

Graft Copolymerization of Methyl Methacrylate onto Sago Starch Using Ceric Ammonium Nitrate and Potassium Persulfate as Redox Initiator Systems

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ABSTRACT: The graft copolymerization of methyl methacrylate (MMA) onto sago starch was carried out in aqueous media by different initiators of ceric ammonium nitrate (CAN) and potassium persulfate (PPS) and under a nitrogen gas atmosphere. Using CAN as an initiator, the maximum percentage of grafting (%G) was ascertained to be 246% at the following optimum conditions: a 70°C reaction temperature, a 2-h reaction period, 2.0 mmol of CAN, 0.4 mmol of nitric acid, and 141 mmol of MMA. The maximum %G achieved with PPS as the initiator was 90%. The optimum conditions were a 50°C reaction temperature, a 1.5-h reaction period, 47 mmol of monomer, and 1.82 mmol of PPS. The grafting of MMA onto sago starch was confirmed by the IR spectra of pure sago starch, MMA, and MMA grafted sago starch. This material may have application as a biodegradable plastic. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 1375–1381, 2001

Key words: sago starch; methyl methacrylate; graft copolymerization; ceric ammonium nitrate; potassium persulfate

INTRODUCTION

Starch is one of the cheapest and most readily available of all natural polymers. It is a high polymer composed of repeating 1,4- α -D-glucopyranosyl units (often called anhydroglucose units or simply AGU) and is generally a mixture of linear and branched components.¹ Sago starch, which is produced from the pith of the sago palm (*Metroxy-*

lon sagu), is a useful resource for commercial raw materials and foodstuffs and is an important product of south Asia.² Sago is an economically important crop of Malaysia. The export of sago starch is the fifth highest revenue earner in the agricultural sector after pepper, rubber, palm oil, and cocoa. Starch in its native form exists in relatively inert granular structures, which are composed of macromolecules arranged in a polycrystalline state.^{3,4} Chemical modification of starch via vinyl graft copolymerization constitutes a powerful means of improving the starch properties, thereby enlarging the range of its utilization. Primarily free-radical initiated processes are used to produce starch graft copolymers. Em-

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phasis is placed on high-energy ionization radiation, ceric ion, and redox systems.⁵

Ceric ions are used to initiate graft copolymerization of many monomers on various substrates. Grafting is generally considered to result from propagation by radical sites generated on the polymer substrate. Graft copolymerization onto starch and other natural macromolecules can also be initiated by transition metal ions such as Fe^{3+} , Cu^{2+} , Co^{3+} , Ce^{4+} , V^{3+} , Cr^{6+} , and their complexes, which are the most commonly used initiators. In particular, Ce^{4+} is widely used in the graft modification of cellulose, fiber, gelatin, and starch. A number of studies investigated the graft copolymerization of vinyl monomers such as methyl methacrylate (MMA) onto curdlan, *N*-vinyl pyrrolidone onto gelatin, methyl acrylate (MA) onto potato starch, MA onto sago starch, and vinyl pyrrolidone onto chitosan.^{6–12} Along this line, we investigated the grafting of MMA onto sago starch, which is a new backbone, by using ceric ammonium nitrate (CAN) and potassium persulfate (PPS) as the redox initiators. The effects of the reaction temperature, reaction period, nitric acid concentration, MMA concentration, and initiator concentration were extensively investigated.

EXPERIMENTAL

Experiments were conducted to investigate the graft copolymerization of MMA onto sago starch using CAN and PPS as redox initiator systems. The materials used and the procedure of the experiments are described.

Materials

Sago starch was purchased from Wee Kwong Sdn. Bhd. and used without further purification. The MMA was supplied by Fluka and used after removing the stabilizer by an aluminum oxide column, and CAN was obtained from Ajax. Analytical grade PPS (AR[®]) was produced by Mallinckrodt and used as received. Acetone was purchased from Merck, and methanol was obtained from J. T. Baker. Concentrated nitric acid was procured from China National Chemicals Import Export Corporation. The spectra of sago starch, the grafted copolymer of sago starch and poly(MMA) (PMMA, sago starch-*g*-PMMA), and side chain polymer were recorded on a Perkin–Elmer 1725X-Fourier transform IR (FTIR) spectrophotometer,

using the potassium bromide disk technique. The scanning of the FTIR spectrophotometer was carried out from 4000 to 400 cm^{-1} .

Preparation of Polymers

The grafting reaction was carried out in a round-bottom flask equipped with a reflux condenser and a nitrogen gas inlet. The flask was placed in a thermostated water bath equipped with a magnetic stirrer to control the reaction temperature. Gelatinized sago starch was used in all experiments and was obtained by heating its slurry in the flask for 30 min at 80°C. The initiation process to produce free radicals onto sago starch chains was carried out after the gelatinized sago starch was cooled to a desired graft copolymerization temperature. The initiator used was either CAN, which was dissolved in nitric acid solution, or PPS, which was added into the gelatinized sago starch 15 min before adding the MMA. All the reactions (gelatinization, initiation, and propagation) were carried out under a nitrogen gas atmosphere, and the reaction mixture was continuously stirred during these reactions. At the end of the propagation reaction the product was precipitated in methanol, filtered using a sintered glass filter of porosity 2, and then dried at 60°C in an oven to a constant weight.

The PMMA, which was also formed during the graft copolymerization reaction, was separated from the grafted polymer by Soxhlet extraction. Acetone was used as the solvent, and each extraction was carried out for 8 h. The purified copolymer was dried in an oven at 60°C to a constant weight. To ensure the complete removal of the homopolymer, the above extraction was carried out 3 times for each sample. The data used in most of the figures was the average of the results of the same three experiments and the percentage of the error was less than 5%. The graft copolymerization reaction was characterized by the percentage of grafting (%*G*), which was calculated as follows:

$$\%G = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the weight of the sago starch and W_2 is the weight of PMMA grafted sago starch.

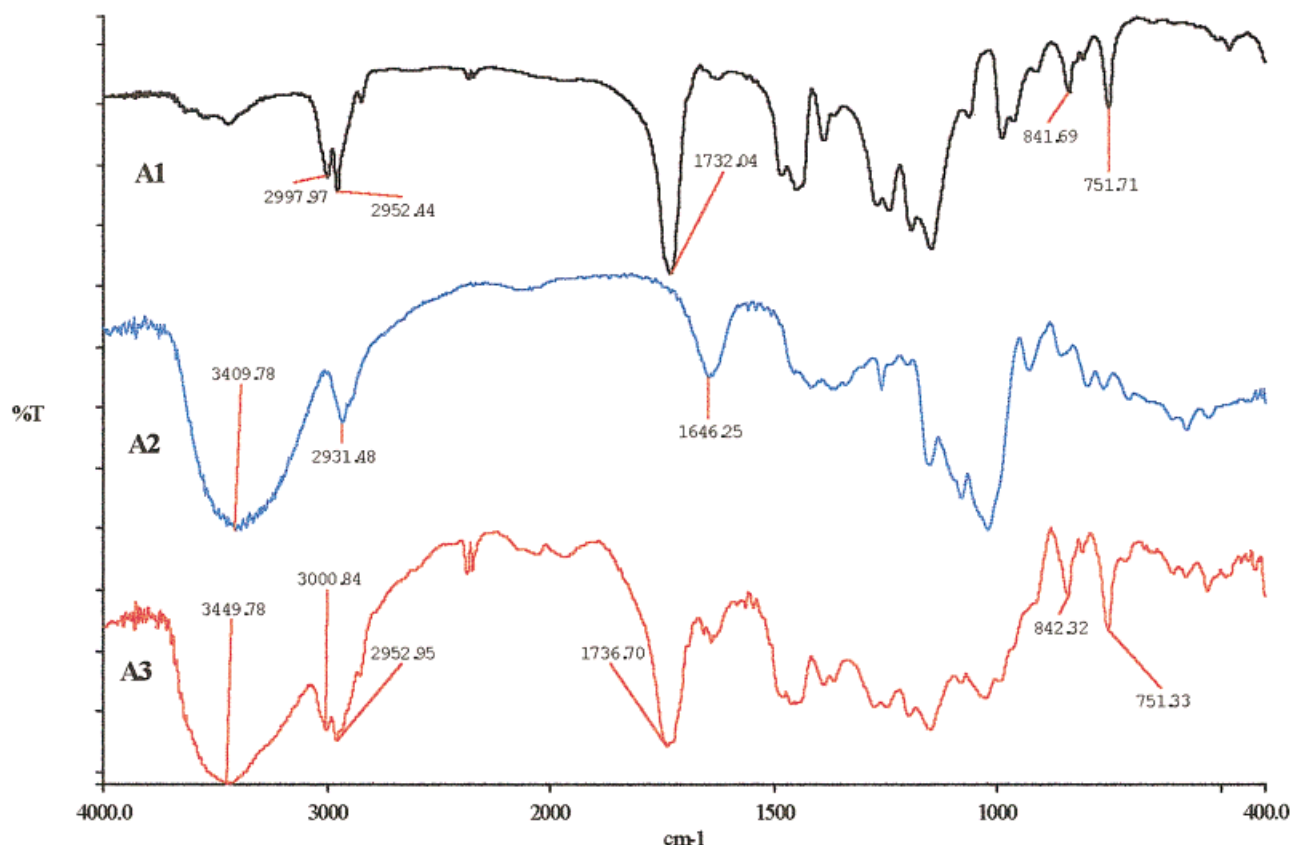


Figure 1 FTIR spectra of PMMA (spectrum A1), sago starch (spectrum A2), and PMMA grafted sago starch (spectrum A3). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

FTIR Spectrum Analysis

The nature of the attachment of MMA in sago starch-*g*-PMMA prepared by using CAN and PPS as initiators was the same as the study reported by Kang et al.¹³ Thus, the same argument may be used for both grafted products. The FTIR spectra of PMMA, sago starch, and sago starch-*g*-PMMA are shown in Figure 1. The FTIR spectrum of the sago starch-*g*-PMMA (Fig. 1, spectrum A3) indicated the appearance of a broad region (1200–1000 cm^{-1}), which was not observed in the spectrum of sago starch (Fig. 1, spectrum A2). At the same time, the FTIR spectrum of the sago starch-*g*-PMMA showed a new absorption band of PMMA at 1736.70 cm^{-1} of the C=O stretching mode in addition to the same absorption bands of sago starch shown in spectrum A2 in Figure 1. However, there was a broad peak at approximately 3449.78 cm^{-1} , which could be due to the stretching frequency of the other hydroxyl

group. The new peaks that appeared at 842.32 and 751.33 cm^{-1} were due to the stretching of the CH_2CH_2 group. The other two small peaks at 3000.84 and 2952.95 cm^{-1} were assigned to the $-\text{OCH}_3$ group and the CH-aliphatic group, respectively. There was also a strong peak for the C=O group that occurred at 1732.04 cm^{-1} in the spectrum of PMMA (Fig. 1, spectrum A1), which was shifted to the position of 1736.70 cm^{-1} in the spectrum of sago starch-*g*-PMMA. However, the appearance of the new peaks in the spectrum of sago starch-*g*-PMMA gave supporting evidence for the grafted product and suggested that MMA had been successfully grafted onto sago starch.^{14,15}

Effects of Reaction Temperature

Temperature is one of the important factors in determining the extent of grafting. The effects of the reaction temperature on the grafting of PMMA onto sago starch prepared by using CAN and PPS as initiators were studied by varying the

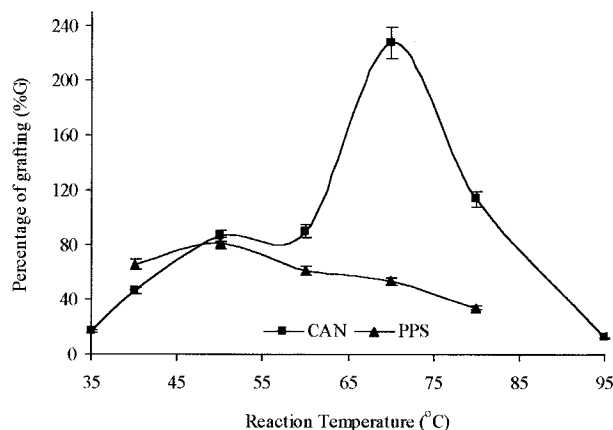


Figure 2 The effects of the reaction temperature on the grafting of PMMA onto sago starch prepared by using CAN and PPS as initiators. The other reaction conditions for the CAN initiator: 1.00 g of sago starch, 0.2742 g of CAN, 1 mL of 0.1M nitric acid, 10 mL of MMA, 2-h reaction period; for the PPS initiator: 1.00 g of sago starch, 1.00 g of PPS, 5 mL of MMA, 1-h reaction period.

reaction temperature from 35 to 95°C. The results obtained are presented in Figure 2. The %G of the copolymers prepared by using CAN as the initiator increased with the increase of temperature up to 70°C, while the %G for the copolymers prepared by using PPS as the initiator increased with the increase of temperature up to 50°C. A further increase of the reaction temperature led to the decrease of the %G, probably because of the formation of the unstable complex of ceric salt with the starch. This result is in agreement with that of Lagos and Rayes,¹⁴ Guthrie and Tune,¹⁶ and Trimmell et al.¹⁷ who used Fenton's reagent and a ceric initiating system to graft MMA onto chitosan and MA onto granular cornstarch, respectively. The same results were also obtained when Rahman et al. grafted MA onto sago starch.¹²

Effects of Reaction Period

The investigation of the effects of reaction periods on the %G was also carried out and the results are shown in Figure 3. The %G increased with the increase of the reaction period up to 2 and 1.5 h for CAN and PPS, respectively. The decrease of the %G after the maximum reaction period could be due to the reduction of the reactive sites exposed to the MMA as the result of the increase in the viscosity of the solution, which made it very difficult for MMA to react with these sites. Simi-

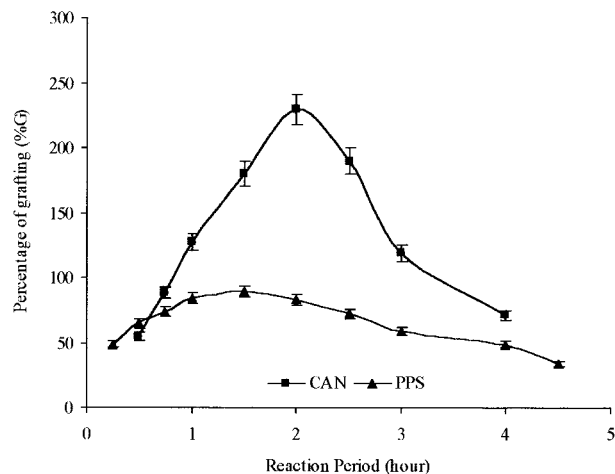


Figure 3 The effects of the reaction period on the grafting of PMMA onto sago starch prepared by using CAN and PPS as initiators. The other reaction conditions for the CAN initiator: 1.00 g of sago starch, 0.2742 g of CAN, 1 mL of 0.1M nitric acid, 10 mL of MMA, 70°C reaction temperature; for the PPS initiator: 1.00 g of sago starch, 1.00 g of PPS, 5 mL of MMA, 50°C reaction temperature.

lar results were obtained in tributylborane initiated grafting of MMA onto chitin¹⁸ and ceric ion initiated grafting of MA onto sago starch.¹²

Effects of Initiator Concentration

The effects of the CAN concentration on the %G is given in Figure 4. The maximum %G was observed at initiator amounts of 2.0 and 1.82 mmol for CAN and PPS, respectively. The %G decreased with the increase of the initiator concentration beyond the optimum condition. This was probably due to the formation of ceric salt, which took part in the termination of the growing grafted chain in the copolymerization. At a higher ceric ion concentration an increase was expected in the reaction steps involving ceric ions, leading to an increase in the number of starch radicals terminated prior to monomer addition.¹² Another factor contributing to the decrease in grafting levels at higher initiator concentration was an increase in the homopolymer formation, which competed with the grafting reaction for available monomer.^{11,12} The maximum grafting of MMA on himachali wool¹⁹ was attained at 7.5×10^{-3} mol L⁻¹ of CAN. A similar concentration of CAN gave maximum grafting of acrylonitrile onto starch.¹¹

Effects of Nitric Acid Concentration

The effects of the nitric acid concentration with CAN as the initiator on the %G are shown in

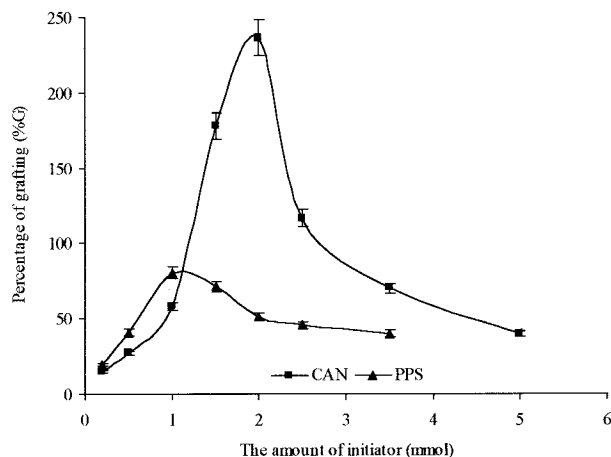


Figure 4 The effects of the initiator concentration on the grafting of PMMA onto sago starch. The other reaction conditions for the CAN initiator: 1.00 g of sago starch, 1 mL of 0.1M nitric acid, 10 mL of MMA, 2-h reaction period, 70°C reaction temperature; for the PPS initiator: 1.00 g of sago starch, 5 mL of MMA, 1-h reaction period, 50°C reaction temperature.

Figure 5. The maximum %G was achieved at 0.4 mmol of nitric acid. A further increase of the nitric acid concentration led to the decrease of the %G, which was due to the reduction of the ceric-starch complex. For higher %G, the acid enhanced the oxidizing power of the initiator.¹⁹ Acids also acted as a catalyst in the hydrolysis of starch, leading to uncoiling of the chains and improvement of the monomer's accessibility.¹² It was

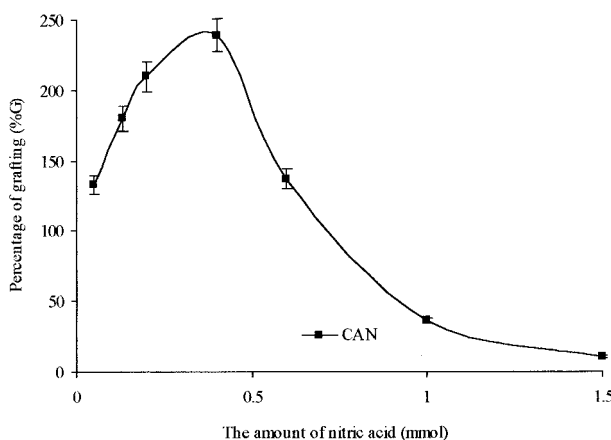


Figure 5 The effects of the nitric acid concentration on the grafting of PMMA onto sago starch prepared by using CAN as the initiator. The other reaction conditions for the CAN initiator: 1.00 g of sago starch, 1.0965 g of CAN, 10 mL of MMA, 2-h reaction period, 70°C reaction temperature.

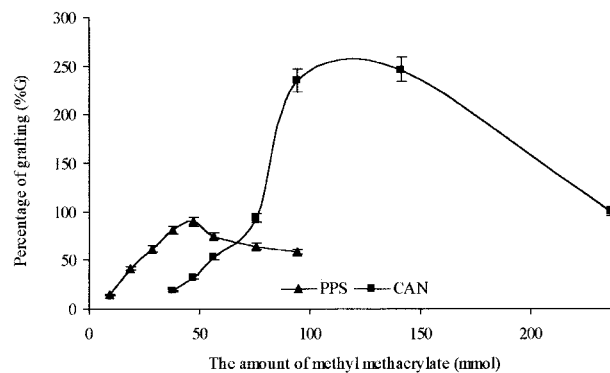


Figure 6 The effects of the monomer concentration on the grafting of PMMA onto sago starch prepared by using CAN and PPS as initiators. The other reaction conditions for the CAN initiator: 1.00 g of sago starch, 1.0965 g of CAN, 4 mL of 0.1M nitric acid, 2-h reaction period, 70°C reaction temperature; for the PPS initiator: 1.00 g of sago starch, 1.00 g of PPS, 1-h reaction period, 50°C reaction temperature.

clear that the grafting reaction happened in the acidic medium, the sago starch had the ability to be grafted with PPS as the initiator, and no further acid was used.

Effects of Monomer Concentration

The effects of the monomer concentration on the %G are shown in Figure 6. The maximum %G was observed when the amount of MMA was 141 and 47 mmol for CAN and PPS, respectively. However, a further increase of the amount of MMA reduced the %G. The decrease of the %G with the increase of MMA concentration could have been due to the hydrolysis of MMA in the acidic medium in the case with CAN. But in the PPS case, the decrease of the %G with the increase of MMA concentration could have been due to the formation of free radicals in the MMA, which led to the formation of the homopolymer. At a higher concentration of monomer, the %G decreased because the formation of the homopolymer was increased. These observations were also recorded when Fenton's reagent was used.¹⁴

Grafting Sites and Copolymerization Reaction

Several reports were published on the graft copolymerization mechanisms of vinyl monomer onto starch macromolecules.^{1,6,8,13} The proposed mechanism used in this study was based on the same principle as Ceresa¹ and Yoshida et al.⁸ It was assumed that free radicals were formed on

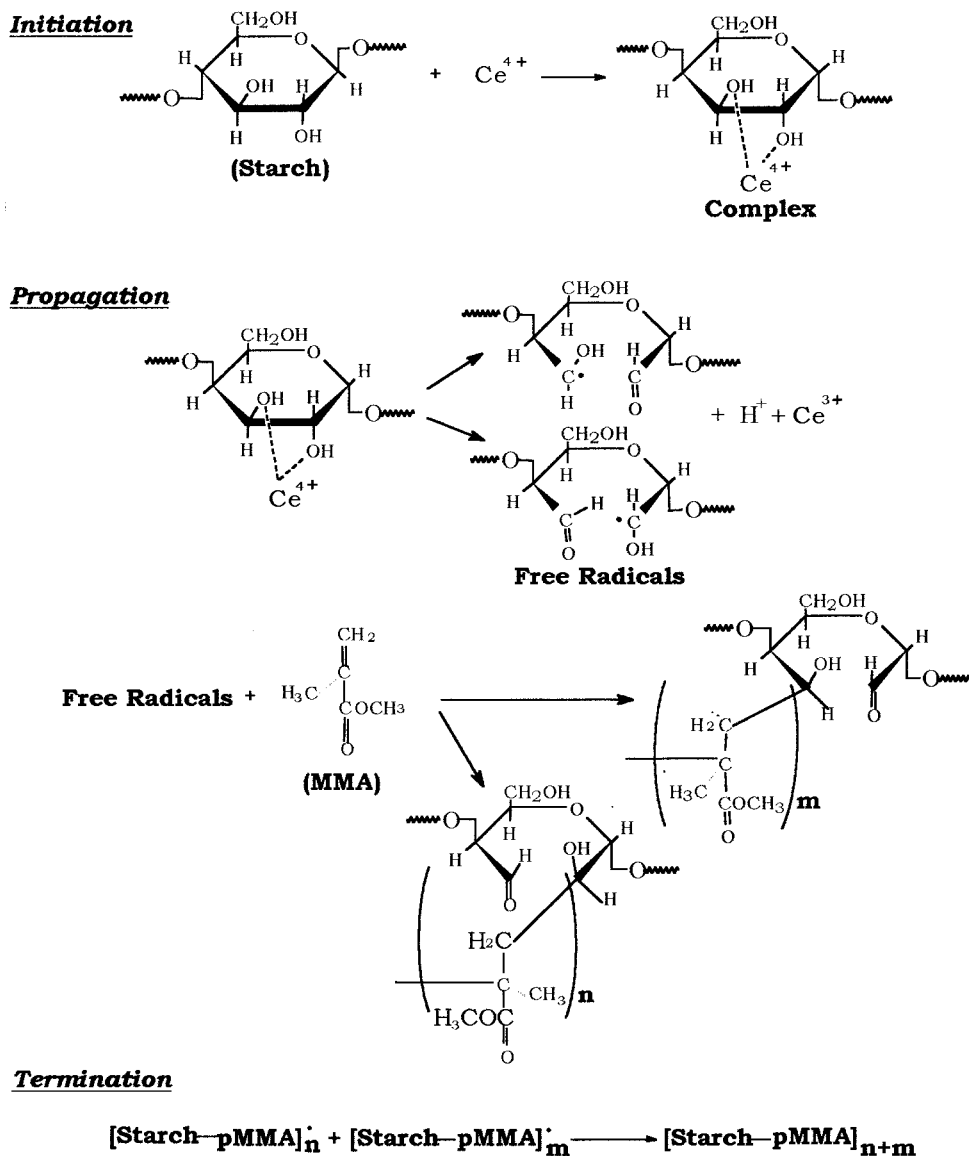


Figure 7 The reaction mechanism for the grafting of PMMA onto sago starch prepared by using CAN as an initiator.

the C₂ of anhydroglucosamine rings when a ceric ion was used to initiate grafting. The ceric ion was attached to sago starch to produce a sago starch-ceric complex (Fig. 7). The Ce⁴⁺ ion was reduced to a Ce³⁺ ion with the release of a proton. When the bond between C₂ and C₃ was broken, free radicals of sago starch were formed. The free radicals formed then reacted with MMA to produce the copolymer. The same mechanism (see Fig. 7) was proposed to be used for the grafting of MMA onto sago starch prepared by using PPS (S₂O₈²⁻ ion) as an initiator. The reaction mechanism of grafting of MMA prepared by using CAN (ceric

ion) as the initiator was similar to that prepared by using PPS.^{8,13}

CONCLUSION

This study concluded that gelatinized sago starch could be grafted with MMA using CAN and PPS as redox initiators. The %G values, which were achieved by using CAN and PPS, were 246.3 and 90%, respectively. The optimum condition that gave the maximum %G using the CAN system with 1.00 g of sago starch was as follows: a 70°C

reaction temperature, a 2-h reaction period, 2 mmol of CAN, 141 mmol of MMA, and 0.4 mmol of nitric acid. On the other hand, the optimum conditions that gave the maximum %G using the PPS initiator with 1.00 g of sago starch was as follows: 50°C; reaction temperature, 1.5-h reaction period, 1.82 mmol PPS initiator, and 47 mmol of MMA.

The appearance of 1736.70 and 3447.78 cm^{-1} bands in the FTIR spectrum of the grafted sago starch indicated that MMA had been successfully grafted onto sago starch. The FTIR spectra of the hydrolyzed sago starch-g-PMMA copolymers were identical to the spectrum of pure MMA, which also suggested that the product of the copolymerization was sago starch-g-PMMA.

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