

Graft Copolymers of Starch-Polyacrylonitrile Prepared by Ferrous Ion-Hydrogen Peroxide Initiation

EDWARD I. STOUT, DONALD TRIMNELL, WILLIAM M. DOANE, and CHARLES R. RUSSELL, *Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604*

Synopsis

The effects of concentration, reactant ratios, temperature, and starch pretreatment on grafting of acrylonitrile onto starch were studied. Grafting was efficient at high concentrations (8-12% starch) when granular starch was used. The molecular weights for grafted polyacrylonitrile (PAN) were higher when gelatinized starch was used, but grafting efficiencies (grafted PAN/total PAN) were much lower. The molecular weight of the grafted side chain increased with increased concentration of reactants. The grafting frequency was highest when the reaction mixture was kept at 5°C and decreased with increased swelling of the starch. The starch-polyacrylonitrile graft copolymers were saponified and dried to give products which absorbed 75-440 ml H₂O per gram and 20-70 ml synthetic urine per gram.

INTRODUCTION

The graft polymerization of acrylonitrile (AN) onto starch by cerium(IV) initiation has been extensively studied,¹⁻¹² and products with considerable potential utility have been developed.¹³ Because of the greater abundance and lower cost of ferrous salts compared to cerium salts, the ferrous ion-hydrogen peroxide initiation system was investigated for the preparation of the starch-polyacrylonitrile (S-PAN) graft copolymers. Fanta et al.⁴ prepared S-PAN by ferrous ion-hydrogen peroxide initiation and found similar trends of molecular weight and grafting frequency compared to those obtained by cerium(IV) initiation. Brockway and Seaberg¹⁴ have also reported on S-PAN graft copolymers prepared by ferrous ion-hydrogen peroxide initiation. However, when we prepared S-PAN graft copolymers by their method, we did not get reproducible results and found that the order and method of addition of the reactants were critical factors. Therefore, we have made a detailed study of this grafting reaction. The effects of concentration, starch pretreatment, temperature, and reactant ratios were studied. Some of the S-PAN copolymers were hydrolyzed with sodium hydroxide, and the properties of the resulting products were examined.

EXPERIMENTAL

Materials

Starch. Pearl corn starch (10–12% H₂O).

Monomer. AN (Eastman Kodak, practical grade) was used without further purification.

Initiator. Ferrous ammonium sulfate (Fisher Scientific Company, reagent grade) or ferrous sulfate (J. T. Baker Chemical Company, reagent grade) and hydrogen peroxide, 30% (J. T. Baker, reagent grade).

Other Reagents. All other reagents were reagent grade and used without further purification.

Graft Polymerization

The grafting reactions were run in a three-neck flask fitted with a nitrogen bubbler tube, stirrer, and dropping funnel. The starch, suspended in distilled water, was brought to the desired temperature and nitrogen bubbled through the suspension for 1 hr. The temperature of the mixture was then adjusted and the ferrous salt (dissolved in a small amount of H₂O) was added. After 10 min, AN was added and the mixture was stirred for 5 min. Then a dilute solution of hydrogen peroxide (0.3–1.5%) was added dropwise over a 20-min period. After the mixture had been stirred under nitrogen for 4 hr, it was filtered. The solid was washed twice with H₂O and three times with acetone, and then air dried. The homopolymer content was determined by extracting the product with DMF.⁴

Isolation of Grafted PAN

A portion (10 g) of the product, which had been extracted with DMF, was suspended in 1N HCl (50 ml) and the mixture kept on the steam bath for 4 hr to remove the starch moiety. The insoluble PAN was collected on a filter, washed thoroughly with H₂O, and dried. The intrinsic viscosity was determined at 25°C in DMF solution with Cannon-Fenske viscometers. The molecular weight was calculated from the equation¹⁵ $[\eta] = 3.92 \times 10^{-4} \bar{M}_n^{0.75}$.

From the molecular weight of the grafted PAN and the nitrogen content of the DMF insoluble copolymer, the average number of anhydroglucose units (AGU) per grafted chain (grafting frequency) was determined.

RESULTS AND DISCUSSION

Graft Copolymerization Reaction

The results in Table I show that the amount of ferrous ion used to initiate polymerization may be varied considerably without greatly affecting the reaction. However, at the lower amounts (runs 1 and 2), the yields and grafting frequencies are decreased, while the molecular weights are increased; at the highest amount (run 6), total conversion of monomer to polymer is high, but the efficiency of grafting is considerably lowered. Therefore, at high iron ratio, homopolymerization is favored.

TABLE I
Effect of Fe²⁺ Concentration on Graft Polymerization Reaction^a

Run no.	Fe ²⁺ g ^b	Total polymer, g	DMF insol.		Mol. wt of graft	AGU per chain	% Conversion ^c	Grafting efficiency, % ^d
			g	% PAN				
1	0.05	32.2	31.0	29	43,200	655	29	95
2	0.1	38.5	36.0	36	50,697	505	50	81
3	0.2	40.8	35.1	39	29,500	286	60	71
4	0.2	43.4	35.6	39	29,500	233	63	70
5	0.5	45.0	34.5	40	27,600	267	69	63
6	1.0	44.0	26.8	22	23,400	591	70	26

^a All runs were made using 21 g starch (granular), 31.8 g acrylonitrile (AN), and 1.0 ml 30% H₂O₂ diluted to 100 ml; reactions were run at 25°C and 4% starch concentration under nitrogen for 4 hr. DMF = Dimethylformamide; PAN = polyacrylonitrile; AGU = anhydroglucose units.

^b Grams of Fe(NH₄)₂(SO₄)₂·6H₂O.

^c Weight of total PAN (homopolymer and grafted PAN)/weight of monomer.

^d Weight of grafted PAN/total PAN.

TABLE II
Effect of H₂O₂ Concentration on Grafting Reaction^a

Run no.	H ₂ O ₂ , ml ^b	Total polymer, g	DMF insol.		Mol. wt of graft	AGU per chain	% Conversion	Grafting efficiency, %
			g	% PAN				
7	0.05	38.0	28.5	26.0	40,300	592	52	45
8	0.05	37.5	27.4	22.7	35,000	738	52	37
9	0.10	43.3	31.2	37.7	32,900	336	79	49
10	0.25	43.2	34.6	38.5	32,900	325	71	60
11	0.50	42.8	36.0	42.0	38,500	328	71	67
3	1.00	40.8	35.1	39.0	29,500	286	60	71

^a All runs were made using 21 g starch (granular), 31.8 g AN, and 0.2 g Fe(NH₄)₂(SO₄)₂·6H₂O; reactions were run at 25°C and 4% starch concentration under nitrogen for 4 hr.

^b Volume of hydrogen peroxide (30%) which was diluted to 100 ml before addition.

TABLE III
Effect of Swelling the Starch on Grafting Reaction^a

Run no.	Pretreat-ment, °C	Total polymer, g	DMF insol.		Mol. wt of graft	AGU per chain	% Conversion	Grafting efficiency, %
			g	% PAN				
3	25	41.1	35.1	39	29,500	286	60	71
12	40	36.0	32.6	36	28,500	309	47	79
13	60	41.2	34.9	39	38,500	369	59	74
14	90	40.1	27.0	26	203,800	3338	58	40

^a All runs were made using 21 g starch, 31.8 g AN, 0.2 g Fe(NH₄)₂(SO₄)₂·6H₂O, and 1.0 ml 30% H₂O₂ diluted to 100 ml; the grafting reaction was run at 4% starch concentration under nitrogen at 25°C for 4 hr. Pretreatment consisted of treating the starch at the designated temperature for 1 hr.

TABLE IV
 Dilution Effect on Grafting Reaction^a

Run no.	% Starch	Total polymer, g	DMF insol.		Mol. wt of graft	AGU per chain	% Conversion	Grafting efficiency, %
			g	% PAN				
3	4	40.8	35.1	39	29,500	286	60	71
15	8	49.5	41.8	50	74,500	458	83	70
16	12	45.0	39.4	50	72,600	413	78	79
17	12	—	—	57	106,500	571	98	85

^a All runs were made using 21 g starch (granular), 31.8 g AN, 0.2 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4) \cdot 6\text{H}_2\text{O}$, and 1.0 ml 30% H_2O_2 diluted to 100 ml; reaction temperature of the 8% and 12% mixtures rose to 40–45°C during first 30 min, but temperature of the 4% mixture only reached 30°C.

 TABLE V
 Effect of Reaction Temperature on Grafting^a

Run no.	Re-act-tem-perature °C	Con-ten-tration, %	Total polymer, g	DMF insol.		Mol. wt of graft	AGU per chain	% Conversion	Graft-ing effi-ciency %
				g	% PAN				
18	5	4	35.5	27.2	28	11,500	188	51	46
3	25	4	40.8	35.1	39	29,500	286	60	71
19	40	4	41.5	34.9	42	56,100	471	72	65
20	60	4	44.0	31.3	34	100,000	1161	63	50
21	25	8	49.5	41.8	50	74,500	458	83	70
22	40	8	47.0	38.2	47	130,200	919	87	65
16	60	8	45.0	28.0	32	206,100	2743	69	42

^a All runs were made using 21 g starch (granular), 31.8 g AN, 0.2 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4) \cdot 6\text{H}_2\text{O}$, and 1.0 ml 30% H_2O_2 diluted to 100 ml; reactions were run under nitrogen for 4 hr.

The effect of varying the hydrogen peroxide ratio to other reactants on grafting and product properties is shown in Table II. As the amount of hydrogen peroxide is increased, the yield of grafted PAN, conversion, grafting efficiency, and frequency of grafting all increased, while the molecular weight of the grafted side chain decreased. However, the change in molecular weight was small and the yield appeared to reach a limiting value. The order and rate of addition of H_2O_2 was critical for obtaining reproducible results. Dropwise addition of the hydrogen peroxide gave the best results even though most of the polymerization appeared to occur before 25% of the total H_2O_2 solution was added.

It may be seen from the data in Table III that pretreatment of the starch in water at 25°, 40°, and 60°C causes relatively small differences in yield, molecular weight, or grafting frequency. However, gelatinization of the starch greatly reduces the grafting efficiency and the number of grafting sites, but the molecular weight of the grafted PAN is greatly increased.

The diluent effect is shown in Table IV. At the higher concentrations, the

TABLE VI
Effect of Monomer:Starch Ratio on Grafting Reaction^a

Run no.	Amount of AN	Total polymer g	DMF insol.		Mol. wt of graft	AGU per chain	% Conversion	Grafting efficiency, %
			g	% PAN				
23	15.9	30.1	27.5	24.8	12,200	228	55	79
24	20.0	32.6	30.0	29.4	18,300	271	58	77
25	25.0	35.6	30.5	34.0	24,700	295	61	68
26	25.0	36.5	31.7	35.4	28,000	314	59	76
3	31.8	40.8	35.1	39	29,500	286	60	71

^a All runs were made using 21 g starch (granular), 0.2 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and 1.0 ml 30% H_2O_2 diluted to 100 ml; reactions were run under nitrogen at 25°C for 1 hr at 4% starch concentration.

conversion of monomer to polymer, the grafting efficiency, and the molecular weight of the grafted side chain increased. Increasing the concentration beyond 8% AN surpasses the solubility of AN in H_2O , which would account for the similar results between runs 15 and 16. However, another reaction at 12% AN gave a graft copolymer of 57% PAN, a grafting efficiency of 85%, and conversion of monomer to polymer of 98%. Some of the differences between the samples prepared at 4% concentration compared to those prepared at higher concentration may be due to the difference in temperature caused by the heat of reaction.

Reaction temperature greatly influences the grafting reaction as shown in Table V. The molecular weight increases considerably as the temperature is increased: At 4% starch concentration, the molecular weight increases from 11,000 at 5°C to 100,000 at 60°C; and at 8% starch concentration, from 74,000 at 25°C to 206,000 at 60°C. A large reduction in the grafting frequency occurred at the higher temperatures.

Results presented in Table VI show the effect of monomer:starch ratio on the grafting reaction. As the ratio of monomer to starch increased, the molecular weight of the graft increased while the number of AGU/chain, the conversion of monomer to polymer, and the grafting efficiency remained relatively constant.

The effect of other variables on the polymerization reaction are given in Table VII. In run 30, in which air was not excluded, the conversion of monomer to polymer was quite low even though the grafting efficiency remained high. Comparison of run 28 with run 27 indicates that CO_2 is essentially equivalent to N_2 for an inert atmosphere. Run 29 shows that tap H_2O reduces both the conversion and the grafting efficiency. When tap H_2O was used with no pH adjustment, very little polymerization occurred. The source of ferrous ion was not critical as indicated by run 31 compared to run 27. These data show ferrous sulfate gave higher conversion and efficiency than ferrous ammonium sulfate.

A number of preparations were made without the nitrogen atmosphere using starch which had been pregelatinized by injecting steam into the mixture to achieve a temperature of 98–99°C for 5 min. These results in Table VIII show

TABLE VII
Effect of Other Variables on Grafting Reaction

Run no.	Atmosphere	Type of H ₂ O	Total polymer, g	DMF insol.		Mol. wt. of graft	AGU per chain	% Conversion	Grafting efficiency, %
				g	% PAN				
27a	N ₂	Distilled	40.8	35.1	39	29,500	286	60	71
28a	CO ₂	Distilled	39.0	34.0	38	34,800	345	52	78
29a	N ₂	Tap, pH 5	37.2	27.5	22	39,300	870	46	39
30a	Air	Distilled	33.5	29.4	28	21,500	343	35	73
31b	N ₂	Distilled	47.3	38.8	45	36,600	276	78	71

^a Made with 21 g starch (granular), 31.8 g AN, 0.2 g Fe(NH₄)₂(SO₄)₂·6H₂O, 1.0 ml 30% H₂O₂; diluted to 100 ml; reactions were run at 25°C for 4 hr at 4% starch concentration.

^b As in footnote above, but using 0.2 g FeSO₄·7H₂O instead of Fe(NH₄)₂(SO₄)₂·6H₂O.

TABLE VIII
Dilution Effect on Grafting Reaction Using Gelatinized Starch^a

Run no.	Starch conc. %	Reaction time, hr	Total polymer, g	DMF insol.		Mol. wt of graft	AGU per chain	% Conversion	Grafting efficiency, %
				g	% PAN				
32	4	1	31.0	23.7	13	27,600	1090	62.6	15
33	8	1	44.1	29.6	24	148,000	2820	71	31
34	8	2	48.0	34.2	36	191,000	2110	97	40

^a Starch was gelatinized with "live steam" and polymerization reaction conducted at 60–70°C using 0.2 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, 1.0 ml 30% H_2O_2 diluted to 100 ml, and 31.8 g AN.

TABLE IX
Absorbancy of Hydrolyzed Starch-PAN

Run no.	% PAN	Mol. wt. of graft	ml absorbed	
			H ₂ O	Synthetic urine ^a
35	14.2	31,100	80	20
36	15.6	31,400	125	30
37	20.1	28,000	125	25
38	34.9	63,500	130	30
39	45.3	89,200	440	70

^a Synthetic urine, 1.28 g CaCl₂, 2.28 g MgSO₄ · 7H₂O, 16.4 g NaCl, 40 g urea in 2 liters H₂O.

that the grafting efficiency is low (15–40%) under these conditions, but that a reasonable add-on (36%) can be achieved at the higher concentration of reactants.

The above results demonstrate that graft copolymers of starch-PAN with a wide range of add-on, molecular weight, and grafting frequency may be readily prepared with the ferrous ion-hydrogen peroxide initiator system.

Saponified Starch-PAN Copolymers

The fluid and synthetic urine uptake of saponified¹⁶ starch-PAN copolymers were measured, and the results are given in Table IX. Products which contain more PAN of higher molecular weight absorbed more water.

Portions of the hydrolyzed gel were isolated by the method described by Gugliemelli et al.¹⁶ The gel was acidified to pH 3.0, centrifuged, dehydrated with alcohol, and oven dried. The resulting powder was then redispersed in H₂O at pH 7.0–9.0 to give highly viscous dispersions.

Although the products reported here do not absorb as much water as the products reported by Weaver et al.,¹³ the preparation from granular starch and the use of the less expensive initiator makes the ferrous ion-hydrogen peroxide-initiated graft polymerization an attractive alternative method of preparation of products of this type.

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.

References

1. L. A. Gugliemelli, C. L. Swanson, F. L. Baker, W. M. Doane, and C. R. Russell, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2683 (1974).
2. Z. Reyes, C. F. Clark, F. Dreier, R. C. Phillips, C. R. Russell, and C. E. Rist, *Ind. Eng. Chem., Prod. Res. Dev.*, **12**, 62 (1973).
3. L. A. Gugliemelli, M. O. Weaver, C. R. Russell, and C. E. Rist, *Polym. Lett.*, **9**, 151 (1971).
4. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Macromol. Sci. Chem.*, **4**(2), 331 (1970).
5. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *Cereal Chem.*, **47**, 85 (1970).
6. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Polym. Sci. A-1*, **7**, 1675 (1969).
7. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **13**, 133 (1969).

8. R. C. Burr, G. F. Fanta, C. R. Russell, and C. E. Rist, *J. Macromol. Sci. Chem.*, **1**, 1381 (1967).
9. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **11**, 457 (1967).
10. Z. Reyes, C. E. Rist, and C. R. Russell, *J. Polym. Sci. A-1*, **4**, 1031 (1966).
11. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **10**, 929 (1966).
12. G. F. Fanta, R. C. Burr, C. R. Russell, and C. E. Rist, *Polym. Lett.*, **4**, 765 (1966).
13. M. O. Weaver, E. B. Bagley, G. F. Fanta, and W. M. Doane, U.S. Pat. 3,935,099, Jan. 27, 1976.
14. C. E. Brockway and P. A. Seaberg, *J. Polym. Sci. A-1*, **5**, 1313 (1967).
15. P. F. Onyon, *J. Polym. Sci.*, **37**, 315 (1959).
16. L. A. Gugliemelli, M. O. Weaver, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **13**, 2007 (1969).

Received July 12, 1976