

# Graft Copolymerization onto Starch. III. Grafting of Acrylonitrile to Gelatinized Potato Starch by Manganic Pyrophosphate Initiation

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## Synopsis

Recent development of synthesis and applications in grafting of acrylonitrile (AN) to gelatinized starch by  $Ce^{4+}$  initiation have been briefly reviewed. Using the  $Mn^{3+}$  method, the effects of starch pretreatment temperature on grafting parameters in grafting of AN onto starch have been studied. Total conversion of AN to PAN and % add-on were almost constant and showed only slight variation with increasing starch pretreatment temperature. Average molecular weight of grafts showed, however, an increase by a factor of nearly 10 (i.e., from  $0.4 \times 10^5$  to  $4 \times 10^5$ ) after swelling and gelatinization of the starch, and the grafting frequency (anhydroglucose units per grafted chain) increased in proportion. In grafting of AN onto gelatinized starch, increasing  $Mn^{3+}$  concentration increased the conversion of monomer and % add-on, whereas the average molecular weight of grafts and the grafting frequency (AGU/chain) decreased. An increase in the amount of starch also increased the conversion of monomer and the grafting frequency (AGU/chain) but decreased the % add-on and the average molecular weight of the grafts. Selective solution of PAN homopolymer by dimethylformamide indicated that grafting efficiencies were high in all cases. The results are interpreted in terms of slow termination rates due to high viscosity of gelatinized starch.

## INTRODUCTION

The definitions of the grafting parameters are the same as those used previously,<sup>1-3</sup> i.e.,

**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.

**Grafting Frequency:** Average number of anhydroglucose units (AGU) separating the grafted branches, i.e., lower value AGU/graft means more frequent grafts.

The effects of reaction conditions on grafting acrylonitrile to gelatinized starch by  $Ce^{4+}$  initiation have been studied extensively, and the work has been reviewed by Fanta.<sup>1</sup> An increase in starch pretreatment temperature had almost no effect on % add-on, whereas average molecular weights of PAN grafts increased by a factor of 5-10 and proportionally less frequent grafts were obtained. Gugliemelli et al.<sup>4</sup> base-hydrolyzed the nitrile groups in starch-polyacrylonitrile (S-PAN) graft copolymers under different conditions to yield products containing variable contents of amide and carboxyl groups. Weaver and coworkers<sup>5</sup> studied the effect of structure on properties of base-hydrolyzed S-PAN (called HS-PAN). They found that HS-PAN products prepared from gelatinized starch by  $Ce^{4+}$  initiation behaved as normal polyelectrolytes, whereas those prepared from granular starch did not. This difference was attributed to higher localization

of PAN grafts to certain starch chain segments in S-PAN prepared from granular starch in comparison with a uniform distribution of PAN grafts in S-PAN prepared from gelatinized starch.

Weaver et al.<sup>6</sup> discovered that dry self-supporting films of HS-PAN prepared from gelatinized starch had extremely high water absorbencies and behaved in a manner similar to films of potassium salt of crosslinked poly(acrylic acid). The mechanism responsible for this unusual behavior with HS-PAN prepared from gelatinized starch has not yet been fully interpreted, but crosslinking and/or ionic associations are suspected.<sup>6,7</sup> Scaled-up studies for production of HS-PAN from granular starch by  $Ce^{4+}$  initiation have been carried out<sup>8</sup> and commercial quantities are now available.<sup>9</sup>

The first successful attempts to graft copolymerize vinyl monomers onto starch and starch derivatives by manganic pyrophosphate initiation was reported in the first paper of this series.<sup>2</sup> The effect of reaction conditions on grafting parameters in grafting acrylonitrile to granular native potato starch were described in the preceding paper.<sup>3</sup> It was found that grafting to starch took place with high grafting efficiency under all conditions studied.<sup>3</sup> The grafting parameters, e.g., % add-on and frequency of grafts, could be varied between appreciable limits by varying the initial ratios of starch substrate/monomer and  $Mn^{3+}/AGU$ . The average molecular weights of PAN grafts were of the order of  $10^5$  and showed a decrease from  $2.6 \times 10^5$  to  $1.5 \times 10^5$  when the initial starch/monomer ratio was decreased by a factor of 3.

In view of the industrial importance of grafting acrylonitrile to gelatinized starch,<sup>9</sup> our work has been extended to manganic pyrophosphate initiation of AN to swollen and gelatinized starch. This paper on  $Mn^{3+}$  initiation reports the effects of gradually increasing the starch pretreatment temperature from 30° to 85°C and the results for grafting of acrylonitrile to gelatinized starch, i.e., starch pretreated at 85°C for 1 hr.

## EXPERIMENTAL

### Materials

All chemicals were the same as previously described.<sup>3</sup> The granular native potato starch used in the grafting reactions was supplied by AB Stadex, Malmö, Sweden. Acrylonitrile monomer was purified according to the procedure previously described.<sup>3</sup>

### Preparation of Initiator

The concentrations of  $MnSO_4 \cdot H_2O$  and  $KMnO_4$  in water were selected so that for each desired  $Mn^{3+}$  concentration in the reaction vessel, 25 ml of  $KMnO_4$  solution was required to oxidize 25 ml  $MnSO_4$  solution. For a particular concentration of  $Mn^{3+}$  ions desired in the reaction vessel, 25 ml of a solution of  $Mn^{2+}$  ions prepared according to Table I was added to a solution of sodium pyrophosphate, prepared by dissolving 13.38 g  $Na_4P_2O_7 \cdot 10H_2O$  in 250 ml distilled water. The pH of the resulting solution was adjusted to 6 by adding conc.  $H_2SO_4$ , using a Beckman Expandomatic pH Meter. The pH values of the solutions 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

TABLE I  
Quantities of  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and  $\text{KMnO}_4$  for the Preparation of the Manganic Pyrophosphate Initiator Solution in Distilled Water

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$ per 100 ml aq. solution $\psi$ , g	0.2434	1.6226	3.246	4.0578	4.868
$\text{KMnO}_4$ per 100 ml aq. solution $\psi$ , g	0.0570	0.3794	0.758	0.9490	1.138
Resulting concentration of $\text{Mn}^{3+}$ ions in reaction vessel, mmol/l.	0.15	1.0	2.0	2.5	3.0

$\text{KMnO}_4$  solution ( $\text{Mn}^{7+}$  ions) by the method of Lingane and Karplus<sup>10</sup> using a Metrohm EA 201 platinum electrode. The weight of  $\text{KMnO}_4$  in 100 ml aqueous solution corresponded to the desired concentration of  $\text{Mn}^{3+}$  ions in the reaction vessel (Table I).

About 25 ml of the permanganate solution was required for each 25-ml batch of  $\text{MnSO}_4$  solution. A total of 300 ml of 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 of native potato starch (5.0, 7.5, or 10.0 g on a moisture-free basis) was slurried in 200 ml distilled water in a reaction vessel which was immersed in a thermostatically controlled water bath. The reaction vessel was equipped with a stirrer, a condenser, a thermometer, an  $\text{N}_2$  bubbler, and a dropping funnel. The dropping funnel consisted of two chambers, each equipped with a nitrogen bubbler and so designed that the content of each of the two chambers could be emptied independently into the reaction vessel under an atmosphere of  $\text{N}_2$ .

A 25-ml portion of the initiator solution (pH 6) of the total 300 ml prepared and corresponding to the concentration of  $\text{Mn}^{3+}$  ions desired in the reaction vessel was emptied into one chamber of the dropping funnel, and 15 ml purified acrylonitrile (AN) was poured into the same chamber. In the second chamber of the dropping funnel, 25 ml acidified water was poured. The acidified water had been previously prepared by adding 25 ml 96%  $\text{H}_2\text{SO}_4$  to 500 ml distilled water.

A brisk stream of oxygen-free nitrogen (purified by passing through a bed of BASF R3-11 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, monomer, and acidified water in the dropping funnel before being led out of the system. Bubbling of  $\text{N}_2$  gas was stopped after a 30-min bubbling period, and an atmosphere of  $\text{N}_2$  was thereafter maintained. At the start of  $\text{N}_2$  bubbling, the temperature of the reaction vessel was raised to the desired starch pretreatment temperature (30°, 40°, 50°, 60°, 75°, or 85°C) and maintained there for 1 hr with stirring. The content of the reaction vessel was then cooled to 30°C, and the monomer, the initiator solution, and the acidified distilled water were emptied into the reaction vessel from the dropping funnel. The initiator solution and the monomer were added first, followed after 1 min by the acidified water.

The reaction mixture was stirred vigorously for 2 min and then allowed to react under slow stirring for 3 hr. All operations were carried out under an atmosphere of purified  $N_2$  gas. The products of the reactions with starch, pretreated at temperatures  $\geq 55^\circ C$ , were filtered, thoroughly washed with water, and dried in air at  $60^\circ C$ . When the starch pretreatment temperatures were  $\geq 60^\circ C$ , the products were poured into an excess of methanol, filtered, and thoroughly washed with methanol and ethanol before being dried.

Nearly 5 g of the dried products was extracted with 250 ml *N,N*-dimethylformamide (DMF) for 72 hr at room temperature, and 50 ml of the clear extract was precipitated in an excess of methanol. The precipitate was dried and weighed. The precipitate was analyzed for N content by Dumas' method to determine the PAN content in the extract. The extracted products were filtered, washed with methanol and then with ethanol, and dried, and 2 g of the dried graft copolymer was refluxed in 200 ml aqueous 1*M*  $H_2SO_4$  to remove the starch moiety. The PAN slurry was then filtered, washed with water and ethanol, and dried in air at  $60^\circ C$ . The molecular weights of PAN grafts were determined by intrinsic viscosity measurements as described previously.<sup>2</sup>

## RESULTS AND DISCUSSION

Acrylonitrile monomer and initiator solution (pH 6) could be placed in the same chamber in the dropping funnel, since at such low acidities (pH 6) the manganic pyrophosphate initiator does not attack the monomer at all.<sup>11</sup> Acidified water was placed in the dropping funnel to prevent any acidic hydrolysis of the starch during the pretreatment step. In principle, acidified water could have been placed together with the initiator solution (pH 6) and the acrylonitrile monomer because acidic manganic pyrophosphate does not attack acrylonitrile.<sup>11</sup> The acidified water was, however, poured separately in the second chamber of the dropping funnel since, in practice, it was found<sup>3</sup> that acidic manganic pyrophosphate does polymerize acrylonitrile to a very slight extent (0.1–1.5% total conversion per batch) in the absence of a suitable substrate.

Initial attempts to graft copolymerize acrylonitrile to gelatinized potato starch (i.e., starch pretreated at  $85^\circ C$  for 1 hr) resulted in PAN yields as low as 40% per batch. The low yields were probably due to the slow diffusion rate of acrylonitrile monomer and manganic pyrophosphate initiator into the starch gel phase due to the high viscosity of gelatinized starch. This problem was solved by stirring the content of the reaction vessel vigorously for 2–3 min immediately after initiator solution, monomer, and acidified water had been emptied into the reaction vessel. High yields of polymer (more than 80%) were then obtained.

To summarize, the total pyrophosphate concentration was kept constant at  $10 \times 10^{-3}M$  while the initial  $Mn^{3+}$  concentration was varied between  $0.15 \times 10^{-3}$  and  $3.0 \times 10^{-3}M$ . The initial  $H_2SO_4$  concentration in the reaction vessel was kept constant at  $85.8 \times 10^{-3}M$ . The starch was pretreated at temperatures between  $30^\circ$  and  $85^\circ C$  for 1 hr and cooled to  $30^\circ C$  before the grafting reaction was conducted. The concentration of anhydroglucose units was varied by increasing the amount of starch from 5.0 to 10.0 g on a moisture-free basis.

Experiments under three sets of conditions were repeated twice. The reproducibility (as shown in Table II) was considered adequate for our purposes. Under all conditions used for synthesis of graft copolymers, the products were extracted with DMF, a good solvent for PAN homopolymer but a poor solvent

TABLE II  
Reproducibility of Grafting Reactions<sup>a</sup>

Expt. no.	Starch pretreatment temperature, <sup>b</sup> °C	Product yield, g	Conversion of monomer to polymer, g/batch (%)	% Add-on	Average weight $\bar{M}_n$ of grafts	Grafting frequency, AGU/chain
1	30	19.3	9.3 (77.5)	47.6	41,400	280
2	30	19.1	9.1 (75.8)	47.1	33,000	230
3	60	19.8	9.8 (81.7)	48.7	370,000	2410
4	60	19.9	9.9 (82.5)	48.4	391,000	2570
5	85	20.0	10.0 (83.3)	49.2	404,000	2580
6	85	20.1	10.1 (84.2)	49.2	430,000	2740

<sup>a</sup> Starch substrate: 10 g potato starch (dry basis);  $[H_2SO_4] = 85.8 \times 10^{-3}M$ ; acrylonitrile (15 ml) = 12 g;  $[Na_4P_2O_7] = 10 \times 10^{-3}M$ ; reaction time = 3 hr; reaction temperature = 30°C;  $[Mn^{3+}] = 1.0 \times 10^{-3}M$ .

<sup>b</sup> Starch was treated at this temperature for 1 hr before the graft copolymerization reaction.

for the graft copolymer. The DMF extract was completely transparent in cases where the starch pretreatment temperature was  $\leq 55^\circ\text{C}$ . Analysis of the extract showed that only 1%–2% of the total PAN content was going into solution. This indicated high grafting efficiencies (i.e., greater than 95%) obtained in these cases. When the starch pretreatment temperature was  $>60^\circ\text{C}$ , the DMF extract was not always completely transparent but showed slight haziness, indicating that some starch on account of its add-on of PAN grafts had been carried into dispersion in DMF. This was confirmed by precipitating the DMF extract in methanol and analyzing the dried precipitate for its N content by Dumas' method. The N contents varied between 7 and 13% (26.4% N in pure PAN), indicating a varying content of starch. The total amount of PAN extractable by DMF from nearly 5 g of reaction product was estimated between 0.1 and 0.25 g. The grafting efficiencies appear to be high (i.e., greater than 95% even if one assumes that all PAN in the DMF extract is homopolymer. There is, however, some starch present in the extract which probably is grafted to PAN.

Under varying conditions we have found that  $\text{Mn}^{3+}$  ions yield PAN in small amounts only (0.1%–1.5%) in the absence of starch substrate,<sup>3</sup> and these results appear to be consistent with similar studies with manganic pyrophosphate as reviewed by Waters.<sup>11</sup> This further supports our observations of high grafting efficiencies (greater than 95%) obtained with manganic pyrophosphate.

The temperature in the reaction vessel remained between  $30^\circ$  and  $32^\circ\text{C}$  under the reaction conditions, and no cooling of the water bath was necessary as in previous cases.<sup>3</sup> The lower heat evolution may be explained by the fact that initiator, starch, and AN monomer concentrations were lower in this study than in those reported previously.<sup>3</sup> Lower AN monomer and starch concentrations would lead to slower polymerization rates and hence lower rates of heat evolution. We also observed that with increasing starch pretreatment temperature, the swelling of the products in DMF increased during extraction. This observation is similar to that reported by Fanta et al.<sup>13</sup>

Figure 1 gives conversion of monomer (g/batch and %) and % add-on as a function of starch pretreatment temperature. There is a slight increase in both conversion and add-on with increasing temperature. Since grafting efficiencies were higher than 90% in all cases, the curve for % add-on has the same shape as the curve for total conversion of monomer to PAN. The conversions at pretreatment temperatures above  $60^\circ\text{C}$  are slightly higher than those where the starch pretreatment temperature was lower than  $60^\circ\text{C}$ . This may be explained by a slightly better accessibility of starch for grafting in swollen and gelatinized state than in granulate form, i.e., for pretreatment temperatures, below  $60^\circ\text{C}$ .

Figure 2 shows plots of average molecular weight of grafts and frequency of grafts as functions of starch pretreatment temperature. Between starch pretreatment temperatures of  $30^\circ$  and  $55^\circ\text{C}$ , the average molecular weights of grafts show only a slight increasing tendency ( $\bar{M}_n$  between 40,000 and 60,000); but when the temperature is increased to  $60^\circ\text{C}$ , the molecular weight of grafts ( $\bar{M}_n$ ) increased to nearly 380,000. Between starch pretreatment temperatures of  $60^\circ$  and  $85^\circ\text{C}$ , there is not much variation. Since % add-on showed only about 10% variation (Fig. 1) between starch pretreatment temperatures of  $30^\circ$  and  $85^\circ\text{C}$ , the curve for grafting frequency is closely related to that for average molecular weight of grafts (Fig. 2).

The average molecular weight of grafts for starch pretreated at  $30^\circ\text{C}$  was nearly 37,000, as compared to values between  $1 \times 10^5$  to  $2 \times 10^5$  reported earlier<sup>3</sup> in

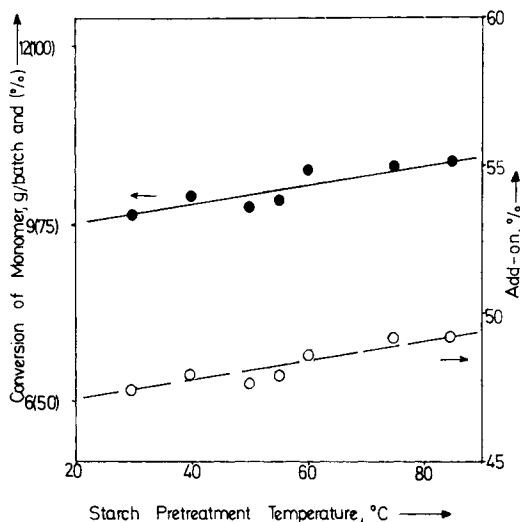


Fig. 1. Total conversion of monomer (—●—) and % add-on (—○—) in grafting of AN onto starch. Reaction conditions: starch substrate = 10 g (dry basis);  $[\text{H}_2\text{SO}_4] = 85.8 \times 10^{-3}M$ ; acrylonitrile (15 ml) = 12 g;  $[\text{Na}_4\text{P}_2\text{O}_7] = 10 \times 10^{-3}M$ ; reaction time, 3 hr; reaction temperature,  $30^\circ\text{C}$ ;  $[\text{Mn}^{3+}] = 1.0 \times 10^{-3}M$ .

grafting to granular starch. We have found that molecular weight of the grafts does not vary much with initial  $\text{Mn}^{3+}$  concentration.<sup>3</sup> Hence, we believe that the lower molecular weights obtained for granular starch in this study are simply a result of slower propagation rates caused by the much lower initial AN monomer concentration (48 g/l.) as compared to previous cases<sup>3</sup> where the AN monomer concentration was 83.4 g/l. Our results appear to be consistent with observations of Fanta et al.<sup>12</sup> using  $\text{Ce}^{4+}$  initiation.

The increase in average molecular weight of grafts when the starch pretreatment temperature is increased to  $60^\circ\text{C}$  and higher appears to be due to autoacceleration of polymerization caused by the well-known diffusion-controlled termination called the gel effect<sup>14</sup> (Trommsdorf-Norrish type). Potato starch granules undergo gelatinization<sup>15</sup> on heating in water between  $59^\circ$  and  $68^\circ\text{C}$ . The granules absorb water, increase in size, swell, and gelatinize to give a viscous paste. Our results are similar to those obtained for  $\text{Ce}^{4+}$  initiation.<sup>1</sup> As a result of gelatinization, the average molecular weight of grafts increases by a factor of 10 in manganic pyrophosphate initiation and a factor of nearly 8 in  $\text{Ce}^{4+}$  initiation.<sup>1</sup>

The effect of initiator concentration on grafting parameters was studied in grafting of AN onto gelatinized starch (i.e., starch pretreated at  $85^\circ\text{C}$  for 1 hr). Figure 3 depicts conversion of monomer and add-on as functions of  $\text{Mn}^{3+}$  concentration. The conversion of monomer increased from 51.7% to 81.5% as  $\text{Mn}^{3+}$  was increased from  $0.15 \times 10^{-3}M$  to  $1.0 \times 10^{-3}M$ . This increase is interpreted as due to more frequent grafts. This is depicted in Figure 4 as a sharp decrease. Increased  $\text{Mn}^{3+}$  concentration means lower AGU/ $\text{Mn}^{3+}$  ratio. Between  $\text{Mn}^{3+}$  concentrations of  $1 \times 10^{-3}M$  and  $3 \times 10^{-3}M$ , there was only 10% variation in total conversion of monomer. Since grafting efficiencies were greater than 90% in all cases, the curve for add-on (Fig. 3) takes nearly the same shape as the curve for conversion of monomer.

Figure 4 shows average molecular weight of grafts and frequency of grafts as

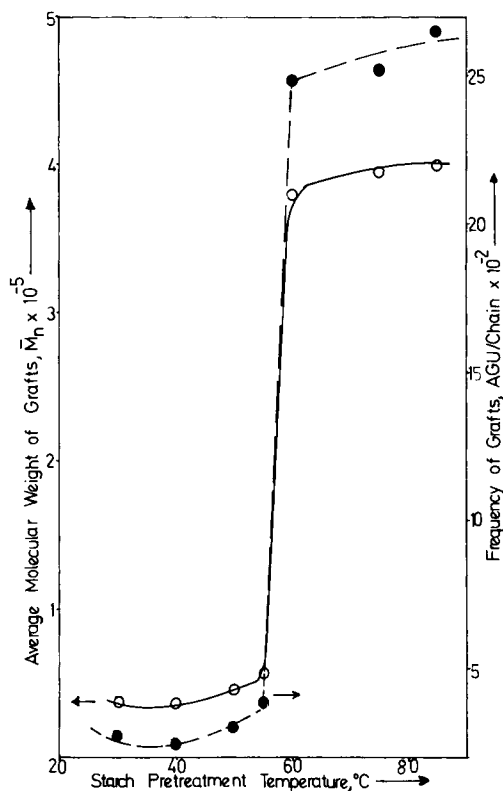


Fig. 2. Average molecular weight of grafts (—○—) and frequency of grafts (—●—) in grafting of AN onto starch. Reaction conditions: starch substrate = 10 g (dry basis);  $[\text{H}_2\text{SO}_4] = 85.8 \times 10^{-3} \text{M}$ ; acrylonitrile (15 ml) = 12 g;  $[\text{Na}_4\text{P}_2\text{O}_7] = 10 \times 10^{-3} \text{M}$ ; reaction time, 3 hr; reaction temperature,  $30^\circ\text{C}$ ;  $[\text{Mn}^{3+}] = 1.0 \times 10^{-3} \text{M}$ .

functions of  $\text{Mn}^{3+}$  concentration. More frequent grafts were obtained as  $\text{Mn}^{3+}$  concentration was raised from  $0.15 \times 10^{-3} \text{M}$  to  $3 \times 10^{-3} \text{M}$  due to decreasing AGU/ $\text{Mn}^{3+}$  ratios. The decrease was more pronounced between  $0.15 \times 10^{-3} \text{M}$  and  $2 \times 10^{-3} \text{M}$  of  $\text{Mn}^{3+}$ . The average molecular weights of grafts ranged between 245,000 and 400,000. A decreasing tendency of the molecular weights was, however, observed between  $\text{Mn}^{3+}$  concentrations of  $1 \times 10^{-3} \text{M}$  and  $2 \times 10^{-3} \text{M}$ . This may be explained by slower propagation rates caused by the decreasing ratio of monomer to the total number of initiation sites on the starch substrate with increasing  $\text{Mn}^{3+}$  concentration. For  $\text{Mn}^{3+}$  concentrations from 2 to  $3 \times 10^{-3} \text{M}$  the values for molecular weight and frequency of grafts are within experimental errors constant.

The effect of the amount of starch used in grafting AN onto gelatinized starch was studied by a twofold variation of the starch concentration (5, 7.5, and 10.0 g on a dry basis). Figure 5 depicts that conversion of AN monomer to PAN increased from 60.8% to 83.7% as the amount of starch was increased from 5 to 10 g, whereas % add-on decreased from 58.7% to 49.2% in the same range. The increase in monomer conversion as amount of starch is increased appears to be due to a larger number of initiation sites leading to grafting. The % add-on shows a decreasing tendency with increasing amounts of starch. This is simply because the monomer starch ratio decreases when the amount of starch charged increases.



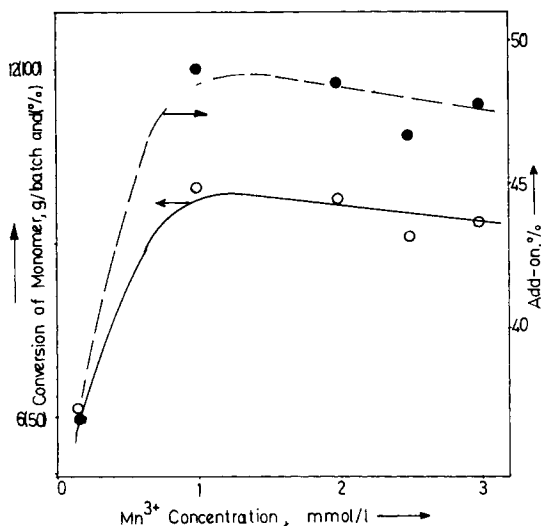


Fig. 3. Total conversion of monomer (—○—) and % add-on (—●—) in grafting of AN onto starch. Reaction conditions: starch substrate = 10 g (dry basis);  $[\text{H}_2\text{SO}_4] = 85.8 \times 10^{-3}M$ ; acrylonitrile (15 ml) = 12 g;  $[\text{Na}_4\text{P}_2\text{O}_7] = 10 \times 10^{-3}$ ; reaction time, 3 hr; reaction temperature, 30°C; starch pre-treatment temperature, 85°C.

A similar observation was reported in connection with grafting to granular potato starch.<sup>3</sup>

A twofold increase in starch/ $\text{Mn}^{3+}$  ratio produced only 15% less frequent grafts, i.e., AGU/chain increased only 15%, as shown in Figure 6. The starch/monomer (AN) ratio also increased twofold, which accounts for the lower molecular weights at higher amounts of starch charged. The  $\text{Mn}^{3+}$  complex is more efficiently used as initiator at high starch concentrations. The AGU/chain values are relatively constant (Fig. 6), which means that the number of grafting sites per starch molecule is rather independent of the starch/initiator ratio at the  $\text{Mn}^{3+}$  concentrations used. This means further that the increase in total number of grafts with increasing amounts of starch is large enough to more than overcome the decrease in molecular weights of grafts. This explanation appears to be consistent with the observation that total conversion increases with increasing amounts of starch charged (Fig. 5). A similar observation was reported previously in connection with grafting to granular starch.

Although our attempts to graft styrene onto starch slurries by manganic pyrophosphate initiation were unsuccessful, we found that styrene together with a readily polymerizable monomer such as acrylonitrile could easily be grafted onto native and oxidized maize starch. This work, together with grafting onto starch slurries of some other monomers such as acrylamide and methyl methacrylate, will be reported in our next paper.

### CONCLUSIONS

The results presented in this paper show that manganic pyrophosphate, in a wide range of reaction conditions, is an efficient initiator for grafting of acrylonitrile (AN) to gelatinized potato starch. Only small amounts of PAN were extractable as homopolymer.

Average molecular weight of grafts and frequency of grafts (number of anhy-

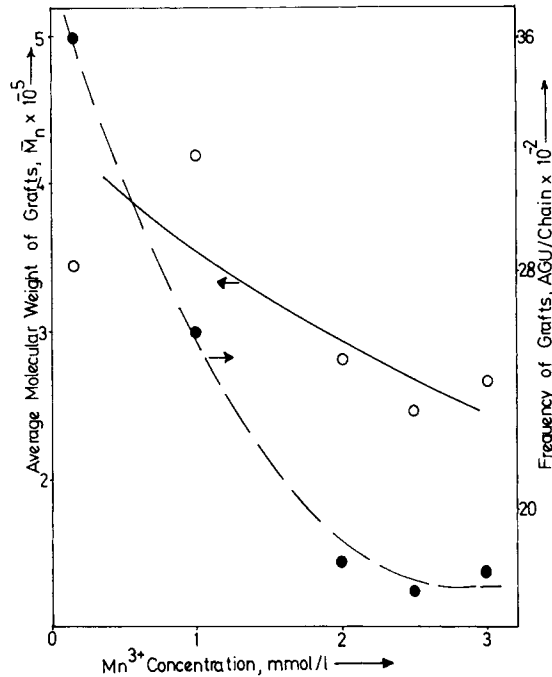


Fig. 4. Average molecular weight of grafts (—○—) and frequency of grafts (—●—) in grafting of AN onto starch. Reaction conditions: starch substrate = 10 g (dry basis);  $[\text{H}_2\text{SO}_4] = 85.8 \times 10^{-3}M$ ; acrylonitrile (15 ml) = 12 g;  $[\text{Na}_4\text{P}_2\text{O}_7] = 10 \times 10^{-3}M$ ; reaction time, 3 hr; reaction temperature, 30°C; starch pretreatment temperature, 85°C.

droglucose units per grafted chain) are increased approximately tenfold by swelling and gelatinizing the starch. In this respect our observations with manganic pyrophosphate initiation are similar to those reported for  $\text{Ce}^{4+}$  initiation.<sup>1</sup> Almost all grafting parameters can be varied substantially by varying the concentration ratio of initiator ( $\text{Mn}^{3+}$ ) to starch in grafting of acrylonitrile to gelatinized starch.

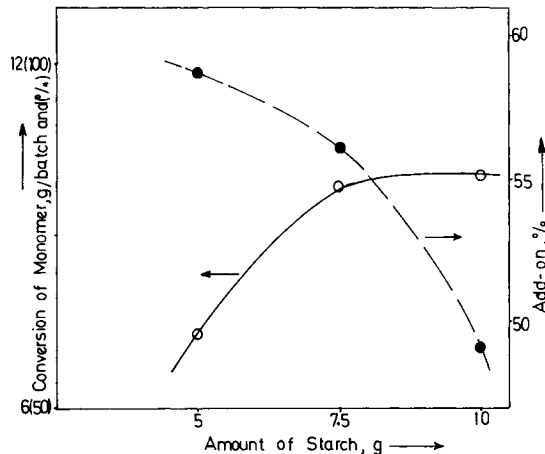


Fig. 5. Total conversion of monomer (—○—) and % add-on (—●—) in grafting of AN onto starch. Reaction conditions:  $[\text{Mn}^{3+}] = 1 \times 10^{-3}M$ ;  $[\text{H}_2\text{SO}_4] = 85.8 \times 10^{-3}M$ ; acrylonitrile (15 ml) = 12 g;  $[\text{Na}_4\text{P}_2\text{O}_7] = 10 \times 10^{-3}M$ ; reaction time, 3 hr; reaction temperature, 30°C; starch pretreatment temperature, 85°C.

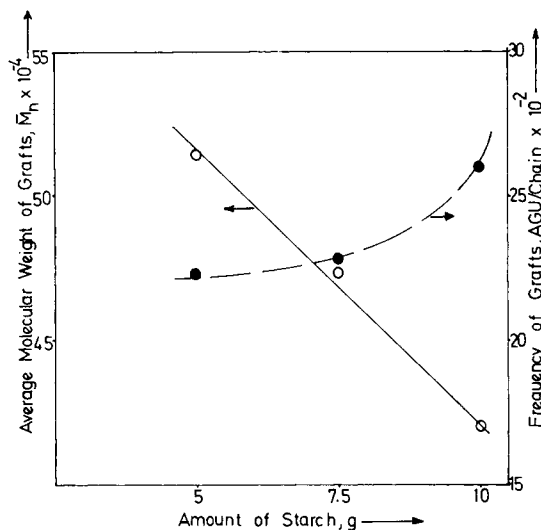


Fig. 6. Average molecular weight of grafts (—○—) and frequency of grafts (—●—) in grafting of AN onto starch. Reaction conditions:  $[\text{Mn}^{3+}] = 1 \times 10^{-3}M$ ;  $[\text{H}_2\text{SO}_4] = 85.8 \times 10^{-3}M$ ; acrylonitrile (15 ml) = 12 g;  $[\text{Na}_4\text{P}_2\text{O}_7] = 10 \times 10^{-3}M$ ; reaction time, 3 hr; reaction temperature,  $30^\circ\text{C}$ ; starch pretreatment temperature,  $85^\circ\text{C}$ .

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