Salt and pH Responsive Property of a Starch-Based Amphoteric Superabsorbent Hydrogel with Quaternary Ammonium and Carboxyl Groups (II)

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ABSTRACT: Swelling behaviors of a starch-based amphoteric superabsorbent hydrogel cationic starch/sodium acrylate (CAS/AA) with quaternary ammonium and carboxyl groups were studied by immersion of the gels in various salt and pH solutions. It was found that swelling behaviors are heavily dependent of feed composition. Besides, it is also sensitive to pH, the concentration, and the ionic charge of the saline solution, but not to temperature. A kinetic study disclosed that the water transport mechanism in the CAS/AA was controlled by polymer relaxation. CAS/AA gels showed a good reversibility in the 0.9% NaCl solution after repeating the absorb-dry process for more than 20 times. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1995–1999, 2006

Key words: hydrogel; swelling; graft copolymer; kinetic

INTRODUCTION

Stimuli-responsive hydrogels have received much attention during the last few decades for applications in bioseparation, medicine, and pharmaceutical fields. These stimuli include temperature,[1–3] pH,[4,5] pressure,[6] and electric field.[7,8] Grafting copolymerization of starch with vinyl monomers (acrylamide, acrylonitrile, acrylic acid) has gained importance in improving some properties of synthetic absorbent polymer, and shown their immense industrial potential with their biodegradability, low cost, and renewability.[9–13] However, so far, more attention is put in the grafting products of original starch.[14–17] Long back in 1976, Masuda et al. obtained water absorbency as high as 219 mL/g of water and 58 mL/g of 0.5% NaCl solution by preparing a hydrogel based on starch grafted with acrylic acid. Some new synthetic ways, like suspension polymerization,[18] or new crosslinkers, such as trimethylol propane triacrylic ester,[19] are applied to improve the water absorbency. Liu[20] reported that cationic copolymer poly(ethylene oxide-ethyleneimine) shows good salt-tolerant property with 50 g/g adsorption capacity in 0.5% NaCl solution. Recently, it is interestingly reported that amphoteic absorbent polymers, compared with the one only with anionic or cationic charges, have the potential salt-tolerant swelling character.[21] In the previous study, we have prepared a series of cationic starch grafting copolymers, which fabricate the amphoteric networks by introducing quaternary ammonium and carboxyl groups. They show good swelling ability and thermal stability.[22] Besides, the products are degradable, causing fewer environmental problems than most synthetic substances. Cationic starch, obtained by etherisation of starch, has been recently used in biomedical and pharmaceutical fields because of its favorable characteristics such as nontoxicity, biocompatibility, biodegradability, and low cost. On the basis of above work, in this article, we tried to give more attention on the reversibility, salt, as well as pH responsive property of amphoteric hydrogel.

EXPERIMENTAL

Materials

Sodium chloride, calcium chloride, ferric chloride, hydrochloric acid, sodium hydroxide, *N, N'*-methylenebisacrylamide (MBAM), acrylic acid, ammonium perdisulfate (analytical reagent grade) were used as received without further purification.

The preparation of the cationic starch has been reported in previous work.[22] Neutralized sodium acrylate solution was firstly prepared by slowly dropping acrylic acid into a flask containing 40% NaOH solution with strong stirring at 0°C (cooled in ice-water bath).

Two gram of the above cationic starch was dissolved in certain amount of deionized water. The starch solution was poured into 250 mL four-neck flask, which was equipped with a mechanical stirrer, reflux condenser, and purged with nitrogen. Then, the monomer AA (varying the dose, 10 mL, 20 mL, and 30 mL, respectively) and crosslinker MBAM (0.02% monomer weight) were added followed by an ammonium perdisulfate solution (2.5% monomer weight). The reaction was carried out at 60°C for 3 h. The resulting product was washed for several times with the deionized water, followed by acetone to remove unreacted monomer and homopolymer, then dried at 50°C.

Nitrogen content is measured by element analysis PE-2400CHN. Hence, the degree of substitution (DS) of quaternary ammonium cationic groups in the copolymer samples was calculated by the equation below[23]

$$DS = \frac{162 \times N\%}{1400 - 152 \times N\%}$$

where N% is the nitrogen content.

Measurement of the swelling capacity of hydrogels

The swelling ratios of the hydrogels were measured over a range of temperatures (35–65°C) in deionized water and solutions of NaCl, $CaCl_2$, and $FeCl_3$ under different concentration using teabag method. After swelling reached equilibrium, water sticking to the surface of teabag was removed, and then the weights of the swollen hydrogels were recorded. The swelling capacity (Q, g/g)) is defined as:

$$Q = (w - w_0)/w_0 \qquad (1)$$

where w_0 (g) and w (g) are the weights of dry and swollen hydrogel, respectively.
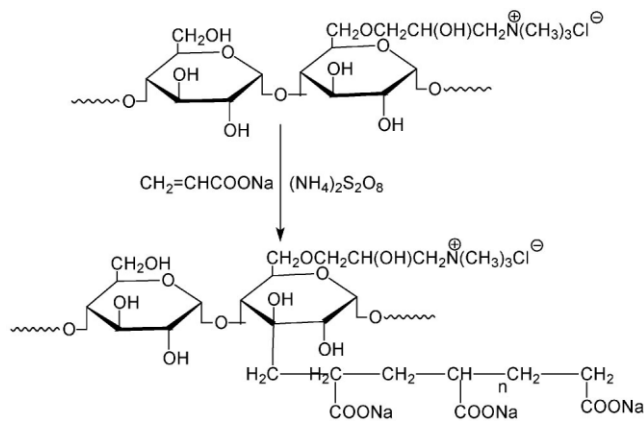
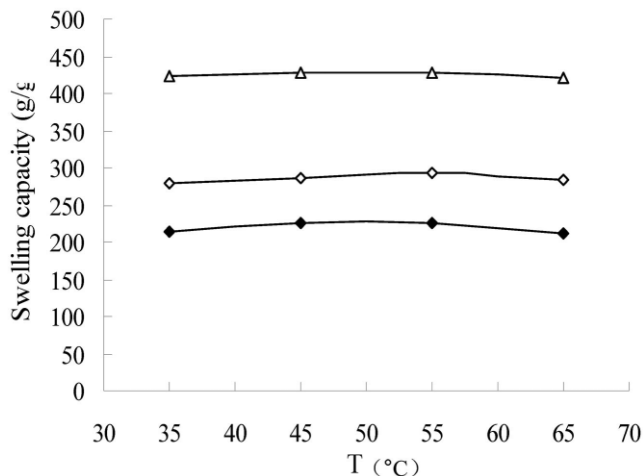Scheme 1   Grafting copolymerization of cationic starch with AA.

Figure 1   Effect of temperature on swelling capacity. ♦, 10 mL AA; ◇, 20 mL AA; △, 30 mL AA.

Swelling kinetics

Dry hydrogel granules (0.1 g) were immersed in 200 mL deionized water at room temperature, and the swelling was measured by weighting the samples at different time intervals.

RESULTS AND DISCUSSIONS

The proposed grafting copolymerization of cationic starch (DS 0.22) involved in the above process is shown in the following Scheme 1:

Effect of temperature on the swelling of CAS/AA hydrogels

The temperature dependency of the swelling ratio in deionized water for cationic starch/sodium acrylate (CAS/AA) hydrogels is shown in Figure 1. It can be seen that CAS/AA hydrogels have stable swelling in a wide range of temperature. The swelling of hydrogel is above 400 g/g, even at 65°C. The results also indicate that the greater the AA content, the higher the hydrophilicity of the gel, which is attributed to the incorporation of more carboxyl groups, which increases the hydrophilicity of the network and provides a greater "driving force" (osmotic pressure) for the water sorption process. In turn, it leads to a high equilibrium swelling degree.

Swelling kinetics of CAS/AA hydrogels

A preliminary study was conducted on the hydrogel swelling kinetics. Figure 2 represents the dynamic swelling behaviors of CAS/AA superabsorbent samples with certain particle size (100 mesh) in deionized water. Initially, the rate of water uptake sharply increases and then tends to level off. The equilibrium
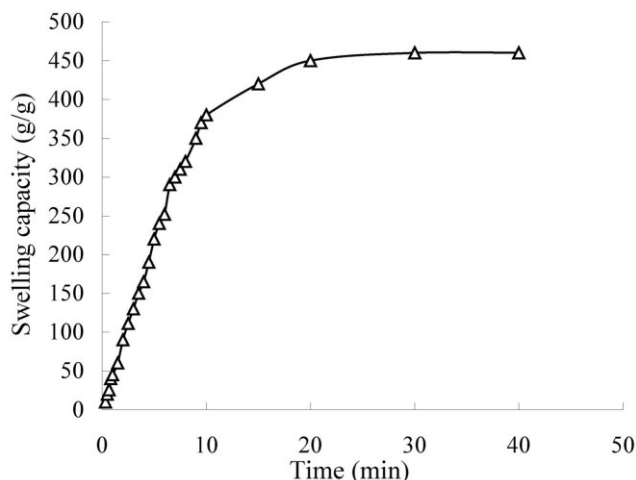
Figure 2 Swelling kinetics of CAS/AA hydrogel at 25°C.

swelling was achieved after 20 min at 25°C. The initial swelling data are fitted to the exponential equation[24]:

$$\frac{M_t}{M_\infty} = Kt^n \text{ for } \left(\frac{Mt}{M\infty} \leq 0.6\right)$$

where K is a characteristic constant of the hydrogel and n is a kinetic exponent of the mode of solute transport. Values of n and K are calculated from the slopes and intercepts of the plot of $\log(Mt/M\infty)$ versus $\log(t)$. For granule samples, if $n = 0.5$, the swelling is Fickian diffusion; n is between 0.5 and 1.0 for non-Fickian diffusion; $n = 1.0$ for case II diffusion; and n is >1 for supercase II diffusion. Table I shows K, n, and D values for the CAS/AA hydrogel with 30 mL AA feed composition. For CAS/AA copolymeric hydrogel, $n = 1.02$, which indicates the swelling transport mechanism is supercase II type. It can be concluded that water transport is controlled by polymer relaxation process. In the case of amphoteric gels, the polymer relaxation is significantly affected by the ionization degree of the functional groups.[25] The electrostatic repulsion between adjacent carboxyl groups or ammonium groups leads to macromolecular chain expansion, making the mechanism more relaxation-controlled.

Swelling behavior in salt solutions

The swelling of CAS/AA hydrogels in saline solutions is illustrated in Figures 3–5. In very dilute salt solu-

TABLE I
The Kinetic Parameters for CAS/AA Hydrogel at 25°C

Hydrogel	K	n	R^a
CAS/AA	0.088	1.0202	0.9957

^{a} R, correlation coefficient.

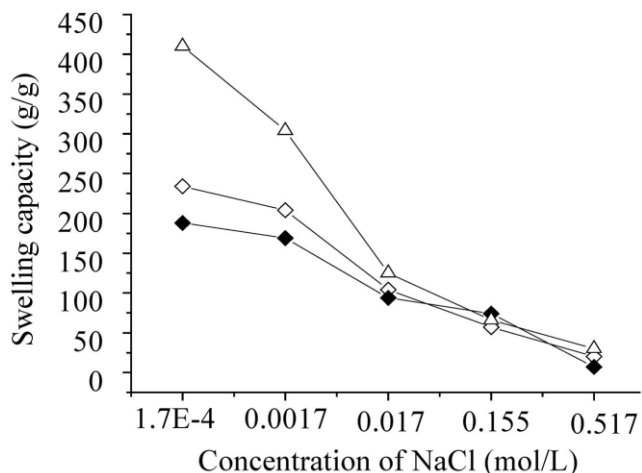**Figure 3** Effect of NaCl concentration on swelling of CAS/AA hydrogels. ◆, 10 mL AA; ◇, 20 mL AA; △, 30 mL AA.

tion, the swelling ratio remains almost constant. As the salt concentration increases, the hydrogel swelling decreases, The decrease of swelling ratio is just caused by the reduction of chemical potential of water with the addition of salt, as well as the screening effect shielding of the anionic or cationic charge of the additional cations or anions causing a feeble anion–anion electrostatic repulsion, leading to a decreased osmotic pressure. Figures 3–5 also show that hydrogels with higher feed composition of AA from 10 mL to 30 mL have higher swelling ratios since the incorporation of AA increases the hydrophilicity of the hydrogel. The swelling reaches 64 g/g in 0.9% NaCl solution for hydrogel with 30 mL AA of feed composition. However, no obvious polyampholyte behaviors were observed among three polymer hydrogels.[25] This may be because the added salt may not break the interchain
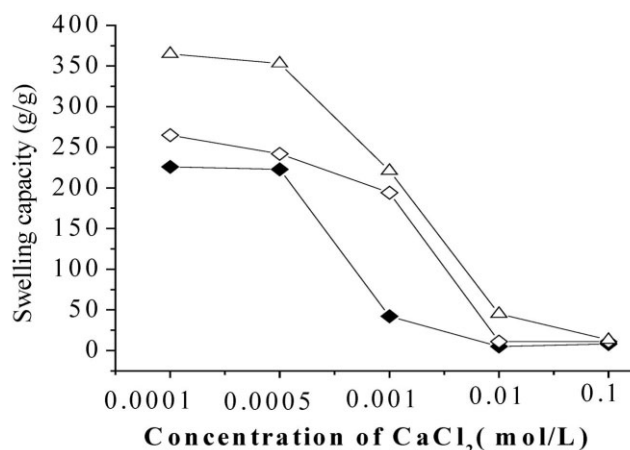

Figure 4 Effect of CaCl$_2$ concentration on swelling of CAS/AA hydrogels. ◆, 10 mL AA; ◇, 20 mL AA; △, 30 mL AA.
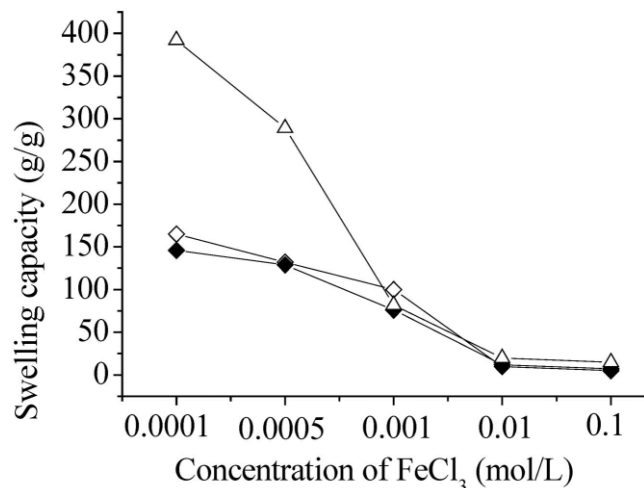
Figure 5 Effect of FeCl$_3$ concentration on swelling of CAS/AA hydrogels. ◆, 10 mL AA; ◇, 20 mL AA; △, 30 mL AA.

Figure 6 Effect of pH on swelling of CAS/AA hydrogels. ◆, 10 mL AA; ◇, 20 mL AA; △, 30 mL AA.

association so easily, or because the polymer gels mainly show anionic property because cationic groups in the starch is in a small fraction compared with anionic groups.

Compared with the equilibrium swelling data obtained in the chloride salt solutions with same concentration, it is found that the swelling capacity decreases with an increase in charge of the metal cation($Na^+ > Ca^{2+}$, Fe^{3+}). It may be explained by complexing ability arising from the coordination of the multivalent cations with CAS/AA carboxylate groups (Scheme 2). It leads to an increase of crosslinking density, which makes network shrink.

pH effect on the swelling behavior

Since the cationic starch-based hydrogels are composed of both acidic and basic groups, they exhibit polyampholytic properties at a wide range of pH. The swelling-pH dependency is shown in Figure 6. The ionic groups play the main role in swelling variations. Therefore, based upon pKa of PAA (~4.7), the involv-
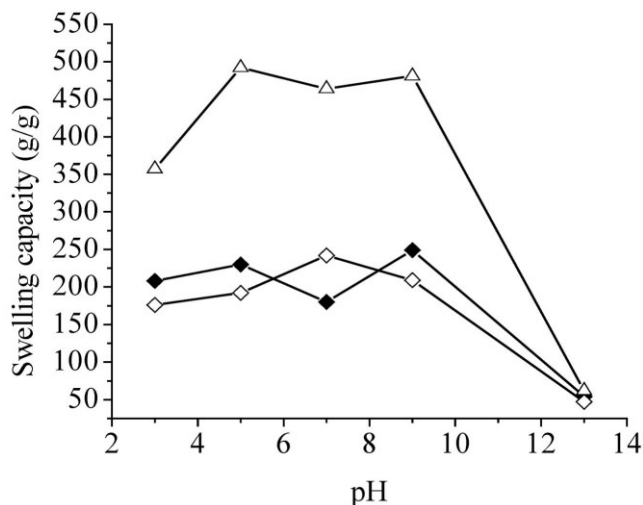
ing species, COOH and COO$^-$, play the main role in swelling variations. At low pH, carboxyl group is predominated as —COOH, so hydrogen bonding between carboxylic acid, as well excessive Cl$^-$ anions may shield the charge of the ammonium cations (N$^+$) and prevent efficient N$^+$–N$^+$ repulsion, thus leading to an decrease in swelling capacity. Meanwhile, at high pH, static attraction between ammonium groups and carboxyl groups may lead to a decrease of network, which, in turn, results in decreased swelling. At a certain pH range 5–9, the concentration of the carboxyl group is greater, either N$^+$ or deprotonated (COO$^-$) groups are in closer proximity to each other. This, in turn, increases charge density on the polymer causing an enhancement of the osmotic pressure inside the gel particles because of the N$^+$–N$^+$ or COO$^-$–COO$^-$ electrostatic repulsion. This osmotic pressure difference between the internal and external solution of the network is balanced by the swelling of the hydrogel.[26]

Swelling reversability

We selected the sample with 30 mL AA of feed composition to investigate the swelling reversability. It is seen in Figure 7 that swelling of CAS/AA in deionized water decrease 410 to 57 g/g after more usage times. This may be explained when the swelling reaches equilibrium in deionized water, the polymer chains fully expanded, while dry process brings water out of network causing hydrogel shrunk. Repeat swollen-shrunk processes will change such an aggregate state in different degree. Furthermore, it is likely that crosslinking will take place among COOH groups by H-bond or forming anhydride, as well as between COO$^-$ and ammonium groups by salt linkage when
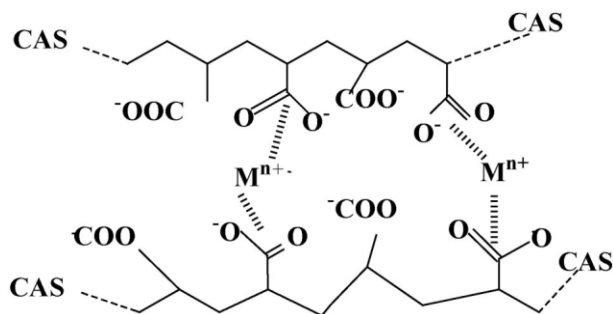
Scheme 2 Crosslinking interaction between a metal cation and anionic groups of CAS/AA hydrogel.
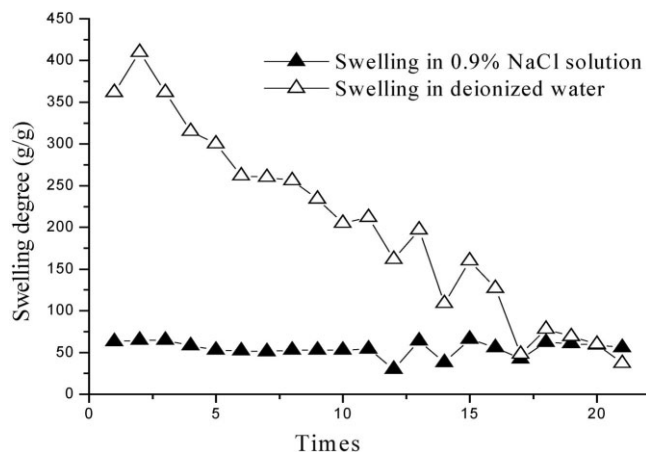
Figure 7 Swelling reversability of CAS/AA hydrogel.

polymer chains are in repeated process. In comparison, CAS/AA hydrogel have good reversibility in 0.9% NaCl solution because of its incomplete expansion.

CONCLUSIONS

The starch-based superabsorbents hydrogels (CAS/AA) were synthesized to investigate the swelling behavior in the various situations. It was shown that the hydrogels exhibited the stimuli responsive behaviors to pH and concentration of salt solution, not to temperature. The swelling ratios for CAS/AA hydrogels are lower in strong acid or alkaline solution, almost plateau from pH 5 to 9. The abrupt pH-dependency of the swelling might be a key factor to their successful application in many fields, such as controlled delivery of bioactive agents, sanitary things; also, the hydrogels are of good reversibility in 0.9% NaCl solution. In the diffusion mechanism study, the results indicate that

the swelling exponents n for CAS/AA copolymeric gels at 25°C is 1.02 when the feed composition of AA is 30 mL. This implies that the diffusion mechanism is super case II transport.

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