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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.

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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, $-\mathrm{C}H_3$), 3.18 (1H, br, $-\mathrm{O}H$), 3.90 (3H, s, $-\mathrm{OC}H_3$), 4.15–4.36 (5H, each m, $-\mathrm{C}H_2-\mathrm{C}H-\mathrm{C}H_2-$), 5.60 and 6.14 (each 1H, s, s, $-\mathrm{C}{=}\mathrm{C}H_2$), 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, $\mathrm{C}H{=}\mathrm{O}$); 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, $-\mathrm{C}H_3$), 3.6 and 3.8 (each 1H, each m, O*H*), 4.1–4.37 (10H, m, $-\mathrm{C}H_2-\mathrm{C}H-\mathrm{C}H_2-$), 5.6 and 6.1 (each 2H, m, $-\mathrm{C}{=}\mathrm{C}H_2$), 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, $\mathrm{C}H{=}\mathrm{O}$); 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, $-\mathrm{C}H_3$), 2.96 (2H, m, O*H*), 4.09, 4.31–4.37 (10H, m, $-\mathrm{C}H_2-\mathrm{C}H-\mathrm{C}H_2-$), 5.62, and 6.16 (each 2H, s, s, $-\mathrm{C}{=}\mathrm{C}H_2$), 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, $\mathrm{C}H{=}\mathrm{O}$); 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

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