Graft Copolymers of Starch and Poly(2-hydroxy-3-methacryloyloxypropyltrimethyl-ammonium chloride).   Preparation and Testing as Flocculating Agents*

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Synopsis

The title monomer (I) has been graft polymerized onto whole wheat starch with both ceric ammonium nitrate and ferrous ammonium sulfate–hydrogen peroxide initiation. Three graft copolymers, which contained 4.5, 12.1, and 15.2% grafted poly(I), were characterized as to molecular weight of grafted branches and grafting frequency.   Graft polymerization was proved by fractional precipitation.   Graft copolymers were tested as flocculating agents for diatomaceous silica and nonmagnetic iron ore.   The graft copolymers with 12.1 and 15.2% grafted poly(I) compared favorably in flocculating ability with a commercial high molecular weight cationic polyacrylamide.

INTRODUCTION

Cationic high polymers are used as flocculating agents to remove finely divided solids from aqueous suspension, and the synthesis of such polymers is currently an active area for research.[1]   Graft polymerization of cationic monomers onto starch offers a good opportunity for developing new and useful products for such applications.   As one step in this direction, we examined the graft polymerization onto whole wheat starch of the commercially available 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride (I):

$$CH_2=\underset{\underset{I}{}}{\overset{\overset{CH_3}{|}}{C}}-CO_2CH_2\overset{\overset{OH}{|}}{C}HCH_2\overset{\oplus}{N}(CH_3)_3Cl\ominus$$
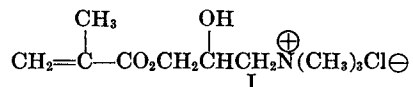
The preparation of starch–poly(I) copolymers, proof of grafting, determination of molecular weight and frequency of grafted branches, and the laboratory testing of graft copolymers as flocculating agents will be described here.

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EXPERIMENTAL

Materials

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

Ceric ammonium nitrate initiator solution was prepared by dissolving 13.9 g of ceric ammonium nitrate (Fisher Certified Reagent) in 250 ml of $1N$ nitric acid.

Ferrous ammonium sulfate hexahydrate and 30% hydrogen peroxide were Baker Analyzed Reagent Grade.

Monomer I (95% purity) was obtained from Shell Chemical Company and, for some reactions, was further purified by recrystallization from isopropanol.

Graft Polymerization

In a typical polymerization initiated with ceric ammonium nitrate, a stirred slurry of 50.0 g, dry basis, of wheat starch [0.308 mole anhydroglucose unit (AGU)] in 375 ml of water was sparged with a nitrogen stream at 25°C for 1 hr. Initiator solution (37.5 ml) was first added, and 5 min later 50.0 g of monomer I was added (as the dry powder). After the mixture was stirred at 25°C for 3 hr, the reaction was terminated by the addition of 0.5 g of hydroquinone. The reaction mixture was centrifuged and the insoluble graft copolymer freed of unreacted monomer and ungrafted poly(I) by washing with water. The copolymer was finally washed with acetone and dried.

In polymerizations initiated by the ferrous ion–hydrogen peroxide system, 0.12 g (3.06×10^{-4} mole) of ferrous ammonium sulfate hexahydrate dissolved in about 2 ml of water was added to the stirred, nitrogen-sparged starch slurry. After 5 min, monomer I was added as the dry solid; and after 5 more min, 0.35 g of 30% hydrogen peroxide (3.09×10^{-3} mole) was added. The mixture was stirred for 2 hr at 25°C, and then the reaction was terminated with hydroquinone.

In reactions where grafting frequencies were to be calculated, per cent poly(I) in the copolymer was calculated from nitrogen and chlorine analyses after all quaternary ammonium groups had been converted to the chloride form. For this conversion, 2 g of copolymer was dispersed in 100 ml of water at 90°C. A solution of 30 g of sodium chloride in 100 ml of water was added to the cooled dispersion, and the resulting mixture was exhaustively dialyzed against distilled water. The copolymer was then isolated by freeze drying.

Values for per cent grafted poly(I) in the copolymer were calculated from nitrogen and chlorine content and also by weight loss after acid hydrolysis of the starch moiety to glucose. For three different graft copolymers these three methods gave values of 13.6, 13.4, and 12.1%; 5.1, 4.6, and 4.5%; and 16.1, 16.5, and 15.2% grafted poly(I), respectively.

Hydrolysis of Graft Copolymer and Molecular Weight of Grafted Poly(I)

To determine the molecular weight of grafted poly(I), starch was removed from the copolymer by refluxing 20 g of graft copolymer in 1 liter of 0.5N hydrochloric acid for 30 min. The mixture was cooled, neutralized to pH 3.8 with 10% sodium hydroxide, and dialyzed against distilled water. The solution was reduced in volume to about 300 ml, and enough concentrated hydrochloric acid was added to give a normality of 0.5. The mixture was again refluxed for 30 min, neutralized, and dialyzed. The solution was filtered and then freeze dried. The infrared spectrum of the freeze-dried product showed less than 5% carbohydrate, as determined by comparison with spectra of synthetic mixtures of poly(I) and starch. The hydrolysis procedure did not degrade poly(I), as determined by refluxing a sample of ungrafted poly(I) in 0.5N hydrochloric acid. Nitrogen and chlorine analyses and intrinsic viscosity in 0.05N sodium chloride were essentially unchanged by acid treatment.

Number-average molecular weights of grafted poly(I) samples 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.).

Proof of Grafting by Fractional Precipitation

A physical mixture of 1.00 g of whole wheat starch (pretreated with dimethyl sulfoxide to improve solubility[2]) and 0.10 g of poly(I) (synthesized in the absence of carbohydrate) was dispersed in 100 ml of water on a steam bath. A 100-ml portion of absolute ethanol was slowly added to the stirred dispersion at room temperature, and the mixture was allowed to stand overnight. Centrifugation afforded 0.98 g of starch, the infrared spectrum of which showed no carbonyl absorption due to poly(I). The supernatant was reduced in volume and freeze dried to give 0.10 g of product. Infrared analysis of this material showed it to be poly(I) containing only about 5% carbohydrate.

When a 1.10-g sample of graft copolymer containing 12.1% poly(I) was dispersed in water in a similar manner, 150 ml of absolute ethanol was required to precipitate 0.90 g of solid. This solid showed carbonyl absorption in the infrared due to poly(I). The soluble fraction weighed 0.13 g, and its infrared spectrum showed strong absorption due to starch in addition to absorption in the carbonyl region.

Flocculation Studies

The starch graft copolymers and the commercial high molecular weight cationic polyacrylamide were dispersed in water by adding 0.2 g of polymer to 150 ml of distilled water at room temperature. The stirred mixture was heated in a boiling water bath for 30 min, cooled to room temperature, and then diluted with water to 1 liter. Final dispersions were clear and color-

less. An alum solution was prepared by dissolving 1 g of $Al_2(SO_4)_3 \cdot 18H_2O$ in 1 liter of distilled water.

Flocculation was studied by means of the jar test.[3] A Phipps and Bird variable-speed six-paddle stirrer was used. Beakers of 1-liter capacity were employed, and flocculant dispersions of varying concentration were added simultaneously to each beaker by a series of test tubes similar to the apparatus used by Packham.[4] After a settling time of 30 min, samples of each supernatant were withdrawn simultaneously from the midpoint of each beaker into sample bottles by means of a vacuum apparatus similar to that described by Cohen.[5] Per cent solids in the withdrawn supernatants was determined by filtration.

Snow Floss Celite (a diatomaceous silica) was from Johns-Manville. The average particle size, quoted by the manufacturer, was 2.1 μ. Dispersions were prepared by addition of 210 g of Celite to 7 liters of rapidly stirred distilled water. The pH (initially about 5) was, for most tests, adjusted to 7 with dilute sodium hydroxide; and 940 ml of the suspension was transferred to each of the six beakers and stirred at 100 rpm. The desired volume of flocculant dispersion was pipetted into each of the six test tubes, and the volume of liquid in each tube was adjusted to 60 ml with distilled water. The six portions of flocculant were then added simultaneously to the six stirred (100 rpm) Celite suspensions. Stirring was continued for 3 min at 100 rpm, 5 min at 50 rpm, and 60 min at 20 rpm. The stirrers were then stopped, sampling tubes inserted, and the contents of the beakers allowed to settle. Samples were then withdrawn simultaneously from each of the six beakers, and the per cent solids in the withdrawn supernatants was determined.

Hematite iron ore contained 62% iron. A suspension was prepared by ball milling 1 kg of solid in 900 ml of water for four days and then diluting the mixture to 30 liters with distilled water; about 70% of the solid suspended in this manner remained in suspension after a settling time of 30 min. The final pH was 7.5 and was not further adjusted. A 940-ml portion of this suspension was transferred to each of the six beakers. For runs without alum, additions of flocculant dispersions were made in the same manner described for Celite. For runs with alum, solutions of alum were added simultaneously to each beaker at 100 rpm, and the suspensions were stirred for 2 min at this speed. Flocculant dispersion was then added to each beaker, and the suspensions were stirred for 1 min more at 100 rpm. Stirring at 50 and 20 rpm, followed by settling, was then carried out in a manner identical to that described for Celite.

RESULTS AND DISCUSSION

Preparation and Characterization of Graft Copolymers

The products from graft polymerization reactions initiated with ceric ammonium nitrate or ferrous ammonium sulfate–hydrogen peroxide are shown in Table I. Although readily dispersible in hot water, the starch–

TABLE I

Graft Polymerization of 2-Hydroxy-3-Methacryloyloxypropyltrimethylammonium Chloride (I) onto Starch

Polymerization recipe[a]				Reaction product				
				Water-soluble poly(I), g	Water-insoluble graft copolymer			
Starch, g	I, g	Initiator	Water, vol		Wt, g	% Poly(I) in copolymer	M_n of grafted poly(I)	AGU[b]/graft
200.0 (1.23 mole AGU)	210.5 (95%) (0.842 mole)	0.0152 mole[c] Ce^{+4}	1500 ml	not determined	225.8	12.1	72,000	3240
200.0 (1.23 mole AGU)	210.5 (95%) (0.842 mole)	0.0152 mole[c] Ce^{+4}	10 liters	74.7	201.2	4.5	80,000	10,500
50.0	52.6[d] (95%)	0.0038 mole[e] Ce^{+4}	375 ml	35.4	57.3	13[f]	...	...
50.0	50.0 (recryst.)	0.0038 mole[e] Ce^{+4}	375 ml	35.5	59.9	15.2	84,000	2900
50.0	50.0 (recryst.)	0.0038 mole[e] Ce^{+4}	180 ml	31.4	56.9	12[f]	...	...
50.0	25.0 (recryst.)	Fe^{+2}/H$_2$O$_2$[g]	200 ml	13.0	54.0	7[f]	...	...
50.0	50.0 (recryst.)	Fe^{+2}/H$_2$O$_2$[g]	200 ml	34.3	54.7	8[f]	...	...

[a] In all but the third reaction, I was added as the dry solid.
[b] Anhydroglucose unit.
[c] 150 ml of initiator solution (see experimental section).
[d] Starch suspended in 300 ml water; I added as a solution in 75 ml water.
[e] 37.5 ml initiator solution (see experimental section).
[f] Estimated from weight gain.
[g] Quantities and order of addition given in experimental section.

poly(I) copolymers, like whole wheat starch, remained as discrete particles when treated with water at room temperature and could be isolated from reaction mixtures as swollen solids by centrifugation. Unreacted monomer and ungrafted poly(I) were soluble in water at room temperature and were removed from graft copolymers by water washing. Infrared analysis of poly(I), isolated from water extracts by dialysis and freeze drying, showed less than 5% carbohydrate; nearly all the starch could be accounted for in the water-insoluble fractions. For the first, second, and fourth reactions of Table I, per cent poly(I) in the copolymer was calculated from weight loss on acid hydrolysis. These values agreed with those calculated from nitrogen and chlorine analyses of graft copolymers before hydrolysis. In the remaining four reactions, per cent poly(I) in the copolymer was estimated from weight gain.

Chemical bonding of poly(I) chains to the starch backbone was proved by fractional precipitation. An aqueous dispersion of starch and ungrafted poly(I) could be separated into its two components by precipitation of starch with ethanol. However, similar treatment of the graft copolymer from the first reaction in Table I gave two fractions, each of which showed infrared absorption for both starch and poly(I).

With ceric ammonium nitrate, addition of monomer I to the reaction mixture as a water solution rather than as a dry solid did not increase per cent grafted poly(I) (compare first and third reactions of Table I); however, a slightly higher conversion to grafted poly(I) was attained with recrystallized monomer (compare first and fourth reactions). As might be expected, a lowering of reactant concentrations reduced the per cent grafted poly(I) in the copolymer (first versus second reaction); however, per cent grafted poly(I) was not increased by high concentrations of reactants (fourth versus fifth reaction). In the last two reactions of Table I, conditions similar to those published by Brockway and Moser[6] were used (ferrous ammonium sulfate–hydrogen peroxide initiation). The per cent grafted poly(I) for both reactions was lower than that for ceric ammonium nitrate. For the reactions in Table I, conversions to ungrafted poly(I) were high; however, optimum reaction conditions were not determined in these exploratory studies.

Number-average molecular weights of grafted poly(I) were determined by membrane osmometry after removal of the starch portion of the copolymer by acid hydrolysis. Heating a solution of ungrafted poly(I) in $0.5N$ hydrochloric acid under reflux had little effect, since the nitrogen and chlorine analyses and the intrinsic viscosity of a sample of poly(I) were essentially unchanged by such treatment. Molecular weights of grafted poly(I) were not greatly different for the first, second, and fourth reactions of Table I.

Laboratory Evaluation of Graft Copolymers as Flocculants

Laboratory tests were run on the three characterized graft copolymers with 4.5, 12.1, and 15.2% grafted poly(I) to get some estimate of the value
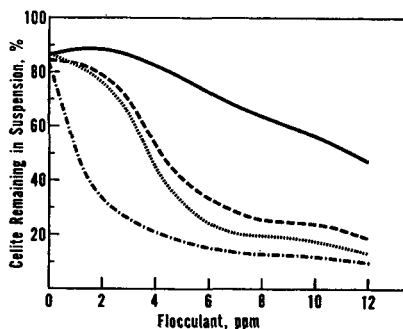
Fig. 1. Flocculation of Celite. Comparison of flocculants. Initial Celite concentration: 30 g/l.; pH 7; flocculant added while suspensions stirred at 100 rpm; mixtures stirred for 3 min at 100 rpm, 5 min at 50 rpm, and 60 min at 20 rpm and allowed to settle for 30 min: (———) starch–poly(I) copolymer with 4.5% grafted poly(I); (- - -) starch–poly(I) copolymer with 12.1% grafted poly(I); (. . .) starch–poly(I) copolymer with 15.2% grafted poly(I); (–··–) commercial cationic polyacrylamide flocculant.
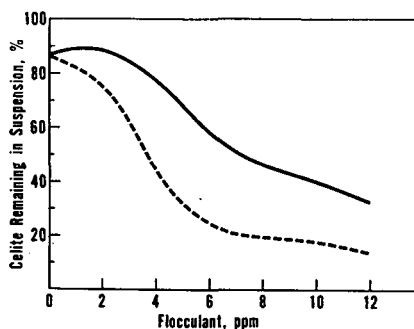
Fig. 2. Flocculation of Celite. Comparison of a physical mixture of starch and poly(I) with starch–poly(I) copolymer. Initial Celite concentration, pH, stirring speeds, and settling time were the same as for Figure 1: (———) physical mixture of starch and poly(I) [isolated from acid hydrolysis of graft copolymer with 15.2% poly(I)]; (- - -) starch–poly(I) graft copolymer with 15.2% poly(I).

of starch–poly(I) graft copolymers as flocculating agents. Figure 1 shows the flocculation of aqueous suspensions of Celite (a diatomaceous silica) with the starch–poly(I) copolymers and also, for comparison, with a commercial high molecular weight cationic polyacrylamide flocculant. Flocculant concentrations in parts per million (ppm) refer to final concentrations in water after addition to the aqueous Celite suspensions. All three starch–poly(I) copolymers showed activity; however, as might be expected, effectiveness as a flocculant depended on the per cent poly(I) incorporated in the graft copolymer. At higher flocculant concentrations, graft copolymers with 12.1 and 15.2% poly(I) approached the flocculating ability of the commercial product; however, the copolymer with 4.5% poly(I) was not so effective.
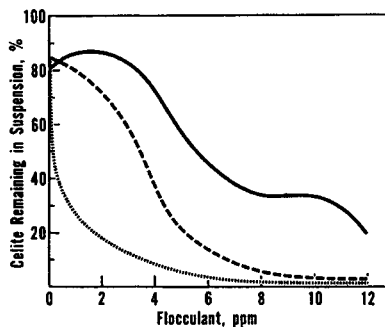
Fig. 3. Flocculation of Celite. Influence of pH. Flocculant was starch–poly(I) copolymer containing 12.1% poly(I). Celite concentration, stirring speeds, and settling times were the same as for Figure 1, pH adjusted with $1M$ HCl or $1M$ NaOH. Ionic strengths kept constant with the addition of $1M$ NaCl: (———) pH 10.5; (- - -) pH 6; (. . .) pH 3.
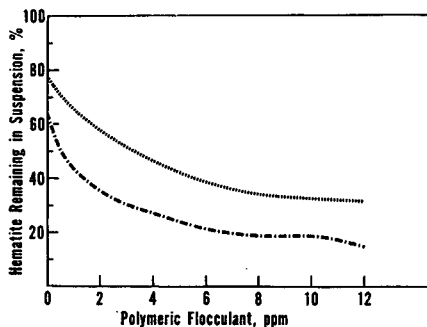

Fig. 4. Flocculation of hematite. Comparison of flocculants. Initial hematite concentration: 33.3 g/l.; pH 7.5. In the absence of alum, stirring speeds were the same as for Figure 1. For runs made with alum, the suspension was stirred at 100 rpm, the alum solution added, stirring continued for 2 min, the flocculant added, and the mixture stirred for 1 min. Stirring was continued at 50 and 20 rpm for 5 and 60 min, respectively. Settling times were 30 min: (. . .) starch–poly(I) graft copolymer with 15.2% grafted poly(I); (–·–) starch–poly(I) graft copolymer with 15.2% grafted poly(I) plus 5 ppm alum.

Since starch–poly(I) copolymers showed activity as flocculants, it was necessary to determine whether the starch part of the graft copolymer was merely acting as a diluent for poly(I) or whether chemical attachment of poly(I) branches to the starch backbone was really an important factor in flocculating ability. The graft copolymer containing 15.2% poly(I) was therefore refluxed with $0.5N$ hydrochloric acid, the liberated poly(I) graft chains were separated from starch hydrolyzate, and a physical mixture was prepared from ungrafted starch and the poly(I) graft chains (now containing only endgroups of carbohydrate). Flocculation of Celite suspensions (Fig. 2) showed that the physical mixture had activity but was inferior to the graft copolymer.

We next examined the influence of some variables in the testing procedure on the flocculation of Celite with the graft copolymer containing 12.1% poly(I). Changes in stirring times at 100, 50, and 20 rpm did not greatly influence results. The length of time at 100°C used in the preparation of flocculant dispersions was also examined, but differences between solutions heated for 30 and 90 min were negligible. Flocculation was more efficient at a low pH (Fig. 3).

The starch–poly(I) graft copolymer containing 15.2% poly(I) was next tested as a flocculating agent for nonmagnetic iron ore (hematite), both with and without alum (Fig. 4). Flocculating ability was comparable to that of the commercial polyacrylamide. To determine whether iron ore components are selectively flocculated by the starch–poly(I) copolymer, solids which remained in suspension after flocculation in the absence of alum were analyzed for iron. With 0, 8, and 12 ppm flocculant, the per cent iron in the suspended solid was 57.2, 57.4, and 56.8, respectively. The flocculation, therefore, shows little selectivity.

In conclusion, copolymers of starch and poly(I) have been prepared, characterized, and shown in laboratory flocculation tests to compare favorably with a commercial high molecular weight cationic polyacrylamide. Because of the encouraging results with I, we intend to study the graft polymerization of additional cationic monomers (and combinations of monomers) to starch.

References

1. Anon., *Chem. Eng. News*, **46**(3), 46 (1968).
2. A. M. Mark, W. B. Roth, C. L. Mehltretter, and C. E. Rist, *Cereal Chem.*, **41**, 197 (1964).
3. A. P. Black, A. M. Buswell, F. A. Eidsness, and A. L. Black, *J. Amer. Water Works Ass.*, **49**, 1414 (1957).
4. R. F. Packham, *Water Wastes Eng.* No. **46**, 105 (1962).
5. J. M. Cohen, *J. Amer. Water Works Ass.*, **49**, 1425 (1957).
6. C. E. Brockway and K. B. Moser, *J. Polym. Sci. A*, **1**, 1025 (1963).