

Kinetics and Mechanism of Graft Copolymerization of Vinyl Monomers (Acrylamide, Acrylic Acid, and Methacrylate) onto Starch by Potassium Dichromate as Redox Initiator

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ABSTRACT

Graft copolymerization of vinyl monomers including acrylamide (AAm), acrylic acid (AAc) and methyl methacrylate (MMA) onto starch (St) has been carried out under nitrogen atmosphere in aqueous solution using potassium dichromate, Cr(VI), as redox initiator, individually. Dependence of graft yield upon monomer, starch and initiator concentration is investigated as well as reaction temperature by using gravimetry method. Rate equations obtained are: $R_g = [AAm]^{0.93}[I]^{0.49}[St]^{0.52}$, $R_g = k[AAc]^{0.95}[I]^{0.44}[St]^{0.46}$ and $R_g = k[MMA]^{0.95}[I]^{0.44}[St]^{0.46}$ for St-g-PAm, St-g-PAAc and St-g-PMMA graft polymers, respectively. The kinetics of grafting process has been evaluated by bromometry titration. Finally, activation energies within temperature 50-55°C for St-g-PAAm, St-g-PAAc and St-g-PMMA syntheses are found to be 48.16, 46.13 and 49.06 kJ/mol.k, respectively. Based on results observed, a suitable mechanism is proposed to justify the results.

Key Words:

kinetics;
starch;
vinyl monomers;
potassium dichromate;
graft copolymerization.

INTRODUCTION

Grafting of various monomers onto macromolecules such as starch, cellulose, etc. has opened a vast horizon to the scientists to amend some attentive properties of such huge homopolymers. For instance, we may use modified starch in health materials [1,2],

cation exchanger membrane [3], and corrosion protection of aluminium [4]. Grafting of acrylic acid onto starch has been reported by potassium bromate/thiocarbonate [5] and permanganate/acid [6]. On other hand, grafting of acrylamide onto

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starch has been reported by potassium persulphate [7]. But it should be noticed that grafting of considered monomers onto starch by Cr(VI) has not been reported [8]. In the present research work, first we aim to determine the optimum condition in the synthesis of St-g-PAAm, St-g-PAAc and St-g-PMMA graft copolymers independently. On other hand, corresponding proper rate equations are presented. In addition, activation energies of these reactions have been calculated. Finally, based on results observed in these experiments, a suitable mechanism is suggested so that it would justify the results.

EXPERIMENTAL

Materials

Starch, acrylamide, methyl methacrylate, potassium dichromate and silver nitrate have been obtained from Merck and acrylic acid from Fluka. Acrylic acid and methyl methacrylate were distilled under a high-reduced pressure to remove inhibitor and acrylamide was recrystallized in benzene. Potassium dichromate and silver nitrate were used as received.

Procedure

A stirred suspension of dried weight of starch (40, 50, and 60 g/L for synthesis of St-g-PAAc, St-g-PAAm and St-g-PMMA graft copolymers, respectively) in a three-necked flask containing water was sparged by a slow stream of nitrogen and/or helium for 1/2 h at 80-85°C. In this temperature range starch swells and so it would be ready to react. Then initiator aqueous solution is added when the reaction temperature is cooled down to 50-55°C, dependent on each synthesis. After reaction time of 2.5-3 h, the contents of vessel were poured by

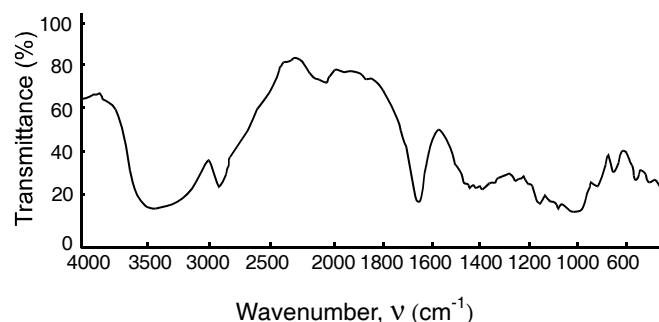


Figure 1. IR Spectrum of St-g-PAAm graft copolymer. Solvent is KBr powder.

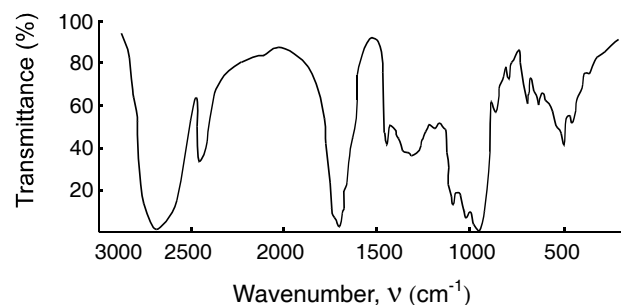


Figure 2. FTIR Spectrum of St-g-PAAc graft copolymer. Solvent is KBr powder.

proper non-solvent to precipitate [9]. Then graft copolymer was separated from homopolymer and unreacted starch by corresponding extractor solvent of homopolymer [9]. Finally, it was passed through soxhlet by the same extractor solvent for 24-36 h. Then, it was washed by slight acidic distilled water to hydrolyze the unreacted starch. The remaining portion of the sediment was dried and weighed. In accordance with the following relation, the graft percentage is calculated:

$$\text{Graft yield} = (w_2 - w_1) / w_1 \times 100$$

where, w_2 and w_1 are the final and initial weight of graft copolymer and starch, respectively. The major part of this paper is concentrated on obtaining the reaction rate and their activating energies. Reaction rate is gained by bromometry titration. To this end, the monomer concentration gradient is followed. At definite times a distinct volume of solution is treated with silver nitrate (0.1 N) to precipitate extra dichromate as $\text{Ag}_2\text{Cr}_2\text{O}_7$. After separating out the solid portion, oral salt (NaCl, 2N) is added to remove extra Ag^+ in the form of AgCl with the help of high speed centrifuga-

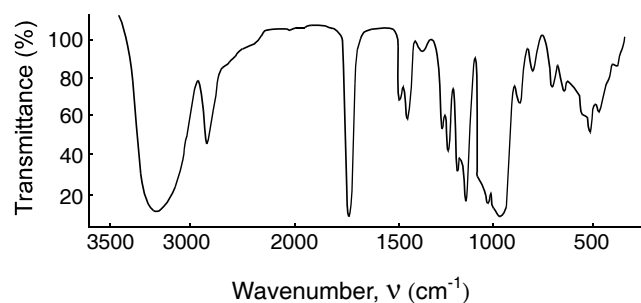


Figure 3. FTIR Spectrum of St-g-PMMA graft copolymer. Solvent is KBr powder.

tion. Bromometry titration is applied as previous works [10]. IR and/or FTIR (Shimadzu FTIR-4300) spectra of objective products are presented as indication of reaction performance (Figures 1-3).

RESULTS AND DISCUSSION

The optimum graft condition for monomer, initiator and starch system was determined by varying the concentration of initiator, monomer and starch.

Effect of Initial Concentration

Graft copolymerization was studied by changing the concentration of initiator at constant monomer and starch concentration. The perusal of results indicate that, with increasing initiator concentration up to 0.032 M, 0.008 M, 0.008 M for AAm, AAc, MMA, respectively, the graft yield increases and thereafter it decreases, Figures 4-6. It indicates that the graft yield increases with the increasing of concentration Cr(VI). The increase of percent grafting with initiator concentration may be related to the increase of active sites on the backbone of the starch arising by the interaction of the starch with the initiator, but beyond 0.032 M, 0.008 M, 0.008 M of the initiators concentrations, respectively, the initiator might interact with the monomer molecules, producing homopolymers, thereby decreasing the graft yield.

Effect of Monomer Concentration

The grafting has been studied by changing the concentration of monomer at constant initiator and starch concentrations. It is observed that, with increasing monomer concentration up to 0.31, 0.31, 0.34 M for AAm, AAc and MMA, respectively, the graft yield

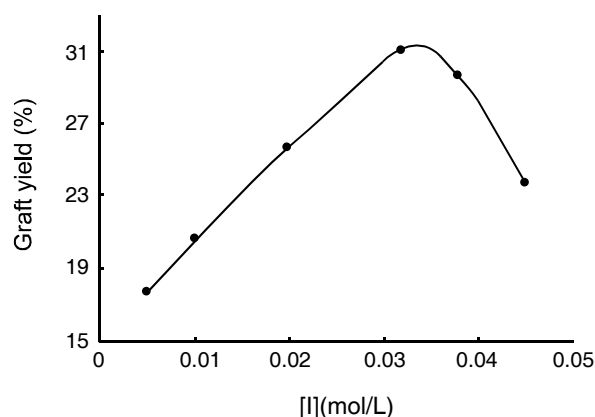


Figure 4. Yield of graft copolymer vs. concentration Cr(VI) in conditions: [AAm] = 0.34 M [St] = 70 g/L, T = 2.5 h, and t = 60°C.

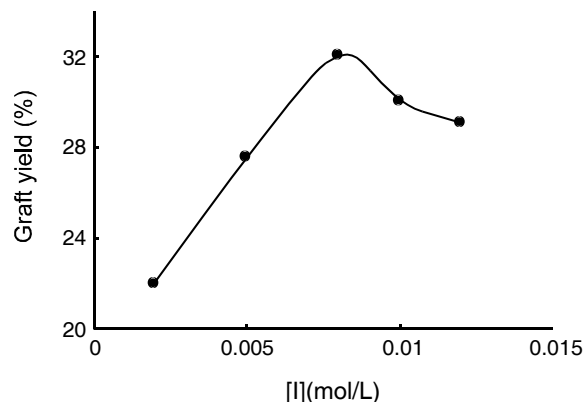


Figure 5. Yield of graft copolymer vs. concentration Cr(VI) and constants: T = 3 h [AAc] = 0.31 M, [St] = 40 g/L and t = 60°C.

increases and thereafter it decreases (Figures 7-9). The graft yield increased because of the rising of grafting rate and a maximum graft yield was achieved at optimum concentrations of monomers, and with the further increases of monomers, there is a pronounced gel effect. The gel effect was more pronounced at higher concentration of the monomer and the chain transfer from starch macroradical onto monomer increased, leading to the lowering of graft yield.

Effect of Starch Concentration

The dependence of grafting on the amount of starch has been studied at constant initiator and monomer concentration. It is observed that, with increasing starch concentration up to 50, 40 and 60 g/L for AAm, AAc and MMA, respectively, the graft yield increases. The significant enhancement in the graft yield by increasing starch concentration makes it understandable that as the

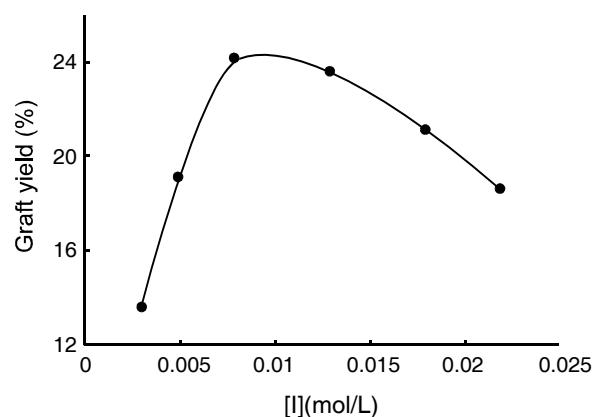


Figure 6. Yield of graft copolymer vs. concentration Cr(VI) and constants: [St] = 60 g/L, [MMA] = 0.34 M, T = 3 h and t = 60°C.

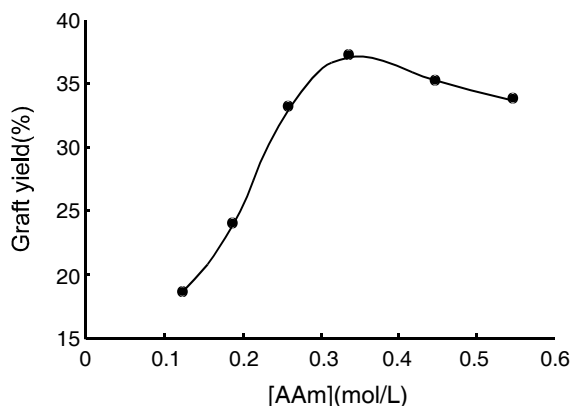


Figure 7. Yield of graft copolymer vs. concentration [AAm] and constants: [I] = 0.02 M, [St] = 70 g/L, T = 2.5 h and t = 60°C.

active centers on starch molecules increase, the graft yield would increase as well. With the further increase in the concentration of starch, grafting is found to decrease. This indicates that beyond optimum concentration, the gel effect becomes pronounced. 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 as the attack on the active sites of starch backbones is decreased, then the homopolymer is formed (Figures 10-12).

The optimum conditions obtained for the synthesis of graft polymers are summarized in Table 1.

Effect of Variation of Time on Graft Yield

The percentage of graft yield versus reaction time studied at indicated temperatures is depicted in Figure 13 and Tables 2- 4. The percentages of graft yield are lin-

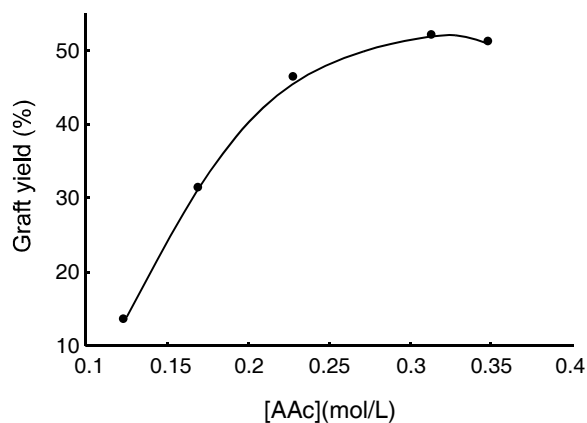


Figure 8. Yield of graft copolymer vs. concentration [AAc] and constants: [I] = 0.01 M, [St] = 70 g/L, T = 3 h and t = 60°C.

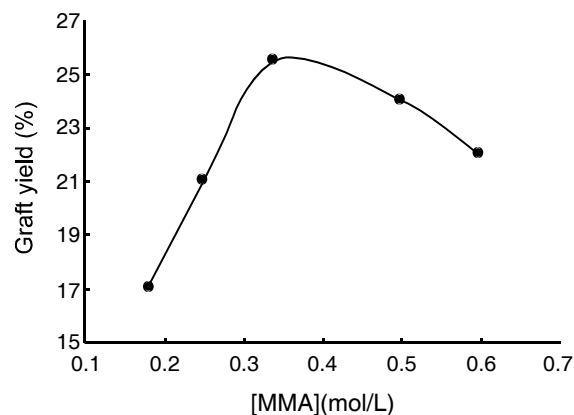


Figure 9. Yield of graft copolymer vs. concentration [MMA] and constants: [I] = 0.01 M, [St] = 70 g/L, T = 3 h, and t = 60°C.

ear with time up to 1200 s for St-g-PAAc and 900 s for St-g-PAAm, and St-g-PMMA.

The graftings of different monomers onto starch under the optimum conditions concentration using Cr(VI) redox system as initiators were examined (Tables 5,6).

Table 7 indicates that the structure of monomers has a great effect on graft copolymerization, and that the order of grafting ability of different monomers onto starch is MMA > AAm > AAc [8].

Kinetics of Graft Polymerization

The rate of graft polymerization (R_g : grafted monomer (mol/s)) depends on reactants concentration, as follows:

$$R_g = k [M]^a [I]^b [St]^c$$

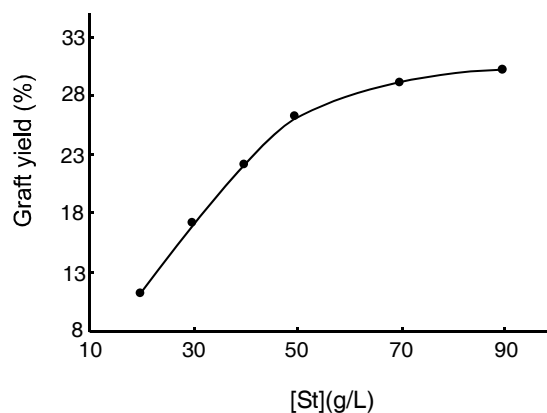


Figure 10. Yield of graft copolymer vs. concentration [St] and constants: [AAm] = 0.34 M, [I] = 0.032 M, T = 2.5 h, and t = 60°C.

Table 1. Optimum conditions for the synthesis of graft copolymers.

Graft copolymer	Starch conc. ^a	Monomer conc. (g/L)	[Cr(VI)]	Temp. ^b (°C)
St-g-PAAc	40	0.31	0.008	55
St-g-PMMA	60	0.34	0.008	55
St-g-PAAm	50	0.31	0.032	60

Table 2. Influence of the reaction time on the grafting of acrylamide onto starch.

Time (min)	5	10	15	20	25
Graft yield (%) AAm	1.5	3.2	4.8	7	8.5

Condition as: [I] = 0.032 M; [AAm] = 0.34M; [St] = 50 g/L; t = 60°C.

Table 3. Influence of the reaction time on the grafting of methylmethacrylate onto starch.

Time (min)	5	10	15	20	25
Graft yield (%)	0.8	1.9	3.1	3.9	5.2

Condition as: [I] = 0.008 M; [MMA] = 0.34 M; [St] = 60 g/L; t = 55°C.

Table 4. Influence of the reaction time on the grafting of acrylic acid onto starch.

Time(min)	5	10	15	20	25
Graft yield (%)	3.2	4.3	5.8	7.7	8.5

Condition as : [I] = 0.008 M; [AAc] = 0.31 M; [St] = 40 g/L; t = 55°C.

Table 5. Effect of monomer concentration on the grafting copolymer at constant initiator and starch concentrations.

[St] = 50 g/L [I] = 0.008 M t = 55°C		[St] = 40 g/L [I] = 0.008 M t = 55°C		[St] = 60 g/L [I] = 0.008 M t = 55°C	
[AAm] ₀ /M	R _g × 10 ⁵	[AAc] ₀ /M	R _g × 10 ⁵	[MMA] ₀ /M	R _g × 10 ⁵
0.125	1.7	0.18	2.41	0.28	3.5
0.19	2.44	0.21	2.67	0.35	4.39
0.34	4.36	0.23	2.98	0.45	5.6
0.45	5.6	0.25	3.19	0.50	6

The graft copolymerization was studied by changing the concentration of monomer at constant [I] and [St] concentration, so the above equation may be rewritten as:

$$\ln R_g = \ln k' + a \ln[M], \text{ where: } k' = k [I]^b [St]^c$$

Table 6. Effect of initiator concentration on the grafting copolymer at constant monomer and starch concentration.

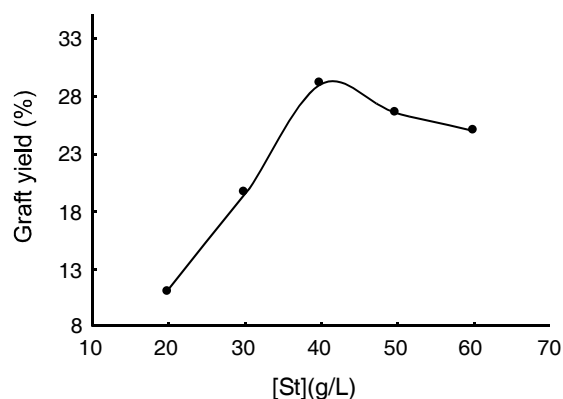
[AAm] = 0.34 M [St] = 50 g/L t = 50°C		[AAc] = 0.31 M [St] = 40 g/L t = 55°C		[MMA] = 0.34 M [St] = 60 g/L t = 55°C	
[I] ₀ /M	R _g × 10 ⁵	[I] ₀ /M	R _g × 10 ⁵	[I] ₀ /M	R _g × 10 ⁵
0.005	2.46	0.005	4.1	0.005	4.1
0.01	3	0.01	5.77	0.009	5.77
0.025	4.72	0.025	8.27	0.025	8.27
0.035	5.94	0.035	9.9	0.035	9.9

Table 7. Effect of starch concentration on the grafting copolymer at constant initiator and monomer concentrations.

[AAm] = 0.34 M [I] = 0.032 M t = 50°C		[AAc] = 0.31 M [I] = 0.008 M t = 55°C		[MMA] = 0.34 M [I] = 0.008 M t = 55°C	
[St] ₀ g/L	R _g × 10 ⁵	[St] ₀ g/L	R _g × 10 ⁵	[St] ₀ g/L	R _g × 10 ⁵
10	3.57	10	2.81	10	5.94
20	4.96	20	3.79	20	8.35
30	6.12	30	4.77	30	10
40	6.63	40	5.43	40	12

The plot of $\ln[R_g]$ vs. $\ln[M]_0$ is linear.

The experimental values of grafted copolymers are given in Table 5 and depicted in Figure 14. The slopes of the curves are 0.93, 0.95, and 0.95, respectively, which suggest that the orders of reaction with respect to monomers are 0.93, 0.95, and 0.95. The graft copolymerization was studied by changing the concentration of initiator at constant [M] and [St] concentration

**Figure 11.** Yield of graft copolymer vs. concentration [St] and constants: [AAc] = 0.31 M, [I] = 0.01 M, T = 3 h, and t = 60°C.

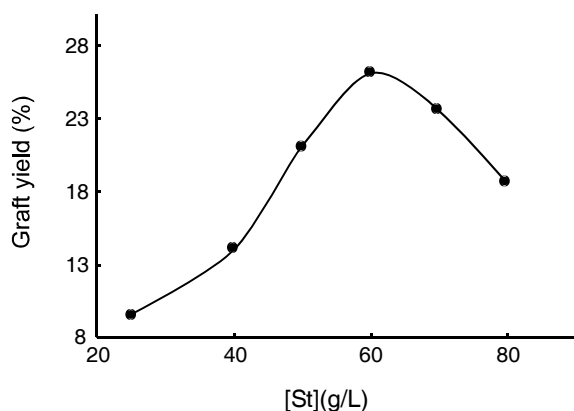


Figure 12. Yield of graft copolymer vs. concentration [St] and constants: [MMA] = 0.34, [I] = 0.008 M, T = 3 h, and t = 55°C.

(Table 6). In these conditions the rate equation is as follows:

$$R_g = k' [I]^b$$

The plots of $\ln[R_g]$ vs. $\ln [I]_0$ are linear and they are shown in Figure 15, the slopes of the plots are 0.49, 0.44, and 0.44, respectively, which suggest that the orders of reaction with respect to initiators are 0.49, 0.44, and 0.44.

The dependence of grafting on the amount of starch was studied at constant initiator and monomer concentrations. The results are given in Table 7. In these conditions the rate equation is as follows:

$$R_g = k' [St]^c$$

The plots of $\ln[R_g]$ vs. $\ln [St]_0$ are linear and they are shown in Figure 16. The slopes of the plots are 0.52,

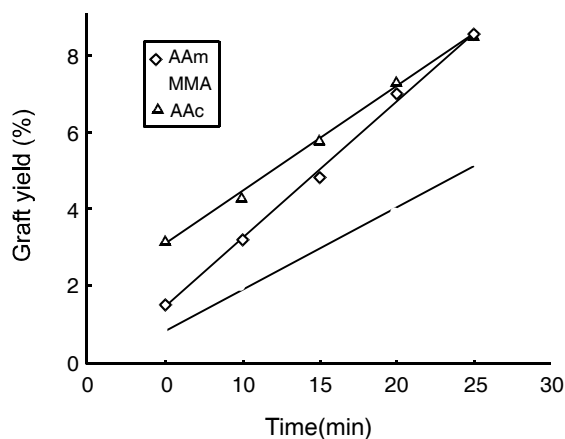


Figure 13. Yield of graft copolymer vs. reaction time.

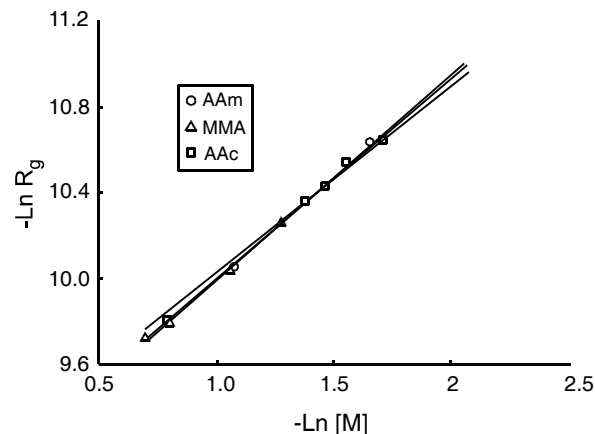


Figure 14. Plot of grafting rate vs. monomer concentration in optimum conditions.

(○) Slope = 0.9, $R^2 = 0.999$ (R is correlation coefficient).

(□) Slope = 0.96, $R^2 = 0.995$.

(△) Slope = 0.9, $R^2 = 0.997$.

0.46, and 0.46, respectively, which suggest that the orders of reaction with respect to initiators are 0.52, 0.46, and 0.46. Therefore, the following rate equations:

$$R_g = k[AAm]^{0.93}[I]^{0.49}[St]^{0.52}$$

$$R_g = k[AAc]^{0.95}[I]^{0.44}[St]^{0.46}$$

$$R_g = k[MMA]^{0.95}[I]^{0.44}[St]^{0.46}$$

Are established for St-g-PAM, St-g-PAAc and St-g-PMMA graft polymers, respectively.

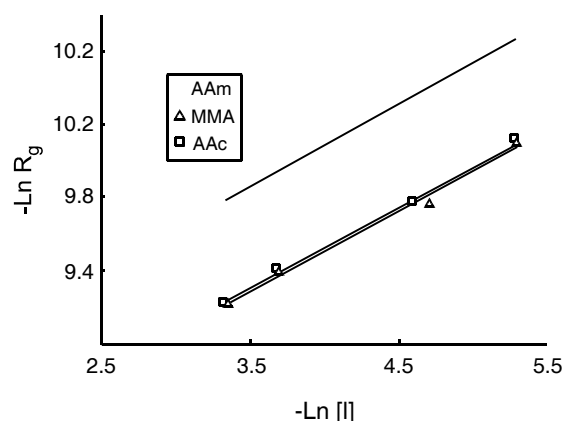


Figure 15. Plot of grafting rate vs. initiator concentration in optimum conditions.

(○) Slope = 0.44, $R^2 = 0.984$.

(□) Slope = 0.4, $R^2 = 0.971$.

(△) Slope = 0.4, $R^2 = 0.997$.

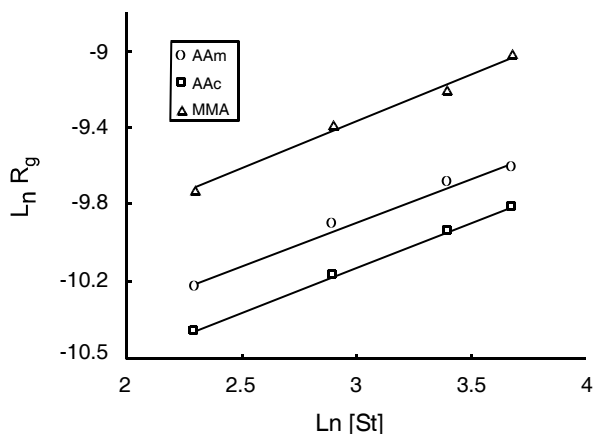


Figure 16. Plot of grafting rate vs. starch concentration \ln optimum conditions.

(○) Slope = 0.52, $R^2 = 0.996$.

(□) Slope = 0.49, $R^2 = 0.997$.

(△) Slope = 0.46 $R^2 = 0.994$.

Effect of Temperature

The grafting reaction was carried out at different temperatures in constant conditions. Then we may equalize the reaction rate to the grafting rate. Substitution of Arrhenius relation in general rate equation yields the following equation: $R_g = A[M]^a[I]^b[St]^c e^{-E_a/RT}$, where A , E_a and T indicate collision parameter in Arrhenius equation, activation energies and absolute temperature, respectively. Other abbreviations have been defined already. In this manner, temperature is the sole variable. Recent equation may be rewritten as:

$\ln R_g = \ln k' - E_a/RT$, where $K' = A[M]^a[I]^b[St]^c$. It means that if $\ln R_g$ versus $1/T$ (K^{-1}) values are fitted with a straight line, the activation energies of reaction, slope of plot, may be derived. The results are presented in Table 8 and depicted in Figure 17, the activation

Table 8. Effect of temperature on R_g in optimum conditions.

[St] = 50 g/L [AAm] = 0.34 M [I] = 0.032 M		[St] = 40 g/L [AAc] = 0.31 M [I] = 0.008 M		[St] = 60 g/L [MMA] = 0.34 M [I] = 0.008 M	
t (°C)	$R_g \times 10^5$	t (°C)	$R_g \times 10^5$	t (°C)	$R_g \times 10^5$
25	3.57	40	2.12	40	2.35
30	4.96	50	2.86	45	2.88
35	6.12	60	3.98	50	4.14
40	6.63	70	5.17	55	5.41

R_g grafting rate is calculated by bromometers titration and is in $M S^{-1}$ units .

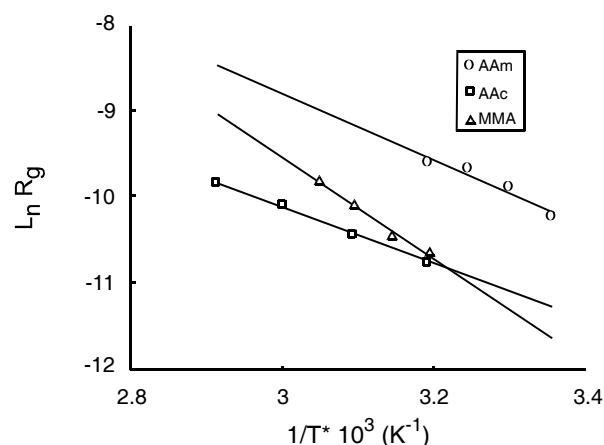


Figure 17. Plot of grafting rate upon the inverse of temperature in optimum conditions.

(○) Slope = -5793 K, $R^2 = 0.987$.

(□) Slope = -5579K, $R^2 = 0.992$.

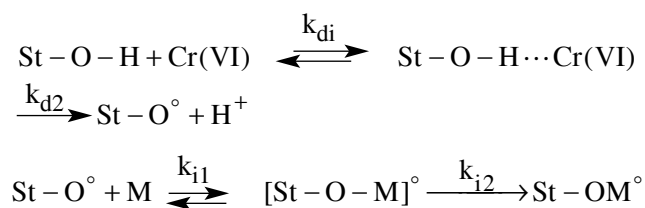
(△) Slope = -5902K, $R^2 = 0.955$.

energy for graft copolymers of St-g-PAAc, St-g-PMMA are 48.16, 46.13 and 49.06 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. IR and or FTIR spectra produce strong bond of carbonyl group near 1720 cm^{-1} after resolution of the graft products. Results observed in our laboratory are consistent with other investigative works [9].

Based on steady state approximation, a proper mechanism is suggested to satisfy observations. According to this hypothesis, the rates of appearing and disappearing of active centres on the starch bulk are the same [11].

Tentative Mechanism

(a) Initiation



(b) Propagation

(c) Termination

Where, k_{i1} , k_{i2} are equilibrium constants and k_{d1} , k_{d2} are rate constants. If polymerization rate is governed by the following general equation:

$$R_p = k_p[M][St-OM_n^\circ] \quad (1)$$

and

$$R_i = k_{d2}[St-O-H-Cr(VI)] = k_{di}k_{d2}[St-O-H][Cr(VI)] \quad (2)$$

where, R_i yields the rate of initiation stage.

The termination rate, R_T , would be a sum of the two phrases:

$$R_T = R_{tc} + R_{td} = 2K_{tc}[St-O-M_n^\circ]^2 + 2k_{td}[St-O-M_n^\circ]^2 \quad (3)$$

$$R_T = (2K_{tc} + 2K_{td})[St-O-M_n^\circ]^2 \quad (4)$$

where, R_{tc} and R_{td} are the combination and dismutation rates, respectively. Based on steady state approximation:

$$R_i = R_T \quad (5)$$

$$K_{d1}K_{d2}[St-O-H][Cr(VI)] = (2K_{tc} + 2K_{td})[St-O-M_n^\circ]^2$$

$$[St-O^\circ] = \left(\frac{K_{d1}K_{d2}}{2K_{tc} + 2K_{td}}\right)^{1/2} [St-O-H]^{1/2} [Cr(VI)]^{1/2} \quad (6)$$

By substituting of $[St-O^\circ]$ in eqn (1) :

$$R_p = K_p \left(\frac{K_{d1}K_{d2}}{2K_{tc} + 2K_{td}}\right)^{1/2} [M][St-O-H]^{1/2} [Cr(VI)]^{1/2} \quad (7)$$

By equalizing the rate constants, $K_p \left(\frac{K_{d1}K_{d2}}{2K_{tc} + 2K_{td}}\right)^{1/2}$ to K , we may rewrite the eqn (7) in a simplified form:

$$R_p = K[M][St-OH]^{1/2} [Cr(VI)]^{1/2}$$

This equation somewhat justifies the observed results.

CONCLUSION

This paper mainly focuses on the kinetics and mecha-

nism of graft copolymers (St-g-PAAm, St-g-PAAc, and St-g-PMMA). First, the optimum conditions for these syntheses, with maximum graft yield, including monomer, initiator and starch concentrations are obtained as well as temperature. Graft yield is calculated through gravimetry and reaction rates by using of bromometry method. Rate equations obtained are: $R_g = [AAM]^{0.93} [I]^{0.49} [St]^{0.52}$, $R_g = k[AAC]^{0.95} [I]^{0.44} [St]^{0.46}$ and $R_g = k[MMA]^{0.95} [I]^{0.44} [St]^{0.46}$ for St-g-PAAm, St-g-PAAc and St-g-PMMA graft polymers, respectively.

A suitable mechanism is suggested to justify observations. This mechanism emphasizes on hydrogen abstraction from hydroxyl functions symmetrically. On other hand, activation energies of St-g-PAAm, St-g-PAAc and St-g-PMMA syntheses are found to be 48.16, 46.13 and 49.06 kJ/mol.K, respectively. Similar values of activation energies imply that this process passes the same pathway specially in the slow step.

The preference of monomer grafted onto starch using Cr(VI) as initiator is: MMA>AAM>AAC

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