

Copolymers of Starch and Polyacrylonitrile: The Dilution Effect

GEORGE F. FANTA, ROBERT C. BURR, C. R. RUSSELL, and
C. E. RIST, *Northern Regional Research Laboratory, Northern
Utilization Research and Development Division, Agricultural Research
Service, U.S. Department of Agriculture, Peoria, Illinois 61604*

Synopsis

In the ceric ammonium nitrate-initiated graft polymerization of acrylonitrile (AN) with starch, grafting frequencies and molecular weights of grafted polyacrylonitrile changed from 600 anhydroglucose units (AGU)/graft and 120000 to 280 AGU/graft and 36000 when concentrations of starch and AN were varied from 0.27 and 1.20 to 0.023 and 0.235 moles/l. of water, respectively. The influence of variety of starch, size of the starch granules, and reaction time was studied, and possible reasons for the influence of reactant concentration on the composition of the copolymer are considered.

INTRODUCTION

Since the work of Mino and Kaizerman in 1958,¹ a considerable amount of research has been published on the subject of starch graft copolymers, and a number of monomers and initiating systems have been investigated.²⁻⁶ Our research is concerned specifically with the ceric ammonium nitrate-initiated grafting of acrylonitrile (AN) and is directed toward an understanding of the influence of reaction conditions on both the molecular weight of grafted chains and the grafting frequency, expressed as the average number of anhydroglucose units separating two given grafts (AGU/graft). Previous work from this laboratory has shown that these structural parameters may be varied by the use of chain modifiers,⁷ by changes in the degree of swelling of the starch granule,⁸ and by the use of an aqueous organic reaction medium rather than water.⁹

We have now found that the frequency and molecular weight of grafted chains is also dependent upon reactant concentration, more polyacrylonitrile (PAN) chains of lower molecular weight being grafted to granular starch at higher dilution in water. In this report, a study of the reaction at high dilution is presented, and possible causes for its difference from reactions at higher concentrations are discussed. Starches of varying amylose content and of varying granule size were examined, and the question whether the granules of starch are surface-grafted with PAN or are also grafted internally is considered.

EXPERIMENTAL

Materials

The wheat starch was Supergel from Industrial Grain Products, Ltd. Waxy maize (a variety of corn starch composed of the branched amylopectin fraction) and Amylon 7 (a variety of corn starch containing about 70% of the linear amylose fraction) were from National Starch and Chemical Corp. Rice starch was from Stein-Hall and Co.

AN (Eastman Kodak, practical grade) was fractionated at atmospheric pressure through a 15 in. Vigreux column. A center cut was collected and stored in amber glass at 5°C.

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

Classification of Wheat Starch

Air classification was carried out in a Pillsbury air classifier, Lab. Model No. 1, at a feed rate of 25 lb/hr. Fraction 1, which contained granules having the smallest diameter, was used without further treatment. The fraction containing the large diameter granules was further fractionated by slurring in water, allowing the suspension to partially settle, and removing the supernatant. This procedure was repeated a total of eight times and effectively removed small diameter granules. The final product (fraction 4) was allowed to air-dry at room temperature to a water content of 12.1%.

Determination of Granule Diameter

The average diameters of starch granules were determined from distribution curves (number of counts versus particle diameter) obtained from a 12-channel Coulter Counter, Model C. A 100 μ aperture was used, and the starch samples were suspended in 0.9% sodium chloride electrolyte. The instrument was calibrated with poly(vinyl toluene) latex having a diameter of 3.49 μ .

Graft Polymerization

In a typical reaction, 3.0 g (dry basis) of starch was slurried with 800 ml of water at room temperature, and a stream of nitrogen was bubbled through the stirred mixture for 1 hr. The required amount of AN was added. After 5 min, 12 ml of initiator solution was added to give a ceric ion concentration of 1.5×10^{-3} mole/l. of water. After the mixture was stirred for the required length of time at room temperature, a solution of 1 g of hydroquinone in about 50 ml of water was added and the mixture filtered. The crude copolymer was washed with both water and ethanol and then dried.

The crude copolymer was freed of ungrafted PAN (of relatively high molecular weight) by extraction with dimethylformamide (DMF). To determine molecular weight of grafted PAN chains, starch was removed from the extracted copolymer by refluxing for 30 min with 0.5*N* hydro-

chloric acid followed by treatment with periodic acid and then aqueous sodium hydroxide.¹⁰ The molecular weight of grafted PAN was determined from the intrinsic viscosity as described previously.¹¹ Grafting frequency was calculated from the per cent PAN in the DMF-extracted copolymer (determined from nitrogen analysis which was corrected for moisture content of the sample) and the molecular weight of grafted PAN.

RESULTS AND DISCUSSION

The influence of reactant concentrations in water upon the composition of the starch-PAN copolymer is shown in Table I. The first reaction was run at concentrations used in previous studies:⁸ 21.9 g of starch (dry basis), 31.8 g of AN, 500 ml of water, and a ceric ammonium nitrate concentration of 1.5×10^{-3} mole/l. of water. Runs 2-4 were made with 3.0 g (dry basis) of starch, 10.0 g of AN, 800 ml of water, and the same ceric ion concentration. These three reactions show both the reproducibility of our results and the shorter and more frequent grafts obtained at high dilution. In the fourth reaction, there was less PAN grafted to starch than in runs 2 and 3. However, the grafting frequency remained essentially constant, and the lower per cent add-on was reflected in the reduced molecular weight of grafted PAN.

Since the same ceric ion concentration (in moles/liter of water) was used in runs 2-4 as was used in the first reaction, the ratio of ceric ion to starch was higher in runs 2-4 than in run 1. To prove that the more frequent grafting under dilute conditions was not simply due to a higher ceric ion concentration in relation to starch, the fifth reaction was made at the same dilution as runs 2-4 but with the same ratio of ceric ion to starch as was employed in run 1. Grafting was less frequent than in runs 2-4, probably due to the lower concentration of ceric ion (1.3×10^{-4} mole/l. of water), but was still more frequent than in the first reaction. The copolymer from run 6 (in which high dilution conditions were used with the same ratio of AN to starch as in run 1) was also more frequently grafted than the product of run 1. However, both the amount and molecular weight of grafted PAN were relatively low.

The influence of granule size and variety of starch on the composition of the copolymer is shown in Table II. The products obtained in reactions with rice starch, Amylon 7, and waxy maize were not greatly different than those reported in Table I with wheat starch. Therefore, neither the origin of the starch nor the relative amounts of amylose and amylopectin affect materially the molecular weights and frequencies of the grafts.

The average diameters of the starch granules studied were determined on a Coulter counter. Rice starch and Amylon 7 showed single peak distribution curves (number of counts versus diameter) with average diameters of 5.8 and 7.3 μ , respectively. Waxy maize showed a two-peak distribution with average diameters of the two components of 5.8 μ (40% of the total number of particles) and 11.6 μ (60% of total number of particles). Classi-

TABLE I
Effect of Dilution

Run ^a	Polymerization recipe				Products			
	Starch, g	AN, g	Ce ⁺⁺ , mole/l. of water	Water, ml	DMF-insoluble, g	PAN in DMF-insoluble, %	Molecular weight of grafted PAN ^b	Grafting frequency (AGU/graft)
1	21.9 ^c	31.8 ^d	1.5×10^{-3}	500	48.4	55.4	122000	606
2	3.0 ^e	10.0 ^f	1.5×10^{-3}	800	5.4	44.7	36700	281
3	3.0	10.0	1.5×10^{-3}	800	5.6	43.6	36600	293
4	3.0	10.0	1.5×10^{-3}	800	5.0	34.9	24000	276
5	3.0	10.0	1.3×10^{-4}	800	4.9	39.7	42500	399
6	3.0	4.35 ^g	1.5×10^{-3}	800	3.6	12.9	9900	413

^a All runs made with granular unclassified wheat starch. Reaction times were 3 hr. Run 1 gave 1.4 g of DMF-soluble polymer. In runs 2-6, DMF soluble polymer varied from 0.1 to 0.3 g.

^b Calculated from intrinsic viscosity in DMF.

^c 0.27 mole/AGU/l. of water.

^d 1.20 mole/l. of water.

^e 0.023 mole AGU/l. of water.

^f 0.235 mole/l. of water.

^g 0.103 mole/l. of water.

TABLE II
Effect of Variety of Starch and Size of Granule^a

Average granule diameter, μ	Starch	DMF insoluble, g	PAN in DMF insoluble, %	Molecular weight of grafted PAN ^b	Grafting frequency (AGU/graft)
5.8	Rice	4.9	36.3	20600	223
7.3	Amylon 7	5.7	44.4	22500	174
5.8(40%) 11.6(60%)	Waxy maize	4.9	38.6	26300	258
4.6	Wheat starch fraction 1	5.3	42.8	27400	225
18.0	Wheat starch fraction 4	5.1	36.3	28100	304

^a All runs made with 3.0 g (dry basis) of granular starch (0.0185 mole AGU), 10.0 g (0.188 mole) AN, 800 ml water, and 1.5×10^{-3} mole, Ce^{+4} /l. of water. Reaction times were 3 hr. DMF-soluble polymer varied from 0.1 to 0.2 g.

^b Calculated from intrinsic viscosity in DMF.

fication of the wheat starch used in Table I according to granule size gave two fractions (1 and 4), each of which showed single peak distributions; average diameters were 4.6 and 18.0 μ , respectively.

Evidence pertinent to the question whether granules of starch were surface grafted or whether grafted PAN was also located in the interior of the granule was obtained by a comparison of the grafting frequencies of Table II with granule diameters. On the basis that starch granules are spherical and that the weight-to-volume ratio is the same for all starches, relative surface areas of 3.9, 3.1, 2.5, and 1.0 were calculated for wheat starch (classified No. 1), rice starch, Amylon 7, and wheat starch (classified No. 4), respectively. Since the relative surface areas for the largest and smallest granules differ by about a factor of 4, we would expect the number of chains grafted also to differ by a significant factor if PAN were grafted mainly on the surface of the granule. Since the grafting frequencies in Table II, as expressed in anhydroglucose units per graft, were not greatly different from each other and showed no dependence on granule size, the evidence suggests that granules of starch are grafted internally. This conclusion is reasonable, since water and some other liquids are known to penetrate rapidly into starch granules.¹²

We next turned our attention to possible reasons for the increase in the number of chains grafted at high dilution. A series of reactions (Table III) with reaction times of 20, 40, and 90 min was run with unclassified wheat starch in high dilution (3.0 g in 800 ml water) but with 50.9 g of AN, the same concentration in moles/liter as was used in the experiment at normal dilution (run 1, Table I). Three additional reactions, run with the same amount of starch for identical periods of time but with 10.0 g of AN, are also presented in the same table along with a reaction run for 22 hr. With 50.9 g of AN and a reaction time greater than 90 min the high AN/

TABLE III
Effect of Time and Increased Acrylonitrile Concentration^a

AN, g	Time, min	DMF- insoluble, g	DMF- soluble, g	PAN in DMF, insoluble, %	Molecular weight of grafted PAN ^b	Grafting frequency (AGU/ graft)
50.9	20	7.4	0.4	57.1	182000	848
50.9	40	8.3	1.4	65.0	175000	581
50.9	90	9.2	4.2	67.3	182000	546
10.0	20	3.4	0.1	10.4	24000	1300
10.0	40	3.9	0.1	22.3	31600	677
10.0	90	4.7	0.1	36.8	28300	300
10.0	1320	5.9	0.3	48.9	34000	219

^a All runs made with unclassified wheat starch (3.0 g dry basis; 0.0185 mole AGU) in 800 ml water with 1.5×10^{-3} mole Ce α^4 /l. of water.

^b Calculated from intrinsic viscosity in DMF.

starch ratio produced a copolymer with such a high percentage of PAN that separation from ungrafted PAN on the basis of solubility differences in DMF was impossible. However, the similarity in grafting frequencies after reaction times of 40 and 90 min indicates that the number of grafted chains with 50.9 g of AN would not change appreciably with longer reaction times and would therefore approximate the 3 hr reaction at normal dilution (run 1, Table I).

If the grafting frequencies in Table III are plotted against reaction time, it is seen that the number of grafted chains levels off more rapidly and to a lower final value with 50.9 g of AN than with 10.0 g, despite the fact that the number of grafts is greater at short reaction times with the larger amount of monomer. These results suggest that at high AN concentration, some of the radicals on the starch backbone, possibly those in less accessible regions of the granule, are prevented from contacting monomer, presumably because of the rapid buildup of large amounts of PAN within the granule. During this rapid graft polymerization, AN adds more readily to the radical end of the growing polymer than to new active sites on starch. At low AN concentration, the rate of propagation has been slowed enough that termination by the usual processes of chain transfer, chain combination, or disproportionation is sufficient to keep the molecular weight of grafted chains low. There is, therefore, less total weight of PAN in the granule per grafted chain, and as a result the monomer may now diffuse past the relatively short terminated PAN chains to new active sites on starch. The idea of an increase in the number of grafted chains due to termination of the growing polymer at low molecular weight is similar to what we proposed earlier to explain our findings in aqueous organic solvent systems.⁹ In fact, the copolymers produced in this work at high dilution were similar in molecular weight and frequency of grafted PAN to some polymers prepared in aqueous methanol, aqueous DMF, and aqueous *tert*-butanol at high concentrations of starch and AN.

TABLE IV
Effect of Granule Size at High Acrylonitrile Concentration^a

Diameter of wheat starch granules, μ	DMF insoluble, g	DMF-soluble, g	PAN in DMF-insoluble, %	Molecular weight of grafted PAN ^b	Grafting frequency (AGU/graft)
4.6	9.2	1.6	66.8	166 000	509
18.0	7.4	0.5	59.1	128 000	547

^a Both reactions run for 40 min with 3.0 g (dry basis) starch (0.0185 mole AGU), 50.9 g (0.959 mole), AN, 800 ml water, and 1.5×10^{-3} mole Ce^{+4} /l. of water.

^b Calculated from intrinsic viscosity in DMF.

Reyes and co-workers¹³ have shown that reducing the amount of AN, with starch present in high concentration (4.0 g starch in 50 ml water), leads only to a lowering of the molecular weight of grafted PAN and does not change significantly the number of chains grafted. Therefore, to obtain an increase in the number of chains grafted, not only must AN be present in high dilution, but a reasonably high ratio of AN to starch must also be maintained.

Although the reactions run at low AN concentration were shown to involve grafting in the interior of the granule, the possibility existed that at high concentrations of AN, the granules might be mainly surface grafted. Evidence against this possibility was obtained by reacting the two fractions of classified wheat starch (fractions 1 and 4) with high concentrations of AN (Table IV). The two reactions gave copolymers with about the same grafting frequencies. The molecular weight of grafted PAN for the larger granules was lower than that for the small granules. This is reasonable, since owing to a smaller surface area in starch fraction 4, a greater percentage of grafted PAN is formed within the interior of the granule where the AN concentration is probably not as high. The amount of ungrafted PAN soluble in DMF was also smaller with the larger granules.

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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.

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