

Kinetics and Reaction Mechanism of Ceric Initiated Graft Copolymerization of Ethyl Acrylate onto Sodium Salt of Partially Carboxymethylated Sodium Alginate

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ABSTRACT

The kinetic and mechanism of grafting of ethyl acrylate (EA) onto Sodium salt of Partially Carboxymethylated Sodium Alginate (Na, PCMSA, $\overline{DS} = 0.605$) was studied. The experimental results were found to be in good agreement with the proposed kinetic scheme.

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) is not 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]. In order to overcome these difficulty in the present work the carboxymethyl derivative can be prepared and that derivative can be further modified by grafting of ethyl acrylate by using ceric ammonium nitrate as a redox initiator in anticipation that grafting enables introduction of special property in the polymer. In the present work we are going to report the kinetics and mechanism of grafting of ethyl acrylate onto sodium salt of partially carboxymethylated sodium alginate using ceric ammonium nitrate as a redox initiator.

EXPERIMENTAL

In order to discover the optimal reaction conditions for affording maximum percentage of grafting of ethyl acrylate onto sodium salt of partially carboxymethylated sodium alginate using ceric ammonium nitrate as a redox initiator, polymerization was carried out under various reaction conditions which are reported elsewhere. The variable studied included the amount of substrate, concentrations of monomer, initiator, nitric acid as well as reaction time and temperature. On the basis of varied reaction variables the grafting yields obtained are %G = 340.45 and %GE = 92.56.

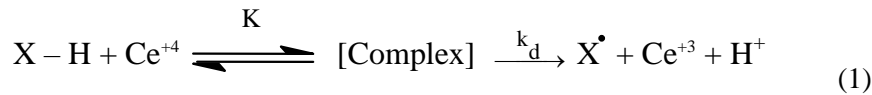
RESULTS AND DISCUSSION

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 ethyl acrylate (EA) onto Na-PCMSA is expected to proceed according to the following scheme:

(i) Radical generation:



(ii) Initiation:



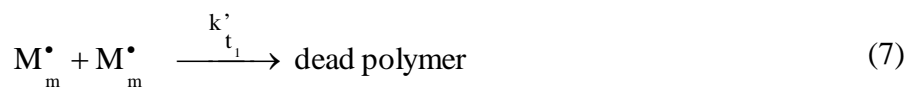
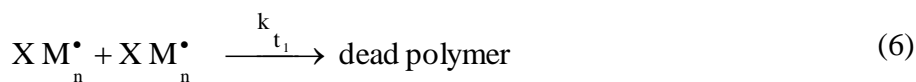
(iii) Propagation:



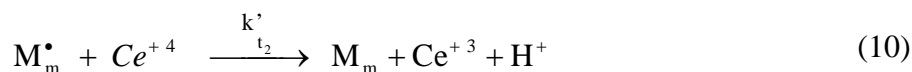
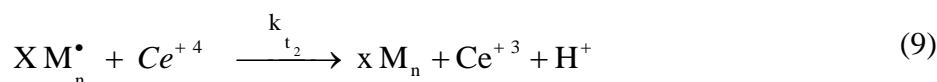
(iv) Termination:

Two types of termination may take place:

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



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





(v) Oxidation:



Where X – H denotes the reactive groups of Na-PCMSA, M is the monomer (EA), K is the equilibrium constant and $k_d, k_i, k'_i, k_p, k'_p, k_{t_1}, k''_{t_1}, k_{t_2}$ and k_o 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

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

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,

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

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

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

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 EA onto Na-PCMSA ($\overline{DS} = 0.605$) at various initiator concentrations^a.

[CAN] x 10 ³ (mol/L)	$R_p \times 10^6$ (mol L ⁻¹ .s ⁻¹)	$R_g \times 10^6$ (mol L ⁻¹ .s ⁻¹)
10.0	7.3	6.5
13.0	10.6	9.9
20.0	10.9	10.1
30.0	11.4	10.6
40.0	12.9	12.2
50.0	11.6	10.9
60.0	10.2	9.4
80.0	7.7	6.8

Na-PCMSA = 1.5 g (dry basis); [HNO₃] = 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 (R_p) for graft copolymerization of EA onto Na-PCMSA ($\overline{DS} = 0.605$) at various monomer concentrations^a.

[Monomer] (mol. L ⁻¹)	$R_p \times 10^6$ (mol L ⁻¹ .s ⁻¹)
0.051	7.3
0.101	10.5
0.203	10.6
0.304	11.1

Na-PCMSA ($\overline{DS} = 0.605$) = 1.5 g (dry basis); [CAN] = 0.04 mol.L⁻¹; [HNO₃] = 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

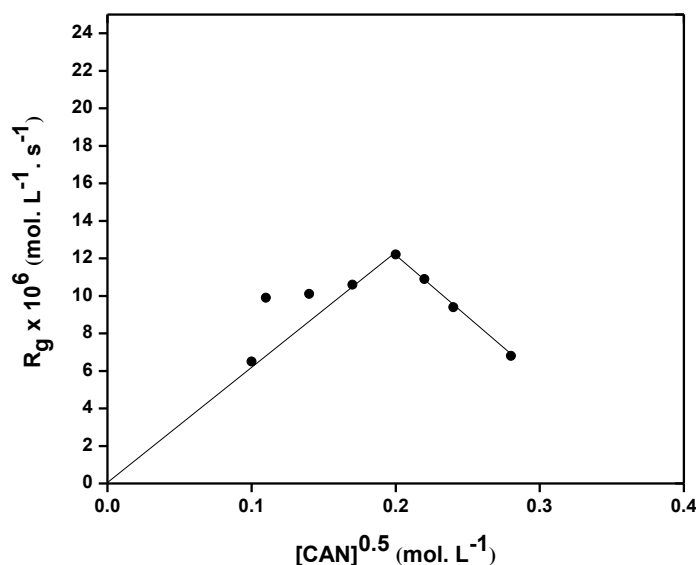


Figure 1. Plot of (●) - $R_g \times 10^6$ versus $[CAN]^{0.5}$

Katai et al. [5] 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:

$$(k_o/k_i) [Ce^{+4}] \gg [M] \tag{18}$$

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

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

and

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

respectively.

The effect of the concentration of EA 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..

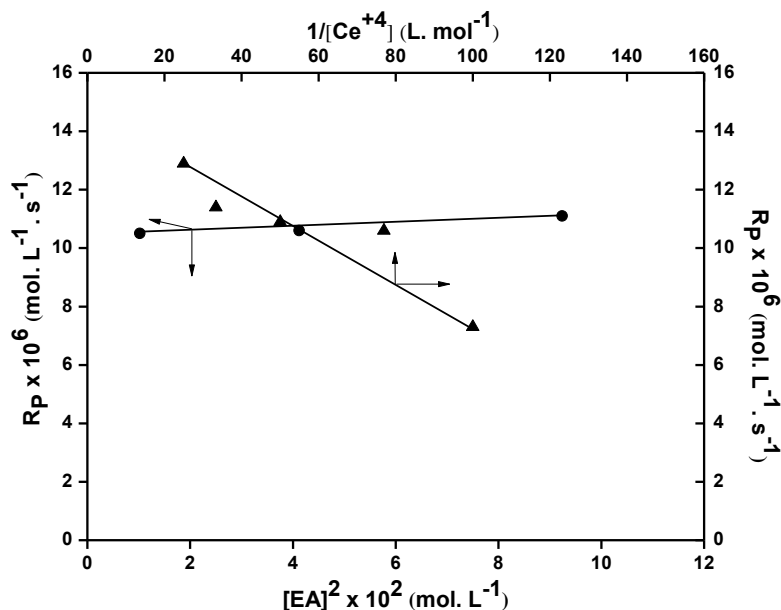


Figure 2. Plot of (●) – $R_p \times 10^6$ versus $[M]^2$ & (▲) - $R_p \times 10^6$ versus $1/[Ce^{+4}]$

CONCLUSION:

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

ACKNOWLEDGEMENTS

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