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Effects of Saccharides and Sulfonic Acid Group on Water Absorption Ability of Cross-linked Polyacrylic Acid

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1. Introduction

Water absorbing resins have numerous uses such as sanitary supplies, soil conditioners, and artificial eye lens. Graft polymers of starch or cellulose with acrylic acid or acrylamide are typical natural-synthetic composite materials whose water absorption ability is considered to be enhanced by a combination of high ionic strength of synthetic polymer and van der Waals and hydrogen bonding forces of natural polymer¹⁻⁴. We have conceived the idea that introduction of constituent units of natural polymers into net-works of cross-linked synthetic polymers may enhance their water absorbing power. We have thus synthesized cross-linked polyacrylic acid including several saccharides such as glucose, maltose, and cyclodextrins to estimate the effects of the saccharides on water absorption abilities.

On the other hand, usual water absorbing resins are known to lose much of their water absorption abilities when metal ions are contained in the water. We think that this point may be improved by introduction of sulfonic acid group into the polymer because of its higher ionic strength and also weak bonding ability to metal ions. We have thus synthesized cross-linked copolymer of acrylic acid and 3-sulfopropyl acrylate including saccharides to estimate the effects of sulfonic acid group and saccharides on water absorption abilities in 0.9 % sodium chloride solution.

2. Experimental

2.1 Reagents

3-Sulfopropyl acrylate was supplied from Sigma-Aldrich Corp.. Other reagents and solvents were supplied from Wako Pure Chemical Industry Ltd.. Solvents were purified by usual procedures.

2.2 Synthesis of cross-linked polyacrylic acid in the presence of saccharides

Into 20 ml of distilled water were placed 2 ml ($M_w=72.06$, 29 mmol) of acrylic acid, 10 mg ($M_w=154.17$, 0.065 mmol) of N, N'-methylene bisacrylamide, 50 mg ($M_w=288.35$, 0.18 mmol) of 2, 2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], and saccharides, and the mixtures were stirred without N_2 gas at 80°C for 8 hrs. The precipitates were collected, dried for 3 hrs, and pulverized. The powders were suspended in 100 ml of 1N-sodium hydroxide solution, the mixtures were stirred for 1 hr, and then into the mixtures was added 200 ml of methanol to give the precipitates which were collected, dried, and pulverized. The yields over 90% were given.

2.3 Synthesis of cross-linked copolymer of acrylic acid and 3-sulfopropyl acrylate in the presence of sccharides

Into 20 ml of distilled water were placed 2 ml (29 mmol) of acrylic acid, 10 mg (0.065 mmol) of N, N'-methylene bisacrylamide, 50 mg (0.18 mmol) of 2, 2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 3-sulfopropyl acrylate ($M_w=194.21$), saccharides, and 1 ml of 10N-hydrogen chloride solution, and the mixtures were stirred without N_2 gas at 80°C for 6 hrs. After-treatments of the precipitates were done in the same way described above. The yields over 90% were given.

2.4 Drying and pulverization of polymers

Polymers were dried in Yamato Kagaku DC-34 drying oven and were pulverized by using Shibata

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Kagaku Personal Mill SCM-40.

2.5 Water absorption test

In a 100 ml bottle was placed the dried polymer and distilled water or 0.9% sodium chloride solution, and the mixture was stood overnight. The polymers swelled without phase separation. The mouth of bottle was covered with non-woven cloth, and the bottle was turned upside down and stood overnight. The amount of water absorption was estimated by the equation.

Amount of water absorption (g of water/g of polymer)

= g of swollen polymer gel/g of dried polymer

3. Results and discussion

At first, the effect of the amount of crosslinking agent on the amount of water absorption was examined and it was found that a maximum amount of water absorption was observed for the polymer obtained in the polymerization of 2 ml (29 mmol) of acrylic acid in the presence of 10 mg (0.065 mmol) of N, N'-methylene bisacrylamide. Hereafter, the polymerizations were done under the same condition.

3.1 Effects of saccharides on water absorption ability

Cross-linked polyacrylic acid including glucose, maltose, and cyclodextrins was synthesized. **Fig. 1** shows the effects of saccharides on the amounts of water absorption in distilled water, indicating that the amount of water absorption increased by introduction of saccharides into the polymer and varied by changing both kinds and additive amounts of saccharides. Especially, an addition of 0.15 g (0.44 mmol) of maltose showed the highest amount of water absorption which is a value 4.3 times as much as that obtained in the absence of saccharide. To examine if saccharide was introduced in the polymer, the filtrate of the reaction mixture obtained in the presence of maltose was subjected to spectrometry to show that maltose was scarcely included in the filtrate. This finding suggests that maltose is trapped in the networks of the polymer to contribute an enhancement of water trapping.

Fig. 2 shows the results of water absorption tests in 0.9% sodium chloride solution. The amounts of water absorption decreased sharply in comparison with that observed in distilled water, however maltose again most effectively increased the amount of water absorption.

Fig. 1 Effects of saccharides on water absorption ability of cross-linked polymer (distilled water)

Fig. 2 Effects of saccharides on water absorption ability of cross-linked polymer (0.9% NaCl aq.)

3.2 Effect of sulfonic acid group on water absorption ability

Cross-linked polyacrylic acid copolymerized with 3-sulfopropyl acrylate was synthesized and was subjected to water absorption test. As shown in **Fig. 3**, an addition of 2 mmol of 3-sulfopropyl acrylate showed the maximum amount of water absorption, hereafter the polymerizations were done under the same condition.

Cross-linked copolymerization of acrylic acid and 3-sulfopropyl acrylate was carried out in the presence of glucose, maltose, and cyclodextrins. **Fig. 4** shows

Fig. 3 Effect of sulfonic acid group on water absorption ability of cross-linked polymer

Fig. 4 Effects of saccharides on water absorption ability of cross-linked polymer containing sulfonic acid group (distilled water)

the results of water absorption tests of these polymers in distilled water. Almost the same water absorption abilities as those observed in Fig. 1 were obtained, however, an addition of 0.15 g of maltose again showed the most effective ability which was 3.8 times as much as that obtained in the absence of saccharide.

Fig. 5 shows the results of their water absorption tests in 0.9% sodium chloride solution. By comparison of the results obtained in the absence of saccharides (Fig. 2 and 5), introduction of the sulfonic acid group resulted in 1.7 times as much water absorption as that obtained in its absence. Here again, the introduction of saccharides increased the water absorption abilities and in case of adding 0.15 g of maltose 3.9

Fig. 5 Effects of saccharides on water absorption ability of cross-linked polymer containing sulfonic acid group (0.9% NaCl aq.)

times as much water absorption as that obtained in the absence of saccharide was detected. Comparison with the results obtained in the absence of saccharides and sulfonic acid group revealed that the introduction of both maltose and sulfonic acid group increased the ability 6.6 times. Polyacrylic acid showed the water absorption ability of 285 g H₂O/g in pure water, while the maltose and sulfonic acid containing polymer had the water absorption ability of 185 g H₂O/g in the sodium chloride solution. Thus, the water absorption ability of the co-introduced polymer in 0.9% sodium chloride solution showed a value 2/3 that observed for polyacrylic acid in pure water.

In conclusion, water absorption ability of cross-linked polyacrylic acid was found to increase by introduction of saccharides, and co-introduction of sulfonic acid group improved the water absorption ability in 0.9% sodium chloride solution.

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