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Robert C. Burr[a]; George F. Fanta[a]; C. R. Russell[a]; C. E. Rist[a]
[a] Northern Regional Research Laboratory, Peoria, Illinois

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Copolymers of Wheat Starch and Polyacrylonitrile. Effect of Aqueous – Organic Solvent Systems on Copolymer Composition*

ROBERT C. BURR, GEORGE F. FANTA, C. R. RUSSELL, and C. E. RIST

Northern Regional Research Laboratory†
Peoria, Illinois

Summary

Starch–polyacrylonitrile graft copolymers prepared in a number of aqueous–organic solvent systems with ceric ammonium nitrate as the initiator had more grafted chains than those prepared in water alone, and these were of lower molecular weight. Substitution of methanol for 80% of the water produced grafted chains with a molecular weight of 15,700 and a grafting frequency of 253 anhydroglucose units per graft. The influence of catalyst concentration, increased reaction temperature, and sodium sulfate on the composition of the copolymer were investigated for the methanol–water system.

Previous work [1–4] has dealt with graft copolymers of polyacrylonitrile (PAN) and starch and the influence of selected variables on copolymer composition. Except for a few runs made with gelatinized starch in dimethylformamide (DMF)–water and ethylene glycol–water mixtures [1], polymerizations in our early work were run in water. To discover the effects on the overall reaction of a solvent system which might be applicable to water-insoluble monomers, the grafting of acrylonitrile to starch was carried out with a mixture of methanol and water as the reaction medium and ceric ammonium nitrate as the initiator. Although acrylonitrile is water-soluble (7.4% at 25°C), it was used here so that a comparison might be made with the

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†A laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

earlier work. Unexpectedly, the water–methanol system produced a product that contained grafted chains considerably higher in number and lower in molecular weight than those we had obtained previously.

This report describes the influence of some reaction conditions on copolymer composition for the aqueous methanol system, and considers possible explanations for the more frequent grafting in the presence of methanol. Reactions in a number of other aqueous–organic solvent systems are also discussed.

EXPERIMENTAL

Materials

The starch used was Supergel* wheat starch from Industrial Grain Products, Ltd.

Acrylonitrile (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 catalyst solution was prepared by dissolving 13.9 g of ceric ammonium nitrate in 250 ml of 1 N nitric acid to give a 0.1 M solution. For the reactions in which ceric ion concentration was varied, solutions 0.5 M, 0.05 M, and 0.02 M were prepared. Catalyst solutions kept at room temperature for more than 3 weeks were discarded.

Tetrahydrofuran, DMF, and t-butanol were fractionated through a 15-in. Vigreux column, and center cuts collected. All other materials were reagent grade and used as is.

Graft Polymerization with Ceric Ion as Initiator

Wheat starch (21.9 g, dry basis) was slurried with 25 ml of water and the mixture purged with a slow stream of nitrogen for 1 hr. Oxygen was displaced in the same manner from the organic solvent. Ceric ammonium nitrate catalyst solution (7.5 ml) was added to the starch slurry, the mixture stirred for 5 min, and a solution of 31.8 g of acrylonitrile in the organic solvent added. After the mixture was stirred under nitrogen for 3 hr at room temperature, it was filtered, and the resulting solid was washed with ethanol and dried. For the reactions run at 50°C, the aqueous slurry of starch was purged with nitrogen at room temperature. The catalyst was added followed by a hot solution of acrylonitrile in methanol. The temperature was then maintained at 50°C.

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

The copolymer was freed of ungrafted PAN by extraction with DMF. The extracted copolymers, dried overnight in a vacuum oven at 60°C, contained 6–8% water. The starch moiety of the copolymer was removed by the periodate–base method [3], and the molecular weight of the grafted PAN determined by intrinsic viscosity as described previously [1].

Graft Polymerization with Ammonium Persulfate–Sodium Metabisulfite Initiator

Two experiments were run with ammonium persulfate–sodium metabisulfide initiator [5] to show that the more frequent grafting in the presence of methanol was not caused by chain transfer to starch via free radicals derived from methanol [6].

Starch (21.9 g, dry basis) was slurried in 25 ml of water and the system purged with nitrogen. Sodium metabisulfite (0.10 g) and ammonium persulfate (0.30 g) were added, followed by 31.8 g of acrylonitrile dissolved in 75 ml of nitrogen-purged methanol. After 40 min the product was separated by filtration, washed, and dried (yield: 32.5 g). Extraction with DMF gave 8.7 g of PAN (molecular weight 141,000) which was free of starch (by infrared). The insoluble fraction (23.0 g) contained 1.93% PAN with a molecular weight of 60,300. The grafting frequency was 18,900 anhydroglucose units (AGU) per graft. When the experiment was repeated in water alone, 31.8 g of product was isolated. Extraction with DMF gave 6.0 g of starch-free PAN with a molecular weight of 384,000. The insoluble fraction (25.2 g) contained 10.5% PAN with a molecular weight of 188,000. A grafting frequency of 9950 AGU/graft was calculated.

RESULTS AND DISCUSSION

Polymerization in Aqueous Methanol

The influence of varying amounts of methanol on the composition of the starch–PAN copolymer is evident from Table 1. The catalyst solution was added to a slurry of starch in 25 ml of water, and after 5 min a solution of acrylonitrile in methanol (75, 115, 150, or 300 ml) was added. For comparison purposes, a run was made under the same conditions except that 115 ml of water was used as a solvent for the monomer instead of methanol. As compared with water, aqueous methanol decreased the molecular weight of grafted PAN and increased the number of chains grafted. Also, the molecular weight of grafted PAN chains was inversely proportional to the volume of methanol used.

It seemed possible that the more frequent grafting in the presence of methanol could have resulted from chain transfer to starch via

TABLE 1. Influence of Methanol Concentration on Copolymer Composition[a]

Solvent, ml				Composition of DMF-insoluble copolymer		
MeOH	Water	Insoluble in DMF[b] wt., g	Soluble in DMF wt., g	% PAN[c] in graft	Mol. wt. of graft	AGU[d]/ graft
0	140	35.1	1.1	37.5	104,000	1,069
75	25	35.6	11.6	35.4	21,400	242
115	25	33.0	9.0	27.7	15,700	253
150	25	30.0	8.4	21.2	8,770	200
300	25	24.4	0.1	5.1	4,320	499

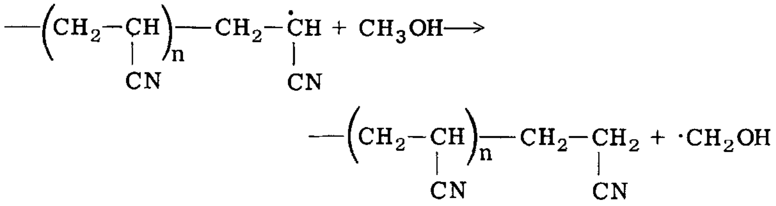
[a] Reactions run at 25°C with 7.5 × 10^{-4} mole of ceric ammonium nitrate.

[b] Dimethylformamide.

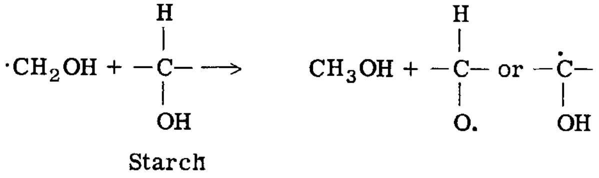
[c] Polyacrylonitrile.

[d] Anhydroglucose unit.

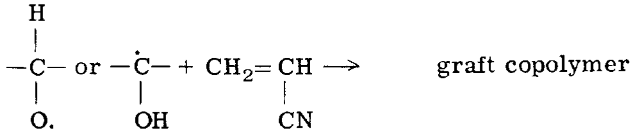
free radicals derived from methanol [6], as shown in the following equations:



$$-\left(\mathrm{CH_2}-\underset{\mathrm{CN}}{\mathrm{CH}}\right)_n-\mathrm{CH_2}-\underset{\mathrm{CN}}{\dot{\mathrm{C}}\mathrm{H}}+\mathrm{CH_3OH}\longrightarrow -\left(\mathrm{CH_2}-\underset{\mathrm{CN}}{\mathrm{CH}}\right)_n-\mathrm{CH_2}-\underset{\mathrm{CN}}{\mathrm{CH_2}}+\cdot\mathrm{CH_2OH} \qquad (1)$$



$$\cdot\mathrm{CH_2OH}+\underset{\text{Starch}}{-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{C}}}-}\longrightarrow \mathrm{CH_3OH}+-\underset{\mathrm{O}\cdot}{\overset{\mathrm{H}}{\mathrm{C}}}-\ \text{or}\ -\underset{\mathrm{OH}}{\dot{\mathrm{C}}}- \qquad (2)$$



$$\underset{\mathrm{O}\cdot}{\overset{\mathrm{H}}{-\mathrm{C}-}} \text{ or } \underset{\mathrm{OH}}{-\dot{\mathrm{C}}-} + \mathrm{CH_2{=}}\underset{\mathrm{CN}}{\mathrm{CH}} \longrightarrow \text{graft copolymer} \qquad (3)$$

This possibility was disproved by two experiments. Acrylonitrile was polymerized in the presence of starch in water and in aqueous methanol under conditions (ammonium persulfate–sodium metabisulfite initiator) designed to minimize the initial formation of free radicals on the starch backbone. The number of chains grafted should then be indicative of the amount of chain transfer to starch. After extraction with DMF to remove ungrafted PAN, the copolymer from the reaction run in water contained 10.5% PAN, had a molecular weight for grafted PAN of 188,000, and showed a grafting frequency of 9950 AGU/graft. The product from the aqueous methanol reaction contained 1.93% grafted PAN of molecular weight of 60,300 and had a grafting frequency of 18,900. Since fewer chains were grafted in aqueous methanol than in water, Eqs. (2) and (3) do not appear to contribute significantly to the overall mechanism. Equation (1) appears valid, however, since the PAN (both grafted and ungrafted) produced in the aqueous methanol system had a lower molecular weight than that formed in water. Moreover, more ungrafted PAN was formed in aqueous methanol than in water, presumably due to initiation by free radicals derived from methanol.

There is probably a combination of factors responsible for the more frequent grafting in the presence of methanol. One such factor is the chain-terminating ability of methanol. If we consider the competition for monomer by free radicals on growing PAN chains and free radicals on the starch backbone, the preference in water seems to be for the radical end of the growing polymer, judging from the comparatively infrequent grafting. In the presence of methanol, however, the growing PAN chains are terminated, and the monomer can now diffuse to new active sites on starch and initiate more grafted chains. Another contributing factor could be a difference between the rate of conversion of the starch–ceric complex to free radicals in methanol–water and this rate in water alone. The apparent inertness of radicals on the starch backbone toward methanol, as evidenced by the large number of chains grafted, is unexpected; and at this time, we have no good explanation.

More DMF-soluble polymer (ungrafted PAN) is formed in the reactions using 75, 115, and 150 ml of methanol than in the reaction using water alone, probably because of initiation by methanol radicals produced either via Eq. (1) or by way of a methanol–ceric ion complex. The decrease in both the amount of ungrafted PAN and the molecular weight of grafted PAN with an increase in the volume of methanol used could be due to increased dilution of monomer as well as to an increased chain-terminating ability of the solvent system at higher methanol concentrations.

Influence of Ceric Ion Concentration, Temperature, and Sodium Sulfate

Reactions run in aqueous methanol with five times, one-half, and one-fifth the ceric ammonium nitrate concentration used earlier are given in Table 2. As with gelatinized starch in water [2], a fivefold increase in ceric ion concentration did not increase the number of chains grafted. With one-half the amount of ceric ion, the number of chains grafted was not significantly reduced and was actually greater than the theoretical number, allowing one grafted PAN chain per ceric ion (268 AGU/graft found vs. 356 AGU/graft theoretical). The greater than theoretical number of grafted chains could be due to a number of factors. Chain transfer to starch by growing PAN chains (without the intermediacy of methanol) to produce more free radicals on the starch backbone is one possibility. Slight errors in the constants K and a in the equation relating intrinsic viscosity to number-average molecular weight [1] could also account for this discrepancy. The resolution of this problem must await further work. With one-fifth the amount of ceric ion, the number of grafted chains

TABLE 2. Effect of Ceric Ion Concentration, Temperature and Sodium Sulfate on Copolymer Composition[a]

Moles Ce^{+4} × 10^4	Temp., °C	Na_2SO_4 wt., g	Insoluble in DMF wt., g	Soluble in DMF wt., g	Composition of DMF-insoluble copolymer: % PAN in graft	Mol. wt. of graft	AGU/ graft
37.5	25	0	30.4	19.6	24.0	12,900	253
7.5	25	0	33.0	9.0	27.7	15,700	253
3.75	25	0	30.0	5.4	26.2	15,500	268
1.5	25	0	24.4	0.3	7.5	14,000	1,067
37.5	50	0	33.5	11.2	32.8	12,600	159
7.5	25	0.87	28.3	1.0	17.6	12,800	369
7.5	50	0.87	26.2	0.6	14.6	16,600	605

[a] Reactions run with 25 ml of water and 115 ml of methanol. Abbreviations used are the same as in Table 1.

was reduced considerably and was less than theoretical. The results of these three experiments suggest that there exists an optimum catalyst concentration where ceric ion is most efficiently utilized.

The influence of increased reaction temperature (50 vs. 25°C) on the composition of the copolymer may be seen by comparing the first and fifth reactions listed in Table 2. A more frequently grafted product and less ungrafted PAN were formed at the higher temperature.

The results of two experiments run at room temperature and 50°C in which 0.87 g of sodium sulfate was added to the reaction mixture are shown in the last two reactions of Table 2. Considerable reduction in the amount of ungrafted PAN resulted from the addition of sodium sulfate (compare with Table 1). These results are consistent with those of Reyes [7], who found a similar effect in the graft polymerization of acrylamide to starch. The starch–PAN copolymer, however, had fewer grafted chains than that formed in the absence of sodium sulfate. Also, in the presence of sodium sulfate, there were fewer chains grafted at 50 than at 25°C.

Polymerization in Other Aqueous Organic Solvents

In Table 3 are collected the results of graft polymerizations run

TABLE 3. Reactions Run in Aqueous Organic Solvents Other Than Methanol–Water[a]

Organic solvent	Insoluble in DMF wt., g	Soluble in DMF wt., g	Composition of DMF-insoluble copolymer: % PAN in graft	Mol. Wt. of graft	AGU/graft
Tetrahydrofuran	25.1	1.0	10.9	8,300	416
DMF	35.9	4.5	34.7	20,700	241
t-Butanol	36.8	4.6	36.7	25,400	270
Acetic acid	31.4	2.2	25.3	39,100	711
Acetic acid[b]	27.8	1.1	18.1	10,100	283
Acetone	35.4	1.0	35.0	51,500	589
Acetonitrile	36.8	0.4	37.8	126,000	1,279

[a] Reactions run at 25°C with 7.5×10^{-4} mole of ceric ammonium nitrate, 25 ml of water, and 115 ml of organic solvent (except where noted). Abbreviations used are the same as in Table 1.

[b] 150 ml.

with organic solvents other than methanol. Tetrahydrofuran, DMF, t-butanol, acetic acid, acetone, and acetonitrile were examined. With the exception of acetonitrile, each of the solvents gave more frequently grafted products with lower molecular weight grafts than were obtained in water. Furthermore, an increase in the volume of acetic acid produced an increase in the number of grafted chains and a decrease in their molecular weight. The mechanism of the action of these solvents is probably similar to that of methanol.

Acknowledgments

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Zusammenfassung

Stärke-Polyacrylnitril-Pfropfpolymere, die in einer Reihe von Wasser-Organische Lösungmittel Systemen mit Ceriammoniumnitrat als Initiator hergestellt worden waren, hatten mehr anpolymerisierte Ketten als nur in Wasser hergestellte Produkte, welche auch geringeres Molekulargewicht aufwiesen. Austausch von 80% des Wassers durch Methanol ergab aufgepfropfte Ketten mit einem Molekulargewicht von 15.700 und einer Pfropfhäufigkeit von 253 Anhydroglucoseeinheiten per Pfropfstelle. Der Eingluss der Katalysatorkonzentration, Erhöhung der Reaktionstemperatur und von Natriumsulfat auf die Zusammensetzung des Copolymeren wurden für das Methanol-Wasser System untersucht.

Résumé

Les copolymères greffés de l'amidon-polyacrylonitrile, preparés dans quelques systèmes de solvants aqueux-organiques à l'aide du nitrate cerique d'ammonium comme initiateur, avaient plus des chaines greffées que les polymères preparés dans l'eau d'une masse moléculaire plus basse. La substitution de 80% de l'eau par le méthanol donna des chaines greffées d'une masse moléculaire de 15,700 et une fréquence de greffage de 253 unites d'anhydroglucose par greffon. L'influence de la concentration du catalyseur, de l'augmentation de température de la réaction, et du sulfate de sodium sur la composition du copolymère dans le système méthanol-eau ont été etudiés.