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

J. H. Trivedi*  
P. G. Department of Chemistry  
Sardar Patel University  
Vallabhbhai Patel University  
Vallabhbhai Patel University

M. K. Prajapati  
Gujarat Industrial Research and Development Agency (GIRDA)  
Vadodara  
Gujarat State

ABSTRACT
The kinetic and mechanism of grafting of ethyl acrylate (EA) onto Sodium salt of Partially Carboxymethylated Sodium Alginate (Na, PCMSA, $M_w = 0.605$) 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 glycosidically linked monomers viz. $\beta$-D-mannuronic acid (M) and $\alpha$-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 derivate 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:

\[ X - H + \text{Ce}^{+4} \xrightarrow{K} [\text{Complex}] \xrightarrow{k_d} X^* + \text{Ce}^{+3} + H^+ \]  

(ii) Initiation:

\[ X^* + M \xrightarrow{k_i} XM^* \]  

\[ \text{Ce}^{+4} + M \xrightarrow{k'_i} M^* + \text{Ce}^{+3} + H^+ \]  

(iii) Propagation:

\[ XM^* + nM \xrightarrow{k_p} XM_{n+1}^* \]  

\[ M^* + nM \xrightarrow{k'_p} M_{n+1}^* \]  

(iv) Termination:

Two types of termination may take place:

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

\[ XM_n^* + XM_n^* \xrightarrow{k_{t_1}} \text{dead polymer} \]  

\[ M_m^* + M_m^* \xrightarrow{k'_{t_1}} \text{dead polymer} \]  

\[ XM_n^* + M_m^* \xrightarrow{k''_{t_1}} \text{dead polymer} \]  

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

\[ XM_n^* + \text{Ce}^{+4} \xrightarrow{k_{t_2}} XM_n + \text{Ce}^{+3} + H^+ \]  

\[ M_m^* + \text{Ce}^{+4} \xrightarrow{k'_{t_2}} M_m + \text{Ce}^{+3} + H^+ \]
(v) Oxidation:

\[
X^* + Ce^{4+} \xrightarrow{k_o} \text{oxidation products} + Ce^{3+} + H^+
\]  

(11)

Where \(X - H\) denotes the reactive groups of Na-PCMSA, \(M\) is the monomer (EA), \(K\) is the equilibrium constant and \(k_d, k_i, k'_i, k_p, k_{i1}, k_{i2}, k_{i1}, k_{i2}\) are the rate constants of the respective reactions it is assumed that \(k_p = k'_p, k_{i1} = k'_i = k''_i\) and \(k_{i2} = k'_{i2}\).

\[
R_g = \frac{k_p k_{i1}^{0.5} K}{k_{t1}^{0.5}} \times \frac{[X - H][M][Ce\ (IV)]^{0.5}}{k_d K[X - H] + k_i [M]^{0.5}}
\]  

(12)

Now the rate of homopolymerization \(R_h\) is

\[
R_h = \frac{k'_p k'_i}{k_{t1}^{0.5}} \times \frac{[M]^2 [Ce\ (IV)]^{0.5}}{(k_d K[X - H] + k_i [M])^{0.5}}
\]  

(13)

and the total rate of polymerization, \(R_p\) would be

\[
R_p = R_g + R_h
\]  

(14)

Similarly, for the case of single radical termination,

\[
R_g = \frac{k_p k_d K}{k_{t2}} \times \frac{[M]^2 [X - H]}{[M] + (k_o / k_i)[Ce(IV)]}
\]  

(15)

\[
R_h = \frac{k_p k_{i1}}{k_{t2}} \times [M]^2
\]  

(16)

\[
R_p = R_g + R_h = \frac{k_p [M]^2}{k_{t2}} \left( \frac{k_d K [X - H]}{[M] + (k_o / k_i)[Ce(IV)]} + k_i \right)
\]  

(17)

The above discussion can more or less be illustrated by the data in Tables 1 and 2.
Table 1. Rates of polymerization (Rp) and graft copolymerization (Rg) for grafting of EA onto Na-PCMSA (DS = 0.605) at various initiator concentrations.

<table>
<thead>
<tr>
<th>[CAN] x 10^3 (mol/L)</th>
<th>R_p x 10^6 (mol L^{-1}.s^{-1})</th>
<th>R_g x 10^6 (mol L^{-1}.s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>7.3</td>
<td>6.5</td>
</tr>
<tr>
<td>13.0</td>
<td>10.6</td>
<td>9.9</td>
</tr>
<tr>
<td>20.0</td>
<td>10.9</td>
<td>10.1</td>
</tr>
<tr>
<td>30.0</td>
<td>11.4</td>
<td>10.6</td>
</tr>
<tr>
<td>40.0</td>
<td>12.9</td>
<td>12.2</td>
</tr>
<tr>
<td>50.0</td>
<td>11.6</td>
<td>10.9</td>
</tr>
<tr>
<td>60.0</td>
<td>10.2</td>
<td>9.4</td>
</tr>
<tr>
<td>80.0</td>
<td>7.7</td>
<td>6.8</td>
</tr>
</tbody>
</table>

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 (Rp) for graft copolymerization of EA onto Na-PCMSA (DS = 0.605) at various monomer concentrations.

<table>
<thead>
<tr>
<th>[Monomer] (mol. L^{-1})</th>
<th>R_p x 10^6 (mol L^{-1}.s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.051</td>
<td>7.3</td>
</tr>
<tr>
<td>0.101</td>
<td>10.5</td>
</tr>
<tr>
<td>0.203</td>
<td>10.6</td>
</tr>
<tr>
<td>0.304</td>
<td>11.1</td>
</tr>
</tbody>
</table>

Na-PCMSA (DS = 0.605) = 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.
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:

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

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

$$
R_g = \frac{k_p k_o K}{k_{i2}} \times \frac{[M]^2 [X - H]}{(k_o / k_i) [Ce(IV)]}
$$

and

$$
R_p = \frac{k_p}{k_{i2}} [M]^2 \left\{ \frac{k_o K[X - H]}{(k_o / k_i) [Ce(IV)] + k_i} \right\}
$$

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.

$$R_p \times 10^6 \text{ (mol. L}^{-1}\cdot\text{s}^{-1})$$

$$[\text{EA}]^2 \times 10^2 \text{ (mol. L}^{-1})$$

$$1/[\text{Ce}^{+4}] \text{ (L. mol}^{-1})$$

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

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

**ACKNOWLEDGEMENTS**
One of us (MKP) is grateful to Ministry of Earth Sciences (MoES), New Delhi for the financial assistance. This project work was financed by MoES, New Delhi, under scheme No. MoES/11-MRDF/1/40/P/07, dt. 21/2/2008.

**REFERENCES**