

Polymerization of Acrylonitrile Initiated by Cerium (IV)-Oxalic Acid Redox System: A Kinetic Study

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Received 17 July 2006; accepted 9 December 2006

DOI 10.1002/app.27378

Published online 29 January 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The kinetics of aqueous polymerization of Acrylonitrile initiated by the Cerium (IV)-Oxalic acid redox system in Sulfuric acid medium has studied under nitrogen atmosphere in the temperature range of 25–50°C. The rate of polymerization (R_p) and the disappearance of Cerium (IV) have been measured. The water-miscible organic solvents and inorganic salts were depressed both the rate and the conversion. The effects of ionic strength, effects of surfactant have been investigated. The temperature dependence of the rate was studied and the activation pa-

rameters were computed using Arrhenius and Eyring plots. A mechanism consistent with the experimental data, involving Ce(IV)-Oxalic acid complexation that generates free radical was suggested. The chain termination step of the polymerization reaction was determined. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1667–1674, 2008

Key words: acrylonitrile; cerium (IV); oxalic acid; redox; kinetic study

INTRODUCTION

Redox polymerization of vinyl monomers initiated by transition metal ions in their higher valence states in aqueous medium can provide valuable information, regarding the mechanistic details of the individual steps. A qualitative survey of Cerium (IV) reactions show that some of them¹ proceed via free radical mechanisms which may be capable of initiating radical-based polymerization. The Cerium (IV) in presence of various inorganic and organic reducing agents has been used as an effective initiator for the polymerization of vinyl monomers.² Some workers are used for Ce(IV)- coupled with alcohols, aldehydes, ketones, and other organic substrates in various acid medium for the polymerization of vinyl monomers.³ Cerium(IV) has been used as an oxidizing agent, especially in an acid medium.⁴ However, there has been little work on the oxidization reactions of Cerium (IV) in aqueous perchloric acid media.^{5–7} In a sulfuric acid medium, Ce (IV) forms^{8–10} several sulfate complexes, although their role has not received much attention so far. Ce (IV) has been used for the oxidation of many organic compounds, in the form of cerium (IV) ammonium nitrate, cerium (IV) ammonium sulfate, cerium (IV) sulfate, and ceric per chlorate.¹¹

The oxidation of alcohols by Ce (IV) is believed to proceed by disproportionation of coordination of complexes. According to the complex mechanism, unimolecular disproportionation of complex yields cerous ion, a proton, and a free radical on the alcohol substrate.^{12–14} Over the past several decades the oxidation of organic compounds by ceric ions has been the subject of numerous studies.¹⁵ However, most reaction mechanisms are highly complex and thus not yet fully understood, possibly because of the lack of direct experimental data on the involvement of radical species. A striking example is the Ce (IV) oxidation of malonic acid, which was first investigated at least as early as 1930.¹⁶ The ceric oxidation of malonic acid is of particular interest because of its relevance for the widely studied Belousov–Zhabolinsky⁴ (BZ) reaction.^{17–19} It is also known that the dynamics of the BZ reaction as well as the kinetics of the oxidation of malonic acid are strongly influenced by molecular oxygen.^{20–24} For these aerobic reaction systems, the formation of the peroxydicarboxymethyl radical had been long postulated as an important intermediate but only very recently were able to identify and characterize this species.²⁵ In the case of the ceric oxidation of malonic acid, we also found that the kinetics of this radical can be readily explained in terms of a standard auto oxidation mechanism. Low temperature redox polymerization of vinyl monomers is of importance especially for industrial view points. Besides its commercial benefits suppression of side reactions, such as branching is its additional

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advantage over common thermal initiation methods. There are many possibilities for redox initiation in aqueous solutions. Fenton reagent, persulfate—various reductant such as metals, metal complexes, thiols, and polyhydric phenols,^{26,27} cerium (IV)—alcohol²⁸ or aminoacids^{29,30} and permanganate with oxalic acid³¹ and ascorbic acid³² redox couples are well known low temperature radical initiators for polymerization water soluble vinyl monomers. In our previous publications redox polymerization of Methylmethacrylate initiated by Ce (IV)—Tartaric acid,³³ polymerization of Acrylonitrile initiated by Chloramine-T/H₂O₂,³⁴ polymerization of Methylmethacrylate initiated by Ce (IV)—lactic acid³⁵ and polymerization of acrylonitrile initiated by Ce(IV)—Tartaric acid.³⁶

This article reports a kinetic study of polymerization reaction of acrylonitrile initiated by Cerium (IV)—Oxalic acid redox systems in aqueous sulfuric acid medium in the temperature range of 25–50°C.

EXPERIMENTAL

Preparation of materials

Acrylonitrile (SISCO-Chem, India) was washed with 5% NaOH, dilute H₃PO₄, and finally with water and dried over anhydrous CaCl₂, distilled under reduced pressure in a nitrogen atmosphere. The middle fraction was collected and stored at 5°C.³⁷

A solution of Cerium (IV) (E-Merk GR) was prepared, it was standardized by iodometry, the value was checked by titrating against standard ferrous ammonium sulfate solution using barium diphenylamine sulfonate as an internal indicator. All other chemicals such as oxalic acid, (E-Merk GR, Mumbai, India), sulfuric acid, ferrous ammonium sulfate, sodium per chlorate, sodium lauryl sulphate, cetyltrimethyl ammonium bromide, and Triton X-100 were of analytical grade (E-Merk, Mumbai, India).

Kinetic measurements

Inhibitor-free Acrylonitrile (0.303M), oxalic acid (0.005M), sulfuric acid (0.002M), and distilled water (for volume constant) were taken in a reaction vessel and thermo stated at 30°C. The system was flushed with oxygen-free nitrogen for about 20–30 min to remove the dissolved oxygen. At the end of the duration, Cerium (IV) solution about (0.005M) was added to the reaction vessel. The reaction vessel was then sealed with rubber gasket to ensure inert atmosphere. Polymerization starts without any induction period. After desired intervals of time and about 60 min, 0.1M of ferrous ammonium sulfate solution was added to stop the polymerization. The polyacrylonitrile was filtered from the reaction mixture

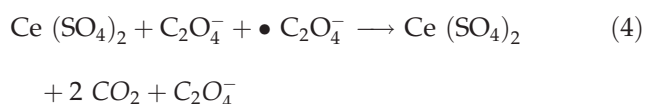
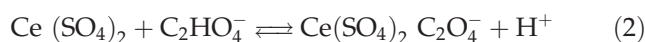
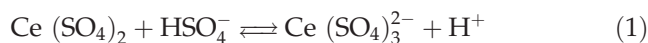
using a glass funnel with Whatman number 41 filter paper and washed several times with distilled water and dried at 60°C to a constant weight. The rate of polymerization (R_p) was determined gravimetrically. The rate of Cerium (IV) disappearance ($-R_m$) was calculated.³⁴

Stoichiometry and product analysis

Reaction mixture of various constituents of [Cerium (IV)], [OA], [AN] and [H₂SO₄] were equilibrated at 30°C for 24 h. The reaction mixture showed that one mole of [Cerium (IV)] was consumed per mole of [OA] according to Eq. (1).

The product polyacrylonitrile was identified by IR spectra. The FTIR spectra of the polyacrylonitrile were taken on a Shimadzu China, Model FTIR1801A instrument in pressed KBr pellets. The formation of PAN in this system was endorsed by FTIR analysis at KMBL, Tabinakere, Mandya.

The FTIR figure (Fig. 7) of the prepared polymer revealed the manifestation of peaks at 2940.16 cm⁻¹ (C—H stretching), 2243.95 (C=N Stretching), and 1454.11 cm⁻¹ (C—H bending), which matched with the reported FTIR spectra for polyacrylonitrile.^{38,39}



RESULTS AND DISCUSSION

The polymerization of acrylonitrile initiated by Cerium (IV)—oxalic acid redox system takes place under stoichiometric conditions at a measurable rate at 30°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 is initiated by free radicals. The steady state was attained within 60 min.

The rate of Cerium (IV) disappearance ($-R_m$) was found to be independent of acrylonitrile concentration. For [Cerium (IV)] = 5.0×10^{-3} mol/dm³, a plot of ($-R_m$) versus [Cerium (IV)] was linear and passed through origin. A plot of $-1/R_m$ versus $1/[\text{OA}]$ was linear with an intercept on the rate axis, indicating Line Weaver and Burk⁴⁰ kinetics for complex formation (Fig. 1) (Table I).

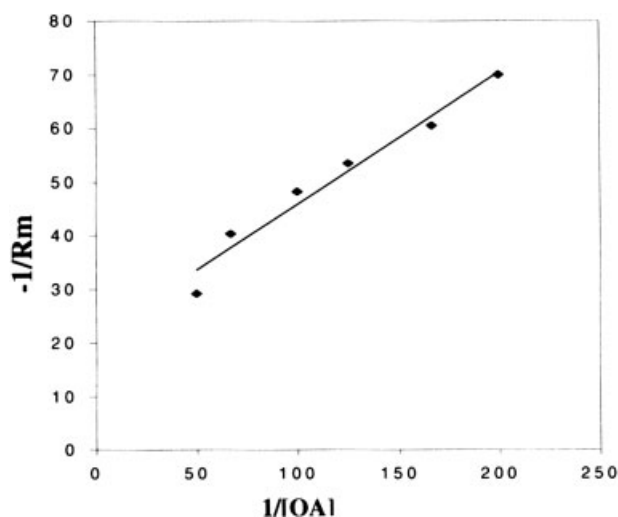


Figure 1 Inverse plots of Cerium (IV) disappearance versus Oxalic acid $[Ce(IV)] = 5.0 \times 10^{-3} \text{ mol/dm}^3$, $[OA] = 5.0 \times 10^{-3} \text{ mol/dm}^3$ $[Monomer] = 0.3033 \text{ mol/dm}^3$, $[H_2SO_4] = 2.0 \times 10^{-3} \text{ mol/dm}^3$ Temperature = 303 K.

Molecular weight determination

The molecular weight M_w of the purified samples of polyacrylonitrile product was determined by viscometry. A 0.1% solution of the polymer in *N,N*-dimethyl formamide (DMF) was filtered through a fritted glass filter and placed in an Ubbelohde type suspended level dilution viscometer. The intrinsic viscosity (η/η_0) was determined and M_w value was evaluated using the following Mark-Houwink equation given by Stock-Mayer and Cleland:⁴¹ $[\eta] = (3.335 \times 10^{-4}) M_w^{0.72}$ at 30°C for polyacrylonitrile in DMF. The molecular weight of the polymer product, under standard condition, was found to be 4.45×10^4 . It increases with increase in monomer concentration and decreases with increase in $[Ce(IV)]$, $[Oxalic]$ or temperature.

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

The rate of polymerization increases with increase of concentration of Cerium (IV), this is due to an increase in the concentration of active species. The

TABLE I
Plots of $-1/R_m$ Versus $1/[OA]$

$1/R_m$	$1/[OA]$
97	200
60.47	166.66
53.47	125
48.17	100
40.34	66.66
29.16	50

$r = 0.982$.
 $s = 0.246$.
 $l = 21.19$.

order of the reaction with respect to cerium (IV) was found to be fractional order (0.8), in the concentration range of $0.005\text{--}0.035 \text{ mol/dm}^3$ (Fig. 2) (Table III). Beyond this concentration, $[Ce(IV)] > 0.02 \text{ mol/dm}^3$, the rate was found to be decreased. Yagci and coworkers⁴² reported a similar observation. This also clearly indicates that the termination occurs through bimolecular interaction of growing polymer chain radical. The molecular weight M_w of PAN decreases with increase in $[cerium(IV)]$. This can be explained by the fact that increasing the concentration of cerium (IV) provides more chances for premature termination of growing chain radicals.⁴³

Effect of [oxalic acid] on rate of polymerization

The rate of polymerization increases with increase of oxalic acid concentration and then decreases gradually. The order of the reaction with respect to oxalic acid (OA) concentration was found to be fractional (0.5) order, from the plot of $\log R_p$ versus $\log[OA]$ in the concentration range of $0.005\text{--}0.035 \text{ mol/dm}^3$ (Fig. 3) (Table III). At higher concentration of oxalic acid, the rate of polymerization decreases, due to chain transfer of oxalic acid or local over concentration of free radicals.⁴⁴

Effect of monomer [M] on rate of polymerization

The effect of monomer concentration on rate of polymerization was studied by varying $[M]$ in the range of $0.151\text{--}1.522 \text{ mol/dm}^3$. The initial rate of polymerization R_p and percentage conversion were found to increase with an increasing monomer concentration up to $0.910M$ of $[M]$, and then the rate decreased. This is probably due to the chain transfer. A plot of $\log R_p$ versus $\log [M]$ was found to be linear with

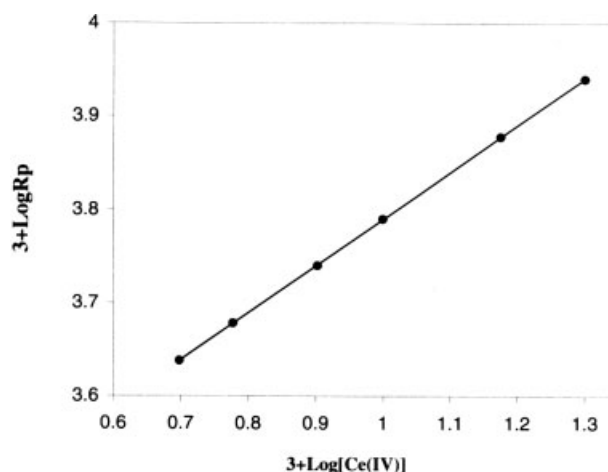


Figure 2 Effect of $[Ce(IV)]$ on rate of polymerization reaction $[Ce(IV)] = 5.0 \times 10^{-3}$ to $35.0 \times 10^{-3} \text{ mol/dm}^3$, $[OA] = 5.0 \times 10^{-3} \text{ mol/dm}^3$ $[Monomer] = 0.3033 \text{ mol/dm}^3$, $[H_2SO_4] = 2.0 \times 10^{-3} \text{ mol/dm}^3$ Temperature = 303 K.

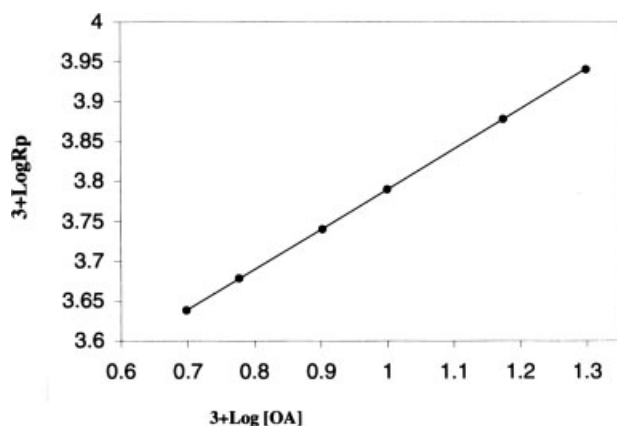


Figure 3 Effect of [OA] on rate of polymerization reaction $[Ce(IV)] = 5.0 \times 10^{-3} \text{ mol/dm}^3$, $[OA] = 5.0 \times 10^{-3}$ to $35.0 \times 10^{-3} \text{ mol/dm}^3$ $[Monomer] = 0.3033 \text{ mol/dm}^3$, $[H_2SO_4] = 2.0 \times 10^{-3} \text{ mol/dm}^3$ Temperature = 303 K.

slope equal to unity (1.0), and the plot of R_p versus $[M]$ was linear and passed through the origin (Fig. 4) (Table III).

Effect of $[H_2SO_4]$ on the rate of polymerization

The rate of polymerization decreases with increase of $[H_2SO_4]$. The effective hydrogen ion concentrations (0.002–0.010 mol/dm³) were evaluated from calibration plot of Kemp and Waters.⁴⁵ The rate of polymerization decreases with an increase 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 oxalic acid is more reactive than the protonated form. The order with respect to H^+ ion concentration was found to be unity (inverse first order) from the plot of $\log R_p$ against $\log [H^+]$ (Fig. 5) (Table III).

Effect of ionic strength on the rate of polymerization

The rate of polymerization increases with increase in ionic strength by adding sodium per chlorate solution. This may be understood in terms of salt catalyzing the propagation step via formation of a complex with the acrylonitrile monomer, Bamford et al.³⁷

Effect of organic solvents on the rate of polymerization

Addition of water-miscible solvents, such as methanol, ethanol, and DMF to the reaction mixture depressed the initial rate as well as the maximum conversion. These solvents 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 the

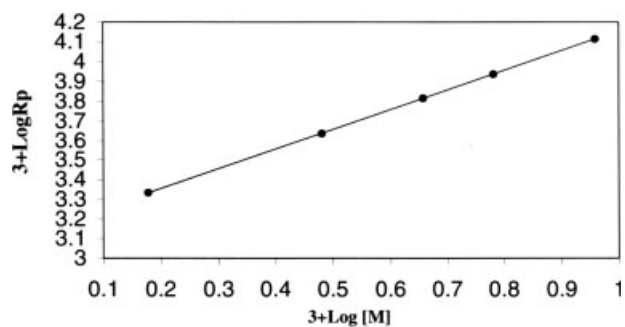


Figure 4 Effect of [AN] on rate of polymerization reaction $[Ce(IV)] = 5.0 \times 10^{-3} \text{ mol/dm}^3$, $[OA] = 5.0 \times 10^{-3} \text{ mol/dm}^3$ $[Monomer] = 0.151$ to 1.522 mol/dm^3 , $[H_2SO_4] = 2.0 \times 10^{-3} \text{ mol/dm}^3$ Temperature = 303 K.

regulated rate of production of primary radicals caused by the solvents which renders the termination rate to be relatively fast as compared with the growth of the polymer chains as shown by Schulz et al.⁴⁶

Konar and Palit⁴⁷ have made similar observations even with a homogeneous medium in which water is the additive. The interchain hydrogen bonding interlocking by the polymer chain is not rigid, causing a premature mutual combination of the polymer chains.

Effect of surfactants on the rate of polymerization

Addition of anionic surfactant like sodium lauryl sulphate (SLS) increases the rate of polymerization R_p above and below CMC value. The cationic surfactants such as Cetyl tri methyl ammonium bromide (CTABr) decreased the rate above and below the CMC value. In contrast, the nonionic surfactants like Triton X-100 have no effect on the rate of polymerization (Table II). The hydrophobic interactions and electrostatic attractions are mainly responsible for

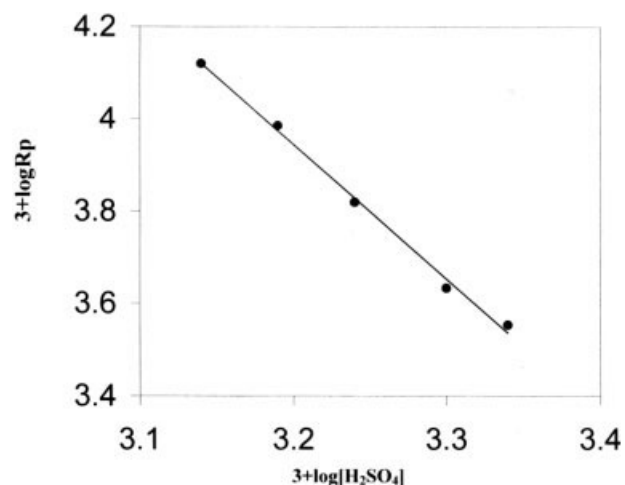


Figure 5 Effect of $[H_2SO_4]$ on rate of polymerization reaction $[Ce(IV)] = 5.0 \times 10^{-3} \text{ mol/dm}^3$, $[OA] = 5.0 \times 10^{-3} \text{ mol/dm}^3$ $[Monomer] = 0.3033 \text{ mol/dm}^3$, $[H_2SO_4] = 2.0 \times 10^{-3}$ to $10.0 \times 10^{-3} \text{ mol/dm}^3$ Temperature = 303 K.

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	0.10–0.25	0.06	Increased above and below CMC
Cationic CTABr	C ₁₉	0.10–1.65	0.824	Decreased above and below CMC
Nonionic Triton X-100	–	–	–	No effect

the enhancement or inhibition of the rate of polymerization.⁴⁸

Effect of temperature on the rate of polymerization

The polymerization reaction has been studied at different temperature range from 25 to 50°C. The initial rate of polymerization and maximum conversion were found to be increasing steadily with an increase of temperature. Thereafter decreases above 45°C. It may be due to an increase in the mobility of growing chain radicals in the system, leading to their efficient termination (Fig. 6) (Table III).

The activation energy (E_a) were calculated from the Arrhenius^{49,50} plot of $\log R_p$ versus $1/T$ in the temperature range of 25–50°C was 56 kJ/mol (Fig. 6). The other activation parameters were calculated from the Eyring plots are:

$$\Delta H^\ddagger = 53.89 \text{ kJ/mole}, \Delta S^\ddagger = -112.67 \text{ JK}^{-1}/\text{mole}, \text{ and } \Delta G^\ddagger = 34.15 \text{ kJ/mole}$$

The reaction, which was initially homogeneous but as soon as the polymerization started, due to the formation of an insoluble product become heterogeneous. Controlling the experiment involving in the individual addition of Cerium (IV) or oxalic acid to the monomer solution did not induce polymerization. Suggesting that the free radicals formed *in situ* by the Cerium (IV)-oxalic acid system was responsible for polymerization. Based on the above results the following mechanistic scheme is proposed.

Mechanism and rate law

It has been assumed that Cerium (IV), species present in sulfuric acid are Ce^{4+} (aq) $\text{Ce}(\text{OH})^{3+}$ (aq) and CeSO_4^+ . Since the effect of HSO_4^- ion on the reaction under investigation is negligible role of CeSO_4^+ is ruled out. Therefore, a combined role of Ce^{4+} (aq) and $\text{Ce}(\text{OH})^{3+}$ (aq) can be envisaged, as observed in many Ce(IV) reactions. In fact $\text{Ce}(\text{OH})^{3+}$ (aq) should be considered as more reactive in view of the decrease in rate with increase in $[\text{H}^+]$.

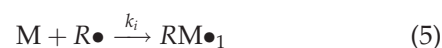
Oxalic acid exists in the form of a cation, $\text{HOOC}-\text{COOH}$ in the strongly acidic medium. The most likely reaction mechanism that can satis-

factorily explain the observed data is as shown in Scheme 1.

Where OA stands for diprotonated oxalic acid, X, R \dot{c} , Z for transient intermediates. In the presence of radical scavenger, i.e., the acrylonitrile monomer, the reaction Step (3) is less probable and the overall rate of Ce (IV) disappearance is given by the forward step of the reaction (2)

$$\frac{-d[\text{Ce}^{4+}]}{dt} = k_2[\text{complex}] \quad (4)$$

Initiation



Propagation



Termination

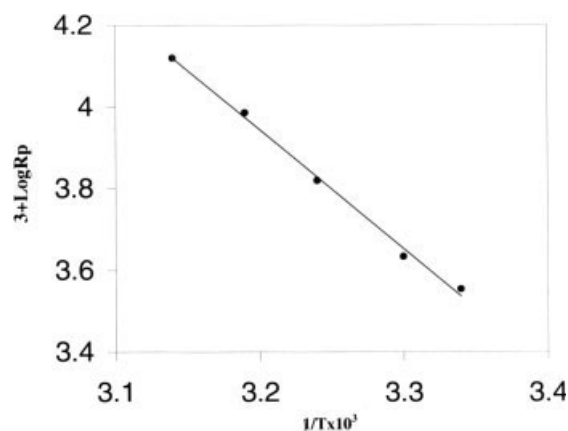
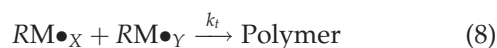


Figure 6 Effect of temperature on rate of polymerization reaction $[\text{Ce}(\text{IV})] = 5.0 \times 10^{-3}$ mol/dm³, $[\text{OA}] = 5.0 \times 10^{-3}$ mol/dm³ $[\text{Monomer}] = 0.3033$ mol/dm³, $[\text{H}_2\text{SO}_4] = 2.0 \times 10^{-3}$ mol/dm³ Temperature = 303–323 K.

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

Ce (IV) × 10 ³ mole/ dm ³	[OA] × 10 ³ mole/ dm ³	[AN] mole/ dm ³	[H ₂ SO ₄] × 10 ³ mol/ dm ³	Temp (K)	R _p × 10 ³ mole/ dm ³
5.0	5.0	0.303	2.0	303	4.33
6.0	5.0	0.303	2.0	303	5.01
7.0	5.0	0.303	2.0	303	5.67
8.0	5.0	0.303	2.0	303	6.29
10.0	5.0	0.303	2.0	303	7.51
15.0	5.0	0.303	2.0	303	10.39
20.0	5.0	0.303	2.0	303	12.21
25.0	5.0	0.303	2.0	303	12.00
30.0	5.0	0.303	2.0	303	11.40
35.0	5.0	0.303	2.0	303	10.97
5.0	5.0	0.303	2.0	303	4.35
5.0	6.0	0.303	2.0	303	4.76
5.0	8.0	0.303	2.0	303	5.50
5.0	10.0	0.303	2.0	303	6.14
5.0	15.0	0.303	2.0	303	7.55
5.0	20.0	0.303	2.0	303	7.72
5.0	25.0	0.303	2.0	303	7.20
5.0	30.0	0.303	2.0	303	6.90
5.0	35.0	0.303	2.0	303	6.80
5.0	5.0	0.151	2.0	303	2.15
5.0	5.0	0.303	2.0	303	4.33
5.0	5.0	0.455	2.0	303	6.50
5.0	5.0	0.606	2.0	303	8.65
5.0	5.0	0.910	2.0	303	13.00
5.0	5.0	1.220	2.0	303	12.0
5.0	5.0	1.522	2.0	303	11.80
5.0	5.0	0.303	2.0	298	3.58
5.0	5.0	0.303	2.0	303	4.30
5.0	5.0	0.303	2.0	308	6.60
5.0	5.0	0.303	2.0	313	9.67
5.0	5.0	0.303	2.0	318	13.18
5.0	5.0	0.303	2.0	323	12.0
5.0	5.0	0.303	1.0	303	8.59
5.0	5.0	0.303	2.0	303	4.30
5.0	5.0	0.303	3.0	303	2.86
5.0	5.0	0.303	4.0	303	2.15
5.0	5.0	0.303	5.0	303	1.72
5.0	5.0	0.303	6.0	303	1.43
5.0	5.0	0.303	7.0	303	1.40
5.0	5.0	0.303	8.0	303	1.40
5.0	5.0	0.303	10.0	303	1.32

Applying the steady state principles to X and R_•, we get

$$\frac{d[\text{complex}]}{dt} = k_1[\text{Ce}^{4+}][\text{OA}] - k_{-1}[\text{complex}][\text{H}^+] - k_2[\text{complex}] = 0 \quad (9)$$

$$[\text{Complex}] = \frac{k_1[\text{Ce}^{4+}][\text{OA}]}{k_2 + k_{-1}[\text{H}^+]} \quad (10)$$

$$\frac{d[\text{Ce}^{4+}]}{dt} = \frac{k_1 k_2 [\text{Ce}^{4+}][\text{OA}]}{k_2 + k_{-1}[\text{H}^+]} \quad (11)$$

$$\frac{d[\text{R}•]}{dt} = k_2[\text{complex}] - k_{-2}[\text{R}•][\text{Ce}^{3+}][\text{H}^+] - k_0[\text{R}•][\text{Ce}^{4+}] - k_i[\text{R}•][\text{M}] = 0 \quad (12)$$

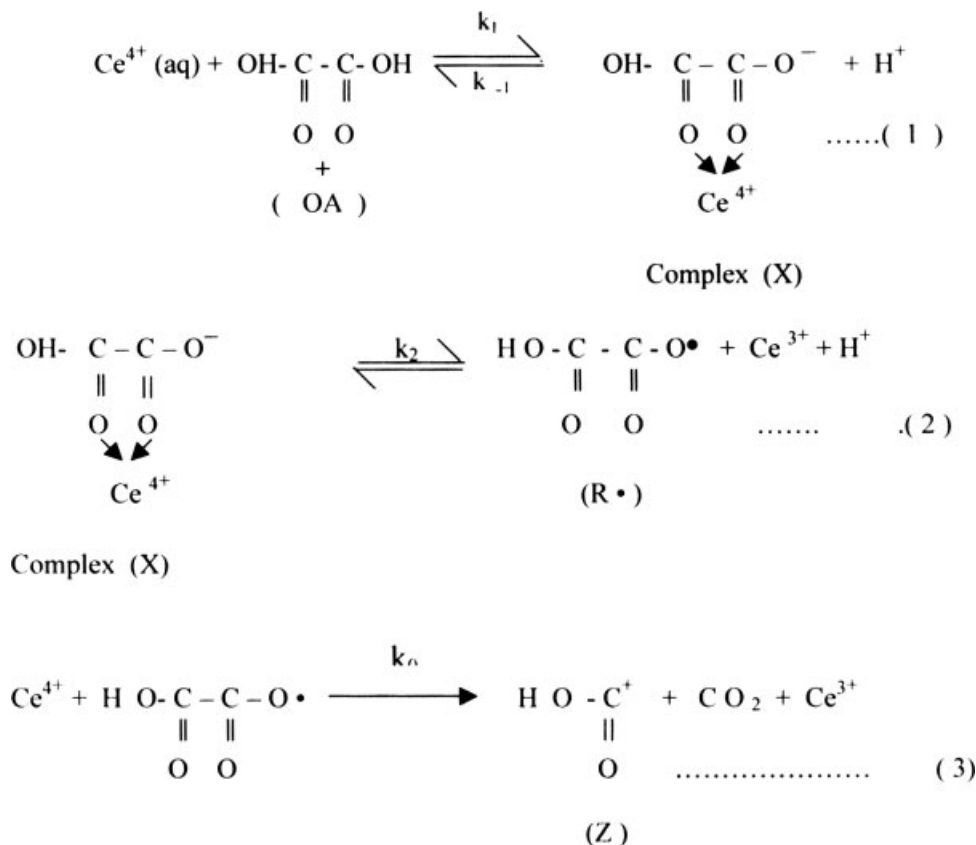
$$[\text{R}•] = \frac{k_1 k_2 [\text{Ce}^{4+}][\text{OA}]}{\{k_2 + k_{-1}[\text{H}^+]\} \{k_2[\text{Ce}^{3+}][\text{H}^+] + k_0[\text{Ce}^{4+}] + k_i[\text{M}]\}} \quad (13)$$

Since the propagation is the stage that involves the major consumption of the monomer, the role of monomer loss can be expressed in terms of propagation only:

$$R_p = \frac{-d[\text{M}]}{dt} = k_p[\text{RM}•_1][\text{M}] \quad (14)$$

Based on the usual assumption that the radical reactivity is independent of the radical chain length, the rate of polymerization becomes,

$$R_p = k_p[\text{RM}•_x][\text{M}] \quad (15)$$



Scheme 1

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

$$k_i[\text{R}\cdot][\text{M}] = k_t[\text{R}-\text{M}\cdot_x]^2 \tag{16}$$

$$[\text{R}-\text{M}\cdot_x] = \left(\frac{k_i}{k_t}\right)^{1/2} [\text{R}\cdot]^{1/2} [\text{M}]^{1/2} \tag{17}$$

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

$$\left(\frac{k_1 k_2 [\text{Ce}^{4+}][\text{OA}]}{(k_2 + k_{-1}[\text{H}^+])(k_2 [\text{Ce}^{3+}][\text{H}^+] + k_0 [\text{Ce}^{4+}] + k_i [\text{M}])}\right)^{1/2} R_p = k_p (k_1 k_2 k_i / k_t)^{1/2} \tag{18}$$

$$= \frac{[\text{M}]^{3/2} [\text{Ce}^{4+}]^{1/2} [\text{OA}]^{1/2}}{k_2 + k_{-1}[\text{H}^+]^{1/2} k_2 [\text{Ce}^{3+}][\text{H}^+] + k_0 [\text{Ce}^{4+}] + k_i [\text{M}]^{1/2}} \tag{19}$$

Thus the dependence of R_p on $[\text{M}]^1$, $[\text{Ce(IV)}]^{0.8}$, $[\text{OA}]^{1/2}$, $[\text{H}^+]^{-1}$, $[\text{Ce}^{3+}]^{-0.5}$, 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 laboratories.

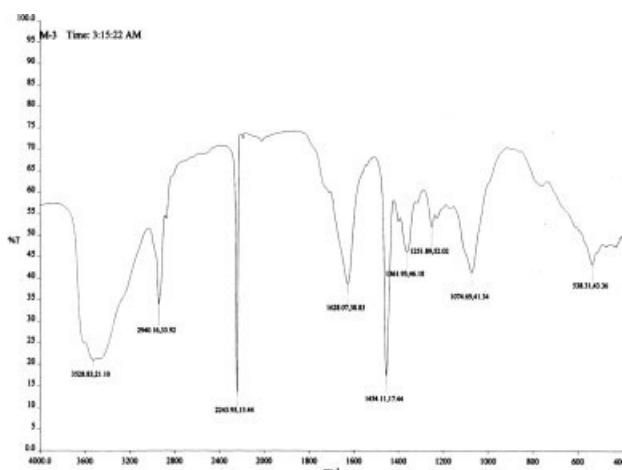


Figure 7 FTIR spectra of polyacrylonitrile Cerium(IV)-oxalic acid Redox system.

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