Synthesis, Characterization, and Properties in Aqueous Solution of Poly(starch-*g*-[1-Amido-ethylene)-co-(Sodium 1-(2-Methylprop-2*N-yl*-1-Sulfonate)Amidoethylene)])

JOHN J. MEISTER, DAMODAR R. PATIL, MARGARET C. JEWELL, and KYLE KROHN, *Department of Chemistry, Southern Methodist University, Dallas, Texas 75275*

Synopsis

Graft terpolymers of starch, 2-propenamide, and sodium 2-methyl-3-imino-4-oxohex-5-ene-1-sulfonate can be made by cerium-IV-initiated, free-radical polymerization of an aqueous monomer mixture on starch. Synthesis is conducted on aqueous, gelled, lintnerized potato starch at 30°C under a nitrogen atmosphere. Yields range from 50 to 100 wt % and products contain 9–52 wt % starch, 1–51 wt % 1-acidoethylene, and 18–65 wt % sodium 1-(2-methylprop-2*N-yl*-1-sulfonate)amidoethylene. Repeat unit ratios in the reaction product approximate monomer ratios in the reaction mixture. Fraction of starch grafted in a reaction decreases as the mole fraction of sulfonated monomer in the reaction mixture increases. No proof has been found for grafting of synthetic side chains to starch in monomer mixtures containing only sulfonated monomer. Starch graft copolymers with side chains composed of 1-amidoethylene units and a sulfonated 1-amidoethylene unit derivative, 1-(sodium[2-methylprop-2*N-yl*-1-sulfonate])amidoethylene, are water-soluble, thickening agents. The rheology of solutions of these copolymers is a function of the ratio of nonsulfonated to sulfonated repeat units in the synthetic chains of the molecule. Aqueous solutions of these products are shear thinning and have power law exponents which decrease 1) with increasing product concentration or 2) as the nonsulfonated to sulfonated repeat unit ratio moves toward 3/1. Limiting viscosity number of product in water decreases with increasing shear rate of measurement or with increasing salt concentration of the solvent. Formulas are derived from the theories of Kirkwood and Flory which show that for copolymers with constant molecular weight, expansion coefficient, and limiting viscosity number increase as the fraction of sulfonate-containing repeat units in the chain increase. This theoretical requirement and the limiting viscosity data for groups of samples prepared under identical synthesis conditions are used to show that molecular weight of the graft copolymer decreases as the fraction of sulfonated repeat units in the copolymer increases. Screen factor measurements show product solutions to be viscoelastic.

INTRODUCTION

Synthetic side chains can be attached to starch by ceric-ion-initiated, graft polymerization. When water-soluble side chains are placed on the starch backbone, water-soluble, graft copolymers are produced.[1,2] Data from a series of such copolymers are already published.[3,4] These data show the aqueous solution behavior of nonionic or weakly anionic graft copolymers. To test the effect of a strongly anionic, synthetic side chain on the rheology of aqueous solutions of graft copolymer, graft copolymers containing sodium 2,2 dimethyl-3-imino-4-oxahex-5-ene-1-sulfonate (monomer II) units were made.

A series of graft copolymers was designed so that the effects of molecular weight and amount of sulfonate-containing monomer on copolymer solution rheology could be measured. The sulfonate containing monomer was incorporated as a randomly occurring part in the synthetic chain with 2-propenamide (monomer I) making up the rest of the chain. Structures for the side chain are

$$(-CH_2-CH-)_m - (-CH_2-CH-)_n$$

$$C=O \qquad NH-C=O$$
$$\diagup$$
$$NH_2 \qquad (CH_3)_2C-CH_2-SO_3Na$$

$$I \qquad\qquad II$$
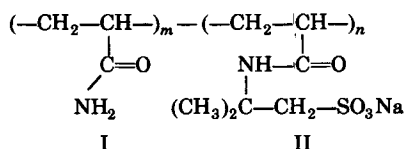
but the occurrence of I and II repeat units in the chain is random.[4]

The ratio of the total number of polymerized 2-propenamide units in a side chain, m, to the number of II units in the side chain, n, is the amide to sulfonate ratio of the polymer, $R_{N/S} = m/n$. Amide to sulfonate ratio of the copolymers varied from 9 to 1, (90% I) to 0 to 1 (100% II) by varying the monomer ratio in the reaction.

As the amide to sulfonate ratio of a given polymer decreases, the size of the polymer in solution should increase. The reason for this change in molecular size at constant molecular weight is that the sodium sulfonate groups in the side chain of the graft copolymer should dissociate in water.[5]

This logic for controlling the size of the graft copolymer in solution was tested by preparing a group of graft copolymers and studying the properties of aqueous solutions of the polymers.

EXPERIMENTAL

Materials. Pfatz and Bauer, S08583, water-soluble starch was used as a backbone for all copolymers. Composition of the starch is 25 wt % amylose, 75% amylopectin. It is a lintnerized[6] 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 cool solution by filtration. Sodium 2-methyl-3-imino-4-oxohex-5-ene-1-sulfonate (II) was purified by heating a 15.2 wt % solution in methanol to 65°C, hot filtering the solution, and recovering precipitated monomer from the cool solution by filtration. Cerium(IV) ion was prepared as an aqueous 0.05M solution of cerium(IV) ammonium sulfate. Nitric and perchloric acid solutions of ceric ion are stronger oxidizing agents but decompose with time.[7] Aqueous solutions of ceric ion are stable indefinitely and give reproducible grafting efficiencies. Deionized-distilled water was used in the reactions. All salts used were reagent grade.

Synthesis. Graft terpolymer was formed in aqueous solution by ceric-ion-initiated, radical polymerization of monomers I and II on starch. Polymerization was conducted in an inert, nitrogen atmosphere.

The water–starch mixture was dispersed thoroughly before it is heated with stirring to 100°C and held there 3 min. This gelatinizes the starch and produces 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 N_2 and stirred while it was 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) the repeat unit mole ratio desired in the product should be maintained in the reaction mixture, and (3) the wt % monomer in the reaction mixture solids should equal the wt % side chain desired in the product. Monomer concentrations were based on the number-average molecular weight of the monomer mixture.

A solution of monomer II (representing one-half of the volume of the starch solution) was adjusted to pH 7 by adding 2.0*M* NaOH or 0.1*M* HCl to the stirred solution. Monomer I was added to the neutral aqueous solution. Both solutions were bubbled with N_2 for 20 min. An appropriate volume of ceric ion solution was added to the starch solution, and the flask was sealed with a septum stopper and stirred. The monomer solution was bubbled with N_2 for 15 more min and added to the starch sample under a nitrogen blanket. The reaction mixture was capped, stirred for 1 min, and placed in a 30°C bath. The mixture was then stirred every 45 min until it becomes 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 viscous or gelatinous reaction mixture was scrapped into a 1-L beaker. The flask was washed with three batches of water, each twice the volume of the reaction mixture, and the wash was placed into the beaker. This mixture was stirred until a viscous, uniform solution has formed. To this solution was added, with stirring, an equal volume of 2-propanone. The resulting two-solvent solution should be less viscous and cloudy than its aqueous predecessor. Product was precipitated by dropwise addition of the cloudy solution to five times its volume of vigorously stirred nonsolvent. For terpolymers containing synthetic chains of 40 mol % or less sulfonated monomer (II), 2-propanone was an effective nonsolvent. For terpolymers with more than 40 mol % monomer II, *n*-butanol was used as 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 aqueous solutions, the solution was made 1*M* in HCl, boiled for 3 h, and then diluted by a factor of 10 with distilled water. A 1-mL sample of this solution was taken and analyzed using the 3-acid anthrone method.[8] For best results, samples should be placed in an ice/water bath for 5 min immediately following the immersion in boiling water. Sample absorbance was then measured at 630 nm.

Solid samples were prepared for analysis by digesting them in stirred, boiling, 5.0*M* HCl for 3 h. The solution was diluted to 50 times its volume with distilled water and was sampled and assayed as described above.

The assay was tested to ensure that accurate results were obtained in the presence of synthetic side chain and despite differences in sample history. Relative precision of the assay is 3%. Side chains did not interfere with the backbone assay.

Assays on starch samples diluted with distilled water, 0.10M HCl, and 0.10M NaCl after digestion all gave the same starch concentration when the diluted solutions were analyzed by the anthrone method. Therefore, the solution sampled for anthrone assay can have a NaCl concentration of up to 0.1M and a pH range from 1 to 7 without affecting the results of the assay.

Terpolymer samples were separated into fractions by stirring 0.2000 g of vacuum-dried solids into 100.0 mL of water for 1 day. Solutions were then allowed to sit for 1 day before being placed in a refrigerator at 4°C, and allowed to sit for 7 days. Insoluble materials were determined by centrifugation.

The supernate and wash from the centrifugation were added dropwise to 80% 2-propanone in water (v/v) (1 to 7.3% v/v for pure II side-chain copolymers), the precipitated solids were recovered by centrifuging, and the solids dried to constant weight.

The second supernate was placed in a sealed still and evaporated between 24 and 30°C and a pressure at 136 Pa N_2. The solids recovered in the evaporation were dried to constant weight. All solids from the fractionation were tested for starch content using the anthrone test.

Elemental assays for C, H, N. O, S, and Na were done by Canadian Microanalytical Services, Ltd., Vancouver, B.C. Canada.

Equipment. All solution viscosities were determined at 30°C using an LTV Brookfield, cone-and-plate microviscometer equipped with an 0.8° cone and calibrated with a Bendix Corp. viscosity standard (16.10 cP at 30°C) and tested against a Cannon Instruments (0.625 cP at 30°C) and Brookfield (105 cP at 30°C) standard. Four measurements of the viscosity of the two test standards gave values of 0.65 cP (6% rel SD) and 105 cP (0.5% rel SD). Cannon-Fenske viscometers, which gave a 0.14% rel SD, were used.

RESULTS AND DISCUSSION

Synthesis

Synthesis data for a dozen products of the grafting reaction of monomers I and II on starch are contained in Table I. All syntheses were designed so that the mole ratio of cerium to starch, N_g, was 1.0, where

$$N_g \text{ (calculated)} = \frac{Ce^{4+} \text{ in reaction (mol)}}{\text{starch in reaction (mol)}}$$

This means that the maximum number of grafts per backbone molecule that could be formed in these syntheses is 1.0.

The composition of the synthesis reactions was also calculated such that if 100% reaction were achieved, the products would cluster into three groups with each group consisting of four samples of approximately equal molecular weight. The planned molecular weights of the three groups were: samples 1–4, 419,000; samples 5–8, 840,000; samples 9–12, 1,275,000. Within each group, the four samples were synthesized to have a ratio of amide to alkylsulfonated

TABLE I

Synthesis Data for Poly(starch-g-[(1-Amidoethylene)-co-(Sodium[2-Methyl-2-N-Propane Sulfonate 1-Amidoethylene)])])

Sample Number	Reaction mixture composition							H$_2$O (g)	Ce^{4+} (mol × 10^5)	$R_{N/S}$	Yield[a] (%)
	Starch		Monomer I		Monomer II						
	g	mol × 10^5	g	mol × 10^2	g	mol × 10^2					
1	1.58	1.25	0	0	3.80	1.66		11.0	1.25	0/1	96.6
2	1.58	1.25	0.87	1.22	2.83	1.23		16.4	1.25	1/1	51.9
3	1.58	1.25	1.74	2.45	1.88	0.820		21.7	1.25	3/1	61.7
4	1.58	1.25	2.58	3.63	0.93	0.406		26.9	1.25	9/1	52.1
5	0.79	0.627	0	0	4.68	2.04		13.5	0.625	0/1	100.5
6	0.79	0.627	1.08	1.52	3.48	1.52		20.2	0.625	1/1	74.8
7	0.79	0.627	2.14	3.01	2.30	1.00		26.7	0.625	3/1	78.0
8	0.79	0.627	3.18	4.47	1.14	0.497		33.2	0.625	9/1	59.7
9	0.53	0.421	0	0	4.97	2.17		14.4	0.415	0/1	78.2
10	0.53	0.421	1.14	1.60	3.70	1.61		21.5	0.415	1/1	70.8
11	0.53	0.421	2.27	3.19	2.45	1.07		28.4	0.415	3/1	75.6
12	0.53	0.421	3.37	4.74	1.22	0.532		35.2	0.415	9/1	48.8

[a]Monomer mole ratio is that of the synthesis reaction mixture.

amide repeat units,

$$R_{N/S} = \frac{\text{amide (monomer I) (mol)}}{\text{sulfonated amide (monomer II) (mol)}}$$

of 0/1, 1/1, 3/1, or 9/1.

Yield and reaction composition data for the samples are given in Table I. These yield data show that monomer ratio sharply affects yield. Yield increases within the three groups of copolymers with decreasing amide to sulfonate ratio. This results in an approximately twofold increase in yield when $R_{N/S}$ decreases from 9/1 to 0/1.

Analysis

Anthrone analyses were run on the products listed in Table I, and the results are shown in Table II. Elemental analyses were also performed on the samples of Table I, and these data were used to calculate the repeat unit content of the products using the following equations:

wt % of sample as sodium 1-(2-methylprop-2 N-yl-sulfonate)amidoethylene repeat units

$$= \text{WP}_S = 7.1499 \times S$$

wt % of sample as 1-amidoethylene units

$$= \text{WP}_N = 5.0745 \times N - 2.217 \times S$$

repeat unit ratio, amide to N-substituted amide

$$= R_{N/S} = \frac{2.2889 \times N - S}{S}$$

mole fraction sodium 1-(2-methylprop-2 N-yl-sulfonate)amidoethylene repeat units in sample

$$= \text{MF}_S = \frac{0.4369 \times S}{N + 1.1117 \times 10^{-4} \times \text{ST}}$$

mole fraction 1-amido-ethylene repeat units in sample

$$= \text{MF}_N = \frac{N - 0.4369 \times S}{N + 1.1117 \times 10^{-4} \times \text{ST}}$$

mole fraction starch in sample

$$= \text{MF}_T = \frac{1.1117 \times 10^{-4} \times \text{ST}}{N + 1.1117 \times 10^{-4} \times \text{ST}}$$

where N, S, and ST are the wt % of nitrogen, sulfur, and starch, respectively, in the sample. These data are contained in Table II.
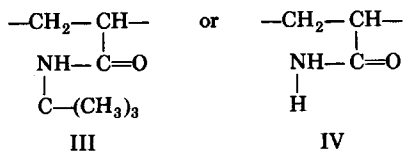
The wt % composition and monomer repeat unit data show that there is some decomposition of the sodium 1-(2-methyl-prop-2 N-yl-sulfonate) amidoethylene repeat unit. This is particularly evident in samples 1, 5, and 9, where small amounts of 1-amidoethylene repeat units are present, but the synthesis mixture contained only the alkyl sulfonated monomer. Decomposition of the sulfonated monomer to produce desulfonated repeat units (III) or

TABLE II
Analysis of Terpolymer Reaction Products

Sample number	Elemental analysis				Wt % composition of reaction product				Mole fraction composition			Limiting viscosity number, water (30°C) $\dot{\gamma} = 225 \, s^{-1}$ (dL/g)
	C	H	N	S	Starch	WP_N	WP_S	$R_{N/S}{}^a$	MF_N	MF_S	$MF_T \times 10^4$	
1	37.11	6.12	3.72	8.04	22.4	1.05	57.4	0.059	0.056	0.943	6.7	26.6
2	39.77	6.07	3.48	4.40	51.8	7.90	31.4	0.810	0.447	0.551	16.5	58.9
3	40.59	6.18	6.53	3.44	33.1	25.5	24.5	3.34	0.769	0.230	5.6	95.8
4	42.13	6.41	7.16	1.81	36.4	32.3	12.9	8.05	0.927	0.072	5.6	74.9
5	35.97	6.23	4.45	8.99	14.2	2.65	64.2	0.133	0.117	0.882	3.5	95.8
6	37.64	5.99	7.12	7.35	11.6	19.81	52.5	1.22	0.549	0.451	1.8	114
7	40.66	6.22	9.62	4.86	18.9	38.0	34.7	3.52	0.779	0.221	2.2	230
8	41.92	6.66	10.62	2.57	25.3	48.1	18.4	8.46	0.894	0.106	2.6	201
9	35.72	5.91	4.77	9.41	10.2	3.34	67.2	0.160	0.138	0.862	2.4	69
10	38.56	6.07	7.74	7.61	9.2	22.4	54.4	1.33	0.570	0.429	1.3	157
11	40.62	6.23	10.41	5.08	11.7	41.5	36.3	3.69	0.787	0.213	1.2	282
12	42.49	6.63	11.11	2.53	12.5	50.7	18.1	9.05	0.900	0.099	1.3	225

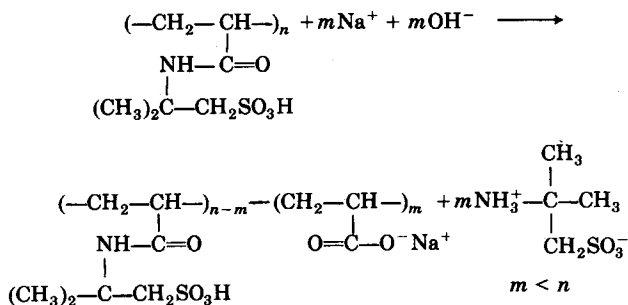[a] Repeat unit mole ratio is that of the reaction product.

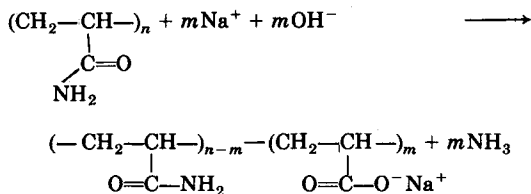dealkylsulfonated (IV) repeat units in the polymer,

$$-CH_2-CH- \quad \text{or} \quad -CH_2-CH-$$
$$\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$NH-C=O \quad\quad\quad\quad NH-C=O$$
$$\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad | $$
$$C-(CH_3)_3 \quad\quad\quad\quad\quad H$$

$$\text{III} \quad\quad\quad\quad\quad\quad\quad\quad \text{IV}$$

would cause $R_{N/S}$ to be greater than 0 for these samples.

The elemental assay results on carbon and hydrogen indicate that dealkyl-sulfonation occurred more frequently than dealkylation. Hydrolysis to remove β,β-dimethyltaurine[9]

$$(-CH_2-CH-)_n + mNa^+ + mOH^- \longrightarrow$$
$$\quad\quad\quad | $$
$$NH-C=O$$
$$\quad\quad | $$
$$(CH_3)_2C-CH_2SO_3H$$

$$(-CH_2-CH-)_{n-m}-(CH_2-CH-)_m + mNH_3^+-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2SO_3^-}{\overset{|}{\underset{|}{C}}}}-CH_3$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad | $$
$$NH-C=O \quad\quad\quad O=C-O^-Na^+$$
$$\quad\quad | $$
$$(CH_3)_2-C-CH_2SO_3H \quad\quad\quad\quad\quad\quad m < n$$

or ammonia[10]

$$(CH_2-CH-)_n + mNa^+ + mOH^- \quad\quad\quad\quad \longrightarrow$$
$$\quad\quad\quad | $$
$$\quad\quad \diagup C=O$$
$$NH_2$$

$$(-CH_2-CH-)_{n-m}-(CH_2-CH-)_m + mNH_3$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad | $$
$$O=C-NH_2 \quad\quad\quad O=C-O^-Na^+$$

occurred and produced the low weight percent compositions shown in Table II.

In general, however, repeat unit ratios are close to but not exactly equal to the repeat unit ratios in the reaction mixture in which the product was synthesized.

Separations: The twelve samples of Table I were fractionated as described in the Experimental section. This fractionation method was de-signed so that (1) unreacted starch, a product component that is insoluble in water,[11] (2) starch and copolymer, product components that are insoluble in water-(2-propanone), and (3) copolymer and poly(1-amidoethylene) homopoly-mer, products that are insoluble in 2-propanone,[12] could be separated from one another. Data on three fractions collected and the assays of these fractions are contained in Table III. Samples 13–16 of Table III are mixtures prepared to test the separation method. The composition of these mixtures is given in Table IV. Samples 14–16 were separated into only two fractions. The first fraction of samples 14–16, labeled fraction 1 in Table III, was recovered as described in the Experimental section. The final fraction, labeled fraction 3 in Table III, was recovered by lyophilizing the supernate obtained from the separation of fraction 1.

TABLE III
Fractionation of Reaction Mixture and Analysis of Fractions

| Number | Fraction 1 precipitate from water | | Total starch in sample recovered in fraction 1 | Fraction 2 precipitate from 2-propanone | | | Fraction 3 solids recovered from fraction 2 supernate | | Total solids recovered |
	Wt % starch	Wt % of original sample		Precipitating solution water to 2-propanone (volume ratio)	Wt % starch in fraction	Wt % of original sample	Wt % starch in fraction	Wt % original sample	(total wt % of sample recovered)
1	98.6	24.9	109	1/7.3(c)	-(d)	0.2	4.8	55.8	85.0
	100	22.6	101						
2	75.3	5.0	7.3	1/4	58.0	12.1	47.8	75.3	92.4
3	96.2	1.3	3.7	1/4	55.6	1.6	26.7	82.4	85.2
4	87.0	1.0	2.3	1/4	51.0	11.8	31.9	70.3	83.0
5	88.4	1.0	2.5	1/7.3	68.2	0.6	5.3	75.4	86.8
	88.5	10.8	67.5						
6	74.1	8.8	46.1	1/4	78.9	1.0	7.1	81.1	82.7
7	74.1	0.8	4.3	1/4	71.4	0.4	4.6	85.4	86.9
8	100	1.2	6.2	1/4	44.4	10.1	23.4	71.4	81.6
	100	0.2	0.8						
9	100	0.2	1.0	1/7.3	78.4	1.3	4.0	77.4	84.9
	84.3	6.2	51.5						
10	100	7.0	68.8	1/4	73.2	1.3	13.8	83.9	85.3
11	76.9	0.3	2.7	1/4	71.4	0.4	17.9	83.4	83.9
12	100	0.1	0.6	1/4	53.6	0.7	13.9	82.7	83.5
	100	0.1	0.8						
13	100	0.1	0.8	1/4	22.7	0.5	5.8	77.3	97.8
	100	20.0	20.0						
14	100	18.8	75.3	—	—	—	10.0	60.8	79.6
15	100	17.3	68.8	—	—	—	8.6	65.6	82.9
16	100	22.2	88.8	—	—	—	2.3	73.1	95.2

[a] This is the ratio of volume of water added to volume of 2-propanone.
[b] Sample too small to analyze.

TABLE IV
Composition of Test Mixtures for Separation Process and Elemental Analysis of Fraction 3

PART A:

| | | Weight percent | |
Number	Starch	Poly(1-amido-ethylene)	Poly(sodium [2-methyl-2-N-propanesulfonate]-1-amidoethylene)
13	25.0	37.5	37.5
14	25.2	—	74.8
15	25.1	74.9	—
16	24.9	37.5	37.6

PART B: Elemental analysis

| | | | | | Compositional assay of fraction 3 (wt %) repeat units | | | |
	Elemental assay (wt %)							
Number	C	H	N	S	Sodium (2-methyl-2-N-propanesulfonate)-1-amidoethylene	1-Amido ethylene	Starch	$R_{N/S}$
14	37.47	6.71	5.78	13.2	94.3	0.06	10.0	0.002
15	44.80	6.81	15.97	1.20	8.57	78.3	8.62	29.5
16	41.33	6.68	11.15	8.01	57.3	38.8	2.27	2.2

Results from the four test mixtures, numbers 13–16, show that between 70 and 90 wt % of the ungrafted starch in a sample is recovered as fraction 1. Also, from the mean of the four test mixtures, 6.7 ± 3.4 wt % starch is carried into fraction 3 by physical entrapment. There is, therefore, a small carryover of unreacted starch into the final fraction.

At the 95% confidence level, there must be more than 18.8 wt % starch in fraction 3 before the high level of starch in this fraction can be attributed to something other than random fluctuation in the amount of starch physically entrapped in the sample. Fraction 3 from samples 2–4 and 8 show a wt % starch in the fraction that is well above the amount expected from physical entrapment (18.8 wt %). The fractionation results thus provide firm proof for the presence of graft copolymer in these four samples.

For evidence of graft copolymer in the other eight samples, the other section of Table III must be considered. Fraction 1 can be consistently extracted from the reaction products as shown from the repeat separations, marked a and b, for samples 1, 4, 5, 8, 9, and 12. Further, this fraction contains between 75 and 100% starch, with a definite slant in the starch-content distribution toward the 100% level.

This fraction consistently decreases in mass as the monomer ratio $R_{N/S}$ increases. Samples in the three sets, 1–4, 5–8, and 9–12, were prepared from reaction mixtures containing the same amount of starch. The first fraction separated from these samples shows a definite pattern, however, with the

mass of fraction 1 for the $R_{N/S} \cong 0$ sample in each set, samples 1, 5, or 9 being 25–70 times larger than fraction 1 for the $R_{N/S} \cong 9.0$ samples of the sets.

The wt % of total starch recovered in fraction 1 for samples 1 (105%), 5 (56%), and 9 (59%) is eight times larger than the highest percent of total starch recovered from samples with higher amide to sulfonate ratios. The highest percentage of total starch recovered in fraction 1 from samples with $R_{N/S} > 0$ is 7.3 wt % recovered from sample 2. The decrease in the amount of ungrafted starch recovered from each set of samples as $R_{N/S}$ increases implies that the capacity of cerium(IV +) to graft starch during this reaction increases as $R_{N/S}$ increases. This hypothesis is confirmed by the higher starch content of the third fraction of the $R_{N/S} \cong 9.0$ sample of each set as compared to the starch content of each fraction 3 from an $R_{N/S} \cong 0.0$ sample. Since $R_{N/S}$ measures the ratio of monomer I to monomer II in the reaction mixture or product, these data are best explained by an interference in grafting produced by monomer II.

Taken together, the data of Table III imply that (1) starch–amidoethylene terpolymer is formed by cerium(IV +)-initiated, free-radical, graft copolymerization of monomer mixture onto starch, (2) capacity of cerium ion to form a grafting site on starch increases as the ratio of monomer I and II in the monomer mixture increases, (3) sodium 2-methyl-3-imino-4-oxohex-5-ene-1-sulfonate disrupts the grafting reaction, and (4) there is no proof of graft copolymer formation in samples (numbers 1, 5, and 9) produced from reaction mixtures containing only monomer II.

Monomer II could disrupt the grafting reaction by (1) complexing the cerium(IV +) initiator, (2) reacting with the initiator, or (3) terminating the growth of grafting side chain by chain transfer. This third mechanism, if it occurred very frequently, would leave the backbone grafted with such small side chains that it would behave like ungrafted starch.

Effects attributed to initiator complexing and chain transfer have been seen by McCormick and Park in their studies of grafting of I and II onto dextran.[12]

Rheology

Viscosities measured at 22.5 s^{-1} of solutions of copolymers 1–4 are given as a function of copolymer concentration in Figure 1. These data show a pattern seen in plots of viscosity vs. concentration results for all of the copolymer samples. The highest solution viscosities are always given by samples with an amide to sulfonate ratio of 3/1. The implications of this result will be discussed below.

Solution viscosity vs. shear rate is plotted for a series in Figure 2. These data show significant decreases in solution viscosity with increasing shear rate.

Product solutions ar shear thinning and have viscosities which are predicted by the power law equation[13]

$$\eta_{apparent} = H\dot{\gamma}(n-1) \qquad (1)$$

In eq. (5), $\eta_{apparent}$ is the viscosity measured at a shear rate of $\dot{\gamma}$, H is the viscosity at a shear rate of 1.0 s^{-1}, and n is the power law exponent. Fluids
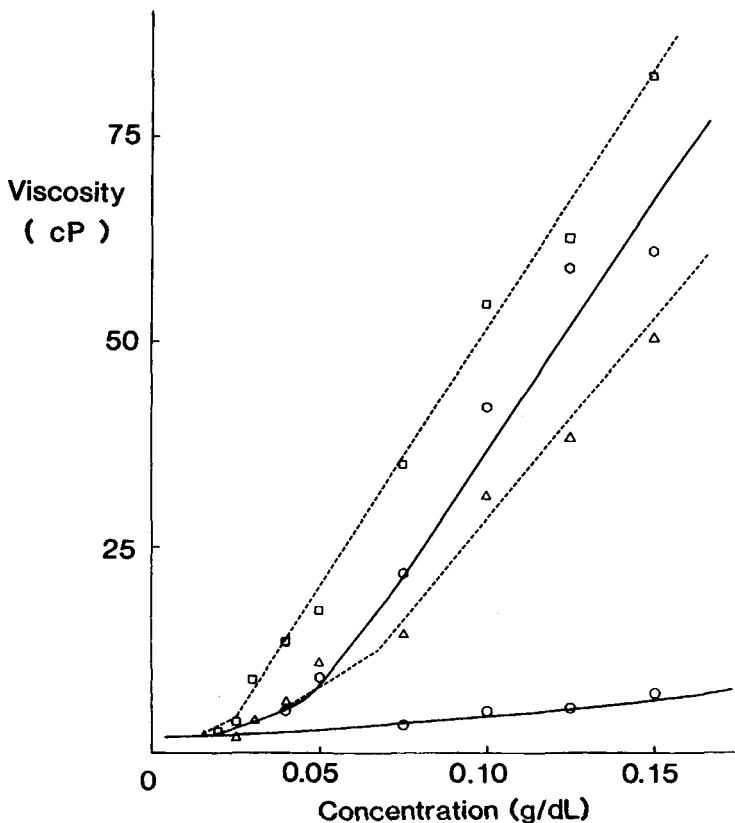
Fig. 1. Solution viscosity at 22.5 s^{-1} as a function of copolymer concentration: $\overline{M}_n$ (from synthesis ratios) = 419,000; (○) sample 1, $R_{N/S}$ = 0/1; (△) sample 2, $R_{N/S}$ = 1/1; (□) sample 3, $R_{N/S}$ = 3/1; (◯) sample 4, $R_{N/S}$ = 9/1.

with an n value of 1.0 are Newtonian while those with an n value less than 1.0 are shear thinning and become more shear thinning as n decreases toward zero. Plots of n vs. polymer concentration for solutions of products of approximately equal amide to sulfonate ratio but varying design molecular weights are given in Figure 3 for copolymers 2, 6, 10, and in Figure 4 for copolymers 3, 7, and 11. Correlation coefficients for these results were generally between −0.98 and −1.0

These data show that reaction product solutions are shear thinning with the degree of shear thinning increasing as (1) polymer concentration increases or (2) the amide to sulfonate ratio changes toward 3/1.

Limiting viscosity number is also a function of shear rate.[14] Limiting viscosity numbers were measured by determining solution viscosity at constant shear rate at three to six different polymer concentrations, and extrapolating the data to zero concentration using the Fuoss equation,[15]

$$C/\eta_{sp} = 1/[\eta] + Q_F C^{1/2} \tag{2}$$

where Q_F is the Fuoss constant.
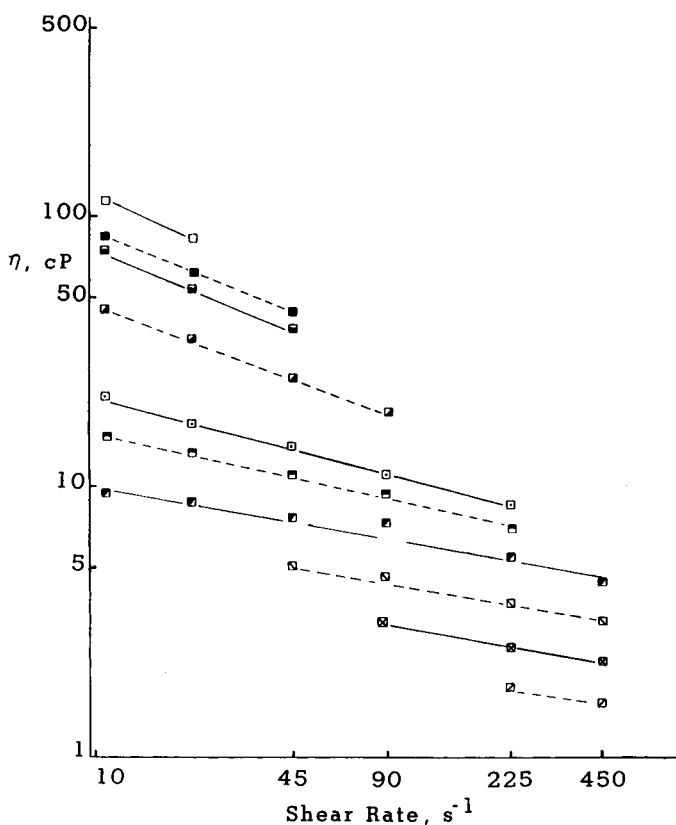
Fig. 2.   Solution viscosity at shear rates from 450 to 10 s^{-1} for aqueous solutions containing different concentrations (g/dL) of copolymer 3: (□) 0.15; (■) 0.125; (▣) 0.10; (▨) 0.075; (▣) 0.05; (▦) 0.04; (▧) 0.03; (▨) 0.025; (▨) 0.02; (▨) 0.01; $\overline{M}_n$ (from synthesis ratios) = 419,000; $R_{N/S}$ = 3/1.

Limiting viscosity numbers for copolymers 5–8 are given as a function of shear rate in Figure 5 and for each copolymer at a shear rate of 225 s^{-1} in Table II. The Flory equation[16]

$$[\eta] = \Phi \langle s^2 \rangle^{3/2} / M_w \tag{3}$$

shows that limiting viscosity number for the same molecule in states i and j is proportional to radius of gyration, $\langle s^2 \rangle^{1/2}$, in that state,

$$\left(\frac{[\eta]_i}{[\eta]_j} \right)^{1/3} = \left(\frac{\langle s^2 \rangle_i}{\langle s^2 \rangle_j} \right)^{1/2} \tag{4}$$

Reductions of limiting viscosity number, as illustrated by Figure 5, imply a reduction in the radius of the solvated polymer molecule. This reduction in radius as a function of shear rate is produced by disruption of polymer–polymer entanglements and compaction of the polymer molecule.[17]

These copolymers were designed and synthesized such that within the three groups (1–4, 5–8, and 9–12) the compounds would have equal molecular
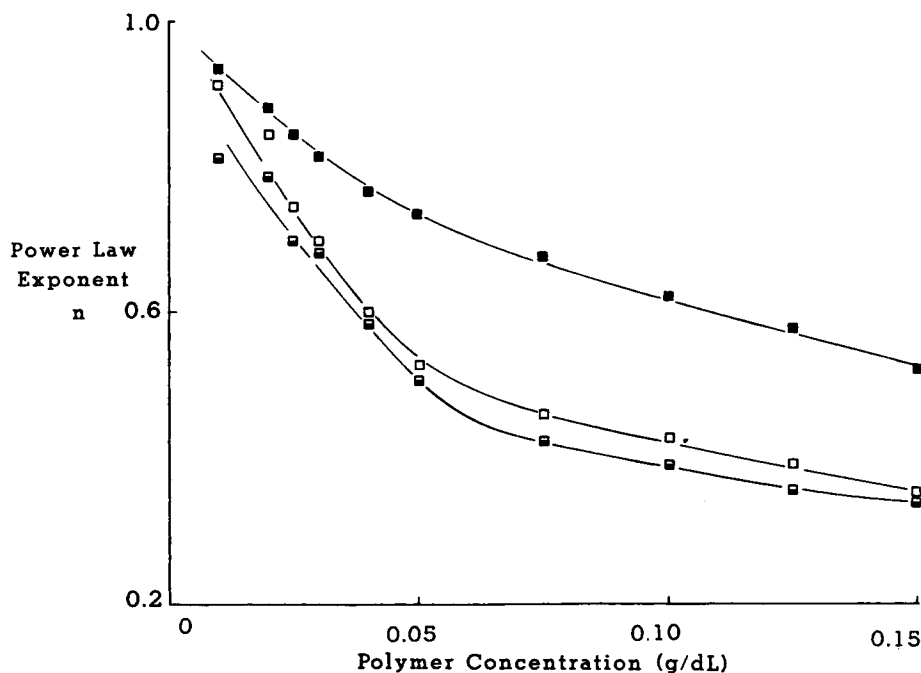
MEISTER ET AL.
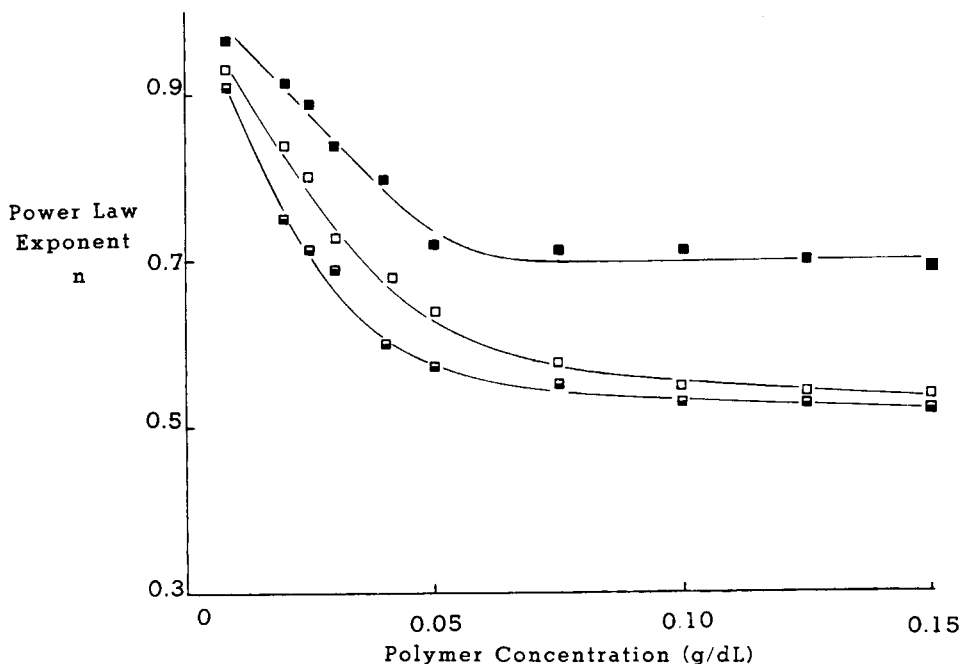
Fig. 3. Power law exponent [see eq. (1)] vs. polymer concentration for solutions of copolymers of different design molecular weight: (■) sample 2 (419,000; 1/1); (□) sample 6 (840,000; 1/1); (◩) sample 10 (1,275,000; 1/1); (#; #) ($\overline{M}_n$ from synthesis ratios; $R_{N/S}$).

weight *if* there were no effect of changing monomer ratio, $R_{N/S}$, on the synthesis. These samples, which were designed to have the same number of grafts per backbone molecule, should give solutions with rheological properties that follow a definite, theoretically predictable pattern. If this pattern of flow properties is not seen, then chemical effects have produced molecular weight variation within the three groups of copolymers. In the following sections, the pattern that must appear in the rheological properties will be derived and will be compared to actual data from the copolymers.

For the values of limiting viscosity number listed in Table II, as $R_{N/S}$ increases, limiting viscosity number increases to a maximum at $R_{N/S} = 3/1$ and then decreases within each set of equal design molecular weight samples.

This pattern in the values of $[\eta]$ has significant structural implications since Debye and Bueche,[18] Kirkwood and Roseman,[19] and Flory[20] have shown $[\eta]$ to be proportional to the cube of the linear expansion coefficient α_e, and Hermans and Overbeek[21] have shown α_e to be a function of chain length and number of charges on the molecule.

Within each of the three sets of samples synthesized, molecular weight of the side chain, X, should be constant unless there are chemical interferences. Degree of polymerization is then

$$D_p = X/M_a \qquad (5)$$

Fig. 4.   Power law exponent [see eq. (1)] vs. polymer concentration for solutions of copolymers of different design molecular weight: (■) sample 3 (419,000; 3/1); (□) sample 7 (840,000; 3/1); (▣) sample 11 (1,275,000; 3/1).

where M_a is the average molecular weight of the monomer. Since

$$M_a = \frac{R_{N/S}M_1 + M_2}{R_{N/S} + 1} \tag{6}$$

where M_1 and M_2 are monomer I and II molecular weights, the derivative of chain length B with respect to monomer ratio at constant side chain molecular weight is

$$\left(\frac{\partial B}{\partial R_{N/S}}\right)_X = \left(\frac{2}{M_2} - \frac{\left(2 \times M_1/M_2^2\right) \times \left(R_{N/S} + 1\right)}{\left(M_1/M_2\right) \times R_{N/S} + 1}\right)$$

$$\times \left(\frac{X}{\left(M_1/M_2\right)R_{N/S} + 1}\right) \tag{7}$$

This derivative is positive for all $R_{N/S} \geq 0$, so that chain length increases with increasing monomer ratio ($R_{N/S}$) at constant molecular weight.

The second variable upon which the linear expansion coefficient of a polyelectrolyte depends is the number of charge sites, CS, on the chain. The change in expansion coefficient as a function of number of charged sites and
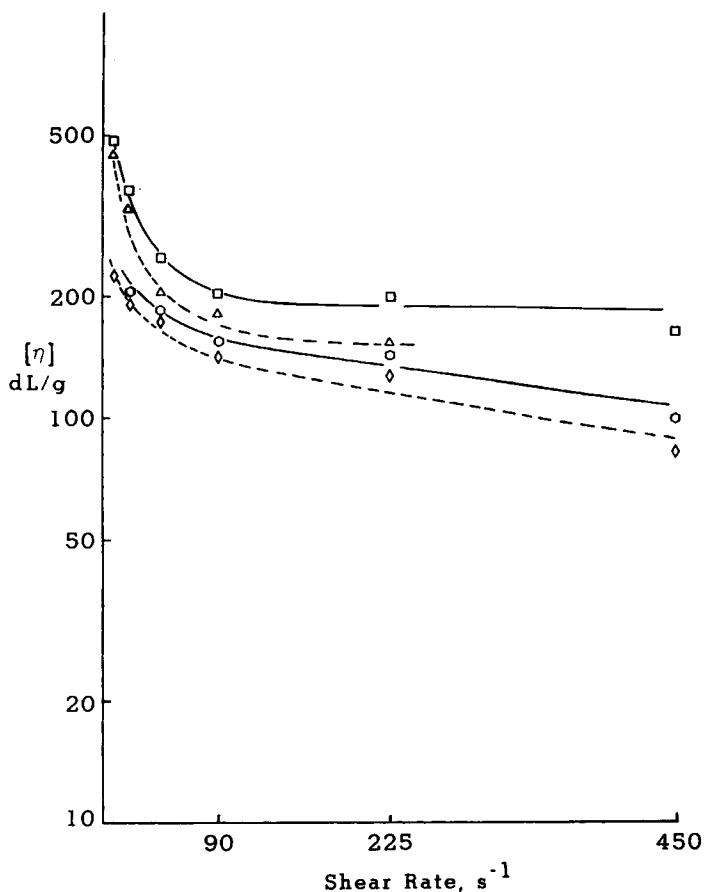
Fig. 5. Limiting viscosity number plotted vs. shear rate at which extrapolated viscosities were measured: (○) sample 8 (840,000; 9/1); (□) sample 7 (840,000; 3/1); (◇) sample 6 (840,000; 1/1); (△) sample 5 (840,000; 0/1).

chain lengths is[21]

$$f(\alpha_e) = \alpha_e^5 - \alpha_e^3 \cong \left(\frac{X}{R_{N/S}M_1 + M_2}\right)^2 \times \sqrt[2]{B} \tag{8}$$

This function is positive for all allowed α_e. The derivative of eq. (8) with respect to $R_{N/S}$ at constant X is

$$\left(\frac{\partial f(\alpha_e)}{\partial R_{N/S}}\right)_X \cong \left[2(R_{N/S} + 1)\right]^{1/2} \times \left(\frac{X}{M_1 R_{N/S} + M_2}\right)^{2.5}$$

$$\times \left(\frac{1}{2(R_{N/S} + 1)} - \frac{2.5}{R_{N/S} + M_2/M_1}\right) \tag{9}$$

The sign of the derivative of $f(\alpha_e)$ depends on the final bracketed term on the

right-hand side of eq. (9). For all $R_{N/S}$ values greater than or equal to zero, this final term and, therefore, $(\partial f(\alpha_e)/\partial R_{N/S})_X$ are negative. Equation (9) shows that linear expansion coefficient *increases* monotonically as $R_{N/S}$ decreases at constant molecular weight. Since $[\eta] \cong \alpha_e^3$, the pattern of properties expected in a given group of copolymers is that the limiting viscosity number increases monotonically as $R_{N/S}$ decreases.

The data of Table II shows that limiting viscosity number initially increases with decreasing $R_{N/S}$ within a given set of samples but decreases beyond $R_{N/S} = 3/1$. This shows that molecular weight is not constant within the sets of samples. Instead, the molecular weight of the reaction product increases as $R_{N/S}$ increases. The rise in molecular weight of polymer with increasing $R_{N/S}$ produces a maximum because the limiting viscosity number difference

$$[\eta]^{1.66} - [\eta] \cong CS^2 \times \sqrt{B} \tag{10}$$

is decreasing in proportion to the square of the number of charge sites and increasing in proportion to the square root of backbone length. Since yield of polymer decreases but molecular weight increases with increasing $R_{N/S}$, the presence of monomer II in the reaction mixture must produce less grafting or more chain transfer during the polymerization. This conclusion from the solution flow properties of the products is consistent with results obtained from the fractionation studies. The fractionation data show that less grafting does take place as monomer II concentration in the reaction mixture increases.

Screen Factor

Water-soluble, graft copolymers of starch have been extensively studied since their development in 1979. Aqueous solutions exhibited the Weissenberg effect,[22] which was more pronounced when the polymer concentration was increased.[23] These polymers were also shown to produce drag reduction in dilute aqueous solution.[24]

A screen viscometer,[26] which requires a fixed volume of fluid to pass through a pack of five 100-mesh screens in close contact and laying perpendicular to the direction of flow, was used to measure screen factor, the ratio of passage time for a given fluid to that for an equal volume of water. Screen factor data for a group of 3 to 1 amide-to-sulfonate-ratio, graft polymer solutions are given in Figure 6. Since screen factor is a measure of viscoelastic losses in a fluid, these representative data and the results of previous experiments show the polymer solutions to be viscoelastic as well as viscous and confirm the presence of entanglements in low-concentration samples.

Electrolyte Effects

The hydrodynamic volume of polyions will decrease if ionic sites in the molecule are neutralized by appropriate counterions. In view of this, the limiting viscosity number of reaction products were measured at 30°C as a function of calcium ion concentration at a shear rate of 600 s^{-1}. The results are shown in Figure 7.
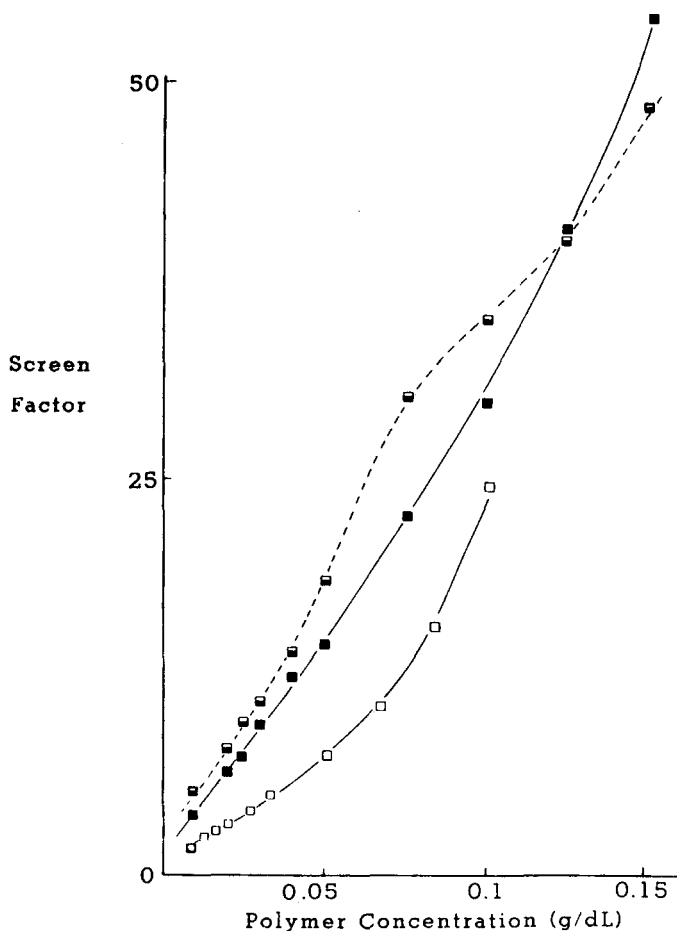
Fig. 6. Screen factor at 2°C vs. polymer concentration in water: (□) sample 3 (419,000; 3/1); (■) sample 7 (840,000; 3/1); (▣) sample 11 (1,275,000; 3/1).

For the three copolymers in Figure 7, the cube root of the ratio of $[\eta]$ in distilled water to $[\eta]$ in $3.5 \times 10^{-2}M$ $CaCl_2$ is 2.5 implying an 80% reduction in the radius of the polymer [Eq. (4)].

Comparison to Other Graft Polymers

Cerium(IV)-initiated, free-radical polymerization has been used to attach side chains from monomers I and II to dextran by McCormick and Park.[12] The products produced by McCormick et al. differ significantly from those described here since (1) the backbones are different, (2) the number of grafts attached to each dextran molecule may be several times larger than the number of grafts on each starch molecule, and (3) the product recovery processes differ.

Burr et al.[26] have synthesized terpolymers of starch using 2-propenenitrile and monomer II. These materials contained only small fractions of soluble product. Because of these differences, no detailed intercomparison of the properties of these polymers can be made. They all do show, however, the
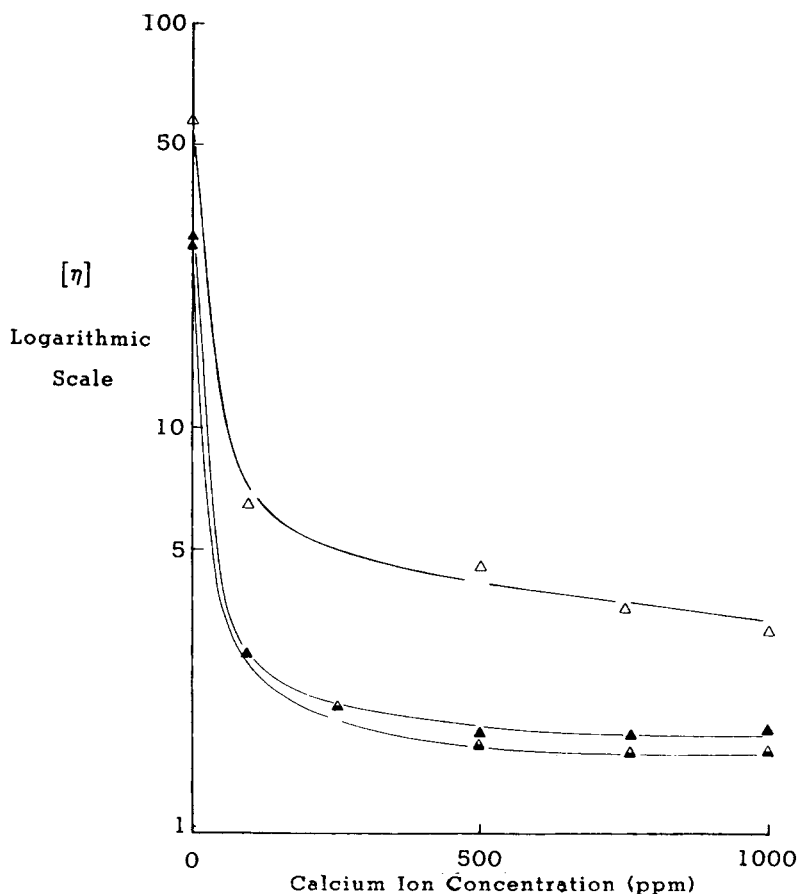
Fig. 7.   Limiting viscosity number of copolymer versus calcium ion concentration: (▲) sample 1 (419,000; 0/1); (△) = sample 5 (840,000; 0/1); (▲) sample 9 (1,275,000; 0/1).

altered solubility characteristics of a graft copolymer and a pronounced capacity to form viscous solutions. The sulfonate-containing polymers show pronounced solubility in polar solvents, a characteristic of polyelectrolytes.

Extensive efforts have been made to graft water-soluble, ethene monomers to cellulose using either ionizing radiation or cerium ion initiation. These products differ from starch copolymers in that the reactions produce graft copolymer but also (1) produce large amounts of homopolymer, (2) are inhibited by common cellulose contaminants such as lignin, and (3) usually do not produce water-soluble, grafted product from pulp or fiber. Reactions, products, and properties for cellulose grafting processes are reviewed in Ref. 27.

CONCLUSIONS

Graft terpolymers of starch, 2-propenamide, and sodium 2-methyl-3-imino-4-oxohex-5-ene-1-sulfonate can be made by cerium(IV)-initiated, free-radical polymerization of an aqueous monomer mixture on starch. Synthesis is con-

ducted on aqueous, gelled, lintnerized, potato starch at 30°C under a nitrogen atmosphere. Product is recovered by dropwise addition of dilute polymer solution to 2-propanone or, for high-sulfonate-content polymers, n-butanol.

Yields range from 50 to 100 wt % and products contain 9–52 wt % starch, 1–51 wt % 1-amidoethylene, and 18–65 wt % sodium 1-(2-methylprop-2 N-yl-1-sulfonate)amidoethylene. Up to 5% of the amide side units are hydrolyzed during synthesis. Repeat unit ratios in the reaction product approximate the monomer ratios of the reaction.

Products can be fractionated to remove unreacted starch with an average removal efficiency of 78 wt %. The mean wt % of unreacted starch that cannot be separated from a homopolymer sample is 6.7 ± 3.4%. Fraction of starch grafted in a reaction decreases as the mole fraction of sulfonated monomer in the reaction monomer mixture increases. No evidence was found for grafting to starch in reactions containing only sulfonated monomer. The capacity of cerium(IV) ion to form grafting sites on starch increases with increasing 2-propenamide mole fraction in the monomer mixture.

The products are readily soluble in water and produce shear thinning solutions. Viscosity of these shear thinning solutions is described by the power law equation. Solutions of these products have lower power law exponents with increasing product concentration or as the $R_{N/S}$ value of the product changes toward 3/1.

Limiting viscosity number of the products in water decreases with increasing shear rate of measurement or with increasing salt concentration of the solvent. This reduction shows that shear and electrolyte concentration cause the polymer molecule to disentangle and compact. Calcium chloride concentrations as low as $0.035M$ cause 80% reductions in hydrodynamic volume.

Both Kirkwood's and Flory's theory show that expansion coefficient and limiting viscosity number must increase as the fraction of sulfonate-containing, repeat units in the copolymer increases ($R_{N/S}$ decreases). This shows that molecular weight within groups of equivalently synthesized copolymers decreases as the fraction of sulfonated repeat units in the polymer increases.

Screen factor and other measurements show product solutions to be viscoelastic.

References

1. G. Mino and S. Kaizerman, J. Polym. Sci., 31, 242 (1958).
2. M. O. Weaver, E. B. Bagley, G. F. Fanta, and W. M. Doane, U.S. Pat. 3,981,100 (1976).
3. J. Meister, J. Rheol., 25, 487 (1981).
4. C L. McCormick and L. S. Park, J. Polym. Sci., 22, 49 (1984).

5. J. W. Lyons, L. Kotin, and J. Binding, *J. Am. Chem. Soc.*, **87**, 1670 (1965).

6. C. J. Lintner, *J. Prakt. Chem.*, **34**, 378 (1886).

7. C. L. McCormick, R. D. Hester, H. H. Neidlinger, and G. C. Wildman, Report BETC-5603-5, U.S. Dept. of Energy, 1979; Report BETC-5603-10, U.S. Dept. of Energy, 1980; *Proceedings of the 5th Dept. of Energy Symposium on Enhanced Oil Recovery*, *1*, D4.1, Petroleum Publishing Company, Tulsa, OK, 1979.

8. M. A. Jermyn, *Anal. Biochem.*, **68**, 332 (1975).

9. *AMPS*^tm *Monomer*, Lubrizol Corp. publication #780-360-43 Wickliffe, OH (1981), p. 5.

10. S. Sawant and H. Morawetz, *Polym. Lett. Ed.*, **20**, 385 (1982).

11. J. Bandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975, pp. IV-245, 262.

12. C. L. McCormick and L. S. Park, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 49 (1984).

13. A. Bondi, *Rheology, Theory and Applications*, F. R. Girich, Ed., Academic, New York, 1960, Vol. 3, Chap. 12, p. 465.

14. W. R. Moore, *Progress in Polymer Science*, A. D. Jenkins, Ed., Pergamon, Oxford, 1967, Vol. 1, pp. 1–43.

15. R. M. Fuoss, *J. Polym. Sci.*, **3**, 603 (1948).

16. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, NY, 1953, p. 611.

17. H. Van Oene and L. H. Cragg, *J. Polym. Sci.*, **57**, 209 (1962).

18. P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

19. J. J. Kirkwood and Jacob Roseman, *J. Chem. Phys.*, **16**, 565 (1948).

20. P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949); P. J. Flory and T. G. Fox, Jr., *J. Polym. Sci.*, **5**, 745 (1950); P. J. Flory and T. G. Fox, Jr., *J. Am. Chem. Soc.*, **73**, 1904 (1951).

21. J. J. Hermans and J. T. G. Overbeek, *Rec. Trav. Chim.*, **67**, 761 (1948).

22. R. Roberts, *Rheology*, F. R. Eirich, Ed., Academic, New York, 1960, Vol. 3, p. 571.

23. H. Pledger, Jr., J. J. Meister, T. E. Hogen-Esch, and G. B. Bulter, Proc. 54th Annual Tech. Conf., Soc. Pet. Eng., Paper Number 8422, Las Vegas, NV, September 1979.

24. G. B. Butler, T. E. Hogan-Esch, J. J. Meister, and H. Pledger, Jr., U.S. Pat. 4,400,496 (1983).

25. D. C. MacWilliams, J. H. Rogers, and T. J. West, in *Water Soluble Polymers*, N. M. Bikales, Ed., Plenum, New York, 1973, p. 105.

26. R. C. Burr, F. Fanta, and W. M. Doane, *J. Appl. Polym. Sci.*, **24**, 1387 (1979).

27. A. Hebeish and J. T. Guthrie, *The Chemistry and Technology of Cellulosic Copolymers*, Springer-Verlag, New York, 1981.