

Synthesis, Characterization, Properties, and Derivatives of Poly(starch-*g*-(1-Amidoethylene)).

I. Synthesis and Characterization

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Synopsis

Poly(starch-*g*-(1-amidoethylene)) can be formed by aqueous, free radical polymerization of 2-propenamide on lintnerized, potato starch. Initiation is by attack of cerium ions (+IV) on the D-glucopyranosyl units of starch. The reaction produces a water-soluble thickener with molecular properties of the product controlled, in part, by the gel effect induced in virtually all syntheses. Yield of product varies from 38 to 100% with yields of 90–100% being common. Products containing less than 50 wt % sidechain were found to be difficult to dissolve once they were recovered from the synthesis mixture. A sample with a design molecular weight of 0.8×10^6 and 4 grafts per backbone formed 3.9 wt % of a water-insoluble solid in the reaction mixture. The solid, which had a composition similar to that of the reaction mixture, may be the result of selective reaction within the distribution of backbone molecules.

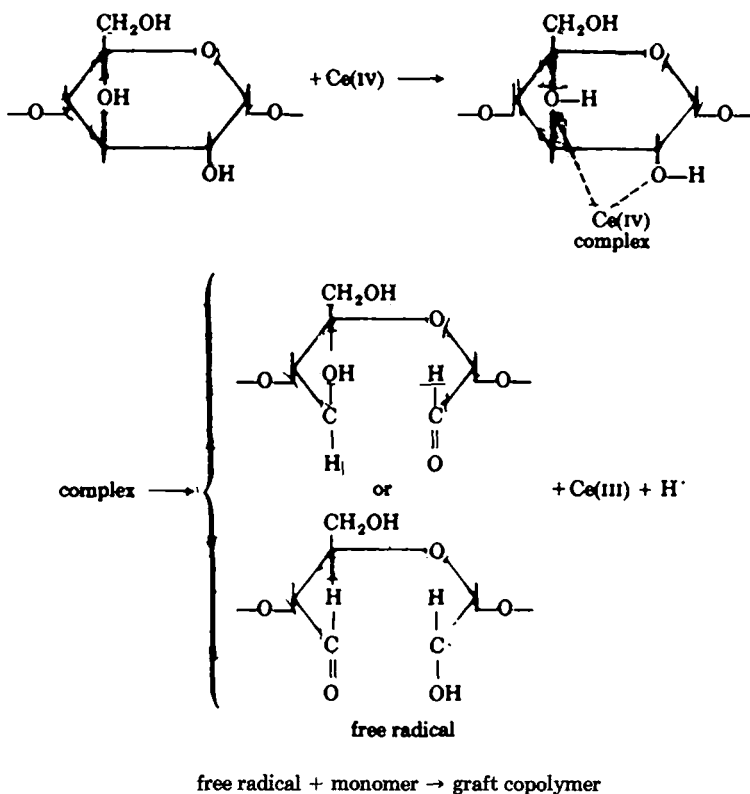
INTRODUCTION

Graft copolymers are molecules composed of at least two chemically distinct parts: a polymeric chain or backbone of one repeat unit type that is used as the site of synthesis or attachment of another chemically distinct polymer chain. Grafting produces a hybrid polymer with properties which are mixtures of or intermediate to the separate backbone and side-chain properties. Grafting is used in such areas as papermaking,¹ textile producing,² and coatings manufacture.³ Graft copolymers are produced both by irradiation and chemical methods. Polysaccharides, the largest and most common class of biopolymers, are grafted by both methods.⁴ Cellulose is grafted by several monomers after initiation by plasma⁵ or X-rays.⁶ However, these methods produce large amounts of homopolymer,⁷ are usually performed on a solid section of backbone polymer, and produce insoluble, crosslinked products.

Chemically initiated grafting can produce much less homopolymer and is particularly effective for producing soluble, grafted products.^{8,9} Polysaccharides, such as cellulose and starch, have been extensively grafted using chemical initiation.^{10–12} Starch has been grafted with poly(1-cyanoethylene),^{7,13} poly(1,1-dimethylethylene),¹⁴ poly(1-methyl-1-[1-oxa-2-oxypyropyl]ethylene),¹⁵ and poly(1-phenylethylene).¹⁶ Starch grafted with poly(1-cyanoethylene) can be hydrolyzed in aqueous base to graft copolymers with amide and carboxylic acid salt¹⁷ units in the sidechain.

These products are water dispersible¹⁸ but have been shown^{19,20} to be swollen gel particles possessing a water-soluble coat of derivatized side chain. Water-soluble graft copolymers can also be formed by these techniques.^{21,22}

The reaction which produces these water-soluble products is the reaction of ceric ion with an alcohol, first developed as a grafting method by Mino and Kaizerman.²³ This method of grafting yields substantially pure graft copolymers since the free radicals are formed exclusively on the backbone.²⁴ The reactions are



These materials formed are very effective thickeners and drag-reducing agents and have a significant potential for commercial application. For these reasons, a series of graft copolymers have been made, characterized, tested for physical and solution properties, and derivatized.

EXPERIMENTAL

Materials

Pfatz and Bauer, S08583, water-soluble starch was used as a backbone for all copolymers. Composition of the starch was 25 wt % amylose, 75% amylopectin by iodine uptake test. It is a lintnerized²⁵ potato starch with molecular weight of 126,000. 2-Propenamide (I) was purified by heating a 21.5 wt %

slurry in trichloromethane to 50–55°C, hot filtering the solution, and recovering precipitated monomer from the cooled solution by filtration. The 2-propanamide was then vacuum dried at 2 Pa and ambient temperature.

Cerium(IV) ion was prepared as a 0.05*M* solution of cerium(IV) ammonium sulfate. This solution is stable indefinitely and gives reproducible grafting efficiencies. Deionized-distilled water was used.

Synthesis

Graft copolymer was formed in aqueous solution by ceric-ion-initiated, radical polymerization of monomer on starch. Polymerization was conducted in an inert N₂ atmosphere.

Starch was dispersed thoroughly in two-thirds of the water used in the reaction. The mixture was heated with stirring to 100°C and held there for 3 min. This gelatinizes the starch and produced a clear, visually homogeneous sample that will cloud and begin to retrograde within 1 h after it cools. The reaction must be initiated within 1 h of boiling. The starch solution was bubbled with N₂ and stirred while it is allowed to cool to 25°C. The total amount of monomer to be added to the reaction mixture was calculated from the restrictions that (1) the final, complete reaction mixture should contain 1–2*m* monomer with 1.5*m* the preferred concentration, (2) with 100% grafting efficiency and 100% reaction, the product will have a specified design molecular weight, and (3) the wt % side chain desired in the product should be maintained in the reaction mixture.

An appropriate amount of 2-propanamide (I) was dissolved in the remaining 1/3 of the water. Both solutions were bubbled with N₂ for 20 min. An appropriate volume of ceric ion solution was added to the starch solution and the flask is sealed with a septum stopper and stirred. The volume of cerium(+IV) solution added was determined by the mole ratios of starch to Ce(+IV) or 2-propanamide to Ce(+IV) desired in the reaction mixture. The monomer solution was bubbled with N₂ for 15 more min and added to the starch sample under an N₂ blanket. The reaction mixture was capped, stirred for 1 min, and placed in a 30°C bath. The mixture was then stirred every hour until it became too viscous to stir.

After 48 h, the reaction was terminated by injection of 0.5 mL of aqueous, 1.0 wt % hydroquinone solution. The thick or gelatinous reaction mixture was scraped into a 1-L beaker using ceramic or plastic tools. The flask was washed with water, and the wash placed in the beaker. This mixture was stirred until a thick, uniform solution has formed. Product was precipitated by dropwise addition of the product solution to five times its volume of vigorously stirred nonsolvent. For poly(starch-*g*-(1-amidoethylene)), 2-propanone was an effective nonsolvent.

The precipitated copolymer was filtered from nonsolvent, slurried in a blender for 30 s in four times the reaction mixture volume of nonsolvent, filtered, and dried under vacuum to constant weight.

Assays

Anthrone assays for starch were performed on both solid and solution copolymer samples. The anthrone test is sensitive to sugars so that starch

must be digested in acid before analysis. For analysis of aqueous copolymer solutions, the solution was made 1*M* in HCl, boiled for 3 h, and was then diluted by tenfold with distilled water. A 1-mL sample of this solution was then taken and analyzed using the 3-acid anthone method.²⁶ For best results, samples should be placed in an ice/water bath for 5 min immediately following the immersion in boiling water.

Solid samples were prepared for analysis by digesting them in stirred, boiling, 5.0*M* HCl acid for 3 h. The solution was then diluted to fifty times its volume with distilled water and is sampled and assayed as described above.

Relative precision of the assay is 3%. All assays were run in triplicate.

Tests on solutions on 32.2 $\mu\text{g}/\text{mL}$ of starch containing 49 $\mu\text{g}/\text{mL}$ of poly(1-amidoethylene) showed equal means at the 95% confidence level when compared with a pure starch sample. Side chains did not interfere with the backbone assay. When starch samples were tested daily for 1 week, there was no deviation of the assay mean at the 95% confidence level. The analysis samples were stable over a 1-week period.

The Kjeldahl test²⁷ was used to determine the amount of 1-amidoethylene repeat units in starch (1-amidoethylene) graft copolymers.

All copolymer samples were separated into fractions by stirring for 1 day 0.200 g of vacuum-dried solids into 100.0 mL of water. Samples were then allowed to sit for 1 day before being placed in a refrigerator at 4°C and allowed to sit for 7 days. Samples were centrifuged to recover all solids, and the solids were dried to constant weight. The supernate were placed in a sealed still and evaporated at between 24 and 30°C under 136 Pa N₂ pressure. Solids from the supernate were dried to constant weight and were tested for starch content using the anthrone test. The wt % unreacted starch in a sample was calculated from:

$$\text{wt \% unreacted starch} = \frac{\% \text{ starch in fraction 1} \times \text{mass fraction 1} \times 100}{\text{mass sample taken for fractionation}}$$

The 10 samples were fractionated as described above. This fractionation method was designed²⁸ so that (1) unreacted starch, a product component that is insoluble in water[†] and (2) poly(starch-*g*-(1-amidoethylene)) copolymer that is soluble in water could be separated from each other.

Size exclusion chromatograms were run using a Toyo Soda TSK-6000-PW, 50-cm column using 0.1*N* pH7 sodium dihydrogen phosphate buffer as the mobile phase. Flow rate was 1 mL/min and injected volume of analyte was 200 μL of 0.05 wt % polymer sample in buffer. The 0.1 wt % dispersion of starch in buffer was made by the same procedure used to make dispersions for grafting. Peaks were detected by both index of refraction change and UV absorbance at 210 nm.³⁰ Standards G to H used to calibrate the SE column are narrow molecular weight poly(1-amidoethylene) standards.

Limiting viscosity number was measured by extrapolating the viscosity measurements on at least four polymer solutions to zero concentration using Huggins equation.³¹

[†]See Ref. 29. Mass balance tests on unreacted starch showed 94 wt % recovery of starch from water.

All solvents, acids, and indicators used in these assays were reagent grade and were used as received. Nonsolvent, 2-propanone, used in precipitation was reused after distillation. Elemental analyses were performed by Canadian Microanalytical Services, Ltd., Vancouver, BC, Canada.

Equipment

Liquid chromatograph used for size exclusion studies was a Waters Associates System equipped with R401 differential refractometer and UV detector. Centrifugations were done in a Sargent S-15699 instrument. Absorbance measurements were done on a Perkin-Elmer, Lambda-3, UV-visible spectrophotometer. Viscosities were measured using Cannon-Fenske capillary viscometers and a Brookfield LV Microvis, cone and plate viscometer with a CP-40, 0.8° cone. Capillary viscometers received 10 mL of a sample for testing while the cone and plate viscometer received 0.50 mL.

RESULTS AND DISCUSSION

Synthesis of the copolymer samples was designed so that a complete reaction would produce products with structural characteristics that changed in a regular pattern. Characteristics controlled were mole ratio of cerium(+IV) to starch, N_g , and mole ratio of grafted 2-propenamide to cerium(+IV), D_p . The mole ratio D_p is the average number of repeat units that would be found in a sidechain if (1) all initiator ions produced a reactive site, (2) the reaction went to completion, and (3) there was no chain transfer. A third characteristic for the reaction mixture is M_{cal} which can be calculated from N_g and D_p :

$$M_{cal} = 71.079 \times N_g \times D_p + M_w (\text{starch})$$

M_{cal} would be a number-average molecular weight of the product if (1) all initiator ions produced a reactive site, (2) the reaction went to completion, and (3) there were no chain transfer. N_g , D_p , and M_{cal} are *design* ratios or characteristics and will not be properties of the reaction product. They are, however, characteristic of the synthesis mixture which produced a product. (Product properties presented in subsequent papers of this series can be compared to these design data.)

A synthesis plan for 12 samples using this formalism is given in Table I and serves as a basis for samples synthesized in this work. Data for the synthesis of these samples is given in Table II. The samples represent an attempted systematic variation in product properties by variation in synthesis conditions. This pattern would produce a series of samples that can be compared for effects of increasing number of grafts or molecular weight.

Physical properties of the samples preclude comparing all products with one another. Samples 1 and 3 with a design mass, M_{cal} , of 2×10^5 were found to be insoluble in water when recovered by precipitation and dried. These materials should contain only 1/3 of product weight as poly(1-amidoethylene). This small fraction of water-soluble part in the molecule may be too small to overcome the forces of crystallization in starch. Products 1 and 3 are dense, translucent, brittle solids while samples with larger 1-amidoethylene side chains are opaque, amorphous, and flaky solids. Sample 2 is the one product

TABLE I
Design of Graft Copolymers from Starch and 2-Propenamide

Sample number	N_g	$D_p \times 10^{-3}$	M calculated ($\times 10^{-5}$)	Maximum yield (g)
1	1/2	2.08	2.0	11.0
2	1	1.04	2.0	11.0
3	4	0.26	2.0	11.0
4	1/2	7.72	4.0	11.0
5	1	3.86	4.0	11.0
6	4	0.96	4.0	11.0
7	1/2	13.35	6.0	11.0
8	1	6.68	6.0	11.0
9	4	1.67	6.0	11.0
10	1/2	18.9	8.0	11.0
11	1	9.45	8.0	11.0
12	4	2.36	8.0	11.0

TABLE II
Composition of Reaction Mixture and Yield of Product
for Samples of Poly(starch-*g*-(1-Amidoethylene))

Sample number	Reaction Mixture Composition				Yield (wt %)
	Starch, (mol $\times 10^{+5}$)	2-propenamide (mol)	Ce(+IV) (mol $\times 10^{+5}$)	H ₂ O (g)	
1 ^a	5.37	0.0563	2.75	38	92.9
2 ^a	5.53	0.0573	5.5	35	91
3 ^a	5.50	0.0573	22.0	35	99.1
4	3.55	0.106	1.27	35	68.3
5	2.75	0.106	2.75	70	102.
6 ^b	2.75	0.106	11.0	70	38.1
7	1.83	0.122	0.95	70	85.5
8	1.83	0.122	1.8	70	94.5
9	1.83	0.122	7.50	70	108
10	1.40	0.130	0.69	84	90.9
11	1.40	0.130	1.38	84	55.0
12 ^c	1.40	0.130	5.5	84	96.9

^aThese samples repeated when the 2-propenamide used was found to be contaminated with poly(1-amidoethylene).

^bThis sample repeated when first reaction failed. Cause: Nonuniform dispersal of starch produced gel sites.

^cA solid formed in the bottom of this sample during reaction. It was insoluble in water and was reproduced and quantified in repetitions of the reaction.

out of six (samples 1-3 and their duplicates) which could be recovered in a water-soluble form. The only difference in the samples that appears to explain this solubility behavior is the nature of the precipitated product recovered from 2-propanone.

If samples designed for low fractions of water-soluble side chain were incompletely dehydrated during precipitation, sections of the starch could crystallize on drying and produce a product which cannot be redissolved. However, X-ray diffraction studies on powdered portions of samples 1-3 and

unreacted starch show that only sample 1 gives any indication of crystalline structure in the sample. Sample 1 gave a very broad diffraction maxima at 21.3° in units of 2θ . Since small amounts of crystallization can change the solubility of starch,³² these data do not eliminate solid morphology as the cause of the solubility difference found in the samples, but do not confirm it either. Samples 1 and 3 were dropped from further study because they were not completely soluble in water.

Sample 6 illustrates a significant problem for correct synthesis of these copolymers. In the initial synthesis of this sample, the starch was incompletely dispersed in water. Undispersed lumps of starch swelled to form gel particles in the synthesis sample which, after grafting and purification, produce insoluble aggregates in the product. To produce a soluble graft copolymer, complete, uniform dispersal of the starch in water *before* heating is mandatory. Sample 6 was successfully prepared in a repeat experiment.

Sample 12 had a unique reaction behavior during synthesis. In the original sample and in three repetitions of the synthesis, a white solid phase formed in the reaction mixture. Further, the extensive gel effect which often solidified reaction mixtures within 1 h was not seen at all in this sample and its repetitions. All of these reaction mixtures remained fluid during the synthesis process. Isolation of the insoluble, white solid from two reaction mixtures showed that it constituted 3.9 wt % of maximum possible yield. Analysis of the solid showed it to be 16.3 wt % starch and 87.1 wt % 1-amidoethylene repeat units. Solids in the reaction mixture are 16.1 wt % starch and 83.9 wt % 1-amidoethylene units. The solids thus model the composition of the reaction mixture. Polymer dissolved in the reaction mixture and recovered by precipitation contains 31.3 wt % starch and 58.2 wt % 1-amidoethylene units. The soluble product does not reflect the composition of the reaction mixture. (The nature of this separation process and what may be causing it will be discussed in later papers of this series.)

In a previous study,²² several "blank" reactions were run to find if homopoly(1-amidoethylene) was initiated by this synthesis procedure. These reactions were the same as those described in Table II but contained no starch. No polymer was formed in these reactions, indicating that starch must be present to act as an initiation site for grafting. These results do not rule out the presence of homopoly(1-amidoethylene) in the reaction products since chain transfer reactions could produce homopolymer. They do show that the concentration of homopolymer will be small, however. The ratio of propagation ($1.8 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$) to chain transfer ($2.2 \times 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$)^{33, 34} rates is 8.2×10^4 . Thus, there will be few chain transfer events during the grafting reaction. Also, homopolymer would be a less massive material than copolymer because the backbone is missing in the homopolymer. Such material would skew the boundary profile of an ultracentrifugation analysis toward lower sedimentation coefficients. Molecular weights of these materials were measured by ultracentrifugation.⁴⁰

Product Composition

Products were analyzed for starch content and 1-amidoethylene repeat unit content. Results of these assays are given in Table III. Since the degree of polymerization in the sidechain attached to the graft copolymer is designed to

TABLE III
 Composition of Reaction Products

Sample number	Nitrogen (wt %)	1-amidoethylene repeat units (wt %)	Starch content (wt %)	Total wt % Material detected	$M_{\text{cal}}^a \times 10^{-5}$	N_g^b
2	6.27	31.78	43.5	75.3	2.0	1
4	11.66	59.10	38.8	97.9	4.0	1/2
5	12.24	62.04	31.3	93.3	4.0	1
6	11.54	58.49	36.4	94.9	4.0	4
7	14.82	75.11	24.6	99.7	6.0	1/2
8	14.85	75.27	20.69	96.0	6.0	1
9	14.24	72.17	16.5	88.7	6.0	4
10	15.17	76.89	16.5	93.4	8.0	1/2
11	14.71	74.56	16.9	91.5	8.0	1
12	11.49	58.24	31.34	89.6	8.0	4

^a M_{cal} is starch plus monomer mass for uniform monomer reaction. It is a design molecular weight, assuming ideal reaction conditions,¹ and will be compared to actual molecular weight.¹⁴

^b N_g is the mole ratio of cerium(+IV) ion to starch in the reaction mixture.¹

be larger in the copolymers with high sample numbers, the poly(1-amidoethylene) content of the samples should increase with increasing sample number, and starch content should decrease with increasing sample number. Both trends occur in the analysis results with the exception of sample 12 which developed a solid aggregate in the synthesis mixture.

Total analysis values below 100% for the copolymer assays are thought to be due to hydrolysis and imine reactions³⁵ in the copolymer side chain during synthesis and/or purification.

While aqueous size exclusion chromatography is used, as later described, to verify grafting, the presence of unreacted starch in the product is not detected by this method. Soluble reaction products were analyzed for unreacted starch by fractionation. Results for this analysis are given in Table IV. This separation is based on the fact that pure starch used in synthesis of these copolymers is insoluble in water. This precipitate was collected and quantified

 TABLE IV
 Fractionation and Composition Data for Copolymers

Sample number	Percent of fraction 1 that is starch	Wt % insoluble starch in copolymer as determined from fraction 1	Wt % of fraction 2 solids that are starch
2	90.7	2.7	54.3
4	79.5	1.2	31.1
5	78.5	1.7	29.1
6	59.8	5.6	32.5
7	80.2	3.0	19.4
8	64.9	5.5	16.0
9	83.8	2.6	17.5
10	71.2	0.8	13.4
11	93.0	0.4	13.4
12	63.1	1.2	12.0

as fraction 1. The starch solubilized by grafting was recovered by drying the supernate of fraction 1 and constituted fraction 2 of the separation. Control samples were run to prove the reliability of the fractionation procedure.

Table IV shows the composition of fraction 1 from 10 copolymer samples. Table IV contains wt % data that show that the insoluble starch that constitutes fraction 1 comprises from 0.4 to 5.6 wt % of the reaction product. Further, as a percentage of starch in the reaction product, the insoluble starch of fraction 1 constitutes from 2.1 to 26.6 wt % of the starch in the copolymer samples.

Median starch content of fraction 1 from copolymer samples is 79.0 wt %, but the starch content of test mixtures containing no graft copolymer was always 100%. Thus, fraction 1 contains more than just ungrafted starch when it is obtained from a copolymer. This separation is based on water solubility and therefore some grafted starch molecules containing small weight fractions of the side chain can also precipitate.

Data on the mass and composition of fraction 2, the soluble solids extracted from the supernate of fraction 1, are also given in Table IV. These data show that fraction 2 from copolymer samples contains between 12.0 and 54.3 wt % starch which decreases as design molecular weight of the copolymer increases. These fractionation data provide evidence that grafting is occurring.

Fraction 2 from test mixtures contains only 2.3–10.0 wt % starch. These data show that, in mixtures representative of copolymer solutions, only 6.7 ± 3.4 wt % ungrafted starch would be carried into fraction 2 by physical entrapment. Since the fractionation data are analytical results and appear normally distributed, they can be tested by use of the student *t*-test and the standard confidence tables for differences of means.³⁶ The hypothesis to be tested is, "Is the copolymer sample merely a polymer mixture and the starch content of fraction 2 from that mixture merely caused by random deviation rather than chemical bonding?" If a statistical analysis gives a "no" answer to this hypothesis at a given confidence level (probability of being right), then the existence of copolymer has been verified by the fractionation results. At the 95% confidence level (19 chances in 20 of being right), any sample producing more than 18.8 wt % starch in fraction 2 must do so because of nonrandom cause (grafting) rather than statistical chance. Samples 2 and 4–7 have more than 18.8 wt % starch in fraction 2 and, therefore, show proof of grafting of 1-amidoethylene side chains to starch backbone by this test.

Samples 8 and 9 can be said to be graft copolymer with better than 90% confidence while samples 10–12 can only be said to be grafted with better than 80% confidence.

Size Exclusion Chromatograms

Elution times for three graft copolymers and starch under the conditions given in the experimental section are given in Figure 1. Elution volumes of copolymers 5, 8, and 11 are significantly smaller than that of the backbone. This indicates that the grafting reaction has sharply increased the molecular volume of the polymer and again confirms that grafting has occurred.³⁷

The values of the elution peaks decrease as reaction variables which should control molecular weight increase. These data thus show that changes in

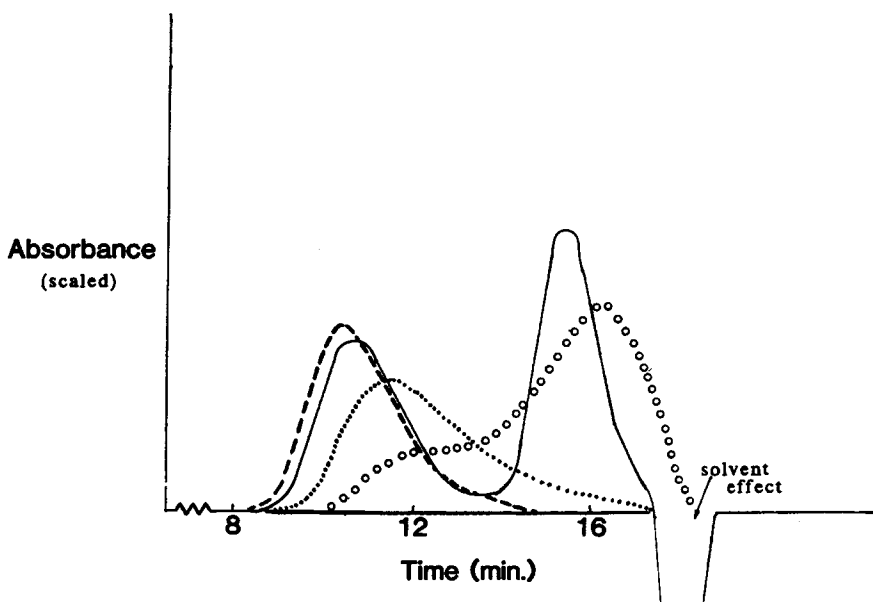


Fig. 1. Size exclusion chromatograms of sample 5 (...), sample 8 (—), sample 11 (---), and starch (○). Sample 8 shows a bimodal size distribution. Detector attenuation = $4 \times$.

reaction variables increase molecular size when those changes increase the degree of polymerization of the side chain. Because SEC results, even with calibration,³⁸ do not measure molecular weight of graft copolymers, these data do not prove that changes in reaction conditions change molecular weight in a predictable manner. They do strongly suggest this, however.

The size exclusion chromatogram of sample 8, shown in Figure 1, is bimodal. Chromatograms of 5 and 11 do not show a second or even a shoulder peak. The second peak of sample 8 is not due to unreacted starch because the elution is at a lower volume than the backbone and the second peak in Figure 1 is a strong absorber at 210 nm. The elution peak of starch does not show a UV absorption response on the chromatograph. Further, spectra of the starch show that it has a molar absorptivity of approximately 920 at 210 nm and tests run at other laboratories³⁹ show the absorbance peak for starch occurs at 255 nm with only slight absorbance at 210 nm. Thus the second peak of sample 8 probably contains poly(1-amidoethylene) which is a strong absorber at 210 nm.

These data show that sample 8 contains two components of different size. Size of a copolymer molecule, however, is a function of molecular weight, average degree of polymerization of side chain, and number and distribution of sidechains on the backbone. Ultracentrifugation has been used to further characterize these samples.⁴⁰

We also found from the ultracentrifugation study that starch retrogrades rapidly, forming aggregates which eventually precipitate from solution. The shoulder at 12 min in the starch chromatogram probably reflects aggregated starch molecules.

TABLE V
Limiting Viscosity Number of Graft Copolymer Solutions at 30°C

Sample number	[η] (L/g)	
	H ₂ O	1M NaNO ₃
2	1.35	1.18
4	3.69	3.01
5	3.99	3.17
6	3.97	3.14
7	4.12	3.32
8	5.84	4.69
9	6.95	5.68
10	11.8	9.94
11	12.2	10.0
12	3.90	3.00

Limiting Viscosity Number

Limiting viscosity numbers for the graft copolymers in water and 1.0M NaNO₃ are given in Table V. Limiting viscosity number of the copolymers is controlled by synthesis variables. Since this is a free radical, graft copolymerization, (1) increasing the 2-propenamide (monomer) to starch (backbone) mole ratio (increasing \bar{M}_{cal}), (2) decreasing the cerium (IV +) (initiator) to starch mole ratio (N_g), or (3) decreasing the cerium (IV +) to 2-propenamide mole ratio would all increase the degree of polymerization (mean side chain repeat units) in the graft copolymer. The degree of polymerization in these samples increases with increasing sample number as can be seen from the reactant amounts of Table II and the reactant mole ratios calculable from that data.

Limiting viscosity number also increases with increasing sample number for all copolymers save 12. Increasing degree of polymerization in the synthesis mixture increases the size of the reaction product in solution and, hence, increases limiting viscosity number.⁴⁰ The exception to this rule is, again, the supernate solids recovered as sample 12 from a two-phase, solids-containing reaction mixture. The process that produced solids formation in this reaction causes a pronounced reduction in molecular size in solution for this copolymer.

CONCLUSIONS

Poly(1-amidoethylene) side chains are grafted on starch backbone by free radical polymerization of 2-propenamide on gelled, aqueous starch after initiation by cerium (IV +) in a nitrogen atmosphere. Grafting was proven for six out of 10 samples by fractionation and size exclusion chromatography and was strongly suggested for the other four samples.

Size exclusion and rheological results show that molecular size of the copolymer is controlled by the composition of the reaction mixture. Changes in reaction composition that increase the degree of polymerization or produce more long chain grafts on a backbone increase molecular size. The reaction produces a water-soluble thickener with molecular properties of the product controlled, in part, by the gel effect induced in virtually all syntheses. Yield of product varies from 38 to 100% with the median yield being 91 wt %.

Products containing less than 50 wt % side chain were found to be difficult to dissolve once they were recovered from the synthesis mixture. A step critical to the formation of a homogeneous water-soluble reaction product is the uniform dispersal of starch before gelation and initiation of the graft polymerization within 1 h of gelation. Rapid reaction of the gelled starch avoids retrogradation of the starch.

All of the copolymers were found to contain unreacted starch which was as high as 5.6 wt % of reaction product. Homopolymer of 1-amidoethylene was not identified in the products. Samples with starch contents as high as 43.5 wt % and poly(1-amidoethylene) contents as high as 76.9 wt % were synthesized and found to be water-soluble, thickening agents.

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