

Superabsorbent Poly(acrylic acid) Complex

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SYNOPSIS

Acrylic acid and crosslinking agent [poly(ethylene glycol)-diacrylate or divinylbenzene] were copolymerized in benzene in the presence of layered sodium silicate (δ - $\text{Na}_2\text{Si}_2\text{O}_5$) powder. The resultant poly(acrylic acid) complex shows large water absorbability, for which dependency on crosslinking degree was investigated. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Many investigators have been studying various superabsorbent polymers.¹⁻⁷ Recently, superabsorbent polyacrylate has been used in various ways.⁸ To prepare the polyacrylate, water must be used, because Na-acrylate should be incorporated into the polyacrylate network to get a large degree of water absorbability. However, the exclusion of water from the resultant polyacrylate gel is energy consuming because water has a relatively larger heat of evaporation and the polyacrylate is hydrophilic.

We have found a new way to prepare a superabsorbent poly(acrylic acid) complex. Namely, acrylic acid and a crosslinking agent, such as poly(ethylene glycol)-diacrylate ($n = 9$, EGDA-9) or divinylbenzene (DVB), were copolymerized in an organic solvent in the presence of an inorganic powder which releases Na^+ in water. Here, the solvent is compatible with the monomers but not with poly(acrylic acid).

In this article we report on the preparation of superabsorbent poly(acrylic acid) complexes: Acrylic acid and EGDA-9 or DVB were copolymerized in benzene in the presence of layered sodium silicate (δ - $\text{Na}_2\text{Si}_2\text{O}_5$) powder. Water absorbability of the poly(acrylic acid) complexes was estimated in relation to the crosslinking degree.

EXPERIMENTAL

Materials

All reagents used were of commercial grade. The average molecular weight of EGDA-9 was 508 and the purity of DVB, a mixture of isomers of DVB and ethylstyrene, was 55%. Initiator of radical polymerization was a redox system: benzoylperoxide (BPO)-*p*-toluyl-diethanolamine (PTEA). The average particle size of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ was 120 μm .

Preparation of Poly(acrylic acid) Complex

A definite amount of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ (15 g) was put into a separable flask (500 mL) containing benzene (150 mL) and evacuated to exclude O_2 from the δ - $\text{Na}_2\text{Si}_2\text{O}_5$. Thereafter, some amount of benzene was added to make its volume 150 mL. Subsequently, acrylic acid (15 g), a definite amount of the crosslinking agent, BPO (0.3 g), PTEA (0.3 g), and benzene (150 mL) were added. The copolymerization was carried out at 40°C with stirring under N_2 atmosphere. The resultant powdery poly(acrylic acid) complex was filtered and dried under reduced pressure.

Measurement

Powdery sample (0.5 g) was put into deionized water or 0.9% NaCl solution (300 mL) overnight at room temperature. Then the swollen gel was filtered with the aid of three piled sieves (openings 22, 38, and 63 μm) and weighed. The pH of the solution was

measured by using a pH meter (pH boy-P1 from Shindengen Kogyo Co., Ltd.).

Scanning Electron Microscopy

The poly(acrylic acid) complex was observed with the aid of a scanning electron microscope (SEM), JSM-840F from JEOL Ltd. The sample was pre-treated by Pt-ion sputtering with the aid of a magnetron sputter coater (JUC-5000 from JEOL Ltd.).

RESULTS AND DISCUSSION

The poly(acrylic acid) complexes were prepared by copolymerizing acrylic acid and the crosslinking agent in benzene in the presence of powdery δ - $\text{Na}_2\text{Si}_2\text{O}_5$. The appropriate molar ratio of (Na in δ - $\text{Na}_2\text{Si}_2\text{O}_5$ /acrylic acid) was preliminarily elucidated to be 0.5–0.8. The monomers are soluble in benzene, but poly(acrylic acid) is not. Then the propagating polymer radicals separate out and the use of the crosslinking agent promotes the phase separation. The resultant polymer particles deposit on the surface of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ particles. Figures 1 and 2 show scanning electron micrographs of the δ - $\text{Na}_2\text{Si}_2\text{O}_5$ particles and the poly(acrylic acid) complexes, respectively. Evidently, the aggregates of very fine poly(acrylic acid) particles deposit on the surface of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ particles, and there is some naked surface. This supports the formation process of the poly(acrylic acid) complex described earlier.

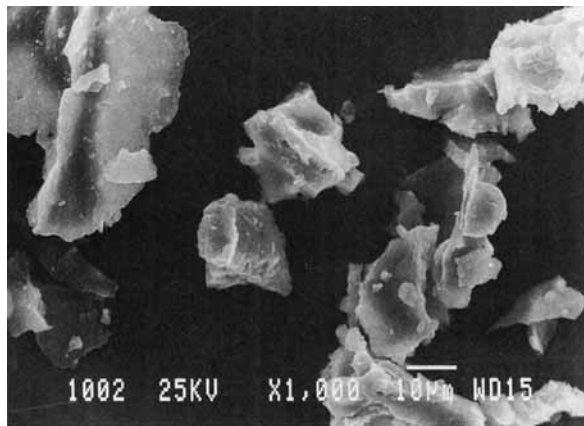


Figure 1 Scanning electron micrograph of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ particles.

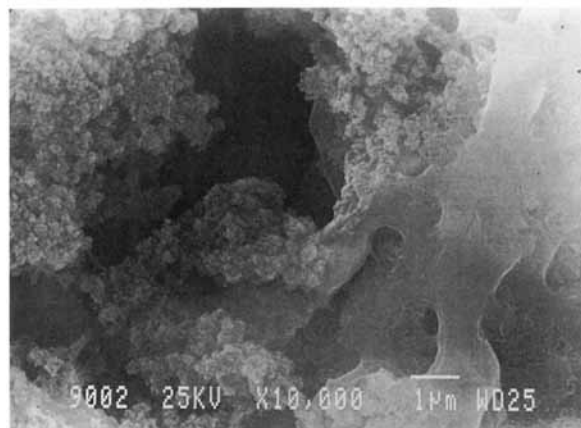
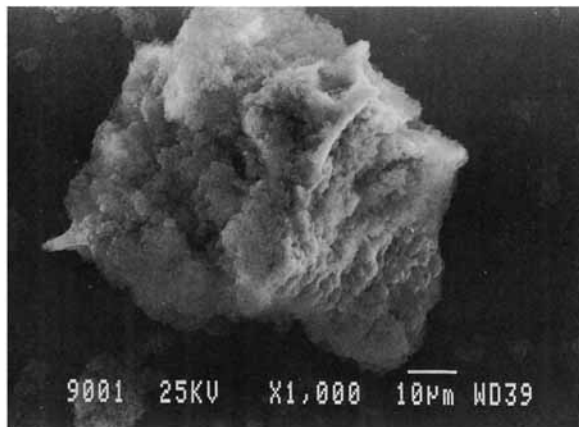


Figure 2 Scanning electron micrograph of a poly(acrylic acid) complex particle.

Acrylic Acid-EGDA-9- δ - $\text{Na}_2\text{Si}_2\text{O}_5$ System

Figures 3 and 4 show the dependencies of monomer conversion, pH of the solution, and absorbency onto the crosslinking degree (molar ratio of EGDA-9/acrylic acid in the recipe) when the poly(acrylic acid) complexes were put into deionized water and 0.9% NaCl solution, respectively. Here,

Absorbency of poly(acrylic acid)

component (g/g polymer)

= absorbency of the complex (g/g complex)

$$\times \frac{\text{yield}}{\text{yield} - \text{weight of } \delta\text{-Na}_2\text{Si}_2\text{O}_5}$$

The monomer conversion increases with increasing the crosslinking degree in the region less than EGDA-9/acrylic acid = 1.5×10^{-2} (molar ratio). This shows that the increase of the EGDA-9 content

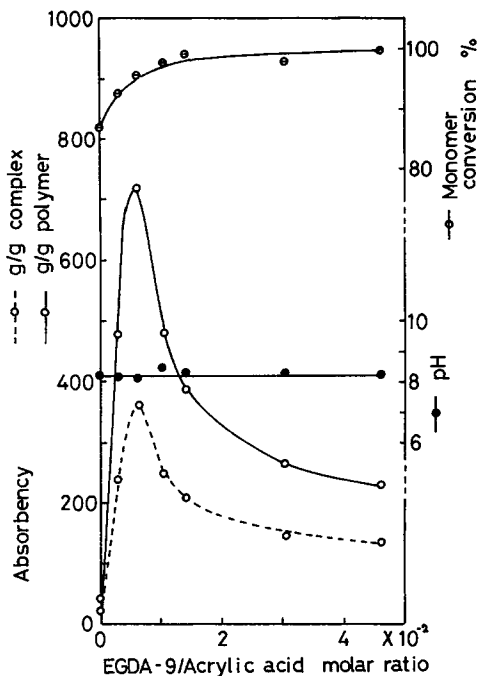


Figure 3 Effect of crosslinking degree to monomer conversion, absorbency, and pH in deionized water.

in the recipe accelerates the copolymerization in this region, and the copolymerization does not complete in 1 h. The pH values are constant in both the cases of deionized water and 0.9% NaCl solution, and the pH values in the case of deionized water are larger than those in the case of 0.9% NaCl solution. As soon as the poly(acrylic acid) complex comes into contact with water, the δ - $\text{Na}_2\text{Si}_2\text{O}_5$ component release Na^+ , which ionizes some part of the acrylic acid unit of the complex. Accordingly, the complex absorbs much more water in deionized water, and in 0.9% NaCl solution the presence of NaCl suppresses the dissociation of acrylate unit, so the absorbency becomes smaller. Regarding the absorbency, there are maximum points at the crosslinking degree less than 1×10^{-2} (molar ratio in the recipe). When the crosslinking degree is less than that at the maximum point, some amount of soluble polymer was observed in deionized water but not in 0.9% NaCl solution. Also, the maximum point in the case of 0.9% NaCl solution moves to the smaller crosslinking degree. When the crosslinking degrees are larger than that at the maximum points, the absorbencies reasonably decrease with increasing crosslinking degree. Furthermore, the absorbencies in the case of 0.9% NaCl solution are reasonably smaller than those in the case of deionized water, due to the salt effect of suppressing the dissociation of the ac-

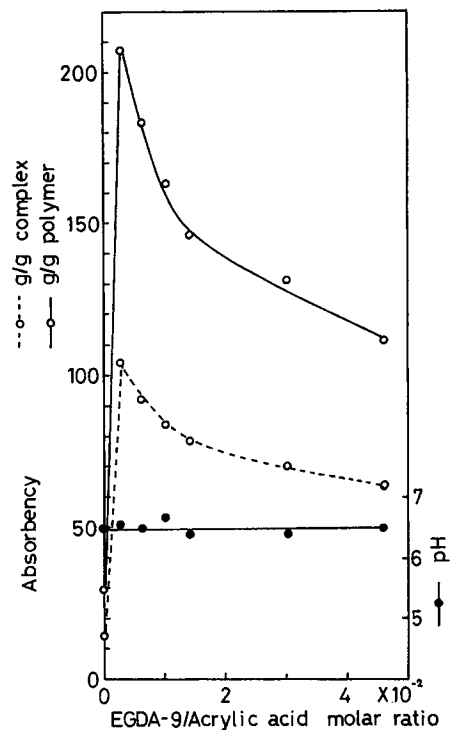


Figure 4 Effect of crosslinking degree to absorbency and pH in 0.9% NaCl solution.

rylate unit—namely, the swelling of the polyacrylate network.

Acrylic Acid-DVB- δ - $\text{Na}_2\text{Si}_2\text{O}_5$ System

Figures 5 and 6 show the dependencies of the monomer conversion, pH of the solution, and absorbency

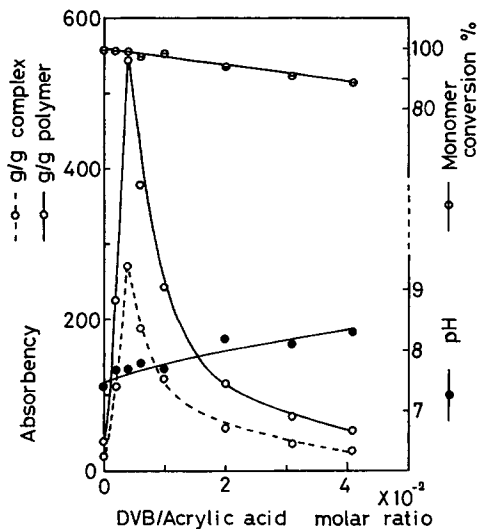


Figure 5 Effect of crosslinking degree to monomer conversion, absorbency, and pH in deionized water.

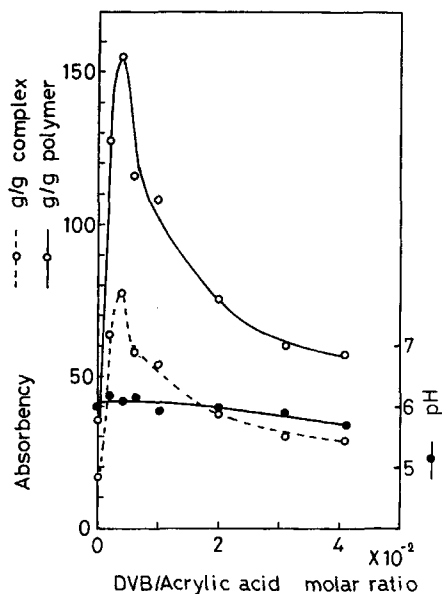


Figure 6 Effect of crosslinking degree to absorbency and pH in 0.9% NaCl solution.

on the crosslinking degree (molar ratio of DVB/acrylic acid in the recipe) when the poly(acrylic acid) complexes were put into deionized water and 0.9% NaCl solution, respectively.

The monomer conversion decreases with increasing crosslinking degree. This is probably attributable to occlusion of the propagating polymer radical in the crosslinked polymer network, which hinders approach of the diffusing monomers. We have already reported a similar situation for the copolymerizations of glycidylmethacrylate-DVB and glycidylmethacrylate-methylmethacrylate-DVB in cyclohexane.^{9,10} The tendencies of absorbency are similar to those of the acrylic acid-EGDA-9 system, although the absorbencies are smaller than those of the acrylic acid-EGDA-9 system. The crosslinking degree to endow the maximum absorbencies is smaller than that shown in Figure 3 and larger than that shown in Figure 4. This should be due to the difference in the crosslinking behavior of EGDA-9 and DVB, but the details are obscure. The pH value increases with increasing crosslinking degree in the case of deionized water. This is probably due to the decrease of the monomer conversion, which means the decrease of the content of acrylic acid unit in the complex. Furthermore, the dissociation degree of the acrylate unit is affected by the crosslinking degree, especially in 0.9% NaCl solution. Then the pH value slightly decreases with increasing crosslinking degree, and the pH values in the case of 0.9%

NaCl solution are smaller than those in the case of deionized water, because NaCl suppresses the dissociation of the sodium acrylate unit. It is interesting that the crosslinking behavior of DVB is presumed to be fairly different from that of EGDA-9. Namely, the distance between the crosslinking points of DVB is shorter than that of EGDA-9, so DVB makes the resultant polymer network tighter. Accordingly, the absorbencies of the acrylic acid-EGDA-9 system are larger than those of the acrylic acid-DVB system when the crosslinking degrees are same.

When the poly(acrylic acid) complexes are swollen in water, no powdery δ - $\text{Na}_2\text{Si}_2\text{O}_5$ can be detected in the resultant gel by visual observation. Accordingly, the state of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ particles in the swollen gel was investigated with the aid of scanning electron microscopy. Namely, a small amount of the swollen gel was put on a sample disc and dried. Figure 7 shows the scanning electron micrographs of the

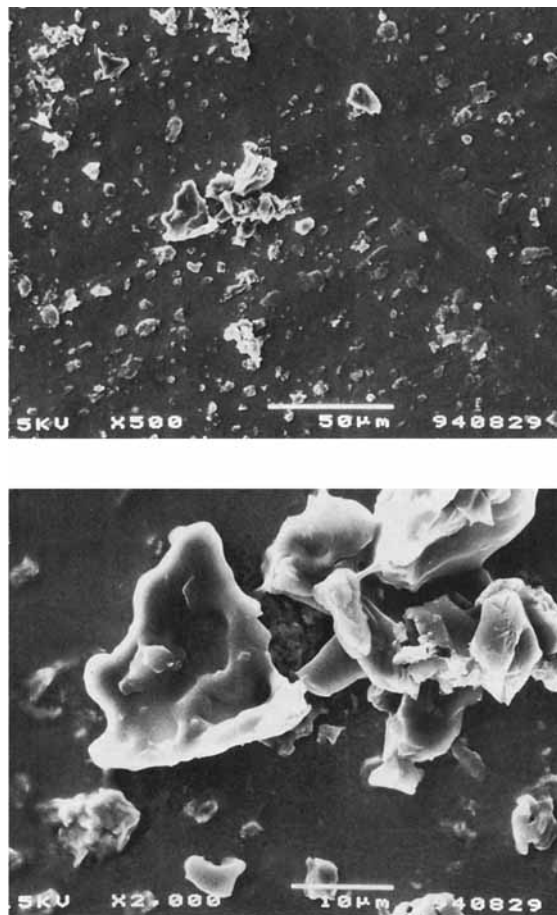


Figure 7 Scanning electron micrograph of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ particles in crosslinked polyacrylate, prepared from swollen gel by drying.

sample prepared from the swollen gel. Evidently, δ - $\text{Na}_2\text{Si}_2\text{O}_5$ particles are observed, which are coated by the polymer component and seem not to be deformed. Therefore, it is elucidated that δ - $\text{Na}_2\text{Si}_2\text{O}_5$ plays a role as the carrier of Na^+ and the poly(acrylic acid) component.

CONCLUSION

Superabsorbent polymer complexes are prepared by copolymerizing acrylic acid and crosslinking agent [poly(ethylene glycol)-diacrylate or divinylbenzene] in benzene in the presence of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ powder as an Na^+ carrier. The resultant poly(acrylic acid) complexes have a large degree of water absorbency. It is elucidated that the crosslinking behavior of poly(ethylene glycol)-diacrylate is different from that of divinylbenzene.

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