Synthesis and Water Absorbility of Base-Hydrolyzed Starch-*g*-Poly(Acrylonitrile-*co*-Sodium Allylsulfonate)

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Synopsis

Grafting of mixed vinyl monomers, acrylonitrile (AN) and sodium allylsulfonate (SAS), onto starch was carried out in aqueous, gelatinized corn starch by using ceric ammonium nitrate (CAN) as an initiator at 30°C under a nitrogen atmosphere. Conversion (%) and percent graft (%) were determined as a function of (1) molar ratios of feed composition, (2) concentration of CAN, (3) HNO_3 concentration, and (4) reaction temperature. The monomer, SAS, is found to decrease percent graft of mixed monomers onto starch. The graft copolymer, starch-*g*-poly(AN-*co*-SAS), can be hydrolyzed by varying amounts of aqueous NaOH at 80–100°C to obtain base-hydrolyzed starch-*g*-poly(AN-*co*-SAS). The hydrolyzed product is an excellent water absorbent, which absorbs 1900 times its weight of deionized water. Water retention reached over 90% at 10 kg/cm^2, and the toleration of electrolyte (synthetic urine) attained was better than that of hydrolyzed starch-*g*-polyacrylonitrile (H-SPAN).

INTRODUCTION

Following the discovery of Mino and Kaizerman[1] that the ceric ion is capable of forming a redox system with alcohol, polyhydroxy compounds such as starch[2,3] have been graft copolymerized with a number of vinyl monomers by using the ceric ion technique. In recent years, numerous attempts have been made to effect grafting of mixed vinyl monomers onto starch by using Ce^{+4} initiator.[4-6]

We reported the grafting of mixed vinyl monomers (AN and SAS) onto corn starch by using Ce^{+4} as an initiator, where synthesis was conducted in aqueous, gelled corn starch. The graft copolymer with the side chain composed of acrylonitrile units and sulfonate units is as follows:

$$-CH_2-CH- \qquad -CH_2-CH-$$
$$\hspace{1.2cm}| \hspace{3.2cm}|$$
$$\hspace{1.2cm}CN \hspace{2.7cm}CH_2SO_3Na$$
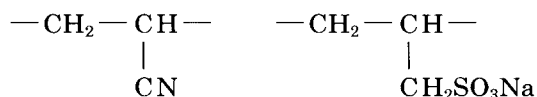
Thereby, we also successfully prepared base-hydrolyzed starch-*g*-poly(AN-*co*-SAS) by alkaline hydrolysis of the graft copolymer. This hydrolyzed product was an excellent water absorbent, in terms of water retention and toleration of electrolyte properties.

Absorbent compositions are valuable for many uses. For example, they can be used in manufacturing sanitary napkins or added to soil to increase its water-retention capability and can be used in other areas of industry where water absorbing and retention is important.

EXPERIMENTAL

Materials

Commercial corn starch was purified in hot methanol, followed by hot filtering the solution. The ceric ammonium nitrate (CAN) was purchased (analytically pure) and used without further purification. Acrylonitrile (AN) was freed from the inhibitor by distillation. Sodium allylsulfonate (SAS), commercial grade, was purified by recrystallization from 90% ethanol twice. All solution were prepared in distilled water.

Grafting Procedure

A weighed quantity of starch was dispersed in water and gelled at 85°C under nitrogen for 30 min. The starch solution was bubbled with N_2 and stirred at 30°C, and a known amount of CAN—HNO_3 solution was added, followed by the addition of AN and SAS. The graft copolymerization was carried out at 30°C and maintained there for 4 h. At the end of the reaction, the reaction mixture was precipitated from solution with ethanol, filtered, and dried under reduced pressure. Crude graft copolymer was extracted with dimethylformamide (DMF) to yield the purified product. From the results, the graft copolymer amount was determined. The percent grafting was calculated using the following equation:

$$\text{Percent graft } (\%) = \frac{w_1 - w_0}{w_0} \times 100$$

where w_1 and w_0 denote, respectively, the weight of the grafted starch and the weight of the original starch.

Base Hydrolysis

A weighed quantity of graft copolymer was taken to a reaction flask and a certain volume of 0.5 M sodium hydroxide solution was added, and the mixture was heated by a steam bath to temperatures within the range of 80–100°C. Graft copolymer rapidly was formed as slurries and had a red-orange color, which then slowly faded to light yellow as the reaction neared completion. The pH of the reaction mixture was adjusted to 7.0, ethanol was added, and the reaction products were filtered, washed, dried, and milled through a 40-mesh screen.

Water Absorbility and Retention Tests

A weighed quantity of hydrolyzed graft copolymer was added to water and allowed to stand to fully hydrate the polymer. Swollen polymer particles were

TABLE I
Effect of the Concentration of Mixed Monomers on Graft[a]

Example	Feed composition molar ratios			Percent graft (%)	DMF extract (%)
	Starch	AN	SAS		
1	1	4.86	0.45	55	3
2	1	9.72	0.90	72	4
3	1	14.58	1.35	79	6
4	1	19.44	1.80	81	7

[a] Reaction conditions: $(Ce^{+4}) = 5.1 \times 10^{-3}$ M, $(HNO_3) = 0.20$ M at 30°C for 4 h.

then separated from unabsorbed water by screening. The mixture on the sieve was allowed to drain for 10 min, and the sieve was then weighed to determine the weight of water-swollen gel and water absorbency was calculated using the following equation:

$$\text{Absorbency (g/g)} = \frac{\text{water-swollen gel (g)} - \text{absorbent (g)}}{\text{absorbent (g)}}$$

Similar absorbency tests were carried out with synthetic urine and NaCl aqueous. Water retention of the swollen gel was determined by the ovenless test and by using the ZNS-2 model fluid-loss meter under various pressures or the HETACHI 55p-72 model centrifuge.

RESULTS AND DISCUSSION

Effect of Variables on Grafting

Monomers Concentration

As seen in Table I, the grafting (%) of the resulting starch-*g*-poly(AN-*co*-SAS) increased with increasing total concentration of mixed vinyl monomers
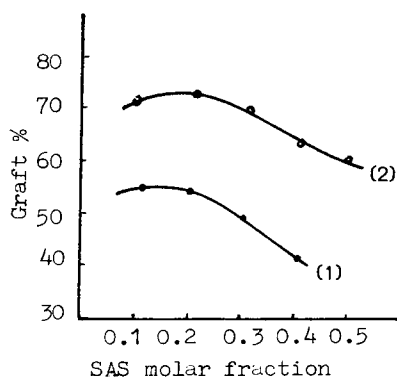

Fig. 1. Effect of SAS molar fraction in feed on percent graft (%) $(Ce^{+4}) = 5.0 \times 10^{-3}$ M, at 30°C for 3 h. (1) starch: (AN and SAS) = 1 : 5; (2) starch: (AN and SAS) = 1 : 10.

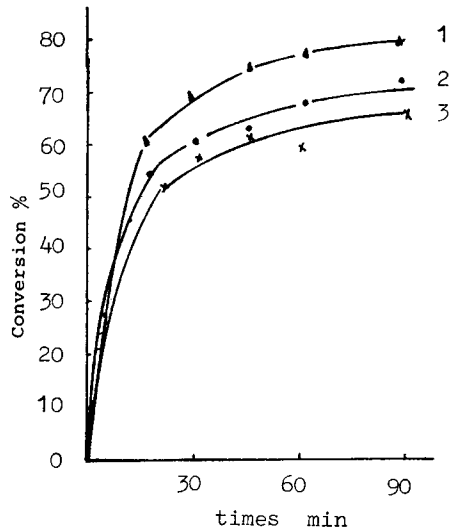Fig. 2.   Effect of SAS concentration on conversion (%) starch 1 M, AN = 4.86 M, Ce^{+4} = 3.1 × 10^{-3} M, at 30°C for 4 h; SAS: (1) 0.226 M, (2) 0.323 M, (3) 0.452 M.

(AN and SAS). In addition, Figure 1 shows that the grafting (%) increased with increasing SAS at lower molar fraction and then decreased after maximum grafting (%). This may be due to the chain transfer of SAS monomer. The conversion (%) and rate of graft copolymerization decreased with increasing SAS concentration (Fig. 2).

Initiator Concentration

Figure 3 shows that the primary grafting (%) increased slowly with increasing initiator (Ce^{+4}) concentration; however, a rise in Ce^{+4} concentration gave rise to enhance grafting (%).
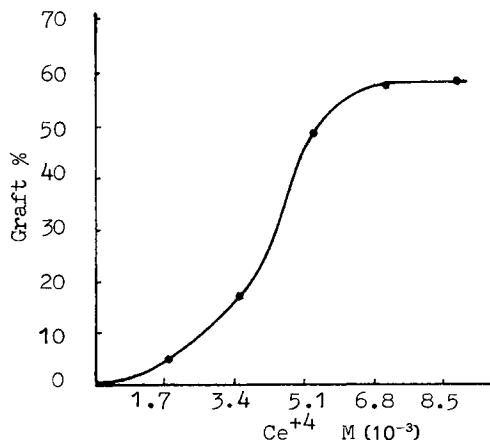

Fig. 3.   Effect of Ce^{+4} concentration on percent graft (%) starch 0.5 M, AN = 2.5 M, SAS = 0.0225 M, at 30°C for 4 h.
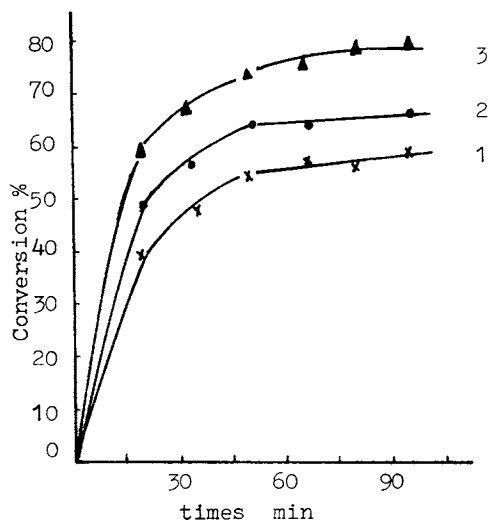
Fig. 4.   Effect of Ce^{+4} concentration on conversion (%) starch 0.31 M, AN = 0.151 M, SAS = 0.14 M, at 30°C for 4 h; Ce^{+4}: (1) 2.1 × 10^{-3} M, (2) 3.1 × 10^{-3} M, (3) 5.1 × 10^{-3} M.

The relation curves of conversion-reaction times under varying Ce^{+4} concentration (2.1 × 10^{-3}–5.1 × 10^{-3}) are plotted in Figure 4. As seen in Figure 4, the greater the Ce^{+4} concentration, the higher the conversion (%).

HNO₃ Concentration

By varying the nitric acid concentration, as seen in Figure 5, a maximum was found between 0.2 and 0.4 M.

Reaction Temperature

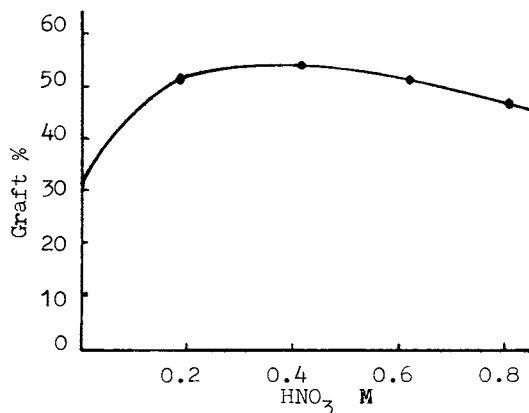Table II shows that the reaction temperature of 30°C facilited the grafting.

Fig. 5.   Effect of HNO$_3$ concentration on percent graft (%) starch 0.5 M; (SAS = 0.225 M, (AN) = 2.5 M at 30°C for 4 h.

TABLE II
Effect of Temperature on Grafting (%)[a]

Example	Time (h)	Temperature (°C)	Grafting (%)	DMF extract (wt %)
5	4	14	51	2.4
6	4	30	55	3.0
7	4	40	46	3.3

[a] Starch: AN : SAS = 1 : 4.86 : 0.45 mol; (Ce^{+4}) = 5.1×10^{-3} M, (HNO_3) = 0.2 M.

TABLE III
Base Hydrolysis of Starch-g-Poly(AN-co-SAS)[a]

Example	NaOH (wt %)	NaOH/Graft copolymer wt ratios	Temp (°C)	N (%)
H1	28.6	0.40	80	6.53
H2	44.4	0.80	80	5.60
H3	28.6	0.40	100	5.39
H4	44.4	0.80	100	4.84
H5	61.5	1.60	100	4.18

[a] Original graft copolymer N (%) = 20.73, S (%) = 5.16.

TABLE IV
Absorbency of Base-hydrolyzed Starch-g-Poly(AN-co-SAS)

| Example | Percent graft (%) | Composition of grafted polymer[a] (mol %) | | | Absorbency | | |
		—AM—	—AA—	—SAS—	Water (g/g)	Synthetic urine[b] (g/g)	0.5% NaCl (mL/g)
H6	80.9	27.3	63.7	9.0	1900	78	700
H7	79.0	27.2	63.4	9.5	1620	74	650
H8	72.1	27.4	64.0	8.6	950	64	630
H-SPAN[c]	78.7	34.5	65.5	—	1060	57	528

[a] —AM—: —CH$_2$—CH—   —AA—: —CH$_2$—CH—
                          | |
                    CONH$_2$ COONa

—SAS—: —CH$_2$—CH—
                |
          CH$_2$SO$_3$Na
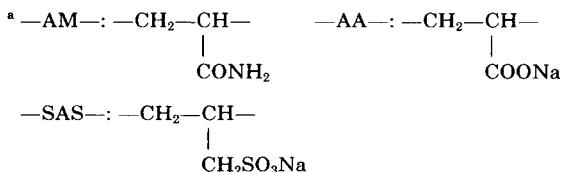
[b] Synthetic urine composition: 97.09% distilled water, 1.94% urea, 0.80% NaCl, 0.11% MgCl$_2$, 0.06% CaCl$_2$.

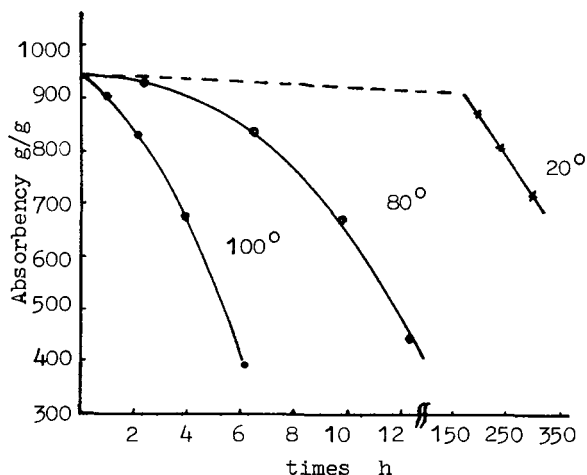[c] H-SPAN: hydrolyzed starch-g-polyacrylonitrile.

Fig. 6.   Heat stability of swollen gel. Temperatures: 100, 80, and 20°C; sample H8.

Alkaline Hydrolysis of Graft Copolymer

Base-hydrolyzed starch-g-poly(AN-co-SAS) was prepared by alkaline hydrolysis of starch-g-poly(AN-co-SAS) by varying the base concentration and temperature (summarized in Table III).

Saponification of the graft copolymer under varying conditions gave a range of products that differed in nitrogen content (Table III). Assuming the original graft copolymer, starch-g-poly(AN-co-SAS), yielded only starch-g-poly-(acrylamide–sodium acrylate–sodium allylsulfonate) (see, also, IR Spectra below), the composition of the saponified product was calculated from nitrogen, sulfur, and carboxyl values.

IR Spectra

As seen in the spectra, distinct characteristic peaks due to constituent co-monomer units appeared for carboxyl absorption at 1585 cm^{-1}, for sulfonate
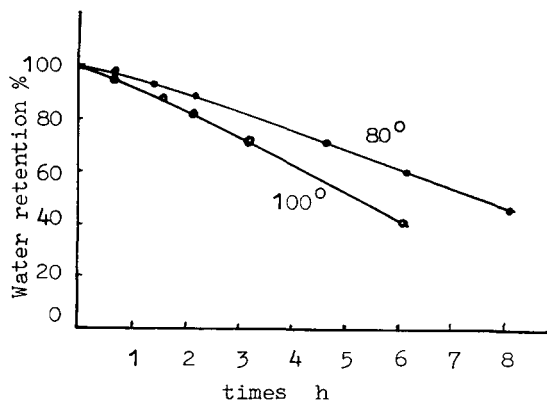

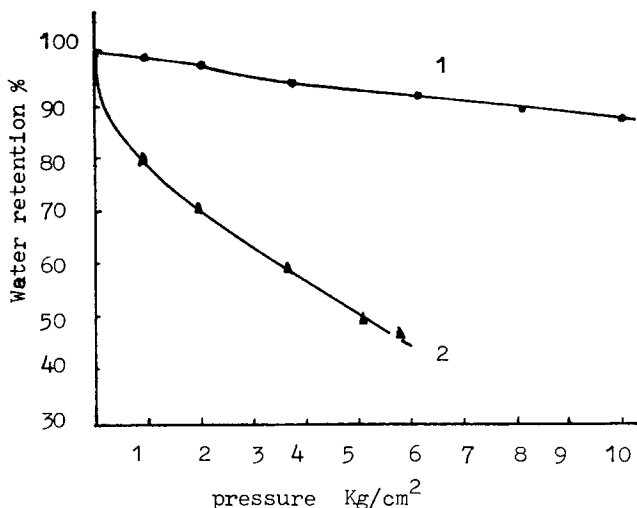Fig. 7.   Water retention of swollen gel. Temperatures: 100 and 80°C, sample H8.

Fig. 8.   Water retention of swollen gel under varying pressures at 1–10 kg/cm² for 30 min: (1) Sample H8; (2) H-SPAN.

at 1048 cm⁻¹, and at 1667 cm⁻¹ because of the —$CONH_2$ group absorption. In addition, starch characteristic peaks at 850 and 750 cm⁻¹ were observed, but the —CN group absorption band (2240 cm⁻¹) had disappeared.

Water Absorbility

Absorbency tests with water and synthetic urine were carried out, and the results are summarized in Table IV.

Figures 6 and 7 show the water retention of swollen gel under varying temperatures. It is found that the absorbent gel is stable.

Figure 8 shows the swollen gel retention under pressure.

The water retention of the swollen absorbent, base-hydrolyzed starch-*g*-poly(AN-*co*-SAS), reached over 90% under 10 kg/cm² in 30 min, and no water was separated by centrifuging at 1.5×10^4 rpm in 15 min. A similar test was run with H-SPAN, which absorbed water at 1060 g/g and synthetic urine at 57 g/g, but the water retention was lower (in less than 50% under 5 kg/cm²).

References

1. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **31**, 242 (1958).
2. G. Mino and S. Kaizerman, *J. Polym. Sci.*, **38**, 393 (1959).
3. M. O. Weaver, L. A. Gugliemzlli, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **15**, 3015 (1971).
4. R. C. Burr, G. F. Fanta, and W. M. Doane, *J. Appl. Polym. Sci.*, **24**, 1387 (1979).
5. C. L. McCormick and L. Park, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 49 (1984).
6. J. J. Melster, M. R. Patil, M. Jewell, and K. Krohn, *J. Appl. Polym. Sci.*, **33**, 1887 (1987).