

## Preparation and properties of macromolecular complexes consisting of chitosan derivatives, iron(III) hydroxide sulfate, and poly(potassium vinyl sulfate)

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### SUMMARY:

Glycol chitosan (GC) and methyl glycol chitosan (MGC) were separately reacted with poly(potassium vinyl sulfate) (PVS)K in the presence of iron(III) hydroxide sulfate (IHS) to form water-insoluble macromolecular complexes (MC's). The chemical compositions and properties of MC's obtained were compared with each other. The solubility of MC in the MGC-IHS-PVS system was lower than that in the GC-IHS-PVS system, and it was suggested that MGC contributes to the properties of MC.

### Introduction

The mixing of a polycation and a polyanion in aqueous solution leads to the formation of macromolecular complexes (MC's). There have been many investigations on the preparation, properties, and applications of MC's consisting of an organic polycation and an organic polyanion, and these complexes are expected to be useful as functional and biomedical materials<sup>1,2</sup>. We have previously reported on the preparation, structures, and properties of a series of MC's consisting of organic macromolecules<sup>3–6</sup>. So far, however, researches on the polyionic interaction between an organic macromolecule and an inorganic macromolecule have little been known<sup>7,8</sup>, and only a few applications of those complexes containing chitosan have been reported<sup>9,10</sup>. We have also presented novel chemical reactions for the formation of MC's consisting of organic and inorganic macromolecules recently<sup>11–13</sup>.

Thus, as a part of series of studies on MC's consisting of organic and inorganic macromolecules, we here report on MC consisting of glycol chitosan (GC), iron(III) hydroxide sulfate (IHS), and poly(potassium vinyl sulfate) (PVS)K and MC consisting of methyl glycol chitosan (MGC), IHS, and PVS)K. The chemical compositions and properties of MC's obtained were compared with each other; elemental analysis, IR spectroscopy, solubility, thermogravimetry, scanning electron microscopy, membrane-forming ability, and electric conductivity were used to characterize these complexes.

### Experimental part

#### Materials

GC (intrinsic viscosity: 179 cm<sup>3</sup>/g in 1 mol/dm<sup>3</sup> NaCl at 25 °C; nitrogen content: 5.93 wt.-%), MGC (intrinsic viscosity: 29 cm<sup>3</sup>/g in 1 mol/dm<sup>3</sup> NaCl at 25 °C; nitrogen content: 3.23 wt.-%), and PVS)K (intrinsic viscosity: 59 cm<sup>3</sup>/g in 1 mol/dm<sup>3</sup> NaCl at 25 °C;

sulfur content: 18,91 wt.-%) were purchased from Wako Pure Chemical Industry Co. Ltd., Osaka, Japan. IHS (compositional formula at pH 0.8:  $[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_m$  ( $0,5 < n < 1,0$ ,  $m = 8-10$ ); iron content: 11,3 wt.-%) was of coagulant grade from Nittetsu Kogyo Co. Ltd., Tokyo, Japan. Methanol was distilled just before use. The other chemicals were reagent grade and used without further purification.

#### *Preparation of macromolecular complexes*

In both the GC-IHS-PVSK and MGC-IHS-PVSK system, MC's were prepared under different conditions of pH. A polycation (or polyanion) solution, which was adjusted to the predetermined pH with HCl or NaOH, was added dropwise to 100 cm<sup>3</sup> of polyanion (or polycation) solution, which was adjusted to the same pH as polycation (or polyanion) solution, at a rate of 50 cm<sup>3</sup>/30 min with stirring at  $22 \pm 2^\circ\text{C}$ . The concentration of each solution was 5 g/dm<sup>3</sup>. The mole ratios of iron (IHS) to nitrogen (GC or MGC) in the polycation mixture solutions of both systems were 1 : 1. By this procedure, we obtained the coagulation points of complexes for both systems only at pH below 2,0. Then MC's to be characterized were freshly prepared again in the titration order of polyanion to polycation at pH 1,5 for the GC-IHS-PVSK and MGC-IHS-PVSK systems. The mole ratios of reactive group of PVSK to those of GC + IHS and MGC + IHS in the reaction mixture are listed in Tab. 1. After standing for 30 min, the precipitate was separated by centrifugation, washed with methanol, and dried in vacuo at room temperature until there was no farther decrease in weight. The nitrogen content was determined by the Kjeldahl method, and the iron content was estimated from the absorbance at 510 nm (Hitachi 100-10 spectrophotometer) by the 1,10-phenanthroline method after wet ashing with HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (1 : 1). The determination of sulfur content was carried out at the Institute of Physical and Chemical Research, Japan.

#### *Characterization of macromolecular complexes*

IR spectra were taken on a Hitachi 270-50 IR spectrophotometer by the use of the KBr pellet method. The solubility of each MC was estimated in different solvents (10 mg/5 cm<sup>3</sup>) for 24 h. The miscibility limit of MC in a ternary solvent mixture, NaBr-acetone-H<sub>2</sub>O, was determined as follows. First the miscibility of the ternary solvent mixture itself was established. NaBr was gradually added into flasks with stoppers, which contained about 10 g of acetone-H<sub>2</sub>O mixtures in different composition, in a thermostat kept at 30 °C, and phase separation was considered as miscibility limit. In a similar manner, acetone (or NaBr) was added to NaBr-H<sub>2</sub>O (or acetone-H<sub>2</sub>O) mixtures in different composition, which included 10 mg of MC, and the cloud point in the homogeneous solvent composition field determined above was considered as miscibility limit of MC. Thermogravimetry was performed in air at a heating rate of 5 °C/min and a flow rate of 100 cm<sup>3</sup>/min with a Seiko Instruments SSC-5000 thermal analyzer and a thermogravimetric module. Scanning electron microscopy was carried out with a JEOL JSM-840 at an acceleration voltage of 10 kV after coating of Au. The electric conductivity was measured by means of the DC four-terminal method with respect to each MC membrane. HCl-dioxane-H<sub>2</sub>O mixture was adopted as solvent for casting MC membranes.

### **Results and discussion**

An attempt to prepare MC's was preliminary made under various pH conditions. Only at pH below 2,0, as a polycation (or polyanion) solution was added dropwise to a polyanion (or polycation) solution, the reaction mixture became turbid gradually,

Tab. 1. Preparation conditions (pH = 1,5; mole ratio S/(N + Fe) = 1,1), yield, and results of elemental analyses of MC's

Titration order <sup>a)</sup>	Yield in wt.-%	Sulfur content in wt.-%	Nitrogen content in wt.-%	Iron content in wt.-%
GC+IHS ← PVSK	51	7,5	1,6	2,3
MGC+IHS ← PVSK	64	8,3	0,30	3,8

a) PVSK solution was added dropwise to GC+IHS and MGC+IHS solution (100 cm<sup>3</sup>).

and then MC was coagulated and precipitated in swollen state. This observation may be interpreted in terms of the fact that the degree of polymerization of IHS decreases with increasing pH. In consideration of such dependence of the coagulation behavior on pH, MC's were prepared by adding the polyanion solution to the polycation solution up to completion of the coagulation at pH 1,5 for the GC-IHS-PVSK and MGC-IHS-PVSK systems in order to obtain invariable products for characterization.

Both MC's thus obtained in the reaction mixture were light brown and swollen products. Preparation conditions, yield, and sulfur, nitrogen, and iron contents of each MC obtained are given in Tab. 1. Their chemical compositions are different from each other. The nitrogen content of MC in the GC-IHS-PVSK system is higher than that in the MGC-IHS-PVSK system. This is essentially due to the difference in nitrogen content between GC and MGC. Fe<sup>3+</sup> ion, which is a co-ion of GC and MGC, seems to act as a compensatory cation in the MGC-IHS-PVSK system.

IR spectra of MC's in the GC-IHS-PVSK and MGC-IHS-PVSK systems are shown in Fig. 1. They are roughly similar to the spectra of the mixtures of GC or MGC, IHS,

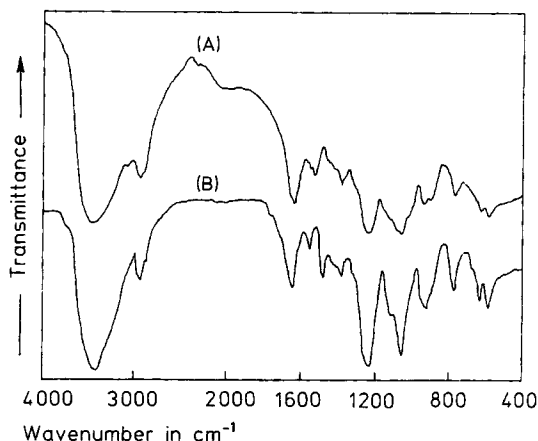


Fig. 1. IR spectra (KBr) of MC's from the GC-IHS-PVSK (A) and MGC-IHS-PVSK (B) systems

and PVSK, without any detectable shift in absorption peaks. This suggests that there are no inter-molecular interactions other than electrostatic. In the GC-IHS-PVSK system the absorption at  $1240\text{ cm}^{-1}$ , which is assigned to S=O group in PVSK, is discernible. In the MGC-IHS-PVSK system, on the other hand, the absorption band at  $1240\text{ cm}^{-1}$  is marked. This is consistent with the results of elemental analyses described above, and IHS (or PVSK) seems to serve as a trap of PVSK (or IHS). The absorption at  $1530\text{ cm}^{-1}$ , assigned to  $-\text{NH}_3^+$  group in GC, is observed only for MC in the GC-IHS-PVSK system.

MC is, generally, insoluble in common organic solvents such as methanol, acetone, and chloroform. Both MC's in this study are only swollen in such organic solvents as ethylene glycol, formalin, formic acid, aqueous ammonia, butylamine, *N,N*-dimethylformamide, and dimethyl sulfoxide, while soluble in hydrobromic acid. It is well known that MC's are well soluble in specific ternary solvent mixtures that consist of water, water-compatible organic solvents, and microions. Fig. 2 shows the phase diagram of MC in the GC-IHS-PVSK system in a ternary solvent mixture, NaBr-acetone- $\text{H}_2\text{O}$ . There is a small region in the solvent composition field where the complex remains in solution to yield a homogeneous liquid. Such a phase diagram was obtained only for MC in the GC-IHS-PVSK system. MC in the MGC-IHS-PVSK system is not soluble at all, even in this ternary solvent mixture. The addition of MGC in forming MC reduces the solubility of MC produced. The bonding through MGC seems to be so tight that NaBr cannot break it.

These results of miscibility, therefore, support the concept that the network structure of each MC is dependent on whether MGC is present in the reaction mixture as a component. These findings are consistent with the difference in the solubility between GC-potassium metaphosphate (MPK) and MGC-MPK systems reported previously<sup>12)</sup>. The strength and thermal stability of three-dimensional polymers result from the fact that the network preserves its structural integrity even after some bonds are broken. Thermogravimetric studies on MC's were conducted to evaluate their thermal stabilities. In view of the results of miscibility in the ternary solvent mixture, the decomposition temperature of MC in the MGC-IHS-PVSK system was expected to be higher than that in the GC-IHS-PVSK system. However, they decomposed at almost

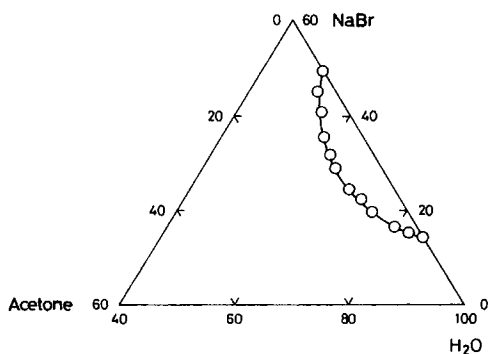


Fig. 2. Phase diagram of MC from the GC-IHS-PVSK system in the ternary solvent mixture NaBr-acetone- $\text{H}_2\text{O}$  at  $30\text{ }^\circ\text{C}$

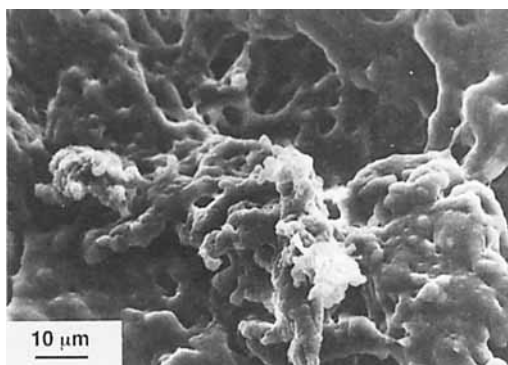


Fig. 3. Scanning electron micrograph of MC from the MGC-IHS-PVSK system

Tab. 2. Stabilities<sup>a)</sup> in acidic and alkaline media and electric conductivities of MC membranes

System	HCl (1 mol/dm <sup>3</sup> )	HCl (0,1 mol/dm <sup>3</sup> )	NaOH (0,1 mol/dm <sup>3</sup> )	NaOH (1 mol/dm <sup>3</sup> )	Conductivity in 10 <sup>-7</sup> S/cm
GC-IHS-PVSK	○	○	○	×	5,3
MGC-IHS-PVSK	○	○	○	×	6,0

a) ○: Stable over 1 week; ×: soluble in 1 day.

the same temperature at thermogravimetric measurements carried out in air; their decomposition temperatures were not obvious, since the thermogravity of each MC decreased continuously between 100 and 200 °C. The morphology of MC in the MGC-IHS-PVSK system was estimated by scanning electron microscopic observation. As shown in Fig. 3, MC from the MGC-IHS-PVSK system has smooth surface in parallel with the other MC's<sup>13)</sup>.

Both MC's were soluble in the mixture HCl-dioxane-H<sub>2</sub>O system. Accordingly, MC membranes were fabricated by casting of those solutions. Tab. 2 shows the results of stability of these membranes in acidic and alkaline media. Our MC membranes are stable in acidic media but unstable in alkali media. Tab. 2 also shows the electric conductivities of MC membranes from the GC-IHS-PVSK and MGC-IHS-PVSK systems in a dry box. The conductivities are about 10<sup>-7</sup> S/cm for both systems. Because both MC's containing IHS are extremely hygroscopic, their conductivities seem to be slightly influenced by moisture.

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