

Graft Copolymerization Onto Starch. II. Grafting of Acrylonitrile to Granular Native Potato Starch by Manganic Pyrophosphate Initiation. Effect of Reaction Conditions on Grafting Parameters

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Synopsis

The effect of reaction conditions on the composition of native potato starch-polyacrylonitrile graft copolymers initiated by manganic pyrophosphate onto starch slurries at 30°C has been examined. In general, when the Mn^{3+} ion concentration was increased from $0.15 \times 10^{-3}M$ to $3.0 \times 10^{-3}M$ (other conditions kept constant), an increase in conversion of monomer to polymer and % add-on was observed, whereas frequency of grafts (anhydroglucose units, AGU, per grafted chain) decreased. Also, the average molecular weights of grafts showed a decrease from 2.2×10^5 to 1.5×10^5 . Increasing the concentration ratio of starch to monomer during polymerization by a factor of 3 produced an increase in the conversion of monomer to polymer, whereas an increase in frequency of grafts (AGU/chain) was obtained. Values of % add-on and average molecular weights of the grafts showed, however, a decreasing tendency. It was observed that grafting onto starch took place readily even at acid additions as low as $10 \times 10^{-3}M$ H_2SO_4 ($pH \approx 1.8$). Selective solvent extraction of homopolymer and extremely low conversions of monomer to polymer (0.1%-1.5%) in duplicate runs without addition of starch indicated that grafting efficiencies were high in all cases. An attempt has been made to interpret the results in terms of variations in factors such as initial ratio of $(Mn^{3+})/(AGU)$, termination rate of acrylonitrile chain radicals by oxidation by Mn^{3+} ions, oxidation rate of radicals formed on anhydroglucose units by Mn^{3+} ions, and physical factors such as diffusion rate of Mn^{3+} ions through the polyacrylonitrile-grafted starch granules for terminating the radicals.

INTRODUCTION

A recent communication in this series described the first successful attempt to graft copolymerize vinyl monomers onto starch and its derivatives using the pyrophosphate complex of Mn^{3+} as initiator.¹ Grafting efficiencies and polymer yields were found to be high when starch and starch derivatives were grafted with acrylonitrile and methyl methacrylate. With acrylamide as monomer, however, low grafting efficiencies were obtained. This was attributed to oxidation of the enol of β -hydroxypropionamide by Mn^{3+} ions, which is an expected side reaction.

For studies of grafting of acrylonitrile onto starch and starch derivatives in granular form using Ce^{4+} initiation, the reader is referred to an extensive review by Fanta² and other papers.³⁻⁷ This paper on Mn^{3+} initiation reports the effects

of the reaction conditions on grafting parameters, i.e., grafting efficiency, % add-on, frequency on grafts, and the average molecular weights of the grafted chains, in grafting of acrylonitrile onto granular native potato starch using manganic pyrophosphate initiation. The definitions of grafting parameters are the same as given previously:^{1,2} Grafting efficiency = percentage of the total synthetic polymer formed that has been grafted to the starch. % Add-on = percent synthetic polymer in the graft copolymer. Frequency of grafts = average number of anhydroglucose units (AGU) separating the grafted branches.

EXPERIMENTAL

Materials

Most chemicals used were analytical-grade reagents from Merck, Darmstadt, Germany, except for anhydrous magnesium sulfate from Mallinckrodt, U.S.A., and sodium hydroxide from EKA, Sweden, both analytical grade. The granular native potato starch used in the grafting reactions was supplied by AB Stadex, Malmö, Sweden. The acrylonitrile (synthetic grade from Merck) contained monomethyl ether of hydroquinone as inhibitor which was removed using aqueous alkali. The monomer was then dried with anhydrous magnesium sulfate, distilled under reduced pressure of N₂, and stored in the dark at 4°C.

Preparation of the Initiator

Concentrations of MnSO₄·H₂O and KMnO₄ in water were selected so that for each desired Mn³⁺ concentration in the reaction vessel, 25 ml KMnO₄ solution was required to oxidize 25 ml MnSO₄ solution. For a particular concentration of Mn³⁺ ions desired in the reaction vessel, 25 ml of a solution of Mn²⁺ ions prepared according to Table I was added to a solution of sodium pyrophosphate, prepared by dissolving 6.69 g Na₄P₂O₇·10H₂O in 250 ml distilled water. The

TABLE I
Quantities of MnSO₄·H₂O and KMnO₄
for the Preparation of the Manganic Pyrophosphate Initiator

MnSO ₄ ·H ₂ O per 100 ml distilled water, g	0.1217	0.2434	0.4057	0.8113	1.623	2.0285	2.434
KMnO ₄ per 100 ml distilled water, g	0.0285	0.0569	0.095	0.1897	0.379	0.4745	0.569
Resulting concentration of Mn ³⁺ in reaction vessel, mmole/l.	0.15	0.3	0.5	1.0	2.0	2.5	3.0

TABLE II
Volumes of Distilled Water Acidified with
Concentrated H₂SO₄ (96 wt-%) to Obtain Different Concentrations of H₂SO₄

Concentration of H ₂ SO ₄ in reaction vessel, mmole/l.	10	20	40	80
Distilled water for 5 ml 96 wt-% H ₂ SO ₄ , ml	7200	3600	1800	900

pH of the resulting solution was adjusted to 6 by adding concentrated H_2SO_4 and using a Beckman Expandomatic pH Meter. The pH values of the solution were checked against standard buffers supplied by Merck. The Mn^{2+} solutions were then oxidized to Mn^{3+} ions by titrating potentiometrically with an aqueous $KMnO_4$ solution (Mn^{7+} ions) by the method of Lingane and Karplus⁸ using a Metrohm EA 201 platinum electrode. The weight of $KMnO_4$ dissolved in 100 ml distilled water corresponded to the desired concentration of Mn^{3+} ions in the reaction vessel in accordance with Table I.

About 25 ml of the permanganate solution was required for each 25-ml batch of $MnSO_4$ solution. A total of 300 ml initiator solution was prepared; 25 ml of this solution was used in grafting each batch. A glass electrode was used for all pH measurements with a saturated calomel electrode as reference.

Graft copolymerization

A known weight (7.5, 10, 15, or 20 g on a moisture-free basis) of native potato starch was slurried in 100 ml acidified distilled water of the desired concentration (prepared as indicated in Table II) in a reaction vessel which was immersed in a thermostatically controlled water bath maintained at 30°C. The reaction vessel was equipped with a stirrer, a condenser, a thermometer, and a dropping funnel. Twenty-five milliliters of the initiator solution (pH 6) of the total 300 ml prepared according to the procedure previously described and corresponding

TABLE III
Reproducibility of Grafting Reactions^a

Expt. no.	Product yield, g	Conversion of monomer to polymer, g/batch (%)	Grafting efficiency, %	% Add-on	Average molecular weight of grafted chains (\bar{M}_n)	Frequency of grafts, AGU/chain
1	37.7	17.7 (88.5)	98.1	46.5	156,000	1100
2	37.5	17.5 (87.5)	97.7	46.1	141,000	1020

^a Starch substrate: 20 g potato starch (dry basis); (H_2SO_4) = $80 \times 10^{-3}M$; acrylonitrile: 25 ml = 20.25 g; ($Na_4P_2O_7$) = $10 \times 10^{-3}M$; reaction time = 3 hr; temperature = 30°C; (Mn^{3+}) = $2.0 \times 10^{-3}M$.

TABLE IV
Effect of Decreasing Acidity on Grafting with Manganic Pyrophosphate^a

Expt. no.	H_2SO_4 concn., mmole/l.	Product yield, g	Conversion of monomer to polymer, g/batch (%)	Grafting efficiency, %	% Add-on	Average molecular weight of grafted chains (\bar{M}_n)	Frequency of grafts, AGU/chain
1	80	37.7	17.7 (88.5)	98.1	46.5	156,000	1100
2	40	37.6	17.6 (88.0)	96.6	45.9	192,000	1400
3	20	37.5	17.5 (87.5)	97.11	45.95	185,000	1340
4	10	37.45	17.45 (87.25)	97.1	45.9	184,000	1340

^a Starch substrate: 20 g (dry basis); acrylonitrile: 25 ml = 20.25 g; ($Na_4P_2O_7$) = $10 \times 10^{-3}M$; reaction time = 3 hr; temperature = 30°C; (Mn^{3+}) = $2.0 \times 10^{-3}M$.

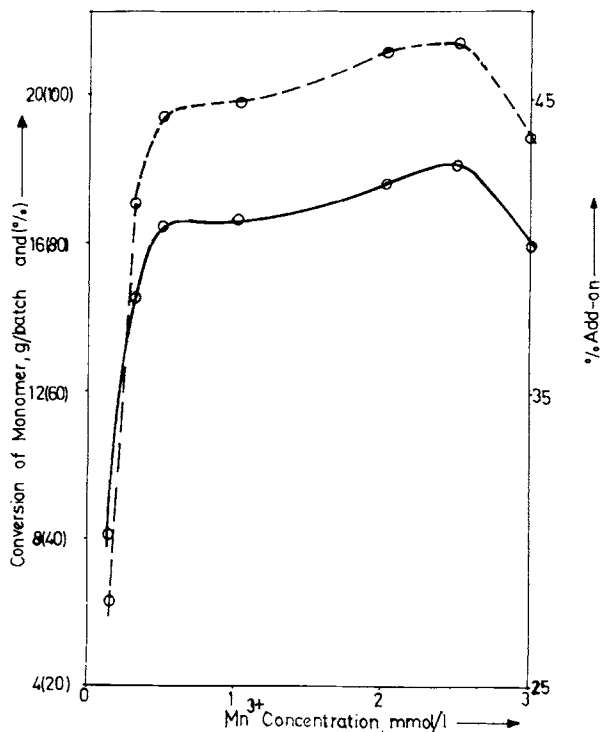


Fig. 1. Total conversion of monomer (—) and % add-on (---) in grafting of AN onto starch. Reaction conditions: starch substrate = 20 g (dry basis); (H_2SO_4) = 80 mmole/l.; acrylonitrile = 25 ml = 20.25 g; ($\text{Na}_4\text{P}_2\text{O}_7$) = $10 \times 10^{-3}M$; reaction time = 3 hr; temperature = 30°C.

to the concentration of Mn^{3+} ions desired in the reaction vessel was placed in one chamber of the dropping funnel together with 25 ml purified acrylonitrile (AN).

A brisk stream of oxygen-free nitrogen (purified by passing through a bed of BASF R 3-11 regenerated catalyst pellets maintained at about 100°C) was bubbled for 30 min through the starch slurry in the reaction vessel and the initiator solution plus monomer in the dropping funnel. At 30°C, the content of the dropping funnel (i.e., initiator plus monomer) was emptied into the reaction vessel and the reaction allowed to proceed for 3 hr (all operations in an atmosphere of purified N_2). The temperature in the vessel was maintained between 30° and 32°C by cooling the water bath with ice. Without cooling, the temperature in the reaction vessel could increase to nearly 55°C owing to the heat of polymerization. After termination of the polymerization by letting air into the vessel, the reaction product was filtered, thoroughly washed with water, and dried overnight in a stream of dry air at 60°C.

The products of the grafting reactions were characterized as described previously.¹ In one case, the reaction products were extracted with hot *N,N*-dimethylformamide (DMF) by the procedure of Houtz.^{9,10} Thus, a sample of approximately 2 g of the reaction product from experiment 1, Table III, was added to 100 ml DMF (being vigorously stirred) which had been previously cooled to 0°C in a flask. After a few minutes, the stirring was discontinued and the slurry heated to 150°C for a period of nearly 45 min. The highly swollen mass was allowed to settle and the content of the flask cooled to room temperature. The

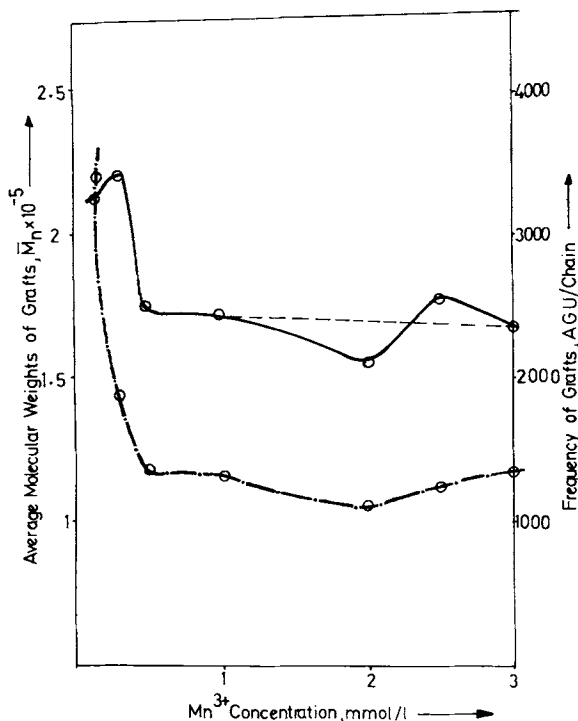


Fig. 2. Average molecular weight of grafts (—) and frequency of grafts (- · - · -) in grafting of AN onto starch. Reaction conditions: starch substrate = 20 g (dry basis); (H₂SO₄) = 80 mmole/l.; acrylonitrile = 25 ml = 20.25 g; (Na₄P₂O₇) = 10 × 10⁻³M; reaction time = 3 hr; temperature = 30°C.

clear extract, 20 ml, was added to an excess of distilled water to precipitate homopolymer (i.e., polyacrylonitrile). The precipitate was filtered, dried, and weighed on a porous glass filter to give the amount of homopolymer in 20 ml of the DMF extract.

RESULTS AND DISCUSSION

Based on studies of low molecular weight glycol compounds,¹¹ a reaction mechanism for initiation of graft copolymerization of vinyl monomers onto starch can be proposed. It should primarily involve the cleavage of glycol groups of the anhydroglucose units (AGU) in amylose and amylopectin as proposed in our previous paper.¹ The rate-determining step in the glycol-cleaving reaction of manganic pyrophosphate¹¹ appears to be the dissociation of the glycol-Mn³⁺ complex. The overall glycol-cleaving rate is governed by several factors,¹² such as Mn³⁺ concentration, "free" pyrophosphate concentration (taken as the difference between the total pyrophosphate concentration and thrice the Mn³⁺ concentration¹²), the acidity, and the glycol concentration.

We have kept the total pyrophosphate concentration constant at 10 × 10⁻³M, while the initial Mn³⁺ concentration has been increased from 0.15 × 10⁻³ to 3.0 × 10⁻³M. The concentration of anhydroglucose units was varied by increasing the amount of starch from 7.5 g to 20 g on a moisture-free basis. The acidity was varied by changing the H₂SO₄ concentration from 10 × 10⁻³M to 80 × 10⁻³M.

Two experiments (Table III) were repeated under identical conditions. They demonstrate adequate reproducibility of our results. Under the different conditions used for synthesis of graft copolymers, negligible amounts of the reaction products could be extracted by DMF, a good solvent for PAN but a poor solvent for the graft copolymer.² Thus, the amount of homopolymer, estimated as described previously,¹ was small, i.e., between 0.3 and 0.5 g of the total product obtained after the graft copolymerization reaction, which means 2%–3% of the polymer formed. As a consequence, grafting efficiencies calculated as described previously¹ were greater than 96% in all graft copolymerization experiments.

Plots of grafting efficiencies as a function of the variables studied give no clear relations. In one case (experiment 1, Table III), extraction of the reaction product was carried out by warm DMF by the method of Houtz^{9,10} to check whether the inability of DMF at room temperature to extract completely all PAN homopolymer was due to any tendency among PAN chains to associate (a phenomenon sometimes observed with PAN chains and referred to as "balling"^{9,10}). We found, however, that extraction of the reaction product by this method removed only a small amount of PAN (0.08 g from nearly 2 g of the reaction product). This indicates that PAN was primarily grafted, i.e., chemically attached to the starch moiety and not merely present as a physical mixture with starch.

Furthermore, under all the different experimental conditions studied in this paper, duplicate runs were carried out without any starch added. Negligible conversion of monomer to polymer (i.e., 0.1%–1.5%) was observed as compared to conversions between 50% and 90% in the presence of starch substrate. These low conversions in the absence of starch substrate are presented as additional evidence for high grafting efficiencies obtained under all experimental conditions investigated in this paper. The results appear to be consistent with previous observations, indicating the high specificity of attack by manganic pyrophosphate on glycols, aldehydes, and ketones in spite of its inactivity toward acrylonitrile as reviewed by Waters.¹¹

Since it is known that the glycol cleaving reaction of manganic pyrophosphate proceeds at a slower rate with decreasing acidity, it was of interest to observe whether or not any substantial grafting occurred at decreased acidity. The results obtained when the H_2SO_4 concentration was decreased from $80 \times 10^{-3}M$ to $10 \times 10^{-3}M$ are presented in Table IV. Normally, the H_2SO_4 concentration was kept at $80 \times 10^{-3}M$. We found that grafting occurred readily even at H_2SO_4 concentrations as low as $10 \times 10^{-3}M$. Grafting efficiencies were high, and both the products yields and the values of % add-on were high and showed only slight variations with acidity. When H_2SO_4 concentration was $80 \times 10^{-3}M$, the average molecular weight of grafted chains of PAN decreased by nearly 25%, and this fact is reflected in the more frequent grafts obtained. The reason for this variation is not clear, but one explanation may be the faster rate of termination at acidities as high as $80 \times 10^{-3}M$ by Mn^{3+} ions like most other oxidation reactions of this ion.¹¹

The effect of the initiator concentration on various grafting parameters was studied by a 20-fold variation in Mn^{3+} concentration from 0.15×10^{-3} to $3.0 \times 10^{-3}M$. Figure 1 shows that conversion of monomer to polymer increased from 40.2% to 82% when Mn^{3+} concentration was increased from $0.15 \times 10^{-3}M$ to $0.5 \times 10^{-3}M$.

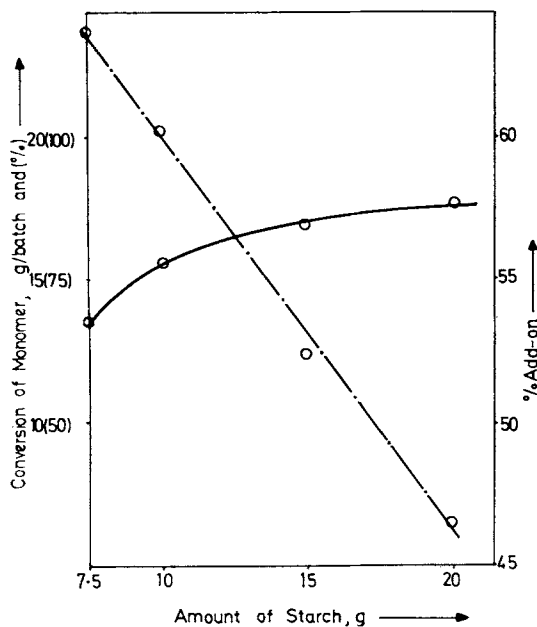


Fig. 3. Total conversion of monomer (—) and % add-on (- · - · -) in grafting of AN onto starch. Reaction conditions: (Mn^{3+}) = $2.0 \times 10^{-3}M$; (H_2SO_4) = $80 \times 10^{-3}M$; acrylonitrile = 25 ml = 20.25 g; ($\text{Na}_4\text{P}_2\text{O}_7$) = $10 \times 10^{-3}M$; reaction time = 3 hr; temperature = 30°C .

Since a 20% decrease in average molecular weights of grafts was observed in this range (Fig. 2), the increased conversion was due to more frequent grafts (shown as a sharp decrease of AGU/chain in Fig. 2). Increased Mn^{3+} concentration means also higher $\text{Mn}^{3+}/\text{AGU}$ ratio. A further increase in conversion of monomer to polymer from 82% to 88.5% was observed when Mn^{3+} concentration was increased from $0.5 \times 10^{-3}M$ to $2.0 \times 10^{-3}M$, and this is also attributable to an increasing number of grafts (Fig. 2) and a slight tendency for decreasing average molecular weights of grafts (Fig. 2). Between Mn^{3+} concentrations $2.0 \times 10^{-3}M$ and $3.0 \times 10^{-3}M$, a slight maximum (i.e., at 91.5%) in conversion of monomer to polymer was observed at $\text{Mn}^{3+} = 2.5 \times 10^{-3}M$ and the value dropped to 80% at $\text{Mn}^{3+} = 3.0 \times 10^{-3}M$ (Fig. 1). Since grafting efficiencies were high (greater than 95%) and almost constant, the curve for % add-on (Fig. 1) takes nearly the same shape as the curve of conversion of monomer to polymer (Fig. 1), and the same explanations hold in this case. The average molecular weights of grafts were nearly 20% higher at 0.15 and $0.3 \times 10^{-3}M$ of Mn^{3+} than at all other concentrations of Mn^{3+} . This may be attributed to a slower termination rate in the former case than in the latter by Mn^{3+} ions. Between Mn^{3+} concentrations of $0.5 \times 10^{-3}M$ and $3.0 \times 10^{-3}M$, the molecular weights of grafts showed only about 10% variation.

We studied the effects of the amount of starch used in the grafting reactions by varying it nearly threefold from 7.5 to 20 g. Figure 3 shows that conversion of monomer to polymer increased from 68% to 88.5% as the amount of starch was increased from 7.5 to 20.0 g (on a dry basis). The add-on (i.e., % synthetic polymer in graft copolymer^{1,2}) decreased from 63.6% to 46.5% with increasing amounts of starch (Fig. 3).

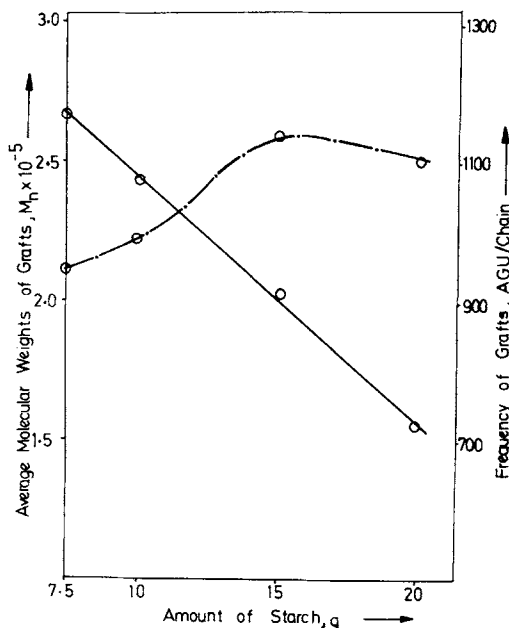


Fig. 4. Average molecular weight of grafts (—) and frequency of grafts (- - - -) in grafting of AN onto starch. Reaction conditions: (Mn^{3+}) = $2.0 \times 10^{-3}M$; (H_2SO_4) = $80 \times 10^{-3}M$; acrylonitrile = 25 ml = 20.25 g; ($Na_4P_2O_7$) = $10 \times 10^{-3}M$; reaction time = 3 hr; temperature = $30^\circ C$.

The slight increase in monomer conversion with increasing amount of starch charged may be attributed to the larger number of sites available for initiation of grafting. The % add-on decreases, however, because the amount of polymer formed increases more slowly than the amount of starch charged. A threefold increase in starch: Mn^{3+} ratio produced only a 20% variation in grafting frequency. The slight reduction in AGU/graft ratio observed at low starch concentration is due to the higher Mn^{3+} : starch ratio.

The increase in average molecular weights of the PAN chains as the amount of starch is decreased (Fig. 4) may be explained by considering that higher values of add-on of PAN at low amounts of starch may act as a stronger barrier to the diffusion of Mn^{3+} ions required for termination of the AN chain radicals by oxidation. It may also be due to higher propagation rates caused by higher ratios of monomer to the total number of radicals initiating grafting at lower amounts of starch. The total conversion of monomer to polymer (expressed as g/batch and % and depicted in Fig. 3) is dependent on the total number of radical sites capable of initiating graft copolymerization and the average molecular weights of the grafted chains so formed. Although the initial availability of Mn^{3+} ions per AGU decreases as the amount of starch charged in a grafting reaction increases, the total number of radicals formed which initiate grafting in the whole batch may be expected to increase with increasing amounts of starch. This increase in the total number of radicals leading to grafting becomes large enough to more than overcome the decrease in average molecular weights of PAN grafts with increasing amounts of starch. This would explain the increasing value of total conversion of monomer to polymer with increasing amount of starch as given in Figure 3.

It is known² that an increase in starch pretreatment temperature from 25° to 60° or 80°C increases the average molecular weights of grafts by a factor of 5–10 while grafting acrylonitrile onto starch by Ce^{4+} initiation. The effect of granule swelling on the graft copolymer composition is being studied and shall be reported in a forthcoming publication.

CONCLUSIONS

Based on the results presented in this paper, we conclude that manganic pyrophosphate is an efficient initiator for grafting of acrylonitrile onto starch under a wide range of experimental conditions. Little or no polyacrylonitrile is formed as homopolymer in physical mixture with the starch substrate.

Grafting parameters such as conversion of monomer to polymer, % add-on, and frequency of grafts can be varied within appreciable limits by varying the $(Mn^{3+})/(AGU)$ ratio, the substrate/monomer ratio, and, to some extent, the acidity. Changes in average molecular weights of grafts were substantial (from 2.6×10^5 to 1.5×10^5) when the substrate/monomer ratio was increased by a factor of 3.

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