

Polymerization Kinetics of Methylmethacrylate by Oxidation: Reduction System Using Cerium(IV)/Lactic Acid in Aqueous Medium

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ABSTRACT: The kinetics of polymerization of methylmethacrylate initiated by cerium(IV)–lactic acid redox system was studied in an aqueous medium in the temperature range of 25–50°C. The rate of polymerization (R_p) and the rate of cerium(IV) disappearance have been measured. The effects of some water-miscible organic solvents, cationic, anionic, non-ionic surfactants, and complexing agents on the rate of polymerization were investigated. The temperature dependence of the rate was studied, and the activation parameters were computed using the Arrhenius and Eyring plots. The effects

of inorganic and organic solvents on polymerization were also investigated. All of them depressed both the initial rate and limiting conversion. A mechanism consistent with the experimental data, involving cerium(IV)–lactic acid complex formation, which generates free radicals, is suggested. The chain termination step of the polymerization reaction is by mutual interaction of the growing macromolecules. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3498–3505, 2007

Key words: cerium(IV)–lactic acid; MMA; redox system

INTRODUCTION

Certain inorganic transition metal ions in their higher valence states coupled with easily reducible organic substrates act as potential initiators for the redox polymerization of vinyl monomers. In earlier studies reported, the various initiating system involving V^{5+} ion coupled with several organic substrates and cerium(IV) has been used for the oxidation of large number of organic substrates. Lactic acid ion coupled with V^{5+} and cerium(IV) has been reported as useful redox pairs toward the polymerization of acrylonitrile in aqueous medium.^{1,2} In our previous publication, the polymerization of methylmethacrylate (MMA) by the cerium(IV)–tartaric acid redox pair has been reported.³ This work has been further extended to investigate the cerium(IV)–lactic acid redox system in the aqueous polymerization of MMA, and its importance in orthopedic surgery, dental laboratory, and contact lenses have stimulated the choice of this study.

Redox polymerization has the advantages of very short induction time, low activation energy (40–85 kJ/mol), production of high-molecular-weight polymers with high yields, easy control of the polymerization reaction at low temperatures due to reduction of the

side reactions, and the direct experimental proof of the transient radical intermediates⁴. In redox systems, oxidants form initially a complex by reacting with simple organic molecules, which then decompose unimolecularly to produce free radicals that initiate polymerization.⁵ Numerous redox pairs containing organic and inorganic compounds as polymerization initiator have been used successively. Commonly used oxidants include peroxides, persulfates, permanganates, etc, and the salts of transition metals. These oxidants form potential redox systems with various reducing agents like alcohols, aldehydes, amines, amides, ketones, acids, thiols, etc., for the aqueous polymerization of vinyl monomers.⁶

Ce(IV) ion 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 perchlorate.⁷ The oxidation of alcohols by Ce(IV) is believed to be produced by disproportionation of coordination of complexes. According to the complex mechanism, unimolecular disproportionation of complex yields a cerrous ion, a proton, and a free radical on the alcohol substrate.^{8,9} Redox polymerization of MMA with allyl alcohol initiated by Ce(IV)/HNO₃ was studied.¹⁰

Low-temperature redox polymerization of vinyl monomers is of importance, especially for industrial view points.¹¹ Besides its economical benefits, suppression of side reactions such as branching is its additional advantage over common thermal initiation methods.

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There are many possibilities for redox initiation in aqueous solutions like Fenton reagent (1), persulfate, and various reductants such as metals, metal complexes, thiols, and polyhydric phenols.^{12,13} Cerium (IV)-alcohol¹⁴ or amino acids,^{15,16} and permanganate with oxalic acid¹⁷ and ascorbic acid¹⁸ redox couples are well-known low-temperature radical initiators, for polymerization of water-soluble vinyl monomers. However, redox initiation in organic solvents is not so much successful. Peroxide tertiary amine¹⁹ or hydroperoxide-cobalt octate²⁰ systems reported are not applicable for all vinyl polymerization. In fact, redox reactions are more complicated than we thought, and presumably water involves in some steps of the reactions.

There are many reports in the literature on the block copolymer synthesis. Initiation by a redox process is the only method used to obtain these types of polymers.²¹⁻²⁴ Redox systems are widely used as initiators in radical polymerization. Compared to other methods, they have the prime advantage of operating at very moderate temperatures. This means that the probability of side reactions can be minimized. Ce(IV) or permanganate coupled with a hydroxyl- or carboxylic group-containing reductant is the initiator most often used.²⁵⁻²⁸

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.²⁹⁻³⁹ Oxidizing agents such as KMnO_4 ,⁴⁰ halogens,⁴¹ chloramine-T,⁴¹ Fe^{3+} ,⁴¹ $\text{S}_2\text{O}_8^{2-}$ ⁴¹ are used. The superiority of the system lies in the molecular weight of the polymer, because glycine itself acts as a modifier.⁴⁰

EXPERIMENTAL

Methylmethacrylate (S.D. Fine Chem, India) was washed with 5% NaOH solution, to remove the inhibitor. The inhibitor-free sample was washed thrice with deionized water to remove the trace of alkali. Water used for the preparation of solutions was obtained by redistilling-distilled water over alkaline permanganate and was deionized by passing through Biodeminrolit resin (Permutite Co., UK).⁴² A solution of cerium(IV) (Nice-Chem) was prepared by distilled water with H_2SO_4 , and it was standardized by iodometric titration against standard ferrous ammonium sulfate solution, using barium diphenylamine sulfonate as an internal indicator.

All other chemicals such as lactic acid, sodium lauryl sulfate, ferrous ammonium sulfate, cetyl trimethyl ammonium bromide, and Triton X-100 were of analytical 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.

Kinetic measurements

Inhibitor-free MMA (0.01873 mol/dm^3), lactic acid (0.005 mol/dm^3), and distilled water were taken in a reaction vessel and thermostated at 30°C . The system was flushed with oxygen-free nitrogen for about 20–30 min to expel the dissolved oxygen. At the end of the duration, cerium(IV) solution (about 0.005 mol/dm^3) was added to the reaction vessel and shaken well. The reaction vessel was then sealed with a rubber gasket to ensure inert atmosphere. Polymerization starts without any induction period. After about 60 min, 0.1 mol/dm^3 of ferrous ammonium sulfate solution was added to stop the polymerization. The polymethylmethacrylate (PMMA) was filtered from the reaction mixture using a glass funnel with Whatman 41 filter paper, washed several times with distilled water, and dried at 60°C to a constant weight. The rate of polymerization (R_p) was determined gravimetrically.⁴³ The rate of cerium(IV) disappearance ($-R_m$) was calculated (Fig. 1).

Stoichiometry and product analysis

Reaction mixture of various constitutions of [cerium(IV)], [LA], and [MMA] were equilibrated at 30°C for 24 h. The reaction mixture showed that one mole

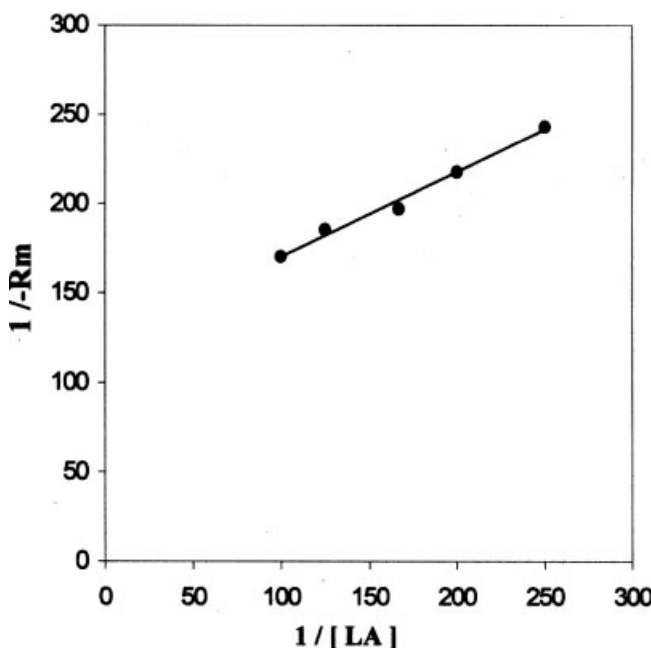


Figure 1 Inverse plot of cerium(IV) disappearance versus [lactic acid]. [cerium(IV)] = $5.0 \times 10^{-3} \text{ mol/dm}^3$, [LA] = $5.0 \times 10^{-3} \text{ mol/dm}^3$, [MMA] = $1.873 \times 10^{-2} \text{ mol/dm}^3$, temperature = 303 K.

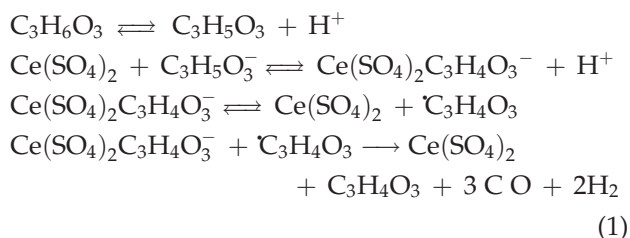
TABLE I
Plots of $-1/R_m$ Versus $1/[LA]$

$\frac{-1}{R_m}$	$\frac{1}{[LA]}$
307.04	500
243.24	250
217.79	200
196.95	166.66
185.44	125
170.27	100

$$r = 0.985, s = 0.336, I = 144.96.$$

of cerium(IV) was consumed per mole of [LA], according to eq (1).

The product PMMA was identified by IR spectra. The wave number $1733\text{--}1735\text{ cm}^{-1}$ corresponds to CH_3COO^-



RESULTS AND DISCUSSION

The polymerization of MMA initiated by cerium(IV)–lactic acid redox system takes place under stoichiometric conditions at 30°C . Although induction period

was not observed under deaerated conditions, there exists an induction period if the solution was not deaerated. Thus, it is evident that the polymerization is initiated by free radicals formed *in situ* by the redox system. The steady state was attained within 60 min.

Molecular weight determination

The molecular weights, M_w , of the purified samples of PMMA product of polymer were determined by viscometry. A 1% solution of the polymer in benzene 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_w value was calculated by using the appropriate Mark–Houwink relationship given by Stockmayer and Cleland.⁴⁴ The intrinsic viscosity ($[\eta]$) was found to be $(5.20 \times 10^3)M_w^{0.76}$ in benzene at 303 K. It has been observed that the molecular weight of the polymer product under standard conditions was found to be 7.464×10^5 . It increases with increasing concentrations of monomer and decreases with increase in Ce(IV), lactic acid, 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.⁴⁵

The rate of cerium(IV) disappearance ($-R_m$) was found to be independent of MMA concentration (Table I). A plot of $-1/R_m$ versus $1/[LA]$ was linear with an intercept on the rate axis, indicating Lineweaver–Burk⁴⁶ equation of kinetics for complex formation.

TABLE II
Effect of Variation of [Lactic Acid], [Cerium(IV)] and [Monomer] on the Rate of Polymerization

[Ce(IV)] (10^3 mol/dm^3)	[LA] (10^2 mol/dm^3)	[MMA] (10^2 mol/dm^3)	Temp (K)	R_p (10^4 s^{-1})
2.0	5.0	1.877	303	6.10
5.0	5.0	1.877	303	8.60
6.0	5.0	1.877	303	9.51
7.0	5.0	1.877	303	10.10
8.0	5.0	1.877	303	11.00
10.0	5.0	1.877	303	10.50
5.0	2.0	1.877	303	5.90
5.0	4.0	1.877	303	7.61
5.0	6.0	1.877	303	8.60
5.0	8.0	1.877	303	9.62
5.0	10.0	1.877	303	11.50
5.0	5.0	0.938	303	4.29
5.0	5.0	1.877	303	8.60
5.0	5.0	2.816	303	13.24
5.0	5.0	3.755	303	17.62
5.0	5.0	1.877	298	7.30
5.0	5.0	1.877	303	8.60
5.0	5.0	1.877	308	14.90
5.0	5.0	1.877	313	16.67
5.0	5.0	1.877	318	26.90
5.0	5.0	1.877	323	21.32

Effect of initiator concentration on the rate of polymerization

As the cerium(IV) concentration increases, the rate of polymerization increases.

This is due to the fact that increase in $[\text{Ce(IV)}]$ increases the rate of production of primary radicals, and hence, the number of propagating polymer radicals, which in turn increases the polymerization rate. Here, the variation of the range is from 0.002 to 0.010 mol/dm³ of cerium(IV) concentration (Table II). These observations indicated that on increasing the initiator concentration the rate of polymerization increases up to 0.008 mol/dm³ of $[\text{Ce(IV)}]$ and then decreases at 0.01M. The decrease is due to the fact that further increase of $[\text{Ce(IV)}]$ provides more chance for premature termination of growing chain radicals, which in turn reduces both the rate and degree of polymerization. To determine the order of the reaction with respect to the initiator, $\log R_p$ has been plotted against $\log[\text{cerium(IV)}]$ (Fig. 2). The value of the slope was found to be fractional (0.51) order. These observations indicated that bimolecular termination occurs.^{47,48}

Effect of lactic acid concentration on the rate of polymerization

With the increase of lactic acid concentration, the rate of polymerization increases.⁴⁹⁻⁵¹ The order of the reaction with respect to lactic acid concentration was found to be fractional (0.42) order in the concentration range of 0.002–0.010 mol/dm³, and above 0.008 mol/dm³ concentration of lactic acid, (Fig. 3) the rate of

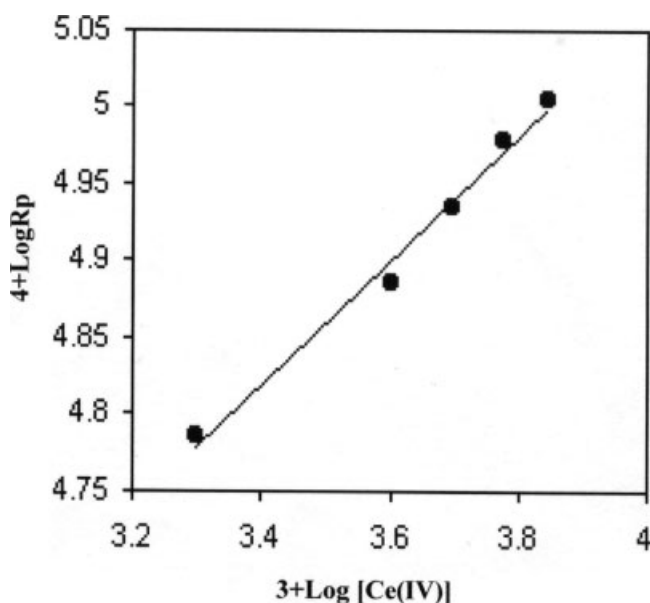


Figure 2 Effect of $[\text{cerium(IV)}]$ on the rate of polymerization. $[\text{Ce(IV)}] = (5.0\text{--}10.0) \times 10^{-3}$ mol/dm³, $[\text{LA}] = 5.0 \times 10^{-3}$ mol/dm³, $[\text{monomer}] = 1.873 \times 10^{-2}$ mol/dm³, temperature = 303 K.

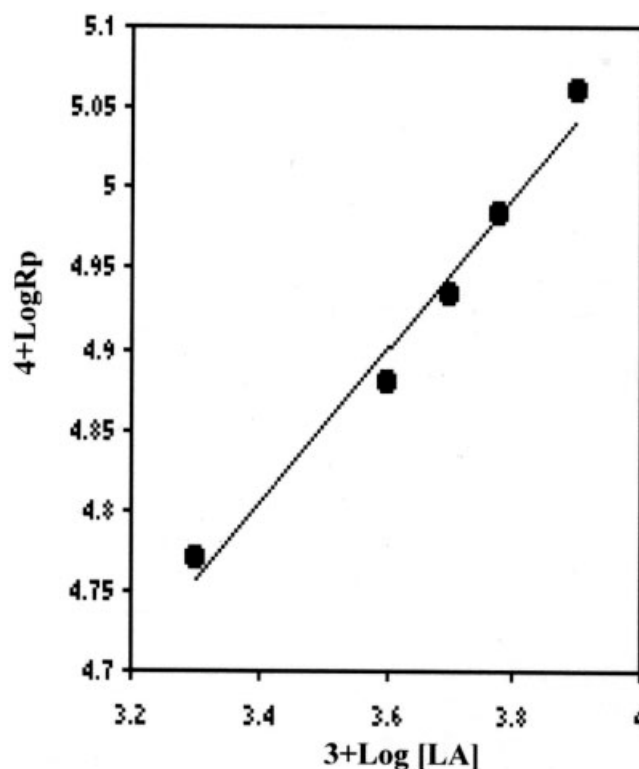


Figure 3 Effect of $[\text{lactic acid}]$ on the rate of polymerization. $[\text{Ce(IV)}] = 5.0 \times 10^{-3}$ mol/dm³, $[\text{LA}] = (5.0\text{--}10.0) \times 10^{-3}$ mol/dm³, $[\text{monomer}] = 1.873 \times 10^{-2}$ mol/dm³, temperature = 303 K.

polymerization decreases due to chain transfer to lactic acid. The molecular weight of the polymer (PMMA) also decreases with increase of lactic acid concentration.⁵² (Fig. 4).

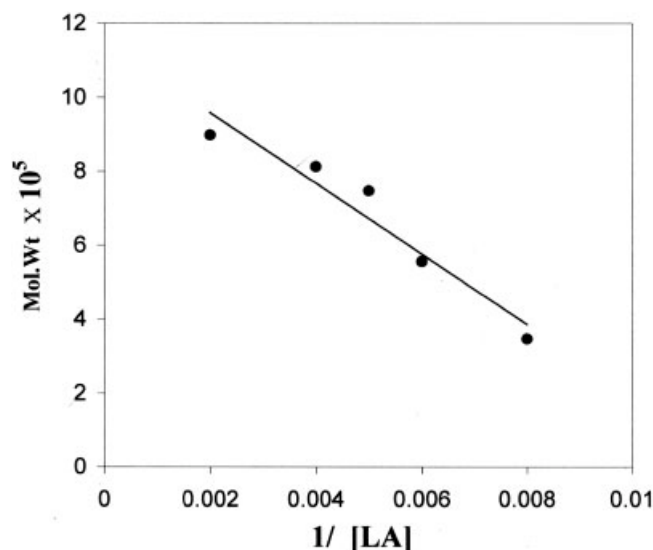


Figure 4 Plot of mol. wt. versus $1/[\text{LA}]$. $[\text{Ce(IV)}] = 5.0 \times 10^{-3}$ mol/dm³, $[\text{LA}] = (2.0\text{--}10.0) \times 10^{-3}$ mol/dm³, $[\text{monomer}] = 1.873 \times 10^{-2}$ mol/dm³, temperature = 303 K.

Effect of monomer concentration on the rate of polymerization

The polymerization reaction was investigated over a wide range of monomer (MMA) concentrations (0.0932–3.755 mol/dm³). The rate of polymerization, R_p , and percentage conversion were found to increase with an increasing monomer concentration. A plot of R_p versus $[M]$ was linear, passed through the origin, and after a certain period the extent of polymerization attained a constant value. A plot of $\log R_p$ versus $\log[MMA]$ shows a first-order dependence on monomer concentration in the aqueous medium. For a monomer MMA, which has a higher affinity for its insoluble polymer than water, generally observation is of first-order dependence on the rate of initial monomer concentration⁵³ (Fig. 5).

Effect of temperature on the rate of polymerization

The effect of temperature on the rate of polymerization was investigated over a range of 25–50°C (Fig. 6). The initial rate as well as the percentage conversion increases with increase of temperature up to 45°C. After 45°C, the rate of polymerization and percentage conversion decreases at 50°C. An increase in temperature causes a decrease in the chain length, which may be due to an increase in the mobility of growing chain radicals in the system, leading to their efficient termi-

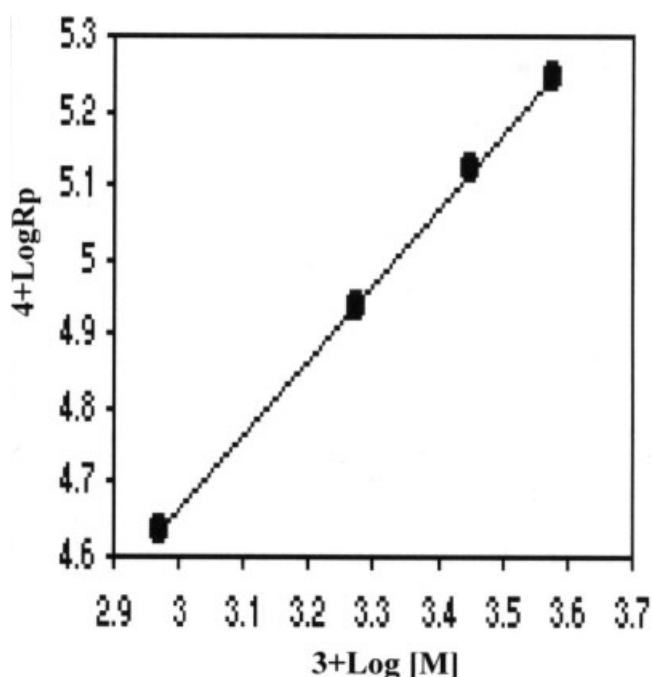


Figure 5 Effect of $[monomer]$ on the rate of polymerization. $[Ce(IV)] = 5.0 \times 10^{-3}$ mol/dm³, $[LA] = 5.0 \times 10^{-3}$ mol/dm³, $[monomer] = (0.938-3.755) \times 10^{-2}$ mol/dm³, temperature = 303 K.

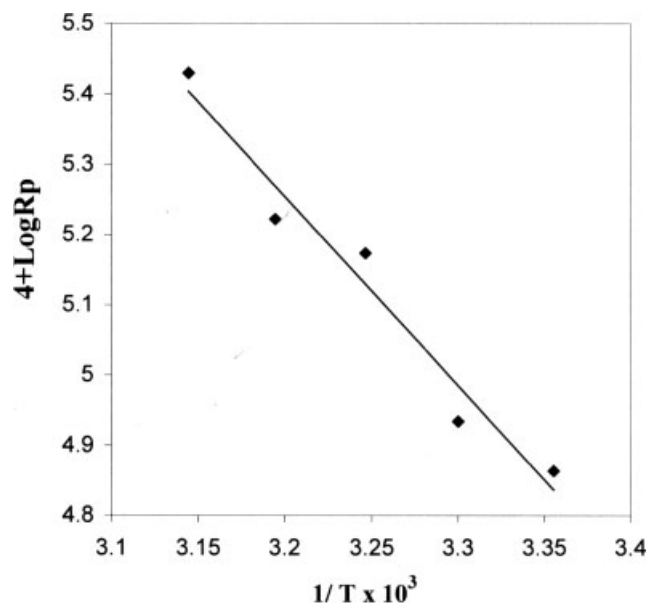


Figure 6 Effect of temperature on the rate of polymerization. $[Ce(IV)] = 5.0 \times 10^{-3}$ mol/dm³, $[LA] = 5.0 \times 10^{-3}$ mol/dm³, $[monomer] = 1.873 \times 10^{-2}$ mol/dm³, temperature = 298–323 K, slope = 2689.99, energy of activation (E_a) = 51.50 kJ/mol.

nation.⁵⁴ The overall energy of activation (E_a) has been calculated from the Arrhenius plot of $\log R_p$ versus $1/T$, in the temperature range of 25–50°C. Activation energy (E_a) = 51.50 kJ/mol.^{55,56} The other activation parameters calculated from the Eyring plot are as follows:

$$\Delta H^\ddagger = 48.93 \text{ kJ/mole}, \Delta S^\ddagger = -141.41 \text{ JK}^{-1}/\text{mole}^{-1}$$

$$\text{and } \Delta G^\ddagger = 92.49 \text{ kJ/mole}$$

Effect of organic solvents on the rate of polymerization

Addition of 5% (v/v) organic solvents such as methanol, ethanol, and DMF to the reaction mixture decreases the rate of polymerization as well as the maximum conversion (Fig. 7). The retardation of the rate by these solvents might be due to the following reasons.

1. Solvent molecules might decrease the area of shielding of the strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain.
2. These solvent molecules might increase the rate of production of primary radicals, which under the existing experimental conditions renders the termination rate relatively fast as compared to the rate of growth of the polymer chain.⁵⁷

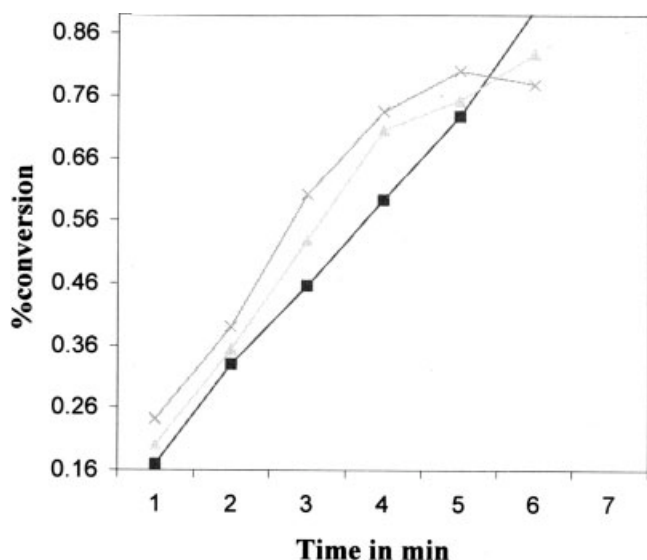


Figure 7 Effect of organic solvents. [Cerium(IV)] = 5.0×10^{-3} mol/dm³, [LA] = 5.0×10^{-3} mol/dm³, standard $R_p = 8.60 \times 10^{-4}$ s⁻¹, temperature = 303 K. [MMA] = 1.873×10^{-2} mol/dm³. ■ [DMF] = 5.0×10^{-3} mol/dm³, $R_p = 5.75 \times 10^{-4}$ s⁻¹. ▲ [CH₃OH] = 5.0×10^{-3} mol/dm³, $R_p = 6.75 \times 10^{-3}$ s⁻¹. X [CH₃OH] = 10×10^{-3} mol/dm³, $R_p = 4.61 \times 10^{-3}$ mol/dm³.

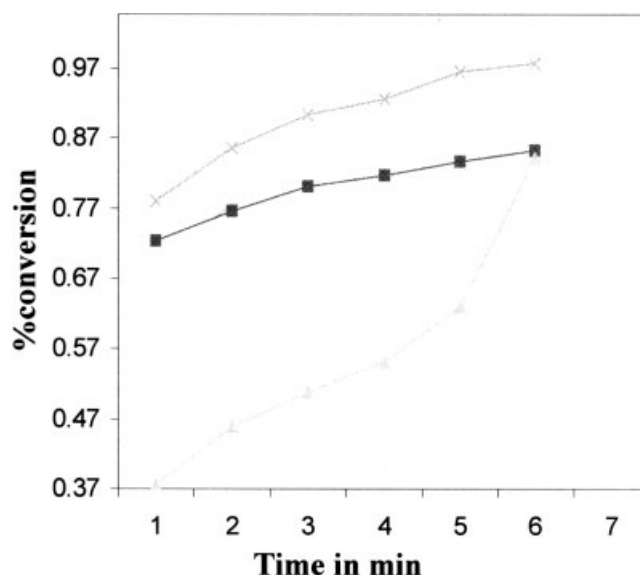


Figure 8 Effect of anionic surfactant. [Cerium(IV)] = 5.0×10^{-3} mol/dm³, [LA] = 5.0×10^{-3} mol/dm³, [MMA] = 1.873×10^{-2} mol/dm³. Temperature = 303 K, ■ [SLS] = 5.0×10^{-3} mol/dm³, ▲ [SLS] = 9.05×10^{-3} mol/dm³, X [SLS] = 10.0×10^{-3} mol/dm³, $R_p = 4.6 \times 10^{-4}$ s⁻¹.

- Further the interchain hydrogen bonding interlocking the polymer chain is not rigid, and therefore the tendency of mutual termination of the polymer chain increases.^{58,59}

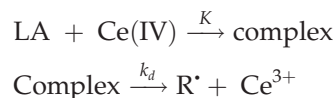
Effect of surfactants on the rate of polymerization

The anionic surfactant, sodium lauryl sulfate concentration increases, the rate of polymerization R_p increases both above and below the CMC value (Fig. 8). The cationic surfactant, cetyltrimethyl ammonium bromide concentration increases, the rate of polymerization decreases both above and below the CMC value (Fig. 9). In contrast, the nonionic surfactant Triton X-100 has no effect on the rate. The hydrophobic interactions and electrostatic attractions are mainly responsible for the inhibition of the rate of polymerization.⁶⁰

Mechanism and rate law

The polymerization of methyl methacrylate (MMA) in aqueous medium initiated by cerium(IV)–lactic acid redox system shows characteristic features of heterogeneous polymerization. The reaction mixture becomes heterogeneous as soon as polymerization starts because of the insolubility of the polymer (PMMA) in the aqueous media. From the kinetic results, a reaction has been proposed involving the initiation by organic free radicals generated by the interaction by the cerium(IV) ion with the COOH

group of the lactic acid via complex formation and termination by metal ion:



Initiation

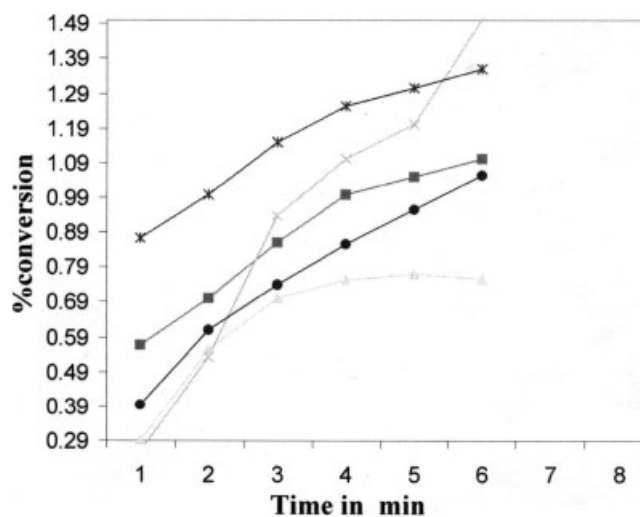
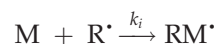


Figure 9 Effect of cationic surfactant on the rate of polymerization. [Cerium(IV)] = 5.0×10^{-3} mol/dm³, [LA] = 5.0×10^{-3} mol/dm³, [MMA] = 1.873×10^{-2} mol/dm³, temperature = 303 K. ■ [CTABr] = 5.0×10^{-4} mol/dm³, ▲ [CTABr] = 7.0×10^{-4} mol/dm³, X [CTABr] = 10.0×10^{-4} mol/dm³, * [CTABr] = 12.0×10^{-4} mol/dm³, ● [CTABr] = 14.0×10^{-4} mol/dm³, $R_p = 8.6 \times 10^{-4}$ s⁻¹.

Propagation



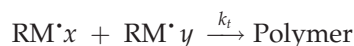
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Termination



Applying steady state approximation

$$-d/dt[\text{R}^*] = k_d[\text{complex}] - k_i[\text{M}][\text{R}^*] = 0$$

$$K = [\text{complex}]/[\text{LA}][\text{Ce(IV)}]$$

$$[\text{complex}] = K[\text{Ce(IV)}][\text{LA}]$$

$$k_dK[\text{Ce(IV)}][\text{LA}] - k_i[\text{M}][\text{R}^*] = 0$$

$$[\text{R}^*] = k_dK[\text{Ce(IV)}][\text{LA}]/k_i[\text{M}]$$

$$k_i[\text{R}^*][\text{M}] = k_t[\text{RM}^*n][\text{RM}^*n] = k_t[\text{RM}^*n]^2$$

$$[\text{RM}^*n]^2 = (k_i/k_t)[\text{R}^*][\text{M}]$$

$$[\text{RM}^*n] = (k_i/k_t)^{1/2}[\text{R}^*]^{1/2}[\text{M}]^{1/2}$$

$$k_p = [\text{RM}^*n][\text{M}]$$

$$R_p = k_p(k_i/k_t)^{1/2}[\text{R}^*]^{1/2}[\text{M}]^{1/2}[\text{M}]$$

$$R_p = k_p[\text{RM}^*n][\text{M}]$$

$$R_p = k_p(k_i/k_t)^{1/2}(k_dK/k_i)^{1/2}$$

$$\{[\text{Ce(IV)}][\text{LA}]/[\text{M}]\}^{1/2}[\text{M}]^{3/2}$$

$$R_p = k_p(k_dK/kt)^{1/2}[\text{Ce(IV)}]^{1/2}[\text{LA}]^{1/2}[\text{M}]^{1/2}/[\text{M}]^{1/2}$$

$$R_p = k_p(k_dK/kt)^{1/2}[\text{Ce(IV)}]^{1/2}[\text{LA}]^{1/2}[\text{M}]$$

Thus the dependence of R_p on $[\text{M}]$, $[\text{Ce(IV)}]$ and $[\text{LA}]$ 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, various vinyl monomers initiated by the reaction of cerium(IV) and other transition metal ions, with suitable reductant is in progress in our laboratory.

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