Preparation of a Polyelectrolyte Complex Gel from Chitosan and κ-Carrageenan and Its pH-Sensitive Swelling

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SYNOPSIS

A polyelectrolyte complex gel was prepared by mixing chitosan and κ-carrageenan solutions in the presence of NaCl. To study the effect of ambient pH on the swelling behavior, the diameter of the cylindrical gel (4 mm × 8 mm) immersed in aqueous NaOH, KOH, or HCl solution was measured. In the range of pH 10–12, the diameter increased with time, and the gel reached swelling equilibrium within 6 days. In an NaOH solution of pH 10.5, the maximum swelling occurred, and the volume of the gel at equilibrium was 10.2 times as large as the initial one. At pH below 9 and at pH 13, no swelling was observed. Thus, the swelling of the complex gel prepared in this study was sensitive to a rather narrow range of pH. The swelling equilibrium in the presence of NaCl was also investigated at various pH. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

When two oppositely charged polyelectrolytes are mixed in an aqueous solution, a polyelectrolyte complex[1] is formed by the electrostatic attraction between the polyelectrolytes. Polyelectrolyte complexes are highly hydrophilic materials,[2] and compose highly swollen systems in water.[3] The equilibrium water content of a polyelectrolyte complex has been reported to vary with the composition of the complex.[3,4] In an aqueous solution of acetone and NaBr, the amount of the solution contained in a polyelectrolyte complex has been reported to depend on the concentrations of acetone and NaBr.[1] Thus, the degree of swelling of a polyelectrolyte complex depends on the composition of the complex and the ambient solution.

The degree of swelling of a polyelectrolyte complex may depend also on pH of the ambient solution as suggested by the extension of polyelectrolyte complex membranes.[5–7] When weak polyelectrolytes are involved in the complex, the net charge fixed on the complex will be affected by pH because of the change in the degree of dissociation of functional groups. Because the ionization of functional groups plays an important role on the swelling of gels made of such monofunctional polymers as polyacrylate,[8] polyelectrolyte complexes may exhibit pH-sensitive swelling. However, the effect of pH on the swelling equilibrium of polyelectrolyte complexes has scarcely been reported. The information on the pH-sensitive swelling of polyelectrolyte complexes might bring novel materials to such application areas as drug delivery systems because pH-sensitive hydrogels have potential for use in oral drug delivery.[9] In such applications, low toxic substances should be used as the components of polyelectrolyte complexes.

Other possible application areas of polyelectrolyte complexes proposed are membranes for separation, microcapsules, coating films, medical implants, and support for catalysts.[2,3] However, it is not easy to make a desired object of a polyelectrolyte complex since polyelectrolyte complexes are obtained generally as precipitates of high water content. To prepare membranes,[5–7] for example, a tedious procedure including dissolution of complex precipitates in a certain solvent, casting, and evaporation of the solvent is needed. If an easily moldable complex gel can be made, it will be useful for these possible applications.

In this study, a polyelectrolyte complex gel in cy-

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lindrical shape is prepared from natural polysaccharides. κ-Carrageenan, which has sulfonate groups, is used as a polyanion component, and chitosan, which has amino groups, is used as a polycation component. With these two polyelectrolytes, strong acid–weak base type polyelectrolyte complexes will be obtained. To study the effect of ambient pH on the swelling equilibrium of the cylindrical complex gel, swelling experiments are performed in solutions of various pH values. The swelling experiments are also performed in the presence of NaCl at various pH because the salt concentration may affect the swelling equilibrium of the complex gel.

EXPERIMENTAL

Materials

Chitosan was obtained from Kimitsu Chemical Industries Co., Ltd., Tokyo, Japan. κ-Carrageenan was obtained from Dai-Nippon Pharmaceutical Co., Ltd., Osaka, Japan. These materials were used without further purification. Other materials were of analytical grade.

Polyelectrolyte Solutions

A solution of chitosan was prepared by dissolving 0.2 g of chitosan in 4.8 g of 1% acetic acid. A solution of κ-carrageenan was prepared by dissolving 0.2 g of κ-carrageenan in 4.8 g of distilled water at 70–80°C. To each solution, a specified amount of NaCl was added.

Preparation of Cylindrical Polyelectrolyte Complex Gel

A cylindrical polyelectrolyte complex gel was prepared as follows. The chitosan and the κ-carrageenan solutions, both of which contained NaCl, were heated and mixed in a boiling water bath. A cylindrical frame (4 mm in inner diameter and 8 mm in length) was put into the mixture. The mixture was centrifuged at 3000 rpm for 30 min to remove air bubbles, and kept at 5°C for 1 day. The cylindrical frame filled with the mixture was taken out and washed in distilled water for 2 days, replacing water each day. Sodium concentration in the waste water was measured with an atomic adsorption spectrophotometer (Hitachi Z-8100) to estimate the amount of NaCl retained in the gel. The polyelectrolyte complex gel in a cylindrical shape was obtained by removing the cylindrical frame.

Swelling Experiments

Swelling experiments for the cylindrical complex gel were performed by the following method, which is similar to that employed by Rička and Tanaka.[10] At first, the initial diameter of the cylindrical gel was measured. In a 300-mL Erlenmeyer flask, the gel was immersed in 150 mL of NaOH or HCl solution of specified concentration. This flask was filled with nitrogen gas, sealed to avoid the dissolution of CO_2, and stored at 5°C. After 24 h, the gel was taken out of the flask to measure its diameter. The gel was then repeatedly immersed for 48 h in 150 mL of the fresh solution under a nitrogen atmosphere until the diameter of the gel ceased to change. In each immersion, the difference between the initial and final values of solution pH was not more than 0.2 pH units. In some experiments, KOH was used instead of NaOH. To study the swelling equilibrium in the presence of salt, NaCl was added to the solution in which the gel was immersed.

Uptake of Na^+ by Swelling Complex Gel

To study the change in charge balance of the swelling complex gel, uptake of Na^+ by the gel was measured as follows. In a 50-mL Erlenmeyer flask, a piece of the cylindrical gel was immersed in 30 mL of NaOH solutions of specified concentrations. The flask was filled with nitrogen gas, sealed, and stored at 5°C. After 24 h, the concentration of Na^+ in the solution was measured with an atomic adsorption spectrophotometer (Hitachi Z-8100). The gel was then repeatedly immersed for 24 h in 30 mL of the fresh solution under a nitrogen atmosphere until the diameter of the gel ceased to change. The uptake of Na^+ by the gel was calculated from the difference between the initial and final concentrations in each immersion. The difference between the initial and final values of solution pH in each immersion was not more than 0.2 pH units.

RESULTS AND DISCUSSION

Preparation of Chitosan-κ-Carrageenan Complex Gel

To study the effect of NaCl addition on the preparation of complex gel, solutions of chitosan and κ-carrageenan, each containing 0, 3.8, or 5.7% NaCl, were tested for the gel preparation without using a cylindrical frame. The results are shown in Figure 1. When the solutions of chitosan and κ-carrageenan were mixed in the absence of NaCl, aggregates were

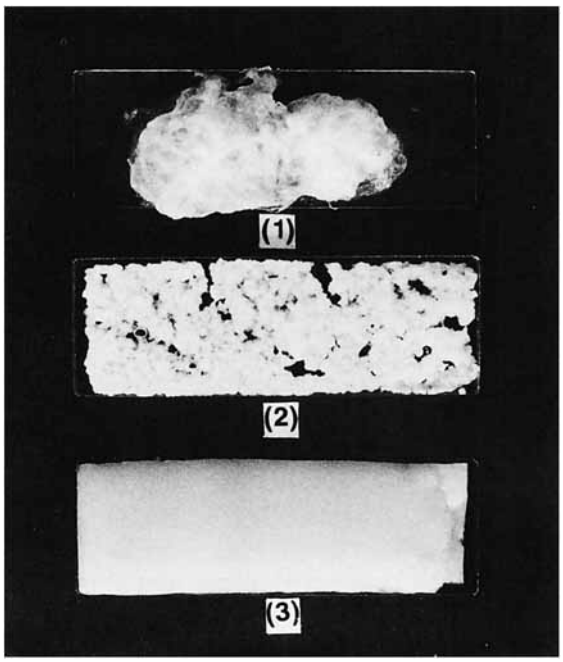

Figure 1 Effect of NaCl addition on the preparation of polyelectrolyte complex gel. Concentration of NaCl: (1) 0%; (2) 3.8%; (3) 5.7%.

formed immediately. Because the pK_a value of chitosan is 6.3,[11] amino groups of chitosan will be protonated, and hence positively charged, in 1% acetic acid (pH = 2.8). On the other hand, sulfonate groups of κ-carrageenan will be negatively charged when dissolved in distilled water. Therefore, the aggregation immediately after mixing the two polyelectrolytes in the absence of NaCl can be ascribed to the electrostatic attraction between the polyelectrolytes. The presence of Na^+ and Cl^- can reduce the electrostatic attraction between oppositely charged polyelectrolytes by contributing to the counterion atmosphere around the polyelectrolytes.[12] However, even in the presence of 3.8% NaCl, aggregated small particles were formed. In the presence of 5.7% NaCl, such phase separation did not occur, and a viscous and macroscopically homogeneous mixture was obtained. This mixture gelled as its temperature went down. In the following washing step, 60.3% of initially added Na^+ was removed from the gel. The removal of Na^+ and Cl^- from the mixture may restore the electrostatic attraction between chitosan and κ-carrageenan, resulting in polyelectrolyte complex formation.

From these results, the concentration of NaCl in the polyelectrolyte solutions was fixed to 5.7% for the preparation of the cylindrical complex gel.

Swelling Equilibrium of Complex Gel

Figure 2 shows swelling behavior of the cylindrical complex gel in NaOH solutions of various pH values. At pH 10.5, the swelling of the gel reached equilibrium in 6 days, and the equilibrium diameter was 2.2 times as large as the initial one. At any other pH, it took not more than 6 days for the complex gel to attain a swelling equilibrium. The length of the cylindrical gel also increased in each experiment. The ratio of the equilibrium length to the initial length agreed with that of the equilibrium diameter to the initial diameter within 4%. Thus, the swelling of the complex gel was isotropic. Consequently, the ratio of the equilibrium gel volume to the initial one, namely the equilibrium swelling ratio, was evaluated as (D_e/D_i),[3] where D_e and D_i are the equilibrium and initial diameters.

The equilibrium swelling ratio of the gel is shown in Figure 3 as a function of pH. In aqueous solutions of NaOH, the gel swelled from pH 10 to 12. The equilibrium swelling ratio was found to take the maximum value (10.2) at pH 10.5. When KOH solutions were used instead of NaOH solutions, swelling of the gel was also observed at pH 11 and at pH 12, although the equilibrium swelling ratio was smaller than that in the NaOH solution at the same pH. In the vicinity of neutral pH and in aqueous solutions of HCl, swelling of the gel was not observed.

Sato et al.[5] measured the extension of polyelectrolyte complex membranes composed of sulfated and aminoacetylyzed derivatives of poly(vinyl al-

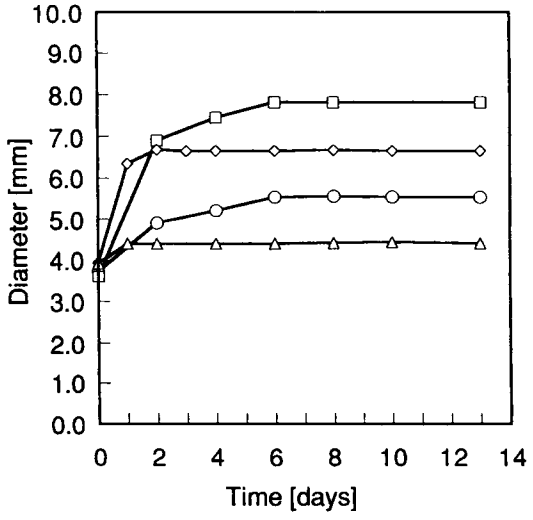

Figure 2 Swelling behavior of the chitosan-κ-carrageenan complex gel in NaOH solutions. pH of solution: (○) 10; (□) 10.5; (◇) 11; (△) 12.

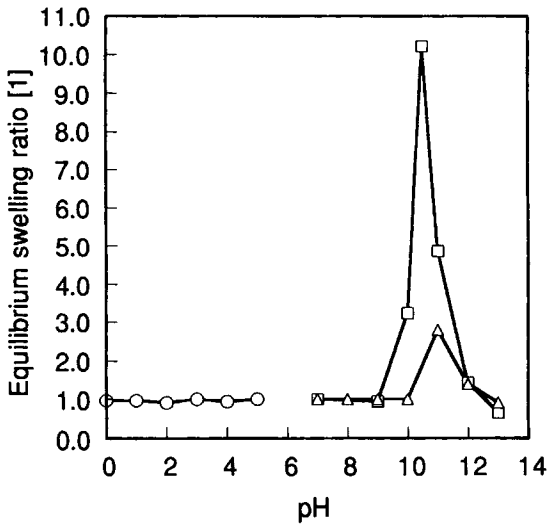

Figure 3 Equilibrium swelling ratio of the chitosan-κ-carrageenan complex gel. Ambient solution: (○) HCl aq.; (□) NaOH aq.; (△) KOH aq.

cohol) in HCl or NaOH solutions of pH 3–11. They showed that the length of the membrane under constant tensile stress increased monotonously with the increase in pH from 10 to 11. Although no tensile stress was applied to the complex gel in this study, a similar increase was observed up to pH 10.5 for the equilibrium swelling ratio in NaOH solution. At higher pH, however, the equilibrium swelling ratio was decreased with the increase in pH, indicating the existence of the swelling maximum. A swelling maximum has been also observed for a polyacrylamide–acrylic acid copolymer gel,[10] which swelled in the range of pH 7–12. Compared with the copolymer gel, the swelling of the complex gel prepared in this study occurred in a rather narrow range of pH.

A possible swelling mechanism for the complex gel is illustrated in Figure 4. The gel prepared in this study contained both sulfonate groups of κ-carrageenan and amino groups of chitosan. In the initial state, these two kinds of functional groups are considered to be oppositely charged and electrostatically bound to each other. In alkaline solution, the amino groups will be neutralized, and the sulfonate groups will remain negatively charged. Therefore, electrostatic linkage between the two functional groups will disappear, and the electrostatic repulsion between sulfonate groups will contribute to the swelling of the gel. Such electrostatic repulsion between the similarly charged groups is known to contribute to the swelling of crosslinked polymer gels.[13] In the acidic solution tested in this study, sulfonate groups will remain negatively charged, and the electrostatic

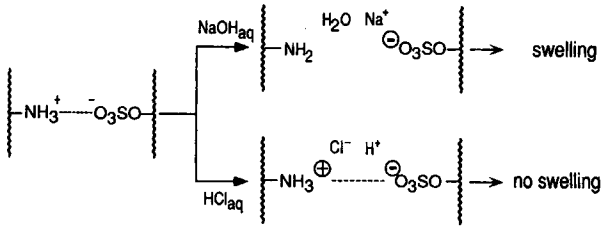

Figure 4 Swelling mechanism of the chitosan-κ-carrageenan complex gel.

bond between the two functional groups will not disappear, resulting in no swelling.

According to the swelling mechanism mentioned above, the gel could swell at pH higher than the pK_a of chitosan (6.3). However, the gel did not swell even at pH 9. This discrepancy may be because of the difference between internal and external pH values. If the gel gets negatively charged even slightly, OH^- may be excluded from the gel.

In NaOH solutions of pH above 10.5, and in KOH solutions of pH above 11, the equilibrium swelling ratio decreased with the increase in pH. It may be ascribed to the increase in Na^+ or K^+ concentration with the increase in pH. An excess of Na^+ or K^+ will shield the electrostatic repulsion between the sulfonate groups to decrease the equilibrium swelling ratio of the complex gel. In the KOH solution, the equilibrium swelling ratio of the gel was smaller than that in the NaOH solution. Because K^+ has the stronger affinity than Na^+ for sulfonate groups,[13]

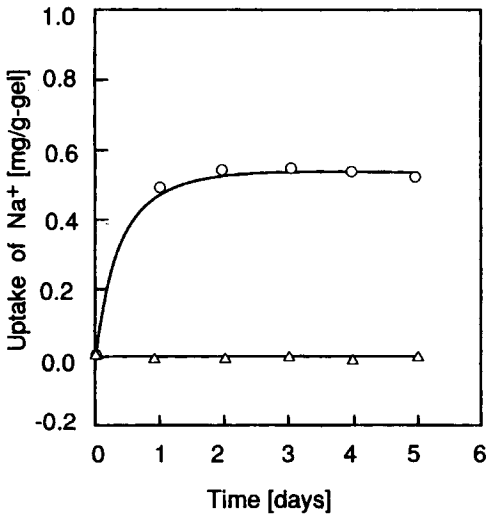

Figure 5 Uptake of Na^+ by the chitosan-κ-carrageenan complex gel in NaOH solutions. pH of solution: (○) 11; (△) 7.

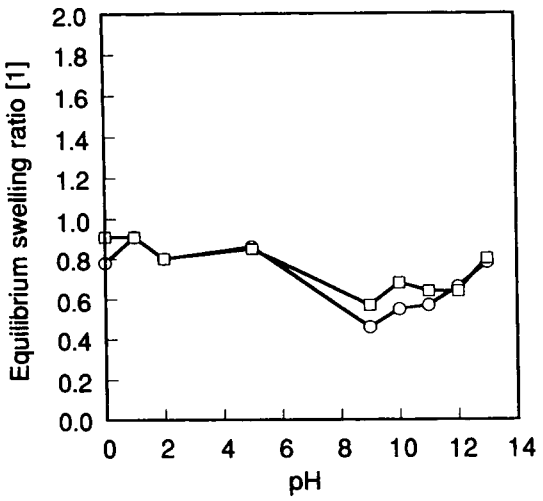

Figure 6 Equilibrium swelling ratio of the chitosan-κ-carrageenan complex gel in NaOH or HCl solutions containing NaCl. Concentration of NaCl: (○) 4%; (□) 6%.

K^+ might reduce the electrostatic repulsion between sulfonate groups more effectively than Na^+.

Figure 5 shows the uptake of Na^+ by the complex gel immersed in NaOH solutions of different pH values. In NaOH solution of pH 11, Na^+ was taken up by the gel for 2 days, and no more uptake was observed in the following immersion. The time course of Na^+ uptake at pH 11 was quite similar to that of the diameter change at pH 11 shown in Figure 2. On the other hand, neither swelling nor Na^+ uptake was observed at pH 7. These results suggested the increase in the net negative charge in the gel during its swelling, and supported the swelling mechanism discussed above.

Figure 6 shows the equilibrium swelling ratio of the complex gel in aqueous NaOH or HCl solutions containing NaCl. At any pH, the equilibrium swelling ratio was less than 1 in the presence of 4 or 6% NaCl. This may be because of the high osmotic pressure of the ambient solutions. However, the equilibrium swelling ratio was somewhat smaller at pH 9–12 than that at other pH, though the osmotic pressure of the ambient solution was considered as approximately constant in the specified concentration of NaCl. Further study is needed to discuss the effect of salt concentration on the swelling behavior of the complex gel.

CONCLUSIONS

A moldable complex gel was prepared by mixing chitosan and κ-carrageenan solutions in the presence of sufficient NaCl. The complex gel swelled in an isotropic manner at ambient pH 10–12, and the swelling maximum was observed in NaOH solution of pH 10.5. Thus, the swelling of the complex gel was revealed to be sensitive to a rather narrow range of pH. The equilibrium swelling ratio was affected also by the kind of alkali. In the presence of 4 or 6% NaCl, however, the complex gel contracted at any pH.

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