with a Yanaco MT-3 CHNcorder.

(Diethylamino)ethylation in Dispersion in Organic Solvents. A dispersion of 0.10 g of powdered chitin in 5 mL of an organic solvent was treated with 0.75 mL of 20% aqueous sodium hydroxide at a given temperature for 1 h. (Diethylamino)ethyl chloride hydrochloride [0.43 g (5 mol equiv per pyranose unit)] was added, and the mixture was stirred at the same temperature for 3 h. The mixture was then poured into 150 mL of acetone/methanol (7:3). The solid was washed with the same mixed solvent thoroughly and dried. DEAE-chitins were obtained as colorless to light brown powdery materials with substitution degrees of up to 1.27: IR (KBr) 2950 (C–H), 1660, 1560 cm^{-1} (C=O).

(Diethylamino)ethylation in Aqueous Solution. Powdered chitin (0.5 g) was dispersed in 10 mL of 42% aqueous sodium hydroxide, and the dispersion was left standing at room

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temperature for 3 h under reduced pressure (water aspirator). The dispersion was stirred vigorously with 25 g of crushed ice made of deionized water at 0 °C to give a clear alkali chitin solution. A given amount of (diethylamino)ethyl chloride hydrochloride dissolved in 10 mL of deionized water was added at 0 °C, and the mixture was stirred at 0 °C for 2 h and then at room temperature for a given time. The mixture was then dialyzed in a cellulose tube for 2 days, and most of the solvent was removed by evaporation under reduced pressure. To the concentrated aqueous solution were added 200 mL of pyridine and 50 mL of acetic anhydride at 0 °C. The mixture was stirred at room temperature for 24 h and poured into 300 mL of acetone. The product was washed with acetone thoroughly and dried. It was then treated with 50 mL of 0.01 mol/L potassium hydroxide in methanol at room temperature for 4 h, washed with acetone, and dried. The DEAE-chitins obtained here were ninhydrin negative, indicating complete N-acetylation.

DEAE-chitins were obtained as colorless to light tan powdery materials with degrees of substitution of 0.30–1.46. IR spectra were identical with those of samples prepared in organic solvents. Though the ^1H NMR spectra in D_2O (containing small amounts of hydrochloric acid and DSS) were rather complicated, characteristic peaks were observed at δ 1.25–1.4 (m, CH_3), 2.05 (br s, $COCH_3$), 3.15–3.45 (m, CH_2), 3.4–4.0 (m, pyranose H), and 4.55 (br d, pyranose H at C1). Elemental analyses were generally satisfactory. A sample with a degree of substitution of 0.59, for example, gave the following analysis data. Anal. Calcd for $[(C_{18}H_{13}NO_5)_{0.41}(C_{14}H_{26}N_2O_5)_{0.59}]\cdot 0.5H_2O$: C, 51.20; H, 8.06; N, 8.22. Found: C, 50.91; H, 8.10; N, 8.02.

(Diethylamino)ethylation in the Presence of a Phase-Transfer Catalyst. An alkali chitin solution was prepared from 0.5 g of chitin, 10 mL of 42% aqueous sodium hydroxide, and 20 g of ice as described above. To the solution was added 5 mL of an aqueous solution of tetramethylammonium chloride of a given concentration, and (diethylamino)ethylation was carried out in a similar manner. The product was worked up by the same method as that mentioned above.

Determination of the Degree of (Diethylamino)ethylation. To 50 mg of a sample were added 5 mL of 1/10 mol/L hydrochloric acid and 60 mL of deionized water, and the mixture was stirred to dissolve or swell the sample. The sample was then titrated conductometrically with 1/30 mol/L sodium hydroxide, and the average number of substituents per pyranose unit was calculated.

Separation of Dyes. In a glass column of 0.6-cm diameter was placed DEAE-chitin swelled in benzene/methanol (1:1) to a height of 7 cm. The amounts required were 0.052 and 0.038 g for the DEAE-chitins with substitution degrees of 0.56 and 1.20, respectively. The original powdered chitin (0.55 g) was also used for a similar packing. After 10 mL of the same mixed solvent was passed through the columns, 10 μL of a solution containing 0.5% each of methylene blue and sudan red in the mixed solvent was placed and developed by the mixed solvent. The eluted solution was fractionated at every 5 drops and diluted with 3 mL of the mixed solvent. The amount of each dye was determined by the absorbance at 661 nm for methylene blue or 533 nm for sudan red.

Results and Discussion

Amination of cellulose has been studied in several methods including 2-aminoethylation with (2-aminoethyl)sulfuric acid,[6,7] 3-aminopropylation through cyanoethylation followed by reduction,[8] and (diethylamino)ethylation with (diethylamino)ethyl halides.[3] Among the products, DEAE-cellulose is practically utilized, and thus (diethylamino)ethylation with (diethylamino)ethyl chloride (DEAE-Cl) was applied to chitin (Scheme I).

Reaction in Organic Solvents. The reaction was first carried out in dispersion in organic solvents. Pulverized chitin dispersed in organic solvents sometimes became sticky on addition of a small amount of aqueous sodium hydroxide depending on the nature of the solvent. It, however, dispersed well again as the reaction with DEAE-Cl proceeded. When dioxane was used as in the case of

Scheme I

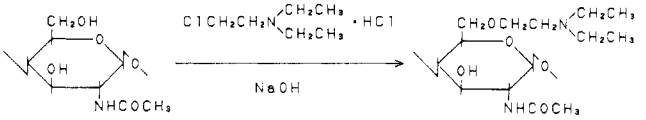

Table I
Preparation of DEAE-Chitins in Organic Solvents[a]

chitin, g	solvent	reacn temp, °C	reactn time, h	yield, g	ds[b]
0.107	dioxane	rt[c]	4	0.123	0.16
0.113	dioxane	60	4	0.116	0.30
0.102	dioxane	95	4	0.119	0.34
0.102	THF	rt	24	0.104	0.40
0.105	THF	reflux	4	0.118	0.64
0.201	DMSO	rt	4	0.226	0.61
0.203	DMSO	60	4	0.219	1.19
0.207	DMSO	95	4	0.151	1.27
0.102	DMAc	rt	24	0.099	0.31
0.105	formamide	95	4	0.095	0.01
0.108	pyridine	rt	24	0.104	0.15

[a] For 0.1 g of chitin, 5 mL of solvent, 0.75 mL of 20% aqueous sodium hdyroxide, and 0.43 g of DEAE-Cl·HCl were used. [b] Degree of substitution determined by conductometric titration. [c] rt = room temperature.

DEAE-cellulose,[9] the products with degrees of substitution (ds) of ca. 0.3 were obtained above 60 °C as shown in Table I. Tetrahydrofuran (THF) was a better solvent than dioxane. Dimethyl sulfoxide (DMSO) resulted in the highest ds values among the solvents tested, probably because of swelling to some extent[10] and favorable dispersion. *N,N*-Dimethylacetamide (DMAc) and pyridine gave low ds values, and formamide turned out to be unsuitable. These results indicate that (diethylamino)-ethylation is affected markedly by the type of solvent and proceeds smoothly in proper solvents. DMSO and THF appeared to be suitable to achieve high substitutions. The suitability of solvent is not dependent on the state of dispersion alone. Formamide, for instance, disperses chitin quite well only to bring about poor substitution, whereas THF is a rather poor solvent in terms of dispersion but enables efficient substitution.

The influence of reaction temperature is evident between room temperature and 60 °C, but not so above 60 °C. The products obtained at 95 °C assumed darker colors and had only slightly higher ds values than those at 60 °C in general. They were light brown when prepared in polar solvents, but colorless or pale yellow when prepared in dioxane or THF. The samples prepared below 60 °C were obtained as off-white to pale tan powdery materials even in polar solvents. These results confirm that the reaction is efficiently conducted in organic solvents at 60 °C in spite of the reaction under heterogeneous conditions on dispersed chitin.

Reaction in Aqueous Solution. Distribution modes of substituents along the chitin main chain affect the properties of the resulting derivatives to great extents, and random substitution improves various properties, especially the hydrophilic nature.[11] In order to realize high affinity to solvents or even solubility, the reaction should be conducted in homogeneous solution to make possible random substitution.

Chitin dissolves in aqueous sodium hydroxide of high concentration, and thus the solution was treated with DEAE-Cl hydrochloride. The mixture was composed of two immiscible phases initially, an aqueous alkali chitin solution and an organic phase of DEAE-Cl. It, however, became a homogeneous solution as the reaction pro-

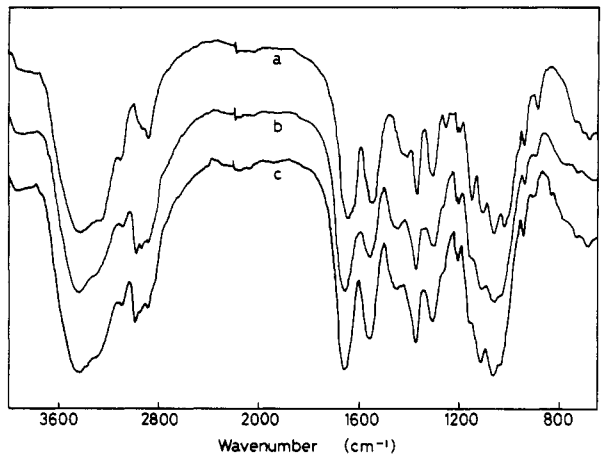

Figure 1. IR spectra of (a) chitin, (b) DEAE-chitin with a ds of 0.73 before N-acetylation, and (c) sample b after N-acetylation (KBr pellets).

Table II
Preparation of DEAE-Chitins in Aqueous Solution[a]

chitin, g	DEAE-Cl·HCl/ pyranose unit[b]	reacn time, h	yield, g	ds[c]
0.503	1	24	0.489	0.30
0.506	3	24	0.577	0.45
0.504	5	24	0.596	0.56
0.508	8	24	0.605	0.64
0.506	10	2	0.465	0.31
0.502	10	5.5	0.368	0.66
0.508	10	8.5	0.590	0.69
0.502	10	15	0.532	0.73
0.501	10	24	0.463	0.78
0.500	20	24	0.329	1.46
0.502	30	24	0.412	1.33
0.505	50	24	nd[d]	0.61

[a] Concentration and volume of aqueous sodium hydroxide: 9.3% and 45 mL; reaction temperature and time: 0 °C for 2 h and then at room temperature for a specified time. [b] Molar ratio. [c] Degree of substitution determined by conductometric titration. [d] Not determined.

ceeded. The product was isolated by concentrating the solution, dialyzing, and freeze-drying. The IR spectra had a strong peak at 2950 cm^{-1} characteristic of saturated hydrocarbons. The amide I and II bands, however, seemd to become weak to a small extent compared to those of the original chitin after prolonged reactions as shown in Figure 1. This might have happened owing to possible partial deacetylation during the substitution reaction in strong alkali. In addition, the original chitin itself had some free amino groups, and to prepare derivatives of definite structure, it was necessary to ensure full N-acetylation after (diethylamino)ethylation. The product was thus treated with acetic anhydride in pyridine. The acetylation took place in homogeneous solution when the extent of (diethylamino)ethylation was high or in a highly swelled state when the extent was low. The IR spectra showed strong amide bands but showed a new weak band at 1730 cm^{-1} of ester linkages at the hydroxyl groups. Subsequent treatment with methanolic potassium hydroxide removed ester linkages completely.

Some typical results are summarized in Table II. The ds increases with reaction time, and 24-h reaction is satisfactory for practical preparations as shown in Figure 2. The influence of the amount of DEAE-Cl on the substitution is evident in Figure 3. The ds increases with an increase in the molar ratio of DEAE-Cl to pyranose units but reaches a maximum at a ratio of 20. The decrease after the maximum is ascribable to the precipitation of chitin from the solution as a result of lowered alkali concentration brought about by a large amount of DEAE-Cl hydrochloride.

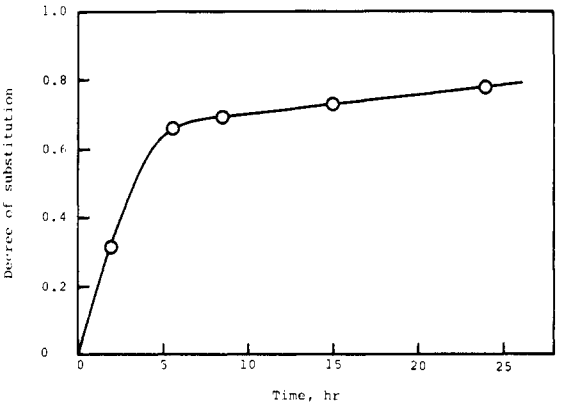

Figure 2. Time course of (diethylamino)ethylation in aqueous solution (conditions: at 0 °C for 2 h and then at room temperature for a given time; DEAE-Cl·HCl/pyranose unit = 10).

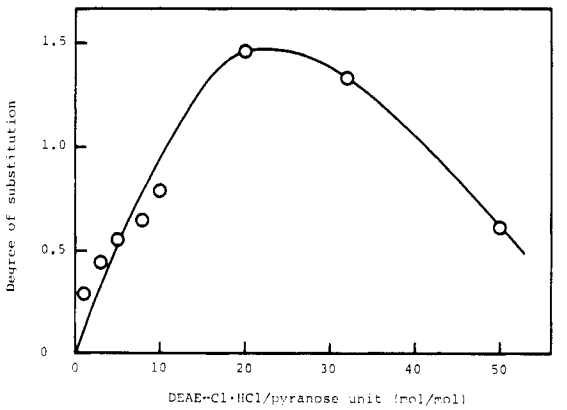

Figure 3. Effect of the amount of DEAE-Cl·HCl on the (diethylamino)ethylation of chitin in aqueous solution (conditions: at 0 °C for 2 h and then at room temperature for 24 h).

The DEAE-chitins prepared in aqueous solution were generally colorless to off-white, and the coloration was much lighter than that in DMSO.

Reaction in Aqueous Solution with a Phase-Transfer Catalyst. Although the (diethylamino)ethylation described above proceeded in aqueous solution smoothly, the reaction actually occurred between the two separated phases. This implies that the use of a phase-transfer catalyst would further improve the reaction efficiently, as in the modifications of cellulose in the presence of tetramethylammonium chloride by Daly and co-workers.[8,12] On addition of the same catalyst, the appearance of the mixture during the (diethylamino)ethylation changed little, but the reaction efficiency was enhanced markedly as shown in Table III. With a slight amount of the catalyst, ds values above 1 were easily attained in a shorter time and with a smaller amount of DEAE-Cl.

In the benzylation of cellulose, the slurry of powdery alkali cellulose was treated with benzyl chloride at 100 °C.[12] Here, because of the solution reaction, the alkylation of chitin proceeded under much milder conditions at 0 °C and room temperature both with and without the catalyst, ensuring that possible degradation of chitin backbones was effectively suppressed.

Structure of DEAE-Chitins. The DEAE-chitins prepared in organic solvents and in aqueous solution showed identical IR spectra. They show a strong C–H stretching band at 2950 cm^{-1}, indicating the introduction of (diethylamino)ethyl groups. The characteristic amide I and II bands become strong after N-acetylation. A typical spec-

Table III
Influence of a Phase-Transfer Catalyst on the Preparation of DEAE-Chitins[a]

chitin, g	TMAC,[b] mmol	reactn time, h	yield, g	ds[c]
0.506	0	2	0.465	0.31
0.504	2	2	0.507	1.05
0.504	10	2	0.483	1.20
0.501	0	24	0.463	0.78
0.502	10	24	0.475	1.39

[a] Concentration and volume of aqueous sodium hydroxide: 9.3% and 45 mL; reaction temperature: 0 °C for 2 h and then room temperature for a specified time; DEAE-Cl·HCl/pyranose unit = 10. [b] Tetramethylammonium chloride. [c] Degree of substitution determined by conductometric titration.

Table IV
Solubility of DEAE-Chitins[a]

	solvent					
ds[b]	water	ethanol	benzene	DMSO	DMAc	DCA[c]
0[d]	–	–	–	–	–	–
0.61[e]	–	–	–	–	–	±
0.83[e]	±	–	–	±	–	+
1.09[e]	±	–	–	±	±	+
0.30[f]	±	±	±	±	±	+
0.59[f]	+	±	±	±	±	+
1.39[f]	+	±	±	±	±	+

[a] + = soluble, ± = partially soluble or swelled, – = insoluble. [b] Degree of substitution. [c] Dichloroacetic acid. [d] Original chitin. [e] Prepared in DMSO. [f] Prepared in aqueous solution.

trum is included in Figure 1. Elemental analyses and NMR spectra supported the structure.

The ds values were determined most conveniently by conductometric titration. Elemental analysis was another useful method as described in the Experimental Section. The ds values were also obtained by NMR spectroscopy on the basis of the methyl and acetyl proton ratio; a sample with a ds of 0.73 determined by the titration was shown to have a ds of 0.69 by NMR.

Crystallinity of DEAE-chitins was studied by X-ray diffraction diagrams by the powder method, and the introduction of (diethylamino)ethyl groups was found to make crystalline chitin completely amorphous. The destruction of the crystalline structure is expected to play an important role in enhancing hydrophilicity.[11]

Solubility of DEAE-Chitins. DEAE-chitins were expected to show improved tractability in contrast to intractable chitin. Qualitative solubility was tested in excess solvents at room temperature. The solubility and swelling ability were much improved by (diethylamino)-ethylation as expected but were highly dependent on the preparation mode and the ds value. The derivatives prepared in aqueous solution exhibited much better solubility than those prepared in organic solvents. This is reasonably interpreted in terms of the difference in distribution of the substituents along the main chain as suggested by high hydrophilicity of randomly substituted derivatives.[11]

DEAE-chitins prepared in aqueous solution in the presence and absence of the phase-transfer catalyst showed the same solubility behavior in addition to the same spectral data, supporting the structural similarity. They were soluble in dichloroacetic acid and swelled highly in ordinary solvents such as benzene, alcohols, DMSO, and DMAc. Furthermore, those with ds values above 0.5 were readily soluble in water. These results are in sharp contrast to the properties of DEAE-chitins prepared in organic solvents; they were soluble in dichloroacetic acid and swelled to small extents in polar organic solvents when the ds values were high, but insoluble in water regardless of the ds. The solubility was improved with an increase in ds, but still poorer than that of DEAE-chitins prepared in aqueous solution. This indicates the superiority of the reaction in aqueous solution over that in organic solvents in terms of not only the randomness of substitution but also the form of isolated products; the products prepared in organic solvents were isolated as rather hard solids whereas those in aqueous solution were obtained as fluffy solids as a result of homogeneous solution reaction. The solubility and swelling ability in some typical solvents are listed in Table IV.

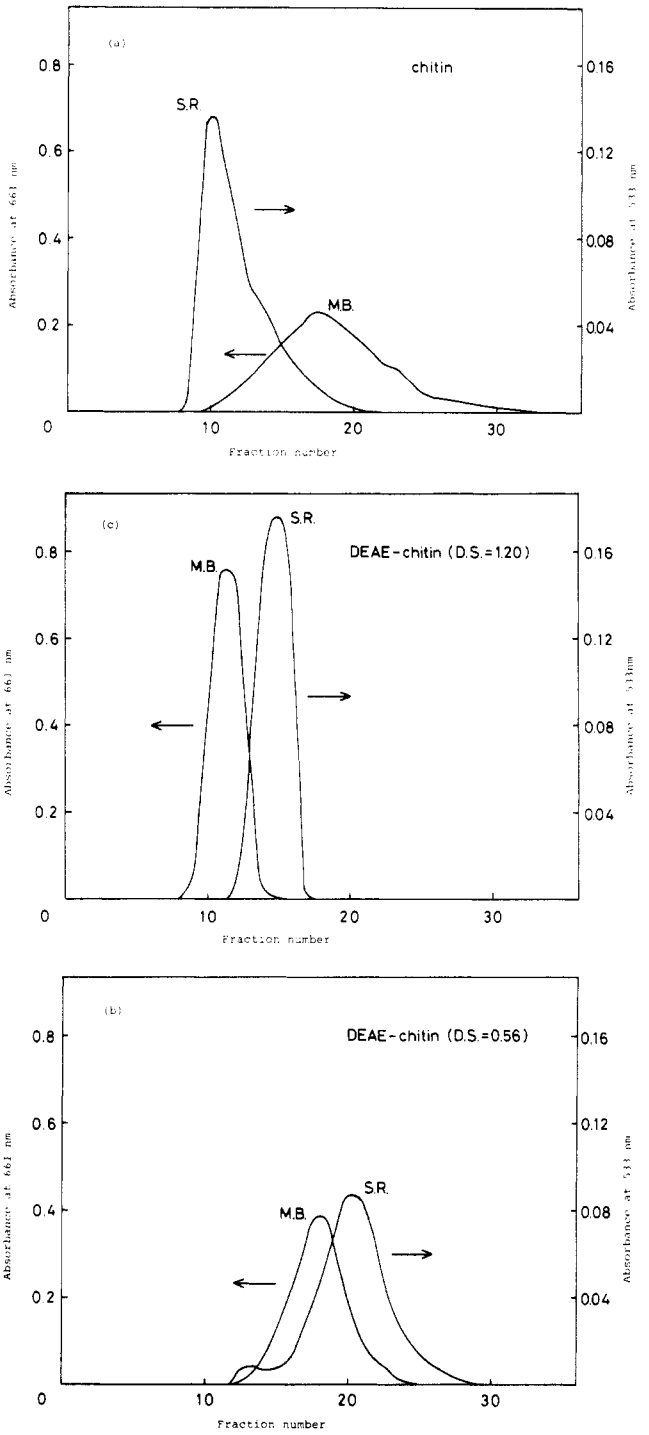

Figure 4. Separation of the organic dyes methylene blue and sudan red by (a) chitin, (b) DEAE-chitin with a ds of 0.56, and (c) DEAE-chitin with a ds of 1.20.

Separation of Organic Dyes. DEAE-chitins obtained here swell in common solvents, and hence they are anticipated to be useful for separation of organic compounds. DEAE-chitins with ds values of 0.56 and 1.20 prepared

in aqueous solution were pulverized and allowed to swell in benzene/methanol (1:1). They were placed in glass columns and subjected to separation of two kinds of dyes, a basic dye (methylene blue) and an acidic dye (sudan red), the same mixed solvent being used as the elution solvent. For comparison, separation by the original chitin was also attempted. The DEAE-chitins swelled so much that the necessary amounts of the derivatives with ds of 0.56 and 1.20 to pack the columns were 1/11 and 1/14 of that of the original chitin, respectively.

The separation behavior for each column is illustrated in Figure 4. In the chitin column, sudan red was eluted first and then methylene blue, but the separation was poor. When DEAE-chitins were used, the development order was reversed, methylene blue being eluted first. With the DEAE-chitin with a ds of 0.56, the separation was not sharp. The DEAE-chitin with ds of 1.20, however, showed improved separation with little tailing and promises to have high potential for use as an adsorbent and separating agent.

Conclusion

DEAE-chitins have been prepared in organic solvents as well as in aqueous solution. Since both reactions proceeded fairly reproducibly under appropriate conditions, the substitution extents were controlled easily. Properties of the products depended on the mode of preparation and substitution extent. DEAE-chitins prepared in aqueous solution showed especially high affinity for both polar and nonpolar solvents. This would be a useful property to explore new advanced utilizations. The high swelling ability in common solvents was of advantage for separation use in that only a very small amount was necessary and that high efficiency was achieved.

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Ring-Opening Polymerizations of Lactone and Epoxide Initiated with Aluminum Complexes of Substituted Tetraphenylporphyrins. Molecular Design of Highly Active Initiators

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ABSTRACT: Ring-opening polymerization of β-propiolactone with a series of aluminum complexes of substituted tetraphenylporphyrins gave polymer with narrow molecular weight distribution, where the aluminum porphyrins (tetrakis(2′,4′,6′-trimethoxyphenyl)porphinato)aluminum chloride, (tetrakis(2′,6′-dimethoxyphenyl)porphinato)aluminum chloride, and (tetrakis(2′,6′-dichlorophenyl)porphinato)aluminum chloride were much more active than nonsubstituted (tetraphenylporphinato)aluminum chloride. These aluminum ortho-disubstituted tetraphenylporphyrins were also active as initiators for the polymerizations of δ-valerolactone and 1,2-epoxypropane both in the absence and presence (immortal polymerization) of methanol as a protic chain-transfer agent.

Introduction

Aluminum porphyrins initiate the living polymerizations of a wide variety of monomers such as lactones,[1] epoxides,[2] and methacrylic esters,[3] affording the corresponding polymers of controlled molecular weight with narrow molecular weight distribution. In these cases, the chain growth takes place at the central aluminum atom–axial ligand bond of the initiator. For example, the polymerization of β-propiolactone initiated with aluminum porphyrin proceeds by the repeated reactions of the monomer with the aluminum–carboxylate bond of (porphina-

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