Kinetics And Reaction Mechanism Of Methyl Acrylate Graft Copolymerization Onto Sodium Salt Of Partially Carboxymethylated Sodium Alginate By Ceric

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Abstract

The kinetic and mechanism of grafting of methyl acrylate (MA) onto Sodium salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA, $\overline{DS}$ = 0.62) was studied. The experimental results were found to be in good agreement with the proposed kinetic scheme.

Keywords: Methyl acrylate, Sodium salt of Partially Carboxymethylated Sodium Alginate, Kinetics and Mechanism

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1. Introduction

Among various water soluble polysaccharides, sodium alginate is composed of two 1 → 4 glycosidically linked monomers viz. β-D-mannuronic acid (M) and α-guluronic acid (G). However, the relative amounts of these monomers (M and G) are note fixed and varies greatly with the origin of the alginate, age of the algae and the method of extraction. SA is abundantly available, cost effective and environment friendly but suffers from certain drawbacks like biodegradability, resistance to chemical and microbial attack and lack of processing which ultimately limit, its use [1-4]. The carboxymethyl derivative can be created to get around these problems in the current work, and that derivative can then be further modified by grafting methyl acrylate using ceric ammonium nitrate as a redox initiator in the hope that grafting will allow the introduction of unique properties in the polymer. The current study will describe the kinetics and process of grafting methyl acrylate onto the sodium salt of sodium alginate that has undergone partial carboxymethylation while employing ceric ammonium nitrate as a redox initiator.

2. Experimental

2.1. Materials

The Mumbai, India-based company Loba Chemie Pvt. Ltd. graciously provided sodium alginate (SA). The sodium salt of carboxymethylated sodium alginate (Na-PCMSA) was prepared, purified, and its degree of substitution measured as previously described [5]. Na-PCMSA sample was discovered to have a 0.62 value. By using an alkali solution, methyl acrylate (MA) (Fluka, Switzerland manufacture) was purified in accordance with standard practice. As received, CAN (Qualigens, Glaxo India, India) was utilized. It was nitric acid of analar grade. The necessary quantity of the initiator (CAN) was dissolved in nitric acid to create fresh solutions. All additional chemicals and solvents employed were of the reagent grade. By passing through a new pyrogallol solution, nitrogen gas was filtered. For the creation of solutions and graft polymerization processes, low conductivity water was employed.

2.2. Methods

When using ceric ammonium nitrate as a redox initiator, polymerization was carried out under a variety of reaction conditions that have been described elsewhere in order to determine the best conditions for providing the highest percentage of grafting of methyl acrylate onto sodium salt of

partially carboxymethylated sodium alginate. The quantity of substrate, the concentrations of monomer, initiator, and nitric acid, as well as the reaction time and temperature, were among the variables examined. The grafting yields that were achieved are %G = 289.45 and %GE = 96.56 based on various reaction factors.

3. Results and Discussion

3.1. Kinetics and Mechanism

In the ceric-initiated grafting, the backbone (i.e sodium salt of partially carboxymethylated sodium alginate) is having two reactive groups like hydroxyl and carboxylate anion. These groups are known to form a complex with ceric-ion. The complex may dissociate giving rise to free radical sites onto Na-PCMSA. The mechanism of free radical graft copolymerization of methyl acrylate (MA) onto Na-PCMSA is expected to proceed according to the following scheme:

(i) Radical generation:

$$X - H + Ce^{+4} \underset{}{\overset{K}{\rightleftharpoons}} [Complex] \xrightarrow{k_d} X^{\bullet} + Ce^{+3} + H^{+} \quad (1)$$

(ii) Initiation:

$$X^{\bullet} + M \xrightarrow{k_i} XM^{\bullet} \quad (2)$$

$$Ce^{+4} + M \xrightarrow{k_i'} M^{\bullet} + Ce^{+3} + H^{+} \quad (3)$$

(iii) Propagation:

$$XM^{\bullet} + nM \xrightarrow{k_p} XM^{\bullet}_{n+1} \quad (4)$$

$$M^{\bullet} + nM \xrightarrow{k_p'} M^{\bullet}_{n+1} \quad (5)$$

(iv) Termination:

Two types of termination may take place:

(a) At lower Ce^{+4} concentrations, the growing chain is terminated by the recombination of double radicals:

$$XM^{\bullet}_{n} + XM^{\bullet}_{n} \xrightarrow{k_{t_1}} \text{dead polymer} \quad (6)$$

$$M^{\bullet}_{m} + M^{\bullet}_{m} \xrightarrow{k'_{t_1}} \text{dead polymer} \quad (7)$$

$$XM^{\bullet}_{n} + M^{\bullet}_{m} \xrightarrow{k''_{t_1}} \text{dead polymer} \quad (8)$$

(b) At higher Ce^{+4} concentrations, the growing chain is terminated by a single radical:

$$XM^{\bullet}_{n} + Ce^{+4} \xrightarrow{k_{t_2}} XM_{n} + Ce^{+3} + H^{+} \quad (9)$$

$$M_n^{\bullet} + Ce^{+4} \xrightarrow{k'_{t_2}} M_n + Ce^{+3} + H^{+} \quad (10)$$

(v) Oxidation:

$$X^{\bullet} + Ce^{+4} \xrightarrow{k_0} \text{oxidation products} + Ce^{+3} + H^{+} \quad (11)$$

Where X– H denotes the reactive groups of Na-PCMSA, M is the monomer (MA), K is the equilibrium constant and $k_d, k_i, k'_i, k_p, k'_p, k_{t_1}, k'_{t_1}, k''_{t_1}, k_{t_2}, k'_{t_2}$ and k_0 are the rate constants of the respective reactions. It is assumed that $k_p = k'_p$, $k_{t_1} = k'_{t_1} = k''_{t_1}$ and $k_{t_2} = k'_{t_2}$

$$R_g = \frac{k_p k_d^{0.5} K}{k_{t_1}^{0.5}} \times \frac{[X-H][M][Ce(IV)]^{0.5}}{k_d K[X-H] + k_i[M]^{0.5}} \quad (12)$$

Now the rate of homopolymerization R_h is

$$R_h = \frac{k_p k'_i}{k_{t_1}^{0.5}} \text{ x } \frac{[M]^2\,[Ce(IV)]^{0.5}}{\left(k_d K[X-H] + k_i[M]\right)^{0.5}} \quad (13)$$

and the total rate of polymerization, R_p would be

$$R_p = R_g + R_h \quad (14)$$

Similarly, for the case of single radical termination,

$$R_g = \frac{k_p k_d K}{k_{t_2}} \text{ x } \frac{[M]^2\,[X\text{-}H]}{[M] + (k_0/k_i)\,[Ce(IV)]} \quad (15)$$

$$R_h = \frac{k_p k'_i}{k_{t_2}} \text{ x } [M]^2 \quad (16)$$

$$R_p = R_g + R_h = \frac{k_p}{k_{t_2}}[M]^2 \left\{ \frac{k_d K[X-H]}{[M] + (k_0/k_i)\,[Ce(IV)} + k'_i \right\} \quad (17)$$

The above discussion can more or less be illustrated by the data in Tables 1 and 2.

Table 1. Rates of polymerization (R_p) and graft copolymerization (R_g) for grafting of MA onto Na-PCMSA ($\overline{DS}$ = 0.62) at various initiator concentrations[a].

[CAN] x 10^3 (mol/L)	R_p x 10^6 (mol $L^{-1}.s^{-1}$)	R_g x 10^6 (mol $L^{-1}.s^{-1}$)
10.0	7.34	6.4
13.0	10.4	9.7
20.0	10.8	10.0
30.0	11.3	10.4
40.0	12.7	12.1
50.0	11.5	10.8
60.0	10.3	9.3
80.0	7.6	6.7

[a]Na-PCMSA = 1.5 g (dry basis); [HNO_3] = 0.40 mol.L^{-1}; [EA] = 0.304 mol.L^{-1}; Time = 5 h; Temperature = 40°C and Total Volume = 150 mL

Table 2. Rate of polymerization polymerization (R_p) for graft copolymerization of MA onto Na-PCMSA ($\overline{DS}$ = 0.62) at various monomer concentrations[a].

[Monomer] (mol. L^{-1})	R_p x 10^6 (mol $L^{-1}.s^{-1}$)
0.051	7.4
0.101	10.3
0.203	10.4
0.304	11.0

[a]Na-PCMSA ($\overline{DS}$ = 0.62) = 1.5 g (dry basis); [CAN] = 0.04 mol.L^{-1}; [HNO_3] = 0.40 mol.L^{-1}; Time = 5 h; Temperature = 40°C and Total Volume = 150 mL

The plot of R_g versus $[CAN]^{0.5}$ should be linear at lower [CAN], according to Eqn. 12. Such type of typical plot is shown in Figure 1. From this figures it is seen that the plot is linear at lower [CAN], which agrees with termination by recombination of double radicals (Eqn.12), but at higher [CAN], plot deviates from linearity. This may be due to single radical termination (Eqn.15), which decreases the rate of graft copolymerization.

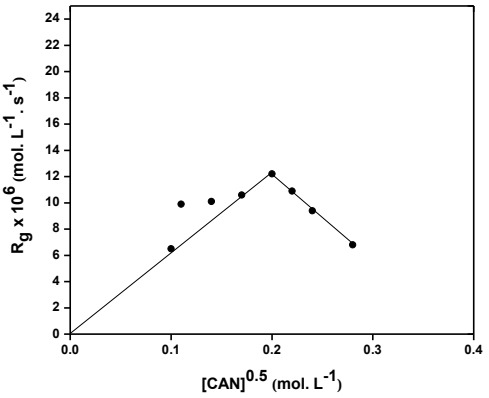

Figure 1. Plot of (●) - R_g x10^6 versus $[CAN]^{0.5}$

Katai et al. [6] reported that k_o/k_i = 50 for the study of the ethylene glycol acrylonitrile system and further stated that k_o is in general considerably larger than k_i. Accordingly one can write:

$$(k_o/k_i)\,[Ce^{+4}] >> [M] \qquad (18)$$

and hence the Eqn.(15) and Eqn.(17) reduces to

$$R_g = \frac{k_p k_d K}{k_{t_2}} \times \frac{[M]^2\,[X-H]}{(k_o/k_i)\,[Ce(IV)]} \quad (19)$$

and

$$R_p = \frac{k_p}{k_{t_2}}\,[M]^2 \left\{ \frac{k_d\,K[X-H]}{(k_o/k_i)\,[Ce\,(IV)]} + k'_i \right\} \quad (20)$$

respectively.

The effect of the concentration of MA as well as that of initiator [CAN] on the overall rate of polymerization (R_p) as expected from the above relation is exemplified in Figure 2. The plots of R_p versus $[M]^2$ and R_p versus 1 / $[Ce^{+4}]$ are found to be linear, supporting the scheme..

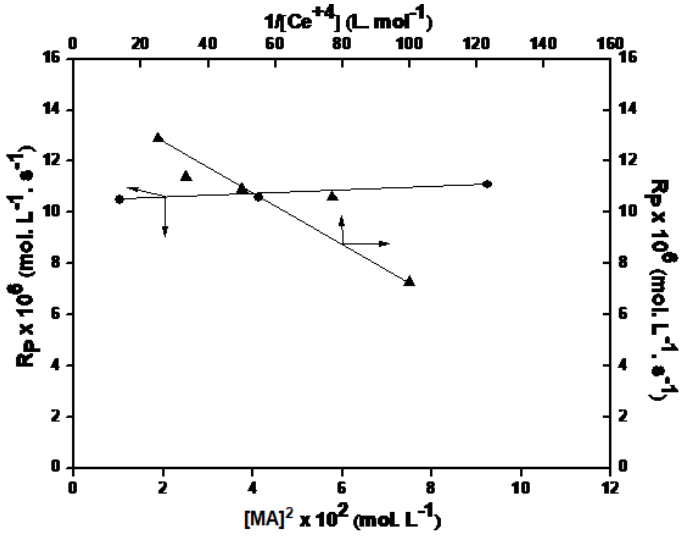

Figure 2. Plot of (●) – R_p x 10^6 versus $[M]^2$ & (▲) - R_p x 10^6 versus $1/[Ce^{+4}]$

4. Conclusion

The experimental results are found to be in very good agreement with the proposed kinetic scheme of free radical graft copolymerzation.

Conflicts of Interest

The authors declare no conflict of interest.

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