Graft Copolymerization onto Starch. IV. Grafting of Methyl Methacrylate to Granular Native Potato Starch by Manganic Pyrophosphate Initiation

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Synopsis

A study has been made of graft copolymerization of methyl methacrylate onto native potato starch in aqueous slurry at 30°C. As Mn^{3+} concentration was increased from $0.15 \times 10^{-3}M$ to $1.0 \times 10^{-3}M$, conversion of monomer to polymer and add-on of polymer to starch increased and frequency of grafts (anhydroglucose units per grafted chain) decreased sharply. The average molecular weights of the PMMA grafts also decreased in this range. At Mn^{3+} concentrations from $1.0 \times 10^{-3}M$ to $3.0 \times 10^{-3}M$, only minor changes in grafting parameters were observed. When the amount of starch charged per batch was increased threefold, the add-on decreased sharply, the molecular weight increased slightly, and the conversion of MMA monomer to polymer remained almost constant. The increase in frequency of grafts (AGU/chain) was almost directly proportional to the increase in the amount of starch charged. In all cases the average molecular weights of grafts were of the order of 10^6 and the grafting efficiencies high, normally greater than 85%. These results were compared with those previously obtained for grafting of acrylonitrile onto starch. They were interpreted in terms of initial $(Mn^{3+})/(AGU)$ ratio, total number of radicals initiating grafting, and compatibility of methyl methacrylate monomer with poly(methyl methacrylate) chains.

INTRODUCTION

For previous work on grafting of methyl methacrylate onto starch and starch derivatives by Ce^{4+} ions and other initiating systems, e.g., Fe^{2+}/H_2O_2, the reader is referred to a review by Fanta[1] and other recent papers.[2,3] The definitions of grafting parameters, i.e., grafting efficiency, % add-on, and frequency of grafts (AGU/chain), are the same as given previously.[1,2,4-6]

We found that manganic pyrophosphate is an efficient initiator for grafting hydrophobic monomers such as acrylonitrile and methyl methacrylate[4-6] to starch. The previous paper in this series dealt with grafting of acrylonitrile to gelatinized starch.[6] We found that gelatinizing the starch increased the average molecular weight of PAN grafts by a factor of nearly 10 and proportionally less frequent grafts, i.e., higher value of AGU/chain, were obtained. It was also found that % add-on and frequency of grafts (AGU/chain) could be varied substantially by varying Mn^{3+} and starch concentrations.

The potential use and technical importance of biodegradable plastics and films has recently been reviewed by Otey.[7] Although unmodified starch has been incorporated as a filler in poly(vinyl chloride) (PVC)–dioctyl phthalate (DOP) plastics to render the PVC plastic products biodegradable,[8] the use of unmodified starch, which is hydrophilic, suffers from the drawback of having poor compatibility with the PVC resin, which is hydrophobic. Compatibility of starch fillers with synthetic resins has been increased by grafting[3] hydrophobic monomers

such as acrylonitrile and methyl methacrylate onto granular starch by Ce^{4+} initiation. High-strength plastic products were obtained with PVC resins filled with such graft copolymers, and these products appear to have industrial significance.

Grafting of acrylonitrile to starch and starch derivatives in granular and gelatinized form by Mn^{3+} initiation has already been studied.[4-6] This paper extends our work on manganic pyrophosphate initiation to grafting of methyl methacrylate onto native potato starch under different reaction conditions.

EXPERIMENTAL

Materials

Most chemicals used were analytical-grade reagents from Merck, Darmstadt, Germany, except anhydrous magnesium sulfate from Mallinckrodt, U.S.A., and sodium hydroxide from EKA, Sweden, both of analytical grade. The granular native potato starch used in the grafting reactions was supplied by AB Stadex, Malmö, Sweden. The methyl methacrylate (synthetic grade from Merck) contained hydroquinone as inhibitor, which was removed using aqueous alkali. The monomer was then dried with anhydrous magnesium sulfate, distilled under reduced pressure of N_2, and stored in the dark at 4°C.

Preparation of Initiator

Concentrations of $MnSO_4 \cdot H_2O$ and $KMnO_4$ solution 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 6.69 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 concentrated H_2SO_4 and 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 an aqueous $KMnO_4$ solution (Mn^{7+} ions) by the method of Lingane and Karplus[9] according to reaction (1):

$$4Mn^{2+} + Mn^{7+} \rightarrow 5Mn^{3+} \tag{1}$$
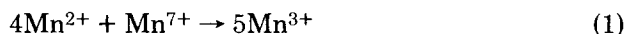
A Metrohm EA 201 platinum electrode was used for all titrations. The weight of $KMnO_4$ dissolved in 100 ml distilled water corresponded to the desired concentration of Mn^{3+} ions in the reaction vessel in accordance with Table I. About 25 ml of the permanganate solution was required for each 25-ml batch of $MnSO_4$ solution. A total of 300 ml of initiator solution of each Mn^{3+} concentration was

TABLE I
Quantities of $MnSO_4 \cdot H_2O$ and $KMnO_4$ for the Preparation of the
Manganic Pyrophosphate Initiator

$MnSO_4 \cdot H_2O$ per 100 ml aqueous solution, g	0.1217	0.4057	0.8113	1.623	2.434
$KMnO_4$ per 100 ml aqueous solution, g	0.0285	0.095	0.1897	0.379	0.569
Resulting concentration of Mn^{3+} in reaction vessel, mmole/l.	0.15	0.5	1.0	2.0	3.0

prepared; 25 ml of such a solution was used as initiator in each grafting 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 (7.5, 10, 15, or 20 g on a moisture-free basis) was slurried in 100 ml acidified water, prepared by adding 5 ml 96% H_2SO_4 (Merck, pro analysi) to 900 ml 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. A 25-ml portion of the initiator solution (pH 6) of the total 300 ml prepared as previously described and corresponding 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 methyl methacrylate (MMA).

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., the manganic pyrophosphate initiator and methyl methacrylate 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 reaction vessel was maintained between 30° and 32°C by cooling the water bath with added ice. After termination of the polymerization by letting air into the vessel, the reaction product was filtered, thoroughly washed with water and ethanol, and dried overnight in a stream of dry air at 60°C.

Nearly 10 g of the methyl methacrylate grafted product was extracted with 500 ml 1,2-dichloroethane after moistening the products with distilled water to a moisture content of around 25%.[10] After 72 hr of extraction at room temperature, 50 ml of the clear extract was added to 300 ml methanol to precipitate the homopolymer. In some cases the homopolymer precipitate was analyzed to determine the PMMA content from the % C of the precipitate. The extracted product was thoroughly washed with water and ethanol and dried in air at 60°C. Nearly 2 g of the graft copolymer was then refluxed for 2 hr in 200 ml $1M$ H_2SO_4 to remove the starch moiety. The PMMA so recovered was filtered, washed with water and ethanol, and dried in air at 60°C. Viscosity measurements were conducted in benzene at 30°C and the average molecular weight of the PMMA chains was estimated from eq. (2) with the parameters from reference 11:

$$[\eta] = 8.69 \times 10^{-5} \, \overline{M}_n^{0.76} \tag{2}$$

RESULTS AND DISCUSSION

Three experiments were conducted under identical conditions, and the results are shown in Table II. The reproducibility of these experiments within 10% appears to be adequate for our purposes. Experiments conducted under other conditions were not repeated. It was of interest to see how the grafting parameters would vary with Mn^{3+} and starch concentrations. Keeping the total pyrophosphate concentration constant at $10 \times 10^{-3} M$, the initial Mn^{3+} concen-

TABLE II
Reproducibility of the Grafting Reactions[a]

Expt. no.	Product yield, g	Conversion of monomer to polymer, g/batch and %	Grafting efficiency, %	% Add-on	Average molecular weight $\overline{M}_n$ of grafted chains	Frequency of grafts (AGU/chain)
1	37.8	17.8 (75.7)	86.4	40.7	935,000	8408
2	36.9	16.9 (71.9)	88	40.3	874,000	7989
3	38.4	18.4 (78.3)	85.8	41.1	1,102,000	9750

[a] Starch substrate = 20 g potato starch (dry basis); $[H_2SO_4] = 80 \times 10^{-3}M$; methyl methacrylate = 25 ml = 23.58 g; $[Na_4P_2O_7] = 10 \times 10^{-3}M$; reaction time = 3 hr; temperature = 30°C; $[Mn^{3+}] = 2.0 \times 10^{-3}M$.

tration was varied from $0.15 \times 10^{-3}M$ to $3.0 \times 10^{-3}M$. The concentration of anhydroglucose units was varied by increasing the amount of starch charged per batch from 7.5 to 20 g on a moisture-free basis. The acidity was kept constant at $80 \times 10^{-3}M$ H_2SO_4, and 25 ml (23.58 g) methyl methacrylate monomer was used for grafting each batch.

Extraction of almost all products by 1,2-dichloroethane, a good solvent for PMMA homopolymer but a poor solvent for the starch–PMMA graft copolymer, dissolved only small amounts of the products, the amounts being between 0.1 and 0.6 g from nearly 10 g of the products. Thus, the grafting efficiencies were high in all these cases and varied between 85% and 99%. This indicated that
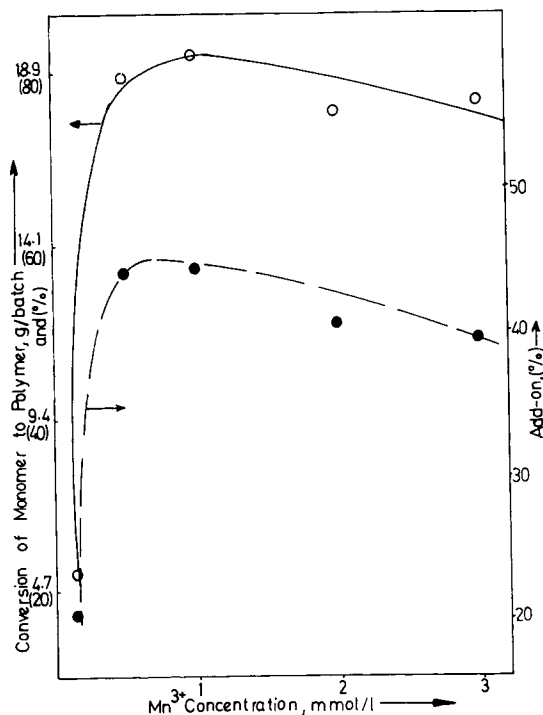

Fig. 1. Total conversion of monomer (——) and % add-on (- - -) in grafting of MMA onto starch. Reaction conditions: starch substrate = 20 g (dry basis); $[H_2SO_4]$ = 80 mmol/l.; methyl methacrylate = 25 ml = 23.58 g; $[Na_4P_2O_7] = 10 \times 10^{-3}M$; reaction time = 3 hr; temperature = 30°C.
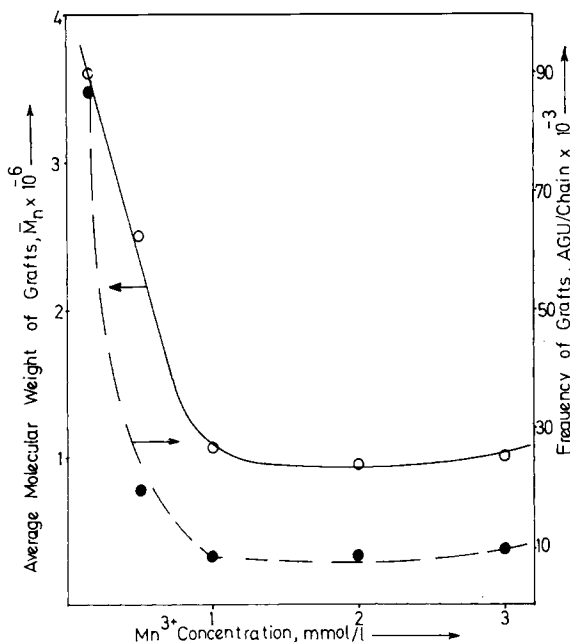
Fig. 2. Average molecular weight of grafts (———) and frequency of grafts (- - -) in grafting of MMA onto starch. Reaction conditions: starch substrate = 20 g (dry basis); [H_2SO_4] = 80 mmole/l.; methyl methacrylate = 25 ml = 23.58 g; [$Na_4P_2O_7$] = 10 × $10^{-3}M$; reaction time = 3 hr; temperature = 30°C.

PMMA was mainly chemically attached to the starch substrate with little homopolymer.   In one case, when the amount of starch was 7.5 g and the reaction was carried out under the conditions given in Figures 3 and 4, a grafting efficiency of 77.4% was obtained.   It was assumed that 1,2-dichloroethane had dissolved some graft copolymer due to high add-on in addition to the PMMA homopolymer.   In order to confirm this, a portion of the clear 1,2-dichloroethane extract was precipitated by pouring into an excess methanol, and the precipitate dried and analyzed for % C.   A value of 55.1% was obtained, corresponding to nearly 33% starch.   Thus, by assuming that all PMMA in this precipitate was present as homopolymer, a grafting efficiency of 83.5% was obtained.   A similar analysis for % C in experiment 2, Table II, indicated that the precipitate of 1,2-dichloroethane extract contained nearly 15% starch.   A grafting efficiency of 88% was obtained by assuming that the precipitate from 1,2-dichloroethane consisted purely of 100% PMMA.

Another observation supporting high grafting efficiencies in synthesis of starch–PMMA graft copolymers is the inability of manganic pyrophosphate solutions to initiate homopolymerization of MMA to PMMA in the absence of a suitable oxidizable substrate.[12]

In general, the grafting efficiencies in synthesis of starch–PMMA graft copolymers are lower than those for starch–PAN graft copolymers as reported earlier.[4-6]   This appears to be due to higher rates of termination of the growing grafted chains to monomer for the former than for the latter case.   This is explained by the fact that the growing PMMA chains are more compatible with MMA monomer than PAN chains with AN monomer in aqueous polymerizations of these monomers.[13]
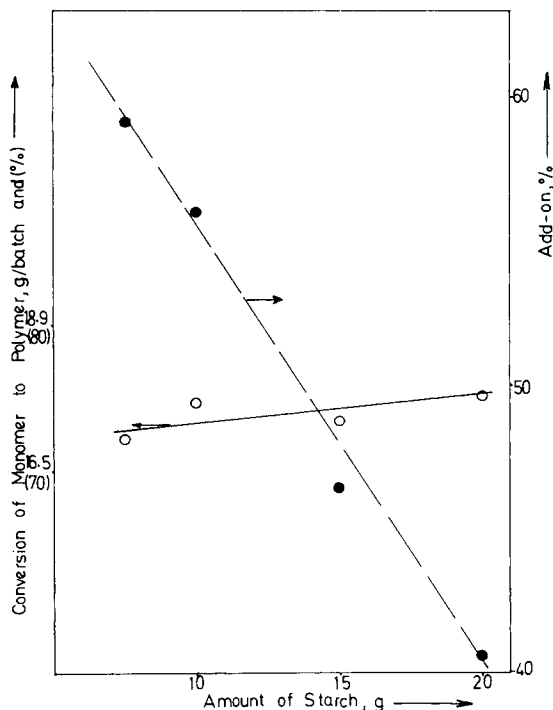
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Fig. 3. Total conversion of monomer (———) and % add-on (- - -) in grafting on MMA onto starch. Reaction conditions: $[Mn^{3+}]$ = 2.0 × $10^{-3}M$; $[H_2SO_4]$ = 80 × $10^{-3}M$; methyl methacrylate = 25 ml = 23.58 g; $[Na_4P_2O_7]$ = 10 × $10^{-3}M$; reaction time = 3 hr; temperature = 30°C.

The initial initiator concentration was varied from 0.15 × $10^{-3}M$ to 3.0 × $10^{-3}M$, and the variations in conversion of monomer to polymer and % add-on are shown in Figure 1. At Mn^{3+} concentrations between 0.15 × $10^{-3}M$ and 1.0 × $10^{-3}M$, a sharp increase in conversion of monomer to polymer was obtained. In this range, the average molecular weight of the grafts decreased by a factor of 3–4. This indicates that the increased conversion of monomer with increasing Mn^{3+} concentration between 0.15 × $10^{-3}M$ and 1.0 × $10^{-3}M$ was due to more frequent grafts. This is shown as a sharp decrease in molecular weight and AGU/chain in this range (Fig. 2). Increasing the Mn^{3+} concentration in this range means higher $(Mn^{3+})/(AGU)$ ratio.

At Mn^{3+} concentrations between 1.0 × $10^{-3}M$ and 3.0 × $10^{-3}M$, only about 10% variation in monomer conversion to polymer was obtained. The curve for add-on versus Mn^{3+} concentration resembles the curve for conversion of monomer to polymer because the grafting efficiencies were relatively constant and high (between 85 and 90%) in this range. The frequency of grafts (AGU/chain) did not show much variation in this range of Mn^{3+} concentrations. At Mn^{3+} concentrations of 0.15 × $10^{-3}M$ and 0.5 × $10^{-3}M$, the grafting efficiencies were 99% and 92%, respectively.

At Mn^{3+} concentrations of 0.15 × $10^{-3}M$ to 1.0 × $10^{-3}M$, the average molecular weights of the PMMA grafts decreased by a factor of 3–4. This appears to be due to higher propagation rates caused by higher ratios of (monomer)/(total number of radicals initiating grafting) at lower Mn^{3+} concentrations. In this range and under similar conditions, only about 20% variation in the average molecular weights of grafts was reported in connection with grafting of acrylo-
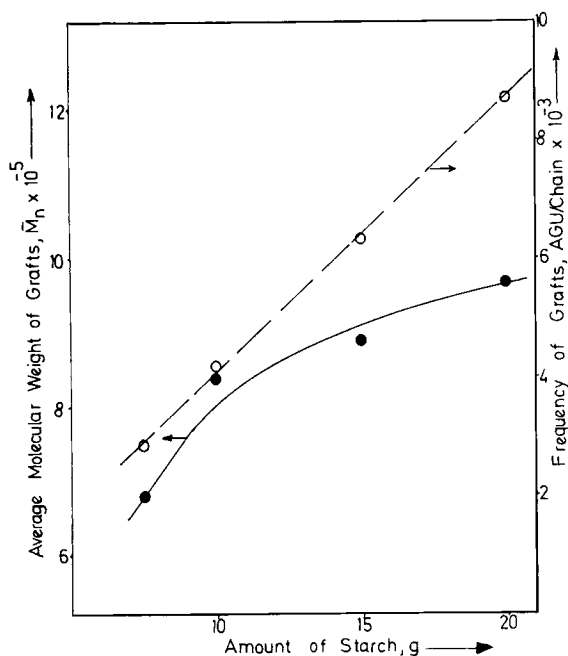
Fig. 4. Average molecular weight of grafts (———) and frequency of grafts (- - -) in grafting of MMA onto starch. Reaction conditions: $[Mn^{3+}] = 2.0 \times 10^{-3}M$; $[H_2SO_4] = 80 \times 10^{-3}M$; methyl methacrylate = 25 ml = 23.58 g; $[Na_4P_2O_7] = 10 \times 10^{-3}M$; reaction time = 3 hr; temperature = 30°C.

nitrile to granular native potato starch.[5] This difference between MMA and AN monomers may be understood by considering the fact that PMMA growing chains are compatible with MMA monomer, whereas PAN growing chains are not soluble in aqueous polymerization systems of these monomers.[13] The growth rate of PMMA chains would be more sensitive to changes in the ratio of (monomer)/(total number of radicals initiating grafting) than the growth rate of PAN chains would be.

The amount of starch was varied nearly threefold, from 7.5 to 20 g. Figure 3 shows that the conversion of MMA monomer to PMMA (g/batch) was almost constant in this range. A much larger variation was reported for acrylonitrile in this range.[5] Since the amount of polymer formed was almost independent of the amount of starch charged, the add-on decreases sharply as the amount of starch charged per batch is increased (Fig. 3).

Increasing the (starch)/(Mn^{3+}) and the (starch)/(monomer) ratios by a factor of 3 (the Mn^{3+} and monomer concertrations remaining constant) increased the frequency of grafts (AGU/chain) almost proportionately (Fig. 4). This is interpreted as due as the lower (Mn^{3+})/(starch) ratio when the amount of starch charged per batch is increased. This variation for grafting of MMA onto granular potato starch is much larger than that previously observed[5] in the grafting of AN. This difference between MMA and AN in grafting may be related to monomer/polymer compatibility: PMMA is soluble in MMA, but PAN is virtually insoluble in AN. This difference may affect the rate of termination with Mn^{3+} ions of the polymer radicals. Figure 4 depicts only about 25% increase in average molecular weights of grafts as the amount of starch is increased nearly threefold. A much larger variation (a decrease) was observed when PAN was grafted to starch.[5] The reason for this difference is not yet clear.

Our attempts to obtain high grafting efficiencies with acrylamide by manganic pyrophosphate initiation were foiled. Although physical methods of activating starch such as simultaneous and preirradiation have been successfully employed, the grafting of acrylamide with high grafting efficiencies by chemically activating the starch remains today an unsolved problem. Results of evaluation of properties of starch graft copolymers and ESR studies to fully understand and elucidate initiating mechanisms for initating grafting onto starch and starch derivatives by manganic pyrophosphate initiation may be published in forthcoming papers.

CONCLUSIONS

It is concluded that methyl methacrylate (MMA) can be graft copolymerized onto granular starch efficiently in aqueous suspension under a wide range of reaction conditions. Changes in the initial concentrations of Mn^{3+} and starch influence the grafting parameters appreciably, e.g., add-on, conversion of MMA monomer to polymer, frequency of grafts (AGU/chain), and average molecular weight of the PMMA grafts. Variations in the grafting parameters were different for grafting of MMA than for AN as reported previously,[5] and the interpretation is discussed.

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