

Graft Copolymers of Starch and Mixtures of Acrylamide and Acrylic Acid

INTRODUCTION

A series of cationic starch graft copolymers was prepared earlier by the simultaneous cobalt 60 irradiation of starch, acrylamide, and *N,N,N*-trimethylaminoethyl methacrylate-methyl sulfate (TMAEMA-MS) in water.¹ In the present study, we used a similar technique to prepare anionic starch graft copolymers from mixtures of acrylamide and acrylic acid and then compared the two monomer systems. Starch-*g*-poly(acrylamide-co-acrylic acid) copolymers have potential use as flocculants and a structural similarity to saponified starch-*g*-polyacrylonitrile, which functions as both a thickener for aqueous systems² and as an absorbent for water.³

EXPERIMENTAL

Materials

Unmodified Globe corn starch was from CPC International and contained 10–14% H₂O. Acrylamide and acrylic acid were Eastman reagent grade and were used as received. Diazyme L-30 was from Miles Laboratories, Inc. Rexyn AG 50 resin was from Fisher Scientific Co.

Graft Polymerization

The cobalt 60 source was a Gammacell 200 unit from Atomic Energy of Canada, Ltd. The dose rate at the center of the chamber was 0.88–0.85 Mrad/hr, as calculated from the initial dosimetry provided by the manufacturer and the decay rate of cobalt 60.

In a typical semidry reaction with unswollen starch and a 20:80 mole ratio of acrylic acid:acrylamide, 5.70 g (0.08 mole) acrylamide and 1.44 g (0.02 mole) acrylic acid were dissolved in 10 ml water, and the solution was blended into 40.5 g (dry basis, 0.25 mole) Globe corn starch. The mixture, which retained an outwardly dry appearance, was transferred to a 4-oz screw-cap bottle, evacuated to 50 mm, and repressured with nitrogen (this procedure was repeated four times). The mixture was then irradiated with cobalt 60 to a total dose of 0.1 Mrad. After the reaction mixture had stood for 2 hr, it was extracted three times with water to remove homopolymer, which was then isolated by dialysis and freeze drying. Since drying the water-extracted solid produced a product from which it was difficult to remove the last traces of starch by hydrolysis (for the purpose of isolating grafted branches for analysis), it was left as a wet cake after the final extraction with water.

A typical reaction with a swollen starch paste and a monomer mixture containing 20 mole-% acrylic acid was run with 5.70 g (0.08 mole) acrylamide and 1.44 g (0.02 mole) acrylic acid dissolved in 40 ml water. This solution was added to 8.1 g (dry basis) Globe corn starch in a 2-oz screw-cap bottle, and the mixture was heated to 68°C in a steam bath to form a thick slurry which would not settle on standing. The bottle was capped, cooled in ice water for 20–30 min, irradiated to 0.1 Mrad, and allowed to stand for 2 hr. The rubbery reaction mass was broken up and extracted three times with water at about 10°C to remove homopolymer and unreacted monomers, and the combined extracts were centrifuged at 40,000×*g* for 70 min at 5°C in a Beckman Model L-4 ultracentrifuge to recover a small amount of graft copolymer carried over during extraction. The supernatant was dialyzed and freeze dried to recover solubles which contained some residual carbohydrate. The water-insoluble starch graft copolymer was left as a wet cake to facilitate hydrolytic removal of starch for analysis of grafted branches.

Hydrolysis of the Starch Moiety

The wet, water-extracted graft copolymer was dispersed in approximately 600 ml water and a portion removed to determine the % solids. If required, the pH of the remaining suspension was adjusted to 3.5–4.0, and the mixture was heated on a steam bath to 90°C and then cooled to 60°C. Diazyme L-30 enzyme (2 ml) was added, and the mixture was placed in a 60°C oven for 16–18 hr to complete hydrolysis. The mixture was then heated to 95°C to destroy the enzyme, cooled to room temperature, and dialyzed against distilled water. The dialyzed mixture was finally centrifuged to remove insolubles (containing both carbohydrate and synthetic polymer and amounting to less than 6% by weight of the graft copolymer hydrolyzed) and then freeze dried to obtain grafted synthetic polymer with less than 5% residual carbohydrate (by infrared). The weight per cent synthetic polymer in the graft copolymer (% add-on) was calculated from the weight loss on enzyme hydrolysis.

Acrylic Acid Content and Molecular Weight of Grafted Polymer

About 0.5–1.5 g grafted synthetic polymer (depending on acrylic acid content) was dissolved in 100 ml water and the solution passed through a column of Rexyn AG 50 (H⁺) ion exchange resin to convert all carboxyl groups to the acid form. The effluent was then freeze dried and an accurately weighed sample of the dry polymer dissolved in water and titrated potentiometrically with 0.1*N* sodium hydroxide.

The titrated solution was dialyzed and freeze dried. Number-average molecular weight of the freeze-dried solid was then determined in 0.15*M* sodium chloride solution on a Melabs Model CSM-2 membrane osmometer equipped with a B-19 membrane (Schleicher and Schuell Co.). When the molecular weight was too high to be determined accurately by membrane osmometry (>500,000), an intrinsic viscosity was obtained in 1*M* sodium nitrate at 30°C with Cannon-Fenske viscometers.

RESULTS AND DISCUSSION

Simultaneous cobalt 60 irradiations of starch with mixtures of acrylamide and acrylic acid were performed with either granular starch, as a semidry blend with monomers in a minimum volume of water, or with starch granules that had been swollen to a paste by heating to 68°C in a larger volume of monomer solution. Graft polymerizations with pasted starch used higher monomer to starch ratios. Polyacrylamide, poly(acrylic acid), and copolymers of the two are soluble in cold water, whereas graft copolymers are largely insoluble due to the granule structure of starch. Consequently, graft copolymers were freed of ungrafted synthetic polymer and unreacted monomer by extraction with cold water, and the extracted water solubles were isolated by dialysis and freeze drying of the water extract.

Graft copolymers were characterized with respect to percent add-on and either the intrinsic viscosity or number-average molecular weight of the grafted synthetic polymer which remained after removal of starch with enzyme. The mole-% acrylic acid incorporated in the grafted polymer was also determined by titration. In reactions with swollen starch, some graft copolymer was dissolved, along with homopolymer, during cold water extraction. This soluble fraction, rich in homopolymer, was also treated with enzyme to remove carbohydrate and then characterized.

Graft polymerizations with acrylamide–acrylic acid mixtures containing 5, 20, and 60 mole-% acrylic acid show higher % add-on values with pasted starch as compared with the semidry reaction conditions because of the higher monomer:starch ratio (Table I). Within each series, however, there were no large variations in % add-on with mole-% acrylic acid. Although mole percentages of acrylic acid in both grafted and water-extractable synthetic polymers approximated those in the initial monomer mixtures under both sets of reaction conditions, the intrinsic viscosities, and thus the molecular weights of grafted branches, were lower for graft copolymers prepared in the semidry state. In each three-reaction series, graft molecular weights did not vary greatly with acrylic acid content. With pasted starch, intrinsic viscosity values were almost identical; however, the molecular weights of the soluble synthetic polymers increased as the acrylic acid content of the reaction mixture was raised from 5 mole-% to 60 mole-%. Two reactions were also run with 20 mole-% acrylic acid in which the acrylic acid was neutralized with sodium hydroxide before polymerization. This procedure produced only small changes in graft copolymer composition.

We compared the anionic polyacrylamide starch graft copolymers of Table I with cationic graft

TABLE I
Starch-g-poly(acrylamide-co-acrylic acid) Graft Copolymers

Polymerization method ^a	Graft copolymer (water-insoluble)					Water-soluble polymer			
	Mole-% acrylic acid	% Total polymer	% Add-on ^b	Grafted branches		Weight % polymer carbohydrate	Mole-% acrylic acid	\bar{M}_n	$[\eta]^d$
				Mole-% acrylic acid	\bar{M}_n^c or $[\eta]^d$				
Unswollen starch (semidry blend)	5	98	14	5.2	168,000	—	—	—	—
	20	99	14	19.1	219,000	—	18	—	—
	60	99	14	54.4	157,000	—	—	—	—
	20 ^e	98	14	17.8	163,000	2	—	—	—
Swollen starch (pasted in monomer solution)	5	58	25	5.4	4.6	29	5.4	280,000	—
	20	69	23	21.6	4.5	15	21.2	>500,000	—
	60	77	29	53.8	4.6	14	58.2	>500,000	—
	20 ^e	66	26	16.5	3.3	29	17.3	252,000	—

^a Unswollen starch: 40.5 g (dry weight) corn starch, 0.1 mole total monomers, 10 ml H₂O, irradiated to 0.1 Mrad. Swollen starch: 8.1 g (dry weight) corn starch, 0.1 mole total monomers, 40 ml H₂O, irradiated to 0.1 Mrad.

^b Determined by weight loss on hydrolysis.

^c Determined by membrane osmometry.

^d dl/g at 30°C in 1N sodium nitrate.

^e Acid neutralized with an equivalent amount of 5N NaOH.

copolymers prepared earlier, under similar conditions, from mixtures of acrylamide with 5 mole-% TMAEMA-MS.¹ Although the cationic system also produced lower molecular weight grafted branches under semidry conditions, as compared with pasted starch, there was less cationic monomer incorporated into the grafted polymer than was initially present in the monomer mixture.

Since polymers of Table I are chemically similar to saponified starch-*g*-polyacrylonitrile, we examined the thickening and water-absorbent properties of a graft copolymer prepared from swollen starch and a monomer mixture containing 60 mole-% acrylic acid. In this experiment, soluble polymer was not removed; but the entire reaction mixture was blended with water, the mixture was dialyzed to remove unreacted monomer, and the pH of the resulting dispersion was adjusted to 6.8 with sodium hydroxide. The Brookfield viscosity of 1400 cp (12 rpm, 25°C) for a 2% dispersion was considerably less than that reported for dispersions of saponified starch-*g*-polyacrylonitrile.² Also, when the 2% dispersion at pH 6.8 was dried to a film and subsequently placed back in water and allowed to stand overnight, the opaque, water-swollen film readily broke up on gentle agitation instead of remaining as a continuous swollen sheet of clear gel, as was observed for saponified starch-*g*-polyacrylonitrile.⁴

Starch-*g*-poly(acrylamide-*co*-acrylic acid) copolymers function as flocculants in laboratory tests with tap water suspensions of diatomaceous silica and bentonite clay. To maximize water solubility, and thus flocculation efficiency, we used a starch of reduced molecular weight (e.g., an acid-modified starch or dextrin) in the preparation of these anionic starch graft copolymer flocculants. At a concentration of 6 mg/l., a dextrin-*g*-poly(acrylamide-*co*-acrylic acid) copolymer prepared (semidry blend) from a monomer mixture containing 20 mole-% acrylic acid reduced suspended silica (3% suspension) by 90% over that of the control. The corresponding product prepared by the pasted procedure was even more effective in reducing suspended silica. This same material, at a concentration of 1 mg/l., removed essentially all the bentonite clay from a 0.5% suspension as determined by % transmission values of the supernatant (99% versus 37% for the control).

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