Influence of Starch Granule Swelling on Graft Copolymer Composition.   A Comparison of Monomers*

GEORGE F. FANTA, ROBERT C. BURR, W. M. DOANE and C. R. RUSSELL, *Northern Regional Research Laboratory, Northern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Illinois 61604*
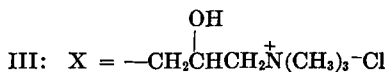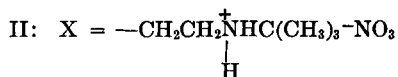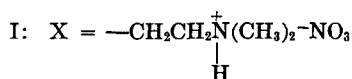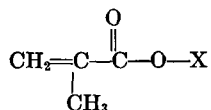
Synopsis

Seven monomers, which varied widely in water solubility and ionic charge, were graft polymerized onto both unswollen starch and starch that had been swollen by heating in water to 60°C. Polymerizations were initiated with ferrous ammonium sulfate hexahydrate–hydrogen peroxide and, where applicable, with ceric ammonium nitrate. Graft copolymers were freed of ungrafted homopolymer by solvent extraction and were characterized by weight percentage of synthetic polymer incorporated in the graft copolymer, molecular weight of grafted branches, and grafting frequency. The influence of starch granule swelling on graft copolymer structure varied with the monomer used and could not be predicted on the basis of water solubility of monomer or its resulting polymer. With acrylonitrile and acrylamide, swollen starch gave higher molecular weight and less frequent grafts than unswollen starch. However, methyl methacrylate, N,N-dimethylaminoethyl methacrylate·HNO₃, N-*t*-butylaminoethyl methacrylate·HNO₃, and 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride produced less frequent grafts of higher molecular weight when starch was unswollen. With acrylic acid, graft molecular weight was independent of starch granule swelling, although grafting was less frequent when swollen starch was used.

INTRODUCTION

The influence of starch granule swelling on the structure of starch–polyacrylonitrile graft copolymers has been described in an earlier publication from this laboratory.[1] Granule swelling, brought about by heating an aqueous starch slurry to 60°C before reaction at room temperature with monomer and initiator, caused a marked increase in the molecular weight of grafted branches as compared with graft copolymers prepared without prior heating of the starch. The reverse was recently observed, however, when the nitric acid salt of N,N-dimethylaminoethyl methacrylate (I) was used as the monomer, a greater number of grafted branches of lower molecular weight being grafted when starch granules were swollen.[2]

To understand better how the structure of the monomer affects the reaction products obtained with swollen versus unswollen starch, seven different monomers were graft polymerized onto swollen and unswollen starch under comparable reaction conditions. The monomers were chosen to encompass a broad range with respect to water solubility and ionic charge. Acrylonitrile and methyl methacrylate have only limited solubility in water and their polymers are water insoluble. Acrylamide, acrylic acid, compound I, the nitric acid salt of N-t-butylaminoethyl methacrylate (II), and 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride (III) are soluble in water, as are their polymers. Polyacrylamide, is a non-

$$CH_2{=}C{-}\overset{\overset{\textstyle O}{\|}}{C}{-}O{-}X$$
$$\underset{\textstyle CH_3}{|}$$

I: X = $-CH_2CH_2\overset{+}{N}(CH_3)_2{}^-NO_3$
$\underset{\textstyle H}{|}$

II: X = $-CH_2CH_2\overset{+}{N}HC(CH_3)_3{}^-NO_3$
$\underset{\textstyle H}{|}$

$\overset{\textstyle OH}{}$
III: X = $-CH_2\overset{|}{C}HCH_2\overset{+}{N}(CH_3)_3{}^-Cl$

ionic polymer, while the other four water-soluble polymers are polyelectrolytes. Poly(I), poly(II), and poly(III) are cationic polyelectrolytes and fall into the general category of polybases.[3] Poly(acrylic acid), however, is a weak polyacid. Graft polymerizations were initiated with ferrous ammonium sulfate hexahydrate–hydrogen peroxide and also, where applicable, with ceric ammonium nitrate. With the ferrous–peroxide initiator, hydroxyl radicals are produced[4] which abstract hydrogen atoms from starch. With ceric initiation, a starch–ceric complex is first formed which then reacts further to give starch-free radicals.[5]

EXPERIMENTAL

Materials

The starch used was unmodified wheat starch (Huron Starbake) from Hercules Incorporated.

Ferrous ammonium sulfate hexahydrate and 30% hydrogen peroxide were Baker Analyzed Reagent Grade. Ceric ammonium nitrate was Fisher Certified ACS Grade.

Methyl methacrylate, acrylamide, and acrylic acid were Eastman Reagent Grade. Acrylonitrile was Eastman Practical Grade. Monomers I and II were from Rohm & Haas and contained 2000 and 1000 ppm of MEHQ, respectively. These six monomers were used without further

purification.   Monomer III was Sipomer Q-1 from Alcolac Chemical Corp. and was recrystallized from isopropanol before use.

Rhozyme H-39, a bacterial diastase, was from Rohm & Haas.   Aqueous solutions containing 1 mg of enzyme per milliliter were freshly prepared before use.   Enzyme activity was not determined.

Graft Polymerization

In ceric ammonium nitrate-initiated polymerizations onto swollen starch, a stirred slurry of 48.6 g, dry basis, of wheat starch, 0.3 mole anhydroglucose unit (AGU), in 400 ml water was sparged with a stream of nitrogen for 1 hr at 60°C and then cooled to room temperature.   With unswollen starch, water was sparged separately and then added to the starch.   A mixture of monomer (0.3 mole in most reactions) in 25 ml of nitrogen-sparged water was then added to the starch slurry followed after 5 min by 1.644 g (3 × 10^{-3} mole) of ceric ammonium nitrate dissolved in 5 ml of $1N$ nitric acid. The mixture was stirred for 2 hr at 25°C, and the reaction was terminated by the addition of 2 g hydroquinone.

In polymerizations initiated by the ferrous–peroxide redox system, 0.12 g (3 × 10^{-4} mole) of ferrous ammonium sulfate hexahydrate dissolved in about 2 ml water was added to the stirred starch slurry.   Monomer and 0.35 g of 30% hydrogen peroxide (3 × 10^{-3} mole) were then added at 5-min intervals, and the mixture was stirred for 2 hr at 25°C.

The nature of some monomers required the following variations in procedure.   Monomer III was added as the dry powder followed by 25 ml water.   In acrylamide polymerizations which used 0.9 mole monomer, starch was suspended in 350 ml water, and acrylamide was added as a solution in 75 ml water.   Monomers I and II were suspended in 25 ml water, and $6N$ nitric acid was added to a pH of 2 (50 ml was required). This solution was then added to the suspension of starch in 350 ml water.

Graft copolymer, which in all reactions was water insoluble, was separated by either centrifugation or filtration and was washed three times with cold water and dried.   In reactions that produced water-soluble homopolymers (acrylamide acrylic acid, I, II, and III), the homopolymer was removed in the water extracts and isolated by dialysis and freeze drying. Polymerizations of acrylonitrile and methyl methacrylate onto swollen starch gave about 1–5 g of solid colloidally dispersed in the water extracts. These solids, which contained both carbohydrate and synthetic polymer (by infrared analysis), were not investigated further.   With acrylonitrile graft copolymerization, the homopolymer was removed by threefold extraction of the dry, water-washed product with dimethylformamide.   With methyl methacrylate graft copolymerization, the dry, water-washed product was first moistened to a water content of 25–30%[6] and then extracted with 1,2-dichloroethane.

In all reactions, 94–100% of the starch was accounted for in the graft copolymer fraction.   A material balance was not obtained since unreacted

monomer was not isolated, but good material balances had been achieved in earlier graft polymerizations with acrylonitrile.[7]

Grafting efficiency was calculated as follows:

grafting efficiency (%)

$$= \frac{\text{wt of polymer grafted to starch}}{\text{wt of polymer grafted to starch} + \text{wt of homopolymer}} \times 100.$$

Although polymer removed by solvent extraction sometimes contained measurable amounts of carbohydrate (5–10%), it was considered to be homopolymer for grafting efficiency calculations.

Per cent add-on was calculated as follows:

$$\text{add-on (\%)} = \frac{\text{wt of synthetic portion of graft copolymer}}{\text{total wt of graft copolymer}} \times 100.$$

Hydrolysis of Graft Copolymer and Molecular Weight of Grafted Branches

Starch was removed by hydrolysis from a portion of each graft copolymer to determine the per cent add-on and also the molecular weight of grafted branches. Grafting frequency was calculated from these two parameters. For all products, except starch–polyacrylamide, hydrolysis to a polymer that contained less than 5% carbohydrate (estimated by infrared spectroscopy) was achieved by refluxing the graft copolymers in $0.5N$ hydrochloric acid. Graft copolymers were normally refluxed for 30 min, separated from glucose and other small carbohydrate fragments by dialysis or filtration, and then refluxed in acid for an additional 30 min.[8] To attain complete hydrolysis of starch grafted with polyacrylonitrile and poly(methyl methacrylate), it was sometimes necessary to dissolve in dimethyl sulfoxide the product from the first 30-min reflux and then precipitate it again with dilute acid before refluxing a second time. In control experiments, refluxing $0.5N$ hydrochloric acid did not significantly alter the molecular weights of poly(methyl methacrylate), poly(II), or poly (acrylic acid).

An enzymatic method was used to hydrolyze starch–polyacrylamide graft copolymers, since both refluxing acid and treatment with periodate followed by base[9] greatly altered the molecular weights of grafted branches. Even the mild conditions of enzymatic hydrolysis reduced the $\bar{M}_n$ of a control sample of polyacrylamide from 150,000 to 120,000. To a suspension of 10 g graft copolymer in 45 ml water was added 7.4 ml sodium chloride solution (10 g/l.), 10.5 ml sodium acetate solution (0.1 g/l.), and 18.8 ml calcium chloride dihydrate solution (0.1 g/l.). The pH was adjusted to 6.0 with sodium hydroxide solution and 3 ml of an aqueous solution of Rhozyme H-39 (1 mg/ml) added. The mixture was stirred at 70°C for 6 hr, heated briefly to 95°C, and cooled. The reaction mixture was dialyzed against distilled water and freeze dried. Solutions of sodium chloride, sodium acetate, and calcium chloride dihydrate were added to the dry solid in

amounts equal to those used above; the pH was adjusted to 6.0, and 3 ml of Rhozyme solution was added. After the mixture was stirred for 3 hr at 70°C, two additional 3-ml portions of Rhozyme solution were added over an interval of 2 hr. The mixture was finally stirred for 2 more hours at 70°C, exhaustively dialyzed against distilled water, and centrifuged to remove insolubles (0.12–0.47 g). The clear supernatant was then freeze dried, and the percentage of polyacrylamide in the dry product was determined from nitrogen analysis. For three starch–polyacrylamide copolymers, this procedure gave final products that contained 74–87% polyacrylamide; however, the copolymer with the lowest molecular weight grafts led to a hydrolysis product that contained only 54% polyacrylamide.

The molecular weights of polyacrylonitrile grafts were calculated from intrinsic viscosities in dimethylformamide at 25°C.[7] The molecular weights of poly(methyl methacrylate) grafts were calculated from intrinsic viscosities in benzene at 30°C.[10] All other 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.). Molecular weights of polyacrylamide grafts were corrected for percentage carbohydrate remaining after enzymatic hydrolysis. Poly(I) and poly(II) were present largely as the hydrochloride salts for molecular weight determination, since hydrolyses were performed with hydrochloric acid. Molecular weights, however, were expressed as the nitric acid salts.

RESULTS

Acrylonitrile

Although the graft polymerization of acrylonitrile onto swollen and unswollen starch has been reported,[1] reactions were repeated since reaction conditions used earlier were different from those chosen for this study. Table I shows the results of graft polymerizations initiated with both ceric ammonium nitrate and the ferrous ammonium sulfate hexahydrate–hydro-

TABLE I
Graft Polymerization of Acrylonitrile[a]

Initiator	Starch pre-treatment temp., °C	Add-on, %	MW of graft	AGU/[b] graft	Grafting efficiency, %
Ce^{+4}	25	21.7	34,200	760	97
Ce^{+4}	60	20.2	248,000	6,050	89
Fe^{+2}/H_2O_2	25	12.6	25,000	1,070	91
Fe^{+2}/H_2O_2	60	5.1	104,000	12,000	39

[a] Polymerization recipe: 0.3 mole anhydroglucose unit wheat starch, 0.3 mole acrylonitrile, 3×10^{-3} mole ceric ammonium nitrate, 430 ml water. Polymerizations with ferrous–peroxide initiation used 3×10^{-4} mole ferrous ammonium sulfate hexahydrate and 3×10^{-3} mole hydrogen peroxide.

[b] Anhydroglucose unit.

gen peroxide redox system. As observed earlier,[1] use of swollen starch with either initiator led to fewer grafted branches of higher molecular weight as compared with unswollen starch. With ceric initiation, per cent add-on was independent of granule swelling, whereas with ferrous–peroxide initiation, per cent add-on was lower with swollen starch. Grafting efficiencies were high in all but the ferrous–peroxide-initiated polymerization onto swollen starch.

Methyl Methacrylate

Results of graft polymerizations are shown in Table II. As observed with acrylonitrile, starch granule swelling did not influence per cent add-on when polymerizations were initiated with ceric ion; however, with ferrous–peroxide initiation, per cent add-on was appreciably higher with unswollen starch. The influence of granule swelling on the frequency and molecular weight of grafted branches was the reverse of that found for acrylonitrile, since grafted branches were less frequent and of higher molecular weight when starch was unswollen. Differences between graft copolymers derived from swollen and unswollen starch were greatest when initiation was with ferrous–peroxide. Also, grafting efficiencies with ferrous–peroxide initiation were somewhat higher than those with ceric initiation.

TABLE II
Graft Polymerization of Methyl Methacrylate[a]

Initiator	Starch pre-treatment temp., °C	Add-on, %	MW of graft	AGU/ graft	Grafting efficiency, %
Ce^{+4}	25	28.3	415,000	6,490	80
Ce^{+4}	60	27.8	338,000	5,420	65
Fe^{+2}/H_2O_2	25	34.3	610,000	7,210	93
Fe^{+2}/H_2O_2	60	13.2	118,000	4,790	82

[a] Same polymerization recipe as for Table I.

Acrylamide

Although ferrous–peroxide initiation with 0.3 mole monomer gave values for per cent add-on of 12–15.7%, ceric ammonium nitrate gave only about 2% and 6% added-on with swollen and unswollen starch, respectively, under the same conditions (Table III). Since a threefold increase in the amount of monomer used with ceric initiation substantially increased per cent add-on, graft molecular weights and grafting frequencies with this initiator were determined for graft copolymers prepared at the higher acrylamide concentration. Values for per cent add-on did not vary greatly with granule swelling (12–16%); however, as with acrylonitrile, both initiating systems led to less frequent grafting of higher molecular weight branches when starch granules were swollen. Grafting efficiencies for all reactions were relatively low.

TABLE III
Graft Polymerization of Acrylamide[a]

Initiator	Starch pre-treatment temp., °C	Mole monomer	Add-on, %	MW of graft	AGU/ graft	Grafting efficiency %
Ce^{+4}	25	0.3	6[b]	—	—	33
Ce^{+4}	60	0.3	2[b]	—	—	12
Ce^{+4}	25	0.9	12.2	8,600	380	30
Ce^{+4}	60	0.9	16	65,000	2,100	31
Fe^{+2}/H_2O_2	25	0.3	15.7	14,000	460	54
Fe^{+2}/H_2O_2	60	0.3	12	38,600	1,750	34

[a] Same polymerization recipe as for Table I, except for the third and fourth reactions.
[b] Estimated from weight gain.

Acrylic Acid

Values for per cent add-on with acrylic acid (Table IV) were lower than those with acrylamide, and even with 0.9 mole monomer, values with ceric initiation were only 5.2% and 1.6% with swollen and unswollen starch, respectively. Graft molecular weights were independent of granule swelling with ferrous–peroxide initiation; however, grafting was less frequent with swollen starch. Ceric-initiated graft polymerization onto swollen starch at the higher monomer concentration produced higher molecular weight grafts than ferrous–peroxide initiation, although the copolymer was less frequently grafted. The corresponding graft copolymer from unswollen starch was not completely characterized because per cent add-on was too low to give sufficient grafted poly(acrylic acid) for molecular weight determination. Grafting efficiencies for acrylic acid were generally poor.

TABLE IV
Graft Polymerization of Acrylic Acid[a]

Initiator	Starch pre-treatment temp., °C	Mole monomer	Add-on, %	MW of graft	AGU/ graft	Grafting efficiency %
Ce^{+4}	25	0.3	2[b]	—	—	48
Ce^{+4}	60	0.3	3[b]	—	—	28
Ce^{+4}	25	0.9	1.6	—	—	10
Ce^{+4}	60	0.9	5.2	280,000	31,500	19
Fe^{+2}/H_2O_2	25	0.3	12.2	47,000	2,090	36
Fe^{+2}/H_2O_2	60	0.3	7.0	49,000	4,020	19

[a] Same polymerization recipe as for Table I, except for the third and fourth reactions.
[b] Estimated from weight gain.

Monomers I and II

Although graft polymerization of I onto swollen and unswollen starch has been described,[2] experiments were reperated to keep reaction conditions constant (Table V). Graft polymerization of II has not been previously reported. All reactions in Table V used ferrous–peroxide initiation, since neither I nor II would graft polymerize to a significant extent in the presence of ceric ammonium nitrate. The per cent add-on for both I and II was higher when swollen starch was used, and for both monomers there was less frequent grafting of higher molecular weight branches when starch was unswollen. Grafting efficiencies were low but were higher for both monomers when starch was swollen.

TABLE V

Graft Polymerization of Nitric Acid Salts of N,N-Dimethylaminoethyl Methacrylate and N-t-Butylaminoethyl Methacrylate[a]

Starch pretreatment temp., °C	Add-on, %	MW of graft	AGU/graft	Grafting efficiency, %
N,N-Dimethylaminoethyl Methacrylate·HNO₃				
25	12.5	567,000	24,500	18
60	18.7	87,000	2,340	27
N-t-Butylaminoethyl Methacrylate·HNO₃				
25	14.8	282,000	10,000	18
60	25.5	104,000	1,880	30

[a] Initiation was with ferrous ammonium sulfate hexahydrate-hydrogen peroxide. Same recipe as for Table I.

Monomer III

As observed with the other cationic monomers I and II, per cent add-on with monomer III was greater, and there was more frequent grafting of lower molecular weight branches when starch was swollen (Table VI). However, differences in graft molecular weight for swollen versus unswollen

TABLE VI

Graft Polymerization of 2-Hydroxy-3-methacryloyloxypropyltrimethylammonium Chloride[a]

Initiator	Starch pre-treatment temp., °C	Add-on, %	MW of graft	AGU/graft	Grafting efficiency, %
Ce⁺⁴	25	14.3	230,000	8,270	13
Ce⁺⁴	60	30.8	219,000	3,040	31
Fe⁺²/H₂O₂	25	6.3	85,400	7,830	9
Fe⁺²/H₂O₂	60	12.7	52,000	2,210	13

[a] Same polymerization recipe as for Table I.

starch were not so great as for I and II. Grafting efficiencies were low for all reactions but were higher when swollen starch was used.

DISCUSSION

The influence of granule swelling on molecular weight and frequency of grafts is highly dependent on monomer structure and cannot be predicted on the basis of solubility of the monomer or its polymer in water. With acrylonitrile and acrylamide, swollen starch gives higher molecular weight and less frequent grafts than unswollen starch; however, methyl methacrylate and the cationic monomers I, II, and III produce less frequent grafts of higher molecular weight when starch is unswollen. Finally, with acrylic acid, graft molecular weight is independent of starch granule swelling, although grafting is less frequent when swollen starch is used.

From the data at hand, we can do little more than speculate on why monomers behave differently when graft polymerized onto swollen and unswollen starch. Differences between acrylonitrile and methyl methacrylate graft polymerizations may be due in part to differences in the compatibility of each monomer with its respective polymer. Acrylonitrile is not compatible with its polymer, and polymerization takes place mainly in the aqueous phase.[11] Methyl methacrylate, however, has a high affinity for polymer, and polymerization takes place largely within the polymer phase. The two polymerizations may also be terminated differently. Transitional metal ions are known to terminate polyacrylonitrile polymerizations, while methyl methacrylate shows little tendency toward this mode of termination.[11]

Any general explanation of how the swelling effect depends on monomer type must consider not only the phase in which the polymerization occurs and the method and rate of termination for each monomer, but also relative rates of initiation and propagation of grafted branches within swollen and unswollen starch matrices. Rates of diffusion of monomer, initiator, and possible chain-terminating species (e.g., Ce^{+4} or Fe^{+3}) into swollen and unswollen starch granules are also important considerations. It is expected that such diffusion would be greatly influenced by the presence of grafted polyelectrolyte branches within the starch matrix.

References

1. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Macromol. Sci.-Chem.*, **A-4**, 331 (1970).

2. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **15**, 1889 (1971).

3. R. W. Armstrong and U. P. Strauss, *Encycl. Polym. Sci. Technol.*, **10**, 781 (1969).

4. J. C. Arthur, Jr., O Hinojosa, and M. S. Bains, *J. Appl. Polym. Sci.*, **12**, 1411 (1968).

5. C. R. Pottenger and D. C. Johnson, *J. Polym. Sci. A-1*, **8**, 301 (1970).

6. C. E. Borkcway, *J. Polym. Sci. A*, **2**, 3733 (1964).

7. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **10**, 929 (1966).

8. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **14**, 2601 (1970).

9. L. A. Gugliemelli, M. O. Weaver, and C. R. Russell, *J. Polym. Sci. B*, **6**, 599 (1968).

10. T. G. Fox, J. B. Kinsinger, N. F. Mason, and E. M. Schuele, *Polymer*, **3**, 71 (1962).

11. S. R. Palit, T. Guha, R. Das, and R. S. Konar, *Encycl. Polym. Sci. Technol.*, **2**, 229 (1965).