

Kinetic Study of the Polymerization of Ethyl Acrylate in an Aqueous Nitric Acid Medium

G. V. Ramana Reddy,¹ J. Arun,² Jayakishore Panda²

¹Polymer Division, Central Leather Research Institute, Adyar, Chennai 600 020, India

²Department of Chemistry, Madras Christian College, Tambaram, Chennai 600 059, India

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ABSTRACT: A kinetic study of the aqueous polymerization of ethyl acrylate (EA) was carried out at 30°C in a dilute nitric acid medium with ammonium ceric nitrate (ACN)-*n*-propanol (*n*PA) and ACN-ethanol as redox initiator systems. The ceric-ion consumption was first-order with respect to the ceric-ion concentration with both initiator systems. The formation of complexes between Ce(IV) and reducing agents was observed. The orders with respect to the Ce(IV), reducing agents, and monomer were evaluated for aqueous polymerizations of EA initiated by Ce(IV)-*n*PA and Ce(IV)-

ethanol redox initiator systems. The overall activation energy for the aqueous polymerization of EA was evaluated in the temperature region of 27–40°C with both initiator systems. A kinetic mechanism for the aqueous polymerization of EA initiated by redox initiator systems is presented. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 218–224, 2006

Key words: activation energy; ESR/EPR; gel permeation chromatography (GPC); kinetics (polym.); UV-vis spectroscopy

INTRODUCTION

Ceric salts show high reactivity in aqueous media and have been used either alone¹ or in combination with reducing agents² as initiators of vinyl polymerization. The oxidation of some of the organic substrates by Ce(IV) is believed to occur by the direct attack of the ceric species on the substrate, appearing to proceed by electron abstraction^{3,4}, whereas in other substrates, the reaction goes through an intermediate complex.^{5–7} Ammonium ceric nitrate (ACN) gives more intense colors with hydroxy compounds than ceric sulfate, mostly because of a complex formation, and with the subsequent liberation of free radicals by the decomposition of the complex. This article describes the study of the kinetics of polymerization of ethyl acrylate (EA) at 30°C in an aqueous nitric acid medium by the use of ACN with *n*-propanol (*n*PA) and ACN with ethanol as redox initiator systems.

EXPERIMENTAL

The monomer EA (Laboratory reagent; Central Drug House Pvt., Ltd., Mumbai, India) was purified by being washed with 5% sodium hydroxide followed by distilled water. The washed monomer was further

purified by vacuum distillation under a nitrogen atmosphere.

*n*PA (Laboratory reagent; Ranbaxy Laboratories, Ltd., S.A.S. Nagar, India), absolute alcohol (analytical reagent, quality ethyl alcohol; Hayman, Ltd., Eastways Park, England), a ferroin solution (analytical reagent; S. D. Fine Chemical Pvt. Ltd., Boisar, India), methanol (analytical reagent; Ranbaxy Laboratories), ACN (analytical reagent; S. D. Fine Chemical), and ammonium ferrous sulfate (AFS; analytical reagent; S. D. Fine Chemical) were used as supplied without further purification.

Tetrahydrofuran (THF; analytical reagent; S. D. Fine Chemical), used for gel permeation chromatography experiments, was purified by distillation over ferrous sulfate.

RESULTS

The aqueous polymerization of EA was carried out in 0.2M nitric acid at 30°C under an inert atmosphere with the redox initiator systems Ce(IV)-*n*PA and Ce(IV)-ethanol. To an aqueous solution (27 mL) of EA and a reducing agent under an inert atmosphere, a solution (3 mL) of ACN in 2M nitric acid was added, and the reaction was carried out at 30°C.

The ceric-ion concentration in the reaction medium at different time intervals was estimated by titration with an AFS solution and with ferroin as an indicator. The rate of ceric-ion consumption (R_{Ce}) was determined from the initial slope of the plot of the consumption percentage of Ce(IV) versus time. The order

Correspondence to: G. V. Ramana Reddy (gvrr2004@yahoo.com).

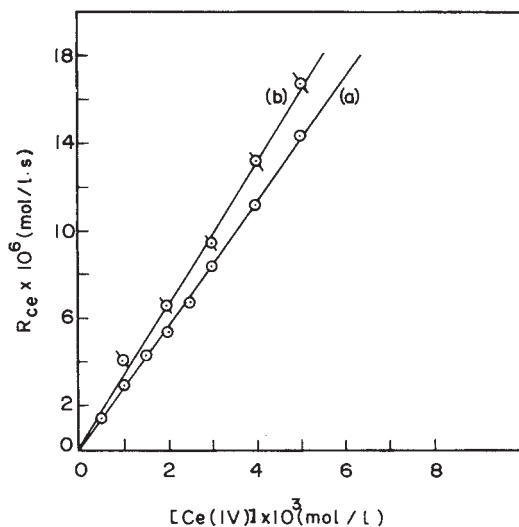


Figure 1 R_{Ce} versus $[Ce(IV)]$ $\{[EA] = 0.0992M, [nPA] = 0.2982M, [ethanol] = 0.3038M, [HNO_3] = 0.2M, \text{temperature} = 30^\circ C\}$: (a) Ce(IV)-*n*PA initiator system and (b) Ce(IV)-ethanol initiator system.

with respect to the Ce(IV) concentration for the reduction of the ceric ion was studied by the variation of the Ce(IV) concentration in the reaction medium in the range of $0.5\text{--}5.0 \times 10^{-3} \text{ mol L}^{-1}$, with all other variables in the reaction medium kept constant. The dependence of R_{Ce} on the reducing agent concentration ($[R]$) was also studied by the variation of $[R]$ in the range of $0.048\text{--}0.601 \text{ mol L}^{-1}$ while all other parameters in the reaction medium were kept constant.

No induction period was observed for the reaction between the ceric ion and reducing agent. The dependence of R_{Ce} on $[Ce(IV)]$ was first-order under these experimental conditions for both initiator systems employed (Fig. 1). The pseudo-first-order rate constant (k^1) for ceric-ion consumption was evaluated from the slope of the plot of $\log [Ce(IV)]$ versus time. The plots of the inverse of the pseudo-first-order rate constants $[(k^1)^{-1}]$ versus the reciprocal of the reducing agent concentration ($[R]^{-1}$) yielded straight lines with positive intercepts on the ordinate for both initiator systems, Ce(IV)-*n*PA and Ce(IV)-ethanol (Fig. 2).

The spectroscopic studies were performed with a Varian Cary 50 Bio UV-vis spectrophotometer and showed shifts in the absorption maximum of a ceric-ion solution in $0.2M$ nitric acid from 246 to 248 and 239 nm when the reducing agents *n*PA and ethanol, respectively, were added. When the monomer was also added with the reducing agent to a ceric solution in a nitric acid medium, the shifts in the absorption maxima were changed to 256 and 249 nm with *n*PA and ethanol, respectively, as the reducing agents in the reaction medium (Fig. 3). Electron paramagnetic resonance (EPR) spectral analysis was carried out with a Bruker EMX 10/2.7 EPR spectrometer (Germany), and

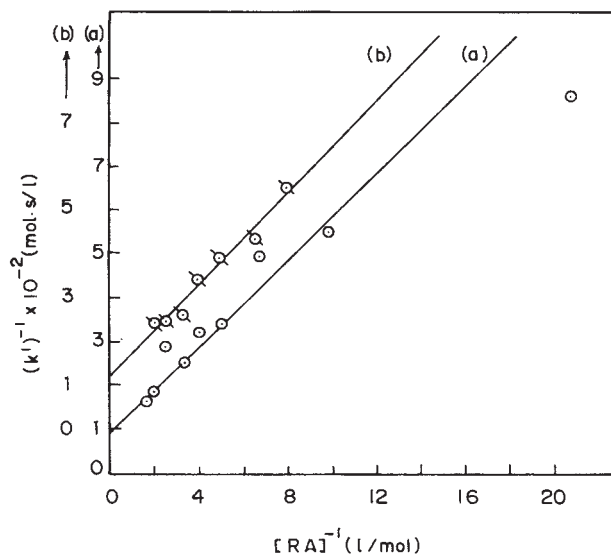


Figure 2 $(k^1)^{-1}$ versus $[RA]^{-1}$ $\{[Ce(IV)] = 0.003M, [EA] = 0.0992M, [HNO_3] = 0.2M, \text{temperature} = 30^\circ C\}$: (a) Ce(IV)-*n*PA initiator system and (b) Ce(IV)-ethanol initiator system.

these EPR spectra showed weak signals at 3460G, indicating the presence of free radicals in the reaction medium with both initiator systems. The hyperfine

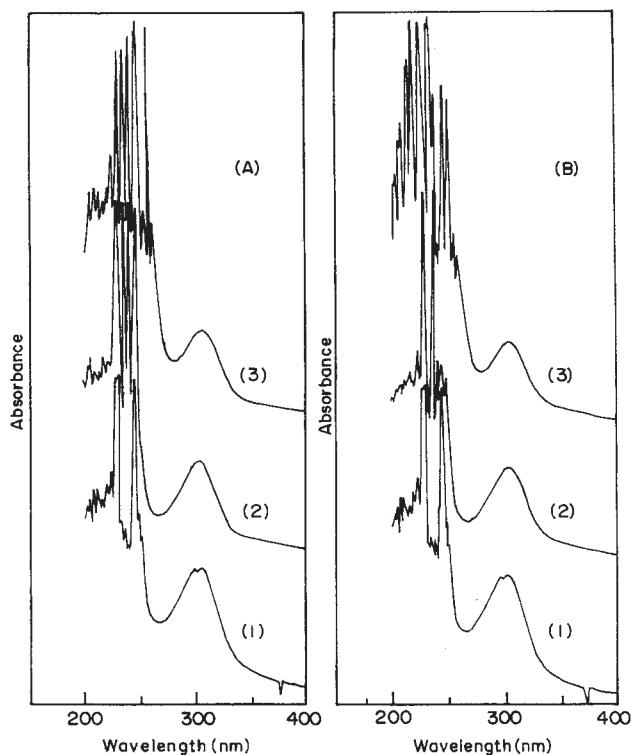


Figure 3 UV-vis absorption spectra of ACN in $0.2M$ HNO_3 : (A-1) ACN, (A-2) ACN with *n*PA, (A-3) ACN with *n*PA and EA, (B-1) ACN, (B-2) ACN with ethanol, and (B-3) ACN with ethanol and EA. The reference solution is water.

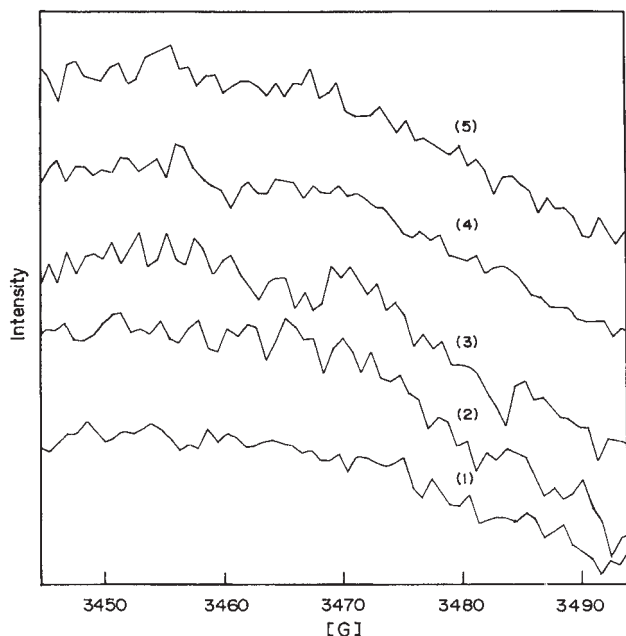


Figure 4 Hyperfine structures of EPR spectra of ACN in 0.2M HNO_3 : (1) ACN, (2) ACN with *n*PA, (3) ACN with ethanol, (4) ACN with *n*PA and EA, and (5) ACN with ethanol and EA.

structures of the EPR spectra showed satellite peaks produced by different types of free radicals in the reaction media (Fig. 4).

Induction periods were observed with all the polymerization reactions, and they varied inversely with the rate of initiation. The polymerization of EA in this study was followed by gravimetry. The rate of polymerization (R_p) of EA in a 0.2M nitric acid medium at 30°C under an inert atmosphere with the redox initiators Ce(IV)-*n*PA and Ce(IV)-ethanol was evaluated from the initial slope of plots of the conversion percentage versus time. Higher R_p 's were observed with the Ce(IV)-*n*PA initiator system in comparison with the Ce(IV)-ethanol initiator system under similar reaction conditions (Figs. 5–8 and Table I). The orders with respect to [Ce(IV)] for EA polymerization were evaluated as the slopes from logarithmic graphs of R_p versus [Ce(IV)] (Fig. 5). The orders with respect to [Ce(IV)] for EA polymerization under these experimental conditions were 0.48 and 0.55 when Ce(IV)-*n*PA and Ce(IV)-ethanol, respectively, were employed as initiators in the reaction medium (Fig. 5).

The orders with respect to [R] for EA polymerization under the experimental conditions were evaluated from the slopes of logarithmic plots of R_p versus [R] and were found to be 0.37 and 0.5 for the Ce(IV)-*n*PA and Ce(IV)-ethanol initiator systems, respectively, in the reaction medium (Fig. 5). The orders with respect to [EA] under these experimental conditions were 1.81 and 1.54 when Ce(IV)-*n*PA and Ce(IV)-ethanol, respectively, were employed as initiators (Fig. 6).

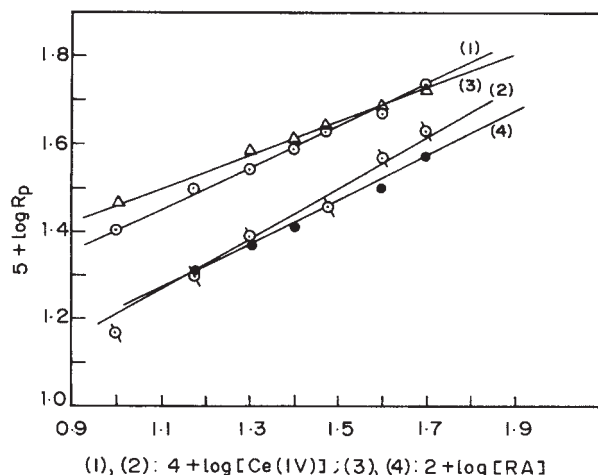


Figure 5 $\log R_p$ versus $\log [\text{Ce(IV)}]$ and $\log R_p$ versus $\log [\text{RA}]$ {[EA] = 0.0992M, [HNO₃] = 0.2M, temperature = 30°C}: (1) [*n*PA] = 0.2982M, (2) [ethanol] = 0.3038M, (3) *n*PA as a reducing agent and [Ce(IV)] = 0.003M, and (4) ethanol as a reducing agent and [Ce(IV)] = 0.003M.

The values of the overall activation energy (E_{overall}) for EA polymerization under these experimental conditions were evaluated from Arrhenius plots of $\log R_p$ versus the reciprocal of the temperature ($1/T$) in the temperature region of 27–40°C with Ce(IV)-*n*PA and Ce(IV)-ethanol as the initiator systems and were found to be 16.75 and 24.51 kJ mol⁻¹, respectively (Table I and Figs. 7 and 8).

The variation of the number-average molecular weight (\bar{M}_n) of the polymer formed at different conversions was determined by gel permeation chromatography (Waters, United States) with THF as an

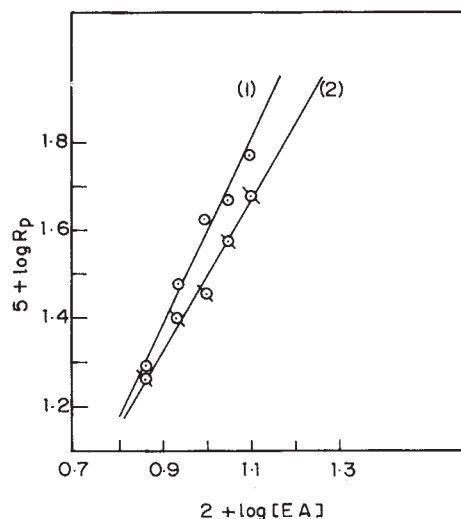


Figure 6 $\log R_p$ versus $\log [\text{EA}]$ {[Ce(IV)] = 0.003M, [*n*PA] = 0.2982M, [ethanol] = 0.3038M, [HNO₃] = 0.2M, temperature = 30°C}: (1) Ce(IV)-*n*PA initiator system and (2) Ce(IV)-ethanol initiator system.

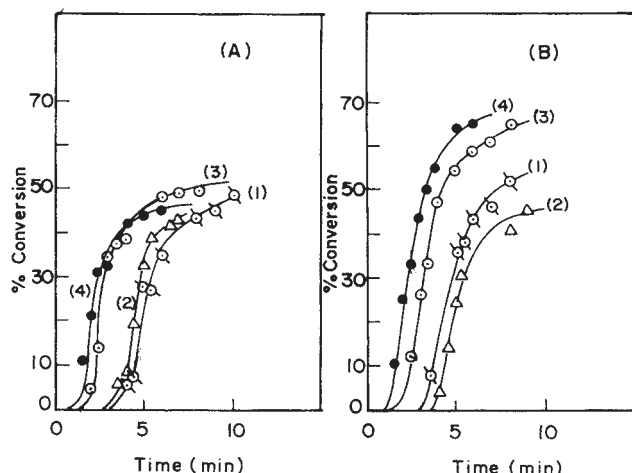


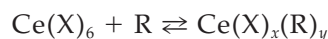
Figure 7 Conversion versus the time $\{[Ce(IV)] = 0.003M, [nPA] = 0.2982M, [ethanol] = 0.3038M, [EA] = 0.0992M, [HNO_3] = 0.2M, \text{temperature} = (1) 27, (2) 30, (3) 35, \text{and} (4) 40^\circ C\}$: (A) *n*PA as a reducing agent and (B) ethanol as a reducing agent.

eluent (Table I and Fig. 9). Higher molecular weights were obtained with the Ce(IV)-*n*PA initiator system in comparison with the Ce(IV)-ethanol initiator system (Table I).

DISCUSSION

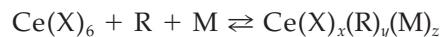
Spectrophotometric observations indicate that both the reducing agents and monomer complexed with the ceric species in the nitric acid medium as there were shifts in the absorption maxima when the monomer was added to solutions of the ceric ion and reducing agent in nitric acid media (Fig. 3). Plots of $(k^1)^{-1}$ versus $[R]^{-1}$ (Fig. 2) indicate the formation of complexes between the ceric ion and reducing agents, and the complex formation between the ceric ion and reducing agent might be maximum in comparison with the monomer liganding with the ceric ion.^{8,9}

Because the tetravalent cerium is known to have a coordination number of six, the reaction between cerate and the reducing agent (R) presents the possibility of the formation of coordination intermediates as indicated:



X represents groups coordinated with tetravalent cerium in a nitric acid solution, which may be OH^- , NO_3^- , and/or H_2O . x lies between 0 and 6, and y lies between 0 and 6.

When the monomer (M) is also complexing with cerate along with the reducing agent in the reaction medium, the coordinate intermediates can be presented by an equilibrium reaction:



where x lies between 0 and 6, y lies between 0 and 6, and z may be a small fraction lying between 0 and 1.

EPR spectra showed weak signals by free radicals at 3460G. The hyperfine structures of EPR spectra showed satellite peaks due to the coexistence of different types of free radicals in the reaction media (Fig. 4). There were variations in the hyperfine structures of EPR spectra obtained by the primary radicals formed by reducing agents, the radicals formed by the monomer, and the radicals on the growing polymer chains (Fig. 4).

The orders with respect to $[Ce(IV)]$ for the aqueous polymerization of EA were 0.48 and 0.55 when Ce(IV)-*n*PA and Ce(IV)-ethanol, respectively, were employed as initiators (Fig. 5). The higher exponent for the ceric-ion concentration when ethanol was employed as a reducing agent shows as confusing a picture as that of the dependence on the monomer concentration.⁹

The variation of R_p with $[R]$ showed a 0.37-order dependence for the Ce(IV)-*n*PA initiator system and a 0.5-order dependence for the Ce(IV)-ethanol initiator system in this study (Fig. 5). This reduced order with respect to $[nPA]$ for EA polymerization under the experimental conditions could be due to a higher oxidative termination rate of primary radicals by Ce(IV) with the Ce(IV)-*n*PA initiator system.

The orders with respect to $[EA]$ were 1.81 and 1.54 when Ce(IV)-*n*PA and Ce(IV)-ethanol, respectively, were employed as initiators (Fig. 6). The higher order dependence of $[EA]$ supports the linear termination (monomolecular termination with ceric species) of the growing chains as well as bimolecular termination of the growing chains.¹⁰ The higher order with respect to

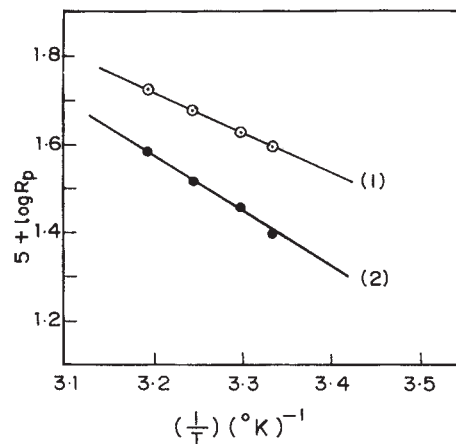


Figure 8 $\log R_p$ versus $1/T$ $\{[Ce(IV)] = 0.003M, [EA] = 0.0992M, [nPA] = 0.2982M, [ethanol] = 0.3038M, [HNO_3] = 0.2M\}$: (1) Ce(IV)-*n*PA initiator system and (2) Ce(IV)-ethanol initiator system.

TABLE I
Determination of E_{overall} and Molecular Weight with Conversion

Temperature (K)	Ce(IV)- <i>n</i> PA initiator system $R_p \times 10^4$ (mol/L/s) ^a	Ce(IV)-ethanol initiator system $R_p \times 10^4$ (mol/L/s) ^b	Ce(IV)- <i>n</i> PA initiator system		Ce(IV)-ethanol initiator system	
			Conversion (%)	$\bar{M}_n \times 10^{-4}$	Conversion (%)	$\bar{M}_n \times 10^{-4}$
300	3.9696	2.5141	34.7	1.232	25.7	1.314
303	4.2342	2.8449	37.3	2.860	33.1	1.409
308	4.7635	3.3080	38.0	2.984	47.0	1.843
313	5.2928	3.8042	38.3	4.442	54.4	1.870
			48.4	2.650	59.2	1.469
			48.9	2.323	60.5	1.460
			49.0	2.521	65.0	1.389

^a $E_{\text{overall}} = 16.75$ kJ/mol.

^b $E_{\text{overall}} = 24.51$ kJ/mol.

[EA] gives support to the complex nature of the initiation reactions involving monomer molecules as participating reactants to generate initiating free radicals.⁸

The E_{overall} values for EA polymerization were 16.75 and 24.51 kJ/mol when Ce(IV)-*n*PA and Ce(IV)-ethanol, respectively, were employed as initiators (Table I and Figs. 7 and 8). These were of the same order as those found in other aqueous polymerization systems.¹¹⁻¹³

The experimental results indicate that the aqueous polymerization of EA under the experimental conditions used, during the early stages of the reaction, obey homogeneous free-radical polymerization kinetics. The following reaction scheme explains satisfactorily the kinetic results obtained. For primary radical formation:

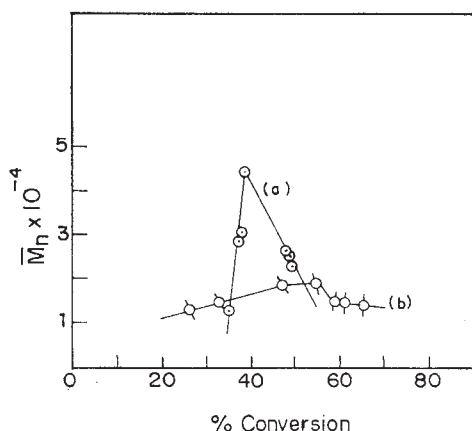
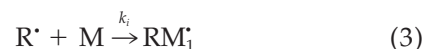
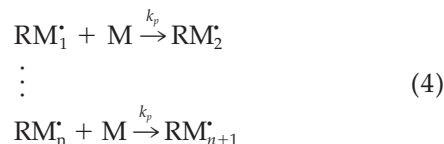


Figure 9 Molecular weight versus the conversion ([Ce(IV)] = 0.003M, [EA] = 0.0992M, [HNO₃] = 0.2M, temperature = 35°C): (a) [nPA] = 0.2982M and (b) [ethanol] = 0.3038M.

For initiation



For propagation



For bimolecular termination



For monomolecular termination with Ce(IV) (linear termination)



For oxidative termination of primary radicals



where $\text{R} \cdot$ is a primary radical, RM_n^* is a growing primary radical, k_t^1 is the rate constant for linear termination of growing chains with ceric species, k is the equilibrium rate constant for the formation of complex between R and Ce(IV) , k_d , k_i , k_p , k_t and k_0 are the rate constants for the decomposition of the complex, initiation of monomer, propagation of growing chains, bimolecular termination of growing chains and oxidative termination of the primary radical by Ce(IV) , respectively. By applying the steady-state principle to the active intermediates $\text{R} \cdot$ and RM_n^* , and by considering only the mutual type of termination as effec-

TABLE II
Rate Constants for the Polymerization of EA by Ce(IV)–Reducing Agent Initiator Systems at 30°C

Initiator system	K (L mol)	(k_i/k_0)	$k_d \times 10^2$ (s ⁻¹)	($k_n/k_t^{1/2}$) (1 ^{1/2} mol ^{-1/2} s ^{-1/2})
Ce(IV)– <i>n</i> PA initiator system	1.800	1.111	0.117	1.343
Ce(IV)–ethanol initiator system	2.240	0.833	0.218	0.903

tive under our experimental conditions, we derived the following equations for R_p and R_{Ce} .¹¹

$$R_p = \frac{-d[M]}{dt} = \frac{k_p}{k_t^{1/2}} \left\{ \frac{k_i k_d K [R] [Ce(IV)]_{eq}}{k_i [M] + k_0 [Ce(IV)]_{eq}} \right\}^{1/2} [M]^{3/2} \quad (8)$$

$$R_{Ce} = \frac{-d[Ce(IV)]}{dt} = k_d K [R] [Ce(IV)]_{eq} \left\{ 1 + \frac{k_0 [Ce(IV)]_{eq}}{k_i [M] + k_0 [Ce(IV)]_{eq}} \right\} \quad (9)$$

In this experimental situation, if the condition $k_i [M] \gg k_0 [Ce(IV)]_{eq}$ is obeyed, then eqs.(8) and (9) can be reduced to

$$R_p = \frac{-d[M]}{dt} = k_p \left(\frac{k_d K}{k_t} \right)^{1/2} [R]^{1/2} [Ce(IV)]_{eq}^{1/2} [M] \quad (10)$$

$$R_{Ce} = \frac{-d[Ce(IV)]}{dt} = k_d K [R] [Ce(IV)]_{eq} \quad (11)$$

Because the measured rate $-d[Ce(IV)]/dt$ applies to total $[Ce(IV)]$, and because $[Ce(IV)]_T = [Ce(IV)]_{eq}(1 + K[R])$, we can obtain

$$R_p = \frac{-d[M]}{dt} = (k_p/k_t^{1/2})(k_d K)^{1/2} \left\{ \frac{[R]^{1/2} [Ce(IV)]_T^{1/2}}{(1 + K[R])^{1/2}} \right\} [M] \quad (12)$$

$$R_{Ce} = \frac{-d[Ce(IV)]}{dt} = k_d K \left\{ \frac{[R] [Ce(IV)]_T}{(1 + K[R])} \right\} \quad (13)$$

On the other hand, if under these experimental conditions the situation is $k_0 [Ce(IV)]_{eq} \gg k_i [M]$, then eqs. (8) and (9) can be reduced to

$$R_p = (k_p/k_t^{1/2})(k_i/k_0)^{1/2}(k_d K)^{1/2} [R]^{1/2} [M]^{3/2} \quad (14)$$

$$R_{Ce} = \frac{2k_d K [R] [Ce(IV)]_T}{(1 + K[R])} \quad (15)$$

The variation in the molecular weight with the conversion percentage was observed with both initiator systems in this study (Table I and Fig. 9). This may be

due to the fact that the polymerization of EA in an aqueous medium initially follows homogeneous polymerization kinetics, then follows emulsion polymerization kinetics for some period in the intermediate stage when the charge-stabilized small particles are dispersed in the aqueous phase in which the monomer is soluble in the polymer and is transferred into these particles, and finally reaches a pseudo-homogeneous-type reaction in which EA is situated in the insoluble phase, coarse particles. Such kinetics can have an effect on the molecular weight of the polymer formed, which varies with the conversion.¹¹

The degree of polymerization (DP) can be expressed as follows:

$$\overline{DP} = \frac{R_p}{\sum R_i} = \frac{k_p [M]}{k_i [M_n] + k_t [Ce(IV)]} \quad (16)$$

The increase in the molecular weight with the conversion seems to be related to the loci of polymerization. In the initial stages of homogeneous polymerization in an aqueous medium, the termination rate between two oligomeric radicals is higher, and this 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, in which bimolecular termination is slower because of the unavailability of a second radical within each particle and also because of the gel effect,¹⁴ and hence the molecular size of the polymer particles is larger. At higher conversions, coarse, precipitated polymer particles, to which most of the monomer is shifted, are big enough to permit the coexistence of more than one polymer radical within them, and hence the termination rate can be higher and cause a reduction in the molecular size. The depletion of the monomer and initiator concentrations and bimolecular termination all influence \overline{DP} at higher conversions [eq. (16)].

The molecular weights of the EA polymer obtained with the Ce(IV)–*n*PA initiator system were higher than the molecular weights obtained with the Ce(IV)–ethanol initiator system (Table I and Fig. 9). This might be due to the higher termination rate of the growing chains with Ce(IV)–ethanol as the initiator system [eq. (16); Table II].

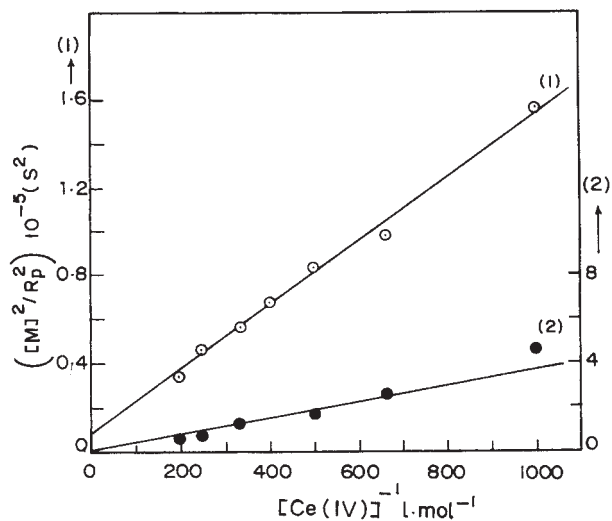


Figure 10 $[M]^2/R_p^2$ versus $[Ce(IV)]^{-1}$ $\{[EA] = 0.0992M, [HNO_3] = 0.2M, \text{temperature} = 30^\circ\text{C}\}$: (a) $[nPA] = 0.2982M$ and (b) $[\text{ethanol}] = 0.3038M$.

Evaluation of the rate constants

In this study, k_d and K were obtained¹¹ from the following relationship:

$$1/k^1 = 1/(k_d K[R]) + 1/k_d \quad (17)$$

The values are reported in Table II (Fig. 2).

When there is a dependence of R_p on $[Ce(IV)]$, the following equation can be used to evaluate the rate constants ratios,¹² k_i/k_0 and $k_p/k_t^{1/2}$:

$$\frac{[M]^2}{R_p^2} = \left(\frac{k_t}{k_p^2}\right) \left\{ \frac{1}{k_d K[R]} + \frac{1}{k_d} \right\} \frac{1}{[Ce(IV)]_T} + \left(\frac{k_t}{k_p^2}\right) \left\{ \frac{k_0}{k_i k_d K[R][M]} \right\} \quad (18)$$

The obtained values are reported in Table II (Fig. 10), and they are comparable to the literature results.^{12,13,15}

CONCLUSIONS

The reduction of the ceric ion showed a first order with both initiator systems. The spectrophotometric observations showed that the monomer also complexed with the ceric ion along with the reducing agent with both initiator systems. The plots of $(k^1)^{-1}$ versus $[R]^{-1}$ yielded straight lines with positive intercepts on the ordinate, which supported the maximum complex formation of the reducing agent with the ceric ion for both initiator systems. There were changes in the hyperfine structures of EPR spectra when the monomer was added to solutions of the ceric ion and reducing agent in a nitric acid medium with both initiator systems. A higher order with respect to the monomer concentration with both initiator systems supported the proposal of linear termination of the growing chains as well as bimolecular termination of the growing chains. The obtained E_{overall} values were comparable to literature results.

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