

# SYNTHESIS OF NOVEL UV-CURABLE CHITOSAN DERIVATIVES AND THEIR PALLADIUM ADSORPTION PROPERTY

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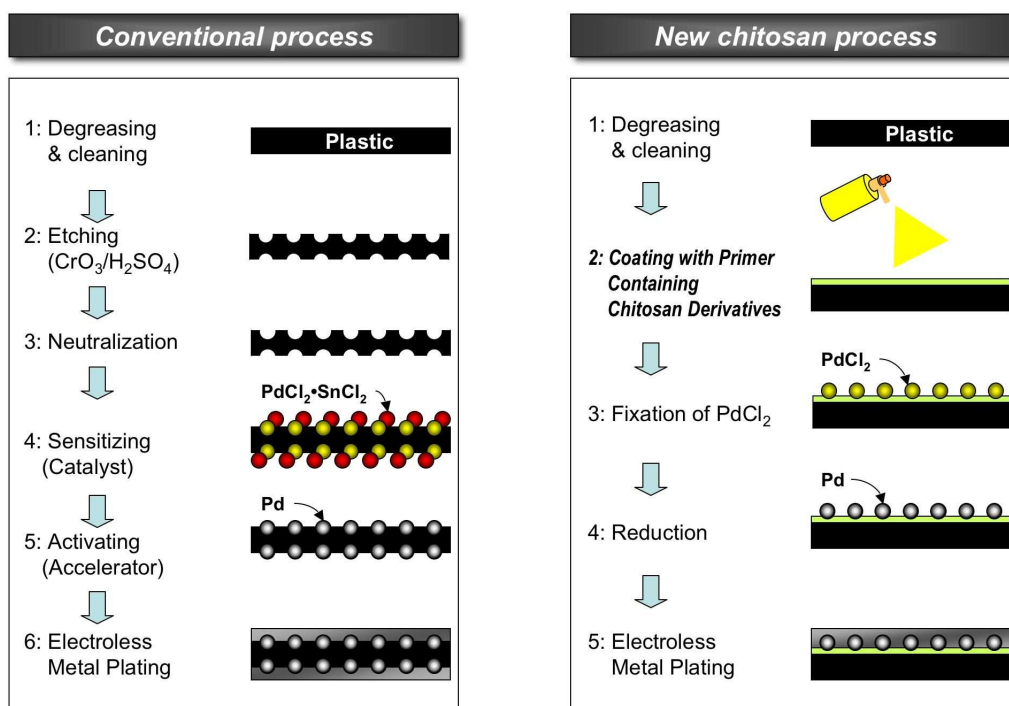
## Abstract

Novel chitosan derivatives with UV-curable functional groups, such as 3-methoxy-4-(2-hydroxy-3-methacryloyloxypropoxy)benzyl group and 3-methoxy-4-methacryloyloxybenzyl 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 with starting chitosan, UV-curable chitosan derivatives showed better solubility in organic solvents, such as DMSO and 70% methacrylic acid. After UV irradiation for 20 seconds under a high-pressure mercury lamp, an acidic solution of these UV-curable chitosan derivatives was transformed to gel in the presence of photoinitiator. Their dried films exhibited good palladium (II) adsorption.

## Introduction

We published the application of chitosan to electroless metal plating [1] because of its excellent adsorption of palladium (II) and other metals [2]. Chitosan-supported palladium plays an important role as a catalyst in the electroless metal plating on non-conductive substance such as wood, plastic and paper. In the usual method, etching treatment of non-conductive substances with a Cr (III)/H<sub>2</sub>SO<sub>4</sub> solution is necessary to attach a metal catalyst, hence, causing environmental pollution (Figure 1). Using the metal absorption ability of chitosan as an alternative method to the Cr (VI) etching treatment, we had established the electroless metal plating process by employing a special paint containing chitosan. However, chitosan itself does not have good affinity for synthetic resins and is not soluble in usual organic solvents and neutral water. Therefore, the chitosan-containing paint did not show enough stability. Furthermore, the paint hardening process requires continuous heating, over thirty minutes, due to the paint having a thermosetting resin property. It is thus necessary to shorten the curing time to improve productivity. In order to find a solution to these problems, we have modified chitosan with hydrophobic side chains, which contain a UV-curable functional group.

Characterization of these derivatives, and palladium adsorption properties, are evaluated in this report.



**Figure 1 :** Electroless metal plating process

## Material and Methods

### Materials

Chitosan (SK-10 · DAC-100; degree of deacetylation, 100%; viscosity 8 cps (1.0% in 1% acetic acid, 20 °C);  $M_w$  86000) was kindly supplied by Koyo Chemical Co., Ltd. and used as received. Photo-initiator, Irgacure<sup>®</sup> 1000, was purchased from Ciba Specialty Chemicals K.K.

### Instrumentation

Derivatives were identified and characterized by <sup>1</sup>H-NMR spectra recorded on a JNM-ECP500 spectrometer 'JEOL' at 500MHz and Fourier transform infrared (FT/IR) spectra obtained using an AVATAR 360 type spectrometer-'Nicolet'. The degree of substitution was calculated from the C / N ratio evaluated by the elemental analysis.

UV irradiation was performed with a UV irradiator (UE-0151-326-01) using a high-pressure mercury lamp (H015-L312 (1.0 kW) 'Eye Graphics Co., Ltd.'). The irradiation time was 20 seconds at a distance of 15 cm from the samples. ICP analysis of palladium was carried out using an ICP optical emission spectrophotometer (SPS7700 'SII NanoTechnology Inc.').

### Preparation of Photosensitive Aldehydes

#### *3-Methoxy-4-(2-hydroxy-3-methacryloyloxypropoxy)benzaldehyde (1).*

The aldehyde **1** was prepared according to the previously described method [3].

A mixture of vanillin (16.74 g, 110 mmol), glycidylmethacrylate (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 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. To the resultant amber syrup, hot toluene was added, and the mixture 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): IR(KBr); 1718, 1672, 1635, 1587, 1512  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 1.94 (3H, s,  $-\text{CH}_3$ ), 3.18 (1H, br s,  $-\text{OH}$ ), 3.90 (3H, s,  $-\text{OCH}_3$ ), 4.10 ~ 4.38 (5H, m,  $-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), 5.60 and 6.14 (each 1H, m,  $-\text{C}=\text{CH}_2$ ), 6.98 and 7.42 (1H, 2H, d, t, aromatic- $H$ ), 9.85 (1H, s,  $\text{CH}=\text{O}$ )

### 3-Methoxy-4-methacryloyloxybenzaldehyde (**2**)

Vanillin (5.0 g, 33 mmol), 4-dimethylaminopyridine (1.2 g, 9.9 mmol) and  $N,N'$ -dicyclohexylcarbodiimide (12 g, 56 mmol) were dried over the  $\text{P}_2\text{O}_5$  for 2 h *in vacuo*. Anhydrous toluene (130 ml) and methacrylic acid (2.8 ml, 33 mmol) were then added to the mixture and stirred at 0 °C for 3h under an atmosphere of 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 **2** as a pale-yellow crystal (6.4 g, 88% yield). IR: 1734, 1693, 1633, 1597, 1506  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 2.1 (3H, s,  $-\text{CH}_3$ ), 3.9 (3H, s,  $-\text{OCH}_3$ ), 5.58 and 6.4 (each 1H, m,  $-\text{C}=\text{CH}_2$ ), 7.2 and 7.6 (3H, m, aromatic- $H$ ), 9.9 (1H, s,  $\text{CH}=\text{O}$ )

**Table 1.** Preparation of Photosensitive Aldehydes

Starting Material	Reagents	Catalysts	Solvents	Products
		$[\text{CH}_3(\text{CH}_2)_3]_4\text{NI}$	DMF	<b>1</b> (43% yield)
		DCC / DMAP	Toluene	<b>2</b> (88% yield)

### Reductive N-Alkylation of Chitosan

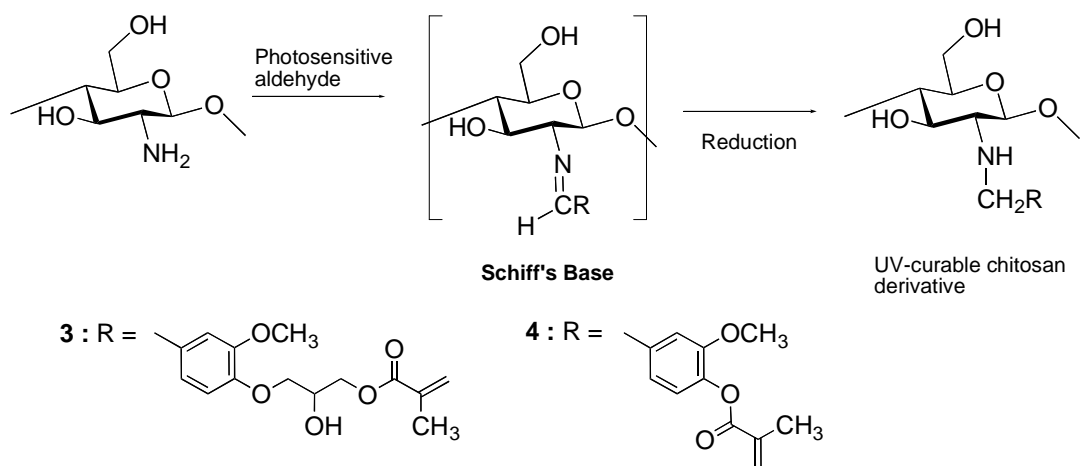
#### *N*-[3-Methoxy-4-(2-hydroxy-3-methacryloyloxypropoxy)benzyl]chitosan (**3**).

Aldehyde **1** (588 mg, 2 mmol) in THF (20 ml) was added to a stirred solution of chitosan (800 mg, 5 mmol as  $-\text{NH}_2$  group) in a mixture of 0.2 M McIlvaine buffer solution (pH 4.5, 60 ml) and methanol (40 ml). Sodium cyanoborohydride (265 mg, 4 mmol)/water (10 ml) solution was added dropwise at 0 °C. The mixture was stirred at 0 °C for 1 h and then at 25 °C overnight. After 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 compound obtained was lyophilized to produce compound **3b**. As shown in Table 2, three kinds of compound **3**'s having different degrees of substitution were prepared (**3a**~**3c**) by changing the molar ratio of aldehyde **1** to  $-\text{NH}_2$  groups of chitosan: IR (KBr): 1710, 1640, 1516, 1320, 1300, 814  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (2% $\text{CD}_3\text{COOD}/\text{D}_2\text{O}$ )  $\delta$ : 1.93 ( $\text{CH}_3$ ), 3.23 (H-2 of GlcN), 3.93 ( $\text{OCH}_3$ ), 5.75 and 6.17 ( $=\text{CH}_2$ ), 7.13~7.20 (aromatic- $H$ ). **3a**: Found: C, 48.81; H, 6.77; N, 5.97 (DS=0.24). **3b**: Found: C, 48.91; H, 6.70; N, 4.77 (DS=0.40). **3c**: Found: C, 54.77; H, 6.64; N, 3.45 (DS=0.84).

#### *N*-(3-Methoxy-4-methacryloyloxybenzyl)chitosan (**4**).

A methanol (50 ml) solution of aldehyde **2** (377 mg, 1.7 mmol) was added to a stirred solution of chitosan (1600 mg, 10 mmol as  $-\text{NH}_2$  group) in a mixture of 0.2 M McIlvaine 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 and cooled to 0 °C, then sodium borohydride (375 mg,

10 mmol) in 10 ml of 0.1% NaOH solution was added dropwise. After stirring at 0 °C for 1h 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 yield compound **4a**. As shown in Table 2, two kinds of compound **4** having different degrees of substitution were prepared (**4a** and **4b**) by changing the molar ratio of aldehyde **2** to -NH<sub>2</sub> groups of chitosan. IR (KBr): 1738, 1640, 1601, 1512, 810 cm<sup>-1</sup>. <sup>1</sup>H-NMR (2 % CD<sub>3</sub>COOD/D<sub>2</sub>O) δ: 1.90 (CH<sub>3</sub>), 3.16 (H-2 of GlcN), 5.95 and 6.39 (-C=CH<sub>2</sub>), 6.9~7.3 (aromatic-H). **4a**: Found: C, 48.18; H, 6.93; N, 6.86 (DS=0.18). **4b**: Found: C, 54.69; H, 6.03; N, 4.55 (DS=0.67).



**Figure 2 :** Structure of UV-curable chitosan derivatives.

#### UV Irradiation and Film Formation of UV-Curable Chitosan Derivatives

A chitosan derivative (20 mg) in 2% aqueous acetic acid (1 ml), methanol (1 ml), and Irgacure<sup>®</sup> 1000 (5 mg) were mixed and cast on a plastic dish. The mixed solution was transformed to a hardened gel by UV irradiation for 20 seconds. After drying at 60 °C for 3 h, a UV cured film was obtained, washed several times with 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 absorption test.

#### Measurement of Palladium Adsorption

According to the previous methods [1], a Pd(II) solution (150 ppm as palladium ion) of pH 1.1 was obtained from PdCl<sub>2</sub> (0.25 g), H<sub>2</sub>O (990 ml), and conc. HCl (10 ml). A pH 5.3 solution was obtained from PdCl<sub>2</sub> (0.25 g) and 1% aqueous NaCl (1000 ml).

The film sample was immersed in 10 ml of palladium chloride solution at 30 °C and subjected to shaking. After 3 minutes, the film was removed and the palladium concentration of the residual solution was measured by ICP analysis. The amount of adsorbed palladium on the film was estimated from the decrease in the palladium concentration.

## **Results and Discussion**

#### Photosensitive Aldehydes

Perfect purification of each aldehyde was difficult because of their high reactivity. Thus all aldehydes included small amount of impurities. Without further purification, the aldehydes were used in the *N*-selective introduction of the chitosan side chains.

Aldehyde **1** can be prepared from vanillin and it seems to be the most suitable, because it can be purified without column chromatography, and a low cost is incurred in synthesizing it.

In the previous report, introduction of the methacryloyl function to vanillin was performed by using methacryloyl chloride to get aldehyde **2** [4], [5]. However, it is often said that acidic chloride is not suitable to 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 **2** in 88% yield.

### UV-Curable Chitosan Derivatives

Reaction conditions and yields of reductive *N*-alkylation products are summarized in Table 2. In preliminary experiments, NaBH<sub>4</sub> was used for the reduction of the Schiff's base to the chitosan derivative **3**, but a part of the ester group (the 2-hydroxy-3-methacryloyloxypropoxy group) in the side chain was hydrolyzed by addition of NaBH<sub>4</sub> (data not shown). Therefore, NaBH<sub>3</sub>CN was used instead of NaBH<sub>4</sub>. On the other hand, reductive *N*-alkylation of chitosan with aldehyde **2** was accomplished by using NaBH<sub>4</sub>. The functional group (the methacryloyloxy group) was stable in high pH conditions.

**Table 2.** Agents for Reductive *N*-Alkylation of Chitosan and Palladium Adsorption on UV-Cured Film Samples

Product	Chitosan mg/mmol <sup>a</sup>	Aldehyde		NaBH <sub>3</sub> CN mmol	Yield g	DS <sup>d</sup>	Amount of Pd adsorbed (mg/film)	
		mmol	Molar equiv. <sup>b</sup>				pH 1.1	pH 5.3
<b>Chitosan</b>							nd <sup>e</sup>	0.28
<b>3a</b>	800 / 5	<b>1</b>	1.0	0.20	2	0.81	0.24	0.28
<b>3b</b>	800 / 5	<b>1</b>	2.0	0.40	4	1.05	0.40	0.30
<b>3c</b>	800 / 5	<b>1</b>	4.0	0.80	8	1.52	0.84	0.30
<b>4a</b>	1600 / 10	<b>2</b>	1.7	0.17	10 <sup>c</sup>	1.91	0.18	0.28
<b>4b</b>	1600 / 10	<b>2</b>	6.8	0.68	40 <sup>c</sup>	2.52	0.67	0.30

a, mmol as -NH<sub>2</sub> group. b, Molar equivalent relative to GlcN unit of chitosan. c, NaBH<sub>4</sub>. d, degree of *N*-substitution by reductive *N*-alkylation. e, The chitosan film dissolved in this condition.

### Solubility of UV-Curable Chitosan Derivatives

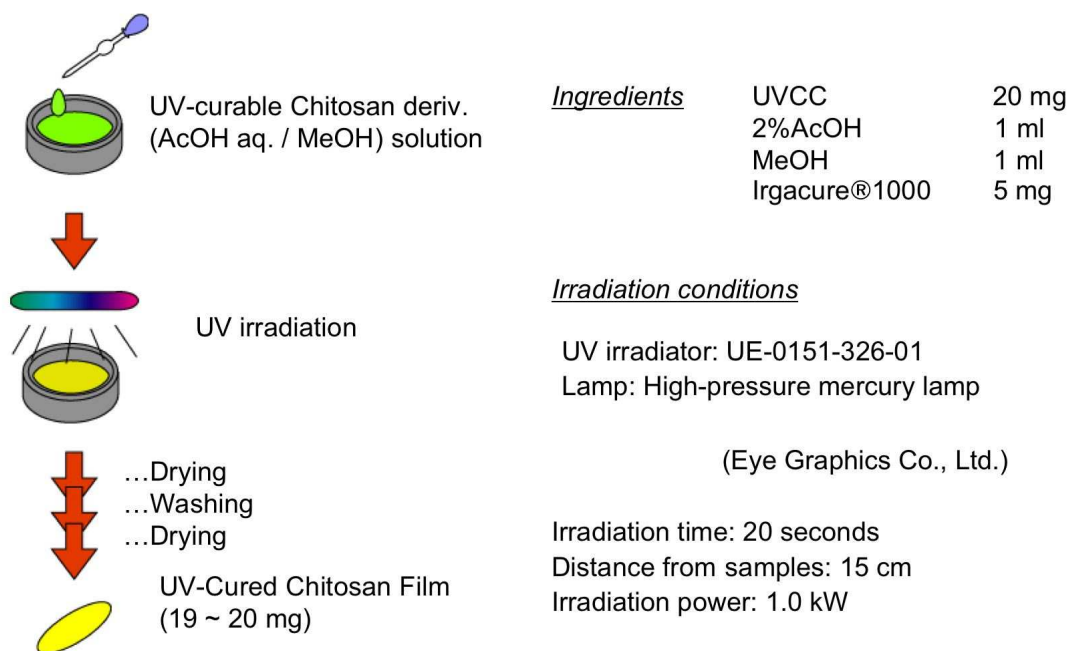
The solvent solubilities of UV-curable chitosan derivatives are summarized in Table 3. In the case of **3**, the solubility of chitosan derivatives in organic solvents, such as DMSO, DMF and NMP, increased with an increase in the DS of each UV-curable side chain. With the exception of **4b**, all of these compounds were soluble in a 2% acetic acid solution. But in a 2% methacrylic acid solution, the solubility of these compounds decreased as an increase in the DS of the side chain occurred. Moreover, all chitosan derivatives showed good miscibility to a methacrylic acid solution of the 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 a 70% methacrylic acid solution is advantageous.

**Table 3.** Solubility of UV-Curable Chitosan Derivatives

Com- pound	Organic solvents			2% aq	aq Methacrylic acid (%)		
	DMSO	DMF	NMP	Acetic acid	2	70	100
Chitosan	---	---	---	+++	+++	+++	---
<b>3a</b>	---	---	---	+++	+++	+++	---
<b>3b</b>	---	---	---	+++	+++	+++	---
<b>3c</b>	++-	+-	+-	+++	---	+++	---
<b>4a</b>	---	---	---	+++	+++	+++	---
<b>4b</b>	++-	---	+-	+-	+-	+++	---

DMSO: dimethyl sulfoxide; DMF: dimethyl formamide; NMP: *N*-methyl pyrrolidinone. Sample (10 mg)/ solvent (1 ml). +++: Soluble; ++-: highly viscous; +-: partly insoluble; ---: insoluble.

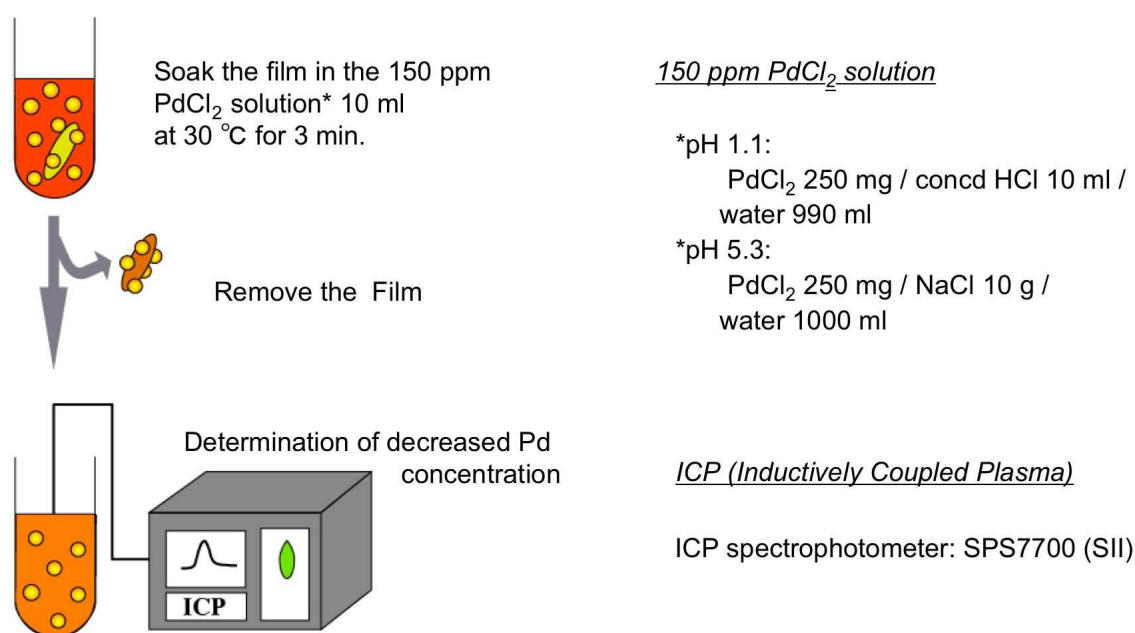
## UV-Cured Films



**Figure 3 :** Film formation and UV irradiation conditions

After UV exposure, the sample solution (UV-curable chitosan derivative/2% AcOH/MeOH) became increasingly viscous and then became a hardened gel. The resultant gels did not re-dissolve in 2% acetic acid solution. After drying, UV-treated films were flexible and strong. The films hardly swelled even when immersed in a hydrochloric acid solution at pH 1.1. Furthermore, the film made from chitosan derivative **3c**, which had a high degree of substitution, was not flexible.

## Palladium Adsorption



**Figure 4 :** Estimation of adsorbed palladium by ICP analysis.

As shown in Table 2, UV exposed UV-curable chitosan derivative film showed good palladium adsorption behavior at pH 1.1 and 5.3 as well as the previously reported chitosan derivatives [6]. At

pH 5.3, the amount of palladium adsorbed on the UV-treated films, prepared from the low DS derivatives was as much as that on chitosan film. Comparison of **3a**, **3b** and **3c** revealed that the amount of palladium adsorbed decreased with an increase in the DS of chitosan derivative **3**. A similar phenomenon was observed in cases of **4a** and **4b**. These phenomena were explained by the hardness in swelling of sample films in a solution of PdCl<sub>2</sub> due to the high level of crosslinking between the chitosan main chains after UV-curing in the high DS chitosan derivatives. Therefore, crosslinking caused by UV-curing gave chitosan an increased resistance to acidic conditions.

Thus, the UV-curable chitosan derivative was found to be a very useful material to immobilize palladium catalysts at a low pH, which is suitable for electroless plating in industrial application. We expect that the UV-curable chitosan derivative will be a potential material to be applied to a variety of fields.

### Acknowledgements

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### References

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