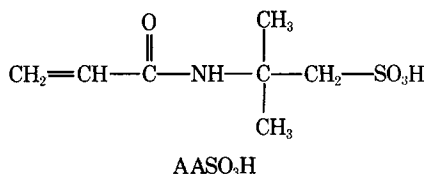


Graft Polymerization of Starch with Mixtures of Acrylonitrile and 2-Acrylamido-2-Methylpropanesulfonic Acid

INTRODUCTION

Acrylonitrile readily graft polymerizes onto starch in an aqueous system in the presence of ceric ammonium nitrate initiator.¹ When starch-*g*-polyacrylonitrile (PAN) copolymers are saponified and their suspensions are dried, the resulting polymers show remarkable absorbent properties for aqueous fluids.² In a recent study,³ we have found that highly absorbent graft copolymers containing starch and acrylonitrile can be prepared in which the nitrile substituents are left unsaponified, provided that a suitable comonomer such as 2-acrylamido-2-methylpropanesulfonic acid (AASO₃H) is polymerized along with the acrylonitrile:



The object of the present work is to study this system in detail by preparing a series of starch-*g*-poly(acrylonitrile-*co*-AASO₃H) copolymers with varying monomer ratios, measuring the water absorbency of each, and determining certain parameters such as weight percent of synthetic polymer in the graft copolymer and AASO₃H content of the grafted branches.

EXPERIMENTAL

Materials

Globe pearl corn starch (Globe 3005) was from CPC International. Acrylonitrile, Eastman practical grade, was distilled at atmospheric pressure through a 14-in Vigreux column, and a center cut was collected and stored at 5°C. Reaction-grade, special process AASO₃H was from the Lubrizol Corporation. Ceric ammonium nitrate was Fisher Certified ACS grade.

Graft Polymerization of Acrylonitrile and AASO₃H

A stirred slurry of 10.0 g, dry basis, of corn starch in 167 ml of water was heated for 30 min at 85–87°C while a slow stream of nitrogen was allowed to bubble through the mixture. The mixture was then cooled back to 25°C. Either 20.0 g of acrylonitrile or a mixture of acrylonitrile and AASO₃H (20.0 g total) was added to the starch dispersion, followed after 5 min by addition of a solution of 0.338 g (6.17 × 10⁻⁴ mol) of ceric ammonium nitrate in 3 ml of 1*N* nitric acid. The reaction mixture was allowed to stir under nitrogen for 2 hr with the temperature maintained between 25 and 28°C by means of an ice bath. The reaction mixture was then dispersed in acetone and centrifuged. The solid was washed with isopropanol to remove unreacted monomers, isolated by either filtration or centrifugation, and allowed to air dry. The weight percent of synthetic polymer in the starch-containing copolymer was calculated from the gain in weight due to polymerization.

Portions of the resulting starch-containing copolymers were subjected to repeated extractions at room temperature with dimethylformamide (DMF), which contained 0.25% lithium bromide to reduce swelling. Products were separated by centrifugation into DMF-insoluble and DMF-soluble fractions and were isolated by freeze drying after exhaustive dialysis against distilled water to remove DMF and lithium bromide.

Hydrolysis of the Starch Moiety

Removal of starch from the copolymers was effected by refluxing accurately weighed samples in 150 ml of 0.5*N* HCl for 1.5 hr followed by dialysis against distilled water. Synthetic polymer fractions were isolated by freeze drying, and their AASO₃H content was determined by sulfur analysis using the method of White.⁴

Measurement of Water Absorbency

Water absorbencies of copolymers (not extracted with DMF) were determined by allowing accurately weighed 2–15-mg samples (amount used depended on absorbency) to soak in 50 ml of deionized water for 30 min. The swollen polymer was then separated from unabsorbed water by screening through a tared 280-mesh sieve that was 4.8 cm in diameter. The polymer on the sieve was allowed to drain for 20 min, and the sieve was weighed to determine the weight of water-swollen polymer. Absorbency was calculated as grams of water per gram of polymer.

Intrinsic Viscosity

Intrinsic viscosities of synthetic polymer fractions were determined in DMF that contained 0.25% lithium bromide to suppress ionization of the AASO₃H repeating units. Viscosities were determined at 25°C using Cannon-Fenske viscometers. Control experiments showed that the conditions of acid hydrolysis used to isolate synthetic polymer fractions did not change the intrinsic viscosity of PAN or poly(AASO₃H).

RESULTS AND DISCUSSION

Mixtures of acrylonitrile and AASO₃H, containing 0–62.5% AASO₃H, were graft polymerized onto gelatinized corn starch in the presence of ceric ammonium nitrate to give products containing about 50–60% synthetic polymer (Table I). Increasing the percentage of AASO₃H in the monomer mixture to 75% drastically reduced the conversion to polymer and afforded a product containing only 6% synthetic polymer. As expected, water absorbencies of the products of Table I increased with increasing AASO₃H content of the monomer mixtures and had a value of 580 g/g when an AASO₃H:acrylonitrile monomer ratio of 62.5:37.5 was used.

Since PAN and poly(AASO₃H) are both soluble in DMF, we attempted to get some measure of the amounts of ungrafted homopolymer in the products of Table I by extracting them with DMF which contained 0.25% lithium bromide. In the absence of lithium bromide, the excessive swelling of the products precluded any separation of fractions. The amount of synthetic polymer in each fraction was then determined from the weight loss on removal of the starch moiety by acid hydrolysis. The synthetic polymers were isolated by dialysis and freeze drying, and the percent AASO₃H in each synthetic polymer fraction was determined from its sulfur analysis. A separate experiment confirmed that the sulfur content of poly(AASO₃H) was not changed by treatment with refluxing HCl.

In contrast to starch-*g*-PAN, major fractions of the AASO₃H-containing products were soluble in DMF/LiBr. Although these soluble fractions showed larger amounts of synthetic polymer than the respective insoluble fractions and obviously contained some ungrafted homopolymer, their significant carbohydrate content suggested that graft copolymer was also present. It is evident from Table I that the amount of AASO₃H incorporated in the synthetic polymer was, in all cases, less than that in the original monomer mixture and did not vary greatly between the DMF-soluble and -insoluble fractions.

To obtain some estimate of the molecular weights of synthetic polymer fractions, the intrinsic viscosities in DMF (containing 0.25% lithium bromide) were determined for those polymer fractions isolated from the runs that employed 25% and 62.5% AASO₃H in the reaction mixture (Table I). In the 25% run, the synthetic polymer isolated from the DMF-insoluble fraction was considerably higher in intrinsic viscosity than that from the DMF-soluble fraction. A similar comparison of intrinsic viscosity for the 62.5% run was not possible, however, due to the insolubility of the synthetic polymer isolated from the DMF-insoluble fraction.

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

TABLE I
Graft Polymerization of Acrylonitrile (AN) and 2-Acrylamido-2-Methylpropanesulfonic Acid (AASO₃H) Onto Gelatinized Corn Starch

Monomer composition of reaction mixture, (wt.%)	Unfractionated polymer		DMF ^a -soluble fraction			DMF ^a -insoluble fraction			[η] ^d of synthetic polymer
	Synthetic polymer, ^b wt %	Absorbency, g H ₂ O/g polymer	% of Total	Synthetic polymer, ^c wt %	AASO ₃ H in synthetic polymer, wt %	[η] ^d of synthetic polymer	Synthetic polymer ^c wt %	AASO ₃ H, in synthetic polymer, wt %	
—	100	2	7	79	—	—	60	—	—
25	75	6	52	53	16	—	52	12	10
37.5	62.5	26	36	75	19	—	43	16	—
50	50	190	15	71	28	—	40	32	—
62.5	37.5	580	47	53	44	3	42	45	(insoluble)
75	25	6	—	—	—	—	—	—	—

^a Dimethylformamide (containing 0.25% LiBr).

^b As determined by weight gain due to graft polymerization.

^c As determined by weight loss on hydrolysis with HCl.

^d Intrinsic viscosity (dl/g) at 25°C in DMF/LiBr.

References

1. G. F. Fanta, *Block and Graft Polymerization*, Vol. 1, R. J. Ceresa, Ed., Wiley, London, 1973, p. 5.
2. G. F. Fanta, M. O. Weaver, and W. M. Doane, *Chem. Technol.*, **4**, 675 (1974).
3. G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *Staerke*, **30**, 237 (1978).
4. D. C. White, *Mikrochim. Acta*, 807 (1962).

ROBERT C. BURR
GEORGE F. FANTA
WILLIAM M. DOANE

Northern Regional Research Center
Agricultural Research
Science and Education Administration
U.S. Department of Agriculture
Peoria, Illinois 61604

Received February 21, 1979