Chemical Modification of Chitosan 12[1]: Synthesis of Organo-soluble Chitosan Derivatives toward Palladium Absorbent for Chemical Plating

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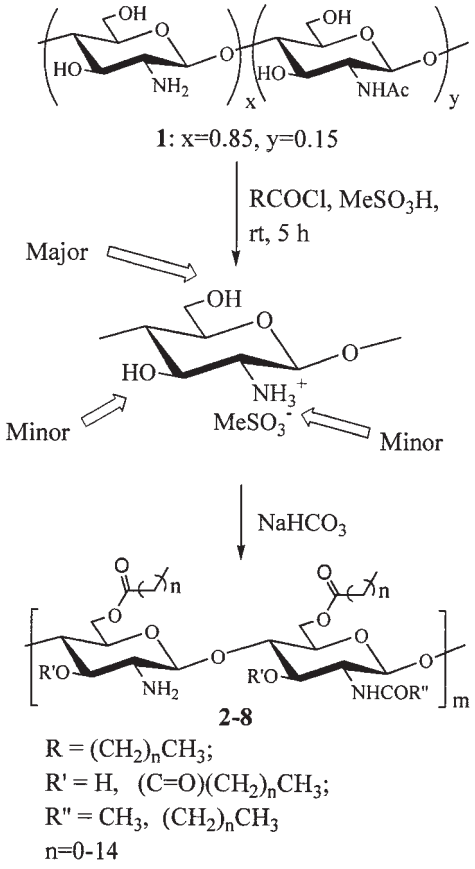
Toward the electromagnetic wave shielding materials for the electronic equipment, organo-soluble, palladium chelating, and biodegradable chitosan derivatives were successfully prepared.

The purpose of this study is to prepare organo-soluble chitosan derivatives as coating materials in order to give electromagnetic radiation shielding function by chemical plating to light-weight electric appliances such as mobile phones and portable computers. In conventional method of chemical plating, the body of the appliance made of plastic is etched to adsorb palladium (Pd) ion. After that, it is plated with layers of copper to conduct electricity, and nickel to prevent corrosion of copper. Etching with chromium, however, is not suitable for earth environment owing to its toxicity. An alternative way is to utilize a binder, which is possible to adhere on plastic surface and adsorb Pd ion. Chitosan is a polymer of choice, because the amino group can adsorb Pd ion. Moreover chemical plating on the glass surface could be achieved by coating with chitosan.[2] Chitosan itself, however, is hydrophilic, while plastics used are hydrophobic. Therefore, chemical modification of chitosan is necessary to improve its adhesion to the plastics as well as its organo-solubility so as to be sprayed on the surface of the plastics. Herein, we report the synthesis of organo-soluble and palladium chelating acylchitosans toward the electromagnetic shielding materials for the electronic equipment.

Chitosan (SK-10) derived from crab shell was purchased from Koyo Chemical Co., Ltd. The Mn and Mw of chitosan and its derivatives were determined by GPC using hexafluoro-2-propanol (HFP) as eluent and poly(methyl methacrylate) as standard (column, Tosoh TSK-gel super H-RC and HM-N; column temp., 40 °C; flow rate, 0.2 mL/min; detector, RI). ^{1}H and ^{13}C NMR were taken on a JEOL A-500 NMR spectrometer. Typical procedure is as follows. Chitosan (1 g) was dissolved in $MeSO_3H$ (20 mL) at room temp for 1 h. To a solution was added acyl chloride (3 equiv/repeating unit of chitosan). After stirring at room temp for 5 h, ca. 30 g of ice was added to stop the reaction. The acidic mixture was dialyzed for 1 day to remove most of acid, followed by neutralizing remained acid and ammonium salt in chitosan with $NaHCO_3$. Finally the mixture was dialyzed again for more than 3 days and lyophilized. The degree of substitution (DS) was estimated by ^{1}H NMR in 0.5 M DCl/D_2O for **2** and **3** from the peak area at δ 0.90 (CH_3) against 3.2–4.0 (H-2–6 of chitosan). The DS for **4–8** was also estimated by ^{1}H NMR in $CDCl_3$ at δ 0.90 (CH_3) against 2.7–5.2 (H-1–6 of chitosan). DS of NH_2 for **4–8** was evaluated at δ 2.7–2.8 (H-2 of GlcN) against 3.2–5.2 (H-1–6 of chitosan except for H-2 of GlcN).[3]



Scheme 1.

Although the selective *O*-acylation of chitosan in $MeSO_3H$ owing to the salt formation of primary amino group in chitosan with $MeSO_3H$ was partly reported,[4] the detailed chemical structure or the protecting effect of amino group was unclear yet. While, the preparation of *O*, *O*′-decanoylchitosan[5] was also reported through protecting *N*-phthaloylchitosan[6] as an intermediate. This method, however, needs several steps for the protection and deprotection of *N*-phthaloyl groups. Moreover, it would be difficult to maintain ester linkage under the deprotecting conditions like hydrazine treatment. Therefore, we chose the selective *O*-acylation of chitosan with $MeSO_3H$ system (Scheme 1). Table 1 shows the chemical structures of prepared chitosan derivatives from original chitosan **1**. The protecting effect of amino group in chitosan by salt formation with $MeSO_3H$ was

Table 1. Chemical structure of chirosan derivatives

Compd.	Reagent		Yield[a]	DS			
	n	equiv.	%	NH_2	NHCOR	NHAc	OCOR
2a	0	1	60	0.82	—	0.18	0.43
2b	0	3	65	0.59	—	0.41	1.04
2c	0	5	65	0.11	—	0.89	1.67
3	2	3	65	0.55	0.32	0.13	1.64
4	4	3	67	0.79	0.16	0.05	1.28
5	6	3	70	0.70	0.20	0.10	1.28
6	8	3	72	0.73	0.22	0.05	1.61
7	10	3	75	0.31	0.60	0.09	0.98
8	14	3	66	0.22	0.68	0.10	1.24

[a]Yield was determined by weight recovery and change in FW according to the DS determined by ^{1}H NMR.

much associated with the amount of reagent in the case of **2**. The amino groups were protected 96% (0.82/0.85) at 1 equiv., 69% (0.59/0.85) at 3 equiv., and 13% (0.11/0.85) at 5 equiv. of reagent. These results indicate that the protection of amino groups was effective at a small amount of reagent, but gradually decreased with increasing the amount of acetyl chloride. The DS of acyl groups at hydroxyl groups, however, did not increase at 1 equiv. of reagent, so that organo-soluble property did not accomplish. So we selected the addition of 3 equiv. of reagent, which showed moderate protection of amino groups and produced organo-soluble derivatives. Although a part of amino groups were *N*-acylated for **3–6**, 65–93% (0.55/0.85–0.79/0.85) of amino groups were protected at 3 equiv. of reagent. In the case of **7** and **8**, protected amino groups were decreased to 26–36%, which would be caused by the ester exchange reaction from *O*-acyl to *N*-acyl groups. The position of *O*-acyl group was mainly at C-6 OH group. A part of acyl group, however, was also substituted at C-3 OH group from the ^{13}C NMR analysis. Nevertheless the reaction was carried out under the strong acidic condition with $MeSO_3H$, the moderate yield (60–75%) of product could be accomplished. Table 2 shows the molecular weights of chitosan derivatives determined by GPC. The degree of polymerization (DP) of these derivatives was much decreased from original chitosan, which was owing to the partial hydrolysis of glycoside linkage with $MeSO_3H$. The moderate molecular weight to appear polymeric property, however, could be maintained for these derivatives. The solubility and adsorption of Pd ion were shown in Table 3. Acetylchitosan **2b** was dissolved in aqueous AcOH (0.1 M) although it did not dissolve in organic solvent such as THF and $CHCl_3$. Butyrylchitosan **3** also dissolved in aq AcOH. Hexanoylchitosan **4** having moderate length of alkyl chain showed both aq. AcOH and organo-soluble property. Octanoyl **5**, decanoyl **6**, lauroyl **7**, and palmitoyl derivatives **8** dissolved in THF and $CHCl_3$ but not dissolved in aq AcOH. These results indicate that the solubility was much associated with the hydrophobic property of alkyl chain in chitosan derivatives. The adsorption ability for Pd ion was tested using organo-soluble derivatives **4–8**.[7] All of chitosan derivatives showed good adsorption property of Pd ion independent on the length of alkyl chain or slight decrease of DS of NH_2 groups. We successfully prepared organo-soluble and palladium chelating chitosan derivatives. And we expect further study for biodegradable property and practical use of these chitosan derivatives for electromagnetic radiation shielding agent to be published in the near future.

Table 2. Molecular weight of chitosan derivatives

Compd.	FW	Mn	Mw	DP	Mw/Mn
1	167	13000	44000	263	3.38
2b	222	6800	14000	63	2.06
3	281	8270	18900	67	2.29
4	306	10000	19000	62	1.90

Table 3. Solubility and Pd absorption of chitosan derivatives

Compd.	Solubility			Pd adsorbed
	aqAcOH	THF	$CHCl_3$	μg/cm^2
2b	O	X	X	—
2c	O	X	X	—
3	O	X	X	—
4	O	O	O	4.4
5	X	O	O	4.6
6	X	O	O	3.2
7	X	O	O	4.4
8	X	O	O	4.0

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References and Notes

1 a) Part 11 of this series: H. Sashiwa, Y. Shigemasa, and R. Roy, *Carbohydr. Polym.*, (2002) in press. b) Part 10: H. Sashiwa, Y. Shigemasa, and R. Roy, *Macromolecules*, **34**, 3905 (2001).
2 T. Hamaya, *Kobunshi Ronbunshu*, **47**, 649 (1990).
3 Selected data for **2b**: ^{1}H NMR (0.5 M DCl/D_2O) δ 2.0–2.1 (brm, 4.35 H, NHAc), 3.2 (s, 0.59 H, H-2 of GlcN residue), 3.3–4.3 (m, 5.41 H, H-2, 3, 4, 5, 6 of chitosan except for H-2 of GlcN); ^{13}C NMR δ 23.7, 23.9, and 25.0 (OAc and NHAc), 56.8–58.0 (C-2 of chitosan), 61.8 (C-6), 64.3 (C-6S), 73.4–74.5 (C-3), 73.3–76.6 (C-5), 79.2–81.1 (C-4), 102.5–103.1 (C-1), 175.4–176.3 (NH*C*O and O*C*O). Data for **4**: ^{1}H NMR ($CDCl_3$) δ 0.90 (s, 4.32 H, CH_3), 1.31 [s, 5.76 H, CH_2 (χ, δ)], 1.62 [s, 2.88 H, CH_2 (β)], 1.9-2.1 (brm, 0.15 H, NHAc), 2.34 [s, 2.88 H, CH_2 (α)], 2.7-2.8 (br, 0.79 H, H-2 of GlcN), 3.3–5.2 (m, 6.21 H, H-1-6 of chitosan except for H-2 of GlcN); ^{13}C NMR δ 13.93 (CH_3), 22.32 and 22.42 [CH_2 (δ)], 24.46, 24.51, and 24.58 [CH_2 (χ) and NHAc], 31.29 and 31.44 [CH_2 (β)], 33.94 and 34.14 [CH_2 (α)], 56.0–56.5 (C-2), 62.0–63.0 (C-6 and C-6S), 73.3–75.4 (C-3 and C-5), 81.3–81.6 (C-4), 103.4–104.4 (C-1), 173.2–173.6 (NH*C*O and O*C*O).
4 T. Seo, Y. Ikeda, K. Torada, Y. Nakata, and Y. Shimomura, *Chitin and Chitosan Res.*, **7**, 212 (2001).
5 K. Inoue, K. Yoshizawa, K. Ohto, and H. Nakagawa, *Chem. Lett.*, **2001**, 698.
6 S. Nishimura, O. Kohgo, K. Kurita, C. Vittavatvong, and K. Kuwahara, *Chem. Lett.*, **1990**, 243.
7 Sample (4.5 mg), poly(vinyl alcohol) butyl acetal (4.5 mg) as a supporting polymer, and poly(ethylene glycol) mono lauryl eter (1 mg) as surfactant which dissolved in THF were coated on glass dish (10 cm^2). $PdCl_2$ (0.15 mg/mL, 1 mL) containing 0.17 M NaCl was dropped on coated dish. After 1 h, the amount of Pd ion in a supernatant was evaluated by HPLC (column, TSK gel IC-Anion-SW; eluent, 5 mM EDTA-2Na; 1.2 mL/min; 40 °C; detection, UV 254 nm).