Swelling and Thermal Behaviors of a Starch-Based Superabsorbent Hydrogel with Quaternary Ammonium and Carboxyl Groups

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ABSTRACT: A starch-based superabsorbent hydrogel with quaternary ammonium and carboxyl groups is synthesized in aqueous solution. Various factors, including the initiator dose, the crosslinker dose, and the dose and the concentration of the acrylate monomer, as well as the polymerization temperature, are investigated in terms of the swelling in distilled water and in a 0.9% NaCl solution. Furthermore, the thermal degradation of the modified starch graft copolymer is studied under an air atmosphere. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2392–2398, 2005

Key words: hydrogels; graft copolymers; swelling; thermogravimetric analysis (TGA)

INTRODUCTION

Superabsorbent polymers, as a newly developed product in the last 30 years, have been applied widely in many fields, such as disposable diapers in the field of sanitation,[1,2] water-retaining materials in the field of agriculture,[3–5] controlled release in drug delivery systems,[6–8] etc.[9–14] Vinyl monomers, especially acrylic acid and its derivates, are the main monomers in the synthetic absorbent polymers,[15–19] which are of great absorbent capacity, but have weak salt-tolerant ability. Graft copolymerization of starch with vinyl monomers (viz. acrylamide, acrylonitrile, acrylic acid) has gained importance in improving some properties of synthetic absorbent polymers.[20–24] Moreover, the graft products have received considerable attention because of their immense industrial potential with their biodegradability, low cost, and renewability. However, so far more attention has been put only in the graft products of original starch.[25–28] Compared with anionic or cationic graft copolymers, amphoteric absorbent polymers have potential salt-tolerant swelling character.[29] In the literature, no previous attempt appears to have been made to study the synthesis and the properties of graft copolymers of cationic starch (CAS) with acrylic acid.

In the present study, we have prepared a series of cationic starch graft copolymers, which produce amphoteric products with quaternary ammonium and carboxyl groups. The swelling and thermal degradation behaviors of these graft copolymers are studied.

EXPERIMENTAL

Materials

Corn starch (food grade) is dried before use; acrylic acid (AA), ammonium persulphate (APS), 3-chloro-2-hydroxypropyltrimethylammonium chloride (65% aqueous solution), epichlorohydrin, chloroacetic acid (analytical reagent grade), and *N*-N′-methylenebisacrylamide (MBAM) (chemical purity) were used as received.

Graft copolymerization

The procedures for preparing water-soluble cationic starch (CAS) have been described earlier[30]; nitrogen content, and hence the degree of substitution (DS) of quaternary ammonium groups in the CAS, was measured with elemental analysis using PE-2400CHN.[31]

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

Neutralized sodium acrylate solution was prepared first by slowly dropping acrylic acid into a flask containing 40% NaOH solution with strong stirring at 0°C (cooled in ice-water bath). 2 g of the above cationic starch was dissolved in a certain amount of distilled water. The starch solution was poured into a 250 mL four-neck flask, which was equipped with a mechanical stirrer and reflux condenser, and purged with nitrogen. Then, the monomer AA (varying the dose, 10 mL, 20 mL, 30 mL, and 40 mL, respectively) and crosslinker MBAM (0.02% monomer weight) were

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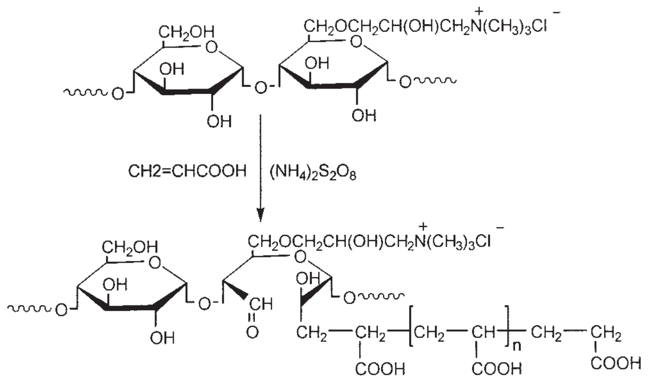

Scheme 1

added. After a certain time, an APS solution (2.5% monomer weight) was added to the reaction system, and the reaction was carried out at 60°C. After 3 h, the resulting product was washed several times with distilled water, then treated with acetone to remove the homopolymer, and finally was dried at 50°C. The infrared (IR) spectra of copolymer samples were taken in KBr pellets using a BRUKER EQUINOX55 FTIR spectrophotometer.

Absorption in distilled water and saline solution (0.9 wt % NaCl aqueous solution) was measured by the "tea bag" method,[19] and the swelling was calculated by the following equation:

$$swelling\ (g/g) = (w - w_0)/(w_0 \times 100)$$

where W is the weight of the swollen polymer, and W_0 is the weight of the dehydrated polymer.

Thermal analysis

Thermal analysis was conducted with the help of a Netzsch STA 449C, using heating rates of 10, 20, 30, and 40K/min.

RESULTS AND DISCUSSION

The proposed graft copolymerization of cationic starch involved in the above process is shown in the following scheme:

Analysis of FT-IR spectra

Elemental analysis data of CAS is as follows: C, 41.67%; H, 7.19%; N, 1.60%, so the DS of quaternary ammonium cationic groups in the CAS is calculated as 0.22. In Figure 1a is shown the infrared spectrum of the corn starch. The O-H stretching and bending modes appear at 3317 cm^{-1} and 1658 cm^{-1}, respectively. Additional characteristic absorption bands of corn starch appear at 2931 cm^{-1} and 993 cm^{-1} due to C-H stretching and bending, respectively. In Figure 1b, the peak becomes sharp when cationic groups are introduced into the starch and destroy the H bonds between the O-H groups. In Figure 1c, the presence of an additional sharp peak at 1608.80 cm^{-1} and 1405cm^{-1} is due to the COO$^-$ groups in the copolymer samples. In contrast to the spectrum of the PAA in Figure 1d, the spectrum indicates that the grafting process has taken place.

Effect of dose of initiator

In Figure 2, the effect of varying the initiator dose on the absorbent swelling in distilled water and in the salt

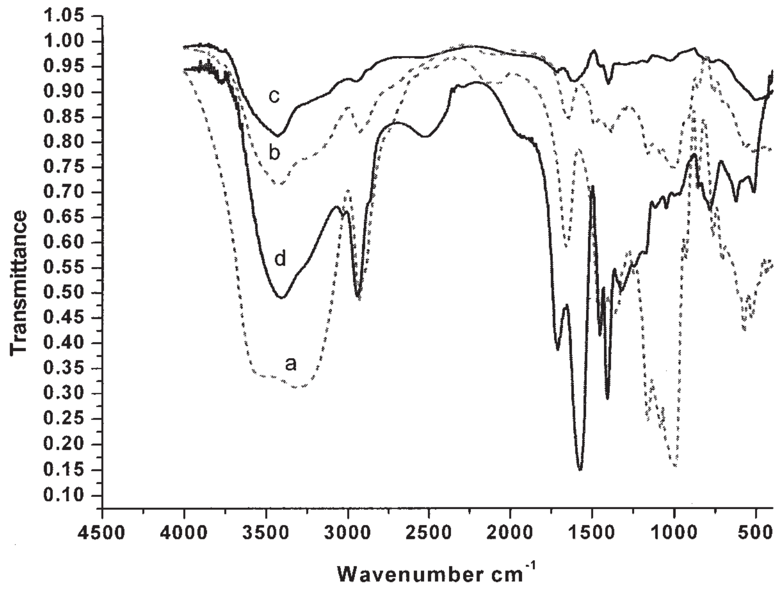

Figure 1 FT-IR spectra of: (a) corn starch; (b) CAS; (c) copolymer; (d) PAA.

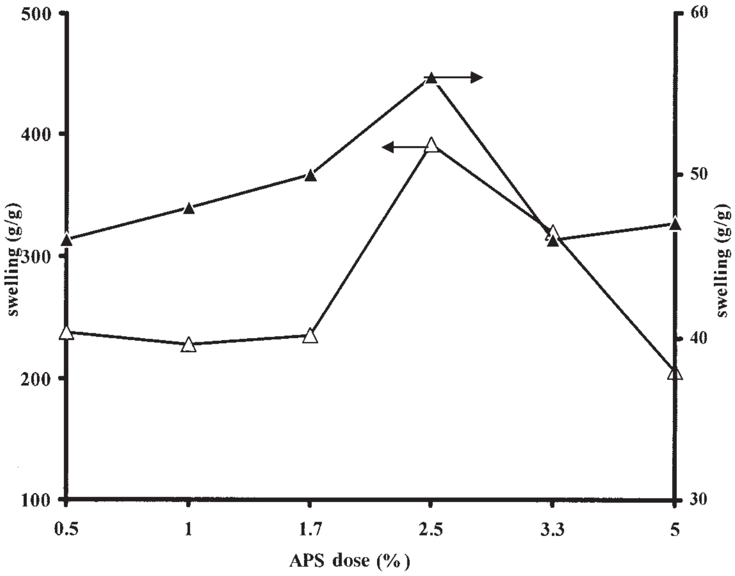

Figure 2 Effect of dose of APS on swelling (cationic starch 2g; MBAM 0.02%; 40°C; 3h; AA 30mL). (▲) 0.9%NaCl; (△) distilled water.

solution is shown. It is seen that increasing the dose of APS from 0.5% to 2.5% (of monomer weight) is accompanied by an increase of swelling in distilled water from 238 g/g to 391g/g and swelling in the salt solution from 46 g/g to 56 g/g. The graft copolymerization of the cationic starch takes place in a free-radicals-initiated process. The rate of reaction increases with the increasing dose of the initiator. However, when the dose of APS increases up to 5%, the polymerization proceeds so fast that it is difficult to remove the heat in a short time; hence, this leads to popcorn polymerization. The resulted wide distribution in the molecule weights causes the low swelling.

Effect of dose of crosslinker

As shown in Figure 3, when the dose of MBAM increases from 0.01% to 0.02% (of monomer weight), the swelling increases from 270 g/g to 360 g/g in distilled water, and 51 g/g to 55 g/g in the 0.9% NaCl solution. The copolymer dissolves slightly in a low MBAM dose, and hence shows small swelling. When the MBAM dose increases further, the absorption increases markedly. It is obvious that the crosslinker produces a big network between the cationic starch and acrylate, thus improving the swelling of hydrogels. However, the absorption decreased gradually

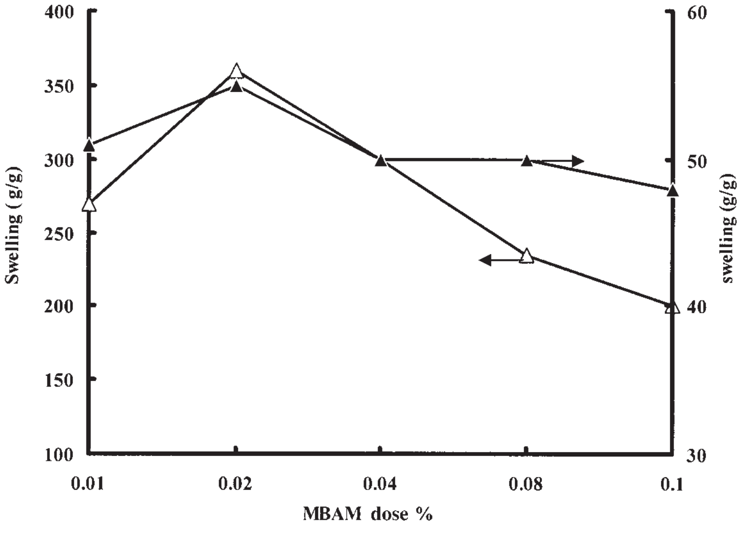

Figure 3 Effect of MBAM dose on swelling(cationic starch 2g; APS 2.5%; 40°C; 3h; AA 30mL). (▲) 0.9%NaCl; (△) distilled water.

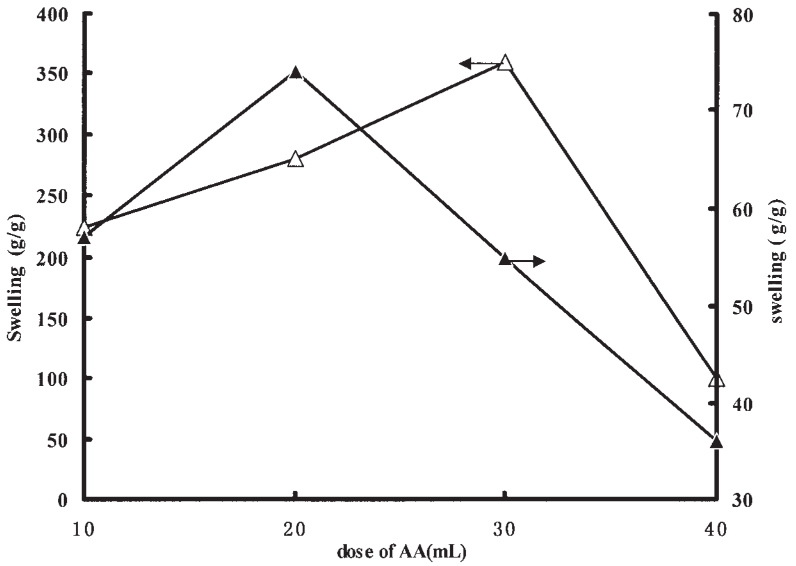

Figure 4 Effect of dose of AA on swelling (cationic starch 2g; APS 2.5%; MBAM 0.02%; 40°C; 3h). (▲) 0.9%NaCl; (△) distilled water.

with the MBAM dose being more than 0.02%. It may be due to an increase of the crosslinking density, which results in the small network space.

Effect of feed composition of AA

Figure 4 demonstrates the effect of the feed composition of AA on the graft copolymerization of the cationic starch; increasing the dose of AA from 10 to 30 mL is accompanied by a significant enhancement in the swelling. This could be interpreted as more AA molecules being grafted in the backbone of the cationic starch at the higher feed composition of AA. The water absorption strongly depends on the number of the carboxyl groups, so the swelling increases with the increasing dose of AA. When the dose is more than 30 mL, the possible rigid chain would not facilitate the higher water adsorption, so the swelling decreases. However, the absorbency in saline solution is slightly different from that in distilled water, which shows a

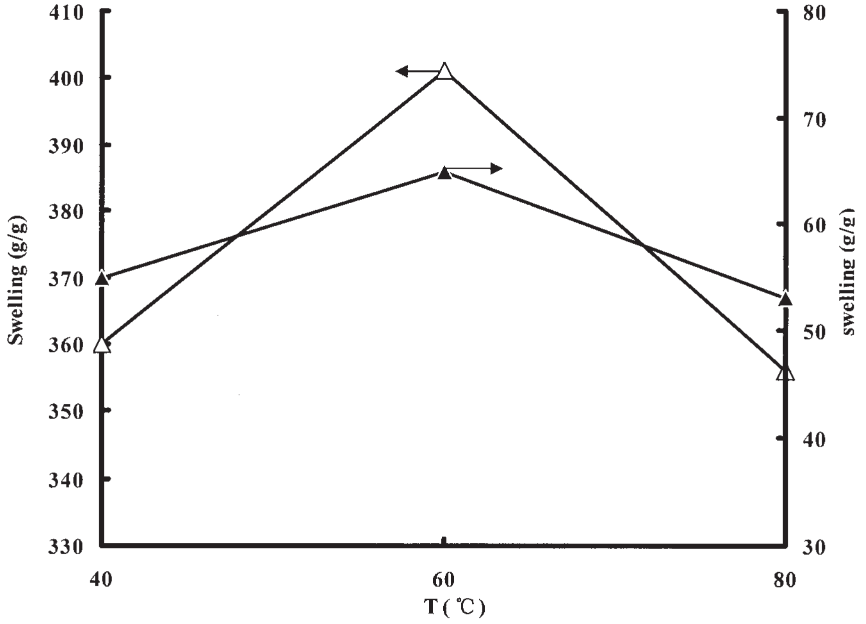

Figure 5 Effect of temperature on swelling (cationic starch 2g; APS 2.5%; MBAM 0.02%; 3h; AA 30mL). (▲) 0.9%NaCl; (△) distilled water.

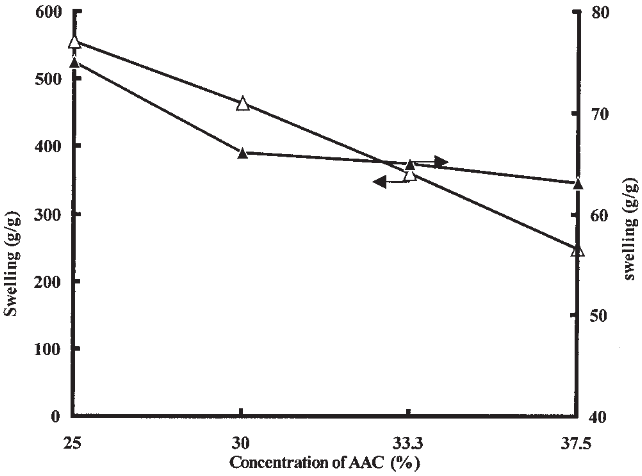

Figure 6 Effect of concentration of AA on grafting (cationic starch 2g; APS 2.5%; MBAM 0.02%; 60°C; 3h). (▲) 0.9%NaCl; (△) distilled water.

good salt-tolerant ability at 20 mL AA. It is because the anionic groups are less salt-tolerant than the cationic groups, so the higher feed composition of AA results in more swelling capacity in the distilled water, but less swelling in the saline solution.

Effect of temperature

The effect of the polymerization temperature on the grafting reaction is also investigated by varying the temperature from 20 to 80°C (Fig. 5). It was observed that the reaction did not happen sudden gelation after 3h at 20°C. When the temperature increased, an obvious gel point is observed. An increase in temperature from 40 to 60°C improves the swelling; further increasing the reaction temperature leads to a decrease of water absorption. The generation of free radicals is accomplished by heat, so increasing the temperature favors the producing of free radicals. But excessive free radicals will result in popcorn polymerization. In this work, the optimum reaction temperature is 60°C.

Effect of concentration of AA

As shown in Figure 6, with increasing concentration of AA, water absorption decreases from 555g/g to 248g/g in distilled water, and 75 g/g to 63 g/g in the 0.9% NaCl solution. The graft polymerization takes place with water as a medium. A reduction in the amount of water increases the possibility of popcorn polymerization and results in worse swelling. The water can favor a steady copolymerization and produces well-molecular-weight-distributed copolymers under low concentration of AA.

Thermal degradation of cationic starch graft copolymer

Thermogravimetry (TG) and derivative thermogravimetry (DTG) curves for thermal degradation of the copolymer (swelling 460 g/g) are shown in Figure 7, using a heating rate of 20 K/min in an air atmosphere. It can be seen that the thermal degradation of such graft copolymer occurs in three stages, and the corresponding DTG curve shows maximum peaks at 158°C, 360°C, and 452°C, respectively. In the first stage, the weight loss starts below 100°C, and continues up to 240°C, resulting in an 8.95% weight loss. It is estimated that free and bound water in the absorbent polymer results in the wide weight-loss temperature

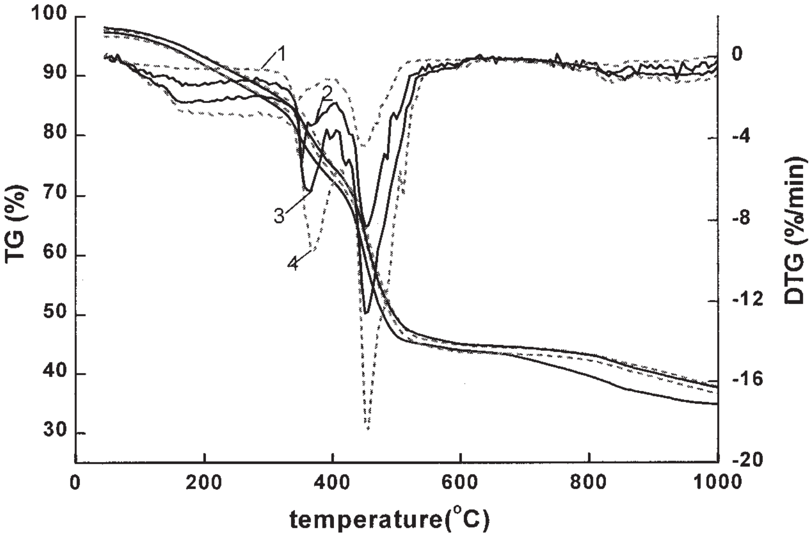

Figure 7 TG and DTG curves under air atmosphere at different heating rates. 1–10 K/min; 2–20 K/min; 3–30 K/min; 4–40 K/min.

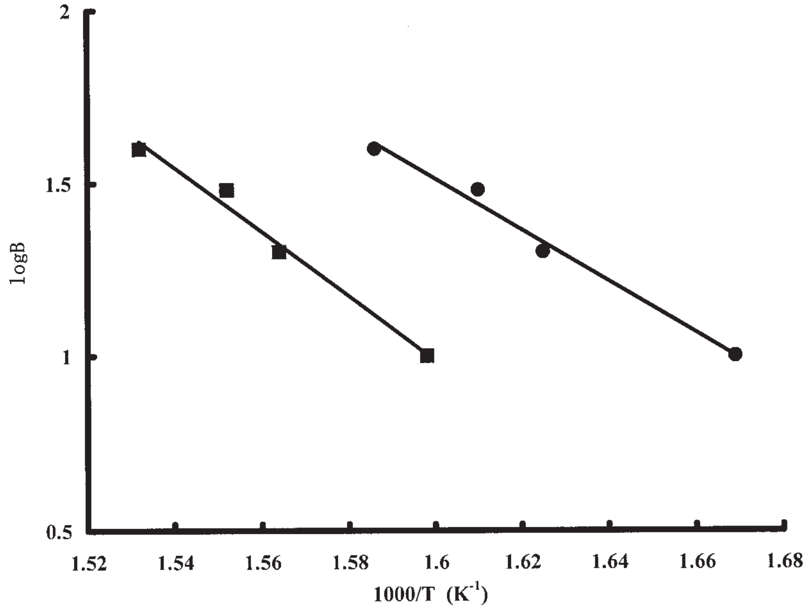

Figure 8 Plots of logarithms of heating rate versus reciprocal of absolute temperature.

range. The second stage is complete with a 17.11% weight loss at 389°C, and the third stage with a 29.93% weight loss is completed at 592°C.

To obtain the activation energy of the degradation of the graft copolymer, its TG curves are recorded at different heating rates of 10, 20, 30, and 40°C/min under an air atmosphere. Thus, the active energy of decomposition (E/J/mol) is obtained from the following equation[32]:

$$E = -R/0.4567[d \log \beta / d(1/T)]$$

where β is the heating rate (°C/min), R is the gas constant (8.314 J/mol K), and T is the absolute temperature. The plot of the logarithm of the heating rate versus the reciprocal of the temperature at each decomposition level obtained from Figure 7 shows a better linear relationship (see Fig. 8), so for the two degradation stages, the first at 16.92% weight loss, and the second at 21.88% weight loss, the E values are calculated as 135.32 KJ/mol and 168.31 KJ/mol, respectively.

CONCLUSIONS

The graft copolymerization of acrylate onto cationic starch is studied by varying the concentrations of the initiator and crosslinked agent, the dose and concentration of the acrylate monomer, and the polymerization temperature. It is found that the swelling reaches to 460 g/g in distilled water and 64 g/g in a 0.9% NaCl solution when 2 g cationic starch is grafted with 30 mL AA; the concentration of APS, MBAM, and AA is 2.5%, 0.02%, and 25%, respectively, and the copolymerization temperature is 60°C. Thermal degradation consists of three stages: the first range of weight loss is wide, attributed to the loss of bond water in the graft copolymer, and the corresponding activation energy in the other two thermal degradation stages is calculated.

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