

# Graft Copolymerization Onto Starch. I. Complexes of $Mn^{3+}$ as Initiators

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## Synopsis

Advantages in using the pyrophosphate complex of trivalent manganese over the sulfate complex as initiator for graft copolymerization onto starch are discussed. The first successful attempts to graft copolymerize acrylonitrile, methyl methacrylate, and acrylamide to starch and starch derivatives are described using manganic pyrophosphate as initiator. Selective solvent extraction of the reaction products and very low conversions of monomer to homopolymer in absence of starch substrates provide evidence for high grafting efficiencies obtained with acrylonitrile and methyl methacrylate. With acrylamide as monomer, however, low grafting efficiencies and considerable amounts of homopolymer are obtained under the experimental conditions investigated. Reaction mechanisms responsible for initiation of graft copolymerization are discussed. These are (a) glycol cleavage in the anhydroglucose units by  $Mn^{3+}$  ions leading to formation of a radical, and (b) enolization and further oxidation of oxidized starch by  $Mn^{3+}$  ions also leading to radical species. Mechanisms are also proposed for homopolymerization through  $Mn^{3+}$  oxidation of enols which probably are formed by "vinylous" addition of water molecules to acrylamide and methyl methacrylate.

## INTRODUCTION

The attainment of high grafting efficiencies in graft copolymerization is a problem of paramount importance. Grafting of vinyl monomers onto starch has been the subject of extensive investigations by several research groups using tetravalent cerium as initiator.<sup>1</sup> They obtained high grafting efficiencies with hydrophobic monomers such as acrylonitrile and methyl methacrylate.

As a result of these investigations, hydrolyzed starch-polyacrylonitrile graft copolymers (called H-SPAN) were developed.<sup>2</sup> These products have extremely high water absorbencies and, therefore, hold industrial promise for the future.

Singh et al.<sup>3</sup> have reported the use of  $Mn^{3+}$  ions as initiator for grafting to polysaccharides. Due to the instability and disproportionation of these ions in sulfuric acid media of low acidities<sup>4</sup> according to the reaction (1)



the use of the sulfate complex of  $Mn^{3+}$  introduces a problem. Because of the high acidities necessary to prevent disproportionation, acidic hydrolysis of carbohydrate chains may occur during the grafting reactions. In spite of the high specificity of attack of  $Mn^{3+}$  ions,<sup>4</sup> Patra et al.<sup>5</sup> obtained low grafting efficiencies

in grafting of vinyl monomers to amylose using the sulfate complex of  $Mn^{3+}$  ions. This may be explained by a substantial simultaneous acidic hydrolysis of the carbohydrate chains during the grafting reaction. This would lead to an extraction of a larger fraction of the reaction product by the solvent for homopolymer than would occur in the absence of hydrolysis. Furthermore, there is also a possibility for "vinylogous" addition of water molecules to the acrylate and methacrylate monomers at such high acidities. This could lead to homopolymerization by oxidation of the enol so formed (a mechanism similar to scheme III).

On the other hand, the pyrophosphate complex of  $Mn^{3+}$  ions is stable to disproportionation and exists as  $[Mn(H_2P_2O_7)_3]^{3-}$ . It can be prepared by the oxidation of  $Mn^{2+}$  ions by  $Mn^{7+}$  ions in the presence of an excess of pyrophosphate and can conveniently be used as a one-equivalent oxidant in the pH range of 1 to 6. Studies of low molecular weight organic compounds<sup>4</sup> indicate a high specificity of attack of manganic pyrophosphate on certain organic substrates, such as glycols, aldehydes, and ketones, in spite of the inactivity of this reagent toward olefinic compounds such as vinyl monomers. Polymerization of vinyl monomers in the glycol cleaving reactions of this complex has been used as evidence for the formation of free radicals.<sup>11</sup> A patent describes<sup>7</sup> grafting of vinyl monomers to cellulose and cellulose derivatives.

This communication reports the first successful attempt to graft copolymerize vinyl monomers onto starch and, in particular, the synthesis of starch-polyacrylonitrile graft copolymers using the pyrophosphate complex of trivalent manganese as initiator.

## EXPERIMENTAL

### Materials

Most chemicals were analytical grade reagents from Merck, Darmstadt, Germany. Anhydrous magnesium sulfate (Mallinckrodt, USA) and sodium hydroxide (EKA, Sweden) were of analytical grade. Hydroquinone (Carlo Erba, Italy) was reagent grade. Native potato starch and other starch derivatives used in the grafting reactions were supplied by AB Stadex, Sweden. Acrylonitrile (Synthetic Grade, Merck) and methyl methacrylate (Kebo, Sweden), however, contained monomethyl ether of hydroquinone as inhibitor, which was removed using aqueous alkali. The monomers were then dried with anhydrous magnesium sulfate and stored in the dark at 4°C. Acrylamide (Eastman Kodak, USA) was used as received.

### Preparation of the Initiator

Five milliliters of a solution of  $Mn^{2+}$  ions prepared by dissolving 0.876 g  $MnSO_4 \cdot H_2O$  in 100 ml distilled water was added to a solution of 2.890 g sodium pyrophosphate ( $Na_4P_2O_7 \cdot 10H_2O$ ) in 50 ml distilled water. The pH of the resulting solution was adjusted to 6 by adding concentrated  $H_2SO_4$  using a Beckman Expandomatic pH Meter. The pH values of the solutions were checked against standard buffers supplied by Merck. The  $Mn^{2+}$  ions were then oxidized to  $Mn^{3+}$  ions by titrating potentiometrically with  $Mn^{7+}$  ions (obtained by dis-

solving 0.205 g  $\text{KMnO}_4$  in 100 ml distilled water) by the method of Lingane and Karplus<sup>6</sup> using a Metrohm EA 201 platinum electrode. About 5 ml of the permanganate solution was required. A glass electrode was used for all pH measurements with a saturated Calomel electrode as reference.

### Graft Copolymerization

Five milliliters 95–97%  $\text{H}_2\text{SO}_4$  (Merck, pro analysi) was added to 1.05 l distilled water. Native potato starch or a starch derivative, 7.5 g (on a moisture free basis), was slurried together with 100 ml of the acidified distilled water 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 with a nitrogen bubbler. The initiator solution (pH = 6), 25 ml, and 10 ml purified acrylonitrile (AN) were added to the dropping funnel. A brisk stream of oxygen-free nitrogen was bubbled first through the contents of the dropping funnel and then through the starch slurry in the reaction vessel before the gas was led out of the system. This was continued for 30 min while the temperature in the reaction vessel was raised to 30°C. The content of the dropping funnel was then emptied into the reaction vessel and the reaction carried out under a slow stream of  $\text{N}_2$  gas for 75 min. The polymerization was terminated by adding 0.5 g hydroquinone dissolved in 25 ml distilled water. The products were filtered, thoroughly washed with water, and dried overnight in a stream of dry air at 60°C.

Nearly 10 g of the acrylonitrile-grafted product was extracted with 500 ml  $\text{N,N}$ -dimethylformamide (henceforth referred to as DMF) at room temperature. After 30 hr of extraction, the products were centrifuged and 50 ml of the clear extract added to 450 ml methanol to precipitate the homopolymer. The extracted product was thoroughly washed with water and ethanol and dried in air at 60°C. The graft copolymer, 2 g, was then refluxed for 2 hr in 200 ml 1M  $\text{H}_2\text{SO}_4$  to remove the starch moiety. The PAN slurry was then filtered, washed with water and ethanol, and dried in air at 60°C. Viscosity measurements were conducted in DMF at 25°C and the molecular weights of the grafted chains of PAN estimated from eq. (2) with the parameters from reference 8:

$$[\eta] = 3.92 \times 10^{-4} (\bar{M}_n)^{0.75} \quad (2)$$

In the case of methyl methacrylate (MMA), the procedure was the same as for AN, but the products were moistened<sup>9</sup> with distilled water to a moisture content of around 25% before extraction with 1,2-dichloroethane. The molecular weight was estimated by viscosity measurements in benzene at 30°C.<sup>10</sup>

When grafting acrylamide, the only difference in the polymerization procedure was that the monomer (a powder) was added to the reaction vessel containing the starch slurry in acidified water in the beginning and the initiator solution later using the dropping funnel. After termination of the polymerization reactions, the products were centrifuged and a portion of the clear solution was precipitated in methanol to determine the amount of homopolymer formed (polyacrylamide is water soluble). The % add-on was determined by the increase in weight of the starch after extraction of the grafted product expressed as per cent of the weight of the graft-copolymer. Molecular weight determinations in this case have not yet been carried out and shall be reported later.

## RESULTS AND DISCUSSION

The definitions of grafting parameters agree with those of reference 1 and are as follows:

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 (or AGU) separating each grafted branch

The copolymerization results are presented in Table I. Initially, we encountered problems regarding reproducibility and obtained deviations of around 20% in the product yields. This was probably due to inefficient removal of O<sub>2</sub> from the system. However, a dropping funnel with a N<sub>2</sub> bubbler eliminated the deviations since all operations were then conducted under sufficiently pure atmosphere of N<sub>2</sub>. Experiments 1, 2, and 3 (carried out under exactly the same conditions) demonstrate good reproducibility of our results. Experiments 4 to 7 were not repeated. Kjeldahl analyses of nitrogen for determinations of “% add-on” and “product yields” were not conducted for this set of experiments, because earlier analyses were in excellent agreement with the values obtained by gravimetric measurements.

Extraction of nearly 10 g of the reaction products by 500 ml of DMF (in case of AN) removed only negligible amounts of synthetic polymer. Thus, the inability of DMF, a good solvent for PAN (homopolymer) but a bad solvent for the graft copolymer, to extract any considerable amount of PAN from the reaction products is highly indicative of the chemical attachment of the PAN chains to starch. This is proof of the high grafting efficiencies obtained with this initiating system. A very low conversion of AN to PAN (4.4%) under exactly the same conditions, but in the absence of starch substrate as compared to conversions to polymer of the order of 75% in the presence of substrate, is presented as additional evidence for the high-grafting efficiency. In the case of MMA, no polymerization was observed in the absence of substrate. The slightly lower grafting efficiency obtained with MMA (expt. 6, Table I) compared with PAN could be due to chain transfer to MMA monomer during the polymerization. The high average molecular weight of the grafted PMMA chain may be due to slow rate of termination of the MMA chain radicals. Such effects are expected since the methyl group on the  $\alpha$ -carbon atom in MMA would impose steric hindrance to the oxidation by Mn<sup>3+</sup> ions as compared with the oxidation of AN chain radicals by Mn<sup>3+</sup> ions. Other normal termination reactions, such as disproportionation and coupling, may also influence the systems.

Furthermore, acrylonitrile is not compatible with its polymer, and therefore polymerization would take place in the aqueous phase or on the substrate. Methyl methacrylate, on the other hand, has a high affinity for its polymer, which means that the polymerization would occur in the polymer phase to a large extent. As a result, the availability of Mn<sup>3+</sup> ions for termination would be much higher for AN chain radicals than for MMA chain radicals.

With acrylamide, a fairly low “% add-on” and a much higher homopolymer content were obtained. The conversion of acrylamide to polyacrylamide in the presence of native potato starch was 30.9%. Furthermore, in the absence of any

TABLE I  
Graft Copolymerization of Vinyl Monomers Onto Starch and Starch Derivatives Initiated by Manganic Pyrophosphate<sup>a</sup>

| Expt. no. | Substrate            | Monomer             | Product yield, g | Conversion of monomer to polymer, g/batch and (%) | Homo-polymer, % of total synthetic polymer formed | Grafting efficiency, % <sup>b</sup> | % Add-on <sup>b</sup> | Molecular weight of grafted chains $\bar{M}_n$ | Frequency of grafts, AGU/chain |
|-----------|----------------------|---------------------|------------------|---------------------------------------------------|---------------------------------------------------|-------------------------------------|-----------------------|------------------------------------------------|--------------------------------|
| 1         | Native potato starch | Acrylonitrile       | 13.6             | 6.10 (75.3)                                       | 4.9                                               | 95.1                                | 44.7                  | 86,000                                         | 650                            |
| 2         | Native potato starch | Acrylonitrile       | 13.75            | 6.25 (77.2)                                       | 4.4                                               | 95.6                                | 45.3                  | 87,900                                         | 655                            |
| 3         | Native potato starch | Acrylonitrile       | 13.78            | 6.20 (76.5)                                       | 4.2                                               | 95.8                                | 45.0                  | 83,500                                         | 640                            |
| 4         | Farinex A90          | Acrylonitrile       | 13.0             | 5.5 (67.9)                                        | 5.9                                               | 94.1                                | 40.9                  | 112,200                                        | 997                            |
| 5         | Posamyl E            | Acrylonitrile       | 13.15            | 5.65 (69.7)                                       | 6.8                                               | 93.2                                | 41.6                  | 190,500                                        | 1648                           |
| 6         | Native potato starch | Methyl Methacrylate | 12.4             | 4.90 (52.1)                                       | 13.3                                              | 86.7                                | 36.2                  | $2.5 \times 10^6$                              | 27,250                         |
| 7         | Native potato starch | Acrylamide          | 9.31             | 3.09 (30.9)                                       | 41.4                                              | 58.6                                | 19.4                  | —                                              | —                              |

<sup>a</sup> Starch substrate: 7.50 g (dry basis); monomer: acrylonitrile (10 ml = 8.1 g); methyl methacrylate (10 ml = 9.4 g); acrylamide = 10 g; ( $M_n^{3+}$ ) =  $1.08 \times 10^{-3}$  m/l.; ( $Na_4P_2O_7$ ) =  $21.6 \times 10^{-3}$  m/l.; ( $H_2SO_4$ ) =  $68.61 \times 10^{-3}$  m/l.; reaction time = 75 min; temperature = 30°C. Farinex A 90 and Posamyl E are commercial names of hypochlorite oxidized and quaternary cation derivatives of native potato starch, respectively, manufactured by AB Stalex, Sweden.

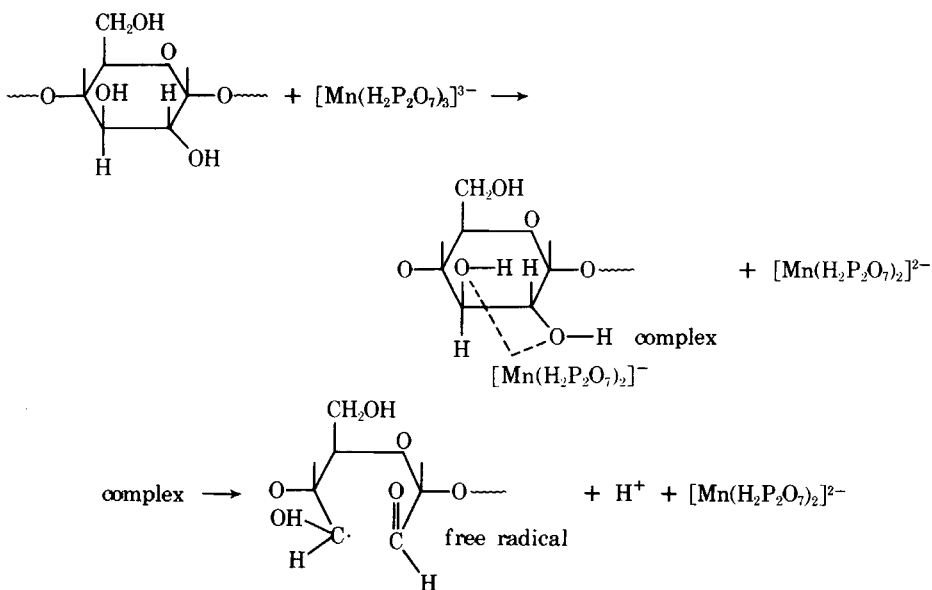
<sup>b</sup> Definition by G. F. Fanta.<sup>1</sup>

substrate, the conversion to polyacrylamide under otherwise exactly similar conditions was 21.6%. An interesting observation (not tabulated in Table I) was that, when oxidized starch (Farinex A 90) was used as the substrate with acrylamide, the temperature in the reaction vessel rose from 30° to 38°C within a few minutes of adding the initiator from the dropping funnel, and the conversion of monomer to polymer at the end of the 75-min reaction period was 87%. However, most of this polymer was soluble in water, and a highly viscous product was obtained. It is possible that most of this polymer is a graft copolymer which had been solubilized on account of its high % add-on.

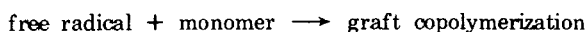
Two reaction mechanisms are presented to account for the synthesis of starch graft copolymers:

(a) Cleavage of glycol groups<sup>4</sup> of the anhydroglucose units in amylose and amylopectin by manganic pyrophosphate (scheme I) where the dissociation of the glycol-Mn<sup>3+</sup> complex should be the rate determining step:

Initiation:



Propagation:

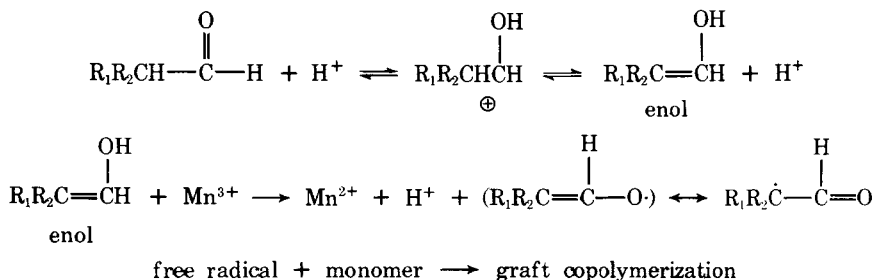


Termination:



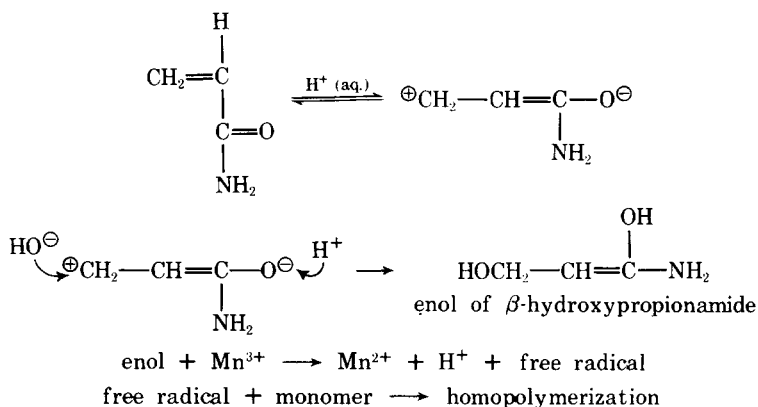
Scheme I: glycol cleavage mechanism with Mn<sup>3+</sup> ions leading to initiation of graft copolymerization

(b) Oxidation of carbonyl groups present in oxidized starch (Farinex A 90). Oxidation through enolization would be the intermediate step in this case,<sup>13</sup> as shown below in scheme II. Aldehydic, ketonic, and carboxyl groups present in oxidized starch are all capable of undergoing enolization. The mechanism for oxidation of an aldehydic group is shown below:



Scheme II: enolization of oxidized starch and subsequent oxidation with  $\text{Mn}^{3+}$  ions leading to initiation of graft copolymerization

Our observations on the polymerization of vinyl monomers in the absence of starch substrates were rather unexpected due to the known inactivity of  $\text{Mn}^{3+}$  ions with vinyl monomers.<sup>4</sup> However, Land and Waters<sup>12</sup> have found that acrolein (acrolein),  $\alpha$ -methacraldehyde ( $\alpha$ -methylacrolein), and crotonaldehyde could easily be oxidized by manganic pyrophosphate. In case of acrylamide, initiation of polymerization in the absence of any substrate may proceed through the oxidation of the enol of  $\beta$ -hydroxypropionamide formed by vinylogous addition of a water molecule to the monomer catalyzed by  $\text{H}^+$  ions (scheme III):



Scheme III: proposed mechanism for homopolymerization of acrylamide by  $\text{Mn}^{3+}$  initiation

With acrylonitrile, the mechanism is not yet clear. With MMA, no conversion to polymer was observed in the absence of starch substrates. This observation may be understood, considering that the methyl group (on the  $\alpha$ -carbon atom) through its inductive effect (electron donating) would decrease the chances of acid-catalyzed vinylogous addition by partly compensating the polar effect of the carbonyl group. Besides, it is known that  $\alpha$ -methacraldehyde is oxidized much more slowly than crotonaldehyde.<sup>12</sup> Thus, it is not surprising that methyl methacrylate (an  $\alpha$ -carbon-substituted vinyl monomer) was less susceptible to attack by  $\text{Mn}^{3+}$  ions than vinyl monomers unsubstituted at the  $\alpha$ -carbon atom (e.g., acrylonitrile and acrylamide). The effect of reaction conditions (acidity, free pyrophosphate concentration, monomer-to-substrate ratio, and  $\text{Mn}^{3+}$  concentration) on grafting to both native and oxidized starches by vinyl monomers is being investigated and shall be reported in forthcoming papers.

## CONCLUSIONS

Using the manganic pyrophosphate initiation method as described in this paper, the results show that grafting efficiencies and polymer yields are high when starch and starch derivatives are grafted with acrylonitrile and methyl methacrylate. The results compare favorably with those obtained with  $Ce^{4+}$  ions as initiators.<sup>1</sup> With acrylamide, however, lower grafting efficiencies and considerable amounts of homopolymer are obtained under the experimental conditions investigated. This has been attributed to the oxidation of enol of  $\beta$ -hydroxypropionamide by  $Mn^{3+}$  ions.

The average molecular weights of the grafted synthetic polymer chains were of the order of  $10^5$  for acrylonitrile and of the order  $10^6$  for methyl methacrylate as monomer. Consequently, the average number of anhydroglucose units (AGU) separating the grafted chains was in the range of 600–1600 for acrylonitrile and over 25,000 for methyl methacrylate.

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