CHAPTER III

CHITOSAN GRAFTED WITH OXYETHYLENE AND AZAETHYLENE CHAINS AND ITS METAL IONS ADSORPTION CAPACITY AND SELECTIVITY

Abstract

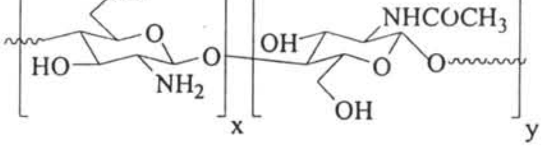
Chitosan conjugated with linear oxyethylenes and azaethylenes to achieve chitosan derivatives are proposed. The conjugation of a series of ethyleneglycol and ethylenealkylamine onto chitosan is succeeded by using carbonyl diimidazole coupling agent. The derivatives show a significant alkali, and transition metals adsorption capacity including the Ag^+ selectivity in the coexistence with Cr^{3+}, Cu^{2+} and Ni^{2+}.

Keywords: Chitosan; Ion adsorbent; Ion adsorption; Selectivity; Metal Ions

Introduction

Chitin-chitosan is the second most naturally abundant copolysaccharide of β-(1-4)-2-acetamido-2-deoxy-β-D-glucose and β-(1-4)-2-amino-2-deoxy-β-D-glucose (Scheme 3.1) found in shells of crustaceans, cuticles of insects, cell-walls of fungi and yeasts. Due to its specific properties, especially, bioactivity,[1] biocompatibility,[2] biodegradability,[3] non-toxicity[4] including the potential for physical[5] and chemical[6] modifications, the material has been developed as a value-added biopolymer for decades.

Scheme 3.1



It is known that chitin-chitosan exhibits specific properties to form complexes with metal ions. Cervera et al.[7] and Minasawa et al.[8] proposed that the complexation with transition metals, for example, Cd^{2+}, Co^{2+} or Cr^{3+} were based on the amino group of chitosan. Ngah et al.[9] demonstrated a simple materialization by crosslinking chitosan to form beads with good mechanical properties and showed that the material obtained could be applied for Cu^{2+}, Fe^{2+} and Fe^{3+} adsorbent.

Functionalization polymer with supramolecules is an alternative way to obtain ion adsorbent with selectivity. Yang et al.[10, 11] demonstrated that chitosan grafted with crown ether showed the selectivity for Cu^{2+} in the mixture of Pb^{2+}, Cu^{2+} and Cd^{2+}, whereas, chitosan-hydroxyl azacrown ether exhibited selectivity for Ag^{+} in coexistence with Pb^{2+} and Cd^{2+}. Although the approach is unique and the chitosan obtained gives metal adsorption with selectivity, the fact that the introduction of macrocyclic unit results in the high cost and the multi-step synthesis. Tan et al.[12] showed that imprinting is another method to achieve Ni^{2+} selectivity by demonstrating the simple preparation of a chitosan with nickel sulfate imprinted network.

It is important to note that, in recent years, amino sugars and their derivatives, especially, chitin-chitosan and hyaluronic acid, have received much attention as efficient ligands or hosts for metal ions delivery in the biological fields. For chitosan, Burke et al.[13] reported about the iron adsorptivity on crosslinked chitosan microsphere and proposed the potential application for the treatment of iron overload in humans. Considering chitosan as ligands in biosystem, it is necessary to develop a compound with sensitivity and selectivity combining with the awareness about toxicity of the introduced cyclic compounds or functional groups.

Based on this viewpoint, we pay our attention to the functionalization of chitosan with simple alkylether and alkylamine chains. Here, it can be expected not only for the low risks of toxicity based on the simple structure of alkyl units but also the possibility to give pseudoether-crown or aza-crown structure in forming the complexation with metals.

Experimental

Chemicals. Low molecular weight chitosan (M_v = 85 000 g mol^{-1}) with degree of deacetylation (DD) 95% was provided by Seafresh Chitosan (Lab) Company Limited, Thailand. *N'-N* carbonyldiimidazole (CDI) was obtained from TCI, Japan. Benzaldehyde, acetic acid, acetone, chloroform, ethanol, and methanol were purchased from Carlo Erba Reagenti, Italy. Sodium hydroxide and hydrochloric acid were provided by Lab-Scan, Ireland. Triethylamine was obtained from Unilab, Australia. Sodium acetate was purchased from Univar, Australia. Triethyleneglycol monomethylether, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyethyleneglycol 1100 monomethylether, copper sulphate pentahydrate, nickel chloride hexahydrate, silver nitrate, and chromium chloride hexahydrate were provided by Fluka Chemika, Switzerland. Poly(ethylene glycol) methylethers; M_w 350, 550, 2000, and 5000 were obtained from Aldrich Chemical Company, Inc., USA. Potassium hydroxide, cesium carbonate, and picric acid were purchased from Ajax chemicals, Australia. All chemicals were analytical grade and were used without further purification.

Instruments and Equipment. Qualitative and quantitative Fourier transform infrared spectra were obtained from a Thermo Nicolet Nexus 670 with 32 Scans at a resolution of 2 cm^{-1}. A frequency range of 4000-400 cm^{-1} was observed using a deuterated triglycinesulfate detector (DTGS) with a specific detectivity, D*, of 1×10^9 cm $Hz^{1/2}$ w^{-1}. Powder X-ray diffraction (XRD) patterns were recorded over a 2θ range of 2-60° by a RIGAKU RINT 2000 using CuKα as an X-ray source and operating at 40 kV and 30 mA with Ni filter. Elemental analyses were obtained from a Yanako CHN CORDER MT-5 with a combustion temperature at 950°C under air with O_2 as a combustion gas (flow rate, 20 mL/min) and He as a carrier (flow rate, 200 mL/min). TG-DTA thermogravimetric analyses were carried out using a Perkin Elmer Pyris Diamond with N_2 flow rate of 20 mL/min and a heating rate of 10°C/min starting from 30 to 650°C. Intrinsic viscosity $[\eta]$ was measured with a calibrated viscometer Cannon-Ubbelohde (No. 2, A149) in 0.2 M CH_3COOH/0.1 M CH_3COONa aqueous solution at 30 ± 0.05°C. The molecular weight was calculated using the Mark-Houwink equation with $K = 1.64 \times 10^{-30} \times DD^{14}$ and $a = (-1.02 \times 10^{-2} \times DD) + 1.82$ as proposed by Wang et al.[14] Concentration of transition metal aqueous solution was determined by a Varian, SpectrAA 300 atomic adsorption spectrophotometry. Alkali metal ion picrate concentration was determined by a Shimadzu UV-2550 spectrophotometry.

Procedures.

***N*-benzylidene chitosan, 2.** Compound **2** was prepared as proposed by Yang et al.[15] In brief, low molecular weight chitosan, **1** (1.00 g), was dissolved in 2% (v/v) acetic acid aqueous solution. The solution (20.0 mL) was stirred with benzaldehyde (4.35 mL, 7 moles equivalent to pyranose rings) and methanol (80.0 mL) at room temperature for 15 h. The crude product was washed thoroughly by methanol and dried *in vacuo* at 60°C to give **2** (Scheme 3.2).

Analysis: Found: C, 56.18; H, 6.29; N, 5.44%. Calculated for $(C_{13}H_{15}O_4N)_{0.95}(C_8H_{13}O_5N)_{0.05}$: C, 62.02; H, 6.04; N, 5.68%. IR (KBr, cm^{-1}) 1644 (C=N), and 756, 692 and 1581 (aromatic ring).

***N*-benzylidene chitosan-carbonyldiimidazole, 3.** Coupling reaction was carried out based on the report by Yoksan et al.[16] Compound **2** (1.00 g) and CDI (1.97 g, 3 moles equivalent to pyranose rings) were mixed in chloroform (20.0 mL). The reaction was carried out at 60°C under N_2 atmosphere for 6 h to obtain yellowish powder. The product was collected and washed thoroughly with acetone and dried *in vacuo* at 60°C to give **3** (Scheme 3.2).

Analysis: Found: C, 54.12; H, 5.95; N, 11.83%. Calculated for $(C_{17}H_{17}O_5N_3)_{0.53}(C_{14}H_{15}O_6N_5)_{0.42}(C_{12}H_{15}O_6N_3)_{0.05}$: C, 53.12; H, 4.59; N, 15.36%. IR (KBr, cm^{-1}) 1761 (C=O reactive ester), 1644 (C=N), and 756, 692 and 1581 (aromatic ring).

***N*-benzylidene chitosan-triethyleneglycol monomethylether, 4.** Compound **3** (1.00 g) was dispersed in chloroform (20.0 mL) and triethyleneglycol monomethylether (1.27 mL, 2 moles equivalent to pyranose rings) was added with a catalytic amount of triethylamine. The reaction was carried out at 60°C for 8 h followed by at room temperature for overnight. The crude product was collected and washed thoroughly with methanol for several times and dried *in vacuo* to yield **4**.

4: Analysis: Found: C, 53.40; H, 5.86; N, 7.96%. Calculated for $[(C_{21}H_{29}O_9N)_{0.53}(C_{22}H_{39}O_{15}N)_{0.42}(C_{16}H_{27}O_{10}N)_{0.05}]_{0.76}$ $[(C_{13}H_{15}O_4N)_{0.53}(C_6H_{11}O_4N)_{0.42}(C_8H_{13}O_5N)_{0.05}]_{0.24}$: C, 52.72; H, 6.75; N, 3.34%. IR (KBr, cm^{-1}) 1755 (carbonate bond), 1644 (C=N), and 756, 692 and 1581 (aromatic ring).

***N*-benzylidene chitosan-triethylenetetramine, 6, *N*-benzylidene chitosan-tetraethylenepentamine, 7, *N*-benzylidene chitosan-**

pentaethylenehexamine, 8. Compounds **6 - 8**, were prepared similarly as **4** but using triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine as the reactants, respectively.

6: Analysis: Found: C, 47.49; H, 6.79; N, 13.48%. Calculated for $[(C_{20}H_{31}O_5N_5)_{0.53}(C_{20}H_{43}O_7N_9)_{0.42}(C_{15}H_{29}O_6N_5)_{0.05}]_{0.76}$ $[(C_{13}H_{15}O_4N)_{0.53}(C_6H_{11}O_4N)_{0.42}(C_8H_{13}O_5N)_{0.05}]_{0.24}$: C, 52.04; H, 7.61;, N, 18.55%. IR (KBr, cm^{-1}) 1712 (carbamate bond), 1644 (C=N), and 756, 692 and 1581 (aromatic ring).

7: Analysis: Found: C, 47.02; H, 7.23; N, 14.06%. Calculated for $[(C_{22}H_{36}O_5N_6)_{0.53}(C_{24}H_{53}O_7N_{11})_{0.42}(C_{17}H_{34}O_6N_6)_{0.05}]_{0.76}$ $[(C_{13}H_{15}O_4N)_{0.53}(C_6H_{11}O_4N)_{0.42}(C_8H_{13}O_5N)_{0.05}]_{0.24}$: C, 52.43; H, 8.03; N, 20.00%. IR (KBr, cm^{-1}) 1712 (carbamate bond), 1644 (C=N), and 756, 692 and 1581 (aromatic ring).

8: Analysis: Found: C, 44.01; H, 7.24; N, 12.08%. Calculated for $[(C_{24}H_{41}O_5N_7)_{0.53}(C_{28}H_{63}O_7N_{13})_{0.42}(C_{28}H_{63}O_7N_{13})_{0.05}]_{0.76}$ $[(C_{13}H_{15}O_4N)_{0.53}(C_6H_{11}O_4N)_{0.42}(C_8H_{13}O_5N)_{0.05}]_{0.24}$: C, 52.75; H, 8.36; N, 21.40%. IR (KBr, cm^{-1}) 1712 (carbamate bond), 1644 (C=N), and 756, 692 and 1581 (aromatic ring).

Chitosan-triethyleneglycol monomethylether, 5. Compound **4** (1.00 g) was reacted with ethanolic hydrochloride solution (0.5 N, 20 mL) at room temperature for 2 h. The solution was neutralized by NaOH. The product was washed with distilled water followed by methanol and dried *in vacuo* at 60°C to yield **5**.

5: Analysis: Found: C, 34.50; H, 6.34; N, 5.62%. Calculated for $[(C_{14}H_{25}O_9N)_{0.53}(C_{22}H_{39}O_{15}N)_{0.42}(C_{16}H_{27}O_{10}N)_{0.05}]_{0.76}[(C_6H_{11}O_4N)_{0.95}(C_8H_{13}O_5N)_{0.05}]_{0.24}$: C, 47.37; H, 7.02; N, 3.76%. IR (KBr, cm^{-1}) 1755 (carbonate bond).

Chitosan-triethylenetetramine, 9, chitosan-tetraethylenepentamine, 10, chitosan-pentaethylenehexamine, 11. Compounds **9 - 11**, were obtained from similar procedures as **5**.

9: Analysis: Found: C, 33.75; H, 6.63; N, 11.35%. Calculated for $[(C_{13}H_{27}O_5N_5)_{0.53}(C_{20}H_{43}O_7N_9)_{0.42}(C_{15}H_{29}O_6N_5)_{0.05}]_{0.60}$

$[(C_{10}H_{13}O_5N_3)_{0.53}(C_{14}H_{15}O_7N_5)_{0.42}(C_{12}H_{15}O_6N_3)_{0.05}]_{0.16}[(C_6H_{11}O_4N)_{0.42}(C_8H_{13}O_5N)_{0.05}]_{0.24}$: C, 46.33; H, 7.51; N, 20.26%. IR (KBr, cm^{-1}) 1712 (carbamate bond).

10: Analysis: Found: C, 38.66; H, 6.89; N, 12.00%. Calculated for $[(C_{15}H_{32}O_5N_6)_{0.53}(C_{24}H_{53}O_7N_{11})_{0.42}(C_{17}H_{34}O_6N_6)_{0.05}]_{0.59}$ $[(C_{10}H_{13}O_5N_3)_{0.53}(C_{14}H_{15}O_7N_5)_{0.42}(C_{12}H_{15}O_6N_3)_{0.05}]_{0.17}[(C_6H_{11}O_4N)_{0.42}(C_8H_{13}O_5N)_{0.05}]_{0.24}$: C, 47.25; H, 7.88; N, 21.41%. IR (KBr, cm^{-1}) 1712 (carbamate bond).

11: Analysis: Found: C, 40.55; H, 6.83; N, 11.55%. Calculated for $[(C_{17}H_{37}O_5N_7)_{0.53}(C_{28}H_{63}O_7N_{13})_{0.42}(C_{19}H_{39}O_6N_7)_{0.05}]_{0.52}$ $[(C_{10}H_{13}O_5N_3)_{0.53}(C_{14}H_{15}O_7N_5)_{0.42}(C_{12}H_{15}O_6N_3)_{0.05}]_{0.24}[(C_6H_{11}O_4N)_{0.42}(C_8H_{13}O_5N)_{0.05}]_{0.24}$: C, 47.87; H, 7.93; N, 21.87%. IR (KBr, cm^{-1}) 1712 (carbamate bond).

Ion adsorption studies. A series of transition metal salts, i.e. $CuSO_4.5H_2O$, $NiCl_2.6H_2O$, $CrCl_3.\ 6H_2O$, and $AgNO_3$, were prepared as aqueous solutions for 300 ppm. Compounds **1**, and **4 - 11** (25 mg) were added to 25 mL of metal ion aqueous solutions. The mixtures were stirred for 24 h at room temperature. The supernatant was collected to determine the metal ion concentration by atomic adsorption technique. The extraction efficiency was evaluated by equation (1).

$$E = [(C_0 - C)/ C_0] / 100 \qquad (2)$$

(E: extraction efficiency of adsorbents, C_0: metal ion concentration before adsorption (ppm), C: concentration of metal ion after adsorption (ppm). The adsorption capacity was calculated from equation (2).

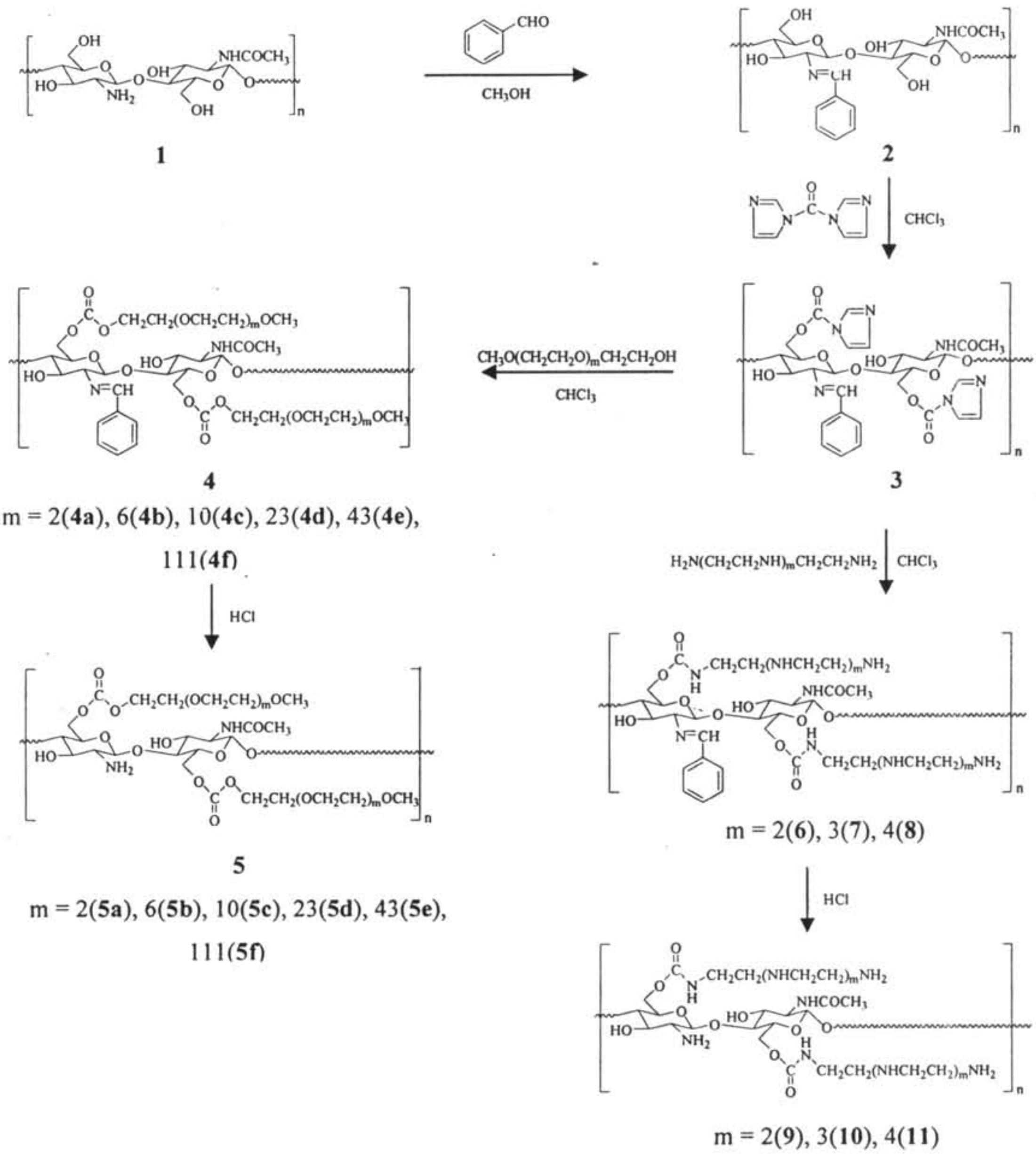
$$Q = V(C_0 - C) / W \qquad (2)$$

(Q: adsorption capacity of adsorbents, V: volume of metal ion solution (mL), C_0: metal ion concentration before adsorption (ppm), C: concentration of metal ion adsorption (ppm), and W: weight of adsorbents (mg)). The selectivity coefficient of the adsorbent was evaluated by equation (3).

$$K_{M(1)/M(2)} = Q_1/Q_2 \qquad (3)$$

($K_{M(1)/M(2)}$: selectivity coefficient of adsorbents, Q_1, Q_2: adsorption capacities of the adsorbents for metals M(1) and M(2), respectively).

Scheme 3.2



Ion extraction studies. In the cases of alkali metals, the ion solutions (7×10^{-5} M) were prepared by using potassium, sodium, and cesium picrate salts. Each metal picrate aqueous solution (25 mL) was added to the compounds, i.e. 1, and 4 - 11 (25 mg) and stirred for 24 h at room temperature. The solutions were collected and quantitatively analyzed by UV-Vis spectrophotometry at 356 nm. The extraction efficiency was calculated from equation (4)

$$E = [(A_0 - A) / A_0] / 100 \tag{4}$$

(E: extraction efficiency of adsorbents, A_0: absorbance at 356 nm of metal ion picrate before adsorption, A: absorbance at 356 nm of metal ion after adsorption.

Results and discussion.

Structural Characterization.

As the present work aims to develop a supramolecular structured chitosan with pseudocyclic structure induced from the oxyethylene and azaethylene chains, low molecular weight chitosan (95% DD) with Mv = 85,000 (~500 repeat unit), **1**, was applied. The preliminary structural studies of **1** about the degradation temperature (at 322°C), the packing structure (9° and 19° 2θ) and the FT-IR spectrum (Figure 3.1(a)) confirmed that **1** maintains its chitosan structure and properties for functionalization in further steps.

In order to maintain chitosan as an amino saccharide, substitution at only hydroxyl groups was considered. The amino group was protected by benzaldehyde[15] in the first step to obtain **2**. Compound **2** was successfully prepared as confirmed from the peaks 756, 692 and 1581 cm^{-1} (aromatic ring), and 1644 cm^{-1} (C=N) (Figure 3.1(b)). Benzylidene substitution was found to be 56% as determined by elemental analysis. The changes in XRD pattern give us indirect information about the chemical reaction of chitosan. Compound **2** showed the XRD peak at 0 2 0 shifting of 9° 2θ to the lower angle at 5° 2θ. This implied the loose packing structure of **2** as a result from the introduction of the bulky benzaldehyde group.

For the introduction of oxyethylene or azaethylene, CDI, a coupling agent with high reactivity with alcohols, carboxylic acids and amines,[17, 18] was applied. As the amino group of **2** was protected, the reaction was expected to occur mainly at the OH groups, either C-3 or C-6. The reaction was carried out in a heterogeneous system in chloroform under N_2 to avoid the moisture for the reactive CDI protection along the reaction.

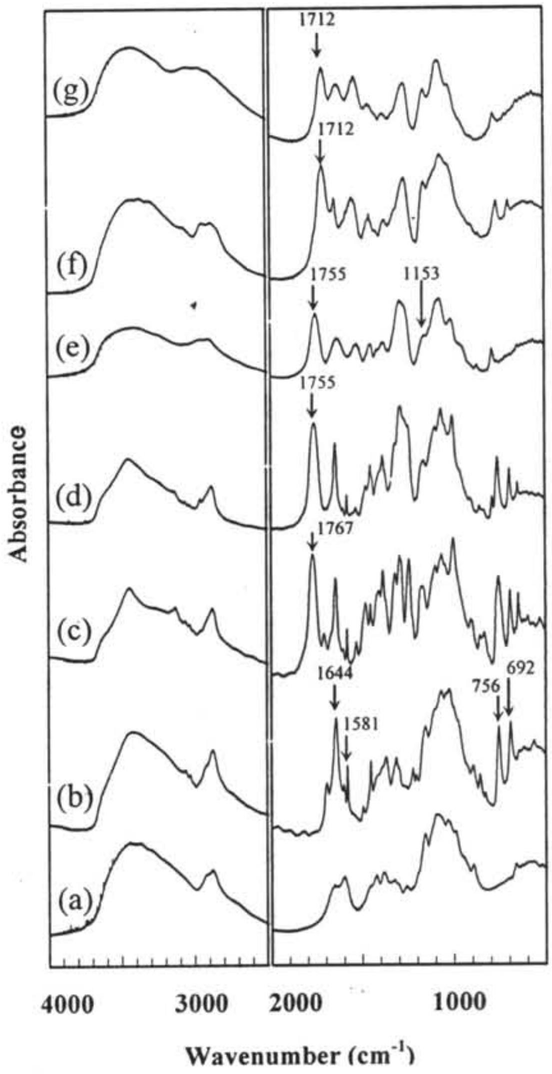


Figure 3.1 FT-IR spectra of compounds: (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5a**, (f) **6**, and (g) **9**.

The reaction was traced by FT-IR at 1767 cm^{-1} (reactive ester) to confirm the achievement of **3** (Figure 3.1(c)). Here, Scheme 3.2 shows a representative structure where the substitution occurs only at C-6 for the ease of expression. As the compound was hardly dissolved in almost all deuterated solvents, the substitution had to be determined by elemental analysis. Based on the structure which the substitution is assumed to occur at only C-6, the degree of substitution is found to be 76% as referred to the C/N ratio. Thermal analysis was also applied to investigate the derivatization. Compound **3** showed the two weight loss peaks at 168°C, and 319°C of which the former one indicates the ester linkage decomposition whereas the latter one shows the saccharide degradation.

Introduction of Oxyethylene Chain.

The introduction of triethyleneglycol monomethylether onto **3** was expected to occur at the reactive carbonyl group. Figure 3.1(d) shows that the reactive ester imidazole group was consumed after the reaction as evidenced, from the disappearance of the peak at 1767 cm^{-1}. The peak at 1755 cm^{-1} (carbonate group) also confirms the successful reaction to obtain **4**. The removal of the benzylidene group was carried out to obtain **5** (Scheme 3.2). In order to study the effect of the ethylene unit, **5a** - **5f** were prepared. Figure 3.1(e) shows **5a** as a representative result for the introduction of oxyethylene chain. Although the peak at 1153 cm^{-1} (C-O-C) gave us information of oxyethylene unit grafted on the chitosan chain, the fact that this peak is overlapped with the ether group of saccharide unit obstructs our interpretation. The disappearance of the peak at 1644 cm^{-1} (C=N) implies the successful benzylidene removal. The peak at 1755 cm^{-1} (carbonate group) is maintained after treating with HCl confirms that the condition of benzylidene removal was not affected much to the ester bonds between chitosan and triethyleneglycol monomethylether.

The degradation temperatures of **5a** – **5f** are approximately 250°C which are lower than that of **1** (Figure 3.2). The decrease in T_d suggested that the introduction with oxyethylene unit onto chitosan might initiate the loose in packing structure. This speculation was supported by the XRD patterns of **5a** – **5f** which showed a single board peak over 18° 2θ.

Introduction of Azaethylene Chain.

Similar to the introduction of oxyethylene chains, for those of azaethylene chains, a series of alkylamine, i.e. triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine were introduced onto **3** to obtain **6** - **8** followed by deprotecting amino group to obtain **9** - **11** (Scheme 3.2). Figure 3.1(f) shows the peak at 1712 cm^{-1} implying the successful introduction of azaethylene chain via the carbamate bond. Compounds **7** – **8** also gave the similar FT-IR spectra. After treating with HCl, those aromatic ring peaks (756, 692 and 1581 cm^{-1}) are disappeared to confirm the achievement of **9** – **11** (Figure 3.1(g)). The C/N ratios were calculated to find the substitution of azaethylene chain for **9** – **11** to be 80, 78, and 68%, respectively. Compounds **9** – **11** show the significant decrease in degradation temperature for 80 ~ 90°C (Table 3.1) as comparing to **1** suggesting the azaethylene chain might affect the hydrogen bonded semi-crystalline structure of chitosan.

Metal Ion Adsorption Capacity.

Interaction with Alkaline Metals.

For alkali metals, the metal ion adsorption capacity of the derivatives were evaluated by using metal picrate solutions. As metal picrate solution gives the peak at 356 nm, the decrease in metal picrate concentration or ion extraction reflects the ion adsorption capacity of the derivatives.

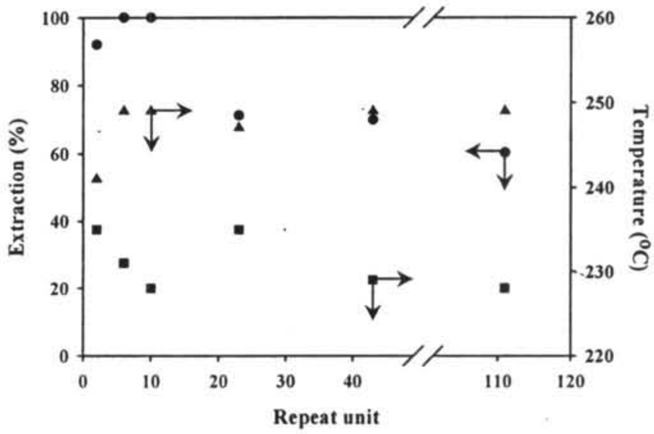


Figure 3.2 Performances **5** evaluated in the number of repeat unit (see structure in Scheme 2) for: potassium picrate ion extraction efficiency (●), degradation temperature before complexation (▲), and degradation temperature after complexation (■).

Compound **1** shows the ion extraction capacity for Na^+, K^+, and Cs^+ to be 13.3, 9.67, and 10.84%, respectively. This implies that **1** performs the interaction with metal ions. Here, a series of **5** with various oxyethylene repeat units, i.e. m = 2 (**5a**), 6 (**5b**), 10 (**5c**), 23 (**5d**), 43 (**5e**), and 111 (**5f**) were studied. Figure 3.2 evaluates the potassium ion entrapment ability of **5** in term of ethylene repeat unit.

The extraction percentages or in other words the potassium ion entrapments are almost 100% when the repeat units are about 6 ~ 10. For the ethylene repeat unit of 23 or above, the extraction percentage is decreased gradually.

Considering the effect of ethylene glycol repeat unit, it might be possible that ethylene glycol formed pseudocyclic crown ether structure to play an important role in ion entrapment. Previously, Yamagishi et al.[19] illustrated the case that the oxyethylene chain on *p*-position of phenols possibly formed pseudocrown in recognizing alkali, and alkaline earth metal ions, especially, Ba^{2+}. In our case, it is suspected that the pseudocyclic structure might form between chitosan repeat unit, either from the same or different chitosan chain as illustrated in Scheme 3.3. Thermal stability is one of the indications to confirm the complex formation. In the cases of crown ethers, the changes in melting temperatures, either increase or decrease, were reported.[20] Here, the degradation temperatures after treating **1,** and **5** – **11** with metal ion solutions were investigated. Figure 3.2 shows the changes in temperature of each derivative after ion adsorption implying the complex formation. The degradation temperatures of **5a** – **5f** are averagely about 250°C and decrease to ~ 230°C after complexation.

In order to verify the pseudo crown structure formation, other types of chitosan but with various azaethylene chains, i.e. **6** - **10**, were investigated. In the cases of **7** – **8** the metal picrate extractions are about 60 ~ 80% in average (Figure 3.3), whereas **10** – **11**, which are the derivatives with amino group, give the metal picrate extraction for almost 100% (Figure 3.3). This implies that amino group onto chitosan might involve with azaethylene chain in complexation. The decreases in degradation temperature of all compounds after metal ion adsorption are observed (Table 3.1). Here, one of the possibilities in complex formation with pseudocyclic structure is illustrated in Scheme 3.3.

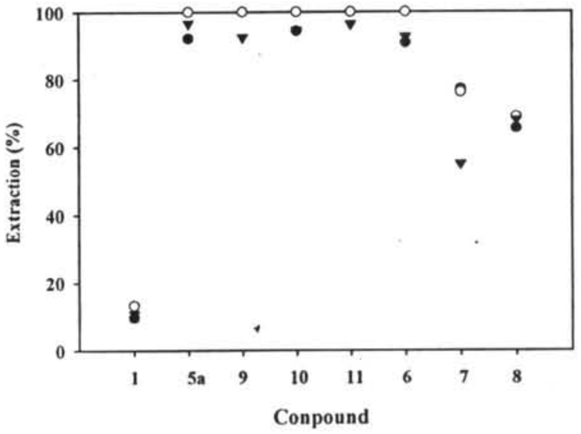
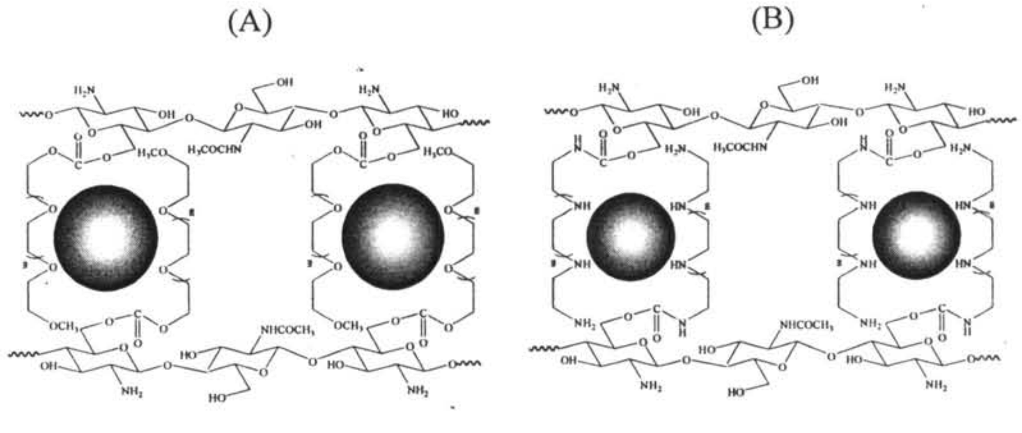


Figure 3.3 Extraction efficiency of **1**, **5a**, and **6** - **11** for metal picrates: K^+ (●), Na^+ (○), and, Cs^+ (▼).



Scheme 3.3 (A) pseudocyclic crownether formed by chitosan conjugated with oxyethylene chains, and (B) pseudocyclic azacrownether formed by chitosan conjugated with azaethylene chains.

Table 3.1 Degradation temperature (T_d) of low molecular weight chitosan (**1**), chitosan with oxyethylene chain (**5a**), and chitosan with azaethylene chain (**6 - 11**)

Compound	T_d (°C)	T_d (°C) after adsorption with						
		Na^+	K^+	Cs^+	Ag^+	Cu^{2+}	Ni^{2+}	Cr^{3+}
1	322	312	306	311	302	226	303	283
5a	241	306	235	310	233	230	223	228
6	290	304	306	304	296	249	288	253
7	295	298	300	299	294	248	291	259
8	289	289	289	287	284	252	289	260
9	231	238	238	237	236	233	237	238
10	238	241	243	243	239	235	243	241
11	244	241	243	239	237	236	240	244

Interaction with Transition Metals.

Figure 3.4 shows ion extraction efficiency of **1**, **5a**, **9**, and **11** to compare how the oxyethylene and azaethylene units induce the transition metal ion adsorption capacity. Peng et al.[21] reported that the ion extraction efficiency of chitosan with crown ether (18-crown-6) for Ag^+ was about 52.32%. Here, **5** shows the significant ion extraction efficiency for Ag^+ as high as 97%. This implies that when chitosan was conjugated with oxyethylene unit, the interaction between chitosan and Ag^+ might be satisfied under the pseudocrown formation.

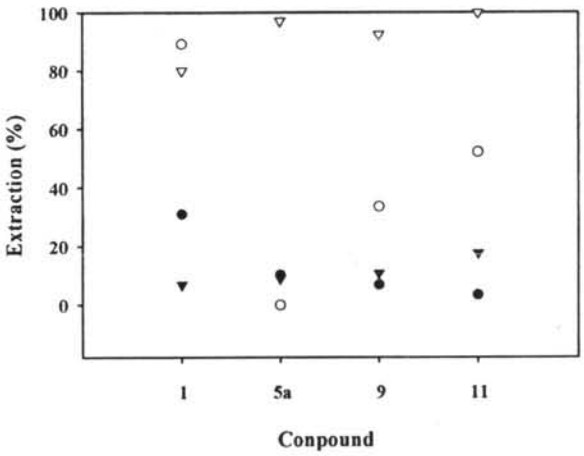


Figure 3.4 Extraction efficiency of **1**, **5a**, **9**, and **11** for: Cr^{3+} (●), Cu^{2+} (○), Ni^{2+} (▼), and, Ag^+ (▽).

Figure 3.4 clarifies that the derivatives with azaethylene chain, i.e. **9** and **11** show much higher value to adsorb Ag^+ than that of chitosan with azacrown ether (52.67 %) as reported by Yang et al.[15] This suggested that the chain length of azaethylene unit and its flexibility to perform pseudocyclic might initiate an effective interaction with Ag^+. Table 3.1 summarizes the decrease of degradation temperature after each derivative was treated with metals.

Selectivity of Metal Ion Adsorption

As all derivatives showed its adsorptivity on Ag^+ to be much more significant than other types of metals, the selectivity of Ag^+ in the coexistence with other transition metals was then calculated. Table 3.2 summarizes the selectivity of Ag^+ over other transition metal ions adsorption. Compounds **9** and **11** show the selectivity of Ag^+ above Cu^{2+} and Cr^{3+} for almost 3, and 80 times, respectively, whereas **5** gives the selectivity of Ag^+ over Ni^{2+} for 13 times. The selectivity of **1**, or in other words chitosan without modification, is significant in the case of $K_{Ag^+/Ni^{2+}}$ for almost 14 times. This implies that chitosan performs its selectivity on Ag^+ at a certain amount. Yang et al.[11] showed that the selectivity of Ag^+ in the coexistence of Pb^{2+} and Cd^{2+} was enhanced after introducing ary azacrown ether onto chitosan chain for 20 and 33 times, respectively, as compared to chitosan. Here, it is suspected that the unit of azaethylene chain might form a pseudocyclic structure to enhance the selectivity in entrapping Ag^+.

Table 3.2 Adsorption selectivity of adsorbents in aqueous at pH = 7.0 for Cr^{3+}, Cu^{2+}, Ni^{2+}, and Ag^+

	$K_{Ag^+/Cr^{3+}}$	$K_{Ag^+/Cu^{2+}}$	$K_{Ag^+/Ni^{2+}}$
1	7.11	1.26	13.91
5a	25.87	n.d.	13.27
9	36.93	3.52	10.40
11	79.85	2.46	6.88

Considering the mechanism involved in ion entrapment, the pseudocyclic cavity related to the ionic size is another point to be concerned. Here, the ionic diameter of Ag^+, Cr^{3+}, Cu^{2+}, and Ni^{2+} are 2.52, 1.64, 1.44, and 1.38 Å, respectively.[21] It should be noted that Ag^+ shows the largest ionic diameter, whereas **5**, and **6 - 11** give the highest Ag^+ adsorptivity. This suggests that the pseudocyclic unit might be in the size appropriate for Ag^+.

Conclusions

A series of ethylene glycol and ethylene amine was successfully conjugated onto low molecular weight chitosan at hydroxyl group via CDI coupling agent. The compounds obtained showed the ion adsorption capacity through various types of metals (alkali, and transition metals) and was comparable to chitosan with crownethers reported in the past implying the possibility that the compounds form pseudocyclic structure to adsorb ions. The studies on transition metal ion adsorption declared the selectivity for Ag^+ with coexistence of Cr^{3+}, Cu^{2+}, and Ni^{2+} in aqueous. The work proposed that instead of introducing the macrocyclic compounds to achieve ion interaction property, we can develop pseudocyclic chain on chitosan by simple conjugating with oxy or aza alkyl chains to achieve the advantages about low risks of toxicity which might come from those macrocyclic units.

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