

Polymerization of Acrylonitrile Initiated by Ce(IV)-Sucrose Redox System: A Kinetic Study

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ABSTRACT: The polymerization of acrylonitrile (M), initiated by the free radicals formed *in situ* in the Ce (IV)-sucrose redox system, was studied in aqueous sulfuric acid medium under nitrogen atmosphere in the temperature range of 30–60°C. The rate of polymerization is proportional to $[M]^{1.0}$, $[R]^{0.76}$, $[Ce(IV)]^{0.8}$, and $[H^+]^{-0.46}$. The rate of Ceric ion disappearance and the rate of polymerization R_p have been measured. The effects of some water-miscible organic solvents, surfactants, ionic strength, and complexing agents on the rate of polymerization were investi-

gated. The temperature-dependence of the rate was studied and the activation parameters were computed using the Arrhenius and Eyring plots. A mechanism consistent with the experimental data, involving Ce(IV)-sucrose complex formation, which generates free radicals, is suggested. The chain termination step of the polymerization reaction was determined. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3760–3768, 2008

Key words: acrylonitrile; Ce(IV)-sucrose; redox

INTRODUCTION

Redox polymerization of vinyl monomers initiated by transition metal ions in their higher oxidation states in an aqueous medium can provide valuable information regarding the mechanistic details of the elementary steps.^{1–11} Sucrose is an ordinary table sugar. It occurs mainly in cane sugars followed by sugar beet. Other sources are honey, pineapples, banana, and several other fruits. Sucrose does not contain a free aldehydic or ketonic group. When sucrose boiled with a dilute acid or treated with enzyme invertase, sucrose is hydrolyzed to equal amounts of glucose and fructose. The kinetics of oxidation of sugars with various metal ions^{12,13} and strong oxidants¹⁴ in alkaline medium has been extensively studied. Oxidations of reducing sugars with oxidants like Ce(IV) are not found in literature. Monosaccharides such as glucose and fructose have wide synthetic applications. Glucose is a source of energy in plants and animals and also serves as the monomeric units of cellulose, the structural framework in woody plants. Hence, the reactions involving carbohydrates are of considerable interest. In the recent years, the use of tetravalent cerium as an initiator of

the graft polymerization of vinyl monomers on cellulose and other textile materials has gained considerable importance on account of its high grafting efficiency,^{15,16} compared with the other known redox systems such as ferrous-hydrogen peroxide and thiosulfate-persulfate.^{17,18} There is a research programmed to investigate the vinyl graft polymerization onto various natural fibers using Ce(IV) as catalyst and carbohydrates i.e., glucose, sucrose etc, as catalyst with a view to achieving higher grafting efficiency. The use of sucrose in particular, as the reducing component is of great industrial importance.

Several reports^{19,20} have been appeared on the mechanism and kinetics of polymerization involving Ceric ion-alcohols redox system, Ceric ion-aldehydes redox system²¹ and Ceric ion-D-glucose²² and Ceric ion-ketones²³ for the polymerization of vinyl monomers. Recently D-glucose has been used with Ceric ion for the polymerization of various vinyl monomers. In the present investigation Ce (IV)-sucrose pair²⁴ has been used for the polymerization of acrylonitrile with elucidate the mechanism involved in the process.

EXPERIMENTAL

Materials and methods

Acrylonitrile (S.d fine Chem.) was free from inhibitor and purified by the method of Bamford and

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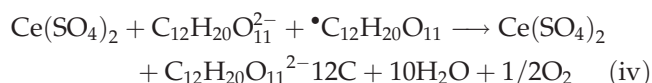
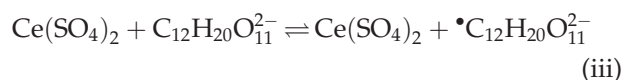
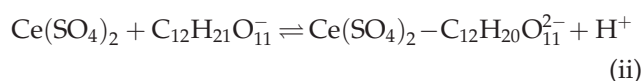
Jenkins.²⁵ Ceric ammonium sulfate (S.d.Fine Chem), sucrose, H₂SO₄, sodium bisulfate, sodium perchlorate, ferrous ammonium sulfate, sodium oleate, zinc sulfate, cetyltrimethyl ammonium bromide and Triton-X-100, methanol, DMF were used of analar grade. Triple distilled water was used throughout the experiment. Pure nitrogen, obtained by passing through a column of Fieser's solution and distilled water, was used for the deaeration of all experimental systems. Ceric ion concentration was determined by titration against standard ferrous ammonium sulfate solution in sulfuric acid medium, barium diphenylamine sulfonate as an internal indicator.

Kinetic measurements

Reactions were performed under the inert atmosphere of nitrogen in Pyrex glass vessels. In a typical kinetic run, a mixture of solutions containing requisite amounts of the acrylonitrile monomer (M), sucrose, Ce(IV), the acid (sulfuric acid + sodium sulfate to maintain a known acid concentration), zinc sulfate, (to maintain a constant ionic strength), and water (to keep the total volume constant) was thermally equilibrated in a water bath at a desired temperature. A wash bottle containing an aqueous solution of acrylonitrile, whose concentration is the same as in the reaction vessel was interposed between the nitrogen train and the reaction vessel to avoid any loss of monomer due to deaeration. Oxygen-free nitrogen was bubbled through the solution for a given period (ca. 30 min) and then the solution of the oxidant, Cerium (IV), was added. The reaction vessel was sealed with a rubber gasket. The reaction was arrested by adding a known amount of standard ferrous ammonium sulfate or by cooling the reaction mixture to 0°C and blowing air in. The rate of Cerium (IV) disappearance ($-R_m$) was followed spectrophotometrically at its λ_{\max} (440 nm) by determining [Cerium (IV)] before and after polymerization. The rate of polymerization (R_p) was determined gravimetrically.²⁶⁻²⁹

Stoichiometry and product analysis

Reaction mixture of various constitutions of Ce (IV), sucrose, acrylonitrile, and H₂SO₄ were equilibrated at 50°C for 24 h. The reaction mixture showed that 1 mole of Ce (IV) was consumed per mole of sucrose according to equations as follows:



Molecular weight determination

The molecular weight (M_v) of the purified samples of polyacrylonitrile product were determined by viscometry. A 0.1% solution of the polymer in *N,N*-dimethyl formamide (DMF) was filtered through a fitted glass filter and placed in an Ubbelohde-type suspended-level dilution viscometer. The intrinsic viscosity ($[\eta]$) was determined and the M_v value was evaluated using the following Mark-Houwink equation given by the Stockmayer and Cleland³⁰ $[\eta] = (3.335 \times 10^{-4}) \times M_v^{0.72}$ at 30°C for polyacrylonitrile in DMF. The molecular weight of the polymer product, under standard condition, was found to be 1.41×10^6 . It increases with increase in monomer concentration and decreases with increase in [Ce (IV)], [Sucrose], or temperature. This effect is attributed to the fact that increases in [Ce (IV)], [Sucrose], or temperature provides more chances for premature termination of growing chain radicals, thus reducing the degree of polymerization. Similar effects have been reported by Behari et al.³¹

RESULTS AND DISCUSSION

The polymerization of acrylonitrile initiated by Ce (IV)-sucrose redox system takes place at a measurable rate at 50°C. Although no induction period was observed under deaerated conditions, there exists an induction period if the solution was not deaerated. Thus, it was evident that the polymerization was initiated by free radicals formed *in situ* by the redox system. The steady state was attained within 60 min. The rate of Ce (IV) disappearance ($-R_m$) was found to be independent of monomer concentration. For [Ce (IV)] = 4.0×10^{-3} mol/dm³, a plot of ($-R_m$) versus [Ce (IV)] was linear and passes through origin. A plot of $-1/R_m$ versus $1/[\text{sucrose}]$ was linear with an intercept on the rate axis, indicating Line Weaver and Burk³² kinetics for complex formation (Fig. 1, Table I). Density of the polymer was found to be 1.20 g/cm³, the refractive index of the polyacrylonitrile is found to be 1.433.

Effect of [Ce (IV)] on the rate of polymerization

The initial rate, as well as the maximum conversion increases with increase in the Ce(IV) concentration in the range (2.0×10^{-3} mol/dm³ to 25.0×10^{-3}

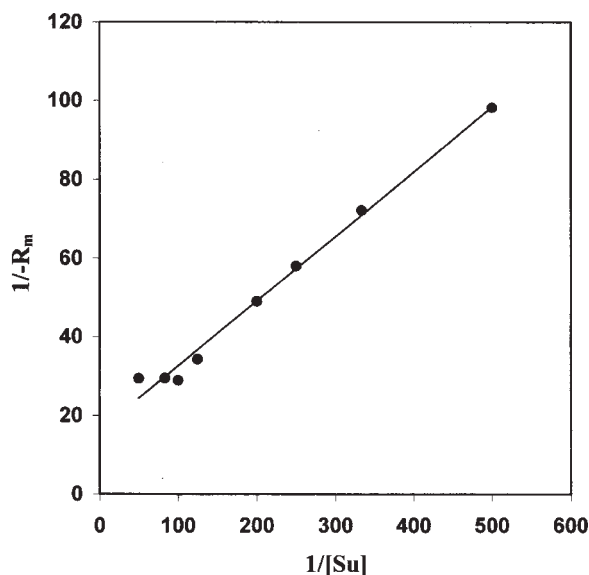


Figure 1 Inverse Plot of Ce(IV) disappearance versus $1/[\text{Sucrose}]$, $[\text{Ce(IV)}] = 4.0 \times 10^{-3} \text{ mol/dm}^3$, $[\text{Su}] = 4.0 \times 10^{-3} \text{ mol/dm}^3$, $[\text{AN}] = 1.5168 \times 10^{-3} \text{ mol/dm}^3$, $[\text{H}_2\text{SO}_4] = 2.0 \times 10^{-3} \text{ mol/dm}^3$, temperature = 323°K .

mol/dm^3). This is due to the fact that increase in Ce (IV) concentration increases the rate of production of primary radicals, and hence, the number of propagating polymer radicals, which in turn increases the polymerization rate and the maximum conversion. The order with respect to $[\text{Ce (IV)}]$ was found to be fractional from a plot of $\log R_p$ versus $\log [\text{Ce (IV)}]$ (Fig. 2, Table III), which clearly indicate that termination occurs through bimolecular interaction of growing polymer chain radicals.^{33,34} The M_p decreases with increase of Ce(IV) concentration, which can be explained by the fact that increasing concentration of Ce(IV) provides more chance for premature termination of growing chain radicals, which in turn reduces the degree of polymerization.^{33,34}

Rate of Ce (IV) disappearance ($-R_m$) on the rate of polymerization

The rate of Ce (IV) disappearance ($-R_m$) was found to be independent of monomer concentration. For

TABLE I
Plots of $-1/R_m$ Versus $1/[\text{Su}]$

| $-1/R_m$ | $1/[\text{Su}]$ |
|----------|-----------------|
| 98.167 | 500 |
| 72.149 | 333.33 |
| 57.980 | 250 |
| 48.958 | 200 |
| 34.270 | 125 |
| 28.924 | 100 |
| 29.525 | 83.33 |
| 29.412 | 50 |

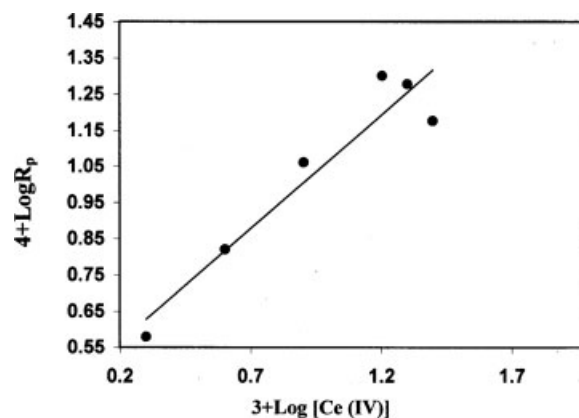


Figure 2 Effect of $[\text{Ce (IV)}]$ on the rate of polymerization, $[\text{Ce(IV)}] = 4.0 \times 10^{-3} - 25.0 \times 10^{-3} \text{ mol/dm}^3$, $[\text{SU}] = 4.0 \times 10^{-3} \text{ mol/dm}^3$, $[\text{AN}] = 1.5168 \times 10^{-3} \text{ mol/dm}^3$, $[\text{H}_2\text{SO}_4] = 2.0 \times 10^{-3} \text{ mol/dm}^3$, temperature 323°K .

$[\text{Ce (IV)}] = 4.0 \times 10^{-3} \text{ mol/dm}^3$, a plot of $(-R_m)$ versus $[\text{Ce (IV)}]$ was linear and passed through origin. A plot of $(-1/R_m)$ versus $1/[\text{su}]$ was linear with an intercept on the rate axis, indicating Line Weaver Burk kinetics for complex formation Table I.

Effect of [sucrose] on the rate of polymerization

The rate of polymerization increases with increase of sucrose concentration, and gradually decreases. The order of the reaction with respect to sucrose concentration was found to be (0.76) fractional order, from the plot of $\log R_p$ versus $\log [\text{sucrose}]$ in the concentration range ($2.0-20.0 \times 10^3 \text{ mol/dm}^3$). When the initial concentration of sucrose was increased, the rate increases due to the production of primary radicals. The exponent of sucrose concentration was found to be fractional. At higher concentration of sucrose rate of polymerization decreases due to chain transfer of sucrose (Fig. 3, Table III).

Effect of monomer concentration on the rate of polymerization

The effect of monomer concentration on polymerization rate (R_p) was studied in the region ($1.5168-3.792 \times 10^3 \text{ mol dm}^{-3}$). The initial rate and percentage conversions were found to increase with the increase in monomer concentration, when the concentration of the monomer is increased. The availability of monomer molecules in the propagation step increases which obviously increase the rate of polymerization. The exponent with respect to monomer concentration was found to be 1.0. The order of the reaction with respect to monomer concentration is calculated from the plot of $\log R_p$ versus $\log [\text{M}]$ (Fig. 4, Table III). The order with respect to monomer concentration was found to be unity in the

TABLE II
Effect of Surfactants on the Rate of Polymerization

| Surfactants added | Hydrocarbon chain length | Concentration 10^{-3} mol/dm ³ | CMC mol/dm ³ | Effect on the rate |
|------------------------|--------------------------|---|-------------------------|-------------------------------|
| Anionic SLS | C ₁₂ | 0.10–0.26 | 0.09 | Increased above and below CMC |
| Cationic CTABr | C ₁₉ | 0.10–1.67 | 0.845 | Decreased above and below CMC |
| Non-ionic Triton X-100 | – | – | – | No effect |

range $1.5168\text{--}3.792 \times 10^3$ mol dm⁻³. At higher concentration of monomer, the rate decreases because of increases in viscosity of the medium, due to the solubility of the polymer in the monomer rendering the diffusion of the ions higher than unity is indicative of the occurrence of cage effect.³⁵

Effect of H₂SO₄ concentration on the rate of polymerization

Kinetic measurements were performed in H₂SO₄–NaHSO₄ solutions of different H⁺ ion concentration.

The effective hydrogen ion concentrations were evaluated from the calibration plot of Kemp and Waters.³⁶ The rate of polymerization decreases with an increasing in H⁺ ion concentration indicating that the hydrolyzed species of Ce (IV) is more reactive than the unhydrolyzed species, and also that the unprotonated form of sucrose is more reactive than the protonated form. The order with respect to H⁺ ion concentration was found to be fractional from the plot of log R_p against log [H⁺] (Fig. 5, Table III).

TABLE III
Effect of Variation of [Sucrose], [Ce (IV)], [H₂SO₄] [Monomer], and Temperature

| Ce (IV) $\times 10^3$ mole/dm ³ | [SU] $\times 10^3$ mole/dm ³ | [AN] $\times 10^3$ mole/dm ³ | [H ₂ SO ₄] $\times 10^3$ mol/dm ³ | Temp (K) | $R_p \times 10^4$ mole/dm ³ |
|--|---|---|---|----------|--|
| 2.0 | 4.0 | 1.5168 | 2.0 | 323 | 3.80 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 323 | 6.62 |
| 8.0 | 4.0 | 1.5168 | 2.0 | 323 | 11.52 |
| 16.0 | 4.0 | 1.5168 | 2.0 | 323 | 20.00 |
| 20.0 | 4.0 | 1.5168 | 2.0 | 323 | 18.98 |
| 25.0 | 4.0 | 1.5168 | 2.0 | 323 | 15.03 |
| 4.0 | 2.0 | 1.5168 | 2.0 | 323 | 3.91 |
| 4.0 | 3.0 | 1.5168 | 2.0 | 323 | 5.32 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 323 | 6.62 |
| 4.0 | 5.0 | 1.5168 | 2.0 | 323 | 7.84 |
| 4.0 | 8.0 | 1.5168 | 2.0 | 323 | 11.20 |
| 4.0 | 10.0 | 1.5168 | 2.0 | 323 | 13.27 |
| 4.0 | 12.0 | 1.5168 | 2.0 | 323 | 13.00 |
| 4.0 | 20.0 | 1.5168 | 2.0 | 323 | 13.05 |
| 4.0 | 4.0 | 0.3792 | 2.0 | 323 | 1.09 |
| 4.0 | 4.0 | 0.7584 | 2.0 | 323 | 2.50 |
| 4.0 | 4.0 | 1.1376 | 2.0 | 323 | 4.42 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 323 | 6.62 |
| 4.0 | 4.0 | 1.896 | 2.0 | 323 | 9.05 |
| 4.0 | 4.0 | 2.275 | 2.0 | 323 | 11.67 |
| 4.0 | 4.0 | 2.651 | 2.0 | 323 | 14.48 |
| 4.0 | 4.0 | 3.033 | 2.0 | 323 | 17.45 |
| 4.0 | 4.0 | 3.792 | 2.0 | 323 | 17.00 |
| 4.0 | 4.0 | 1.5168 | 1.0 | 323 | 9.10 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 323 | 6.62 |
| 4.0 | 4.0 | 1.5168 | 3.0 | 323 | 5.49 |
| 4.0 | 4.0 | 1.5168 | 4.0 | 323 | 4.81 |
| 4.0 | 4.0 | 1.5168 | 8.0 | 323 | 3.49 |
| 4.0 | 4.0 | 1.5168 | 10.0 | 323 | 3.45 |
| 4.0 | 4.0 | 1.5168 | 14.0 | 323 | 3.50 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 303 | 3.47 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 308 | 3.98 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 313 | 4.90 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 318 | 5.62 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 323 | 6.62 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 333 | 9.12 |
| 4.0 | 4.0 | 1.5168 | 2.0 | 338 | 8.01 |

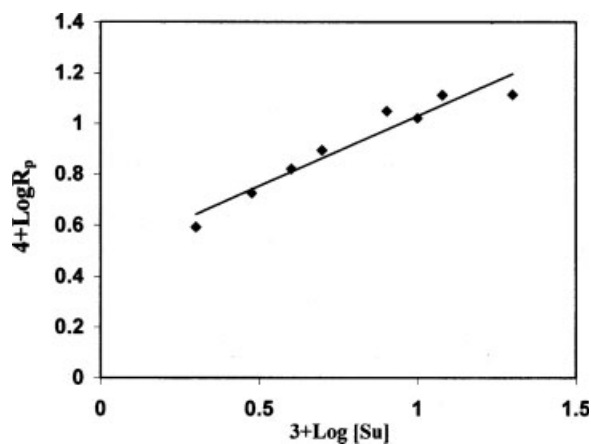


Figure 3 Effect of [sucrose] on the rate of polymerization, $[Ce(IV)] = 4.0 \times 10^3 \text{ mol/dm}^3$, $[SU] = 4.0\text{--}8.0 \times 10^3 \text{ mol/dm}^3$, $[AN] = 1.5168 \times 10^3 \text{ mol/dm}^3$, temperature 323°K , $[H_2SO_4] = 2 \times 10^3 \text{ mol/dm}^3$.

Effect of organic solvents on the rate of polymerization

Addition of water-miscible organic solvents (5% (V/V)) such as methanol, ethanol and DMF, to the reaction mixture depresses the initial rate as well as the maximum conversion. This is due to the decrease in the area of shielding of a strong hydration layer in the aqueous medium, resulting in the termination of the radical end of the growing chain, or due to the increase in the regulated rate of production of primary radicals caused by the solvent which renders the termination rate to be relatively fast as compared to the growth of the polymer chains as shown by Schulze et al.³⁸ Konar and Palit³⁸ have made sim-

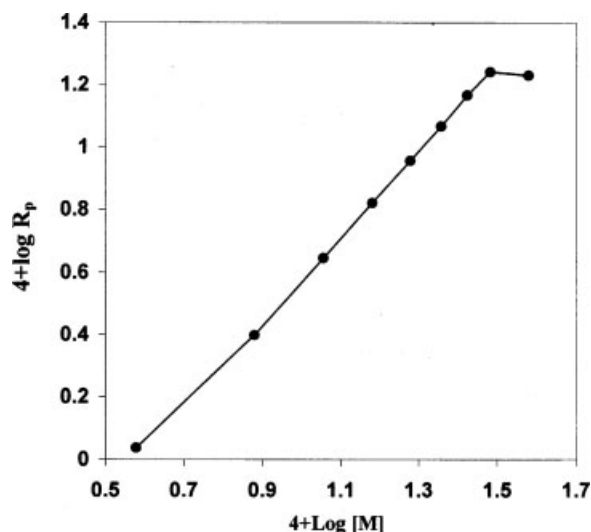


Figure 4 Effect of [monomer] on the rate of polymerization, $[Ce(IV)] = 4.0 \times 10^3 \text{ mol/dm}^3$, $[SU] = 4.0 \times 10^3 \text{ mol/dm}^3$, $[AN] = 0.3792\text{--}3.792 \times 10^3 \text{ mol/dm}^3$, $[H_2SO_4] = 2.0 \times 10^3 \text{ mol/dm}^3$, temperature 323°K .

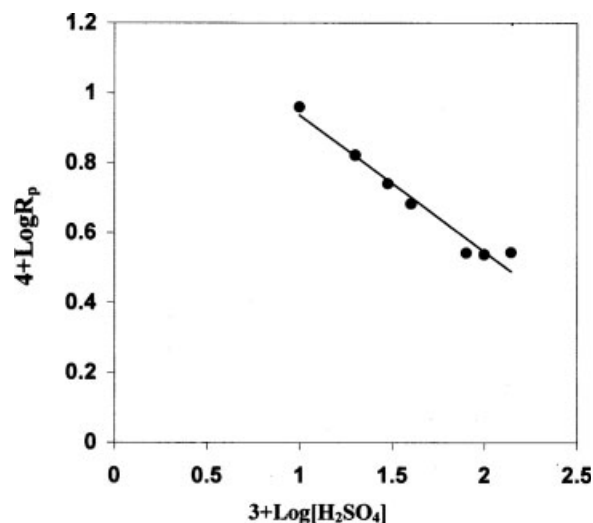


Figure 5 Effect of $[H_2SO_4]$ on the rate of polymerization, $[Ce(IV)] = 4.0 \times 10^3 \text{ mol/dm}^3$, $[SU] = 4.0 \times 10^3 \text{ mol/dm}^3$, $[AN] = 1.5168 \times 10^3 \text{ mol/dm}^3$, $[H_2SO_4] = 1.0\text{--}14.0 \times 10^3 \text{ mol/dm}^3$; temperature 323°K .

ilar observations even with a homogeneous medium in which water is the additive. The interchain hydrogen bonding interlocking the polymer chain is not rigid causing premature mutual combination of the polymer chains or it may also be due to a change in the termination rate arising from a change in the degree of occlusion of the radicals.

Effect of surfactants on the rate of polymerization

Addition of anionic surfactant such as sodium lauryl sulfate (SLS) increased the rate of polymerization R_p

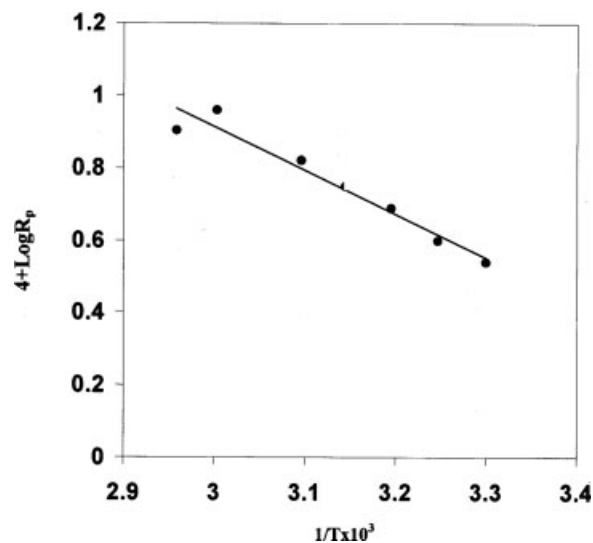
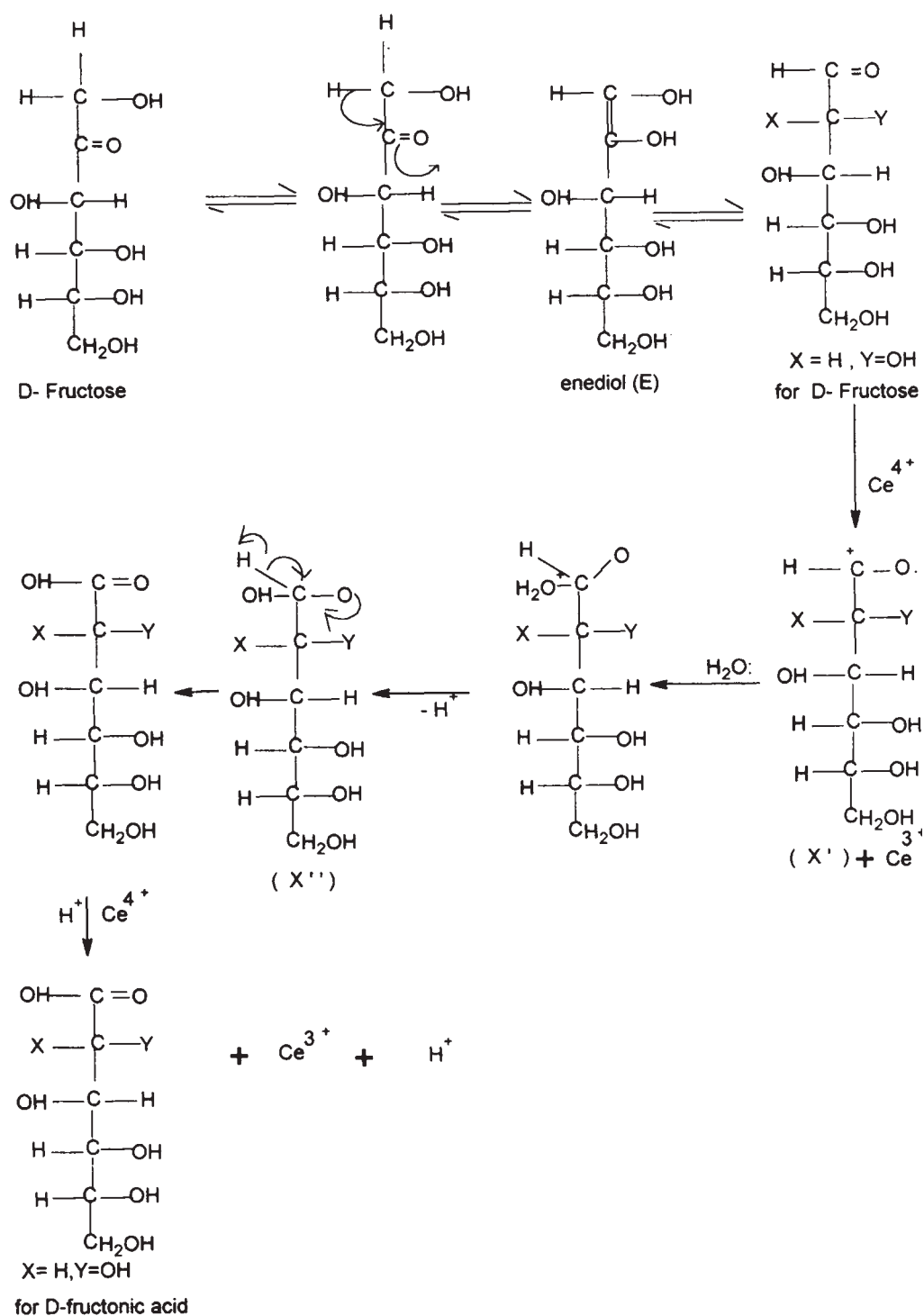


Figure 6 Effect of temperature on the rate of polymerization, $[Ce(IV)] = 4.0 \times 10^3 \text{ mol/dm}^3$, $[SU] = 4.0 \times 10^3 \text{ mol/dm}^3$, $[AN] = 1.5168 \times 10^3 \text{ mol/dm}^3$, $[H_2SO_4] = 2.0 \times 10^3 \text{ mol/dm}^3$; temperature $303\text{--}338^\circ\text{K}$.



Scheme 1 Reaction mechanism.

above and below CMC value. The cationic surfactant such as Cetyl tri methyl ammonium bromide (CTABr) decreases the rate above and below CMC value. In contrast, the nonionic surfactants like Triton-X-100 have no effect on the rate. Hydrophobic interactions and electrostatic attractions are mainly responsible for the enhancement or inhibition of the rate of polymerization³⁸ Table II.

Effect of ionic strength (I)

The rate of polymerization decreases when the ionic strength of the medium increased by varying NaClO_4 concentration, showing a negative salt effect. But when the ionic strength was varied by using ZnSO_4 , there was an increase in the rate of polymerization due to the catalyzing effect of SO_4^{2-} .

In the overall polymerization, the rate of initiation and the rate of termination become equal, resulting in a steady concentration of free radicals.

$$k_i[R^\bullet][M] = k_t[R - M_x^\bullet]^2 \quad (16)$$

$$[R - M_x^\bullet] = \left(\frac{k_i}{k_t}\right)^{1/2} [R^\bullet]^{1/2}[M]^{1/2} \quad (17)$$

$$\text{Thus; } R_p = k_p \left(\frac{k_i}{k_t}\right)^{1/2} [M]^{3/2}$$

$$\left(\frac{k_1 k_2 [Ce^{4+}][SU]}{(k_2 + k_{-1}[H^+])(k_{-2}[Ce^{3+}][H^+] + k_0[Ce^{4+}] + k_i[M])}\right)^{1/2} \quad (18)$$

$$R_p = k_p(k_1 k_2 k_i / k_t)^{1/2} \frac{[M]^{3/2} [Ce^{4+}]^{1/2} [SU]^{1/2}}{k_2 + k_{-1}[H^+]^{1/2}(k_{-2}[Ce^{3+}][H^+] + k_0[Ce^{4+}] + k_i[M]^{1/2})} \quad (19)$$

Thus the dependence of R_p on $[M]^1$, $[Ce(IV)]^{0.8}$, $[SU]^{0.76}$, $[H^+]^{-0.46}$, all of which are observed, are consistent with the experimental results. The low energy of activation is an indication of the high reactivity of the initiator and provides direct experimental evidence of the existence of transient radical intermediates generated in redox reactions. It also enables the identification of these radicals as end groups of the polymer. Further work on the kinetics of polymerization of various vinyl monomers initiated by the reaction of Cerium (IV) and other transition metal

ions with suitable reductants are in progress in our laboratory.

Spectroscopic analysis of the prepared polymer

The formation of polyacrylonitrile in this system was endorsed by spectroscopic analysis FTIR.³⁹ The FTIR of the prepared polymer revealed the manifestation of peaks at 1454.76, 2243.93, and 2939.61 cm^{-1} corresponds to CH_2 , CH, CN (Fig. 7).

CONCLUSION

Acrylonitrile is polymerized in a nitrogen atmosphere by the redox system of Cerium (IV)-sucrose via free radical mechanism. The polymerization reaction with respect to monomer concentration is 1.0, and reaction order related to cerium (IV) and sucrose are 0.80 and 0.76, respectively, which indicates that bimolecular mechanism is suggested and the following rate equation is derived:

$$V_p = k[M]^{1.0}[Ce(IV)]^{0.8}[Su]^{0.76}[H^+]^{-0.46}$$

From the Arrhenius plot, the overall energy of activation (E_a) has been calculated to be 27.22 kJ/mol in the investigated range of temperatures.

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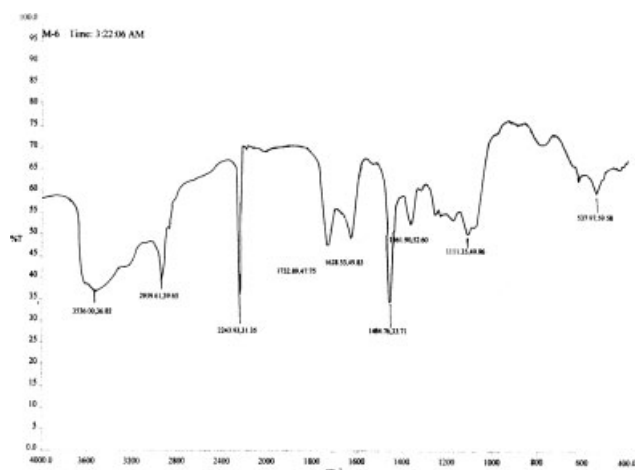


Figure 7 FTIR Spectra of Polyacrylonitrile-Ce (IV)-Sucrose system.

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