

Starch-poly(acrylamide-co-2-acrylamido-2-methylpropanesulfonic acid) graft copolymers prepared by reactive extrusion

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Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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ABSTRACT: Graft copolymers of starch with acrylamide and 2-acrylamido-2-methylpropanesulfonic acid (AMPS) were prepared by reactive extrusion in a twin-screw extruder. The weight ratio of total monomer to starch was fixed at 1 : 3, while the molar fraction of AMPS in the monomer feed ranged from 0 to 0.119. Monomer to polymer conversions were 85% or greater, with grafting efficiencies of 68% (highest AMPS content) to 85% (no AMPS). Absorbency in distilled water at pH 7 increased linearly with the mole fraction AMPS in the grafted polymer, while absorbencies in 0.9% NaCl were independent of AMPS content. When swollen in water/ethanol mixtures, swelling decreased gradually with increasing ethanol volume fraction, followed by a large decrease over a narrow ethanol concentration. This behavior is similar to that observed for AMPS-acrylamide gels. The swelling properties suggest these graft copolymers may have applications as responsive materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42405.

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INTRODUCTION

There is considerable interest in the development of starch-based copolymers for uses such as superabsorbents, hydrogels, and controlled release. In particular, graft copolymers of starch with water-soluble polymers such as hydrolyzed polyacrylonitrile, polyacrylamide, and polyacrylic acid have been investigated. Starch graft copolymers are typically prepared using batch processes with relatively low solids contents (20% or less) and reaction times of several hours. The low solids content are needed to prevent excessive viscosities which cause processing difficulties and can lead to inhomogeneous products. We have recently demonstrated the efficacy of reactive extrusion in producing starch-polyacrylamide graft copolymers. Using a twin screw extruder, graft copolymers were produced in a continuous manner, with high reaction and grafting efficiencies.¹⁻⁴ Starch-polyacrylamide graft copolymers require saponification to produce swelling values greater than 100 g/g.⁵

AMPS (2-acrylamido-2-methylpropanesulfonic acid) is commonly used in water soluble or swellable polymers in applications such as hydrogels, thickeners, adhesives, and water treatment (AMPS is a registered trademark of the Noveon Corporation). Acrylamide-AMPS copolymers have been extensively

studied in recent years, either as soluble polymers⁶ or as cross-linked gels.⁷⁻¹¹ AMPS has been investigated as a comonomer with acrylamide in starch graft copolymers, since the strongly dissociating AMPS groups reduces pH effects on swelling and water absorbency. Fanta *et al.* polymerized starch with mixtures of acrylamide (AAM) and AMPS using Co60 radiation.¹² Absorbency and water solubility increased with increasing AMPS fraction for a fixed monomer/starch ratio of 1/1. Incorporation of 10% AMPS (monomer weight basis) increased absorbency more than tenfold compared to the copolymer with acrylamide only. At a fixed AMPS/AAM ratio of 1/1, absorbency and water solubility increased as the monomer/starch ratio increased from 1/10 to 1/1. It has also been reported that AMPS significantly reduces saponification times for hydrolyzed starch-polyacrylonitrile superabsorbents.¹³ Xu *et al.* characterized the swelling properties of starch/acrylic acid/AMPS graft copolymers prepared with ammonium persulfate and microwave heating.¹⁴ They found that maximum swelling of approximately 450 g/g in water occurred with a starch/acrylic acid/AMPS ratio of 2 : 5 : 3, yielding a graft copolymer of 20% by weight starch. Amylopectin was grafted with p(Aam-co-AMPS) using CAN in solution.¹⁵ Graft copolymer properties were controlled by varying the ratios of constituents. Flocculation and water absorption

Table I. Starting Compositions Based on Feed Rates

Sample	Weight fraction (total feed) ^a		Molar fraction (monomer feed)	
	AAM	AMPS	AAM	AMPS
SGP0	0.260	0.0	1.00	0
SGP1	0.229	0.030	0.957	0.043
SGP2	0.215	0.044	0.934	0.066
SGP3	0.209	0.057	0.915	0.085
SGP4	0.187	0.071	0.885	0.115

^aWeight fractions are calculated on solids basis. Balance of solids is starch.

was maximized at a monomer ratio of 2 : 1 AM : AMPS. Dextran (MW = 500 K) were grafted with AMPS¹⁶ and Aam/AMPS⁷ also using CAN in a batch process. Complex initiators were also investigated for corn starch-g-(Aam-co-AMPS).¹⁷ Soluble starch-Aam-AMPS copolymers have been prepared and evaluated for use in oil recovery applications,¹⁷ fire retardants,¹⁸ metal chelators,¹⁵ and as gel polyelectrolytes.¹⁹

Here we report the properties of starch/AAM/AMPS graft copolymers prepared using reactive extrusion. The total monomer/starch ratio was fixed at 1 : 3, with AMPS molar fraction in the monomer feed up to 0.115. Conversion, grafting, and copolymer composition were determined, as were swelling in distilled water and 0.9% NaCl. Swelling properties in ethanol/water mixtures were also measured. For the first time, we report on the composition of the soluble and insoluble products generated from reactive extrusion as well as the copolymer molecular weight distributions.

EXPERIMENTAL

Materials

The starch used was unmodified dent cornstarch (PFP, Tate and Lyle NA). Acrylamide was obtained from Kemira as a 50 wt % solution (nominal) and used as received. Ammonium persulfate (APS) and AMPS were obtained from Sigma and used without further purification. Deionized water was used. APS was fed as a 2 wt % solution and AMPS as a 20 wt % solution. Solutions were pumped using triple piston oscillating pumps (Eldex) and flow rates were measured by following the weight changes in the fluid reservoirs. Formulations are listed in Table I as weight

fractions (based on total solids) and molar fractions (based on monomer feed).

Polymerization

Reactive extrusion was performed using a Werner and Pfleiderer ZSK-30 twin screw extruder.² The extruder had fourteen barrel sections (BS) and eight temperature control zones with a *L/D* ratio of 44. The extruder and screw configuration is shown in Figure 1. Starch (ambient moisture content \approx 10%) was fed gravimetrically in the feed throat, followed by water injection and a series of mixing elements on the screw. Acrylamide was injected after initial water, mixed, and AMPS was injected next and mixed again with kneading blocks. One-half of the APS initiator was then injected, followed by two mixing sections. The remaining APS was injected at the end of the barrel, also followed by two mixing sections. A two-strand die (4 mm diameter) with temperature and pressure readout was used, and enclosed in a ventilated polycarbonate sampling chamber to minimize exposure to unreacted monomers. The feed throat was maintained at room temperature and the first heating zone at 60°C. All remaining barrel sections were maintained at 90°C. The screw speed was 150 rpm, and the total feed rate including water to give moisture content of 50% was 180 g/min (\pm 5 g/min). The total APS concentration was 3.8×10^{-3} mol/kg (based on feed rate).

After adjusting pump rates to give the desired monomer feed composition, 10–12 min (approximately 3 retention periods) were allowed to reach steady state. Samples were then collected for approximately 30 s, and immediately quenched in ethanol with 0.1% hydroquinone while stirring for 4 min in a Waring blender. Extrudates were steeped in the ethanol solution overnight to remove unreacted monomer. After filtering and drying, extrudates were extracted using a 70/30 water/ethanol solvent to remove ungrafted polymer. Nitrogen contents were measured using a Perkin-Elmer 2400 Series Dumas-type HCN analyzer. Sulfur contents were determined by Galbraith Laboratories.

Evaluation

Conversion of monomer to polymer was determined as the ratio of monomer weight fractions in the quenched extrudates to the feed rates. AMPS weight fractions (w_{AMPS}) were calculated using the *S%* values, and acrylamide weight fractions (w_{AAM}) using % *N* results:

$$w_{AMPS} = \frac{S\%}{15.4\%}$$

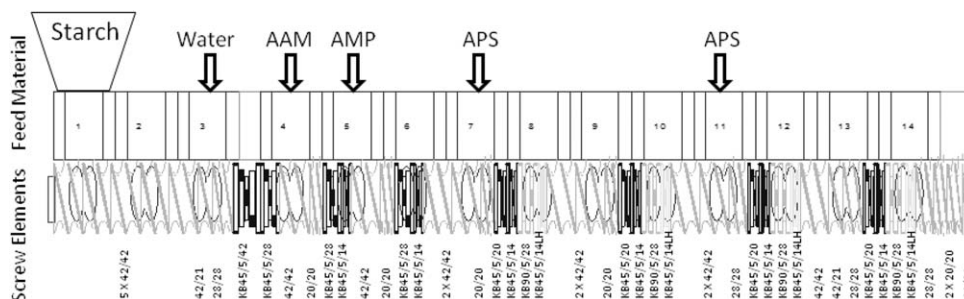


Figure 1. Extruder and screw configuration.

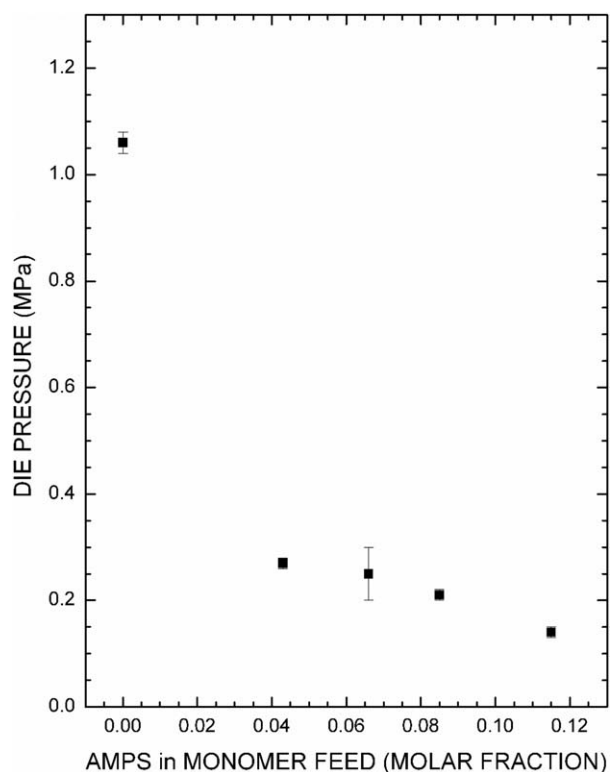


Figure 2. Relation between extruder die pressure and AMPS in the reaction feed.

$$w_{\text{AAm}} = \frac{N\% - 0.437(S\%)}{19.72}$$

Molar fractions (f) of AMPS were calculated following McCormick²⁰

$$f_{\text{AMPS}} = \frac{14.1(S\%)}{32.1(N\%)}$$

Swelling properties of the unextracted graft copolymers were measured in deionized water and 0.9% NaCl solutions at pH 7.⁵ Swelling was also measured in water–ethanol solvents of varying ethanol content using the same procedure.

Molecular weights were determined using size exclusion chromatography as described previously.¹ After extraction with

aqueous ethanol, the starch fraction was removed by enzymatic hydrolysis. The remaining graft soluble copolymers were filtered and eluted at 1.0 mL/min using 0.1M NaNO₃ mobile phase at 40°C. Weight average molecular weights were determined using polyethylene oxide standards.

RESULTS AND DISCUSSION

Extrusion was performed with a monomer/starch ratio of 1 : 3 and a total feed rate of 180 g/min. Molar fractions of AMPS in the monomer feed ranged from 0 to 0.115. For all compositions, extrusion was stable with no major fluctuations in die pressure or torque. Figure 2 shows the die pressure dependence on AMPS molar fraction during extrusion. With no AMPS present, die pressure was approximately 1.1 MPa. The addition of 4.4 mol % AMPS reduced the pressure by roughly 75%, to 0.3 MPa. Die pressure decreased gradually to approximately 0.15 MPa as the AMPS content was increased to 11.9 mol %. The significant drop in die pressure on addition of AMPS is most likely due to acid-catalyzed starch hydrolysis during extrusion. AMPS was used in its acid form without neutralization. AMPS is a strongly dissociating acid ($pK_a \approx 2$)⁸ and the effective pH in the extruder would be quite low. Specific mechanical energy values showed a similar trend, decreasing from 185 kJ/kg with no AMPS to 109 kJ/kg at the highest AMPS level, consistent with the die pressure results.

Conversion and grafting results are shown in Table II. Monomer weight fractions in the feed were calculated using the measured feed rates during extrusion, while the compositions of the extrudates and graft copolymer (after extraction) were calculated using S% and N% analyses. Both monomers are converted to polymer with high efficiency during the extrusion process, with the AAm-only feed giving the lowest conversion (86.1%). In all other cases, conversions exceed 90% for each monomer. The conversion data suggest that AMPS improves the overall conversion of AAm, but no definitive conclusions can be drawn from the data in Table II regarding this effect although our results are consistent with conversion rates for dextran-g-p(AAm-co-AMPS).⁷

Graft contents are given in the last column of Table I. The lowest graft content (21.3%) was obtained with the AAm-only feed, while graft contents with AMPS range from 25.5 to 28.3%. The

Table II. Conversion and Grafting Data

Sample	Extrudate composition (wt. fractions) ^a		Graft composition (wt. fractions) ^a		Conversion (%)			Graft content (wt %)
	AAm	AMPS	AAm	AMPS	AAm	AMPS	Total	
SGP0	0.224	–	0.213	–	86.1	–	86.1	21.3
SGP1	0.212	0.031	0.225	0.030	92.4	103.3	93.8	25.5
SGP2	0.210	0.042	0.239	0.044	97.8	95.4	97.3	28.3
SGP3	0.192	0.054	0.205	0.055	91.9	94.7	92.5	26.0
SGP4	0.188	0.070	0.197	0.078	100.5	98.6	100.0	27.5

^aWeight fractions are calculated on solids basis. Balance of solids is starch.

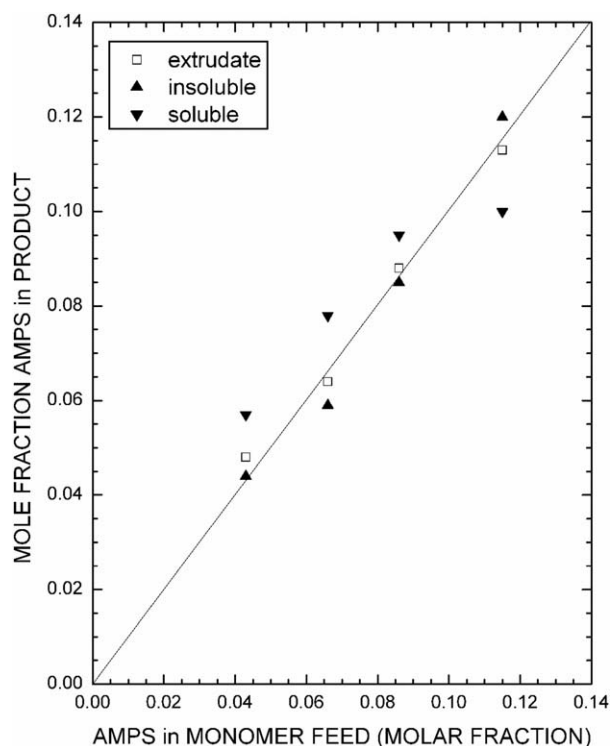


Figure 3. Correlation between graft copolymer composition and feed composition (extrudate prior to extraction \square ; insoluble fraction \blacktriangle ; soluble fraction \blacktriangledown).

AMPS-containing copolymers have graft contents greater than the nominal monomer-starch feed ratio of 1/3. The enhanced graft contents are primarily a result of the increase in soluble starch in the presence of AMPS (see below).

Figure 3 shows the relationship between feed composition and copolymer (PAAm-*co*-AMPS) composition. The copolymer composition in the unextracted extrudate is equal to the monomer feed. This result is consistent with the high conversions shown in Table II. In addition, it is seen in Figure 3 that the insoluble grafted copolymer and the soluble polymer fraction have the same composition as the extrudate. The lack of composition variation in the various polymer fractions indicates that grafting reactions with starch do not affect the copolymerization of AAm and AMPS. The copolymer composition results

in Figure 3 are consistent with results reported for copolymerization of AAm and AMPS at lower conversions.^{6,8–10,20,21}

Graft efficiency, defined as the fraction of polymer grafted relative to total polymer formed, was determined by extraction with 70/30 water/ethanol solvent. Solubility and grafting efficiency data are given in Table III. The addition of AMPS has a significant impact on the solubility of the product and graft efficiency. With AAm as the only monomer, 11.0% of the extrudate is soluble in the water/ethanol solvent. The presence of AMPS increases the amount soluble by a factor of three or more. The composition of the soluble fraction is also dependent on AMPS content. The soluble fraction is approximately 20% polymer when AMPS is present, but almost 31% when AAm only is used. The increase in solubles is due to increased solubility of both starch and polymer compared to the AAm-only extrudate. Examination of Table II shows that when AMPS is absent, approximately 10% of the total starch and 15% of the polymer in the extrudate are soluble. The amount of soluble polymer approximately doubles with addition of AMPS, while the amount of soluble starch increases nearly fourfold to approximately 40%. This increase in soluble material is consistent with the large decrease observed in die pressure (Figure 2) and indicates that acid-catalyzed hydrolysis of starch occurs during extrusion.

The increase in soluble starch has the effect of increasing the graft content, which is based on analysis of the insoluble fraction. With no AMPS, the graft content is 21.4%, giving a graft efficiency of 84.6%. Graft contents with AMPS ranged from 25.6 to 28.2%, which are all in excess of the monomer/starch ratio in the feed. As a result of the increased solubility of starch and polymer fractions with AMPS, the graft efficiencies are lower, ranging from 68.3 to 72.7%. Grafting of corn starch with (Aam-*co*-AMPS) using a dual initiator system showed a similar trend as grafting efficiency decreased with increasing AMPS concentration.¹⁷ Differences in the grafting content can be attributed to the reaction parameters including time, solids content, and initiator systems.

Gel permeation chromatograms which reflect the molecular weight distributions (MWD) of the grafted copolymers are shown in Figure 4. Grafted copolymers were isolated after extracting the soluble polymer in the ethanol/water solvent and enzymatic removal of the starch component. Peaks at

Table III. Extraction and Graft Efficiency Data

Sample	Soluble fraction			Insoluble fraction			Graft Efficiency (%)
	Wt % ^a	Starch (wt %)	Polymer (wt %)	Wt % ^b	Starch (wt %)	Polymer (wt %)	
SGP0	11.0	69.1	30.9	89.0	78.6	21.4	84.6
SGP1	31.0	78.7	21.3	69.0	74.4	25.6	72.7
SGP2	36.1	80.1	19.9	63.9	71.8	28.2	71.5
SGP3	35.1	78.1	21.9	64.9	74.0	26.0	68.6
SGP4	35.9	77.2	22.8	64.1	72.5	27.5	68.3

^aPercentage by weight of extrudate which is soluble in 70/30 water/ethanol.

^bPercentage by weight of extrudate which is insoluble in 70/30 water/ethanol.

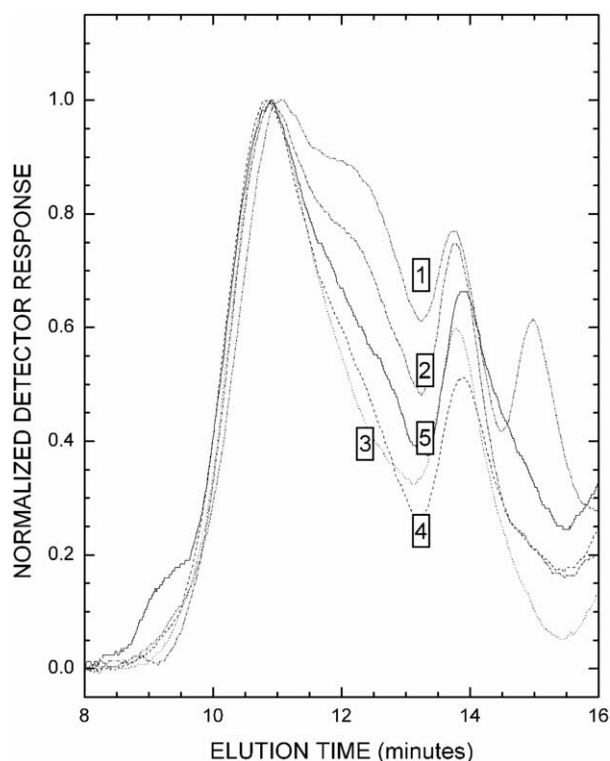


Figure 4. Elution curves of grafted PAAm-AMPS. Copolymer molar fractions AMPS: (1) no AMPS; (2) 0.043; (3) 0.066; (4) 0.085; (5) 0.115.

approximately 14 and 15 min are due to the enzymes used in the starch digestion. The chromatogram of the PAAm homopolymer with no AMPS shows two distinct peaks at approximately 11 and 12 min. As the AMPS molar fraction increases, the higher molecular peak shifts slightly (≈ 0.2 min) to shorter elution time, indicating an increase in molecular size. The elution time of this peak is independent of the AMPS content. The peak at roughly 12 min decreases in magnitude with increasing AMPS content. In addition, the copolymer with the highest AMPS content displays a small shoulder eluting at approximately 9.5 min.

Figure 4 shows that the incorporation of AMPS into the copolymer results in a narrower MWD and higher average molecular weight. Similar elution patterns have been observed in previous work on starch-polyacrylamide graft copolymers and depend strongly on the initiator and acrylamide concentrations.² It has been shown that under comparable conditions of persulfate concentrations (0.2 to 0.8%) and temperature (78°C), persulfate initiation leads to branching in polyacrylamide.²² If the longer eluting shoulder reflects the formation of branched polymer, then the data of Figure 6 suggest that inclusion of AMPS may decrease the degree of branching during reactive extrusion. This might be expected if the charged sulfonate groups in the polymer inhibit hydrogen abstraction by either a negatively charged persulfate ion or a growing chain end. Regardless of the exact mechanism, Figure 4 demonstrates that incorporating AMPS into the graft copolymer strongly influences the resulting MWD and average molecular weight. It is noted that in a previous report of acrylamide-AMPS copolymerization, no change in

number-average molecular weight was observed when AMPS was present at 10 mol %, albeit at lower polymerization temperature (30°C) and solids content (8.4%).⁶

Molecular weights (M_w) are shown in Figure 5. The PAAm homopolymer (no AMPS) has a molecular weight of 478,000 g/mol. As the AMPS content in the monomer feed increases, the resulting copolymer molecular weight increases, reaching a value of 873,000 g/mol² at an AMPS mole fraction of 0.085. Increasing the AMPS content to 0.115 results in a decrease in molecular weight to 732,000 g/mol, which is approximately 50% greater than the PAAm with no AMPS. As shown in Figure 4, the molecular weight increase is largely due to reduction in lower molecular fraction which elutes at approximately 12 min. The lower molecular weight of the copolymer with the highest AMPS content appears to be due to the increased amount of lower molecular weight fraction elution past the peak, as seen in Figure 4.

Graft frequencies (grafts/1000 AGU) are shown in Figure 6. As the AMPS mole fraction of the monomer feed increases to 0.085, the graft frequency decreases from 0.185 to 0.130. Increasing the AMPS mole fraction to 0.115 results in an increase in graft frequency to 0.168. Therefore, incorporating AMPS as a comonomer yields starch graft copolymers with fewer grafts of higher molecular weight compared to using AAm alone, up to an AMPS mole fraction of approximately 0.09. Apparently higher AMPS levels reduce the copolymer molecular weight and the graft frequency.

Swelling or absorbency data are shown in Figure 7. Since a viable commercial process would not involve an extraction step, swelling was determined using the extrudates without

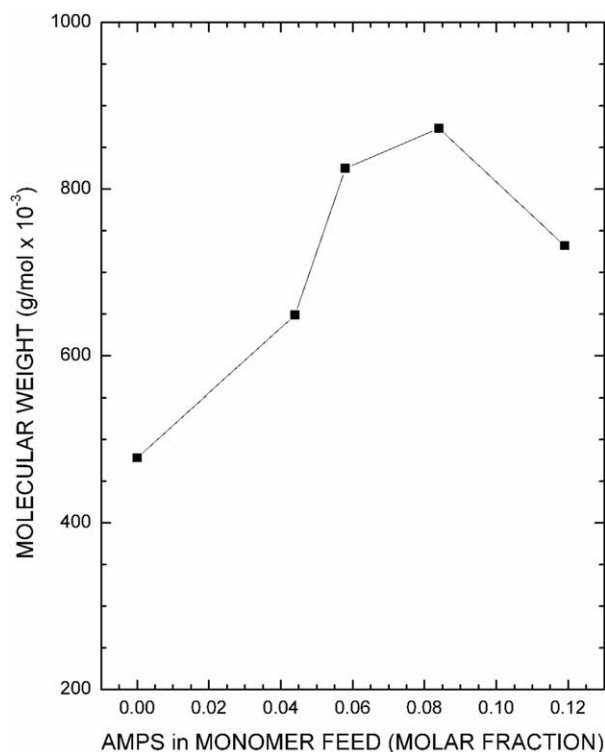


Figure 5. Molecular weights of graft PAAm-AMPS.

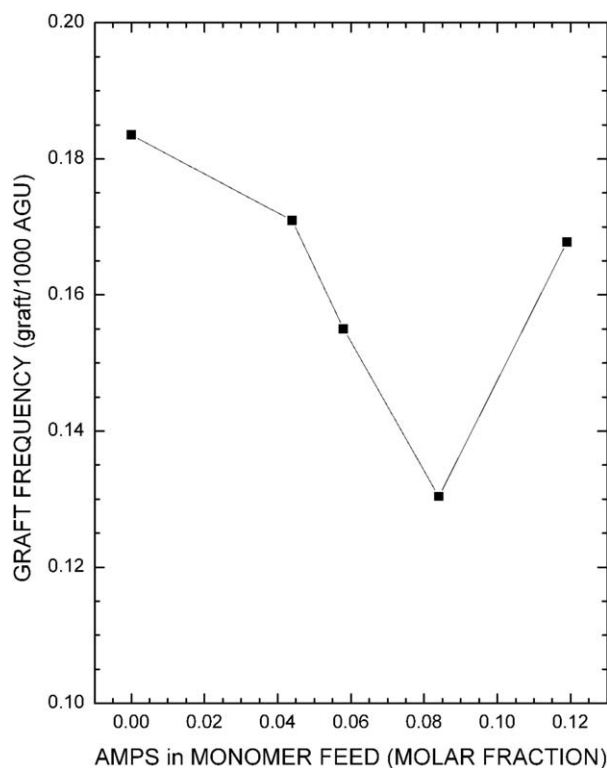


Figure 6. Grafting frequency (grafts/1000 AGU) of PAAm-AMPS copolymers.

extraction. Swelling was measured in deionized water at pH 7 and in 0.9% NaCl. In water, swelling increased from approximately 25 g/g with AAm only to nearly 200 g/g at an AMPS molar fraction of 0.115. There is a linear correlation between the molar fraction AMPS in the copolymer and swelling ($r^2 = 0.99$). This result demonstrates the critical role of ionized AMPS groups in swelling. Swelling of AAm-AMPS gels has also been shown to increase significantly with increasing AMPS content.¹⁰ In comparison, Fanta *et al.* obtained swelling of 160 g/g in a starch/AAm/AMPS copolymer with 50% copolymer content and an AMPS molar fraction of 0.037.¹² With a polymer content of approximately 28% and an AMPS molar fraction of 0.255, swelling of 710 g/g was obtained. Xu *et al.* reported swelling values of approximately 300 to 450 g/g, but with copolymers containing 80% polymer and high levels of AMPS.¹⁴

Also shown in Figure 7 are swelling data obtained in 0.9% NaCl solution. At this concentration of electrolyte, swelling is independent of AMPS content with an average value of 31 (± 8) g/g. The lower swelling values are due to the screening of electrostatic interactions between AMPS groups, and are consistent with the effect of electrolytes on swelling of AAm-AMPS gels.^{8,11} Xu *et al.* found a maximum in swelling in 0.9% NaCl of approximately 55 g/g, for a copolymer consisting of 80% AAm-AMPS polymer and only 20% starch.

During extraction with 70/30 water/ethanol, it was noted that the materials with AMPS swelled significantly to a degree dependent on the AMPS content. This effect was further examined using a series of solvents with varying water/ethanol ratios. As shown in Figure 8, the graft copolymer with no AMPS

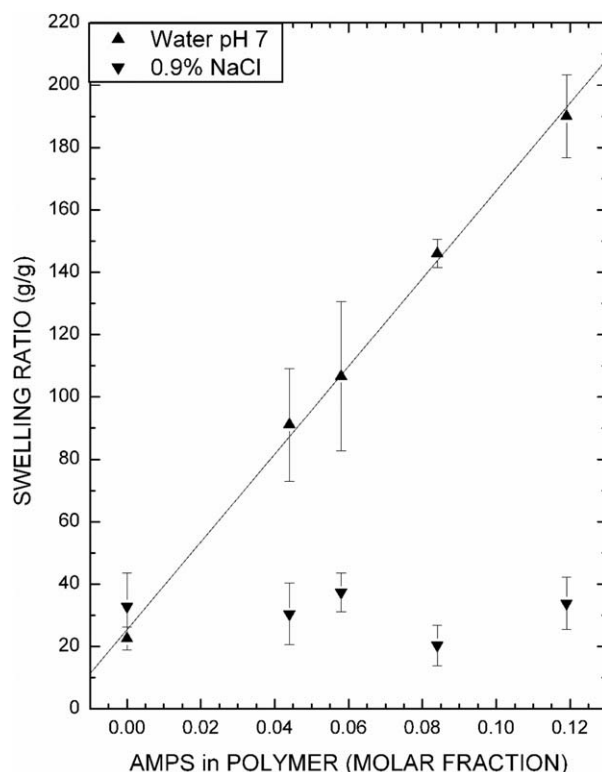


Figure 7. Swelling of starch-PAAm-AMPS graft copolymers in water (deionized water \blacktriangle ; 0.9% NaCl \blacktriangledown).

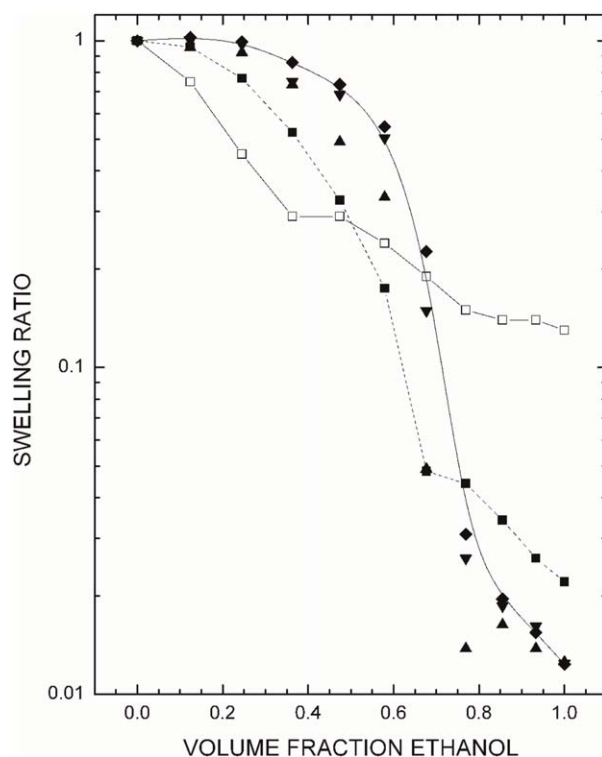


Figure 8. Swelling curves of starch-PAAm-AMPS graft copolymers in aqueous ethanol solvents. (molar fractions AMPS in copolymer: AAm only \square ; 0.044 \blacksquare ; 0.058 \blacktriangle ; 0.084 \blacktriangledown ; 0.115 \blacklozenge).

shrank (deswelled) steadily as the volume fraction ethanol (φ) increased. Incorporation of AMPS had two effects on swelling. First, AMPS increases swelling at low ethanol fractions. Second, a large decrease in swelling occurred over a relatively narrow range of ethanol content, typically between $\varphi \approx 0.6$ and 0.7 . The inflection point of the swelling curves occurred at higher ethanol fractions as the AMPS content increased. It is noted that the large decreases in swelling shown in Figure 8 are continuous, with transitions that become sharper as the AMPS content increased. The reversible nature of swelling in aqueous ethanol was demonstrated by adding sufficient ethanol to previously equilibrated samples to give $\varphi = 0.80$. The gels deswelled to a value comparable to that of samples exposed only to this same solvent.

Discontinuous changes in swelling of AAm–AMPS gels in water–acetone solvents have been reported.⁸ Discontinuous transitions in AAm–AMPS gels have been interpreted in terms of the effect of AMPS on the critical interaction parameter (χ_{cr}): as the AMPS content in the gel increases, χ_{cr} increases and shifts the transition to higher acetone contents. The data of Figure 8 are consistent with this interpretation, and indicate that the swelling and deswelling properties of starch–PAAm–AMPS graft copolymers depend primarily on the copolymer fraction.

CONCLUSIONS

Graft copolymers of starch with acrylamide and AMPS can be easily prepared at high yield using reactive extrusion. Incorporation of AMPS gives grafted copolymers with fewer grafts of higher molecular weight compared to AAm alone. AMPS also hydrolyzes starch into soluble oligomers and increases the soluble fraction, reducing the overall yield. In deionized water at pH 7, swelling is directly proportional to AMPS content in the copolymer, whereas as swelling in 0.9% NaCl is constant. The graft copolymers with AMPS swell in aqueous ethanol solvents, and show a sharp deswelling transition over a narrow ethanol volume fraction range. The critical ethanol range increases with increasing AMPS content. The swelling properties of these copolymers suggest they may be useful as stimuli-responsive materials.

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