Kinetics and Reaction Mechanism of Fenton's-Reagent-Initiated Graft Copolymerization of Acrylonitrile onto Sodium Alginate

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SYNOPSIS

The kinetics and mechanism of grafting of acrylonitrile (AN) onto sodium alginate (SA) using Fenton's reagent ($Fe^{2+}-H_2O_2$) has been studied. The experimental results are found to be in good agreement with the proposed kinetic scheme. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In our previous studies we have reported Ceric-induced[1] as well as Fenton's-reagent-initiated[2] grafting of acrylonitrile (AN) onto sodium alginate (SA) and investigated the biodegradable behavior of sodium alginate–graft–acrylonitrile by studying its interactions with different microorganisms.[3] This note is a report on the kinetics and mechanism of grafting of AN onto sodium alginate using Fenton's reagent as an initiator.

EXPERIMENTAL

In order to discover the optimal conditions for grafting of acrylonitrile onto sodium alginate using Fenton's reagent as an initiator, polymerization was carried out under various conditions as described earlier.[2] The variables studied included sulfuric acid concentration, concentrations of initiator components, monomer concentration, reaction time, temperature, and amount of sodium alginate. The results of our previous study[2] have been used in the present work.
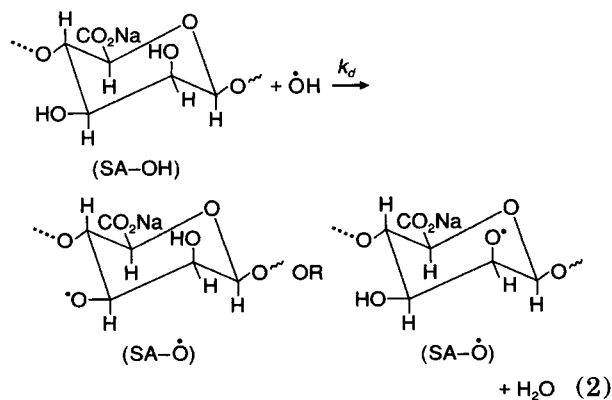
RESULTS AND DISCUSSION

Kinetics and Mechanism

In a system containing H_2O_2, ferrous ammonium sulfate (FAS), and sodium alginate, H_2O_2 may react with FAS (Fe^{2+}) to form $^\bullet OH$. The hydroxyl radical thus formed abstracts hydrogen from the hydroxyl groups present on the reactive sodium alginate (SA–OH) backbone to produce sodium alginate macroradicals (SA–O$^\bullet$), which react with the monomer (M) to initiate grafting. The following reaction mechanism scheme is proposed for this graft copolymerization:
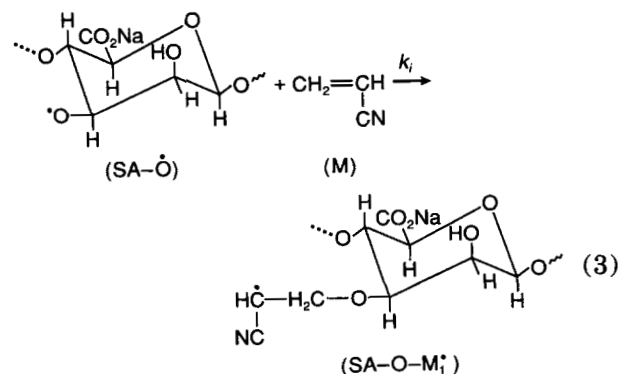
$$Fe^{2+} + HO-OH \xrightarrow{k_1} Fe^{3+} + HO^- + {}^\bullet OH \quad (1)$$
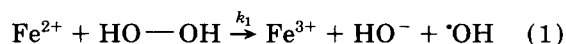
The free radicals ($^\bullet OH$) formed in the above manner attack sodium alginate (SA–OH), giving rise to sodium alginate macroradicals (SA–O$^\bullet$).
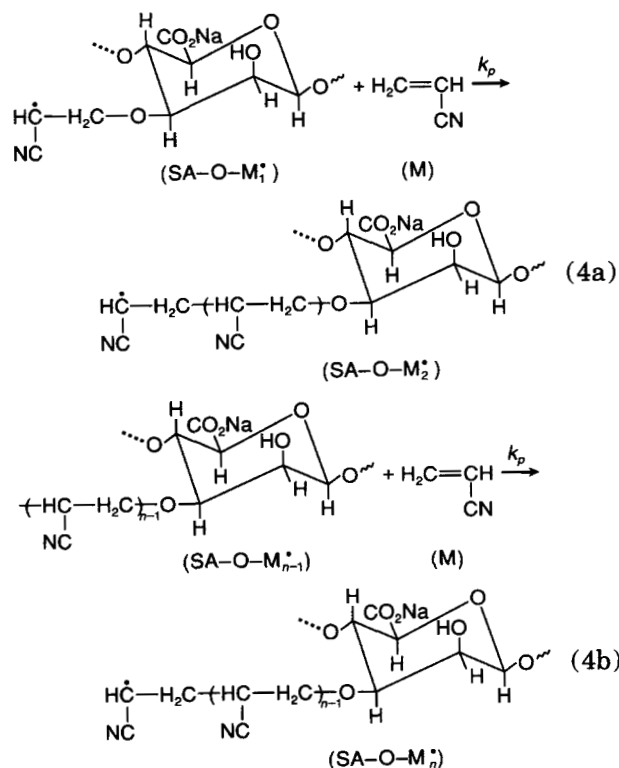

$$+ H_2O \quad (2)$$

(i) Initiation

(SA–Ȯ)   (M)

$$+ CH_2{=}CH \xrightarrow{k_i}$$

$$\tag{3}$$

(SA–O–M$_1^\bullet$)

(ii) Propagation

(SA–O–M$_1^\bullet$)   (M)

$$+ H_2C{=}CH \xrightarrow{k_p}$$

$$\tag{4a}$$

(SA–O–M$_2^\bullet$)

(SA–O–M$_{n-1}^\bullet$)   (M)

$$+ H_2C{=}CH \xrightarrow{k_p}$$

$$\tag{4b}$$

(SA–O–M$_n^\bullet$)

(iii) Termination

(SA–O–M$_n^\bullet$) +

$$\xrightarrow{k_t}$$

(SA–O–M$_m^\bullet$)

graft copolymer $\tag{5}$

(iv) Oxidation

$$+ H_2O_2 \xrightarrow{k_0} \text{oxidation products} \tag{6}$$
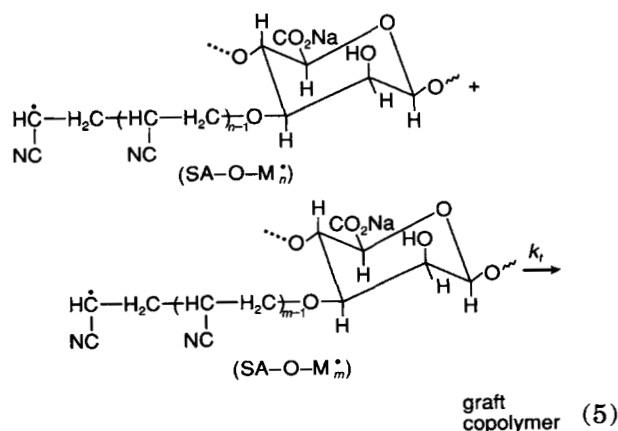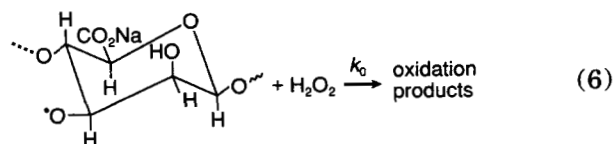
The lives of the growing polymers are relatively short and hence the steady-state approximations may be applied to these radicals. The following equations thus follow:

$$\frac{d[\text{SA–O–M}_1^\bullet]}{dt} = k_i[\text{SA–O}^\bullet][\text{M}]$$

$$- k_p[\text{SA–O–M}_1^\bullet][\text{M}]$$

$$- k_t[\text{SA–O–M}_1^\bullet]\{[\text{SA–O–M}_1^\bullet]$$

$$+ [\text{SA–O–M}_2^\bullet] + \cdots\} = 0 \tag{7}$$

$$\frac{d[\text{SA–O–M}_2^\bullet]}{dt} = k_p[\text{SA–O–M}_1^\bullet][\text{M}]$$

$$- k_p[\text{SA–O–M}_2^\bullet][\text{M}]$$

$$- k_t[\text{SA–O–M}_2^\bullet]\{[\text{SA–O–M}_1^\bullet]$$

$$+ [\text{SA–O–M}_2^\bullet] + \cdots\} = 0 \tag{8}$$

$$\frac{d[\text{SA–O–M}_n^\bullet]}{dt} = k_p[\text{SA–O–M}_{n-1}^\bullet][\text{M}]$$

$$- k_p[\text{SA–O–M}_n^\bullet][\text{M}]$$

$$- k_t[\text{SA–O–M}_n^\bullet]\{[\text{SA–O–M}_1^\bullet]$$

$$+ [\text{SA–O–M}_2^\bullet] + \cdots\} = 0 \tag{9}$$

Adding Eqs. (7), (8), and (9), we get

$$k_i[\text{SA–O}^\bullet][\text{M}] - k_p[\text{SA–O–M}_n^\bullet][\text{M}]$$

$$- k_t \sum [\text{SA–O–M}_n^\bullet]^2 = 0 \tag{10}$$

The [SA–O–M$_n^\bullet$] is the concentration of the longest polymeric radical and as it is small, its concentration can be neglected. Therefore, we get

$$k_i[\text{SA–O}^\bullet][\text{M}] - k_t \sum [\text{SA–O–M}_n^\bullet]^2 = 0$$

$$\therefore \sum [\text{SA–O–M}_n^\bullet] = \sqrt{\frac{k_i}{k_t}[\text{SA–O}^\bullet][\text{M}]} \tag{11}$$

Similarly for $^\bullet$OH radical the following equation can be written:

$$\frac{d[{}^{\cdot}OH]}{dt} = k_1[H_2O_2][Fe^{2+}] - k_d[SA][{}^{\cdot}OH] = 0$$

$$\therefore [{}^{\cdot}OH] = \frac{k_1[H_2O_2][Fe^{2+}]}{k_d[SA]} \qquad (12)$$

Further, we can write

$$\frac{d[SA\text{-}O^{\cdot}]}{dt} = k_d[SA][{}^{\cdot}OH] - k_i[SA\text{-}O^{\cdot}][M]$$

$$- k_0[SA\text{-}O^{\cdot}][H_2O_2] = 0$$

$$\therefore [SA\text{-}O^{\cdot}] = \frac{k_d[SA][{}^{\cdot}OH]}{\{k_i[M] + k_0[H_2O_2]\}} \qquad (13)$$

Putting Eq. (12) in (13), we get

$$[SA\text{-}O^{\cdot}] = \frac{k_1[H_2O_2][Fe^{2+}]}{\{k_i[M] + k_0[H_2O_2]\}} \qquad (14)$$

Substituting Eq. (14) in (11), we get

$$\sum [SA\text{-}O\text{-}M_n^{\cdot}]$$

$$= \sqrt{\frac{k_i}{k_t} [M] \frac{k_1[H_2O_2][Fe^{2+}]}{\{k_i[M] + k_0[H_2O_2]\}}} \qquad (15)$$

The rate of polymerization, R_p, is given by

$$R_p = k_p[M] \sum [SA\text{-}O\text{-}M_n^{\cdot}] \qquad (16)$$

Upon substituting Eq. (15) in (16), we get

$$R_p = k_p[M] \sqrt{\frac{k_i}{k_t} [M] \frac{k_1[H_2O_2][Fe^{2+}]}{\{k_i[M] + k_0[H_2O_2]\}}}$$

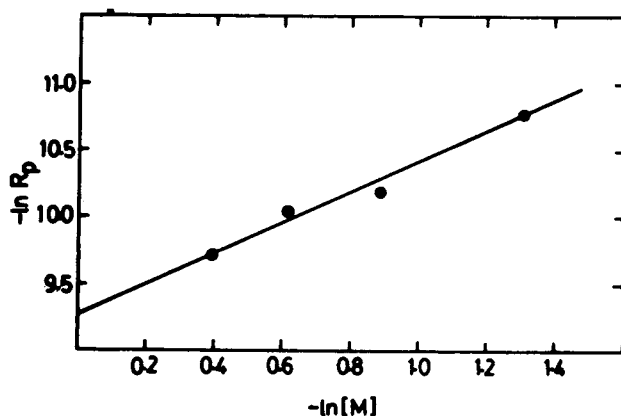**Figure 1**   Plot of ln R_p vs. ln[M]. (Data taken from Ref. 2.

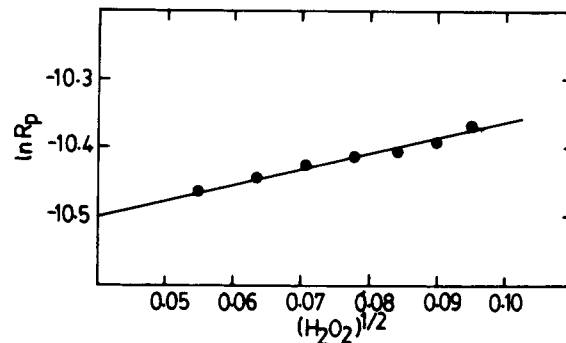**Figure 2**   Plot of ln R_p vs. $[H_2O_2]^{0.5}$. (Data taken from Ref. 2).

or

$$R_p = k_p[M]^{3/2} \frac{k_i^{1/2} k_1^{1/2}}{k_t^{1/2}}$$

$$\times \frac{[H_2O_2]^{1/2}[Fe^{2+}]^{1/2}}{\{k_i[M] + k_0[H_2O_2]\}^{1/2}} \qquad (17)$$

$$\ln R_p = C_1 + \tfrac{1}{2} \ln[H_2O_2] + \tfrac{1}{2} \ln[Fe^{2+}]$$

$$+ \tfrac{3}{2} \ln[M] - \tfrac{1}{2} \ln k_i[M]\left\{1 + \frac{k_0[H_2O_2]}{k_i[M]}\right\} \qquad (18)$$

where $C_1 = \ln k_p + \tfrac{1}{2} \ln k_i + \tfrac{1}{2} \ln k_1 - \tfrac{1}{2} \ln k_t$. Since $k_i \gg k_0$ and $[M] \gg [H_2O_2]$, then $k_0[H_2O_2] \ll k_i[M]$ and let $x = k_0[H_2O_2]/k_i[M]$

$$\ln R_p = C_1 + \tfrac{1}{2} \ln[H_2O_2] + \tfrac{1}{2} \ln[Fe^{2+}] + \tfrac{3}{2} \ln[M]$$

$$- \tfrac{1}{2} \ln k_i[M] - \tfrac{1}{2} \ln(1 + x)$$

$$\ln R_p = C_1 + \tfrac{1}{2} \ln[H_2O_2] + \tfrac{1}{2} \ln[Fe^{2+}]$$

$$+ \tfrac{3}{2} \ln[M] - \tfrac{1}{2} \ln k_i - \tfrac{1}{2} \ln[M]$$

$$- \tfrac{1}{2}\left\{x - \frac{x^2}{2} + \frac{x^3}{3} - \cdots\right\} \qquad (19)$$

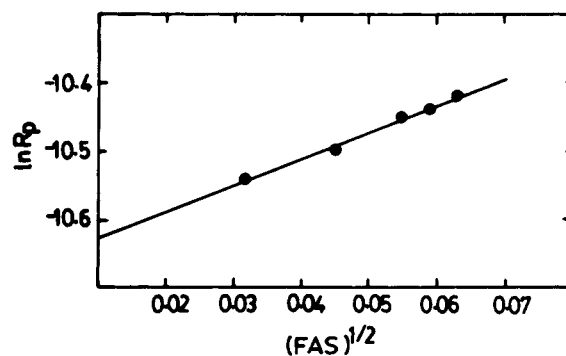**Figure 3**   Plot of ln R_p vs. $[FAS]^{0.5}$. (Data taken from Ref. 2.

Since the value of x is very small, the terms involving x^2, x^3, etc. can be neglected and we get,

$$\ln R_p = C_1 + \tfrac{1}{2} \ln[H_2O_2] + \tfrac{1}{2} \ln[Fe^{2+}]$$
$$+ \tfrac{3}{2} \ln[M] - \tfrac{1}{2} \ln k_i - \tfrac{1}{2} \ln[M] \quad (20)$$
$$\ln R_p = C_2 + \tfrac{1}{2} \ln[H_2O_2]$$
$$+ \tfrac{1}{2} \ln[Fe^{2+}] + \ln[M] \quad (21)$$

where $C_2 = C_1 - \tfrac{1}{2} \ln k_i$.

According to Eq. (21), the plots $\ln R_p$ versus $\ln[M]$, $\ln R_p$ versus $\ln[H_2O_2]^{1/2}$, and $\ln R_p$ versus $\ln[Fe^{2+}]^{1/2}$ should be linear and are found to be so as shown in Figures 1, 2, and 3, respectively, thus confirming the validity of the above reaction scheme.

REFERENCES

1. S. B. Shah, C. P. Patel, and H. C. Trivedi, *High Performance Polym.,* **4,** 151 (1992).
2. S. B. Shah, C. P. Patel, and H. C. Trivedi, *J. Appl. Polym. Sci.,* to appear.
3. S. B. Shah, C. P. Patel, and H. C. Trivedi, Communicated to *J. Polym. Mat.,* to appear.