

KINETICS AND MECHANISM OF GRAFT POLYMERIZATION OF ACRYLIC ACID ONTO STARCH INITIATED WITH CERIC AMMONIUM NITRATE

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ABSTRACT

Graft polymerization of acrylic acid (AA) onto tapioca starch was carried out using ceric ammonium nitrate (CAN) as initiator in aqueous nitric acid medium. The kinetics of the graft polymerization of AA onto starch was studied by gravimetric method. The following rate expression (rate of graft polymerization) $R_g = k \cdot [AA]^{1.02} [CAN]^{0.478} [Starch]^{0.543}$ was obtained and a suitable mechanism was suggested. The overall activation energy was found to be 41.33kJ/mol within the temperature range of 30 - 40°C.

I - INTRODUCTION

Graft polymerization of vinyl monomers is one of the universal, effective and accessible methods of chemical modification of high molecular weight compounds, natural polymer in particular. Considerable work on graft polymerization of natural polymers such as starch, cellulose, chitosan, etc. with the vinyl monomers has been reported [1 - 3].

Graft polymerization of starch can be initiated by various initiator system such as potassium persulfate [4], redox pair of Fe^{2+}/H_2O_2 [5], $KMnO_4$ /organic acid [6], transition metal ions/organic reductors [7] and also irradiation initiation [8]...Of the redox systems investigated so far the Ce(IV) ion has received considerable interest [9, 10] because of its high graft yield and very low homopolymer formation.

In previous work, optimum conditions for grafting of acrylic acid onto tapioca starch by ceric ammonium nitrate (CAN) as initiator were investigated. Some physicochemical characteristics of graft copolymer were also

characterized [11]. In this article, the graft polymerization was kinetically studied and the percentage of grafting as a function of various parameters that influence the grafting reactions and consequently, a reaction scheme and an expression for the polymerization rate have been proposed and activation energy and order of reaction were determined.

II - EXPERIMENTAL

1. 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. Acrylic acid (AA) (Merck) was distilled in decreased pressure and stored in refrigerator before use. Ceric ammonium nitrate (CAN) (Merck) was used as aqueous solution in nitric acid of 0.01 M. Methanol, acetone, hydroquinone were of laboratory grade reagents and used as received.

Oxidation of tapioca starch by sodium hypochlorite [12]

Oxidation of tapioca starch was carried out at 35°C, pH = 7, with starch concentration of 700g/l and ratio of hypochlorite to starch was 1% (w/w). The viscosity molecular weight of oxidized starch was 1.36.10⁴.

Graft polymerization

The reactions were carried out in 250 ml three-neck flask equipped with a stirrer and condenser and immersed into thermostat water bath. A mixture of 10 g of oxidized starch and 30ml of distilled water was preheated at 80°C for about 30 min with stirring. After it was gelatinized, the flask contents were cooled to the required temperature and treated with a predetermined quantity of CAN/HNO₃ under N₂ atmosphere for 10min to facilitate free radical formation on starch. This treatment was followed by the addition of monomer and then the total volume of the reaction mixture was adjusted with distilled water. The reaction was proceeded under N₂ atmosphere and the reaction temperature was controlled by thermostatic water bath. After the desired reaction period, 2ml of 0.1M hydroquinone was immediately added to each reaction for ceasing the polymerization. The product was poured into 200ml of methanol to induce precipitation. The grafted product was washed several times with methanol- water solution (4:1 v/v) and then oven dried under vacuum at 60°C to a constant weight. Exactly 5g of crude grafted products was taken and extracted with distilled water in a Soxhlet extractor for 24h to remove the poly(acrylic acid) (PAA) homopolymer and the pure copolymer was then dried under vacuum at 60°C to a constant weight.

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

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

and

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

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

III - RESULTS AND DISCUSSION

The optimum conditions for synthesis of Starch-g- PAA were obtained: $t = 60\text{min}$, $[AA] = 1.25\text{M}$, $[\text{Starch}] = 125\text{g/l}$, $[\text{CAN}] = 0.012\text{M}$, $T = 40^\circ\text{C}$. The graft yield (%GY) and total conversion (%TC) obtained at these conditions were 14.7% and 88.2%, respectively [11].

Kinetics of graft polymerization

The rate of graft polymerization (R_g : grafted monomer (mol/l.min)) depends on the concentration of initiator, monomer and starch as following:

$$R_g = k. [AA]^a [\text{CAN}]^b [\text{Starch}]^c$$

*Effect of initiator concentration

Effects of CAN concentration within the range of 0.003 - 0.012 M on the graft yield (%GY) with constant monomer and starch concentrations are shown in table 1.

The plot of $-\ln(R_g)$ vs. $-\ln[\text{CAN}]$ is linear and plotted in figure 1. The slope of the line is 0.478, which suggests that the order of the reaction with respect to initiator is 0.478.

*Effect of monomer concentration

Effects of AA concentration within the range of 0.75 - 1.25 M at constant initiator and starch concentration on the graft yield are shown in table 2.

The plot of $-\ln(R_g)$ vs. $-\ln[AA]$ is linear and plotted in figure 2 and indicating that the order of the reaction with respect to monomer is 1.02.

*Effect of starch concentration

Effects of starch concentration within the range of 80 - 125 g/l at constant initiator and monomer concentration on the graft yield are shown in table 3.

Table 1: Effect of CAN concentration on the grafting copolymer at 40°C with [AA] = 1.25M and [Starch] = 125g/l

Time, min	[CAN], M	GY, %				
		0.003	0.006	0.009	0.01	0.012
5		0.64	0.85	1.13	1.19	1.25
10		1.26	1.81	2.07	2.31	2.4
20		2.63	3.41	4.39	4.37	5.0
40		4.87	7.29	8.36	9.19	9.6
60		7.8	10.13	13.16	13.21	14.7
$\overline{R_g} \cdot 10^3$ (mol/l.min)		2.213	3.03	3.753	3.949	4.253

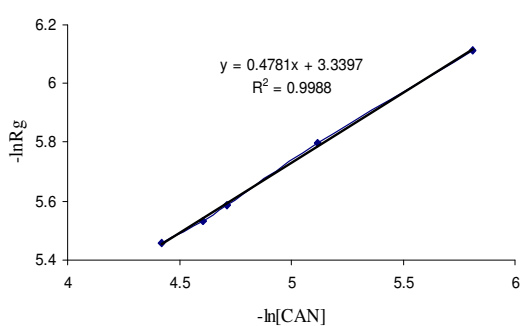


Fig. 1: Plot of $-\ln[\text{CAN}]$ vs. $-\ln(R_g)$ with constant AA and starch concentrations

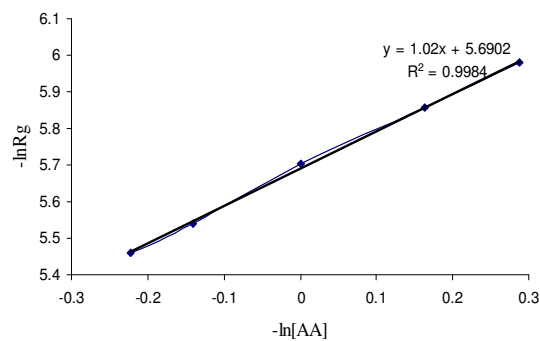


Fig. 2: Plot of $-\ln[\text{AA}]$ vs. $-\ln(R_g)$ with constant CAN and starch concentrations

Table 2: Effect of AA concentration on the grafting copolymer at 40°C with [CAN] = 0.012 M and [Starch] = 125 g/l

Time, min	[AA], M	GY, %				
		0.75	0.85	1	1.15	1.25
5		0.79	0.86	0.94	1.1	1.25
10		1.36	1.57	1.99	2.32	2.4
20		3.01	3.39	3.65	4.46	5.0
40		5.46	6.27	8.06	9.38	9.6
60		8.88	10.14	11.25	13.25	14.7
$\overline{R_g} \cdot 10^3$ (mol/l.min)		2.531	2.862	3.328	3.925	4.253

Table 3: Effect of starch concentration on the grafting copolymer at 40°C with [CAN] = 0.012 M and [AA] = 1.25 M

Time, min	[Starch], g/l	GY, %				
		200	180	160	150	125
5		1.02	1.07	1.12	1.19	1.25
10		1.88	1.99	2.11	2.19	2.4
20		4.09	4.27	4.49	4.6	5.0
40		7.55	7.99	8.47	8.78	9.6
60		12.25	12.89	13.48	13.84	14.7
	$\overline{R}_g \cdot 10^3$ (mol/l.min)	5.497	5.206	4.871	4.738	4.253

The plot of $\ln(R_g)$ vs. $\ln[\text{Starch}]$ is linear and plotted in figure 3. The slope of line is 0.543, which suggests that the order of the reaction with respect to starch is 0.543.

Therefore, the following reaction rate equation is established:

$$R_g = k \cdot [\text{AA}]^{1.02} [\text{CAN}]^{0.478} [\text{Starch}]^{0.543} \quad (*)$$

**Effect of temperature*

The grafting reaction was carried out at different temperatures ranging from 30 - 40°C in constant experimental conditions. Graft yield increases with increasing of temperature (table 4). Then we may equalize the reaction rate to the grafting rate. Substitution of Arrhenius

relation in general rate equation yields the following equation: $R_g = A [\text{AA}]^a [\text{CAN}]^b [\text{Starch}]^c e^{-E_a/RT}$, where A, E_a and T indicate collision parameter in Arrhenius equation, activation energies 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 $k' = A [\text{AA}]^a [\text{CAN}]^b [\text{Starch}]^c$. It means that if $\ln(R_g)$ vs. $1/T$ (K^{-1}) values are fitted with a straight line, the activation energies of reaction, slope of plot may be derived. The plot of $\ln(R_g)$ vs. $1/T$ is linear and activation energy was obtained as 41.33 kJ/mol according to the Arrhenius equation (figure 4).

Table 4: Effect of temperature on R_g with [CAN] = 0.012 M, [AA] = 1.25 M and [Starch] = 125 g/l

Time, min	Temperature, °C	GY, %		
		30	35	40
5		0.73	0.98	1.25
10		1.39	1.8	2.4
20		2.95	3.91	5.0
40		5.88	7.21	9.6
60		8.83	11.72	14.7
	$\overline{R}_g \cdot 10^3$ (mol/l.min)	2.523	3.288	4.253

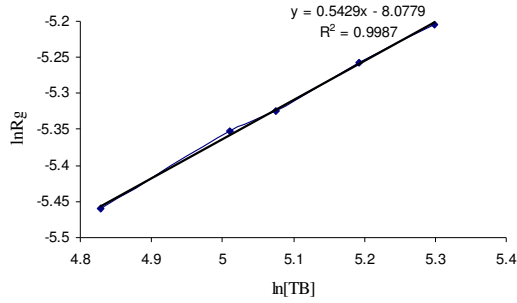


Fig. 3: Plot of $\ln[\text{Starch}]$ vs. $\ln(R_g)$ with constant AA and CAN concentrations

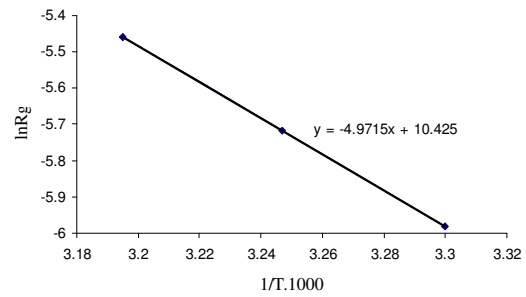


Fig. 4: Plot of $\ln(R_g)$ vs. $1/T$

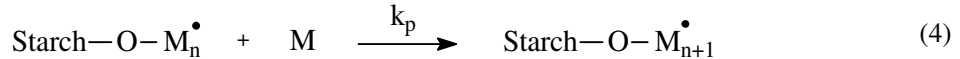
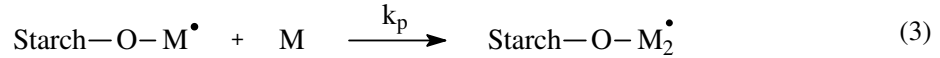
Mechanism

The mechanism of grafting reaction of vinyl monomer onto starch initiated by CAN was proposed by Lutfor et al. as follow [13]:

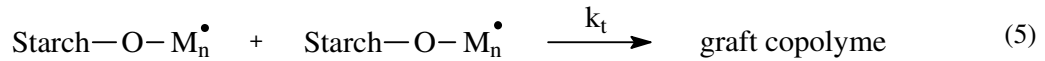
* Initiation:



* Propagation:



* Termination:



in which Starch-OH is starch, Starch-O[•] is starch macroradical, M is monomer, K_d is equilibrium constant and k_d , k_i , k_p 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:

$$R_g = k_g [M] [\text{Starch-M}_n^\bullet] \quad (6)$$

$$R_i = R_d = k_d \{\text{Starch-OH-Ce(IV)}\} = k_d \cdot K_d [\text{Starch-OH}] [\text{Ce(IV)}] \quad (7)$$

$$R_t = 2k_t [\text{Starch-M}_n^\bullet]^2 \quad (8)$$

By considering steady state principle:

$$R_i = R_t \quad (9)$$

$$k_d \cdot K_d [\text{Starch-OH}] [\text{Ce(IV)}] = 2k_t [\text{Starch-M}_n^\bullet]^2 \quad (10)$$

$$[\text{Starch-M}_n^\bullet] = (k_d \cdot K_d / 2k_t)^{1/2} [\text{Starch-OH}]^{1/2} [\text{Ce(IV)}]^{1/2} \quad (11)$$

By replacing equation (11) into equation (6):

$$R_g = k_g \cdot (k_d \cdot K_d / 2k_t)^{1/2} [M] [\text{Starch-OH}]^{1/2} [\text{Ce(IV)}]^{1/2} \quad (12)$$

Equation (12) is identical with equation (*) established from our experiment. This indicate that the reaction mechanism suggested above is acceptable.

IV - CONCLUSION

From the present results, it can be concluded that CAN can initiate the graft polymerization of starch with AA efficiently, and the graft yield and R_g can be adjusted by changing the reaction conditions. Under the experimental condition, a suitable rate equation was proposed as follows:

$$R_g = k. [AA]^{1.02} [CAN]^{0.478} [Starch]^{0.543}$$

and the overall activation energy was 41.33 kJ/mol. It has been possible for us to gather sufficient experimental evidence in favour of the mechanism suggested.

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