

Graft Copolymerization of Acrylic Acid onto Cocoyam Starch by Ceric Ion in the Presence of *N,N'*-Dimethylacetamide

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ABSTRACT: Grafting of acrylic acid onto cocoyam starch, *Xanthosoma sagittatum* was initiated by ceric ion—*N,N'*-dimethylacetamide redox pair in aqueous media. The reaction was characterized by high graft yields of up to 676%, and infrared spectroscopy affirmed the presence of grafted polymer. Graft yield was enhanced by *N,N'*-dimethylacetamide (DMAc) in the concentration range, $9.0\text{--}36.0 \times 10^{-4}M$ but lower concentrations were more favorable with the ratio of percentage graft, P_g/P_{g0} , in the presence and absence of DMAc respectively, of up to 1.34 at $9.0 \times 10^{-4}M$ of the latter. Ceric ion was nonterminating of the graft reaction and a 10-fold increase in its concentration of $4.16 \times 10^{-3}M$ resulted in high efficiency

of graft of 50.2% in monomer conversion to grafted polymer. Enhanced homopolymer formation and low efficiency of graft were observed at monomer concentration greater than $0.69M$. Long reaction time, greater than 30 min, was unfavorable to the graft reaction and the latter showed negative dependence on temperature in the range, 30–50°C. At 30-min reaction time, the graft yield at 50°C was not more than 70% of the corresponding value at 30°C. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2676–2680, 2008

Key words: graft copolymer; cocoyam starch; infrared spectroscopy; radical polymerization

INTRODUCTION

Starch is an important raw material for a number of industrial processes and applications, notably as a flocculating agent¹ and as a thickener for textiles.² A range of other industrial applications are possible when starch is modified through graft copolymerization of vinyl monomers. Starch-*g*-polyacrylamide and starch-*g*-polyacrylic acid copolymers are of great interest for enhanced oil recovery operations.³ For the latter copolymer, its application as sizing agent for improved physical properties of textile fabrics has been demonstrated.⁴ Furthermore, the presence of hydrophilic polyacrylic acid has been reported to impart water sorbency and ion exchange properties on the graft copolymer.⁵ There are a number of other reports on the graft copolymerization of vinyl monomers onto starch.^{6–9} For the graft copolymerization of methylmethacrylate onto sago starch by ceric ions and potassium persulfate redox initiators, significant graft levels at 70°C were reported.⁶

Apart from cassava and to a smaller extent sweet potato, starch from other tuber crops has not been exploited for industrial applications. Yet, physico-

chemical properties of starch vary widely depending on the sources and varieties. The relative amounts of amylose and amylopectin components of starch vary for starches from different sources and may thus exert profound effect on their properties and grafting characteristics. Cocoyam (tannia) *Xanthosoma sagittatum*, a tuber crop, is an edible aroid, and one of the most important species of the family, Araceae.¹⁰ It is a major staple in the Caribbean and West Africa. In some places, it is used in small quantities as soup thickener. Yet, there is paucity of information on the physicochemical properties, industrial application and grafting characteristics of the starch derivable from cocoyam. This study is on grafting of acrylic acid onto cocoyam starch by ceric ions—*N,N'*-dimethylacetamide redox pair. The results are presented and discussed.

EXPERIMENTAL

Materials

Acrylic acid (AA, Sigma–Aldrich Chemie, Germany) was purified by fractional distillation after washing successively with 5% solution of sodium hydroxide and sodium chloride. *N,N'*-dimethylacetamide (DMAc, BDH, UK) was fractionally distilled and the middle fraction collected. Other reagents, namely glacial acetic acid, nitric acid, ceric ammonium nitrate,

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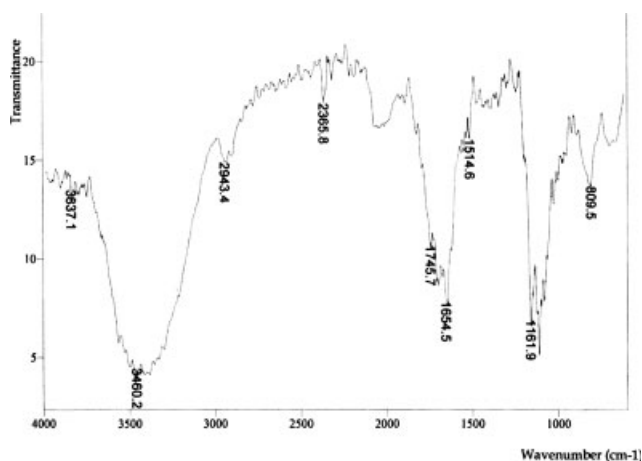


Figure 1 Infrared spectrum for cocoyam starch.

potassium permanganate and methanol were used as supplied. The white variety of cocoyam, *X. sagittifolium* was obtained locally in Abeokuta, Nigeria.

Methods

The cocoyam tuber was peeled, washed, and finely grated. The grate was put into a fine sieve to which was added some quantity of water and then agitated. The soluble part was collected in a container leaving behind in the filter some chaff and fibrous materials which were discarded. The soluble extract was allowed to settle for 12 h and the supernatant decanted leaving a mass of cocoyam starch. The starch was oven-dried at 30°C, pulverized into a fine white powder using pestle and mortar and sifted.

The graft copolymerization reaction using gelatinized starch was based on the method of Lepoutre and Hui¹¹ as previously reported.¹² In a typical experiment, 0.1 g of starch was weighed into a conical flask containing distilled water. The slurry was heated for 30 min at 75°C for gelatinization. The gel was cooled to the operating temperature before addition of other reagents namely, nitric acid, glacial acetic acid, *N,N'*-dimethylacetamide (DMAc) and the oxidant, ceric ammonium nitrate or potassium permanganate at the required concentrations. Specifically, DMAc and the oxidant were allowed to interact in the reaction medium for a given period, the preoxidation time (POT) before addition of the monomes, which marked the onset of the graft reaction. The reaction was terminated by the addition of methanol which precipitated the graft copolymer.⁶ The latter was filtered using a sintered glass and dried in an oven at 40°C to constant weight. Percentage grafting and grafting efficiency were calculated from the relation:

$$\% \text{ Grafting} = [(W_2 - W_1)/W_1] \times 100$$

$$\% \text{ Efficiency} = [(W_2 - W_1)/W_3] \times 100$$

where W_1 , W_2 , and W_3 are the weights of the starch, the grafted starch and the monomer, respectively.

Infrared spectroscopy

The infrared spectra for the starch and for the starch-g-polyacrylic acid copolymer were recorded on Buck Scientific Spectrophotometer M500 using the potassium bromide disk technique.

Infrared spectroscopy of cocoyam starch and starch-g-polyacrylic acid copolymer

Figure 1 represents the infrared spectrum for cocoyam starch. The peaks at 3460.2 cm^{-1} and 1161.9 cm^{-1} are for bonded OH stretching and alcoholic C—O stretching vibrations, respectively.¹³ The spectrum for starch-g-polyacrylic acid copolymer is shown in Figure 2. Evidence for graft are provided by the peaks at 1697 cm^{-1} and 1650 cm^{-1} for C=O and COO⁻ anion stretching vibrations respectively, characteristics for carboxylic acids. This is corroborated by OH bending vibration for carboxylic acid at 1417.5 cm^{-1} and C—O—C stretching vibration at 1113.5 cm^{-1} . The latter arises from the reaction of starch alkoxy radicals with acrylic acid which is the initiation of graft polymerization.

Effect of *N,N'*-dimethylacetamide on grafting of acrylic acid onto cocoyam starch

The conversion profile in graft yields at different concentrations of *N,N'*-dimethylacetamide (DMAc) is represented in Figure 3. The redox reaction of ceric ions and DMAc is expected to generate methylacetylaminomethyl radical (I) initiating species as follows:

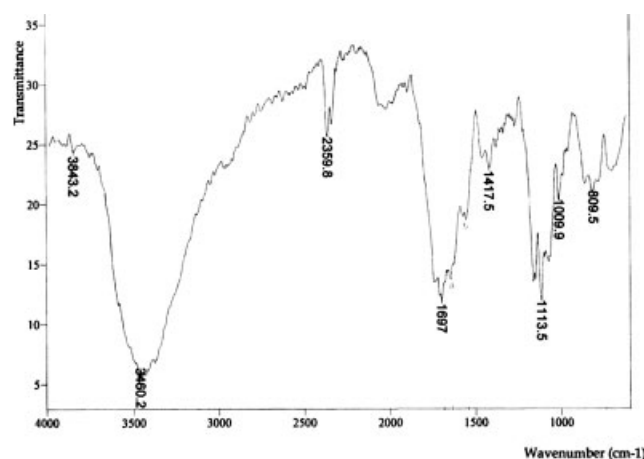
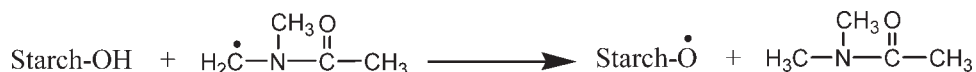


Figure 2 Infrared spectrum for starch-g-polyacrylic acid copolymer.



Starch macroradicals are formed by interaction of starch molecules with I. That is,



Direct oxidation of starch molecules by ceric ion to produce macroradicals is possible and the grafting characteristics will depend on the relative rates of the latter reaction and the one by interaction of starch with species I above. From Figure 3, it is evident that graft yield is enhanced by DMAc in the concentration range, $9.0\text{--}36.0 \times 10^{-4}\text{M}$ with ratio of percentage graft P_g/P_{g0} , in the presence and absence of DMAc greater than one as shown in Table I. However, graft yields are favored at lower concentrations of DMAc i.e., at $9.0 \times 10^{-4}\text{M}$ of DMAc, P_g/P_{g0} is highest at 1.34. Reduction in graft yield at high concentration of DMAc may arise from termination of graft reaction by radical coupling of starch macroradicals and methylacetylaminomethyl radical species (I). A cursory examination of the infrared spectrum for starch-g-polyacrylic acid copolymer (Fig. 2) shows no evidence in support of the latter reaction. Thus, it is plausible to adduce the observed reduction in graft yield to transfer reaction of DMAc with growing graft polymer chain with resultant

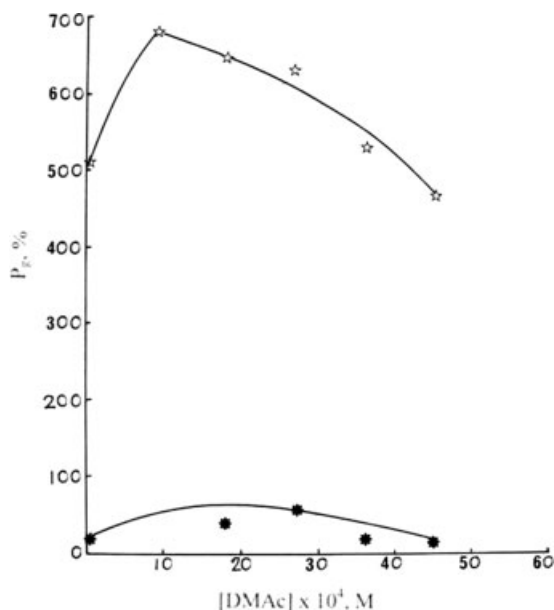


Figure 3 Effect of DMAc concentration on graft yield. $[\text{H}^+] = 0.54\text{M}$; $[\text{Ce}^{+4}] = 8.33 \times 10^{-3}\text{M}$; $[\text{AA}] = 0.46\text{M}$; $[\text{AcOH}] = 0.5\text{M}$; starch = 0.1 g; POT = 10 min; temperature = 30°C ; time = 3 h. (☆) ceric ion; (●) permanganate.

formation of polyacrylic acid homopolymer. From Table I, such homopolymerization reaction is competitive because a five-fold increase in DMAc concentration is accompanied by 30% reduction in graft yield. The preponderant effect of DMAc in transfer reaction with growing graft polymer chain is buttressed by the graft yield profile with permanganate as oxidant in place of ceric ion. First, it is evident that permanganate is less effective than ceric ion for the graft reaction having much lower yields at corresponding concentrations of DMAc. Second, the graft yield increases with DMAc and thereafter shows negative dependence at higher concentrations of the latter.

Effect of ceric ions on graft yield

Figure 4 represents the effect of ceric ion on grafting of acrylic acid on starch. Increase in the concentration of ceric ion from 4.16 to $41.70 \times 10^{-3}\text{M}$ is accompanied by a corresponding increase in graft yield with value of up to 501.9% at the latter concentration and efficiency in monomer conversion to graft polymer of 50.2% (Table II). A reduction in graft yield was observed at certain concentrations of ceric ions at 70°C for the graft copolymerization of methylmethacrylate onto sago starch⁶ and was attributed to termination reactions by the ions. The increase in graft yield with ceric ion concentration (Fig. 4) suggests that the latter is nonterminating of the graft reactions under the experimental conditions. The high efficiency in monomer conversion to graft is further evidence that the graft polymerization is

TABLE I
Effect of DMAc on Graft Yield

$[\text{DMAc}] \times 10^4$	P_g/P_{g0}
9.0	1.34
18.0	1.27
27.0	1.24
36.0	1.05
45.0	0.93

$[\text{H}^+] = 0.54\text{M}$; $[\text{Ce}^{+4}] = 8.33 \times 10^{-3}\text{M}$; $[\text{AA}] = 0.46\text{M}$; starch = 0.1 g; $[\text{AcOH}] = 0.5\text{M}$; temperature = 30°C ; time = 3 h.

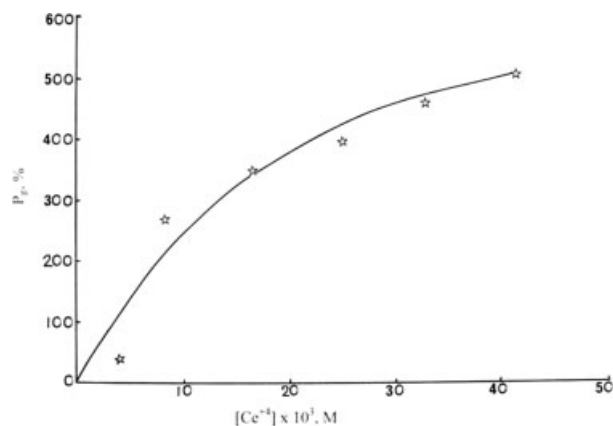


Figure 4 Effect of ceric ion concentration on graft yield. $[H^+] = 0.54M$; $[AcOH] = 0.5M$; $[DMAc] = 18.0 \times 10^{-4}M$; $[AA] = 0.46M$; starch = 0.1 g; POT = 10 min; temperature = $30^\circ C$; time = 3 h.

competitive to assuage the effects of possible homopolymerization reaction on graft yield.

Effect of monomer on graft yield

Graft yield increases with monomer concentration in the range 0.23–1.38M and approaches a plateau as represented in Figure 5. The efficiency of monomer utilization in graft reaction increases with monomer concentration up to 0.69M with value of up to 50.7% at the latter concentration. At higher concentrations, i.e., $>0.69M$, the efficiency decreases and explains the approach to a plateau observed in the graft yield profile. The reduction in efficiency in graft may be ascribed to enhanced homopolymerization reaction initiated by methylacetyl amino methyl radical species and ceric ion. Similar reduction in graft yield at high concentrations of monomer has been reported for the graft copolymerization of methylmethacrylate onto sago starch initiated by ceric ions.⁶

Effect of starch weight on graft yield

Figure 6 shows the effect of starch weight on graft yield. Graft yield increases with the weight of starch

TABLE II
Effect of Ceric Ion on Graft Yield

$[Ce^{4+}] \times 10^3 (M)$	Efficiency (%)
4.16	3.71
8.33	26.5
16.70	34.4
25.0	39.1
33.3	45.3
41.7	50.2

$[AA] = 0.46M$; $[DMAc] = 18.0 \times 10^{-4}M$; $[H^+] = 0.54M$; $[AcOH] = 0.5M$; starch = 0.1 g; temperature = $30^\circ C$; time = 3 h.

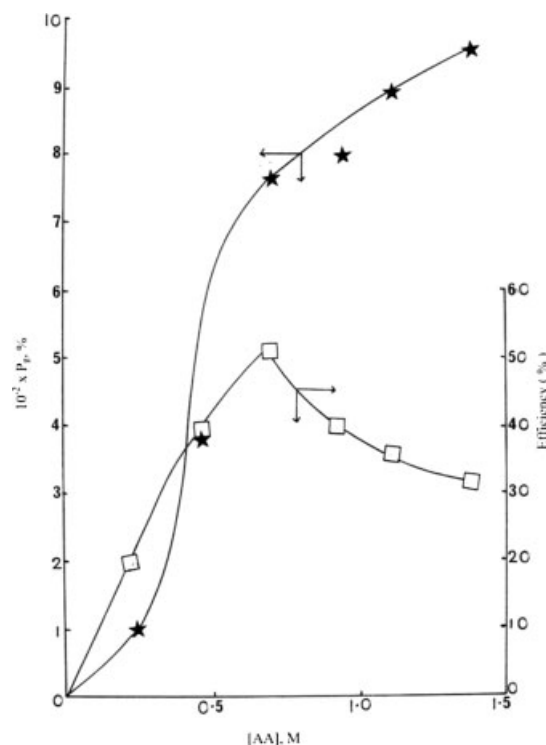


Figure 5 Effect of acrylic acid concentration on graft yield. $[H^+] = 0.54M$; $[AcOH] = 0.5M$; $[Ce^{4+}] = 8.33 \times 10^{-3}M$; $[DMAc] = 18.0 \times 10^{-4}M$; starch = 0.1 g; POT = 10 min; temperature = $30^\circ C$; time = 3 h.

in the range, 0.1–0.6 g at $30^\circ C$. However, it is noteworthy that the yield increases markedly, by 180% in the lower weight range, 0.1–0.2 g of starch and thereafter approaches a plateau, where further increase in weight by the same magnitude results in graft yield increases of not higher than 17%. The

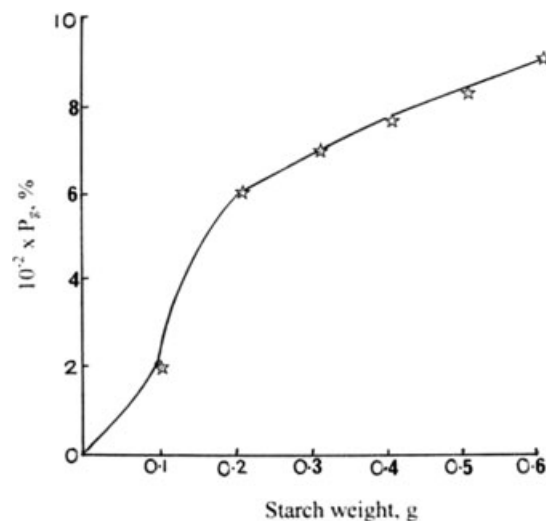


Figure 6 Effect of starch weight on graft yield. $[H^+] = 0.54M$; $[AcOH] = 0.5M$; $[Ce^{4+}] = 25.0 \times 10^{-3}M$; $[AA] = 0.46M$; $[DMAc] = 18.0 \times 10^{-4}M$; POT = 10 min; temperature = $30^\circ C$; time = 3 h.

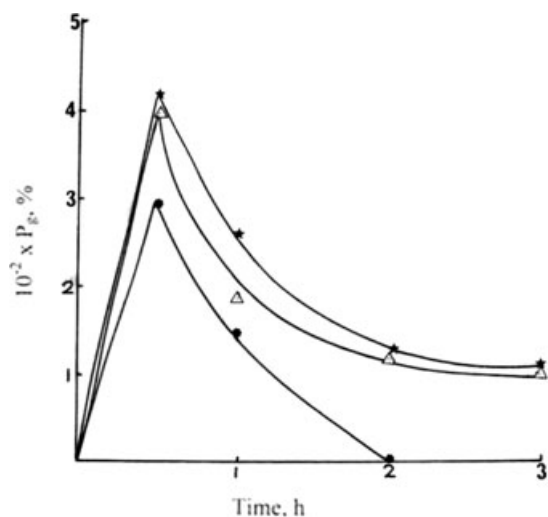


Figure 7 Effect of temperature on graft yield. $[H^+] = 0.54M$; $[AcOH] = 0.54M$; $[Ce^{+4}] = 25 \times 10^{-3}M$; $[DMAc] = 18.0 \times 10^{-3}M$; $[AA] = 0.46M$; POT = 10 min; (★) 30°C; (Δ) 40°C; (●) 50°C.

latter may be adduced to increased viscosity of the medium and its limiting effects on diffusion of monomeric units to radical sites of the starch molecules.

Effect of temperature

The time–temperature conversion for the graft reaction in the range, 30–50°C is represented in Figure 7. The conversion profiles are characterized by an initial increase in graft yield with time up to 30 min and thereafter decreases. Thus, long reaction time is inimical to the graft reaction. This was demonstrated for sago starch where for grafting of methylmethacrylate onto it, the yield decreased after 2 h reaction time.⁶ The latter was ascribed to viscosity effects on the accessibility of monomer to the grafting sites on the starch molecule. From Figure 7, it can be seen that graft yield shows negative dependence on temperature. At 50°C, there is zero yield at 2-h reaction time. This may be adduced to two factors; first, increased gelation of the starch solution with temperature and the attendant increase in the viscosity of the medium, and second, hydrolysis of grafted polymer chains exacerbated by high temperature

conditions. At 30-min reaction time, the graft yield at 50°C is 70% of the value at 30°C.

CONCLUSIONS

Ceric ion, *N,N'*-dimethylacetamide redox pair was effective for grafting of acrylic acid onto cocoyam starch in aqueous media with graft yields of up to 676%. Low concentrations of *N,N'*-dimethylacetamide (DMAc) were favorable to graft yields with the ratio of percentage graft, P_g/P_{g0} in the presence and absence of DMAc of 1.34 at $9.0 \times 10^{-4}M$ of the latter.

Ceric ion was nonterminating of the graft reaction and a 10-fold increase in its concentration of $4.16 \times 10^{-3}M$ resulted in high efficiency of 50.2% in monomer conversion to grafted polymer.

Long reaction time, greater than 30 min, was unfavorable to the graft reaction and the latter showed negative dependence on temperature in the range, 30–50°C. At 30 min reaction time, the graft yield at 50°C was not more than 70% of the value at 30°C.

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