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Synthesis of UV-curable chitosan derivatives and palladium (II) adsorption behavior on their UV-exposed films

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Abstract

Novel chitosan derivatives with UV-curable functional groups, such as 3-methoxy-4-(2-hydroxy-3-methacryloyloxypropoxy)benzyl, 3,4-bis(2-hydroxy-3-methacryloyloxypropoxy)benzyl, 3-methoxy-4-methacryloyloxybenzyl, and 3,5-dimethacryloyloxybenzyl groups, were prepared. Introduction of photosensitive functional groups to chitosan was accomplished by reductive *N*-alkylation *via* Schiff's bases using corresponding photosensitive aldehydes. Compared to starting chitosan, UV-curable chitosan derivatives showed better solubility in several organic solvents, such as DMSO and 70% methacrylic acid. The solubility of these compounds increased with an increase in the degree of substitution of the *N*-alkyl side chains. After UV irradiation for 20 s under a high-pressure mercury lamp at a distance of 15 cm from the samples, acidic methanol solutions of these derivatives were transformed to gels in the presence of photo-initiator, and their dried films adsorbed palladium (II) at pH 1.1 and pH 5.3. The UV-curable chitosan derivatives were successfully used as coating materials for electroless plating on non-conductive substances.

Keywords: Photosensitive aldehyde; Chitosan derivatives; UV-curable; Palladium adsorption; Metal deposition; Electroless plating

1. Introduction

One of the most popular properties of chitosan is metal adsorption due to the presence of an active amino groups. There are many chitosan derivatives which have the ability to chelate metals (Varma, Deshpande, & Kennedy, 2004).

We have previously reported on the application of chitosan to electroless metal plating (Omura, Nakagawa, & Murakami, 1998; Omura, Renbutsu, Morimoto, Saimoto, & Shigemasa, 2003) because of its excellent adsorption of palladium (II) (Baba, Kawano, & Hirakawa, 1996). Palladium immobilized on chitosan plays an important role as a catalyst in the development of environmentally friendly electroless metal plating on non-conductive substances such as wood, plastic, ceramics, paper, glass, and fiber. In the general method, etching treatment of non-conductive substances with a Cr (VI)/H_2SO_4 solution is necessary to attach metal catalyst, and this has caused environmental pollution. Using the metal adsorption ability of chitosan as an alternative method to Cr (VI) etching, we established electroless metal plating by using a special paint containing chitosan (Omura et al., Jpn. Patent. 2000). However, chitosan itself does not have good affinity for synthetic resins and is not soluble in usual organic solvents or neutral water. Thus, the chitosan-containing paint was not stable enough. Furthermore, the paint hardening process requires long heating times of over 30 min due to the thermosetting resin of the paints. It is necessary to shorten the curing time

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to improve productivity. Therefore, we modified chitosan with hydrophobic side chains, which contain UV-curable functional groups (Renbutsu et al., 2005).

In this paper, we report on UV-curable palladium-chelating chitosan derivatives prepared using photosensitive aldehydes as side chain precursors. In addition, these novel derivatives are characterized and their palladium adsorption properties are evaluated.

2. Experimental

2.1. Materials

Chitosan (SK-10 · DAC-100; Lot. No. L90831; degree of deacetylation (DDA), 100%; viscosity, 8 cps (1.0% in 1% acetic acid, 20 °C); Mw 86000) was kindly supplied by Koyo Chemical Co. Ltd, and used as received. The photo-initiator, Irgacure®1000, was purchased from Ciba Specialty Chemicals K.K. Glycidyl methacrylate (GMA), 3-methoxy-4-hydroxybenzaldehyde (vanillin), 3,4-dihydroxybenzaldehyde, 4-dimethylaminopyridine (DMAP), *N*,*N*′-dicyclohexylcarbodiimide (DCC), and sodium borohydride ($NaBH_4$) from Wako, 3,5-dihydroxybenzaldehyde from Avocado, sodium cyanoborohydride from Aldrich, dimethylamine-borane (DMAB) from TCI and palladium (II) chloride from Hayashi were used without further purification. Methacrylic acid from Kishida was used for esterification after drying over 4Å molecular sieves.

2.2. Instrumentation

Compounds were identified and characterized by ^{1}H NMR spectra recorded on a JNM-ECP500 spectrometer ‘JEOL’ at 500 MHz in a 2% CD_3COOD/D_2O solution at a concentration of 10 mg/ml, and by Fourier transform infrared (FT/IR) spectra obtained using an AVATAR 360 type spectrometer ‘Nicolet’. The degree of substitution (DS) was calculated from the C/N ratio evaluated from the elemental analysis.

UV irradiation was performed with a UV irradiator (UE-0151-326-01) with a high-pressure mercury lamp (1.0 kW) ‘Eye Graphic’. Inductively coupled plasma (ICP) analysis of palladium was carried out by an ICP optical emission spectrophotometer SPS7700 ‘SII NanoTechnology Inc’.

2.2.1. Preparation of photosensitive aldehydes by using glycidyl methacrylate (Method A)

*2.2.1.1. 3-Methoxy-4-(2-hydroxy-3-methacryloyloxypropoxy)benzaldehyde (**1**).* The aldehyde **1** was prepared according to the previously described method (Ichimura & Oohara, 1987). A mixture of vanillin (16.74 g, 110 mmol), glycidyl methacrylate (14.2 g, 100 mmol) and tetra-*n*-butylammonium iodide (370 mg, 1 mmol) in DMF (50 ml) was stirred overnight at 80 °C. The mixture was then diluted with ethyl acetate, and the organic layer was washed with cold 10% KOH, cold distilled water and brine. After drying over anhydrous sodium sulfate, the organic layer was concentrated. Hot toluene was added to the resultant amber syrup, and it was heated, followed by the immediate removal of the insoluble amorphous portion by filtration. The filtrate was concentrated at 60 °C to remove excess toluene and cooled to room temperature. After the precipitate appeared, the mixture was kept in cold storage. The precipitate was collected by filtration to give aldehyde **1** (14.01 g, 43% yield). – ^{1}H NMR ($CDCl_3$) δ 1.94 (3H, s, –CH_3), 3.18 (1H, br, –OH), 3.90 (3H, s, –OCH_3), 4.15–4.36 (5H, each m, –CH_2–CH–CH_2–), 5.60 and 6.14 (each 1H, s, s, —C=CH_2), 6.98 (1H, d, $J = 8.3$ Hz, aromatic-H), 7.40 (1H, d, $J = 1.7$ Hz, aromatic-H), 7.43 (1H, dd, $J = 1.7$, 8.3 Hz), 9.85 (1H, s, CH=O); IR (KBr, cm^{-1}) 1718, 1672, 1635, 1587, 1512.

*2.2.1.2. 3,4-Bis(2-hydroxy-3-methacryloyloxypropoxy)benzaldehyde (**2**).* 3,4-Dihydroxybenzaldehyde (6.90 g, 50 mmol) and tetra-*n*-butylammonium iodide (370 mg, 1 mmol) were dried *in vacuo* for 2 h in the presence of P_2O_5. Glycidyl methacrylate (35.40 g, 250 mmol) and anhydrous DMF (50 ml) were added to the mixture and it was stirred at 80 °C overnight. The mixture was then diluted with ethyl acetate, and the organic layer was washed with water. After drying over anhydrous sodium sulfate, the organic layer was concentrated. The resultant syrup was purified by silica gel chromatography (dichloromethane → ethyl acetate/hexane = 1:1 → ethyl acetate/hexane = 2:1) to give aldehyde **2** as a pale yellow syrup (4.72 g, 22% yield). – ^{1}H NMR ($CDCl_3$) δ: 1.94 (6H, s, –CH_3), 3.6 and 3.8 (each 1H, each m, OH), 4.1–4.37 (10H, m, –CH_2–CH–CH_2–), 5.6 and 6.1 (each 2H, m, —C=CH_2), 7.0 (1H, d, $J = 8.3$ Hz, aromatic-H), 7.44 (1H, s, aromatic-H), 7.48 (1H, d, $J =$ 8.3 Hz, aromatic-H), 9.84 (1H, s, CH=O); IR (IR card Type 61, cm^{-1}) 1716, 1690, 1635, 1510, 814.

*2.2.1.3. 3,5-Bis(2-hydroxy-3-methacryloyloxypropoxy)benzaldehyde (**3**).* The above procedure was applied to the synthesis of **3**. From 3,5-dihydroxybenzaldehyde (1.0 g, 7 mmol), aldehyde **3** (1.93 g, 64% yield) was obtained as a pale yellow amorphous solid. – ^{1}H NMR ($CDCl_3$) δ: 1.96 (6H, s, –CH_3), 2.96 (2H, m, OH), 4.09, 4.31–4.37 (10H, m, –CH_2–CH–CH_2–), 5.62, and 6.16 (each 2H, s, s, —C=CH_2), 6.76 (1H, t, $J = 2.3$, 2.8 Hz, aromatic-H), 7.04 (2H, d, $J = 2.3$ Hz, aromatic-H), 9.88 (1H, s, CH=O); IR (KBr, cm^{-1}): 1718, 1633, 1597 cm^{-1}.

2.2.2. Preparation of photosensitive aldehydes by using methacrylic acid (Method B)

*2.2.2.1. 3-Methoxy-4-methacryloyloxybenzaldehyde (**4**).* Vanillin (5.0 g, 33 mmol), 4-dimethylaminopyridine (1.2 g, 9.9 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (12 g, 56 mmol) were dried *in vacuo* for 2 h in the presence of P_2O_5. Anhydrous toluene (130 ml) and methacrylic acid (2.8 ml, 33 mmol) were then added to the mixture and it was stirred at 0 °C for 3 h under argon. The mixture was diluted with water and extracted with toluene. The organic layer was then separated, dried over anhydrous sodium sulfate, and concentrated. The resultant syrup was purified by silica gel chromatography (toluene/diethyl ether = 20:1) to give the aldehyde **4** as a pale yellow crystal (6.4 g, 88% yield). – ^{1}H NMR ($CDCl_3$) δ: 2.08 (3H, s, –CH_3), 3.89 (3H, s, –OCH_3), 5.80 and 6.38 (each 1H, s, s, $-C{=}CH_2$), 7.27 (1H, s, aromatic-H), 7.49 (2H, d, $J = 7.6$ Hz, aromatic-H), 10.0 (1H, s, C$H{=}O$); IR (KBr, cm^{-1}): 1734, 1693, 1633, 1597, 1506.

*2.2.2.2. 3,4-Dimethacryloyloxybenzaldehyde (**5**).* 3,4-Dihydroxybenzaldehyde (50 mg, 0.36 mmol), 4-dimethylaminopyridine (15 mg, 0.12 mmol) and N,N'-dicyclohexylcarbodiimide (126 mg, 0.61 mmol) were dried *in vacuo* for 2 h in the presence of P_2O_5. Anhydrous toluene (3 ml) and methacrylic acid (305 μl, 3.6 mmol) were added to the mixture and it was stirred at 75 °C for 2 h under argon. The mixture was diluted with ethyl acetate, and the organic layer was washed with brine and concentrated. The resultant syrup was purified by thin layer chromatography (toluene/ethyl acetate = 4:1) to give aldehyde **5** as a pale yellow syrup (47 mg, 48% yield). – ^{1}H NMR ($CDCl_3$) δ: 2.02 (6H, s, –CH_3), 5.78 and 6.32 (each 2H, s, s, $-C{=}CH_2$), 7.46 (1H, d, $J = 7.8$, aromatic-H), 7.81 (1H, d, $J = 1.5$ Hz), 7.82 (1H, dd, $J = 1.5$, 7.8 Hz), 9.99 (1H, s, C$H{=}O$); IR (KBr, cm^{-1}): 1747, 1701, 1638, 1605, 1500.

*2.2.2.3. 3,5-Dimethacryloyloxybenzaldehyde (**6**).* 3,5-Dihydroxybenzaldehyde (2.0 g, 14.5 mmol), 4-dimethylaminopyridine (531 mg, 4.35 mmol) and N,N'-dicyclohexylcarbodiimide (5.1 g, 24.7 mmol) were dried *in vacuo* for 2 h in the presence of P_2O_5. Anhydrous toluene (130 ml) and methacrylic acid (6.1 ml, 72.5 mmol) were added to the mixture and it was stirred at room temperature for 2 h under argon. The mixture was diluted with ethyl acetate, and the organic layer was washed with brine. Then the organic layer was dried over anhydrous sodium sulfate, and concentrated. The resultant syrup was purified by silica gel column chromatography (toluene/ethyl acetate = 4:1) to give the aldehyde **6** as a pale yellow syrup (2.0 g, 50% yield). – ^{1}H NMR ($CDCl_3$) δ: 2.07 (6H, s, –CH_3), 5.82 and 6.38 (each 2H, s, s, $-C{=}CH_2$), 7.29 (1H, t, $J = 1.9$, 2.3 Hz, aromatic-H), 7.58 (2H, d, $J = 2.3$ Hz, aromatic-H), 9.98 (1H, s, C$H{=}O$); IR (KBr, cm^{-1}): 1738, 1699, 1633, 1597.

2.2.3. Reductive N-alkylation of chitosan

*2.2.3.1. N-[3-Methoxy-4-(2-hydroxy-3-methacryloyloxypropoxy)benzyl]chitosan (**7**).* Aldehyde **2** (588 mg, 2 mmol) in THF (20 ml) was added to a stirred solution of chitosan (800 mg, 5 mmol as $-NH_2$ groups) in a mixture of 0.2 M AcOH/AcONa buffer solution (pH 4.5, 60 ml) and methanol (40 ml). After stirring at 25 °C overnight, the reaction mixture was cooled to 0 °C, then sodium cyanoborohydride (265 mg, 4 mmol) in water (10 ml) was added dropwise. After stirring at 0 °C for 1 h and then at 25 °C overnight, the reaction mixture was neutralized with 10% NaOH solution. The precipitate was collected by centrifugation, washed with ethanol and water, and dialyzed against distilled water. The wet product obtained was lyophilized to give compound **7b**. As shown in Table 2, three kinds of compound **7** having different degrees of substitution were prepared (**7a–c**) by changing the molar ratio of aldehyde **1** to $-NH_2$ groups of chitosan. – ^{1}H NMR (2% CD_3COOD in D_2O) δ 1.93 (–CH_3), 3.23 (H-2 of GlcN residue), 3.73–4.0 (m (chitosan chain) + s (δ 3.9, –OCH_3)), 4.19 and 4.38 (–CH_2–CH–CH_2–), 5.75 and 6.17 ($-C{=}CH_2$), 7.13–7.20 (aromatic-H); IR (KBr, cm^{-1}) 1710, 1640, 1516, 1320, 1300, 814. **7a**: found: C, 48.81; H, 6.77; N, 5.97% (DS = 0.24). **7b**: found: C, 48.91; H, 6.70; N, 4.77% (DS = 0.40). **7c**: found: C, 54.77; H, 6.64; N, 3.45% (DS = 0.84).

*2.2.3.2. N-[3,4-Bis(2-hydroxy-3-methacryloyloxypropoxy)benzyl]chitosan (**8**).* The above procedure was applied to the synthesis of **8** (Table 2). – ^{1}H NMR (2% CD_3COOD in D_2O) δ: 1.90 (–CH_3), 3.16 (H-2 of GlcN), 3.7–4.4 (chitosan chain and –CH_2–CH–CH_2–), 5.71 and 6.12 ($-C{=}CH_2$), 7.11–7.15 (aromatic-H); IR (KBr, cm^{-1}) 1713, 1635, 1595, 1514, 814. **8a**: found: C, 44.09; H, 6.38; N, 6.20% (DS = 0.11). **8b**: found: C, 50.26; H, 6.23; N, 4.44% (DS = 0.34).

*2.2.3.3. N-(3-Methoxy-4-methacryloyloxybenzyl)chitosan (**9**).* A methanol (50 ml) solution of aldehyde **4** (377 mg, 1.7 mmol) was added to a stirred solution of chitosan (1600 mg, 10 mmol as $-NH_2$ groups) in a mixture of 0.2 M AcOH/AcONa buffer solution (pH 4.5, 100 ml) and methanol (50 ml). After stirring at 25 °C overnight, the reaction mixture was neutralized by adding 10% NaOH solution. After cooling to 0 °C, sodium borohydride (375 mg, 10 mmol) in 10 ml of 0.1% NaOH solution was added dropwise. After stirring at 0 °C for 1 h and then at 25 °C overnight, the reaction mixture was neutralized with acetic acid and dialyzed against distilled water. The wet compound obtained was lyophilized to give compound **9a**. As shown in Table 2, two kinds of compound **9** having different degrees of substitution were prepared (**9a** and **b**) by changing the molar ratio of aldehyde **4** to $-NH_2$ groups of chitosan. – ^{1}H NMR (2% CD_3COOD in D_2O) δ 1.90 (–CH_3), 3.16 (H-2 of GlcN residue), 3.72–4.14 (m (chitosan chain) + s (δ 4.0, –OCH_3)), 5.95 and 6.39 ($-C{=}CH_2$), 6.9–7.3 (aromatic-H); IR (KBr, cm^{-1}) 1738, 1640, 1601, 1512, 810. **9a**: found: C, 48.18; H, 6.93; N, 6.86% (DS = 0.18). **9b**: found: C, 54.69; H, 6.03; N, 4.55% (DS = 0.67).

*2.2.3.4. N-(3,5-Dimethacryloyloxybenzyl)chitosan (**10**).* The above procedure was applied to the synthesis of **10** (Table 2). – ^{1}H NMR (2% CD_3COOD in D_2O) δ 1.90 (CH_3), 3.16 (H-2 of GlcN residue), 3.7–4.0 (chitosan chain), 5.95 and 6.4 ($-C{=}CH_2$), 6.45–7.0 (aromatic-H); IR (ATR, cm^{-1}) 1730, 1641, 1591, 806. Found: C, 48.19; H, 6.49; N, 6.28% (DS = 0.20).

2.2.4. Solubility of chitosan derivative

One milliliter portions of various solvents were added to samples (10 mg) of all chitosan derivatives. After standing at 25 °C for 24 h, the solubility was evaluated.

2.2.5. UV irradiation and film formation of UV-curable chitosan derivatives

Chitosan derivatives (20 mg) in 2% aqueous acetic acid (1 ml), methanol (1 ml), and Irgacure® 1000 (5 mg) were mixed and cast on a plastic dish (polypropylene; diameter 30 mm). The mixed solution was transformed to a hardened gel by UV irradiation. The irradiation time was 20 s at a distance of 15 cm from the sample in an ambient atmosphere. Drying at 60 °C for 3 h gave a UV-cured film, which was washed several times with a solution of 1% NaOH in 90% aqueous methanol, and then rinsed with methanol to remove excess solvent. After drying, each dried film sample (ca. 20 mg; thickness, 0.04–0.07 mm; diameter, 20–25 mm) was subjected to the metal adsorption test.

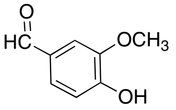
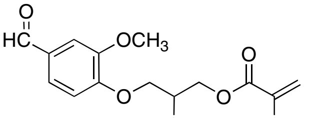
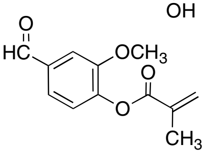
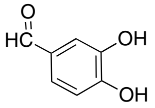
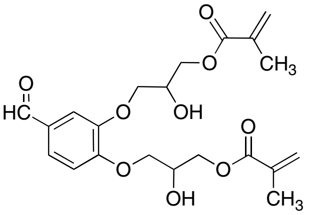
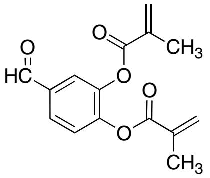
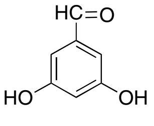
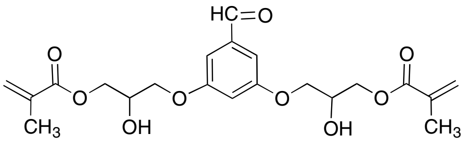
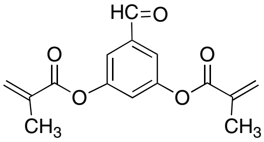
UV-untreated film was prepared in a similar manner as above, only without UV-exposure.

2.2.6. Measurement of palladium adsorption

A palladium (II) solution (150 ppm as palladium ions) of pH 1.1 was obtained from $PdCl_2$ (0.25 g), concentrated hydrochloric acid (10 ml) and H_2O (990 ml) and a solution of pH 5.3 was obtained from $PdCl_2$ (0.25 g) and 1% aqueous NaCl (1000 ml) (Omura et al., 2003).

The film sample was immersed in 10 ml of palladium chloride solution at 30 °C with shaking. After 3 min of treatment, the film was removed and the palladium concentration of the residual solution was measured by ICP analysis. The amount

Table 1
Photosensitive aldehydes

Starting material	Method	Product		Yield
	A		**1**	43%
	B		**4**	88%
	A		**2**	22%
	B		**5**	48%
	A		**3**	64%
	B		**6**	50%

Methods A and B are shown in Fig. 1.

of adsorbed palladium on the film was estimated from the decrease in the palladium concentration.

2.2.7. Electroless plating on wood using UV-curable chitosan derivatives

A solution of 1% UV-curable chitosan derivative in 2% aqueous acetic acid was diluted two times with *N*-methyl-2-pyrrolidinone. Photo-initiator (equivalent to 1 wt% of the chitosan derivatives) was then added to the mixture. The mixture was applied to a piece of *Japanese cypress* (12 × 65 × 5 mm), which had been degreased in advance with methanol, by spraying or dipping. The coated test piece was exposed to UV light for 20 s at a distance of 15 cm and then dried at 60 °C for 30 min. The test piece was then immersed in 0.1 M aqueous NaOH at 40 °C, and soaked in a palladium (II) solution at pH 1.1, as described above, for 3 min at 30 °C. For the reduction of Pd (II) to Pd (0), the test piece was submerged in 0.5% dimethylamine-borane at 25 °C for 5 min. Between each treatment, the test piece was washed with deionized water at 40 °C. Finally, soaking the test piece in an electroless nickel-plating solution (HR-TA and HR-TB mixture, Okuno Chemical, Japan) at pH 9 at 40 °C for 4 min gave a nickel-plating surface. The nickel-plated test piece was rinsed with deionized water and then dried at 60 °C for 1 h.

3. Results and discussion

3.1. Photosensitive aldehydes

The structures and yields of photosensitive aldehydes are summarized in Table 1. Complete purification of the aldehydes was difficult because of their high reactivity. Thus all aldehydes included small amounts of impurities. Without further purification, the aldehydes were used for the *N*-selective introduction of chitosan side chains.

Aldehyde **1** can be prepared from vanillin and seems to be the most suitable agent for use in the chemical industry at a lower cost, because it can be purified without column chromatography. The similar glycidyl derivative **2** needs purification by column chromatography, which is not suitable for industrial applications. Of the aldehydes prepared in this study, purification of aldehyde **3** was extremely difficult, because it formed a plastic-like amorphous mass during the concentration process after purification by column chromatography. The plastic-like

Table 2
Reductive *N*-alkylation of chitosan

Product	Chitosan (mg/mmol)[a]	Aldehyde			NaBH$_3$CN (mmol)	Yield (g)	DS
			mmol	Molar equiv.[b]			
7a	800/5	**1**	1.0	0.20	2	0.81	0.24
7b	800/5	**1**	2.0	0.40	4	1.05	0.40
7c	800/5	**1**	4.0	0.80	8	1.52	0.84
8a	1600/10	**2**	1.0	0.10	1.75	1.57	0.11
8b	1168/7.25	**2**	2.9	0.40	5	1.63	0.34
9a	1600/10	**4**	1.7	0.17	10[c]	1.91	0.18
9b	1600/10	**4**	6.8	0.68	40[c]	2.52	0.67
10	1600/10	**6**	2.0	0.20	10[c]	1.77	0.20

[a] mmol as –NH$_2$ groups.
[b] Molar equivalent relative to GlcN unit of chitosan.
[c] NaBH$_4$.

Table 3
Solubility of UV-curable chitosan derivatives

Compound	Organic solvent			2% Acetic acid	Aq. methacrylic acid (%)		
	DMSO	DMF	NMP		2	70	100
Chitosan	− − −	− − −	− − −	+ + +	+ + +	+ + +	− − −
7a	− − −	− − −	− − −	+ + +	+ + +	+ + +	− − −
7b	− − −	− − −	− − −	+ + +	+ + +	+ + +	− − −
7c	+ + −	+ − −	+ − −	+ + +	− − −	+ + +	− − −
8a	+ − −	+ − −	+ − −	+ + +	+ + +	+ + +	− − −
8b	+ − −	+ − −	+ − −	+ + +	+ − −	+ + −	− − −
9a	− − −	− − −	− − −	+ + +	+ + +	+ + +	− − −
9b	+ + −	− − −	+ − −	+ − −	+ − −	+ + +	− − −
10	+ + −	− − −	− − −	+ − −	− − −	+ + −	− − −

DMSO, dimethyl sulfoxide; DMF, dimethyl formamide; NMP, *N*-methyl pyrrolidinone. Sample (10 mg)/solvent (1 ml). + + +, soluble; + + −, swelling; + − −, partly insoluble; − − −, insoluble.

mass was hardly soluble in usual solvents such as ethanol, methanol, acetone, toluene, ethyl acetate, and dichloromethane. Therefore, aldehyde **3** was not used for the reaction with chitosan in this study.

In the previous report, aldehyde **4** was obtained by introduction of the methacryloyl function to vanillin using methacryloyl chloride (Brown & Racois, 1972; Imoto, Maeda, & Ouchi, 1978). However, it is often stated that alkanoyl chloride is not suitable for use in industrial applications. Therefore, in this study, we employed an industrially suitable method, esterification using DCC and methacrylic acid under mild conditions, to give aldehyde **4** with a yield of 88%. This esterification using DCC and organic acid was applied to the synthesis of **5** and **6**. Thin layer chromatography was used in the purification of diester **5**, and it was difficult to separate the diester from the corresponding monoesters. For this reason, aldehyde **5** was not used in the *N*-selective alkylation of chitosan.

3.2. UV-curable chitosan derivatives

Some photosensitive chtiosan derivatives have been prepared by using azide functional groups (Ono et al., 2000) or allyl functional groups (Tokura, Uraki, Ohmiya, Tsutsumi, & Sashiwa, 1990). However, these derivatives have not been applied to metal chelating techniques.

The reductive *N*-alkylation method is useful for introducing functional side chains to chitosan under mild condi-

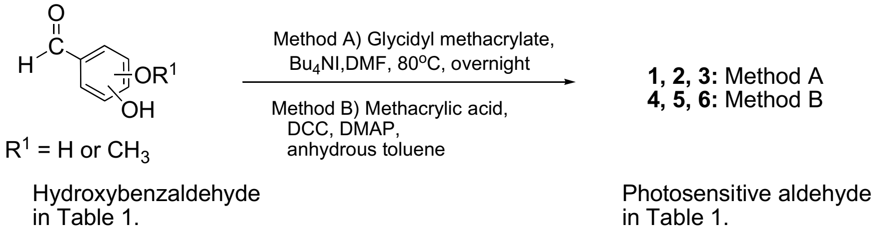


Fig. 1. Preparation of photosensitive aldehydes.

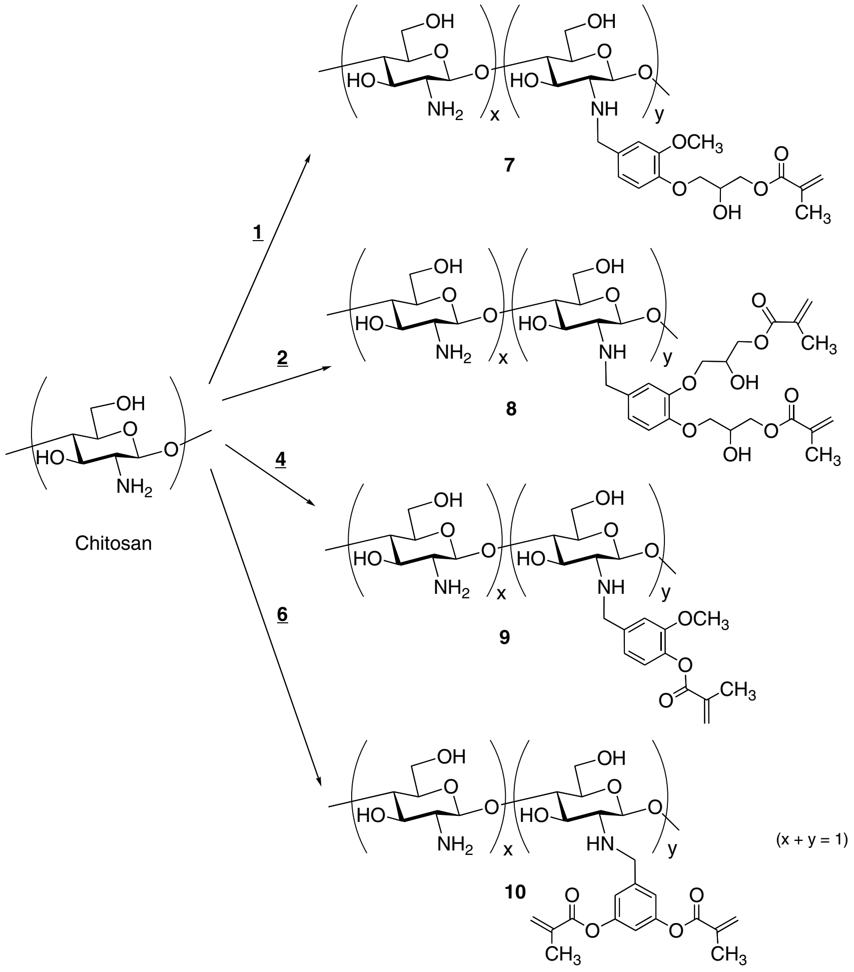


Fig. 2. Preparation of UV-curable chitosan derivatives.

tions – at pH 4–5 and room temperature (Muzzarelli, Tanfani, Emanuelli, & Mariotti, 1982). In some cases, chitosan having *N*-alkyl residues exhibits a higher metal chelating ability than the original chitosan (Delben, Muzzarelli, & Terbojevich, 1989).

Reaction conditions and yields of reductive *N*-alkylation products are summarized in Table 2. In preliminary experiments, $NaBH_4$ was used for the reduction of the Schiff's base to chitosan derivative **7**, however, a part of the ester group in the side chain (the 2-hydroxy-3-methacryloyloxypropoxy group) was hydrolyzed by addition of $NaBH_4$ (data not shown). Therefore, to prepare chitosan derivatives **7** and **8**, $NaBH_3CN$ was used instead of $NaBH_4$. In contrast, reductive *N*-alkylation of chitosan with aldehydes **4** and **6** was accomplished by using $NaBH_4$ to prepare compounds **9** and **10**. In fact, this functional group, the methacryloyloxy group, was able to withstand high pH conditions when $NaBH_4$ was used as a reducing agent.

3.3. Solubility of UV-curable chitosan derivatives

The solvent solubilities of UV-curable chitosan derivatives are summarized in Table 3. In the cases of compounds **7** and **9**, the solubility of chitosan derivatives in organic solvents, such as DMSO, DMF, and NMP increased with an increase in the degree of substitution (DS) of each UV-curable side chain. Except for **9b** and **10**, all the compounds studied here were soluble in 2% aqueous acetic acid. However, in 2% aqueous methacrylic acid, the solubility of these compounds decreased with an increase in the degree of substitution of the side chain. On the other hand, all chitosan derivatives showed good miscibility with methacrylic acid of higher concentration (70%). Because a methacrylic acid solution of high concentration can be used as a UV-reactive solvent, good solubility of UV-curable chitosan derivatives in 70% aqueous methacrylic acid is advantageous.

Compounds **7c** and **10** were not soluble in 2% aqueous methacrylic acid. None of the compounds tested were sol-

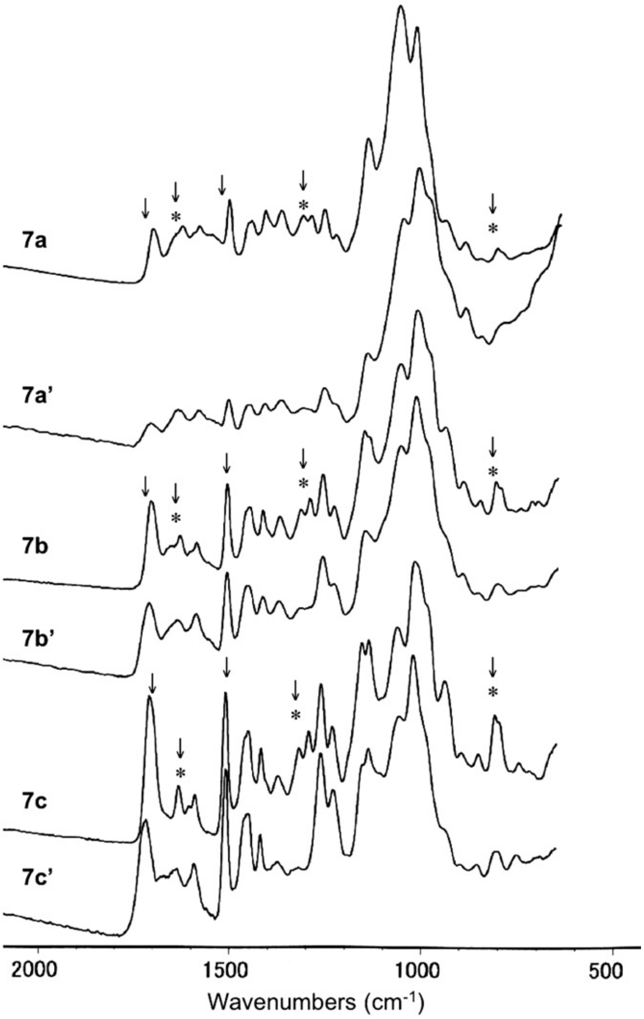


Fig. 3. FT/IR spectra of untreated films **7a**, **b**, and **c** and those of UV-treated films **7a′**, **b′**, and **c′**. Peaks corresponding to the side chains are indicated by arrows. Arrows with an asterisk indicate that the peaks disappeared after UV irradiation. (ATR; ZnSe crystal).

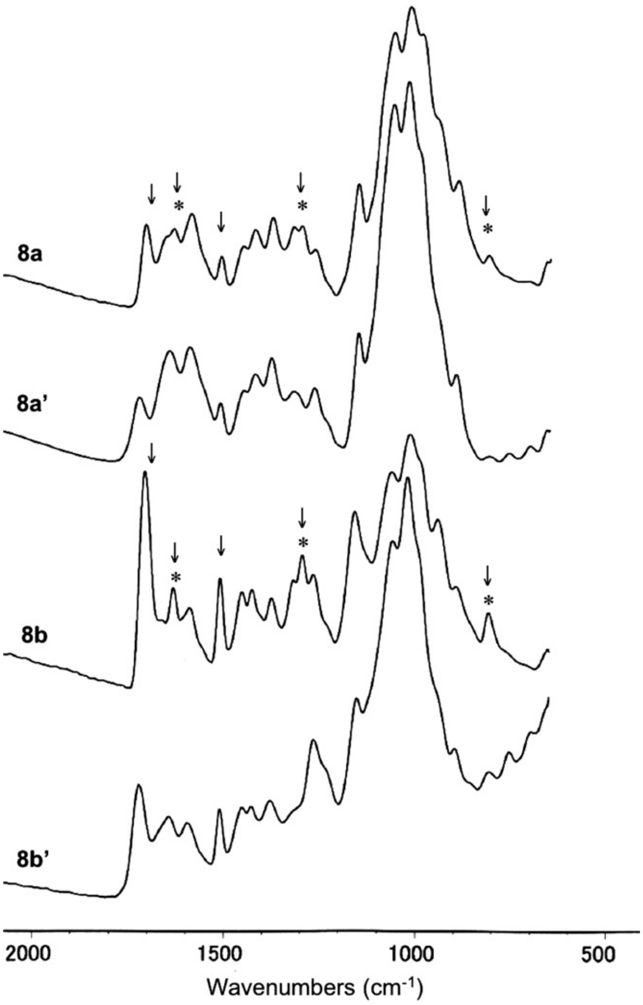


Fig. 4. FT/IR spectra of untreated films **8a** and **b** and those of UV-treated films **8a′** and **b′**. Peaks corresponding to the side chains are indicated by arrows. Arrows with an asterisk indicate that the peaks disappeared after UV irradiation. (ATR; ZnSe crystal).

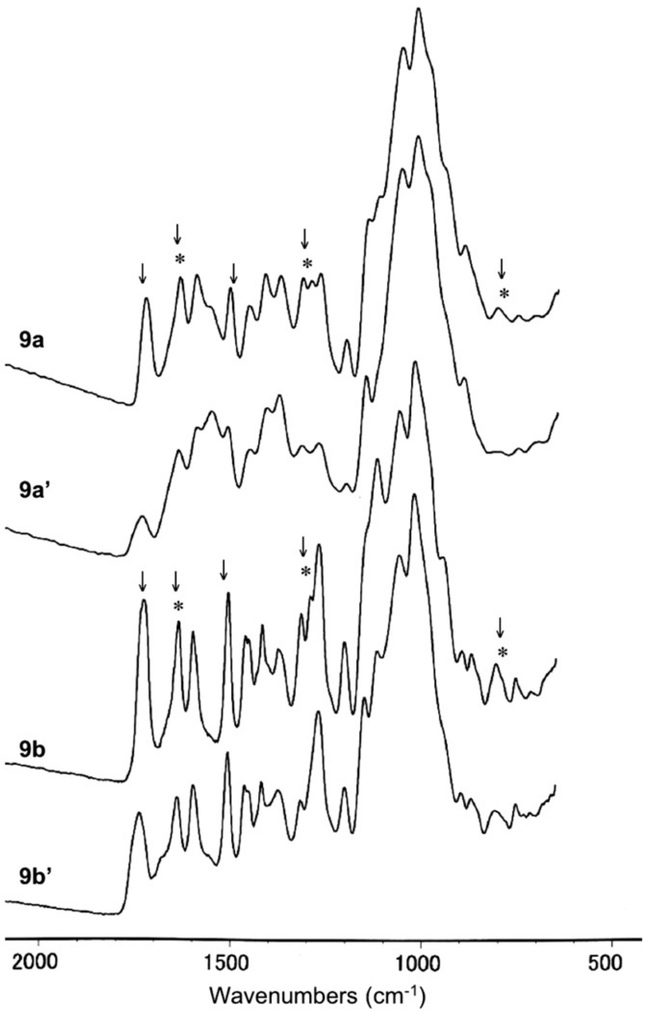


Fig. 5. FT/IR spectra of untreated film **9a** and **b** and those of UV-treated films **9a**′ and **b**′. Peaks corresponding to the side chains are indicated by arrows. Arrows with an asterisk indicate that the peaks disappeared after UV irradiation. (ATR; ZnSe crystal).

uble in 100% methacrylic acid. However, compounds **7a**, **b**, and **c** swelled in 90% aqueous methacrylic acid (data not shown). These results suggest that the presence of water is one of the important factors for the solubility of UV-curable chitosan derivatives in methacrylic acid.

3.4. UV-cured derivative films

After UV exposure, the sample solutions (UV-curable chitosan derivative/2% AcOH/MeOH mixture) became increasingly viscous and then hardened into gels. These gels did not redissolve in 2% aqueous acetic acid. After drying, UV-treated dried films were flexible and strong except the one prepared from **7c**. All the films hardly swelled at all, even when they were immersed in aqueous hydrochloric acid at pH 1.1. Exceptionally, the film made from chitosan derivative **7c**, which has a high degree of substitution, was not flexible. The high degree of substitution of *N*-alkyl side chains in compound **7** was probably responsible for the low flexibility (Figs. 1 and 2).

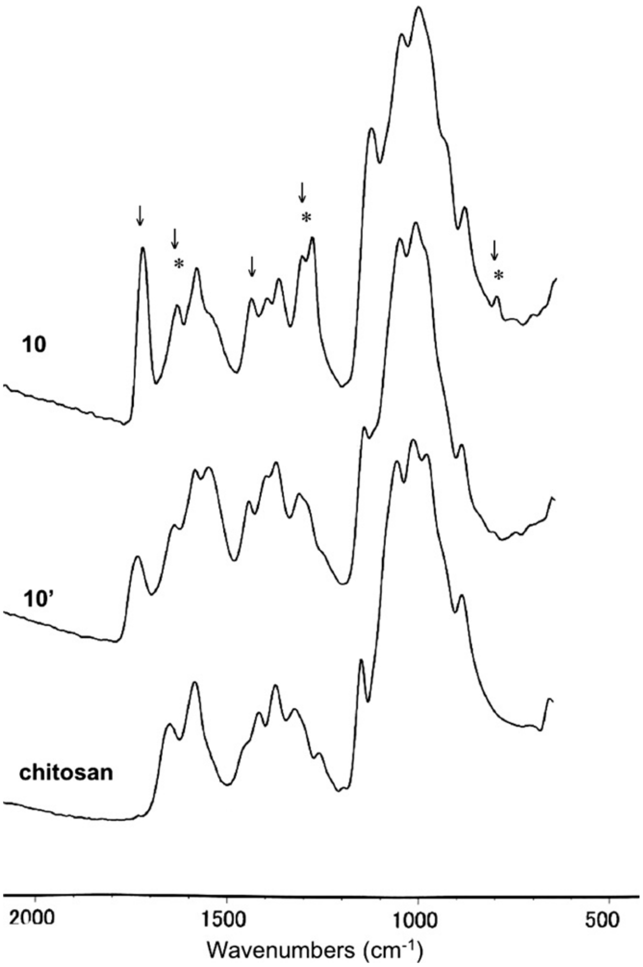


Fig. 6. FT/IR spectra of chitosan, untreated compound **10** film and its UV-treated film **10**′. Peaks corresponding to the side chains are indicated by arrows. Arrows with an asterisk indicate that the peaks disappeared after UV irradiation. (ATR; ZnSe crystal).

FT/IR spectra of film samples of **7**, **8**, **9**, and **10** are shown in Figs. 3–6. These IR spectra were measured by ATR methods using ZnSe crystal. The arrows indicate the peaks corresponding to the side chain. – IR: 1710–1720 (C=O), 1640 (C=C), 1510 (aromatic), 1300–1320, 814 (C=C) cm^{-1}. Arrows with an asterisk show the peaks

Table 4
Palladium adsorption on film samples

Compound	Amount of palladium adsorbed (mg/film)	
	pH 1.1	pH 5.3
Chitosan	nd[a]	0.28
7a	0.28	0.18
7b	0.30	0.06
7c	0.30	0.01
8a	0.46	0.25
8b	0.32	0.09
9a	0.28	0.31
9b	0.30	0.05
10	0.46	0.28

[a] The chitosan film dissolved under this condition.

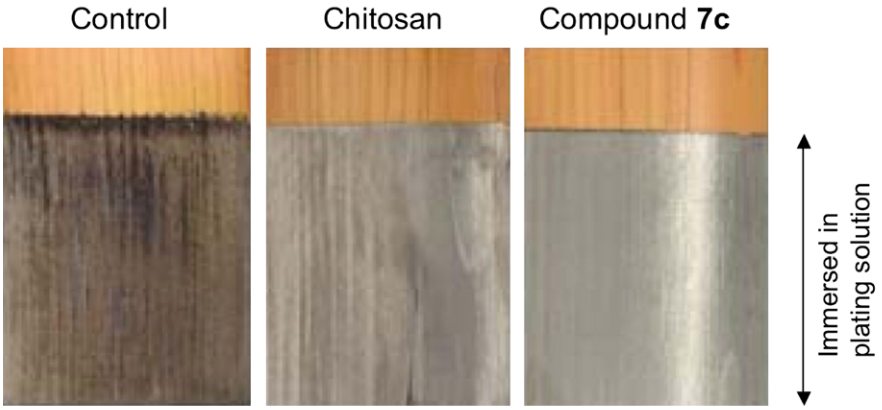


Fig. 7. Electroless nickel-plating on wood (*Japanese cypress*) coated by chitosan and UV-curable chitosan compound **7c**.

that disappeared after UV irradiation. – IR: 1640, 1300–1320, 814 cm^{-1}. Comparison of IR spectra of **7a**, **b**, and **c** in Fig. 3 shows that the intensities of these specific peaks derived from the side chains increased in proportion to the amount of the corresponding aldehyde used for the reductive *N*-alkylation reaction. Similar phenomena were also observed in the cases of IR spectra of chitosan derivatives **8** and **9**, which are shown in Figs. 4 and 5. This tendency is consistent with the fact that the degree of substitution of the side chain group is dependent on the proportion of each aldehyde shown in Table 2. This tendency was also confirmed by ^1H NMR analysis.

3.5. Palladium adsorption

As shown in Table 4, the UV-treated chitosan derivative films exhibited good palladium adsorption behavior as well as the previously reported chitosan derivative films (Omura et al., 2003; Sashiwa et al., 2002). At pH 5.3, the amount of palladium adsorbed on the UV-treated films prepared from the derivatives with a low degree of substitution was as much as that on the chitosan film. Comparison of **7a**, **b**, and **c** reveals that the amount of palladium adsorbed decreased with an increase in the degree of substitution of chitosan derivative **7**. Similar phenomena were observed in the cases of the other chitosan derivatives reported in this paper. This is explained by the difficulty in swelling of sample films in a solution of $PdCl_2$, because the chitosan derivatives having a high degree of substitution have much more crosslinking between the chitosan main chains after UV-curing. Therefore, crosslinking caused by UV-curing gave chitosan an acid resistant property.

Although, the amount of palladium adsorbed at pH 5.3 on UV-treated films made from chitosan derivatives with a low degree of substitution was comparable to that on the original chitosan film, a large amount of palladium was adsorbed on all UV-treated films at pH 1.1. That is to say, at pH 1.1, palladium adsorption behavior did not depend on the degree of substitution. On the other hand, chitosan derivatives having a low degree of substitution and many crosslinkage sites, such as compounds **8** and **10**, have a tendency to adsorb much more palladium than the other derivatives **7** and **9**.

3.6. Electroless plating

The results of electroless nickel-plating on *Japanese cypress* are shown in Fig. 7. On the control piece, nickel was deposited inconsistently. The chitosan-treated test piece showed partial metal deposition. Uniform metal deposition was observed on the test piece treated with the UV-curable chitosan derivative **7c**. The homogeneous metallic thin film formed looked good and exhibited excellent adhesion to the wood surface.

Thus, the UV-curable chitosan derivative was found to be a very useful material for immobilizing palladium catalyst at a low pH, which is suitable for electroless plating in manufacturing. We expect that the UV-curable chitosan derivatives have the potential to be applied to a variety of fields.

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