

# Kinetic Study of Graft Polymerization of Acrylic Acid and Ethyl Methacrylate onto Starch by Ceric Ammonium Nitrate

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**ABSTRACT:** Graft polymerization of acrylic acid (AA) and ethyl methacrylate (EMA) onto starch (St) were carried out in aqueous solution using ceric ammonium nitrate (CAN) as redox system under  $N_2$  atmosphere. The effect of pH, reaction time, temperature, concentrations of CAN, St, and monomers on the graft yield was investigated. Monomer reactivity was in the following order: AA>EMA.

The kinetics of the graft polymerization of AA and EMA onto starch in same system with CAN was studied by acid-base and borometric titration, respectively. The rate expressions for graft polymerization are  $R_g = k[AA]^{0.92}[CAN]^{0.56}[St]^{0.46}$  and  $R'_g = k'[EMA]^{0.92}[CAN]^{0.53}[St]^{0.48}$  and a suitable mechanism is suggested. The graft copolymers were investigated by FT-IR spectroscopy. The overall activation energy of graft polymerization of AA onto starch was found to be 36.25  $\text{kJ}\cdot\text{mol}^{-1}$  within the temperature range 20-40°C, and for graft polymerization of EMA onto starch is found to be 11.88  $\text{kJ}\cdot\text{mol}^{-1}$  within the temperature range 25-45°C.

**KEY WORDS:** Kinetics, Starch, Acrylic acid, Ethyl methacrylate, Ceric ammonium nitrate, Graft polymerization.

## INTRUCTION

The syntheses of vinyl polymer-starch composites have been investigated by many authors [1-4]. These composites have been synthesized in order to add new properties to the starch without major change in its natural characteristics and to expand the market for starch-based products. Polymerization of vinyl monomers with starch can be initiated through generation of free radicals along the starch backbone as well as on the monomers. Among the various methods allowing the

generation of radicals of the starch, redox systems have been the subject of several investigations [5-9]. Using transition metals as initiators in the graft copolymerization of vinyl monomers onto natural macromolecules has received considerable attention in recent years [10, 11]. Hebeish and et al. [12-14] have reported the grafting of acrylonitrile onto starch by using  $\text{KMnO}_4$  as an initiator. Other metals such as Cr (VI) [15], V(V) [16], Co(III) [17] and especially Co(VI) [18] are also reported for use

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as initiators in the graft polymerization onto starch. They have initiated and yielded free radicals directly on backbone. The monomer was then grafted at those active sites. Another type of initiator that is commonly used is Fenton reagent ( $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ ) [19, 20] which behaves in a contrary fashion. It first reacts with itself to give free radicals, which reacts further with starch leading to the formation of free radical centers on the backbone. Similarly, hydrazine redox systems [21], persulfate [22], as well as metal acetyl acetonate [23] have also been reported as chain-transfer initiators used in the graft copolymerization of natural macromolecules. Though much work has been reported on the grafting of acrylonitrile [24-26], methylacrylates [27-29] onto starch, via free radicals initiated by using potassium permanganate acid, less attention has been paid to the grafting of vinyl monomers with ceric ammonium nitrate (CAN) as initiator. Mino and Kaiserman suggested for the first time the ceric ions could form very efficient redox systems in the presence of organic reductors, and help in reducing the extent of homopolymerization during graft copolymerization, thereby yielding a pure and uncross-linked graft copolymer [30]. Many specialists have studied the copolymerization of starch grafted vinyl monomers initiated by ceric salts [5, 31-33].

This method is one of the most interesting methods of graft copolymerization of vinyl monomers onto polymer presenting oxidizable functional groups. Russell, et al. [34] have studied grafting of acrylonitrile (AN), methyl methacrylate (MMA) and vinyl acetate (VAC) onto starch using ceric ion technique. They observed that the relative activity of monomers towards grafting followed the order: AN>MMA>VAC.

No attempt, however, has been made to determine the relative activity of acrylic acid and ethyl methacrylate towards of grafting onto starch, using Ce (IV) as initiator. It was therefore, thought desirable to compare the monomer reactivities and investigates the kinetics of grafting onto starch using the ceric ion method.

The object of present work is graft polymerization of AA and EMA onto starch in aqueous media using ceric ammonium nitrate as initiator to prepare starch-g-poly acrylic acid (St-g-PAA) and starch-g-poly ethyl methacrylate (St-g-PEMA) copolymers, evaluating and comparing the properties of the poly acrylic starch composites obtained under various polymerization

conditions. The graft polymerization was kinetically studied and tentative mechanisms for the polymerization reactions involved in the redox system are also reported.

## EXPERIMENTAL

### Materials

Acrylic acid (AA), ethyl methacrylate (EMA) were from Merck (Darmstadt, Germany), contained hydroquinone as inhibitor were freshly distilled under reduced pressure and stored in the dark at 4°C until used. Starch and Ceric ammonium nitrate,  $(\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6)$  used were analytical-grade reagents from Merck.

### Graft Polymerization Procedure

A weighed amount of starch ( $w_0$ ) was slurried in 30 ml and 50 ml (for synthesis of St-g-AA and St-g-PEMA, respectively) distilled water in a three-necked flask, which was equipped with a stirrer, a condenser and a dropping funnel. The slurry was heated at 70°C for about half an hour under the nitrogen atmosphere and cooled to the desired reaction temperature (40-45°C), dependent on the synthesis case. After that, initiator was first added, followed by monomer ( $w_3$ ) after 30 min [35]. The reaction mixture was allowed to react under slow stirring for 3 hours. After the desired reaction time, the products were taken out and washed thoroughly with acetone in the case of AA and with ethanol in the case of EMA, dried and weighed ( $w_1$ ) [13]. Finally, the copolymers (St-g-PAA, St-g-PEMA) were Soxhlet extracted with DMF and  $\text{CCl}_4$  respectively for 24 hour to remove the homopolymers [36]. They were then dried in an oven, cooled to room temperature, and weighed ( $w_2$ ). The percentage of grafting and percent conversion on monomer was calculated by weighing the original starch and grafted product [37, 38].

$$\text{Graft}(\%) = \left[ \frac{w_2 - w_0}{w_0} \right] \times 100$$

$$\text{and Graft}(\%) = \left[ \frac{w_2 - w_0}{w_0} \right] \times 100$$

The optimum conditions for synthesis St-g-PAA were determined as follows:  $[\text{CAN}] = 5 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $[\text{AA}] = 0.9 \text{ mol.lit}^{-1}$ ,  $m_{\text{st}} = 1.4 \text{ g/50 cm}^3$ ,  $\text{pH} = 2$ ,  $T = 40^\circ\text{C}$ ,  $\text{Time} = 3 \text{ hr}$  and for synthesis St-g-PEMA is:  $[\text{CAN}] = 8 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $[\text{EMA}] = 0.16 \text{ mol.lit}^{-1}$ ,  $m_{\text{st}} = 0.5 \text{ g/30 cm}^3$ ,  $\text{pH} = 7.2$ ,  $T = 45^\circ\text{C}$  and  $\text{Time} = 2.5 \text{ hr}$ .

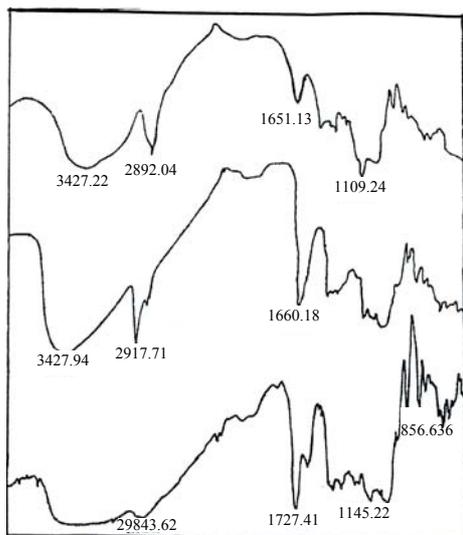


Fig.1: FT- IR spectra of (A) starch, (B) graft copolymer (St-g-PAA) and (C) graft copolymer (St- g- PEMA).

### IR Spectral Analysis

The infra-red spectra of grafted and ungrafted starch were recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the FT-IR Shimadzu model 4300, (Japan) in the range 650-4000  $\text{cm}^{-1}$  at 25°C.

## RESULTS AND DISCUSSION

### Evidence of Graft

The IR spectra of ungrafted starch and grafting samples (St-g-PAA, St-g-PEMA) showed both the characteristic absorption of starch at 3000-3800  $\text{cm}^{-1}$  and characteristic absorption of St-g-PAA and St-g-PEMA at 1670  $\text{cm}^{-1}$  and 1730  $\text{cm}^{-1}$ , respectively which were not present in starch, this testified the existence of grafting (Fig. 1).

### The Effect of Reaction Time

The effect of reaction time on AA and EMA grafting onto starch has been shown in Fig. 2. The percentage of grafting, graft %, was obtained by acid-base and bromometry titration, respectively at time ranged from 200-4000 second by keeping constant other parameters. The rate of AA and EMA grafting increased linearly with increasing reaction time up to 2000 and 2400 s respectively, and gradual leveling off thereafter. The leveling off of graft yield is perhaps, a direct consequence of depletion of monomer available for grafting [27].

### The Effect of Initiator Concentration

The concentration of initiator has a decisive effect on the grafting. The effect of CAN concentration on the % graft yield was studied in the range of  $0.5 \times 10^{-3}$ – $1.2 \times 10^{-3}$   $\text{mol.lit}^{-1}$  for St-g-PAA and  $4 \times 10^{-3}$ – $12 \times 10^{-3}$   $\text{mol.lit}^{-1}$  for St-g-PEMA at constant starch, monomer concentration, pH, temperature and time are presented in table 1. It is observed that with increasing initiator concentration up to  $5 \times 10^{-3}$   $\text{mol.lit}^{-1}$  for St-g-PAA and  $8 \times 10^{-3}$   $\text{mol.lit}^{-1}$  for St-g-PEMA. The graft yields increases and thereafter it decreases. In the initial stage with the increasing the initiator concentration, the number of grafting sites on the backbone of the starch increases by the interaction of the starch with the initiator, results the increasing in graft yield. But with further increasing of [CAN] over  $5 \times 10^{-3}$   $\text{mol.lit}^{-1}$  in the case of AA and  $8 \times 10^{-3}$   $\text{mol.lit}^{-1}$  in the case of EMA, the initiator might interact with the monomer molecules producing homopolymer, thereby decreasing graft yield.

### The Effect of Monomer Concentration

The effect of monomer concentration on the % graft yield within the range 0.4-1.4  $\text{mol.lit}^{-1}$  for St-g-PAA and 0.01-0.36  $\text{mol.lit}^{-1}$  for St-g-PEMA at constant starch, initiator, pH, temperature and time are presented in table 2. With the increase in [AA] from 0.4-0.9  $\text{mol.lit}^{-1}$  and [EMA] from 0.01-0.16  $\text{mol.lit}^{-1}$ , the graft yield increased because of the rising in grafting rate, and a maximum graft yield was achieved at [AA]=0.9  $\text{mol.lit}^{-1}$  and at [EMA]=0.16  $\text{mol.lit}^{-1}$ . The increase in the rate of grafting with the increase in monomer concentration was obviously owing to the greater availability of monomer in the proximity of starch macroradicals [39]. This is in close agreement with the result of grafting of ethyl acrylate onto gelatin [40]. With the further increase in [AA] and [EMA], the chain transfer from starch macroradical onto monomer increased, it may be due to the formation of more  $M_n^o$  radicals, that leading to the lowering of graft yield and leads to preferential formation of homopolymer. The growing polymeric radical at higher concentrations may terminate grafting by process [13, 41] leading to a decrease in grafting.

### The Effect of Starch Concentration

The effect of concentration of starch on the % graft yield within the range 0.2-2.6  $\text{g}/50 \text{ cm}^3$  for St-g-PAA and

**Table 1: The Effect of initiator concentration on the grafting of AA and EMA onto starch.**

St=1.4 g/50 cm <sup>3</sup> , [AA]=0.9 mol.lit <sup>-1</sup> , pH=2, T=40°C, Time=3 hr		St=0.5 g/30 cm <sup>3</sup> , [EMA]=0.16 mol.lit <sup>-1</sup> , pH=7.2, T=45°C, Time=2.5 hr	
[CAN]×10 <sup>3</sup> mol.lit <sup>-1</sup>	%Graft yield (AA)	[CAN]×10 <sup>3</sup> mol.lit <sup>-1</sup>	%Graft yield (EMA)
0.5	30	4	55
2.5	49	5	64
5	58	6	68
6	55	7	72
8.6	50	8	75
10.6	47	10.5	65
12	44	12	47

**Table 2: The Effect of monomer concentration on the grafting of AA and EMA onto starch.**

St=1.4 g/50 cm <sup>3</sup> , [CAN]= 5×10 <sup>-3</sup> mol.lit <sup>-1</sup> , pH=2, T=40°C, Time=3 hr		St=0.5 g/30 cm <sup>3</sup> , [CAN]= 8×10 <sup>-3</sup> mol.lit <sup>-1</sup> , pH=7.2, T=45°C, Time=2.5 hr	
[AA] mol.lit <sup>-1</sup>	% Graft yield	[EMA] mol.lit <sup>-1</sup>	% Graft yield
0.4	12	0.01	30
0.5	20	0.06	46
0.6	28	0.11	58
0.7	40	0.16	67
0.8	65	0.20	65
0.9	72	0.26	60
1	70	0.31	55
1.2	60	0.36	45

**Table 3: The Effect of starch concentration on the grafting of AA and EMA.**

[CAN]=5×10 <sup>-3</sup> mol.lit <sup>-1</sup> , [AA]=0.9 mol.lit <sup>-1</sup> pH=2, T=40°C, Time=3 hr		[CAN]=8×10 <sup>-3</sup> mol.lit <sup>-1</sup> , [EMA]=0.16 mol.lit <sup>-1</sup> pH=7.2, T=45°C, Time=2.5 hr	
[St] g/50 cm <sup>3</sup>	% Graft yield (AA)	[St] g/30 cm <sup>3</sup>	% Graft yield (EMA)
0.2	15	0.1	25
0.6	34	0.2	38
1	48	0.3	45
1.4	65	0.4	55
1.8	62	0.5	70
2.2	61	0.7	68
2.6	20	0.8	66
		1	64

0.1-1 g/30 cm<sup>3</sup> for St-g-PEMA at constant initiator, monomer concentration, pH, temperature and time are presented in table 3.

It is observed that the graft yield increased with the increase in [St] and reached a maximum at [St]=1.4 g/50 cm<sup>3</sup> for St-g-PAA and [St]=0.5 g/30 cm<sup>3</sup> for St-g-PEMA and thereafter remained almost constant. There exists an optimum starch concentration at which the percent of grafting reaches maximum. This indicates that, the integrated surface area of the starch greatly affects the diffusion of the monomer and free radical formation on the starch backbone [42]. It is also possible that at higher concentrations, some of the starch molecules react with primary radicals to generate backbone macroradicals [43], and therefore with further increase in the concentration of starch, grafting is found to become almost constant. This indicates that beyond the optimum concentration, there is a pronounced gel effect [44].

The gel effect was more pronounced at higher concentrations of the monomer. The formation of a large amount of gel increases the viscosity of the reaction medium and as such the movement of the growing grafted polymeric chain is restricted with the result that in the attack on the active sites of starch backbone is decreased and homopolymer is formed. The homopolymerization of PAA and PEMA being relatively much faster than the grafting of AA and EMA onto starch.

#### The Effect of Temperature

Reaction temperature is another important reaction condition in the graft copolymerization. The grafting reaction was carried out at different temperatures ranging from 25-65°C for St-g-PAA and 25-55°C for St-g-PEMA under constant experimental conditions, and are presented in table 4. With the increase in temperature from 25°C to 40°C in the case of St-g-PAA and from 25°C to 45°C in the case of St-g-PEMA, the graft yield increased and maximum graft yield was achieved at 40°C and 45°C respectively, and then decreased.

The favorable effect of temperature (up to 40°C in the case of St-g-PAA and 45°C in the case of St-g-PEMA) on grafting could be ascribed to:

- diffusion of AA and EMA into the starch structure,
- mobility of AA and EMA molecules and their collision with starch macroradicals for initiating of grafting,

**Table 4: The Effect of reaction temperature on the grafting of AA and EMA onto starch.**

Temp. (°C)	St=1.4 g/50 cm <sup>3</sup> [CAN]=5×10 <sup>-3</sup> mol.lit <sup>-1</sup> , [AA]=0.9 mol.lit <sup>-1</sup> pH=2, Time=3 hr	St=0.5 g/30 cm <sup>3</sup> [CAN]=8×10 <sup>-3</sup> mol.lit <sup>-1</sup> , [EMA]=0.16 mol.lit <sup>-1</sup> , pH=7.2, Time=2.5 hr
	% Graft yield	% Graft yield
25	30	24
30	50	40
35	62	50
40	74	58
45	70	66
50	68	64
55	64	60
60	60	-
65	58	-

- (c) swellability of starch,  
 (d) solubility of monomers and,  
 (e) propagation of the graft.

Similar observations have been noted by Mostafa [31] while grafting AA onto starch using KMnO<sub>4</sub> along with an acid as initiated. On the other hand, a probable explanation given by them, the lower grafting observed at 60°C is perhaps due to the faster termination rate a greater amount of homopolymer formation at higher temperatures. Moreover, it is likely that at higher temperatures starch undergoes modification, such as partial hydrolysis in the presence of nitric acid, partial dissociation of soluble amylose part [27].

#### The Effect of pH

It has been observed that change in the [HNO<sub>3</sub>] affects the rates of oxidation by ceric ion to and polymerization [45]. The changes observed in these rates have been attributed to the formation complexes between ceric ion and nitrate ions, hydroxyl ions and water molecules. An increase in [HNO<sub>3</sub>] makes the rates of initiation and termination by ceric ion to increase [10].

Table 5 shows the effect of concentration of nitric acid on the graft yield. The results of varying nitric acid concentration at the stages of the polymerization reaction indicate that grafting yield increase rapidly with pH reaching the maximum value in the cases of AA and EMA at pH=2 and pH=7.2 respectively and thereafter it decreases.

**Table 5: The Effect of concentration of nitric acid on the grafting of AA and EMA onto starch.**

St=1.4 g/50 cm <sup>3</sup> [CAN]= 5×10 <sup>-3</sup> mol.lit <sup>-1</sup> , T=40°C, [AA]=0.9 mol.lit <sup>-1</sup> , Time=3 hr		St=0.5 g/30 cm <sup>3</sup> [CAN]=8×10 <sup>-3</sup> mol.lit <sup>-1</sup> , T=45°C, [EMA]=0.16 mol.lit <sup>-1</sup> , Time=2.5 hr	
PH	% Graft yield	PH	% Graft yield
0	25	4	20
1	45	5	30
2	58	6	45
3	53	7	60
4	40	8	55
5	24	10	40

The increase in grafting yield with [HNO<sub>3</sub>] up to a certain value can be a result of the higher increase in the rate of initiation than in the rate of termination. On the other hand, the further decrease of grafting yield is the result of a decrease in the number of starch radicals, which add monomer, because of their increased oxidation by Ce (IV).

#### Kinetics of Graft Polymerization

It is observed that in Figs. 2 and 3 up to 2000 sec in the case of AA and 2400 sec in the case of EMA, the percentage of graft yield is linear with time; thereby the reaction rate remained constant. The rate of graft copolymerization of St-g-PAA (R<sub>g</sub>) and St-g-PEMA (R'<sub>g</sub>) on the concentration of the initiator, monomer and starch as in the following:

$$R_g = k[CAN]^a[AA]^b[St]^c, R'_g = k'[CAN]^a[EMA]^b [St]^c$$

Graft copolymerization was studied by changing the concentration of CAN with constant monomer and starch concentrations. In these conditions, the rates of equations are as follows:

$$R_g = k_1[CAN]^a, R'_g = k'_1[CAN]^a$$

The effects of initiator concentration on the graft yield are shown in Figs. 3 and 4. They indicate that the graft yield increase with the increasing of concentration CAN. The plots of -Ln(R<sub>g</sub>)<sub>0</sub> versus -Ln[CAN]<sub>0</sub> and -Ln (R'<sub>g</sub>)<sub>0</sub> versus. -Ln[CAN]<sub>0</sub> are linear and plotted in Figs. 5 and 6.

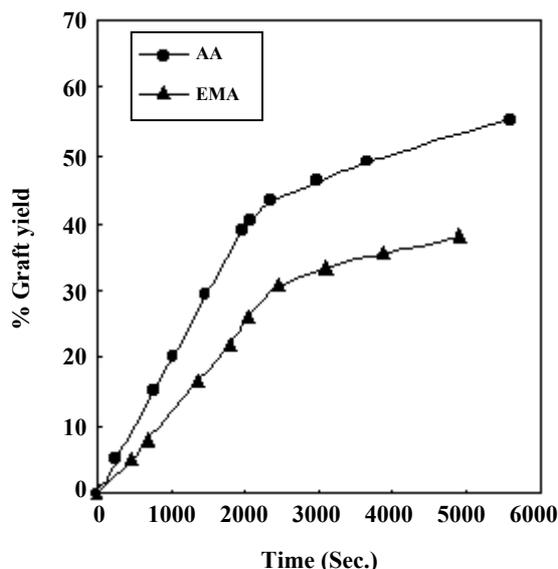


Fig.2: The Effect of polymerization time on the grafting of AA onto starch at  $\text{pH}=2$ ,  $[\text{CAN}]=5 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $[\text{AA}]=0.9 \text{ mol.lit}^{-1}$ ,  $m_{\text{St}}=1.4 \text{ g/50 cm}^3$ ,  $T=40^\circ\text{C}$  and EMA onto starch in conditions of  $[\text{EMA}] = 0.16 \text{ mol.lit}^{-1}$ ,  $[\text{CAN}]=8 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $m_{\text{St}} = 0.5 \text{ g/30 cm}^3$ ,  $\text{pH}=7.2$ ,  $T= 45^\circ\text{C}$ .

The slopes of the lines are 0.56 and 0.53, respectively, which suggest that the orders of the reactions with respect to initiator are 0.56 and 0.53. The grafting has been studied by changing concentration of monomer with constant initiator and starch concentrations. In these conditions the rate of equations are as follows:

$$\text{Rg} = k_2[\text{AA}]^b, \text{R}'\text{g} = k'_2[\text{EMA}]^b$$

Experimental values of grafted copolymer are which depicted in Figs. 7 and 8, increase in percent grafting were observed upon increasing the monomer concentration. The plots of  $-\text{Ln}(\text{Rg})_0$  versus  $-\text{Ln}[\text{AA}]_0$  and  $-\text{Ln}(\text{R}'\text{g})_0$  versus  $-\text{Ln}[\text{EMA}]_0$  in constant concentrations of starch and initiator are linear and plotted in Figs. 9 and 10 which indicate that the order of the reaction with respect to monomers are 0.92 and 0.92, respectively, which suggest that the orders of the reaction with respect to monomer are 0.92 and 0.92.

The dependence of grafting on the amount of starch was studied at constant initiator and monomer concentration. In these conditions the rates of equations are as follows:

$$\text{Rg} = k_3[\text{St}]^c, \text{R}'\text{g} = k'_3[\text{St}]^c$$

The plots of % graft are shown in Figs. 11 and 12. These indicate that the graft yield increases with increasing of concentration starch. The plots of  $-\text{Ln}(\text{Rg})_0$

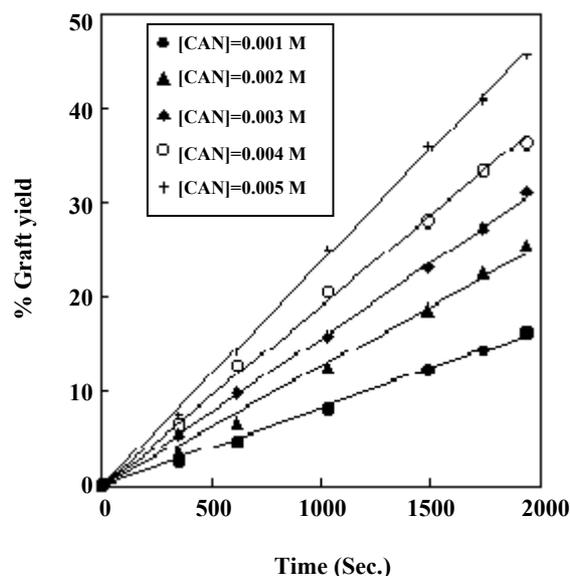


Fig. 3: The Effect of initiators concentration (CAN) on the grafting of AA onto starch at  $[\text{AA}]=0.9 \text{ mol.lit}^{-1}$ ,  $m_{\text{St}}=1.4 \text{ g/50 cm}^3$ ,  $\text{pH}=2$ ,  $T=40^\circ\text{C}$ .

versus  $-\text{Ln}[\text{St}]_0$  and  $-\text{Ln}(\text{R}'\text{g})_0$  versus  $-\text{Ln}[\text{St}]_0$  are linear and plotted in Figs. 13 and 14. The slopes of lines are 0.46 and 0.48, respectively, which suggest that the orders of the reactions with respect to initiator are 0.46 and 0.48. Therefore, the following reactions rates equations are established:

$$\text{Rg} = k[\text{CAN}]^{0.56}[\text{AA}]^{0.92}[\text{St}]^{0.46} \quad (\text{a})$$

and

$$\text{R}'\text{g} = k'[\text{CAN}]^{0.53}[\text{EMA}]^{0.97}[\text{St}]^{0.48} \quad (\text{b})$$

The effects of temperature on the graft yield within the range of  $20\text{--}40^\circ\text{C}$  for St-g-PAA and  $25\text{--}45^\circ\text{C}$  for St-g-PEMA shown in Figs. 15 and 16. These indicate that the graft yield increase with the increasing of temperature. The effect of temperature on the grafting rate is shown in table 6.

The plots  $-\text{Ln}(\text{Rg})$  and  $-\text{Ln}(\text{R}'\text{g})$  versus  $1/T$  are linear (Fig. 17). According to the Arrhenius equations, the overall activation energy for graft copolymer was obtained  $36.25 \text{ kJmol}^{-1}$  for St-g-PAA and  $11.88 \text{ kJmol}^{-1}$  for St-g-PEMA.

The grafting of two different monomers onto starch under the optimum conditions using Ce(IV) as initiator was examined. The data in table 4 indicate that the structure of monomer has a great effect on graft copolymerization and that the order of grafting ability of

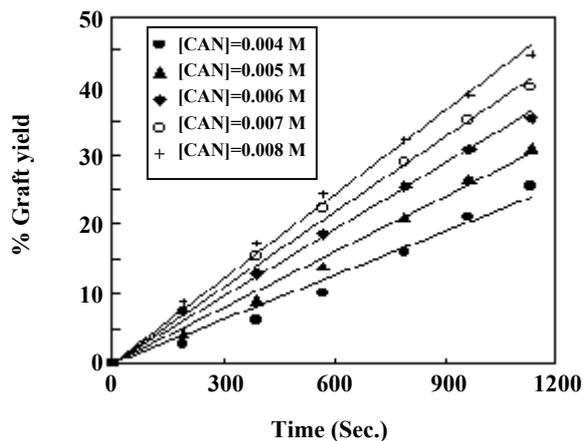


Fig. 4: The Effect of initiator concentration (CAN) on the grafting of EMA onto starch at  $[EAM]=0.16 \text{ mol.lit}^{-1}$ ,  $m_{st}=0.5 \text{ g/30 cm}^3$ ,  $pH=7.2$ ,  $T=45^\circ\text{C}$ .

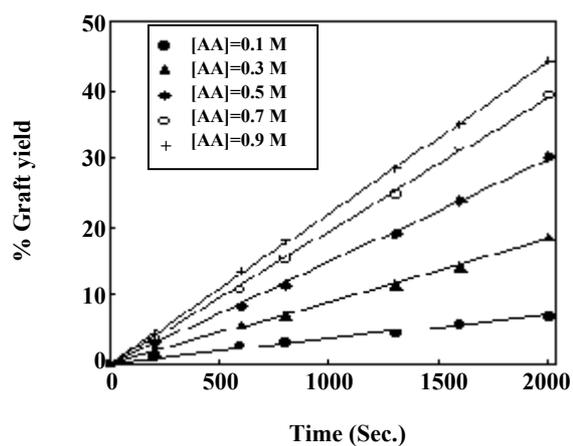


Fig. 7: The Effect of monomer concentration (AA) on the grafting of AA onto starch at  $pH=2$ ,  $[CAN]=5 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $m_{st}=1.4 \text{ g/50 cm}^3$ ,  $T=40^\circ\text{C}$ .

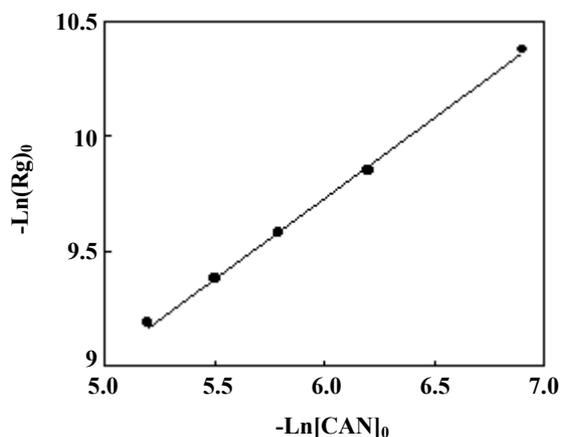


Fig. 5: Plot of  $-\ln(Rg)_0$  versus  $-\ln[CAN]_0$ , other conditions are as in Fig. 3.

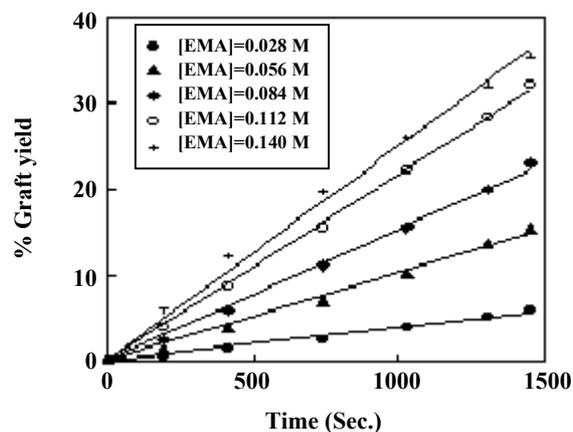


Fig. 8: Effect of monomer concentration (EMA) on the grafting of EMA onto starch in conditions of  $pH=7.2$ ,  $[CAN]=8 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $m_{st}=0.5 \text{ g/30 cm}^3$ ,  $T=45^\circ\text{C}$ .

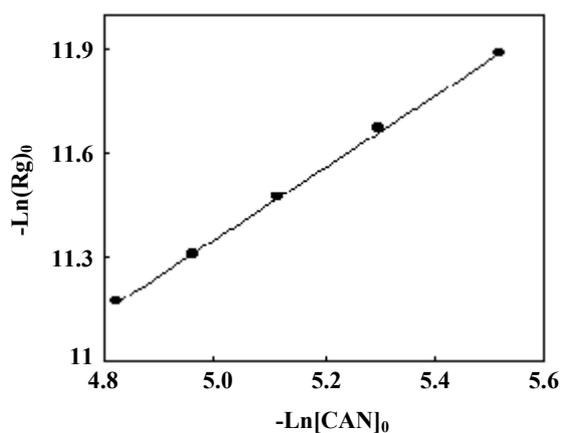


Fig. 6: Plot of  $-\ln(Rg)_0$  versus  $-\ln[CAN]_0$ , other conditions are as in Fig. 4.

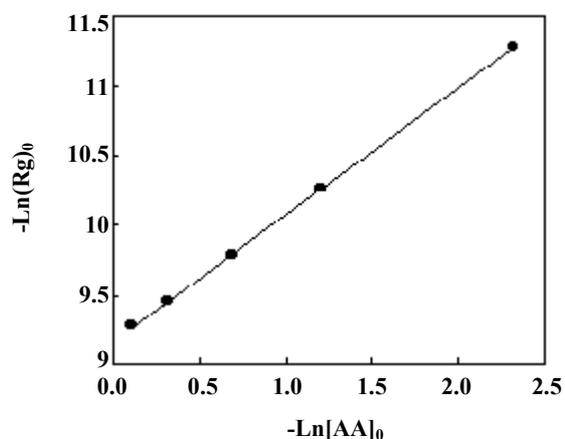


Fig. 9: Plot of  $-\ln(Rg)_0$  versus  $-\ln[AA]_0$ , other conditions are as in Fig. 7.

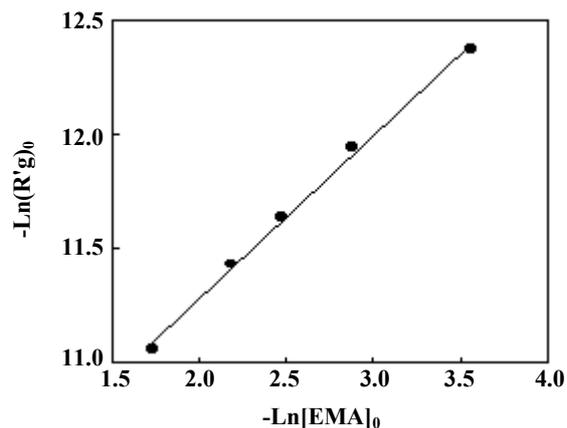


Fig. 10: Plot of  $-\ln(R'g)_0$  versus  $-\ln[EMA]_0$ , other conditions are as in Fig. 8.

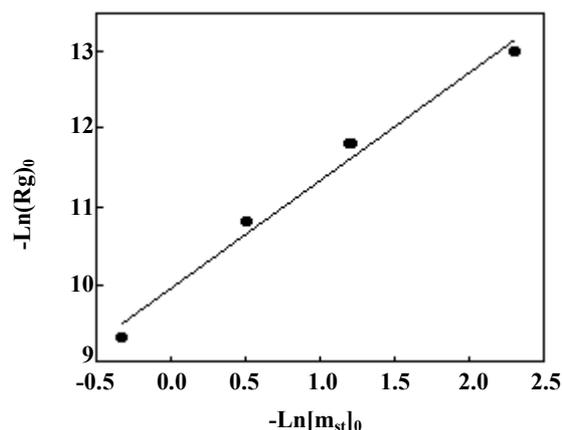


Fig. 13: Plot of  $-\ln(Rg)_0$  versus  $-\ln[St]_0$ , other conditions are as in Fig. 11.

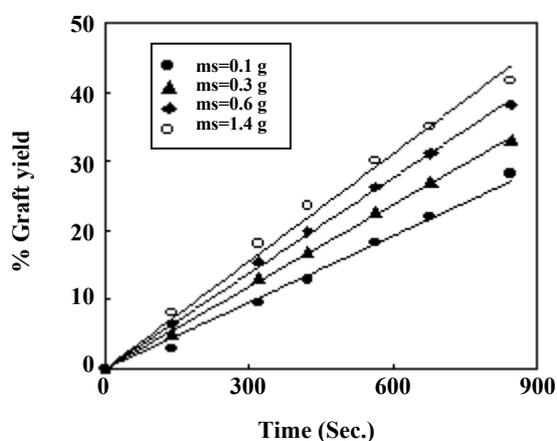


Fig. 11: The Effect of starch concentration ( $St$ ) on the grafting of AA onto starch at  $pH = 2$ ,  $[CAN]=5 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $[AA]=0.9 \text{ mol.lit}^{-1}$ ,  $T=40^\circ\text{C}$ .

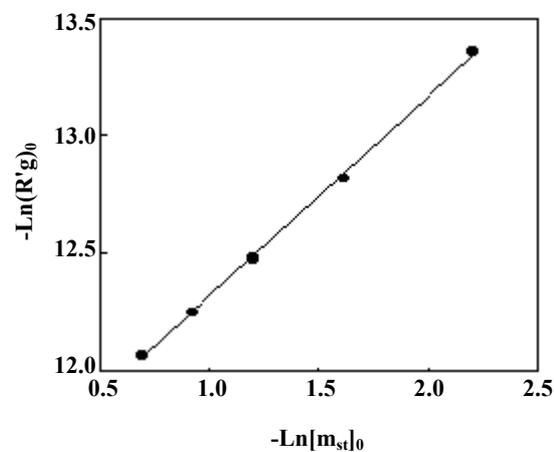


Fig. 14: Plot of  $-\ln(R'g)_0$  versus  $-\ln[St]_0$ , other conditions are as in Fig. 12.

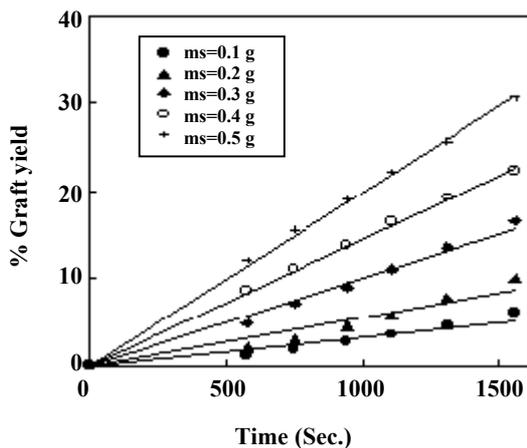


Fig. 12: The Effect of starch concentration ( $St$ ) on the grafting of EMA onto starch at  $[EMA] = 0.16 \text{ mol.lit}^{-1}$ ,  $[CAN]=8 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $pH=7.2$ ,  $T=45^\circ\text{C}$ .

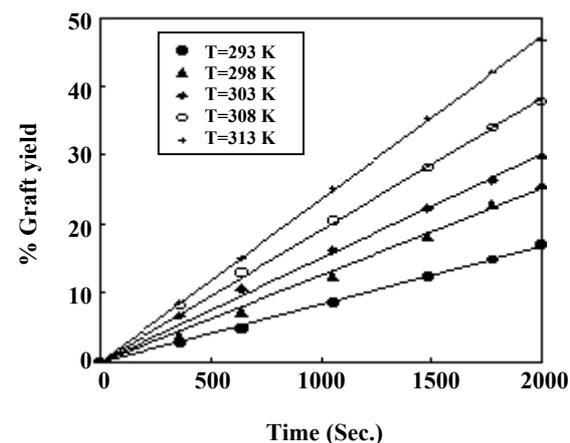


Fig. 15: The Effect of reaction temperature on the grafting of AA onto starch at  $pH=2$ ,  $[CAN]=5 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $[AA]=0.9 \text{ mol.lit}^{-1}$ ,  $m_{St}=1.4 \text{ g}/50 \text{ cm}^3$ .

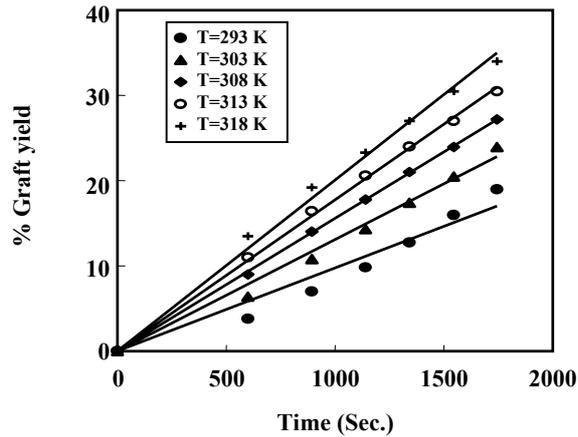


Fig. 16: The effect of reaction temperature on the grafting of EMA onto starch at  $[EMA]=0.16 \text{ mol.lit}^{-1}$ ,  $pH=7.2$ ,  $[CAN] = 8 \times 10^{-3} \text{ mol.lit}^{-1}$ ,  $m_{St}=0.5 \text{ g/30 cm}^3$ .

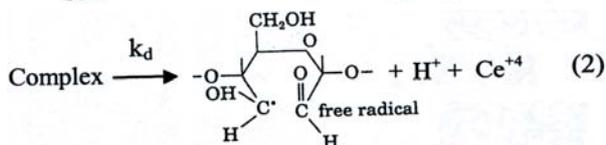
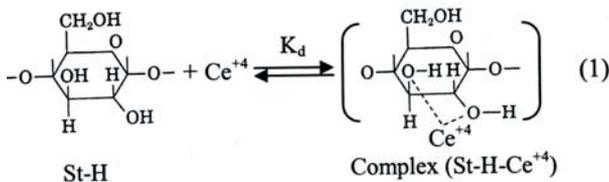
two different monomer onto starch is  $AA > EMA$ .

Thus as the size of the monomer is increased, the diffusion of monomer to all available sites on the starch is not possible resulting in the decrease of the percentage of graft in the case of bulkier monomers [46].

## MECHANISM

The mechanism of polymerization vinyl monomers onto starch with ceric ammonium nitrate as a redox system was suggested as follows [31, 47]:

### Initiation



In the presence of vinyl monomer the starch radical is added to the double bond of the vinyl monomer; resulting in a covalent bond between monomer and starch with creation of a free radical on the monomer; i.e., a chain is initiated.

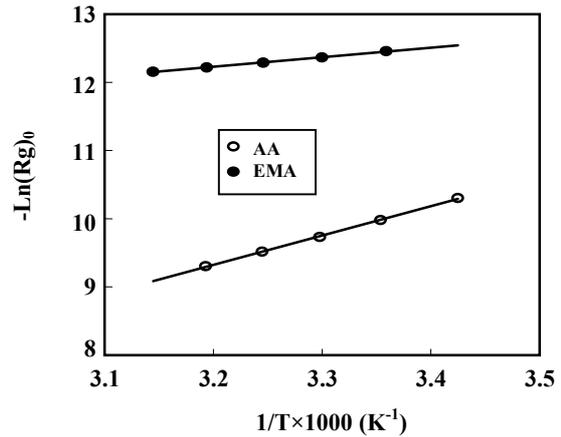
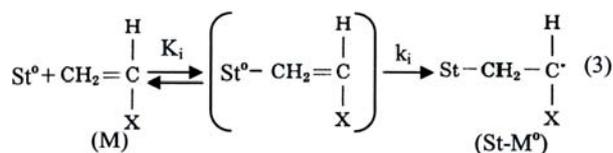
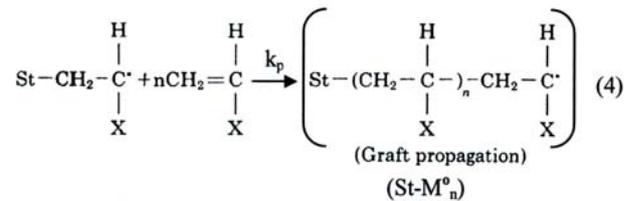


Fig. 17: Plot of  $-\ln(Rg)_0$  versus  $1/T$  and  $-\ln(R'g)_0$  versus  $1/T$ , other conditions are as in Figs. 15 and 16.

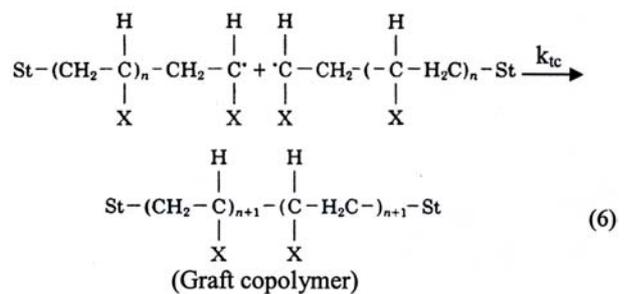
### Propagation

Subsequent addition of monomer molecules to the initiated chain propagates the grafting reaction onto starch as follows:



### Termination

Termination of the growing grafted chain may occur via coupling as follows:



On the basis of the above reaction scheme and consider steady state approximation, the following expressions were derived.

$$R_p = k_p[M][\text{St-M}_n^{\bullet}] \quad (7)$$

$$R_i = R_d = k_d[\text{St-H-Ce(IV)}] = k_d K_d [\text{St-H}][\text{Ce(IV)}] \quad (8)$$

Table 6: The effect of temperature on the grafting rate.

Temperature (°C)	R <sub>g</sub> × 10 <sup>5</sup>	R' <sub>g</sub> × 10 <sup>6</sup>
20	3.227	-
25	4.651	3.816
30	5.992	4.237
35	7.384	4.522
40	8.384	4.929
45	-	5.221

$$R_t = 2k_{tc}[\text{St-M}^{\circ}_n]^2 \quad (9)$$

By considering steady state principle:

$$R_i = R_t \quad (10)$$

$$k_d K_d [\text{St-H}][\text{Ce(IV)}] = 2k_{tc}[\text{St-M}^{\circ}_n]^2 \quad (11)$$

$$[\text{St-M}^{\circ}_n] = \left( \frac{K_d k_d}{2k_{tc}} \right)^{\frac{1}{2}} [\text{St-H}]^{\frac{1}{2}} [\text{Ce(IV)}]^{\frac{1}{2}} \quad (12)$$

By replacing equation (12) into equation (7),

$$R_p = K_p \left( \frac{k_d K_d}{2k_{tc}} \right)^{\frac{1}{2}} [\text{St-H}]^{\frac{1}{2}} [\text{Ce(IV)}]^{\frac{1}{2}} [M] \quad (13)$$

$$\text{if } K = K_p \left( \frac{k_d K_d}{2k_{tc}} \right)^{\frac{1}{2}}$$

$$R_p = K [\text{St-H}]^{\frac{1}{2}} [\text{Ce(IV)}]^{\frac{1}{2}} [M] \quad (14)$$

where M, St-H and Ce (IV) represent monomer, starch and initiator (Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>), respectively and St is starch radical. K<sub>d</sub>, K<sub>i</sub> are equilibrium constant and k<sub>p</sub>, k<sub>d</sub> are rate constants. Equation (14) is identical with equations a and b, established from the experiment. This indicates that the reaction mechanism suggested above was acceptable.

## CONCLUSIONS

Based on the results presented in this paper, we conclude that ceric ammonium nitrate is an efficient initiator for grafting of AA and EMA onto starch under a wide range of experimental conditions. Only small amounts of PAA and PEMA were extractable as homopolymer. The graft yield can be adjusted by changing the reaction conditions, such as reaction temperature, concentration of monomer, initiator, starch and PH under the experimental conditions.

Grafting parameters such as conversion of monomer to polymer, graft yield can be varied substantially by varying the concentration ratio of initiator (Ce<sup>4+</sup>) to starch and monomer to starch, and to some extent, the acidity. Variations in the grafting parameters were different for grafting of AA than for EMA. The capability of monomer grafted onto starch using Ce (IV) as initiator is: AA>EMA

The two suitable rate conditions were proposed as follows:

$$R_g = k[\text{AA}]^{0.92}[\text{CAN}]^{0.56}[\text{St}]^{0.46} \text{ and}$$

$R'_g = k'[\text{EMA}]^{0.92}[\text{CAN}]^{0.53}[\text{St}]^{0.48}$  for St-g-PAA and St-g-PEMA, respectively.

A suitable mechanism is suggested to justify observation. This mechanism emphasizes on hydrogen abstraction from hydroxyl function symmetrically. The apparent activation energies of St-g-PAA and St-g-PEMA syntheses are found to be 36.25 kJ.mol<sup>-1</sup> and 11.88 kJ.mol<sup>-1</sup> respectively.

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