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Graft Copolymers of Starch with Mineral Acid Salts of Dimethylaminoethyl Methacrylate. Preparation and Testing as Flocculating Agents*

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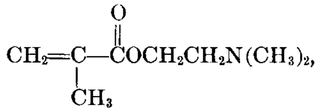
Synopsis

Mineral acid salts of dimethylaminoethyl methacrylate (DMAEMA) have been graft polymerized onto starch with ferrous ammonium sulfate–hydrogen peroxide initiation. The nitric acid salt was used in most reactions, and graft polymerizations were run in both water and aqueous–organic solvent systems. Increased monomer concentration in water led to an increase in both the percentage of poly(DMAEMA·HNO_3) in the graft copolymer (percent add-on) and the molecular weight of grafted branches. Variations in initiator concentration altered the percent add-on only slightly but affected the molecular weight of grafted polymer significantly. When swollen starch, in contrast with unswollen starch was used in graft polymerization reactions run in water, the product had a higher per cent add-on and a larger number of grafted branches of lower molecular weight. The efficiency of starch–poly(DMAEMA·HNO_3) graft copolymers as flocculants for diatomaceous silica increased with per cent add-on; however, variations in grafting frequency and graft molecular weight had less effect on the behavior of these materials as flocculants.

INTRODUCTION

In a previous publication,[1] we described graft polymerization of 2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride onto starch and tests of the resulting cationic graft copolymers as flocculants. As a continuation of our study of cationic starch graft copolymers, we now describe graft polymerization of mineral acid salts of dimethylaminoethyl methacrylate (DMAEMA),



$$CH_2{=}\underset{\displaystyle CH_3}{C}{-}\overset{\displaystyle O}{\overset{\|}{C}}OCH_2CH_2N(CH_3)_2,$$

and, in particular, the influence of selected reaction variables on structure of the starch graft copolymer; i.e., percentage of synthetic polymer incorpo-

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rated in the graft copolymer (per cent add-on), molecular weight of grafted branches, and grafting frequency. A number of these starch graft copolymers were tested as flocculants for diatomaceous silica (Celite) to determine how graft copolymer structure influences flocculating ability. Except for two reactions, graft polymerizations were carried out with whole wheat starch.

EXPERIMENTAL

Materials

Unmodified wheat starch was Huron Starbake from Hercules, Inc. Amylon 7, high-amylose corn starch, and Amioca, waxy maize starch, were obtained from National Starch and Chemical Corp.

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

DMAEMA was purchased from Rohm & Haas and contained 2000 ppm hydroquinone methyl ether as inhibitor. This monomer was used without removal of inhibitor.

Graft Polymerization

For a typical graft polymerization run in water, 100 g (0.636 mole) DMAEMA and 50 ml water were mixed and acidified to pH 2 with 6*N* nitric acid (106 ml acid was required). A slurry of 118 g starch (100 g dry basis, 0.618 mole anhydroglucose unit, AGU) in 350 ml water was prepared, the reaction vessel was flushed with nitrogen, and a solution of 0.24 g (6.12×10^{-4} mole) ferrous ammonium sulfate hexahydrate in 5 ml water was added. After this mixture was stirred for 5 min, the acidified monomer solution was added, followed after 5 additional min of stirring with 0.70 g 30% hydrogen peroxide (6.18×10^{-3} mole) in about 2 ml water. The mixture was stirred for 2 hr at 25°–27°C, and the reaction was terminated by the addition of hydroquinone. The swollen solid was separated by centrifugation and washed four times with cold water by slurrying and centrifuging. The product was finally washed with acetone, collected on a filter, and dried. The combined water extract was dialyzed against water to remove any unreacted monomer, and the ungrafted poly(DMAEMA·HNO_3) was isolated by freeze drying.

In a typical graft polymerization employing water–organic solvent mixtures, a solution of 1.176 g (3×10^{-3} mole) ferrous ammonium sulfate hexahydrate in 15 ml water was intimately mixed with 56.2 g starch (48.6 g dry basis, 0.3 mole AGU), the solid was suspended in 75 ml acetonitrile, and the reaction vessel was flushed with nitrogen. A mixture of 94.2 g (0.6 mole) DMAEMA in 75 ml water was acidified to pH 2 with 6*N* nitric acid (100 ml acid was required), and 3.39 g 30% hydrogen peroxide (3×10^{-2} mole) was added to the acidified monomer solution. The solution of monomer and peroxide was then added to the acetonitrile suspension, and this mixture was stirred for 2 hr at 25°–27°C. The reaction was terminated by addition of hydroquinone, and the products were isolated as in the previous example.

Isolation of Grafted Branches and Determination of Molecular Weight

A suspension of 15 g graft copolymer in 750 ml 0.5*N* hydrochloric acid was heated under reflux for 30 min and cooled to room temperature. The pH was adjusted to 3 with sodium hydroxide solution, and the mixture was dialyzed against distilled water. The dialyzed solution was reduced in volume to about 500 ml, and enough concentrated hydrochloric acid was added to give a normality of 0.5. The mixture was again refluxed for 30 min, the pH adjusted to 3, and the solution dialyzed. The grafted branches, isolated from the dialyzed solution by freeze drying, usuall contained less than 5% carbohydrate, as estimated by comparison of the infrared spectrum with those of known mixtures of starch and synthetic polymer. Per cent add-on was calculated from weight loss on acid hydrolysis, assuming that after treatment with hydrochloric acid the grafted polymer was present as the hydrochloride salt rather than as the salt of the acid used initially for acidification of DMAEMA. These values generally agreed with those calculated from the gain in weight of starch due to graft polymerization.

Number-average molecular weights of grafted synthetic polymer were determined in 0.15*M* sodium chloride on a Melabs Model CSM-2 membrane osmometer equipped with B-19 membranes. Although molecular weights were run on hydrochloride salts, values were expressed in terms of the salt of the acid initially used for acidification of DMAEMA.

Proof of Grafting by Fractional Precipitation

A mixture of 0.111 g poly(DMAEMA·HNO_3), prepared in the absence of carbohydrate, and 0.960 g starch (treated with ferrous ammonium sulfate and hydrogen peroxide under conditions used for graft polymerization but in the absence of monomer[2]) was shaken overnight in a 100-ml volumetric flask with 90:10 (by volume) dimethyl sulfoxide (DMSO)–water. The Brookfield viscosity (12 rpm) of the resulting 1% dispersion at 25°C was 47 cp. A 50-ml portion of this dispersion was mixed with 50 ml water. Dropwise addition of 100 ml absolute ethanol to this 0.5% dispersion precipitated 0.458 g starch(95.5% recovery), the infrared spectrum of which showed little or no poly(DMAEMA·HNO_3). The supernatant contained 0.057 g polymer, which was largely poly(DMAEMA·HNO_3).

A 1.053-g sample of graft copolymer, prepared from wheat starch and containing 12.2% poly(DMAEMA·HNO_3) of molecular weight 521,000, was weighed into a 100-ml volumetric flask and dispersed in 90:10 DMSO–water. The Brookfield viscosity (12 rpm) of the 1% dispersion at 25°C was 1220 cp. A 50-ml portion of this dispersion was mixed with 50 ml water. Dropwise addition of 300 ml absolute ethanol to this 0.5% dispersion precipitated only 69% of the polymer, and infrared analysis showed that both precipitated and soluble fractions contained poly(DMAEMA·HNO_3).

Flocculation Studies

A 5-g sample of graft copolymer was suspended in 200 ml water at room temperature and the pH (3.5–4.0) was adjusted to 6.0 with sodium hydroxide solution. After the mixture was centrifuged and the supernatant decanted, the solid was suspended in acetone, collected on a filter, and allowed to air dry at room temperature. A 1-g portion (dry basis) of this solid (accurately weighed) was suspended in 100 ml DMSO, and the mixture was stirred for 2 hr at 100°C. The solution was then cooled and added to 200 ml water. This mixture was exhaustively dialyzed against distilled water, and the dialyzed solution was diluted to a final concentration of 0.2 g/l. after adjusting the pH to 4.0 with nitric acid.

Graft copolymers were tested as flocculants for Celite (a diatomaceous silica having an average particle size of 2.1 μ) in a manner identical to that described previously.[1] The pH of Celite suspensions was 6.6–6.9 for all tests.

RESULTS AND DISCUSSION

Preparation and Properties of Graft Copolymers

Graft polymerizations of DMAEMA·HX (mineral acid salts of DMAEMA) onto starch were initiated with the ferrous ammonium sulfate–hydrogen peroxide system. A number of attempts were made to initiate graft polymerization with ceric ammonium nitrate, but these were unsuccessful.

Although poly(DMAEMA) is a water-soluble polymer when it is in the form of a mineral acid salt, starch graft copolymers are insoluble in cold water and still exist as granules which resemble ungrafted starch when viewed under a light microscope. The graft copolymer can be freed of both unreacted monomer and ungrafted poly(DMAEMA·HX) by water washing, and ungrafted synthetic polymer is readily isolated from water extracts by freeze drying, after removal of unreacted monomer by dialysis. Starch graft copolymers form smooth pastes in hot water.

The weight per cent grafted poly(DMAEMA·HX) in the copolymer was calculated from weight loss on treatment of the graft copolymer with refluxing 0.5N hydrochloric acid. The starch moiety is depolymerized under these conditions to glucose and other small carbohydrate fragments, which can be separated from grafted branches by dialysis. A grafted synthetic polymer so isolated generally contains less than 5% residual carbohydrate, remaining as endgroups. Refluxing hydrochloric acid does not saponify ester linkages in poly(DMAEMA·HX), in agreement with the inertness of poly(methyl methacrylate)[3] and poly(2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride)[1] to mineral acid. Moreover, since the intrinsic viscosity of poly(2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride) was not affected by refluxing hydrochloric acid,[1] presumably the molecular weight of structurally similar poly(DMAEMA·HX) would also be unchanged by these reaction conditions.

Number-average molecular weights of grafted branches were determined by membrane osmometry. Grafting frequencies, expressed as the average number of AGU per grafted polymer chain, were calculated from the molecular weight of grafted poly(DMAEMA·HX) and the per cent add-on.

Chemical attachment of poly(DMAEMA·HX) to starch, as opposed to an intimate physical mixture of polymers, was demonstrated by fractional precipitation with ethanol from a 0.5% polymer dispersion in DMSO–water. Whereas starch could be precipitated in this manner from a synthetic mixture of starch and poly(DMAEMA·HNO_3) no separation was achieved with a graft polymerization product containing 12.2% poly-(DMAEMA·HNO_3) of molecular weight 521,000.

The influence on graft polymerization of the mineral acid selected to prepare the salt of DMAEMA is shown in the first three reactions of Table I. The nitric acid salt gave a higher conversion to grafted polymer and produced a graft copolymer with a higher synthetic polymer content than did either the hydrochloric or sulfuric acid salts. With sulfuric acid, grafted branches were significantly higher in molecular weight and the starch was infrequently grafted. The nitric acid salt was used for the remainder of this study.

TABLE I
Influence of Mineral Acid Salt and Oxygen Removal on Graft Polymerization onto Wheat Starch[a]

		Graft copolymer			Conversion of monomer, %	
Acid salt	O_2 removed	Poly (DMAEMA·HX) content,[b] %	$\bar{M}_n$ of graft[b]	AGU/branch	To grafted polymer	To ungrafted polymer
HCl	no	9.1	158,000	9,730	8	75
H_2SO_4	no	7.9	665,000	47,800	5	55
HNO_3	no	20.2	239,000	5,830	18	57
HNO_3	yes[c]	16.6	191,000	5,920	14	52
HNO_3	yes[d]	16.9	230,000	6,970	15	57

[a] Polymerization recipe: 118 g unswollen wheat starch (100 g dry basis, 0.618 mole AGU); 100 g (0.636 mole) dimethylaminoethyl methacrylate (DMAEMA); 0.24 g (6.12×10^{-4} mole) $Fe(NH_4)_2(SO_4)_2\cdot6H_2O$; 0.70 g 30% H_2O_2 (6.18×10^{-3} mole); 515 ml water. DMAEMA·HX, mineral acid salt of DMAEMA; AGU, anhydroglucose unit.

[b] Based on the mineral acid used for acidification of monomer.

[c] The water used to prepare the starch slurry was boiled and cooled under nitrogen.

[d] Monomer solution and starch slurry were purged with nitrogen.

Reactions were also run to determine the influence of oxygen removal on the graft polymerization reaction (Table I). In the third reaction, the free space in the flask above the reaction mixture was flushed with nitrogen; however, dissolved oxygen was not removed. In the fourth reaction, the water used to prepare the starch slurry was heated to boiling and cooled

TABLE II

Influence of Monomer and Initiator Concentration on Graft Polymerization onto Wheat Starch[a]

Starting materials			Graft copolymer			Conversion of monomer, %	
DMAEMA, g	$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, g	30% H_2O_2, g	Poly-(DMAEMA · HNO_3) content, %	$\bar{M}_n$ of graft[b]	AGU/branch	To grafted polymer	To ungrafted polymer
Monomer Concentration							
50 (0.318 mole)	0.24 (6.12×10^{-4} mole)	0.70 (6.18×10^{-3} mole)	7.8	154,000	11,200	12	26
100	0.24	0.70	20.2	239,000	5,830	18	57
200	0.24	0.70	25.7	715,000	12,700	12	51
Initiator Concentration							
100	0.12	0.35	17.4	715,000	21,000	15	57
100	0.24	0.70	20.2	239,000	5,830	18	57
100	0.48	1.40	20.2	382,000	9,300	18	54

[a] All reactions used 118 g unswollen wheat starch (100 g dry basis, 0.618 mole AGU) and 515 ml water. Starch slurries and monomer solutions were not purged with nitrogen.

[b] Calculated as the nitric acid salt.

under nitrogen. In the fifth run, both the starch slurry and the acidified monomer solution were purged with nitrogen for 1 hr before reaction. These procedural changes caused only small variations in the composition of the graft copolymer and in the percentage of conversion of monomer to grafted and ungrafted polymer. Rigorous removal of dissolved oxygen is therefore not important in these reactions.

Increasing monomer concentration increased both the percentage of poly(DMAEMA·HNO_3) in the graft copolymer and the molecular weight of grafted branches (Table II). Grafting frequency, however, showed no easily interpreted trend. The most frequent grafting was observed with 100 g each of starch and monomer, and both an increase and a decrease in the amount of monomer resulted in a less frequently grafted copolymer. There was a lower conversion of monomer to ungrafted polymer at the lowest monomer concentration.

Variations in initiator concentration (Table II) altered only slightly the percentage poly(DMAEMA·HNO_3) in the graft copolymer and the percentage conversion to grafted and ungrafted polymer, although significant changes in molecular weights of grafted branches and in grafting frequencies were observed. The highest molecular weight for grafted poly(DMAEMA) and the lowest number of grafted branches were found at the lowest initiator concentration.

When the aqueous starch slurry was stirred for 1 hr at 60°C before reaction at room temperature with monomer and initiator, a more frequently grafted copolymer with lower molecular weight grafted branches was obtained, and the poly(DMAEMA·HNO_3) content of the graft copolymer was higher than when starch was slurried at 25°C before polymerization (Table III). Moreover, the grafting reaction was more efficient with swollen starch; that is, a higher percentage of the synthetic polymer formed in the reaction was grafted to starch. The depencence of both molecular weight of grafted branches and grafting frequency on starch granule swelling when DMAEMA·HNO_3 was used as the monomer sharply contrasts with previous observations with acrylonitrile.[4,5] Polyacrylonitrile branches were higher in molecular weight, and the copolymer was less frequently grafted when the starch granule was swollen at 60°C than when starch was grafted without swelling. Experiments are in progress to determine if these differences stem from the ionic nature of DMAEMA·HNO_3 or arise because poly(DMAEMA·HNO_3) is a water-soluble polymer whereas polyacrylonitrile is not.

Graft copolymers with higher percentages of grafted poly(DMAEMA·HNO_3) were produced with an alternate method of polymerization, based on acetonitrile–water as solvent and a higher ratio of initiator to starch than used in previous reactions. Starch was first intimately mixed with ferrous ammonium sulfate hexahydrate which had been dissolved in a minimum amount of water. The treated starch, which still retained its dry appearance, was next suspended in acetonitrile, and graft polymerization was initiated by addition of a combined water solution of DMAEMA·HNO_3 and

TABLE III
Influence of Starch Granule Swelling on Graft Polymerization onto Wheat Starch

Starting materials							Graft copolymer			Conversion of monomer, %	
Wheat starch,[a] g	Pre-treatment temp.,[b] °C	DMAEMA, g	$Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$, g	30% H_2O_2, g	Water, ml	N_2 purge[c]	Poly (DMAEMA · HNO_3) content	$\bar{M}_n$ of graft[d]	AGU/ branch	To grafted polymer	To un-grafted polymer
100 (0.618 mole AGU)	25	100 (0.636 mole)	0.24 (6.12× 10^{-4} mole)	0.70 (6.18× 10^{-3} (mole)	515	no	20.2	239,000	5,830	18	57
100	60	100	0.24	0.70	515	yes	28.0	67,300	1,070	27	40
50	25	50	0.12	0.35	435	yes	13.8	636,000	24,500	12	52
50	60	50	0.12	0.35	435	yes	20.7	63,600	1,500	18	45
50	60	100	0.24	0.70	460	no	31.7	95,500	1,270	16	53

[a] Figures are given on a dry basis. The starch contained 15% moisture.

[b] Starch–water slurries stirred for 1 hr at this temperature.

[c] Yes, starch slurry and monomer solution were purged with nitrogen; no, apparatus only was flushed with nitrogen and dissolved oxygen was not removed.

[d] Calculated as the nitric acid salt.

hydrogen peroxide. Acetonitrile was chosen since it is miscible with water but will not dissolve ferrous ammonium sulfate. A high concentration of ferrous salt is thus maintained within the starch matrix until such time as the water solution of monomer and peroxide is added. Moreover, a previous study of the starch–polyacrylonitrile system suggested that acetonitrile would not act as a chain transfer agent during polymerization to lower the molecular weight of grafted branches.[6]

A series of graft copolymers prepared by this technique is presented in Table IV. In addition to wheat starch, reactions are also shown for a high amylose corn starch (which is composed largely of the linear amylose starch fraction) and for waxy maize starch (which consists almost entirely of the branched amylopectin starch fraction). The three varieties of starch produced graft copolymers with different compositions. Although the poly(DMAEMA·HNO_3) content was not greatly different for waxy maize and wheat starch, the molecular weight for grafted polymer was greater by about a factor of 2 when wheat starch was used. High-amylose corn starch produced a graft copolymer with an appreciably higher per cent add-on, and the molecular weight of grafted branches was about midway between the values found for the other two starch varieties. Substitution of methanol for acetonitrile in the polymerization with wheat starch did not change the molecular weight of grafted poly(DMAEMA·HNO_3) but gave a lower percent add-on.

TABLE IV

Graft Polymerizations in Water–Organic Solvent Systems[a]

	Graft copolymer				Conversion of monomer, %	
Starch variety	Organic solvent	Poly (DMAEMA·HNO_3) content, %	$\bar{M}_n$ of graft[b]	AGU/ branch	To grafted polymer	To ungrafted polymer
Wheat	CH_3CN	33.1	150,000	1,870	19	63
High-amylose corn	CH_3CN	53.0	119,000	652	34	51
Waxy maize	CH_3CN	37.7	72,400	738	23	50
Wheat	CH_3OH	21.4	146,000	3,310	10	68

[a] Polymerization recipe for the first three reactions: 56.2 g unswollen starch (48.6 dry basis, 0.3 mole AGU), 94.2 g (0.6 mole) DMAEMA, 1.176 g (3×10^{-3} mole) ferrous ammonium sulfate hexahydrate, 3.39 g 30% hydrogen peroxide (3×10^{-2} mole), 75 ml organic solvent, and 190 ml water. The fourth reaction used the same proportions of reactants but was a twofold scale-up. Starch slurries and monomer solutions were not purged with nitrogen.

[b] Calculated as the nitric acid salt.

Graft Copolymers as Flocculants

It was expected that flocculating ability would depend on the percentage of poly(DMAEMA·HNO_3) in the graft copolymer, since a similar dependence was found for starch–poly(2-hydroxy-3-methacryloyloxypropyltrimethylammonium chloride) graft copolymers.[1] In addition to confirming these earlier results, we wished to determine whether variations in the structure of graft copolymers caused by different synthesis procedures would influence the function of these graft copolymers as flocculants. Testing of graft copolymers as flocculants was carried out with 3% aqueous suspensions of Celite, and flocculants were evaluated at different concentrations by determining the percentage of Celite remaining in suspension after 30 min of settling.

To dissolve graft copolymers in water for flocculation tests, the copolymers were first slurried in water, the pH was adjusted to 6.0, and the products were isolated and dried. Dry products were then dissolved in DMSO at 100°C, water was added, and the DMSO was finally removed by dialysis. This procedure gave clear solutions in water and was expected to minimize polymer degradation, based on previous work by Mark et al.[7] with ungrafted starch. When graft copolymers were merely heated in water at pH 6.0, significant amounts of highly swollen but still insoluble product remained, whereas at the natural pH of 3.5–4.0, degradation of the starch moiety was extensive. Steam jet cooking[8] was also investigated; however, this method of solution preparation reduced molecular weights in both the starch portion of the graft copolymer and the grafted branches. The higher molecular weight poly(DMAEMA·HNO_3) branches were most susceptible to degradation. Indeed, even the DMSO procedure reduced the molecular weight of grafted poly(DMAEMA·HNO_3) of $\bar{M}_n$ 715,000, whereas no degradation was observed when the $\bar{M}_n$ of grafts was 230,000.

The molecular sizes of starch moieties in a number of graft copolymers were estimated from intrinsic viscosity measurements on wheat starch sam-

TABLE V

Flocculation of Celite. Reproducibility. Influence of pH Adjustment Before Preparing Water Solution of Graft Copolymer

pH adjusted to 6.0 before preparation of solution	[η] of corresponding starch[a]	Per cent Celite remaining[b] at different concentrations of graft copolymer[c]			
		0 ppm[d]	4 ppm	8 ppm	12 ppm
Yes	0.74	91.1	71.5	51.1	35.3
		90.4	74.1	49.6	35.5
		90.5	75.3	52.0	36.8
		90.9	75.9	52.0	38.3
No		89.8	82.0	58.0	43.0

[a] Treated with Fe^{+2}–H_2O_2. Dissolved according to dimethyl sulfoxide (DMSO) procedure and isolated by freeze drying; [η] in 90:10 DMSO–Water expressed in dl/g; [η] of granular unmodified wheat starch, 1.38.

[b] Per cent remaining in suspension after a settling time of 30 min.

[c] Graft copolymer prepared from wheat starch. Poly(DMAEMA·HNO_3) content, 20.2%; $\bar{M}_n$ of graft, 239,000; grafting frequency, 5,830 AGU/branch.

[d] Parts per million is based on total volume of Celite slurry.

ples that had been treated in the absence of monomer with ferrous ammonium sulfate and hydrogen peroxide under the same conditions used for graft polymerizations. Treated starch samples dissolved by the DMSO procedure were isolated from water solutions by freeze drying, and the intrinsic viscosities were run in 90:10 DMSO–water.

Reproducibility in flocculation tests was determined by dissolving four separate samples of the same graft copolymer and testing each sample as a flocculant for Celite (first four runs of Table V). In the last run in this table, the graft copolymer was dissolved at its natural pH so that the more acidic conditions might reduce the molecular weight of the starch backbone with respect to the first four runs. Test results suggest that flocculation efficiency is lowered somewhat as the molecular weight of the starch backbone is reduced.

Table VI contains the results of flocculation tests run with graft copolymers selected from those described in Tables I–III. Since preparation of water solutions of copolymers with grafted branches of $\bar{M}_n$ 715,000 lowered graft molecular weight, data on these products have not been included. When graft copolymers are arranged on the basis of increasing poly(DMAEMA·HNO_3) content, it is apparent that flocculation efficiency increases as the cationic polymer content of the graft copolymer is increased. Differences are greatest between the copolymers with 7.8% and 16.9% add-on. An increase in add-on from 16.9% to 31.7% does not improve flocculating ability greatly.

The influence of graft molecular weight and grafting frequency on the ability of these copolymers to function as flocculants may be measured by comparing runs 3 and 4 of Table VI. Both graft copolymers have about the same percent add-on, and the intrinsic viscosities of the initiator-treated starches do not differ greatly. The graft copolymer with longer and less frequently grafted branches is the better flocculant; however, differences are minor in view of the fourfold difference in both $\bar{M}_n$ of grafted branches and grafting frequency.

Since the reaction conditions used to prepare graft copolymers in water–organic solvent systems (Table IV) were so widely different from those used in the first three tables, the flocculation tests are presented separately in Table VII. The graft copolymer from wheat starch with 33.1% add-on was a better flocculant than the product with only 21.4% add-on; however, no further improvement in flocculating ability was observed with the graft copolymer from high-amylose corn starch, even though the per cent add-on was 53%. Since the graft copolymer from waxy maize starch was the only one examined that was not completely solubilized by the DMSO procedure, the flocculation results should not be directly compared with flocculation data obtained with other products.

The graft copolymer with 21.4% add-on gave about the same flocculation results as the product in run 4 of Table VI where the poly(DMAEMA·HNO_3) content was 20.7%. The graft copolymer with 33.1% add-on, however, was a somewhat better flocculant than the copolymer in Table VI

TABLE VI

Influence of Graft Copolymer Composition on Flocculation of Celite

Graft copolymer[a]			$[\eta]$ of corresponding starch[b]	Per cent Celite remaining at different concentrations of graft copolymer			
Poly(DMAEMA·HNO_3) content, %	$\bar{M}_n$ of graft	AGU/branch		0 ppm	4 ppm	8 ppm	12 ppm
7.8	154,000	11,200	0.74	89.4	87.5	84.2	75.5
16.9	230,000	6,970	0.74	90.6	78.8	55.7	40.5
20.2	239,000	5,830	0.74	90.7[c]	74.2[c]	51.2[c]	36.5[c]
20.7	63,600	1,500	0.64	90.7	83.0	59.3	42.3
28.0	67,300	1,070	...	90.3	71.3	49.9	33.0
31.7	95,500	1,270	0.45	90.4	71.4	46.6	30.9

[a] Graft copolymer prepared from wheat starch

[b] Treated with Fe^{2+}–H_2O_2. Dissolved according to DMSO procedure and isolated by freeze drying; $[\eta]$ in 90:10 DMSO–water expressed in dl/g; $[\eta]$ of granular unmodified wheat starch, 1.38

[c] Average of the four runs in Table V.

TABLE VII
Flocculation of Celite with Graft Copolymers Prepared in Water–Organic Solvent Systems

Graft copolymer[a]			Per cente Celite remaining at different concentrations of graft copolymer			
Starch variety	Poly-(DMAEMA·HNO_3) content, %	[η] of corresponding starch[b]	0 ppm	4 ppm	8 ppm	12 ppm
Wheat	21.4	...	89.9	83.9	58.3	42.4
Wheat	33.1	0.24	90.1	63.4	39.2	25.3
Waxy maize[c]	37.7	...	90.9	76.5	47.3	32.6
High-amylose corn	53.0	...	90.3	61.3	37.7	24.3

[a] $\bar{M}_n$ of grafts and grafting frequencies given in Table IV.

[b] Treated with Fe^{2+}–H_2O_2. Dissolved according to DMSO procedure and isolated by freeze drying; [η] in 90:10 DMSO–water expressed in dl/g; [η] of granular unmodified wheat starch, 1.38.

[c] This graft copolymer was not fully dissolved.

with 31.7% add-on (run 6). Since the intrinsic viscosity of initiator-treated starch in Table VII was lower than any values in Table VI, apparently reaction conditions used with the higher initiator concentrations and water-organic solvent systems led to more extensive degradation of the starch backbone.

Although our data indicate that the ability of a starch–poly(DMAEMA·HNO_3) graft copolymer with a given add-on to flocculate Celite does not greatly depend on the molecular weight and frequency of grafted branches, it must be emphasized that these conclusions apply only to the ferrous–peroxide initiating system and to the graft frequency and molecular weight ranges encompassed by data in the tables. Another initiating system, for example, gamma or electron beam irradiation, could lead either to a graft copolymer of different architecture or to a product containing a significant amount of block copolymer.[9–11] Regardless, the flocculating properties might be significantly altered. Also, if graft copolymers with extremely low molecular weight branches could be synthesized under our reaction conditions, or if those with high molecular weight branches could be solubilized without degradation, the behavior of these materials as flocculants might well differ from those reported.

The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

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