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KINETICS AND MECHANISM OF FREE RADICAL GRAFTING OF ACRYLAMIDE ONTO TAPIOCA STARCH

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ABSTRACT

Graft polymerization of acrylamide (AM) onto tapioca starch has been carried out in aqueous solution using potassium persulfate as initiator. Dependence of graft yield upon monomer, starch and initiator concentration as well as reaction temperature is investigated by using gravimetry method. Rate equation obtained are: $R_g = k[AM]^{1.045}\,[KPS]^{0.589}\,[Starch]^{0.533}$. *The kinetics of grafting process has been evaluated and the activation energy within temperature 60-70*^{0}*C for starch-g-PAM synthesis is found to be 52.53kJ/mol. A suitable mechanism was also proposed to justify the results.*

I - INTRODUCTION

A graft copolymer is a polymer of molecules with one or more species of block connected to the main chain as a side chains. These side chains have constitutional or configurationally features that differ from those in the main chain. Starch, a high molecular weight polymer composed of repeating anhydroglucose units (AGUs), is generally a mixture of linear and branched components, namely, amylose and amylopectin. Starch has been used as a model substrate for graft investigations mainly because of the ease with which vinyl monomers undergo grafting onto it [1]. Most of graft polymerization was done by chemical means. Grafting of starch with different vinyl monomers was done using different initiators such as $K_2S_2O_8$ [2], $KMnO_4$ [3], Fe^{2+}- H_2O_2 [4]…

In our previous work, the optimum conditions in the synthesis of starch-g- PAM copolymer initiated by potassium persulfate were determined independently [6]. The aim of this article is to establish the corresponding rate equation and to calculate the activation energy of this reaction. Based on the results obtained, a tentative mechanism is also proposed.

II - MATERIALS AND METHODS

Materials

Tapioca starch supplied by Ha Tay Food Company (molecular weight of ~ 860.000), sodium hypochlorite (80g/l of chlorine active content) received from Viet Tri Chemical Company. Acrylamide (AM), potassium persulfate ($K_2S_2O_8$), ethanol, hydroquinone were of laboratory grade reagents and used as received.

Methods

*Oxidation of tapioca starch: Oxidation of tapioca starch was carried out according to a method detailed elsewhere. The viscosity molecular weight of oxidized starch was $1.36.10^4$ [5].

*Graft polymerization: Graft polymerization of acrylic acid (AM) onto oxidized starch using potassium persulfate (KPS) as initiator was carried out according to a method detailed elsewhere [6].

The graft yield (%GY) and total conversion (%TC) were determined by the following formula:

$$\%GY = \frac{m_2 - m_1}{m_1} \text{ x } 100$$

and

$$R_g = \frac{m_2 - m_1}{\overline{M_{AM}} \times t \times V}$$

in which m_1, m_2, $\overline{M_{AM}}$, t and V were weight of oxidized starch, pure graft copolymer (g), molecular weight of AM, reaction time (min) and reaction volume (liter), respectively.

III - RESULTS AND DISCUSSION

The optimum conditions for synthesis of starch-g-PAM initiated by KPS were obtained: t = 45 min; [AM] = 2.4 M; [Starch] = 125 g/l; [KPS] = 0.016 M and T = 70°C. The graft yield (%GY) and total conversion (%TC) obtained at these conditions were 16.9% and 94.7%, respectively [6].

Kinetics of graft polymerization

The rate of graft polymerization (R_g: grafted monomer- mol/l.min) depends on reactants concentration, as following:

$$R_g = k. [AM]^a [KPS]^b [Starch]^c$$

** Effect of monomer concentration*

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

$$\ln R_g = \ln k' + a \ln[AM],$$

where $k' = k [KPS]^b [Starch]^c$

The plot of $\ln(R_g)$ vs. ln[AM] is linear. The experimental values of grafted copolymers are given in table 1 and depicted in Fig. 1. The slope of the curve is 1.045, which suggests that the order of reaction with respect to monomer is 1.045.

** Effect of initiator concentration*

The graft polymerization was studied by changing the concentration of KPS at constant [AM] and [Starch] concentration (table 2). In these conditions, the rate equation is as follows:

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

The plot of $\ln(R_g)$ vs. ln[KPS] are linear and it is shown in Fig. 2, the slope of the plot is 0.589, which suggest that the order of reaction with respect to initiator are 0.589.

Table 1: Effect of AM concentration on the grafting copolymer at 70°C with [KPS] = 0.016 M and [Starch] = 125 g/l

[AM] (M) Time, min	GY, %				
	1.60	1.80	2.00	2.20	2.40
5	1.27	1.33	1.59	1.68	1.92
10	2.37	2.87	3.01	3.49	3.67
20	5.1	5.35	6.41	6.71	7.63
30	7.05	8.59	9.05	10.53	11.02
45	11.46	12.02	14.39	15.02	16.9
$\overline{R_g}.10^3$ (mol/l.min)	4.339	4.838	5.496	6.004	6.604

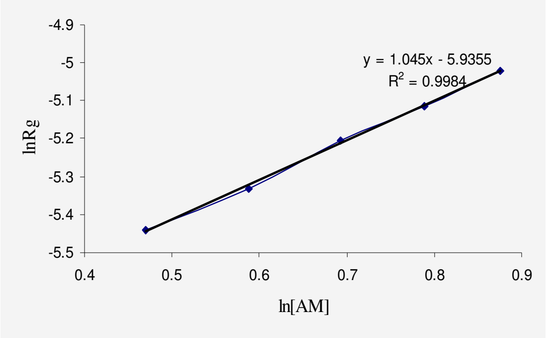

Fig. 1: Plot of ln[AM] vs. ln(R_g) with constant KPS and starch concentrations

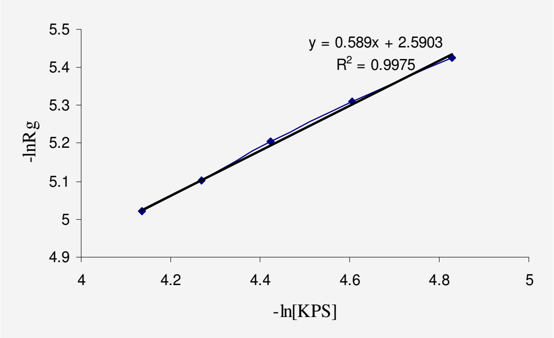

Fig. 2: Plot of -ln[KPS] vs. -ln(R_g) with constant AA and starch concentrations

* *Effect of starch concentration*

The dependence of grafting on the amount of starch was studied at constant initiator and monomer concentrations. The results are given in table 3. In these conditions the rate equation is as follows:

$$R_g = k' \, [\text{Starch}]^c$$

The plot of ln(R_g) vs. ln[Starch] are linear and it was shown in Fig. 3. The slope of the plot is 0.533, which suggest that the order of reaction with respect to starch is 0.533. Therefore, the following rate equation was established for starch-g- PAM:

$$R_g = k \, [\text{AM}]^{1.045} \, [\text{KPS}]^{0.589} \, [\text{Starch}]^{0.533} \quad (*)$$

Calculation of activation energy

The grafting reaction was carried out at different temperatures in constant conditions. Then we equalize the reaction rate to the grafting rate. Substitution of Arrhenius relation in general rate equation yields the following equation:

$$R_g = A \, [\text{AM}]^a \, [\text{KPS}]^b \, [\text{Starch}]^c \, e^{-Ea/RT}$$

where A, E_a and T indicate collision parameter in Arrhenius equation, activation energy and absolute temperature, respectively. In this manner, temperature is the sole variable. Recent equation may be rewritten as:

$$\ln R_g = \ln k' - E_a/RT$$

where $K' = A \, [\text{AM}]^a \, [\text{KPS}]^b \, [\text{Starch}]^c$

Table 2: Effect of KPS concentration on the grafting copolymer at 70°C with [AM] = 2.4M and [Starch] = 125g/l

[KPS], M	GY (%)				
Time, min	0.008	0.01	0.012	0.014	0.016
5	1.28	1.37	1.63	1.7	1.92
10	2.39	2.92	3.06	3.55	3.67
20	5.17	5.46	6.49	6.77	7.63
30	7.14	8.79	9.18	10.68	11.02
45	11.61	12.29	14.61	15.21	16.9
$\overline{R_g}$ .10^3 (mol/l.min)	4.40	4.947	5.481	6.083	6.604

It means that if $\ln R_g$ versus 1/T (K^{-1}) values are fitted with a straight line, the activation energy of reaction, slope of plot, may be derived. The results are presented in table 4 and depicted in Fig. 4, the activation energy for graft copolymer of starch-g- PAM is 52.53 kJ/mol.

Table 3: Effect of starch concentration on the grafting copolymer at 70°C with [AM] = 2.4 M and [KPS] = 0.016 M

[Starch], g/l	GY, %				
Time, min	200	180	160	140	125
5	1.55	1.52	1.71	1.74	1.92
10	2.88	3.27	3.24	3.65	3.67
15	6.24	6.09	6.88	6.93	7.63
25	8.63	9.80	9.71	10.94	11.02
35	14.02	13.70	15.47	15.61	16.9
$\overline{R_g}.10^3$ (mol/l.min)	8.503	7.943	7.56	6.984	6.604

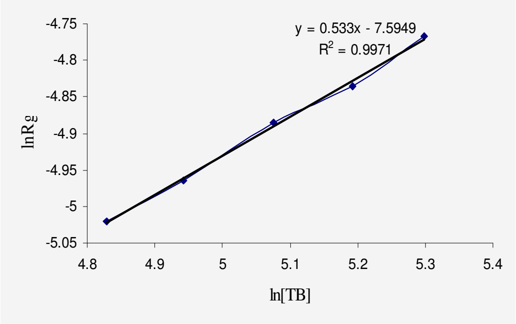

Fig. 3: Plot of ln[Starch] vs. ln(R_g) with constant AM and KPS concentrations

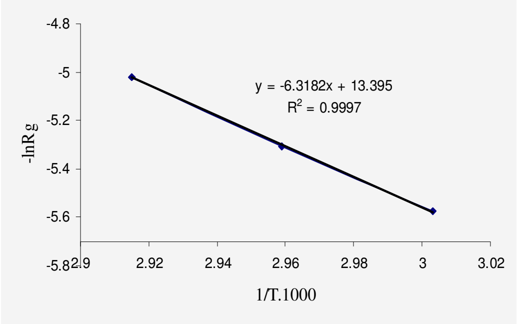

Fig. 4: Plot of ln(R_g) vs. 1/T

Table 4: Effect of temperature on R_g with [AM] = 2.4 M, [KPS] = 0.016 M and [Starch] = 12 5g/l

Temperature, °C	GY, %		
Time, min	60	65	70
5	1.12	1.38	1.92
10	2.03	2.91	3.67
15	4.35	5.64	7.63
25	6.39	8.61	11.02
35	9.81	12.32	16.9
$\overline{R_g}.10^3$ (mol/l.min)	3.787	4.964	6.604

Mechanism

Based on steady state approximation, a tentative mechanism for grafting of vinyl monomers onto starch initiated by potassium persulfate was proposed by Taghizadeh et al. [7]:

* Initiation:

$$\text{Starch—OH} + R^{\bullet} \xrightarrow{k_{i}\cdot} \text{Starch—O}^{\bullet} + RH \tag{1}$$

$$\text{Starch—O}^{\bullet} + M \xrightarrow{k_{i}\cdot} \text{Starch—O—M}^{\bullet} \tag{2}$$

$$\text{* Propagation:}\ \text{Starch—O—M}^{\bullet} + \text{M} \xrightarrow{k_p} \text{Starch—O—M}_2^{\bullet} \tag{3}$$

$$\text{Starch—O—M}_n^{\bullet} + \text{M} \xrightarrow{k_p} \text{Starch—O—M}_{n+1}^{\bullet} \tag{4}$$

$$\text{* Termination:}\ \text{Starch—O—M}_n^{\bullet} + \text{Starch—O—M}_n^{\bullet} \xrightarrow{k_t} \text{graft copolyme} \tag{5}$$

in which Starch–OH is starch, Starch–$O^{\bullet}$ is starch macroradical, M is monomer, and k_d, k_i, k_p, k_t are different rate constants. On the basis of the above reaction scheme and steady state principle in free-radical polymerization, the following results are found:

$$R_g = k_g\,[M]\,[\text{Starch–}M_n^{\bullet}] \tag{6}$$

$$R_i = k_i\,[\text{Starch–OH}]\,[R^{\bullet}] \tag{7}$$

$$[R^{\bullet}] = 2fk_d\,[\text{KPS}] \tag{8}$$

$$R_t = 2k_t\,[\text{Starch–}M_n^{\bullet}]^2 \tag{9}$$

where k_g is rate constant of graft polymerization, f is initiator efficiency for M. By considering steady state principle:

$$R_i = R_t \tag{10}$$

$$k_i\,[\text{Starch–OH}]\,[R^{\bullet}] = 2k_t\,[\text{Starch–}M_n^{\bullet}]^2 \tag{11}$$

$$[\text{Starch–}M_n^{\bullet}] = (k_i/2k_t)^{1/2}\,[\text{Starch–OH}]^{1/2}\,[R^{\bullet}]^{1/2} \tag{12}$$

$$[\text{Starch–}M_n^{\bullet}] = (k_i/2k_t)^{1/2}\,(2fk_d)^{1/2}\,[\text{Starch–OH}]^{1/2}\,[\text{KPS}]^{1/2} \tag{13}$$

By replacing equation (13) into equation (6):

$$R_g = k_g.(k_i/2k_t)^{1/2}\,(2fk_d)^{1/2}[M]\,[\text{Starch–OH}]^{1/2}\,[\text{KPS}]^{1/2} \tag{14}$$

Equation (14) is identical with equation (*) established from our experiment. This indicates that the reaction mechanism suggested above is acceptable.

IV - CONCLUSION

This paper mainly focuses on the kinetics and mechanism of graft copolymer of starch-g-PAM. The rate equation obtained are: $R_g = k[\text{AM}]^{1.045}\,[\text{KPS}]^{0.589}\,[\text{Starch}]^{0.533}$. A suitable mechanism is suggested to justify observations. On the other hand, the activation energy of starch-g-PAM synthesis was found to be 52.53 kJ/mol.

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