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NOTE

Synthesis of Photosensitive Polymers from Chitosan

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Chitin, a natural polymer having *N*-acetylglucosamine units,[1] exists widely in nature as a hard supporting structure for many living things such as crabs, insects and so on, and has a very poor solubility similar to cellulose. On the other hand, chitosan[2] which is derived from chitin by hydrolysis has free amino groups which increase its solubility in organic solvents and has a high reactivity toward chemical reactions such as amidation or esterification.[3-6]

We found that chitosan reacts very easily with strong carboxylic acids such as mono-, di- or trichloroacetic acids under mild conditions to form corresponding chitosan derivatives which are soluble in acetone, and that films obtained from these chitosan derivatives can be easily converted into hard insoluble films owing to a crosslinking reaction when irradiated with UV light. This paper describes the synthesis of a new-type photosensitive polymer derived from chitosan.

EXPERIMENTAL

Reaction of Chitosan with Chloroacetic Acids

A 5 g portion of chitosan was dissolved into 120 ml of mono-, di- or tri-chloroacetic acids for a period of 20 min at 60—70°C. The solution was kept at 70°C for 30 min with stirring. The solution was poured into excess water and the precipitated polymers were collected by filtration, followed by washing with ether. The polymers were purified by repeated dissolution in acetone and precipitation with water twice, and dried under vacuum. Solution viscosities of the resulting polymers were measured in dimethylsulfoxide (DMSO) at 30°C.

UV Irradiation of Films

A 1 to 1.5 g portion of chitosan derivatives having chloroacetyl groups were dissolved in a mixed solution of 10 ml of methylcellosolve and 10 ml of acetone. The solution was casted on a flat glass plate. By evaporating the solvent under vacuum, a flexible film was obtained. Films containing various photosensitizers were prepared by the same method. The films were colorless and transparent with good flexibility.

The films were irradiated by UV light in a given period with a 450 W high pressure mercury lamp situated at a distance of 45 cm from the lamp. The irradiated films were immersed in a mixed solvent of methylcellosolve and acetone or in dimethylformamide (DMF), and the insoluble parts were washed with ether and weighed.

Model Reaction

In order to investigate the crosslinking reaction of chloroacetyl groups with UV irradiation, a model reaction was carried out using isopropyl dichloroacetate. Isopropyl dichloroacetate was dissolved in 2-propanol or tetrahydrofuran at a desired concentration and the solution was irradiated with UV light at 25°C. Reaction products in the solution were analyzed by gas chromatography, infrared, and NMR spectra.

RESULTS AND DISCUSSION

When chitosan was dissolved into chloroacetic

Table I. Haloacetylation of chitosan

Haloacetic acid	$ClCH_2COOH$	$Cl_2CHCOOH$	Cl_3CCOOH	CF_3COOH
η_{sp}/c[a]	Insoluble	1.28	0.46	2.18[b]
Haloacetyl group (number/unit)	—	2.9	2.2	1.0

[a] 0.5 g/100 ml in dimethylsulfoxide at 30°C.
[b] 0.5 g/100 ml in water at 30°C.

acids and the solution was warmed up to 70°C, a rapid reaction took place with both amino and hydroxyl groups to form amide and ester groups, respectively, presumably owing to an auto-catalytic effect of the strong chloroacetic acids. However, trifluoroacetic acid yielded only a salt of the amino group of chitosan and neither amidation nor esterification occurred. Among chloroacetic acids, monochloroacetic acid yielded a product which was not soluble in acetone or DMSO, while di- or trichloroacetic acids produced chitosan derivatives which were soluble either in acetone or DMSO. The products obtained in various hologenated acetic acid indicated a decrease in solution viscosity, as shown in Table I, and this may be ascribed to an acidolysis of the original chitosan caused by the strong acidity of these acids.

Figure 1 indicates the infrared spectrum of the product obtained from chitosan and dichloroacetic acid; it exhibits absorptions due to an ester group at $1750\,cm^{-1}$ and an amide group at 1700 and $1530\,cm^{-1}$, respectively. The absorption maximam of the dichloroacetylated chitosan exhibits 205 nm in the UV spectrum. Elemental analysis of the product indicated that the amount of combined dichloroacetic acid reached about 2.9 per one unit of glucosamine.

Films obtained from dichloroacetylated chitosan were irradiated with UV light. The irradiated film became insoluble in acetone within 20 min. Figure 2 indicates the degree of crosslinking in the irradiated films in terms of insoluble polymer. It is seen in Figure 2 that crosslinking reactions occur in dichloroacetylated chitosan much faster than in trichloroacetylated chitosan. The infrared spectrum of the irradiated film showed a decrease in the absorption at $808\,cm^{-1}$ as is seen in Figure 1, and suggests the elimination of the chlorine atom from the dichloroacetyl group to form the crosslinking bonds among the polymer chains. The irradiated film retained its transparency and flexibility.

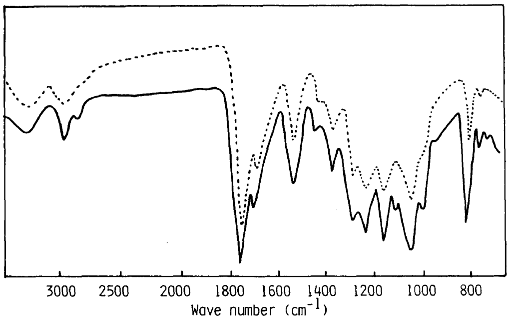


Figure 1. Infrared and UV spectra of dichloroacetylated chitosan and its irradiated film: ——, dichloroacetylated chitosan; ------, dichloroacetylated chitosan after irradiation.

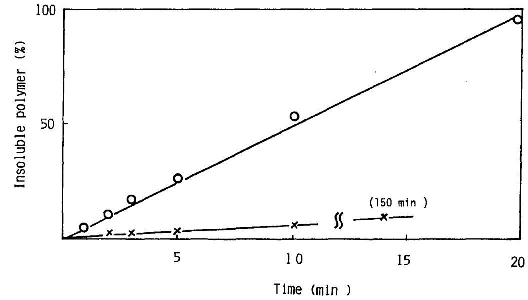


Figure 2. Photosensitivity of di- or tri-chloroacetylated chitosan in UV irradiation: ○, dichloroacetylated chitosan; ×, trichloroacetylated chitosan.

Films of dichloroacetylated chitosan containing various additives were irradiated so as to find an effective sensitizer; the results are summarized in Figure 3. The film containing diphenylaniline developed a deep green color with irradiation, owing perhaps to the formation of di- or triphenylmethane

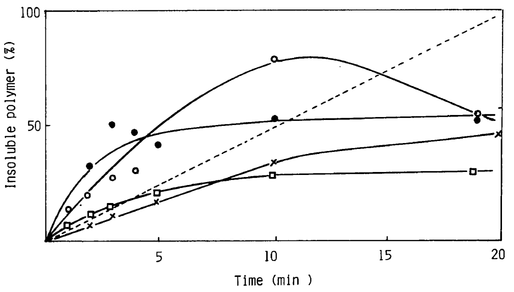


Figure 3. Effect of photosensitizers on the photosensitivity of dichloroacetylated chitosan: ●, anthracene (10%); ○, hydroquinone (10%); □; Michler's ketone; ×, diphenylaniline (14%).

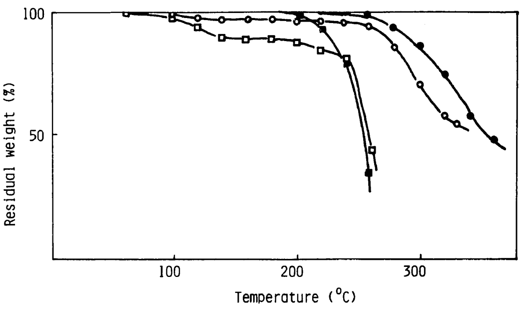


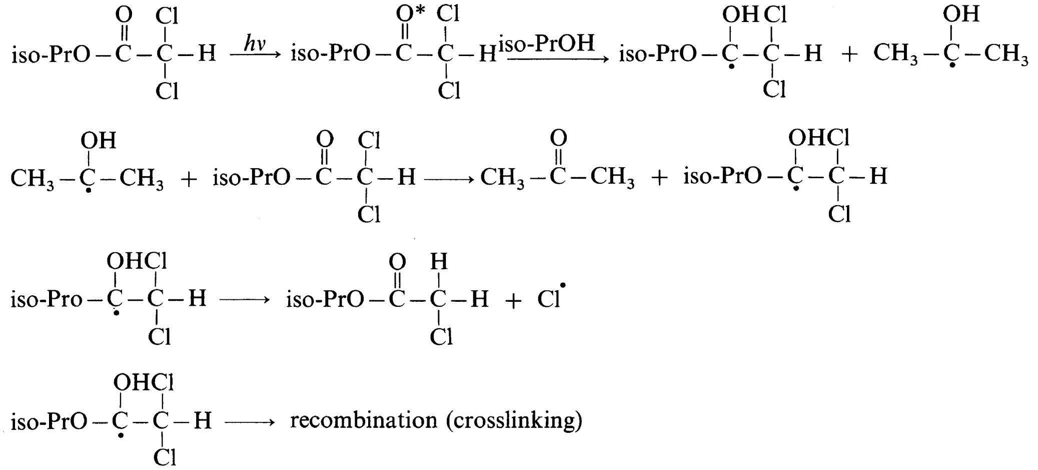
Figure 4. Thermogravimetric analyses of chitosan derivatives: ●, chitin; ○, chitosan; □, dichloroacetylated chitosan; ■, trichloroacetylated chitosan. Heating rate, 10°C/min, in air.

dyes, while diphenylaniline somewhat retarded the crosslinking reaction. Hydroquinone or anthracene enhanced the crosslinking reaction at the initial stage of the irradiation. The irradiated films became brittle.

Figure 4 shows the thermal properties of various chloroacetylated chitosan derivatives from the thermogravimetric analysis. Di- or tri-chloroacetylated chitosan derivatives had less thermal stability than chitin or chitosan, as shown in Figure 4.

In order to investigate the crosslinking reaction of chloroacetyl groups with UV irradiation, a model reaction using isopropyl dichloroacetate was carried out in 2-propanol solution. It was confirmed by gas chromatographic, infrared and NMR analyses that isopropyl monochloroacetate and acetone were produced in the solution with UV irradiation. Table II summarizes the results of the UV irradiation of isopropyl dichloroacetate in isopropanol solution in reference to the yield of isopropyl monochloroacetate. When isopropyl dichloroacetate was irradiated in bulk for 2 days, no reaction products were detected. However, in 2-propanol solution, monochloroacetate was formed rapidly.

The addition of radical scavengers such as hydroquinone inhibited the formation of monochloroacetate which might be produced through a radical mechanism. Therefore, it is presumed that the photochemical reaction of chloroacetyl groups requires a source of hydrogen atoms such as secondary alcohols for the initiation of the radical reaction. From these results, the following mechanism is proposed for the model reaction and the crosslinking reaction of chloroacetylated chitosan:



$$\text{iso-PrO}-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\overset{Cl}{\overset{|}{C}}}-H \xrightarrow{h\nu} \text{iso-PrO}-\overset{O^*}{\overset{\|}{C}}-\underset{Cl}{\overset{Cl}{\overset{|}{C}}}-H \xrightarrow{\text{iso-PrOH}} \text{iso-PrO}-\overset{OH}{\underset{\bullet}{C}}-\underset{Cl}{\overset{Cl}{C}}-H + CH_3-\overset{OH}{\underset{\bullet}{C}}-CH_3$$

$$CH_3-\overset{OH}{\underset{\bullet}{C}}-CH_3 + \text{iso-PrO}-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\overset{Cl}{C}}-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + \text{iso-PrO}-\overset{OH}{\underset{\bullet}{C}}-\underset{Cl}{\overset{Cl}{C}}-H$$

$$\text{iso-Pro}-\overset{OH}{\underset{\bullet}{C}}-\underset{Cl}{\overset{Cl}{C}}-H \longrightarrow \text{iso-PrO}-\overset{O}{\overset{\|}{C}}-\underset{Cl}{\overset{H}{C}}-H + Cl^{\bullet}$$

$$\text{iso-PrO}-\overset{OH}{\underset{\bullet}{C}}-\underset{Cl}{\overset{Cl}{C}}-H \longrightarrow \text{recombination (crosslinking)}$$

The lower photosensitivity of trichloroacetyl group in comparison with dichloroacetyl group may be ascribed to the lower reactivity of the trichloroacetyl radical owing to both steric and inductive effects of chlorine atoms.

Table II. Irradiation of isopropyl dichloroacetate by UV light in 2-propanol in the presence of various additives[a]

Additive (10%)	Yield of isopropyl monochloroacetate/%				
	1 day	2 day	3 day	4 day	5 day
None	3	15	21	28	33
Concd HCl	3	13	24	28	36
AIBN[c]	2	8	13	21	—
BPO[d]	7	7	17	—	19
Benzophenone	6	8	10	—	11
Anthracene	0	1	3	—	5
Michler's ketone[b]	0	1	1	1	1
Hydroquinone	0	0	0	0	0
Triethylamine	0	0	0	0	0

[a] Concn, 2 mol l^{-1} at 30°C in air.

[b] Concn, 1 mol l^{-1} in 2-propanol and tetrahydrofuran (1/1).

[c] Azobisisobutyronitrile.

[d] Benzoyl peroxide.

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