

Graft Copolymers of Starch. III. Copolymerization of Gelatinized Wheat Starch with Acrylonitrile. Influence of Chain Modifiers on Copolymer Composition

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Synopsis

A study was made of the influence of selected chain modifiers on both the molecular weight of grafted polyacrylonitrile and the grafting frequency of the starch-polyacrylonitrile graft copolymer. Gelatinized wheat starch was used with ceric ammonium nitrate as the initiator. The organic chain modifiers investigated were ethyl mercaptan, 1-dodecanethiol, methyl ethyl ketone, acetaldehyde, and chloroform. Sodium chromate, cupric bromide, cupric nitrate, cupric acetate, and cupric chloride were also tested as chain modifiers. In the presence of cupric chloride, there was a tenfold reduction in the molecular weight of grafted polyacrylonitrile; however, fewer chains were grafted to the starch backbone than were observed without cupric chloride.

INTRODUCTION

Previous papers in this series have reported both the fractionation of the starch-polyacrylonitrile graft copolymer¹ and the influence of reaction conditions on copolymer composition.² Since the graft copolymer fractions reported in our earlier work had, for the most part, polyacrylonitrile (PAN) chains with molecular weights in excess of 500,000, an investigation was made of the influence of selected chain modifiers on both the molecular weight of grafted PAN and the grafting frequency.

EXPERIMENTAL

Materials

The starch used was unmodified edible wheat starch, 11-12% moisture (Huron Starbake, Hercules Powder Company).

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, except for one reaction, was prepared by dissolving 13.9 g. of ceric ammonium nitrate (G. Frederick Smith Chemical

Company) in 250 ml. of 1*N* nitric acid. Catalyst solutions more than 3 weeks old were discarded.

Methyl ethyl ketone (technical), ethyl mercaptan (technical), and chloroform (U.S.P.) were fractionated through a 15-in. Vigreux column, and center cuts were collected. Acetaldehyde (Eastman White Label) and 1-dodecanethiol (Aldrich Chemical Company) were used as is. All inorganic chemicals were reagent grade.

Graft Copolymerization

Polymerizations were carried out at 25–28°C. as described previously¹ with 21.9 g. (dry basis) of gelatinized wheat starch in an aqueous medium. If not otherwise indicated, 31.8 g. of acrylonitrile was used, and acrylonitrile and the chain modifier were added to the gelatinized starch 5 min. before addition of the catalyst. With the exception of one reaction, the concentration of ceric ion in the reaction mixture was 1.52×10^{-3} mole/l. In all reactions in which inorganic chain modifiers were used, the inorganic salt was added to the polymerization mixture as a solution in about 20 ml. of water. Except in one run, all reactions were made under an atmosphere of nitrogen.

After the copolymer was washed with water at room temperature, it was freed of ungrafted PAN by extraction with dimethylformamide (DMF). No special techniques were used to ensure removal of ungrafted starch. To determine the molecular weight of grafted chains, the starch moiety was removed from the extracted copolymer by oxidation with periodic acid followed by treatment with methanolic sodium methoxide (method developed by L. A. Gugliemelli³). This method generally gave faster and more complete removal of starch than the α -amylase method used earlier.¹ The molecular weight of grafted PAN was then determined as described previously.¹

RESULTS AND DISCUSSION

To have a comparison for reactions in which chain modifiers were used, three experiments were run in the absence of modifiers (Table I). Run 1 was made with 31.8 g. of acrylonitrile and shows the high molecular weight grafts and infrequent grafting which characterize these reactions. Decreasing the amount of acrylonitrile initially present (run 2, carried out under the same conditions only with 27.7% of the monomer used for run 1) lowered the molecular weight of the grafted PAN to 418,000; however, the grafting frequency of 10,800 anhydroglucose units (AGU) per graft indicated that fewer PAN chains were grafted to the starch backbone. Run 3, made under the same conditions as run 1 but under an atmosphere of air instead of nitrogen, yielded a product with about the same grafting frequency as that from run 1. The molecular weight of grafted PAN was not greatly reduced by the presence of oxygen.

TABLE I
Reactions in the Absence of Modifiers

Fraction	Run ^a	Wt., g.	PAN in graft, %	M.W. of graft	AGU/ graft
Recovered monomer	2, 3	1.4, 5.7			
Water solubles	1, 2, 3	5.3, 3.9, 4.1			
Insoluble in DMF ^b	1	41.2	52.3	923,000	5,200
	2	22.2	19.3	418,000	10,800
	3	34.6	44.3	638,000	4,950
Soluble in DMF ^c	1	2.8	(Contains 10-15% starch)		
	2	1.5	(Contains >15% starch)		
	3	5.3	(Contains about 5% starch)		

^a Runs 1 and 2 made under nitrogen with 31.8 g. and 8.6 g. acrylonitrile, respectively; run 3 made under air with 31.8 g. acrylonitrile.

^b Dimethylformamide.

^c Per cent starch estimated by infrared.

TABLE II
Reactions with Organic Chain Modifiers

Fraction	Run ^a	Wt., g.	PAN in graft, %	M.W. of graft	AGU/ graft
Recovered monomer	3, 5	9.7, 1.7			
Water-solubles	1, 2	2.7, 4.7			
	3, 4, 5	5.2, 6.8, 1.7			
Insoluble in DMF	1	19.6	0.04		
	2	43.0	51.8	881,000	5,060
	3	36.0	45.1	873,000	6,600
	4	23.8	13.8	255,000	9,640
	5	42.8	55.5	881,000	4,330
Soluble in DMF ^b	1	2.1	(Contains about 5% starch)		
	2	6.0	(Contains >15% starch)		
	3	7.7	(Contains about 10% starch)		
	4	15.1	(Contains about 5% starch)		
	5	5.5	(Contains 10-15% starch)		

^a Run 1 used 5 ml. of ethyl mercaptan; run 2, 5 ml. of 1-dodecanethiol; run 3, 10.4 g (0.144 mole) of methyl ethyl ketone; run 4, 6.4 g. (0.145 mole) of acetaldehyde; and run 5, 5 ml. of chloroform.

^b Per cent starch estimated by infrared.

Data for experiments involving organic chain modifiers are collected in Table II. With ethyl mercaptan (run 1), some ungrafted PAN was formed, but no significant grafting was observed. This run, however, demonstrates the efficiency of DMF in removing ungrafted PAN. Before DMF extraction, nitrogen analysis showed 9.2% PAN in the product. After DMF extraction, only 0.04% PAN was present in the DMF-insoluble fraction, and the DMF-soluble fraction had only about 5% starch (by

TABLE III
Reactions with Cupric Nitrate and Cupric Acetate

Fraction	Run ^a	Wt., g.	PAN in graft, %	M.W. of graft	AGU/ graft
Recovered monomer	1, 2, 3	4.5, 18.9, 30.2			
Water solubles	1, 2, 3	5.1, 2.6, 2.2			
Insoluble in DMF	1	36.4	49.8	822,000	5,075
	2	26.7	27.8	626,000	10,000
	3	19.8	2.1	66,700 ^b	19,300
Soluble in DMF ^c	1	5.0	(Contains >15% starch)		
	2	4.7	(Contains about 10% starch)		
	3	0.6	(Contains 10–15% starch)		

^a Run 1 used 1.20 g. (4.97×10^{-3} mole) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; run 2, 12.0 g. (4.97×10^{-2} mole) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; run 3, 0.99 g. (4.97×10^{-3} mole) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$.

^b The infrared spectrum of this material exhibited a medium-intensity —OH band at 3340 cm^{-1} . The rest of the spectrum showed little, if any, absorption due to starch.

^c Per cent starch estimated by infrared.

infrared). With 1-dodecanethiol (run 2), considerable grafting occurred; however, the product, after extraction with DMF, resembled that from run 1 (Table I), where no chain modifier was added. Methyl ethyl ketone⁴ (run 3, Table II) and chloroform (run 5) also gave no significant reduction in the molecular weight of grafted PAN. Acetaldehyde has been employed as a chain modifier in acrylonitrile polymerization;⁵ in our system, some chain shortening was indeed observed (run 4). The product, however, had a grafting frequency of 9,640 AGU/graft; and in addition, a large amount of ungrafted PAN was isolated.

Chromate ion has been described as a modifier for controlling the molecular weight of PAN.⁶ Addition of 0.03 g. (1.85×10^{-4} mole) of sodium chromate to our reaction mixture, however, completely inhibited grafting. Nearly all the monomer was recovered, and after DMF extraction the product showed no nitrile absorption in the infrared. Similarly, grafting was inhibited if polymerization was carried out in the presence of 0.28 g. (1.26×10^{-3} mole) of cupric bromide.

Watanabe and Kiuchi⁷ conducted a mechanistic study of the effects of cupric salts on the polymerization of acrylonitrile in aqueous solution and found that the degree of polymerization was influenced by the anion of the salt. The results of graft polymerizations run in the presence of cupric nitrate and cupric acetate are shown in Table III. These experiments, together with those run with cupric chloride (see below), confirm the influence of the anion on the molecular weight of PAN. When 1.20 g. (4.97×10^{-3} mole) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was added to the polymerization mixture (run 1), the product, after extraction with DMF, was not greatly different from that obtained without chain modifiers. A tenfold increase in the amount of cupric nitrate (run 2) reduced the molecular weight of the

grafted chains only slightly but gave a product containing about twice the number of AGU per grafted chain. When the polymerization was carried out in the presence of 4.97×10^{-3} mole of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, the molecular weight of grafted PAN was 66,700 (run 3); however, the copolymer contained only 2.1% PAN, and the grafting frequency was 19,300 AGU per graft.

TABLE IV
Reactions with Cupric Chloride

Fraction	Run ^a	Wt., g.	PAN in graft, %	M.W. of graft	AGU/ graft
Recovered monomer	1, 2	23.2, 23.9			
	3, 4, 5	25.6, 21.6, 28.7			
Water solubles	1-3	4.1-4.5			
	4, 5	3.0, 2.3			
Insoluble in DMF	1	21.3	5.6	95,500	9,900
	2	21.0	5.3	89,000	9,650
	3	19.2	6.0	83,200	8,120
	4	21.9	10.5	318,000	16,700
	5	21.2	3.9	54,500 ^b	—
Soluble in DMF ^c	1	1.7	(Contains about 15% starch)		
	2	1.3	(Contains >15% starch)		
	3	2.1	(Contains >15% starch)		
	4	6.2	(Contains 10-15% starch)		
	5	1.4	(Contains about 15% starch)		

^a Runs 1 through 4 made with 0.85 g. (4.98×10^{-3} mole) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and the normal concentration of ceric ammonium nitrate. In run 1, cupric salt added with catalyst; in run 2, cupric salt added with monomer; in run 3, cupric salt added with monomer, and catalyst added in seven portions over a period of 1.5 hr.; and in run 4, both cupric salt solution and catalyst added alternately in seven portions over a period of 1.5 hr. Run 5 used 4.25 g. (2.49×10^{-2} mole) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and five times the normal amount of ceric ammonium nitrate (7.6×10^{-3} mole/l.). Both cupric salt solution and catalyst were added alternately in seven portions over a period of 1.5 hr.

^b An infrared spectrum revealed a medium intensity —OH band at 3340 cm^{-1} , while the rest of the spectrum showed <5% unremoved starch. The sample was difficultly soluble in DMF; and in the determination of intrinsic viscosity, it was necessary to correct the weight of solute for 23.4% insoluble material. The value for molecular weight is, therefore, not representative of the entire sample.

^c Per cent starch estimated by infrared.

The results obtained with cupric chloride are collected in Table IV. In run 1, cupric chloride (4.98×10^{-3} mole) was added to the reaction mixture at the same time as the catalyst (5 min. after the addition of monomer); whereas in run 2, cupric chloride was added simultaneously with the monomer. In both cases, grafting frequencies of nearly 10,000 AGU per graft were observed, and the molecular weights of the grafted chains were on the order of 90,000. Addition of the cupric salt with the monomer, followed by addition of the catalyst solution in seven portions over a period of 1.5 hr. (run 3), also did not change the results appreciably.

When both the catalyst and the cupric salt were added portionwise (run 4), the molecular weight of the grafted PAN increased to 318,000, and the grafting frequency assumed a value of 16,700 AGU/graft. When the amounts of both ceric ammonium nitrate and cupric chloride were increased fivefold (run 5), portionwise addition in a manner identical to run 4 gave a product which more closely resembled those obtained from runs 1, 2, and 3.

To determine the amount of water-soluble material in a typical copolymer prepared in the presence of cupric chloride, a portion of the DMF-insoluble fraction from run 3 (Table IV) was extracted four times with water by heating the mixture to boiling and allowing it to stir and cool before centrifugation. Evaporation of a few drops of the supernatant from the fourth extraction indicated that a negligible amount of material was being solubilized. Work-up of the fractions showed that 9.6% of the starting material had been dissolved, and 86.4% remained water-insoluble. The infrared spectrum of the water-soluble fraction had no nitrile absorption at 2250 cm^{-1} . The water-insoluble fraction contained 6.3% PAN and had a grafting frequency of 7630 AGU/graft as opposed to 6.0% PAN and 8120 AGI/graft for a sample of unextracted material. The same molecular weight for grafted PAN was used to calculate both grafting frequencies.

In summary, chain modifiers may be used to lower the molecular weight of grafted PAN; however, the number of chains grafted to starch is also markedly reduced. This is probably due to reaction of the modifier with free radicals on the starch backbone before these radicals can react with monomer.

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

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Résumé

Une étude a été faite sur l'influence des modificateurs de chaînes choisis à la fois sur le poids moléculaire d'un polyacrylonitrile greffé et sur la fréquences des greffages d'un copolymère greffé amidon-polyacrylonitrile. L'amidon de froment gélatinisé a été

utilisé avec le nitrate cérique ammonique comme initiateur. Les modificateurs organiques de chaîne étudiés étaient le mercaptan éthylique, le 1-dodécane-thiol, la méthyle éthyle cétone, l'acétaldéhyde et le chloroforme. Le chromate de sodium, le bromure de cuivre, le nitrate de cuivre, l'acétate de cuivre et le chlorure cuivrique ont également été essayés comme modificateurs de chaîne. En présence de chlorure cuivrique, il y avait une réduction décuple du poids moléculaire du polyacrylonitrile greffé. Toutefois, il y avait moins de chaînes greffées au squelette de l'amidon, que ce qui l'on observe en absence de chlorure cuivrique.

Zusammenfassung

Eine Untersuchung des Einflusses ausgewählter Kettenmodifikatoren auf das Molekulargewicht von aufgepfropftem Polyacrylnitril und die Pflanzungsausbeute beim Stärke-Polyacrylnitrilpflanzcopolymeren wurde durchgeführt. Gelatinierte Weizenstärke mit Cerammonnitrat als Starter wurde angewendet. Die untersuchten organischen Kettenmodifikatoren waren Äthylmercaptan, 1-Dodekandiol, Methyläthylketon, Acetaldehyd und Chloroform. Auch Natriumchromat, Kupferbromid, Kupfernitrat, Kupferacetat und Kupferchlorid wurden als Modifikatoren getestet. In Gegenwart von Kupferchlorid trat eine Herabsetzung des Molekulargewichtes des aufgepfropften Polyacrylnitrils auf eine Zehntel auf; es wurden aber weniger Ketten auf die Stärkmoleküle aufgepfropft als ohne Kupferchlorid.

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