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Aqueous polymerization of ethyl acrylate initiated by ceric ion-reducing agent system in sulphuric acid medium

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Abstract Kinetic study of aqueous polymerization of ethyl acrylate (EA) is carried out at 30 °C in dilute sulphuric acid medium by employing ammonium ceric sulphate–methyl ethyl ketone (MEK) as redox initiator system. The ceric ion consumption is found to be first order with respect to ceric ion and half order with respect to reducing agent concentrations. No complex formation between ceric ion and reducing agent is observed. The orders with respect to ceric ion, reducing agent and monomer concentrations are evaluated for the aqueous polymerization of EA by Ce(IV)–MEK redox initiator system, and are found to be 0.5, 0.5 and 1.4, respectively . The overall activation energy, E_{overall}, for aqueous polymerization of EA in the temperature region of 27–40°C is found to be 20.27 kJ/mol. A kinetic scheme for the aqueous polymerization of EA initiated by Ce(IV)–MEK redox initiator system is presented.

Introduction

Ceric salts show a high reactivity in aqueous media [1] and have been used either alone [2] or in combination with reducing agents [3–5] as initiators of vinyl polymerization. The ceric ion proceeds via a single-electron transfer with the formation of free radicals from reducing agents [6]. The oxidation of some of the organic substrates by Ce(IV) believed to occur by the direct attack of the ceric species on the substrate and appears to proceed by electron abstraction. In some cases, the reaction goes through an intermediate complex. Evidence of complex formation has not been obtained in Ce(IV) oxidations of many compounds in sulphuric and nitric acid media [7–10].

Studies have been reported, in recent literature, on ceric ion initiation of vinyl polymerization including graft and block copolymerizations, in aqueous acid media, by using various types of reducing agents [11–22]. In graft and block copolymerizations the substrate itself can be oxidized [23–25] by Ce^{4+} to initiate the polymerization. Attempts have also been made to study the effects of organic additives on the kinetics of polymerization by ceric salt-reducing agent systems in aqueous acid media [11, 26].

This paper describes the study of the kinetics of polymerization of ethyl acrylate (EA) at 30 °C in aqueous sulphuric acid medium by employing ammonium ceric sulphate (ACS) with methyl ethyl ketone (MEK) as the redox initiator system under inert atmosphere.

Experimental

Materials

The monomer, EA (Central Drug House Pvt. Ltd., Mumbai, India) is purified by washing with 5% sodium hydroxide followed by distilled water. The washed monomer is further purified by vacuum distillation under nitrogen atmosphere.

Methyl ethyl ketone (AR, s. d. fine chem pvt. ltd., Boisar, India), methanol (AR, Ranboxy Laboratory Ltd., S.A.S. Nagar, India), ferroin solution (ferrous o-phenanthroline) (AR, s. d. fine chem pvt. ltd.,), ammonium ceric sulphate (ACS) (LR, Sarabhai M. Chemicals Ltd., Baroda, India) and ammonium ferrous sulphate (AFS) (AR, s. d. fine chem pvt. ltd.,) are used as supplied without further purification.

Analytical reagent grade tetrahydrofuran (THF) (AR, s. d. fine chem pvt. ltd.,) used for gel permeation chromatography experiments is purified by distillation over iron(II) sulphate.

Methods

Aqueous polymerization of EA is carried out in 0.1 M sulphuric acid at 30 °C under an inert atmosphere by using Ce(IV)–MEK redox initiator system. To an aqueous solution (27 ml) of EA and reducing agent (RA) under inert atmosphere the solution (3 ml) of ACS in 1 M sulphuric acid is added and the reaction is carried out at 30 °C. The ceric ion concentration in the reaction medium is determined volumetrically at different time intervals by adding an excess of known quantity of ammonium ferrous sulphate solution to the reaction mixture and the excess ammonium ferrous sulphate in the reaction mixture is back-titrated with standard ACS solution by using O-phenanthroline (ferroin) as an indicator. The rate of ceric ion consumption, R_{Ce}, is determined from the initial slope of the plot of the percentage consumption of Ce(IV) versus time.

The polymerization of EA in the present study is followed by gravimetry. The polymerization reaction in the reaction tube is arrested at the required time interval by adding slight excess of ammonium ferrous sulphate solution to the reaction mixture in the reaction tube. Thus, the polymer formed for different time intervals are separated by filtration in sintered crucibles and the filtered polymers are washed thoroughly in the sintered crucibles and are dried to constant weights at 60 °C in a vacuum oven. The percent conversions of the polymer formed at different times is computed from the weights of the polymers obtained in these time periods. The rate of polymerization, R_p, is evaluated from the initial slope of the plot of percent conversion versus time.

Molecular weight determination

The molecular weights ($\bar{M}_n$) of the polymers formed at different time intervals are determined by gel permeation chromatography (Waters, USA) with tetrahydrofuran as eluent (Table 1; Fig. 7). Molecular weight calibration curve is obtained with polystyrene standards in the molecular weight range 2.3×10^3–3.1×10^6 (Polymer Laboratories, Church Stretton, Shropshire, UK).

Table 1 Determination of energy of activation, E_{overall} and molecular weight with conversion

T (°K)	R_px10^4 (mol l^{-1} S^{-1})	Conversion (%)	$\bar{M}_n \times 10^{-4}$
300	1.261	17.3	1.96
303	1.389	24.6	2.19
308	1.527	33.2	2.53
313	1.792	35.9	2.64
		44.7	2.99
E_{overall} = 20.27 kJ/mol		55.9	3.23
		58.0	2.98
		61.9	2.79

Results and discussion

There is no colour change observed with the addition of reducing agent to the ceric solution in 0.1 M sulphuric acid medium which indicates the absence of complex formation between reducing agent and ceric ion, and the oxidation of RA appears to proceed by direct attack of the ceric species on the RA [6, 10].

The ceric ion concentration in the reaction medium is varied in the range 1.0–5.0×10^{-3} moll^{-1} by keeping all other variables in the reaction medium constant to study the effect of [Ce(IV)] on R_{Ce}. The influence of reducing agent concentration on R_{Ce} in the concentration range 0.48–4.99 M, while keeping constant all the other parameters in the reaction medium is also studied.

The dependence of R_{Ce} on [Ce(IV)] is first order under the present experimental conditions (Fig. 1). The rate of ceric ion consumption shows half-order dependence with respect to [MEK] under present experimental conditions (Fig. 2). The linear plot of R_{Ce} versus $[\mathrm{MEK}]^{0.5}$ passes through the origin, clearly indicating the absence of complex formation between Ce(IV) and reducing agent (Fig. 2) [10].

A short induction period is observed with every polymerization system under present study and is found to vary inversely with the rate of initiation. From the results obtained at different MEK concentrations, under present experimental conditions, it is deduced that with the increase in MEK concentration the primary radical production increases as R_p increases regularly. The order with respect to [MEK] for EA polymerization under present experimental conditions is evaluated from the slope of the logarithmic plot of R_p versus [MEK] and is found to be 0.5 (Fig. 3), which is in agreement with the theoretical value (0.5) for the RA exponent in the rate Eq. (11). The rate of polymerization of EA under present experimental conditions shows increasing trend with [Ce(IV)] and yields an order 0.5 as the slope of loga-

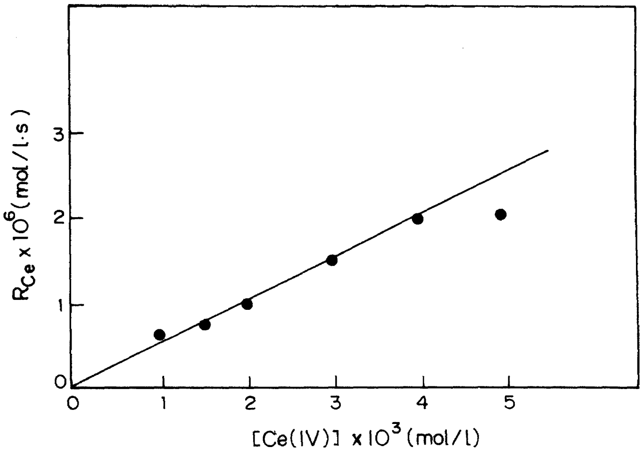

Fig. 1 Plot of R_{Ce} Vs. [CE(IV)]. [EA] = 0.0992M, [MEK] = 0.2978M, $[H_2SO_4]$ = 0.1M, T= 30 °C

rithmic plot of R_p versus [Ce(IV)] (Fig. 3). This order for [Ce(IV)] is in agreement with the theoretical value for [Ce(IV)] exponent (0.5) in the rate Eq. (11). The order with respect to [EA] is also evaluated as slope of the logarithmic plot of Rp versus [EA] and is found to be 1.4 (Fig. 4). This order with respect to monomer concentration under present experimental conditions is higher compared to the monomer exponent in the rate Eq. (11) for EA polymerization. This higher order dependence on [EA] supports the linear termination (monomolecular termination with ceric species) of the growing chains as well as bimolecular termination of the growing chains. The higher order with respect to [EA] gives support to the complex nature of the initiation reactions involving monomer molecules as participating reactants to generate initiating free radicals [27].

The overall activation energy, E_{overall}, under present experimental conditions in the temperature region 27–40 °C is obtained from the Arrhenius plot of log R_p versus 1/T and is found to be 20.27 kJ/mol (Table 1, Figs. 5 and 6), which is of the same order compared to the literature results [28–31].

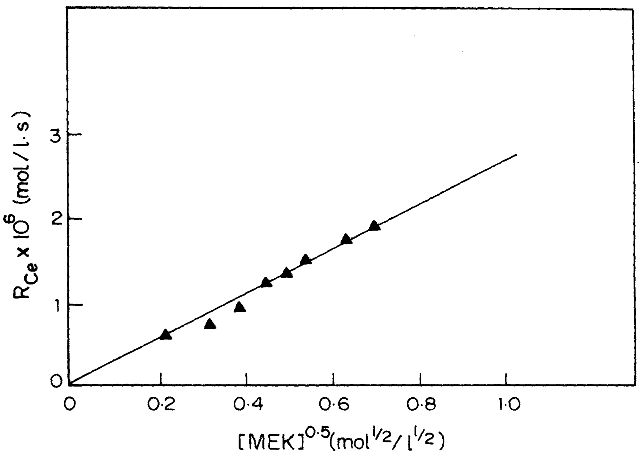

Fig. 2 Plot of R_{Ce} Vs. $[MEK]^{0.5}$. [EA] = 0.0992M, [Ce(IV)] = 0.003M, $[H_2SO_4]$ = 0.1M, T = 30 °C

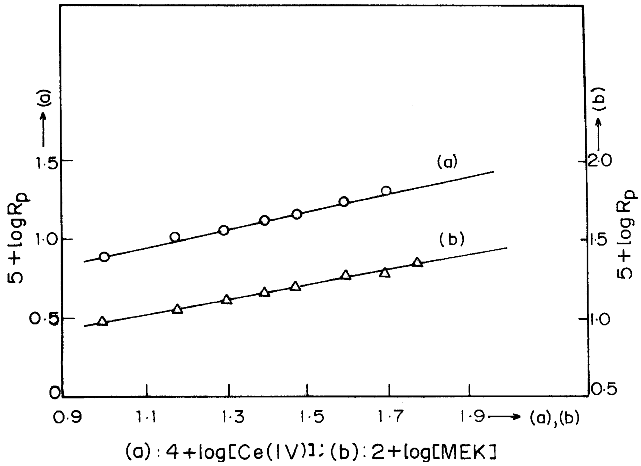

Fig. 3 Determination orders with respect to [CE(IV)] and [MEK] for the polymerization of EA. $[H_2SO_4]$ = 0.1M, T = 30 °C. **a** [EA] = 0.0992M, [MEK] = 0.2978M; **b** [EA] = 0.0992M, [CE(IV)] = 0.003M

The following reaction scheme explains satisfactorily the kinetic results obtained:

Reaction of ceric ion with reducing agent

$$\mathrm{Ce(IV)} + R \xrightarrow{k_r} R^{\cdot} + \mathrm{Ce(III)} + \mathrm{H}^+ \qquad (1)$$

where R is the reducing agent and $R^{\cdot}$ is a primary radical.

Reaction of primary radical with Ce(IV) to give the products

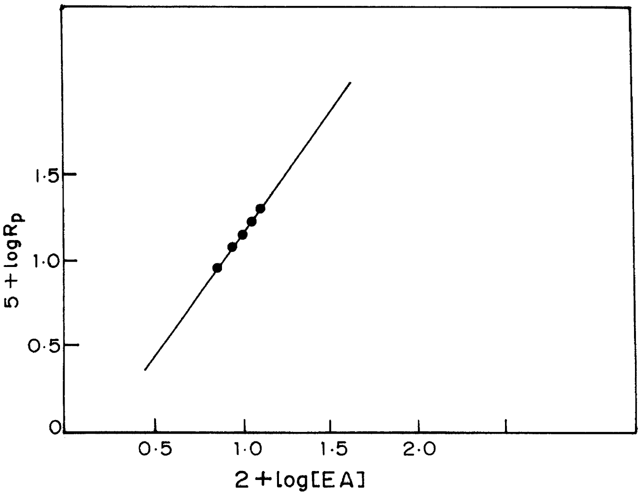

Fig. 4 Determination of order with respect to [EA]. $[H_2SO_4]$ = 0.1M, T = 30 °C, [Ce(IV)] = 0.003M, [MEK] = 0.2978M

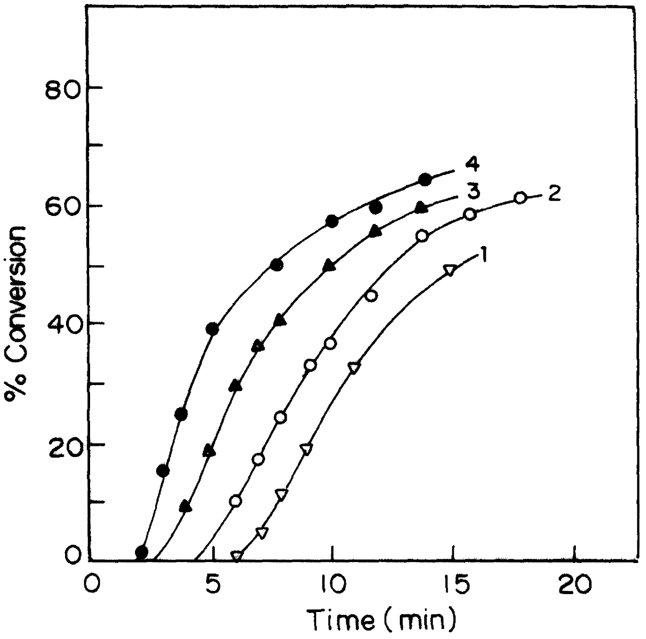

Fig. 5 Conversion Vs. time plots for polymerization of EA at temperatures: (1) 27 °C, (2) 30 °C, (3) 35 °C and (4) 40 °C. [EA] = 0.0992M, [Ce(IV)] = 0.003M, [MEK] = 0.2978M, [H_2SO_4] = 0.1M (Table 1)

$$\mathrm{Ce(IV)} + R^{\cdot} \xrightarrow[\text{fast}]{k_o} \text{products} + \mathrm{Ce(III)} + \mathrm{H^+} \tag{2}$$

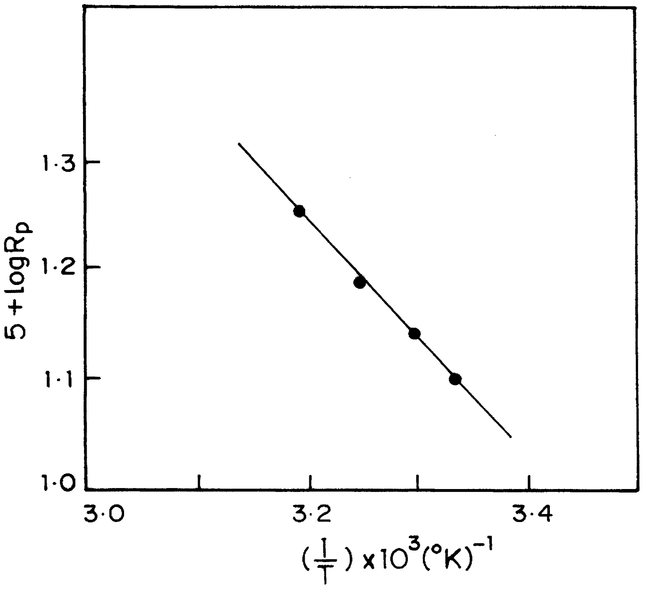

Fig. 6 Determination of overall energy of activation (Table 1). [Ce(IV)] = 0.003M, [EA] = 0.0992M, [MEK] = 0.2978M, [H_2SO_4] = 0.1M

Initiation

$$R^{\cdot} + M \xrightarrow{k_i} R\text{-}M^{\cdot} \tag{3}$$

Propagation

$$R\text{-}M^{\cdot} + M \xrightarrow{k_p} R\text{-}M\text{-}M^{\cdot} \tag{4}$$

$$M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_p} M_{n+1}^{\cdot} \tag{5}$$

Bimolecular termination

$$M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_t} \text{Polymer} \tag{6}$$

Monomolecular termination with Ce(IV) (linear termination)

$$M_n^{\cdot} + \mathrm{Ce(IV)} \xrightarrow{k_t^1} \text{polymer} + \mathrm{Ce(III)} + \mathrm{H^+} \tag{7}$$

A possible alternative to Eq. 2

$$R^{\cdot} + \mathrm{Ce(III)} \longrightarrow R^{-} + \mathrm{Ce(IV)} \tag{8}$$

Equation 8 may arise especially from a consideration of products of Eq. (1) still in the solvent cage, which means competition for $R^{\cdot}$ between Ce(IV) and Ce(III). Occurrence of such a step would mean a decrease in the rate of ceric ion disappearance with time.

Making the usual assumptions for the steady-state concentrations of free radicals (primary and chain) and with the rate constants being independent of chain length, and considering only the mutual type of termination as effective under our experimental conditions, the following equations for R_{Ce} and R_{p} are derived:

$$R_{\mathrm{Ce}} = \frac{-\mathrm{d}[\mathrm{Ce(IV)}]}{\mathrm{d}t} = k_r[\mathrm{Ce(IV)}][R] \tag{9}$$

$$R_p = \frac{-\mathrm{d}[M]}{\mathrm{d}t} = \frac{k_p[M]^{3/2}}{k_t^{1/2}} \left\{ \frac{k_i k_r [R][\mathrm{Ce(IV)}]}{k_i[M] + k_o[\mathrm{Ce(IV)}]} \right\}^{1/2} \tag{10}$$

Under present experimental conditions, if the condition $k_i[M] \gg k_o[\mathrm{Ce(IV)}]$ obeys, then the Eq. (10) reduces to

$$R_p = k_p (k_r/k_t)^{1/2} [\mathrm{Ce(IV)}]^{1/2} [R]^{1/2} [M] \tag{11}$$

And if the condition $k_o[\mathrm{Ce(IV)}] \gg k_i[\mathrm{M}]$ obeys, the Eq. (10) reduces to

$$R_p = \left(k_p/k_t^{1/2}\right)(k_i/k_o)^{1/2}k_r^{1/2}[R]^{1/2}[M]^{3/2} \tag{12}$$

Molecular weight increases with the progress of polymerization and falls at higher conversions after 55.9% (Table 1). The polymerization of EA in aqueous medium initially follows homogeneous polymerization kinetics, situated in the aqueous medium; then, emulsion polymerization kinetics for some period of time in the intermediate stage in the charge-stabilized discrete particles dispersed in the aqueous phase, where the monomer is soluble in the polymer, and finally a pseudo-homogeneous-type reaction situated in the insoluble phase, with coarse particles. This type of kinetics can show an effect on the molecular weight of the polymer formed, which varies with conversion [28].

The degree of polymerization can be expressed by the following Eq. (13)

$$\overline{\mathrm{DP}} = \frac{R_p}{\sum R_t} = \frac{k_p[M]}{k_t[M_n^{\cdot}] + k_t^1[\mathrm{Ce(IV)}]} \tag{13}$$

where $k_t{}^1$ is the rate constant for linear termination of growing chain with ceric species.

The increase of molecular weight with conversion seems to be related with the loci of polymerization [28]. In the initial stages of homogeneous polymerization in aqueous medium, the termination rate between two oligomeric radicals is higher, which results in lower molecular weight polymer particles. During the intermediate stage when most of the monomer shifts to charge-stabilized discrete particles dispersed in the aqueous phase because of the solubility of the monomer in the polymer, sol phase polymerization occurs in these particles where bimolecular termination is slower due to the unavailability of a second radical within each particle and also due to the gel effect [32] and hence, the molecular size of the polymer particles is larger. At higher conversions in coarse precipitated polymer particles to which most of the monomer is shifted are large enough to permit the coexistence of more than one polymer radical within them and hence, the termination rate can be higher to cause the reduction in molecular size. Depletion of monomer and initiator concentrations together with bimolecular termination all influence the degree of polymerization at higher conversions (Eq. 13).

Evaluation of rate constants

In the present study, $R_{\mathrm{Ce}} = k_r[\mathrm{Ce(IV)}][\mathrm{MEK}]^{0.5}$. By plotting R_{Ce} versus [Ce(IV)], we can obtain $k_r[\mathrm{MEK}]^{0.5}$ as the slope from which k_r is evaluated (Fig. 7; Table 2). When there is a dependence of $R_p$on [Ce(IV)], Eq. (10) can be rearranged in the following form:

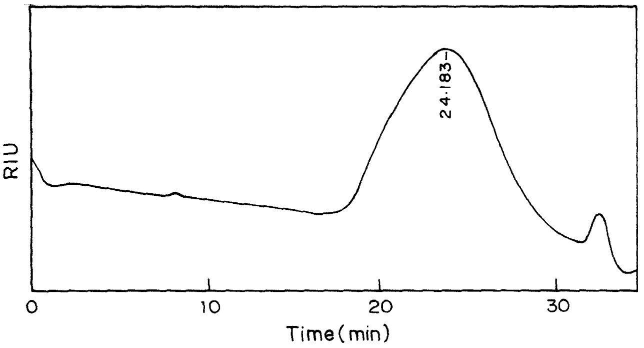

Fig. 7 GPC analysis for the determination of molecular weight

Table 2 Rate constants for the polymerization of EA at 30 °C

Initiator system	k_rx10^3 (S^{-1})	k_i/k_o ($l^{1/2}$ $mol^{-1/2}$ $S^{-1/2}$)	$k_p/k_t{}^{1/2}$
Ce(IV)–MEK	0.8750	1.3856	1.6706

$$\frac{[M]^2}{R_p^2} = \frac{k_t}{k_p^2 k_r[\mathrm{MEK}][\mathrm{Ce(IV)}]} + \frac{k_t k_o}{k_p^2 k_i k_r[\mathrm{MEK}][M]} \tag{14}$$

and by plotting $[\mathrm{M}]^2/R_p{}^2$ versus 1/[Ce(IV)], the rate constants ratios (k_i/k_o) and ($k_p/k_t{}^{1/2}$) can be evaluated (Fig. 8; Table 2). The values of rate constants for EA polymerization by using Ce(IV)–MEK as the initiator are comparable with the values already reported [10, 28 and 33].

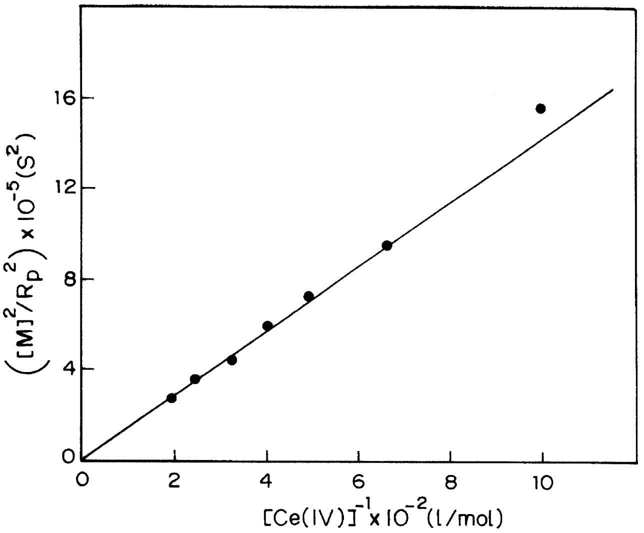

Fig. 8 Determination of rate constants ratios. [EA] = 0.0992M, [MEK] = 0.2978M, $[H_2SO_4]$ = 0.1M, T = 30 °C

Conclusions

The rate of ceric ion consumption shows first-order dependence on Ce(IV) and 0.5-order dependence on reducing agent concentration. The absence of complex formation between Ce(IV) and reducing agent is observed. The rate of EA polymerization shows 0.5 order dependences on Ce(IV) and MEK concentrations and higher order (1.4) dependence on monomer concentration. The higher order with respect to monomer concentration may be due to the simultaneous occurrence of linear termination as well as bimolecular termination. The molecular weight variation with percent conversion shows dependence on loci of polymerization. Initially, homogeneous polymerization takes place in the aqueous phase; in the next stage, polymerization occurs in charge stabilized discrete particles similar to emulsion polymerization; and finally, pseudohomogeneous-type polymerization takes place in coarse suspension. This type of polymerization can bring a change in molecular weight with percent conversion. The overall energy of activation under present experimental conditions in the temperature region 27–40 °C is in accordance with the literature values.

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