Graft Polymerization of Acrylamide and 2-Acrylamido-2-methylpropanesulfonic Acid onto Starch

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Synopsis

Mixtures of acrylamide and 2-acrylamido-2-methylpropanesulfonic acid (AASO$_3$H) were graft polymerized onto starch by cobalt-60 irradiation, and the water absorbency and water solubility of the resulting products were determined. The conversion of monomers to polymer was nearly quantitative when pregelatinized wheat starch and a water solution of the two monomers were simultaneously irradiated (simultaneous irradiation conditions). Products with high water absorbency were obtained with equal weights of starch and total monomers when acrylamide:AASO$_3$H ratios ranged from 9:1 to 1:3. Water solubility of these polymers was over 50%. Neither of the two monomers gave absorbent polymers when graft polymerized individually onto starch. Although highly absorbent products were also obtained at a total monomer:starch ratio of 2:5, ratios of 1:5 and lower gave products with poor absorbency. Neutralization of AASO$_3$H with sodium hydroxide before graft polymerization drastically reduced both the water solubility and absorbency of the final products. A reaction with granular starch was also carried out under simultaneous irradiation with a total monomer:starch ratio of 2:5 and with equal weights of the two monomers. Conversion of monomers to polymer was once again nearly quantitative. To obtain good water absorbency from this granular product, it was necessary to first neutralize the AASO$_3$H portion with alkali, then disperse the polymer in hot water, and finally dry the resulting water dispersion. Graft copolymers with good water absorbency were also obtained by adding preirradiated starch to a water solution of acrylamide and AASO$_3$H, although only partial conversions of monomers to polymer were realized. Selected products from the various graft polymerizations were fractionated by extraction with either water or a 1% solution of sodium chloride. The synthetic polymer content of the resulting fractions and the percentage of AASO$_3$H in the synthetic portion of each polymer were determined. The $\overline{M}_n$ of some of the synthetic polymers was also determined after removal of carbohydrate by enzymatic hydrolysis.

INTRODUCTION

The remarkable ability of some hydrophilic starch graft copolymers (in particular, saponified starch-*g*-polyacrylonitrile[1]) to absorb aqueous fluids has generated considerable interest. Suggested uses for these absorbents range from incorporation into personal care products, such as disposable diapers, to agricultural uses, such as seed and root coating and addition to sandy soils to improve water retention.

In a previous publication,[2] we described the graft polymerization onto starch of mixtures of acrylonitrile and 2-acrylamido-2-methylpropanesulfonic acid (AASO$_3$H), which contained up to 10 mol % AASO$_3$H. Saponification of these

$$CH_2{=}CHCNHC{-}CH_2SO_3H$$

with O (double bond), CH$_3$, and CH$_3$ substituents
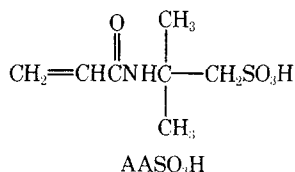
AASO$_3$H

graft copolymers with hot alkali, to convert nitrile substituents to carboxamide and alkali metal carboxylate, gave highly absorbent polymers. As a continuation of our study of $AASO_3H$-containing starch graft copolymers, we now report the cobalt 60-initiated graft polymerization of mixtures of $AASO_3H$ and acrylamide. Since polyacrylamide is hydrophilic, these polymers function as absorbents for aqueous fluids without saponification, and in many instances they show absorbency properties comparable to earlier saponified products.

EXPERIMENTAL

Materials

Pregelatinized wheat starch was MSWS 1000 from Midwest Solvents Company, Inc. Granular globe pearl corn starch was from CPC International.

Acrylamide (97%) was from Polysciences, and $AASO_3H$ (reaction grade, special process) was from the Lubrizol Corp. Both monomers were used as received.

Graft Polymerizations

The cobalt-60 source was a Gammacell 200 unit from Atomic Energy of Canada, Ltd. The dose rate at the center of the chamber was 0.64 to 0.59 Mrad/hr, as calculated from the initial dosimetry data provided by the manufacturer and the decay rate of cobalt 60.

Reactions carried out under simultaneous irradiation conditions were run in 2-oz. screw-cap bottles. A mixture of starch and a water solution of monomers was thoroughly blended with a spatula, and the resulting paste was evacuated to 50 mm Hg and repressured with nitrogen. This evacuation and repressuring procedure was repeated four times to displace dissolved oxygen. The mixture was then irradiated with cobalt 60 and allowed to stand at ambient temperature for 2 hr. For reactions with external cooling, the bottle containing the reactants was allowed to stand in ice water for about 45 min and was then irradiated in an ice-filled container. The tough, rubbery reaction mass was cut into small pieces and was reduced to a granular solid by high-shear blending with isopropanol. The solid was washed thoroughly with isopropanol to remove any unreacted monomer and was then allowed to air dry. The air-dried product was ground to pass 60 mesh.

Reactions carried out with preirradiated starch were run in a 600-ml beaker to facilitate addition of dry solids. The beaker was equipped with paddle stirrer, thermometer, and nitrogen inlet tube and was covered with polyethylene to exclude air. Starch (30 g, dry basis, water content 11–13%) was weighed into a 2-oz. screw-cap bottle, cooled in ice water, and evacuated and repressured with nitrogen to displace oxygen. The bottled starch was irradiated in an ice-filled container in 1.0 Mrad and was then added, within 4 min, to a stirred solution of 20 g $AASO_3H$ and 20 g of acrylamide in 300 ml nitrogen-sparged water in the beaker. The mixture was allowed to stir at 25–28°C for 2 hr and was then dispersed in excess isopropanol. The solid was isolated by centrifugation, washed with isopropanol, and allowed to air dry.

Selected graft copolymers were fractionated by repeated extraction with 1% sodium chloride solution (NaCl added to reduce swelling). Water was used for

the extraction when polymer swelling was not excessive. Sodium chloride was removed by dialyzing the fractions first against water at pH 2 and then against distilled water. Polymers (H$^+$ form) were then isolated by freeze drying.

Polymer Characterization

To rapidly determine polymer solubility, an accurately weighed 1-g sample of polymer was dispersed in 200–800 ml water, and the dispersion was allowed to stand overnight at room temperature. The volume of water was accurately measured, and the amount used depended on the water absorbency or the degree of swelling of the polymer. The mixture was allowed to gravity filter through fluted paper, and an accurately weighed portion of the clear filtrate was freeze dried. Percent water solubles was calculated from the weight of freeze-dried solid.

The percent synthetic polymer incorporated in the graft polymer fractions was determined by refluxing 1 g polymer in 150 ml 0.5N hydrochloric acid for 1.5 hr. The hydrolyzate was dialyzed against distilled water, and the grafted synthetic polymer was isolated by freeze drying. Percent synthetic polymer was calculated by weight loss on hydrolysis.

Weight percent AASO$_3$H in the synthetic polymer was calculated from sulfur analysis.[3] Refluxing hydrochloric acid did not change the sulfur analysis of a known sample of poly(AASO$_3$H).

Carbohydrate was removed from copolymer fractions by enzymatic hydrolysis to obtain synthetic polymers for $\overline{M}_n$ determinations. A dispersion of 1.5 g polymer in 200–300 ml water was prepared, sodium hydroxide solution was added to adjust the pH to 6.2, and 0.1 ml Thermamyl 60L (Novo Enzyme Corp.) was added. The mixture was held at 95 °C for about 18 hr and was then dialyzed against distilled water. The synthetic polymer fraction (containing about 5–10% residual carbohydrate) was isolated by freeze drying.

Number-average molecular weights were determined in 0.15N sodium chloride solution on a Melabs Model CSM-2 membrane osmometer equipped with a B-19 membrane (Schleicher and Schuell Co.)

Measurement of Water Absorbency

An accurately weighed 2 to 10-mg sample of polymer (amount used depended on absorbency) was allowed to stand 30 min in 50 ml deionized water. The swollen polymer was separated from unabsorbed water by screening through a tared 280-mesh sieve that was 4.8 cm in diameter. The polymer on the sieve was allowed to drain 20 min, and the sieve was weighed to determine the weight of water-swollen gel. Absorbency was calculated as grams of water per gram of dry polymer, taking into account the initial moisture content of the polymer (about 10%). No correction was made for the percentage of the polymer that was soluble in water; the absorbency values would thus be higher if based only on insoluble polymer.

RESULTS AND DISCUSSION

Simultaneous Irradiation, Pregelatinized Starch

Graft polymerizations were carried out by first preparing an intimate blend of pregelatinized starch with a water solution of acrylamide and $AASO_3H$ and then irradiating the resulting mixture with cobalt 60. The amount of water in the polymerization recipe was adjusted so that the monomer solution would be totally absorbed by the starch to give a heavy paste which would not separate on standing. In previous work with another monomer system, we realized high grafting efficiencies under conditions similar to these.[4] After irradiation, the reaction mass was allowed to stand at ambient temperature for 2 hr and was then dewatered by blending with isopropanol. Extraction with isopropanol also served to remove any unreacted monomers.

In our first series of reactions (Table I), we prepared starch–monomer–water blends containing varying amounts of acrylamide and $AASO_3H$ and irradiated the resulting mixtures to a total dose of 0.5 Mrad. Each reaction used an equal weight of starch and total monomer (10 g). Since conversion of monomers to polymer was nearly quantitative in these reactions, as judged from the weight gain of starch due to graft polymerization, products of Table I are composed of about equal parts of starch and synthetic polymer.

Water absorbencies and water solubilities were next determined for each of the products in Table I. In the absence of $AASO_3H$ (reaction 1), water solubility was low (14%), and so was the absorbency. With the introduction of 10% $AASO_3H$ in the monomer mixture (reaction 2), water absorbency was increased by a factor of more than 10; however, over 59% of the reaction product was soluble in water. Absorbency continually increased with larger amounts of $AASO_3H$, whereas the water solubility remained at about 75%. A monomer mixture composed of 75% $AASO_3H$ and 25% acrylamide (reaction 5) gave a product with a water absorbency of 1200 g/g. However, with 100% $AASO_3H$, an absorbent polymer was not obtained because the final product was almost totally soluble in water (reaction 6).

Because of our high reactant concentrations, large exotherms were observed during these polymerizations. For reaction 4 of Table I, which used equal weights of the two monomers, the temperature rose from 25°C to 95°C after only

TABLE I
Dependence of Polymer Properties on Comonomer Ratio

Reaction no.	Reactants[a]		Products[b]	
	AA, g	$AASO_3H$, g	Water solubility, %	Absorbency, g H_2O/g polymer
1	10	0	14	12
2	9	1	59	160
3	7.5	2.5	73	540
4	5	5	75	750
5	2.5	7.5	74	1200
6	0	10	97	disperses

[a] AA = Acrylamide; $AASO_3H$ = 2-acrylamido-2-methylpropanesulfonic acid. Monomers dissolved in 10 ml water and blended with 10 g (dry basis) pregelatinized wheat starch. Mixtures irradiated to 0.5 Mrad at ambient temperature (25°C initially).

[b] Conversion of monomers to polymer was nearly quantitative in each reaction.

5.5 min of irradiation. This high temperature, coupled with the acidity of our sulfonic acid-containing system, no doubt caused some starch hydrolysis, which contributed to the observed high percentages of water solubles.

We next varied some of our reaction conditions to determine the effect on water absorbency and amount of water solubles. Initially, we examined variations in irradiation dose and reaction temperature (Table II), because these variables will obviously influence not only starch degradation but also polyacrylamide crosslinking.[5] Polymerizations were run with 5 g of each of the two monomers and 10 g of starch.

The conversion of monomers to polymer was nearly quantitative for each reaction in Table II. Reducing the total dose from 0.5 Mrad (reaction 4) to 0.1 Mrad (reaction 7) did not change the percent water solubles. However, water absorbency of the final product was increased from 750 g/g to 2100 g/g, possibly because of less radiation-induced polyacrylamide crosslinking. The lower temperatures in reactions 8 and 9 were achieved by cooling the starch–monomer–water mixture in ice water before cobalt-60 irradiation and then allowing the sample to remain in the ice bath during irradiation. The exotherm at the center of the reaction mass under these conditions reached a maximum of 60°C after an irradiation time of 6 min. This cooling procedure did not lead to large reductions in percent solubles; moreover, the absorbencies were appreciably reduced.

We next looked at the influence on graft copolymer properties of the total amount of the two monomers used (Table III). Each reaction was run with equal amounts of acrylamide and AASO₃H, and reaction mixtures were irradiated to

TABLE II
Dependence of Polymer Properties on Irradiation Dose and Reaction Temperature[a]

Reaction no.	Dose, Mrad	Initial temp., °C	Water solubility, %	Absorbency, g H_2O/g polymer
4	0.5	25	75	750
7	0.1	25	76	2100
8	0.5	5–10	56	270
9	0.1	5–10	62	800

[a] Reactions were run with 5 g each of acrylamide and 2-acrylamido-2-methylpropanesulfonic acid, 10 ml water, and 10 g (dry basis) pregelatinized wheat starch. Conversion of monomers to polymer was nearly quantitative in each reaction.

TABLE III
Dependence of Polymer Properties on Monomer Amounts

| Reaction no. | Reactants[a] | | Products[b] | |
	AA, g	AASO₃H, g	Water solubility, %	Absorbency, g H_2O/g polymer
7	5	5	76	2100
10	2	2	47	710
11	1	1	22	80
12	0.5	0.5	20	24

[a] Monomers dissolved in 10 ml water and blended with 10 g (dry basis) pregelatinized wheat starch. Mixtures irradiated to 0.1 Mrad at ambient temperature (25°C initially).
[b] Conversion of monomers to polymer was nearly quantitative in each reaction.

0.1 Mrad with no external cooling. Once again, conversion of monomers to polymer was nearly quantitative in each reaction. By reducing the amount of each monomer from 5 g to 2 g, water solubility was decreased to 47% and absorbency was also decreased. However, the product still had a very acceptable absorbency value of 710 g/g (reaction 10). Low absorbencies were obtained when the amount of each of the two monomers was reduced to either 1 g (reaction 11) or 0.5 g (reaction 12).

We next investigated the effect on product properties of either reducing or eliminating the possibility of acid hydrolysis of the starch moiety by partially or completely neutralizing $AASO_3H$ with sodium hydroxide before polymerization (Table IV). When half of the theoretical amount of sodium hydroxide was added to $AASO_3H$ before cobalt-60 irradiation (reaction 13), the water solubility of the final product was reduced from 73% to 48%, and water absorbency was reduced from 540 g/g to 340 g/g. In reaction 14, close to the theoretical amount of sodium hydroxide was used to neutralize $AASO_3H$; however, there was sufficient free acid remaining to give a final pH of 2.1. These reaction conditions lowered the solubles to 15% but gave a product with water absorbency of only 88 g/g. Similar results were obtained in reaction 15, where $AASO_3H$ was completely neutralized to a pH of 7.4. Addition of sodium hydroxide to $AASO_3H$ thus reduces solubles, probably by reducing starch hydrolysis; however, neutralization also leads to low-absorbency products.

Simultaneous Irradiation, Granular Starch

To complete our study of the graft polymerization of $AASO_3H$ and acrylamide under simultaneous irradiation conditions, we substituted 10 g granular pearl corn starch for pregelatinized wheat starch. Equal weights of the two monomers were used, and the monomer concentration in water was the same as that used for most of the reactions with pregelatinized wheat starch (4 g total in 4 ml). Equal weights of starch and total monomer could not be used because granular starch cannot absorb as much monomer solution as pregelatinized starch and still remain as a heavy-bodied paste which will not separate on standing.

Irradiation was carried out without cooling to a total dose of 0.1 Mrad, and the product was again isolated by isopropanol extraction followed by air drying. The conversion of monomers to polymer was nearly quantitative. Although distilled water absorbency of the granular product was only 9 g/g, absorbency

TABLE IV
Dependence of Polymer Properties on Neutralization of 2-Acrylamido-2-methylpropanesulfonic Acid[a]

Reaction no.	Degree of neutralization	Water solubility, %	Absorbency, g H_2O/g polymer
3	not neutralized	73	540
13	half neutralized	48	340
14	neutralized, pH 2.1	15	88
15	neutralized, pH 7.4	17	94

[a] Reactions were run with 7.5 g acrylamide and 2.5 g 2-acrylamido-2-methylpropanesulfonic acid, 10 ml water, and 10 g (dry basis) pregelatinized wheat starch. Mixtures were irradiated to 0.5 Mrad at ambient temperature (25°C initially). Conversion of monomers to polymer was nearly quantitative in each reaction.

was increased to 250 g/g when a 1% dispersion of the polymer was neutralized with sodium hydroxide to pH 7, then heated to 95°C, and finally allowed to air dry to a film on a Teflon-coated tray.

Graft Polymerization onto Preirradiated Starch

Two reactions were next carried out in which 30 g of either pregelatinized wheat starch or granular pearl corn starch was irradiated to 1 Mrad and then immediately added to a solution of 20 g each of $AASO_3H$ and acrylamide in 300 ml water. Free radicals generated within the starch matrix by irradiation are stable for finite periods of time and are thus available for reaction with monomers.[6] Products were again isolated by precipitation and extraction with isopropranol followed by air drying. Both reactions yielded sizable fractions (14–18 g) that were soluble in the isopropranol–water supernatant. These fractions were assumed to be mainly ungrafted poly(acrylamide–co–$AASO_3H$) and were therefore not examined further. Water absorbency of the polymer derived from pregelatinized starch was 270 g/g. Although the polymer prepared from granular starch showed only negligible absorbency, a value of 290 g/g was obtained when a 1% water dispersion of the product was neutralized to pH 7 with sodium hydroxide, heated to 90°C, and allowed to dry to a film at room temperature.

Fractionation and Characterization of Products

Selected graft polymerization products were fractionated by repeated extraction at room temperature with a 1% solution of sodium chloride (Table V). Water was used for the extraction of the product prepared from granular starch by simultaneous irradiation, because the swelling of this polymer was not excessive. Values for percent synthetic polymer in the various fractions were determined by weight loss on acid hydrolysis of the starch moiety, and the weight percent $AASO_3H$ in the remaining synthetic polymer was calculated from the sulfur analysis. Even though polyacrylamide is not inert to hot mineral acid, neither acid hydrolysis nor crosslinking should affect these gravimetric determinations. The sulfur analysis of a sample of poly($AASO_3H$) was not changed by the conditions of acid hydrolysis.

For each product of Table V, the soluble fraction was the lesser component, while the major portion remained insoluble after aqueous extraction. Products from reaction 9, Table II, and reaction 15, Table IV, gave lower percentages of soluble polymer by repeated extraction with 1% sodium chloride than they did by the water solubility determinations used in Tables II and IV. This discrepancy is probably caused by differences between aqueous sodium chloride and water as extraction solvents and by differences in the two experimental methods. Any ungrafted poly(acrylamide–co–$AASO_3H$) formed in these polymerization reactions would, of course, be found in the soluble fractions, and the respective insoluble fractions can therefore be considered as graft copolymers. Since values for percent add-on in the soluble fractions show the presence of considerable carbohydrate (and in some cases a predominance of carbohydrate), graft copolymer is no doubt also present in these fractions along with ungrafted poly(acryalmide–co–$AASO_3H$) and any ungrafted starch fragments.

Although conversions of monomer to polymer were essentially quantitative

TABLE V
Fractionation and Characterization of Selected Products

Product	Soluble fraction			Insoluble fraction		
	% of Total	Synthetic polymer content, %	Characterization of synthetic moiety	% of Total	Synthetic polymer content, %	Characterization of synthetic moiety
9, Table II	43	44	50% $AASO_3H$, 50% AA; $\bar{M}_n = 140{,}000$	57	56	39% $AASO_3H$, 61% AA; partially insol. in H_2O
15, Table IV	11	56	18% $AASO_3H$, 82% AA	89	48	31% $AASO_3H$, 69% AA; partially insol. in H_2O
Granular starch, simultaneous	21	36	48% $AASO_3H$, 52% AA	79	27	36% $AASO_3H$, 64% AA
Pregelat. starch, preirradiated	28	38	43% $AASO_3H$, 57% AA; $\bar{M}_n = 120{,}000$	72	25	39% $AASO_3H$, 61% AA; partially insol. in H_2O
Granular starch, preirradiated	5	70	41% $AASO_3H$, 59% AA	95	36	34% $AASO_3H$, 66% AA; $\bar{M}_n = 126{,}000$

for reactions run by simultaneous irradiation, use of preirradiated starch led to only partial conversion. It is apparent from analyses of synthetic moieties that polymers generally contain a lower percentage of $AASO_3H$ than was present in the initial monomer mixtures. With the exception of the product of reaction 15, Table IV, the synthetic polymers isolated from soluble fractions contained higher percentages of $AASO_3H$ than those resulting from the respective insoluble fractions.

To obtain synthetic polymer moieties which could be used for molecular weight determination, selective fractions of Table V were subjected to hydrolysis with enzyme. Under these mild conditions, starch could be removed without the danger of altering the acid-sensitive, polyacrylamide-containing portion; although polymers generally contained about 5–10% residual carbohydrate. Some of the synthetic polymers isolated from insoluble fractions were partially insoluble in water, and molecular weights of these polymers were therefore not determined. Membrane osmometry was used to determine number-average molecular weights of polymers that were totally soluble; these $\overline{M}_n$ values were in the 120,000 to 140,000 range.

Comparison with Earlier Starch Graft Copolymer Absorbents

Absorbents prepared by graft polymerization of acrylonitrile onto starch followed by saponification in aqueous alkali typically have absorbency values on the order of 1000 g/g when the starch is gelatinized before graft polymerization and about 300 g/g when the graft polymerization is carried out with granular starch.[2] Water solubilities of these absorbent polymers range from about 20% to 35%.[7] Substitution of flour for starch increases absorbencies by about a factor of 3; and when minor amounts of $AASO_3H$ are incorporated with acrylonitrile during the graft polymerization, absorbencies of the saponified starch graft copolymers are also increased appreciably.[2]

Absorbencies of the unsaponified starch graft copolymers prepared in the present study are therefore comparable to those of our earlier products prepared by graft polymerization followed by saponification. Some of the present products, however, contain high percentages of water solubles. This soluble polymer does not contribute to absorbency, and the leaching out of solubles might also be considered objectionable in some end-use applications.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

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