Vinyl Polymerization Initiated by Ceric Ion-Ethyl Cellosolve Redox System in Aqueous Nitric Acid

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VINYL POLYMERIZATION INITIATED BY CERIC ION–ETHYL CELLOSOLVE REDOX SYSTEM IN AQUEOUS NITRIC ACID

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ABSTRACT

Polymerizations of methyl methacrylate (MMA) and acrylonitrile (AN) were carried out in aqueous nitric acid at 30°C with the redox initiator system ammonium ceric nitrate–ethyl cellosolve (EC). A short induction period was observed as well as the attainment of a limiting conversion for polymerization reactions. The consumption of ceric ion was first order with respect to Ce(IV) concentration in the concentration range $(0.2–0.4) \times 10^{-2}$ M, and the points at higher and lower concentrations show deviations from a linear fit. The plots of the inverse of pseudo-first-order rate constant for ceric ion consumption, $(k^{1})^{-1}$ vs $[EC]^{-1}$, gave straight lines for both the monomer systems with nonzero intercepts supporting complex formation between Ce(IV) and EC. The rate of polymerization increases regularly with [Ce(IV)] up to 0.003 M, yielding an order of 0.41, then falls to 0.0055 M and again shows a rise at 0.00645 M for MMA polymerization. For AN polymerization, R_p shows a steep rise with [Ce(IV)] up to 0.001 M, and beyond this concentration R_p shows a regular increase with [Ce(IV)], yielding an order of 0.48. In the presence of constant $[NO_3^-]$, MMA and AN polymerizations

yield orders of 0.36 and 0.58 for [Ce(IV)] variation, respectively. The rates of polymerization increased with an increase in EC and monomer concentrations: only at a higher concentration of EC (0.5 M) was a steep fall in R_p observed for both monomer systems. The orders with respect to EC and monomer for MMA polymerization were 0.19 and 1.6, respectively. The orders with respect to EC and monomer for AN polymerization were 0.2 and 1.5, respectively. A kinetic scheme involving oxidation of EC by Ce(IV) via complex formation, whose decomposition gives rise to a primary radical, initiation, propagation, and termination of the polymeric radicals by biomolecular interaction is proposed. An oxidative termination of primary radicals by Ce(IV) is also included.

INTRODUCTION

Many oxidation-reduced reactions produce radicals that can be used to initiate polymerization. Ceric salts show 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 single-electron transfer with the formation of free radicals from the reducing agents [6]. The oxidation of alcohols by Ce(IV) is believed to proceed through the formation of free-radical intermediates. Evidence of complex formation has been obtained in Ce(IV) oxidations of many compounds in perchloric and nitric acid media [7-9]. This paper describes the study of the kinetics of polymerization of methyl methacrylate and acrylonitrile in aqueous nitric acid under nitrogen atmosphere and initiated by the ammonium ceric nitrate–ethyl cellosolve redox pair.

EXPERIMENTAL

Materials

The monomers, methyl methacrylate (LR, G. S. Chemical Testing Lab & Allied Industries, Bombay, India) and acrylonitrile (LR, s.d. fine chem. Ltd., Boisar, India), were purified by washing with 5% sodium hydroxide followed by distilled water. The washed monomers were further purified by vacuum distillation (<25 mmHg) under nitrogen atmosphere. Acetone (LR, Fischer, Madras, India), methanol (LR, Fischer, Madras, India), and ethyl cellosolve (2-ethoxyethanol) (LR, Sarabhai M. Chemicals, Baroda, India) were purified by distillation. N,N'-Dimethylformamide (LR, s.d. fine chem. Ltd., Boisar, India) was purified by vacuum distillation. Ammonium ceric nitrate (ACN) (AR, Loba Chemie, Bombay, India), ammonium ferrous sulfate (AR, s.d. fine chem. Ltd., Boisar, India) and ammonium nitrate [AR, Glaxo Laboratories (India) Ltd., Bombay, India] were used as supplied without further purification.

Methods

The polymerizations were carried out at 30°C in 50 mL reaction tubes (Pyrex) provided with an inlet and an outlet for the passage of nitrogen through the reaction medium. The mixture of monomer and reducing agent in required concentrations

was taken in aqueous solution, and it was deaerated by the passage of pure dry nitrogen through this reaction mixture. The oxidant solution of ammonium ceric nitrate in nitric acid medium was also deaerated before adding it to the reaction mixture in the reaction tube. The polymerization reactions were arrested at different intervals by the addition of a slight excess of ammonium ferrous sulfate to the reaction mixtures in the reaction tubes, and the polymers formed were separated by filtration in sintered crucibles. The filtered polymers were washed thoroughly in the sintered crucibles with distilled water and methanol. The washed polymers were dried to constant weights at 60°C in a vacuum oven, and percent conversions of monomers into polymers at different intervals were calculated from the weights of these dried polymers. The initial rate of polymerization, R_p, was calculated from the initial slope of the plot, % conversion vs time.

Determination of Total Ceric Ion Concentration

The concentrations of total ceric ion in the reactions were determined volumetrically with ammonium ferrous sulfate, using ferrous O-phenanthroline (ferroin) as indicator. To the reaction mixture in the reaction tube was added a known quantity of excess ammonium ferrous sulfate solution to reduce the Ce(IV) in the reaction medium, and the excess ammonium ferrous sulfate was backtitrated with a standard ammonium ceric nitrate solution. The latter was standardized with ammonium ferrous sulfate using ferroin as indicator. The initial rate of ceric ion disappearance, R_{Ce}, was calculated from the initial slope of the plot, % consumption of Ce(IV) vs time.

Molecular Weight Determination

The molecular weights of the purified polymers at different percent conversions were determined by measuring the intrinsic viscosities, $[\eta]$, of them with an Ubbelohde suspended level dilution viscometer in a thermostatic water bath which can regulate the temperature within ±0.01°C. The following Mark–Houwink relationships were employed.

For poly(methyl methacrylate) [10] in acetone at 30°C:

$$[\eta] = 7.7 \times 10^{-5} \overline{M}_w^{0.7}$$

For polyacrylonitrile [11] in dimethylformamide at 30°C:

$$[\eta] = 20.9 \times 10^{-5} \overline{M}_w^{0.75}$$

Detection of Complex Formation

The complex formation between Ce(IV) and the reducing agent was detected by observing the shift in the absorption maximum of Ce(IV) in nitric acid medium using a Beckman spectrophotometer.

RESULTS

Rate of Ceric Ion Disappearance

In the absence of reducing agent there was no polymerization even after longer time periods (60 minutes). The rate of consumption of Ce(IV) in the presence of monomers was larger than the value obtained without monomers in the reaction medium. The pale yellow solution of ammonium ceric nitrate in nitric acid showed the absorption maximum at 367 nm. With the addition of ethyl cellosolve to the above solution, the pale yellow color turned to orange with a shift in the absorption maximum to 390 nm, which is a clear indication of complex formation between Ce(IV) and the reducing agent. The monomers did not bring about a significant change in the absorption maximum of Ce(IV) (Fig. 1).
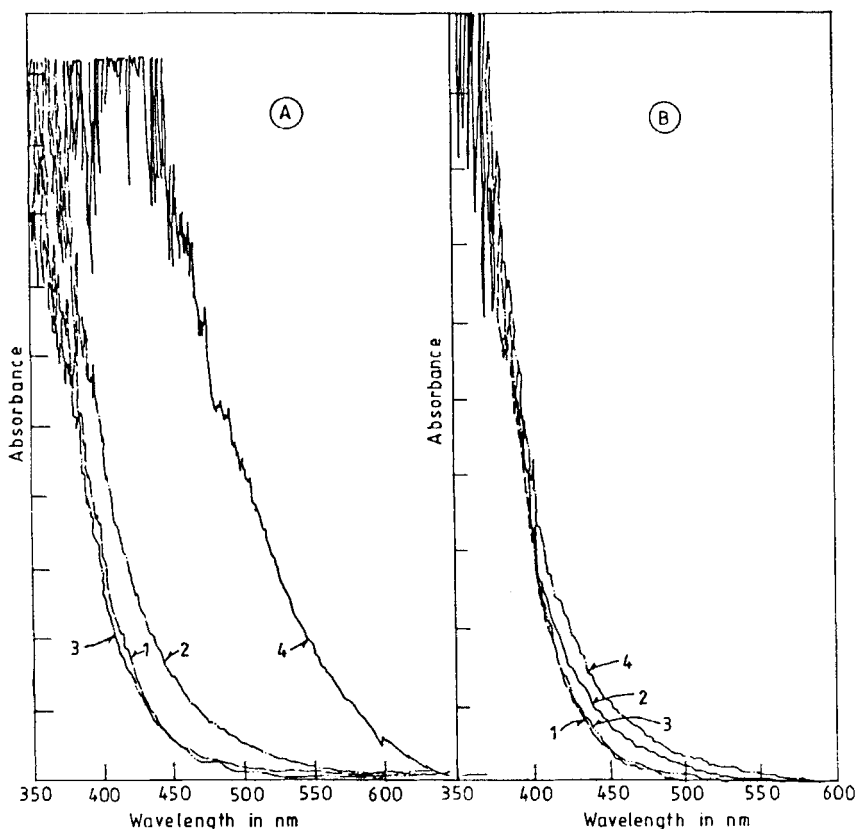

FIG. 1.   UV-Vis absorption spectra of ACN in 0.2 M HNO$_3$. A: (1) ACN in 0.2 M HNO$_3$, (2) ACN with EC in 0.2 M HNO$_3$, (3) ACN with MMA in 0.2 M HNO$_3$, (4) ACN with EC and MMA in 0.2 M HNO$_3$; reference solution is 0.2 M HNO$_3$. B: (1) ACN in 0.2 M HNO$_3$, (2) ACN with EC in 0.2 M HNO$_3$, (3) ACN with AN in 0.2 M HNO$_3$, (4) ACN with EC and AN in 0.2 M HNO$_3$; reference solution is 0.2 M HNO$_3$.

Dependence on Ce(IV)

The rate of ceric ion consumption increased when the Ce(IV) concentration was increased. Figure 2 shows the rate of ceric ion reduction is a first-order reaction with respect to Ce(IV). At higher and lower concentrations the data points deviate from the curves. In the present study the value of R_{Ce} falls when ammonium nitrate is added to maintain constant [NO$_3^-$] in the reaction medium (Fig. 2).

Dependence on EC Concentration

The rate of ceric ion consumption increases with an increase in EC concentration (Figs. 3 and 4). Plots of the inverse of the pseudo-first-order rate constant for ceric ion consumption, $(k')^{-1}$ vs [EC]$^{-1}$ yielded straight lines with nonzero intercepts for both monomer systems (Fig. 5).

Rate of Polymerization

A short induction period was detected, and it showed an inverse dependence on Ce(IV) and EC concentrations. Limiting conversion was attained with the extent of the reaction. Since the consumption of ceric ion was 100% when conversion was maximum, it was concluded that the attainment of maximum conversion was due to exhaustion of the initiator.

Dependence on EC Concentration

The EC concentration was changed from 0.1 to 0.5 M. The maximum conversion increased with an increase in EC concentration up to 0.3 M for MMA polymerization and up to 0.2 M for AN polymerization. However, a decrease in this parame-
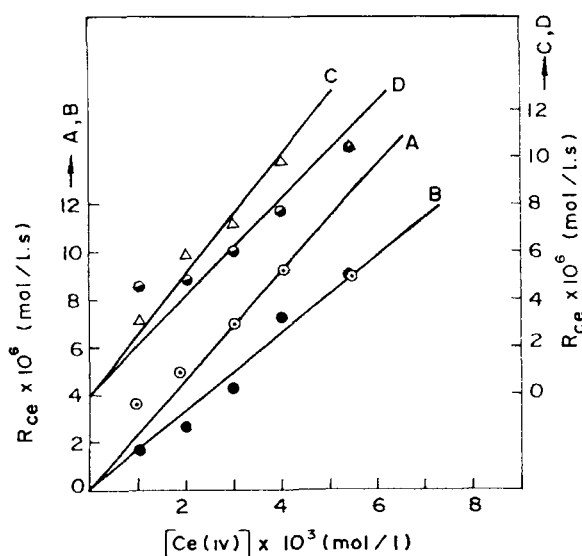

FIG. 2. Verification of first-order reduction of Ce(IV). [EC] = 0.2 M, [HNO$_3$] = 0.2 M, [MMA] = 0.1084 M, [AN] = 0.1748 M, T = 30°C. ($\odot$, ●) MMA, ($\triangle$, $\bigcirc$) AN, (●, $\bigcirc$) [NO$_3^-$] = 0.233 M.

FIG. 3.   Ceric ion consumed vs reaction time at different [EC]. [Ce(IV)] = 0.003 M, [MMA] = 0.1084 M, [HNO$_3$] = 0.2 M, [NO$_3^-$] = 0.233 M, T = 30°C. [EC]: (1) 0.05 M, (2) 0.1 M, (3) 0.2 M, (4) 0.3 M, (5) 0.4 M.
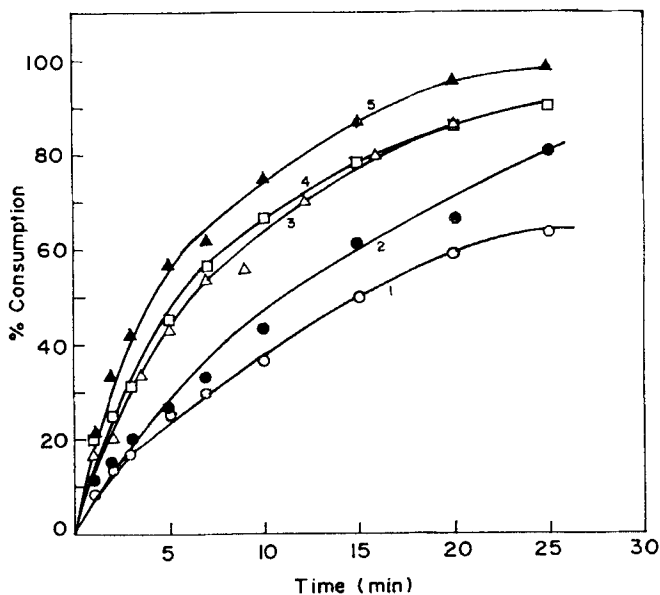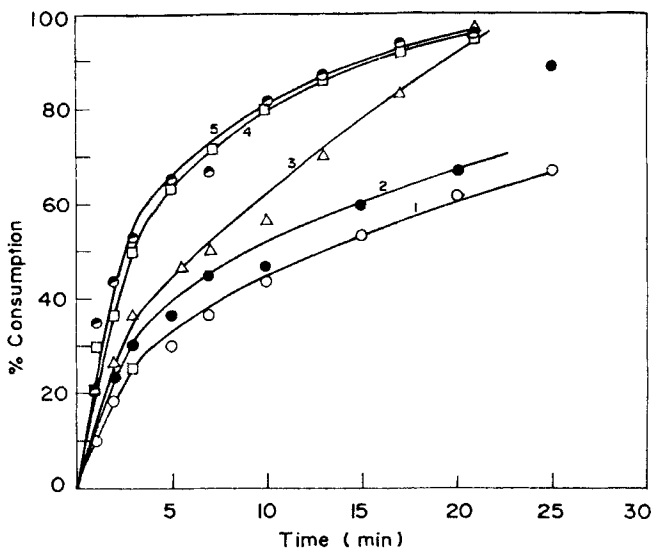

FIG. 4.   Ceric ion consumed vs reaction time at different [EC]. [Ce(IV)] = 0.003 M, [AN] = 0.1748 M, [HNO$_3$] = 0.2 M, [NO$_3^-$] = 0.233 M, T = 30°C. [EC]: (1) 0.05 M, (2) 0.1 M, (3) 0.2 M, (4) 0.3 M, (5) 0.4 M.
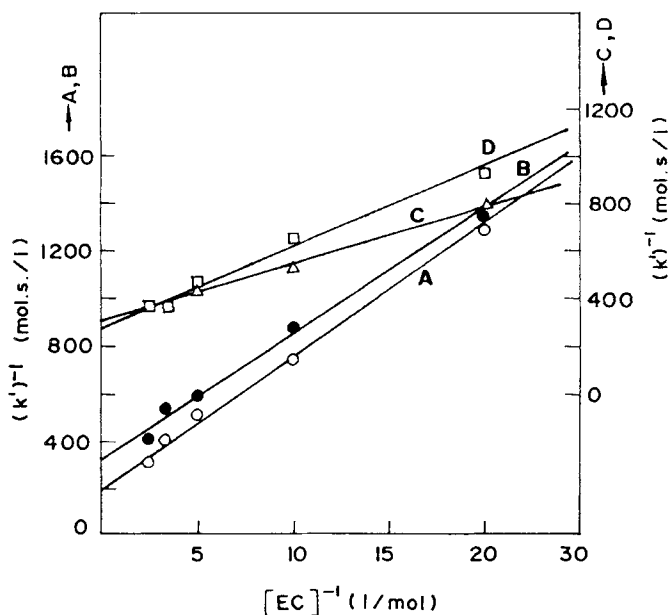
FIG. 5. $(k')^{-1}$ vs [EC]. [Ce(IV)] = 0.003 M, [MMA] = 0.0184 M, [AN] = 0.1748 M, [HNO$_3$] = 0.2 M, T = 30°C. ($\bigcirc$, $\bullet$) MMA, ($\triangle$, $\square$) AN, ($\bullet$, $\square$) [NO$_3^-$] = 0.233 M.

ter with [EC] was observed above these concentrations for both MMA and AN polymerizations. The initial rate of polymerization increased with an increase in EC concentration up to 0.4 M and then fell steeply at higher concentration (0.5 M) for both monomer systems. Similar observations were reported in the literature [12, 13]. The orders with respect to EC for MMA and AN polymerizations were evaluated as slopes from plots of log R_p vs log [EC] and were found to be 0.19 and 0.20, respectively (Fig. 6).

Dependence on Ce(IV) Concentration

The ceric ion concentration was varied in the range (0.5–6.45) × 10^{-3} M whereas all the other parameters for each system remained constant. The same polymerization reactions were also carried out while maintaining [NO$_3^-$] constant in the reaction medium to determine the effect of the constant NO$_3^-$ strength. The initial rate of polymerization increased regularly on increasing Ce(IV) concentration up to 0.003 M for MMA polymerization, then fell up to 0.0055 M, and again rose at 0.00645 M. The initial rate of polymerization increased steeply up to 0.001 M and then showed a "regular" increase with Ce(IV) concentration for AN polymerization. Plots of log R_p vs log[Ce(IV)] yielded orders with respect to Ce(IV) for the polymerization of MMA and AN (Fig. 7). The rates were dependent on [Ce(IV)]$^{0.41}$ and [Ce(IV)]$^{0.48}$ in the concentration ranges (0.5–3.0) × 10^{-3} M and (2.0–6.45) × 10^{-3} M for MMA and AN polymerizations, respectively. When the NO$_3^-$ concentration was kept constant in the reaction medium, the initial rate of
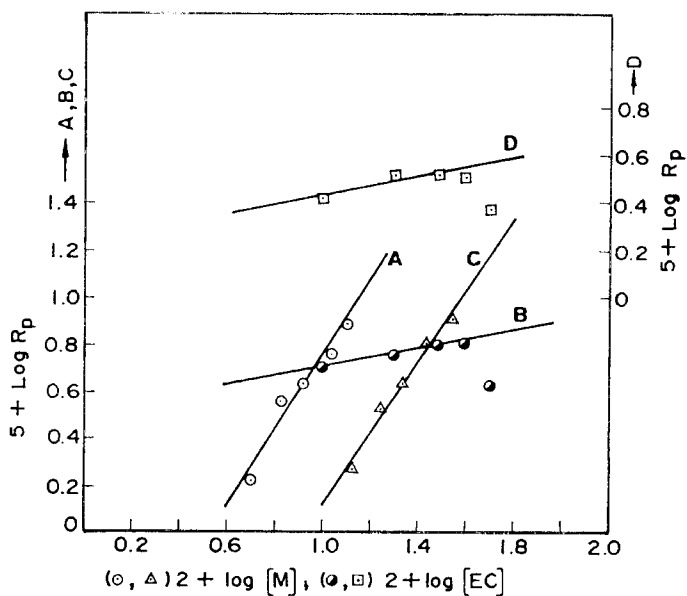
FIG. 6.   Log R_p vs log [M] and log R_p vs log [EC] plots. [Ce(IV)] = 0.003 M, [HNO$_3$] = 0.2 M, T = 30°C, (●) [MMA] = 0.1084 M, (▣) [AN] = 0.1748 M, (⊙, △) [EC] = 0.2 M.
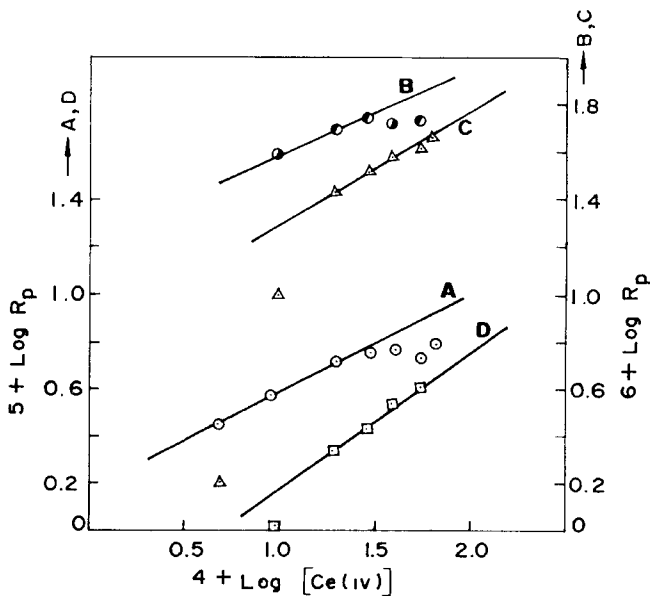
FIG. 7.   Log R_p vs log [Ce(IV)]. [EC] = 0.2 M, [HNO$_3$] = 0.2 M, T = 30°C, (⊙, ●) [MMA] = 0.1084 M, (△, ▣) [AN] = 0.1748 M, (●, ▣) [NO$_3^-$] = 0.233 M.

polymerization was reduced and the rates were found to yield orders of 0.36 and 0.58 with respect to Ce(IV) for MMA and AN polymerizations, respectively.

Dependence on Initial Monomer Concentration

The effect of monomer concentration on R_p was investigated at a ceric ion concentration of 3.0 × 10^{-3} M. The polymerization was always carried out within the solubility range of the monomer. MMA concentration was varied in the range (5.08–12.87) × 10^{-2} M and AN concentration was varied in the range (13.65–35.50) × 10^{-2} M. R_p was found to increase with monomer concentration in the concentration range employed for both the monomers studied. Plots of log R_p vs log[M] are linear (Fig. 6) with slopes of 1.60 and 1.50 for MMA and AN polymerizations, respectively.

Molecular Weight

The molecular weights of the polymers determined from the intrinsic viscosities of the polymer samples at different percent conversions are reported in Table 1 (Fig. 8). The molecular weights show increases with percent conversion for MMA polymerization up to 44% conversion and then decrease. Similar variations of molecular weight with percent conversion have been reported in the literature for many polymer systems [12, 16, 22]. In the polymerization of AN the molecular weights show an increase with percent conversion up to 15.74% conversion and then fall.

Effect of Temperature

The effect of temperature on the polymerization rates of MMA and AN was investigated over the 27–40°C range. A short induction period was detected in this range for both the monomer systems and was found to decrease with a rise in temperature. The rate of polymerization increased on increasing the temperature, and the maximum conversion decreased with a rise of temperature (Table 1, Figs. 9 and 10). The overall activation energies, $E_{overall}$, of polymerizations as calculated from the Arrhenius plots (Fig. 11) for the monomer systems MMA and AN were found to be 7.01 and 11.28 kcal/mol, respectively, within the 27–40°C temperature range.

DISCUSSION

The proportionality found between the inverse of the pseudo-first-order rate constant for ceric ion consumption, $(k^1)^{-1}$, and $[EC]^{-1}$ proves that the oxidation proceeds via complex formation between EC and Ce(IV). The observations made with a Beckman spectrophotometer clearly support complex formation between Ce(IV) and the reducing agent (Fig. 1). The scattering of the points in Fig. 2 might be due to the presence of various types of Ce(IV) complexes which formed under different sets of reaction conditions due to variations in the relative proportions of Ce(IV) and reducing agent concentrations in the reaction medium [14].

The induction period observed at the beginning of polymerization can be related to EC–Ce(IV) complex formation as well as to subsequent decomposition

TABLE 1. Determination of Energy of Activation, $E_{overall}$, and Molecular Weight with Percent Conversion

No.	T, °K	MMA, $R_p \times 10^5$ mol/L·s	AN, $R_p \times 10^5$ mol/L·s	No.	MMA % Conversion	MMA $\overline{M}_w \times 10^{-4}$	AN % Conversion	AN $\overline{M}_w \times 10^{-4}$
1	300	5.281	2.428	1	5.0	3.946	3.0	1.039
2	303	5.721	3.367	2	11.0	4.628	4.5	1.103
3	308	6.949	4.370	3	17.5	4.934	6.3	0.643
4	313	8.431	5.327	4	42.7	5.440	13.1	1.655
				5	44.0	5.985	15.7	2.142
				6	44.1	4.397	17.4	1.619
				7	45.7	3.467	19.1	1.876

$E_{overall}$ for MMA polymerization = 7.01 kcal/mol

$E_{overall}$ for AN polymerization = 11.28 kcal/mol

FIG. 8. $\overline{M}_w$ vs conversion. [Ce(IV)] = 0.003 M, [EC] = 0.2 M, [HNO$_3$] = 0.2 M, T = 30°C, (○) [MMA] = 0.1084 M, (●) [AN] = 0.1748 M.

FIG. 9. Percent conversion vs time plots for MMA polymerization at various temperatures. [Ce(IV)] = 0.003 M, [MMA] = 0.1084 M, [EC] = 0.2 M, [HNO$_3$] 0.2 M. T: (1) 27°C, (2) 30°C, (3) 35°C, (4) 40°C.
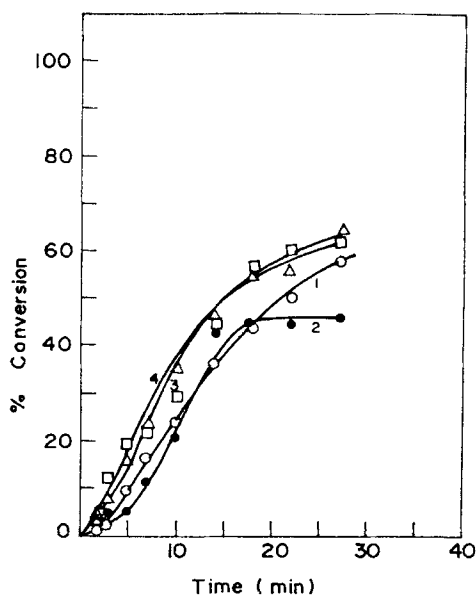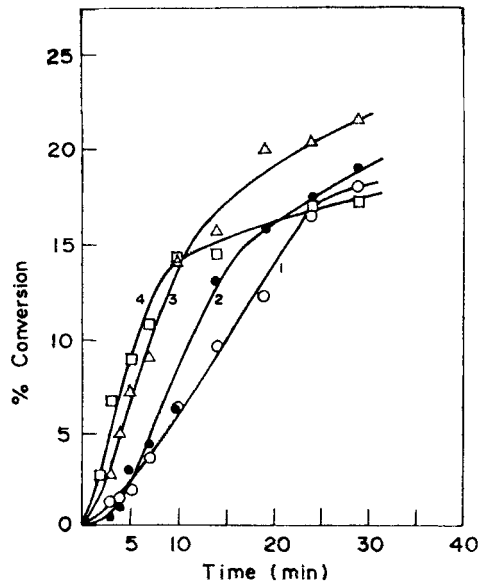
FIG. 10.   Percent conversion vs time plots for AN polymerization at various temperatures. [Ce(IV)] = 0.003 M, [AN] = 0.1748 M, [EC] = 0.2 M, [HNO$_3$] = 0.2 M. T: (1) 27°C, (2) 30°C, (3) 35°C, (4) 40°C.
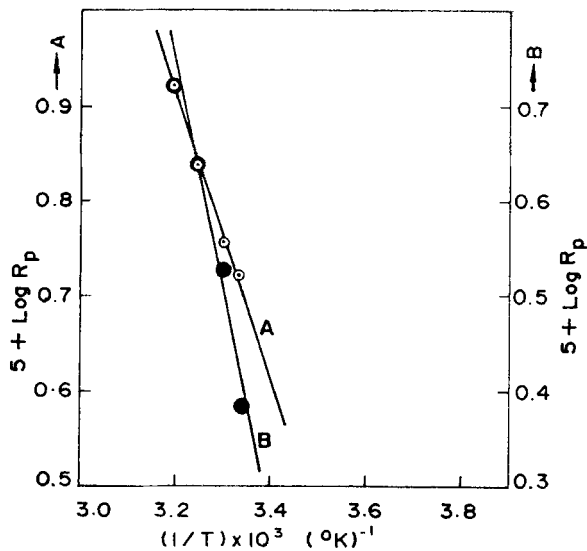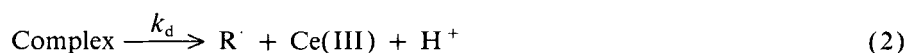

FIG. 11.   Log R_p vs ($1/T$) plots for the determination of overall energy of activation. [Ce(IV)] = 0.003 M, [EC] = 0.2 M, [HNO$_3$] = 0.2 M, (☉) [MMA] = 0.1084 M, (●) [AN] = 0.1748 M.

of this complex, since a high activation energy for Ce(IV)-alcohol complex decomposition reaction has been reported [3].
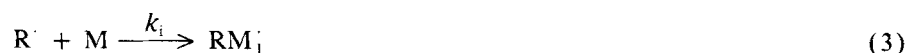
From the results obtained at different EC concentrations, it is observed that R_p increases regularly with an increase of EC concentration in the concentration range 0.1-0.4 M and falls steeply at higher concentration of EC (0.5 M). The orders with respect to EC for the polymerizations of MMA and AN under present experimental conditions are 0.18 and 0.20, which are lower than the theoretical value (0.5) for the reducing agent exponent. This fall in the order with respect to EC, and the steep fall in R_p at a higher concentration of EC (0.5 M) under present experimental conditions for both monomers can be attributed to the generation of an excess of primary radicals which leads to premature termination of the growing chains and, on the other hand, causes the oxidative termination rate of primary radicals by Ce(IV) to be relatively higher than at a lower concentration of EC. Termination of growing chains may occur either by interaction between them or by oxidation with ceric ion, depending on the concentration of Ce(IV). In the present study the rate of polymerization is proportional to $[Ce(IV)]^{0.41}$ and $[Ce(IV)]^{0.48}$ for MMA and AN polymerizations, respectively. This slow variation of R_p with Ce(IV) concentration for MMA polymerization can be attributed to the simultaneous effect of ceric ion on the initiation rate and on the oxidative termination rate of primary radicals [12]. Addition of ammonium nitrate to the reaction medium to maintain constant NO_3^- concentration brought down the rate of polymerization, and yielded orders of 0.36 and 0.58 with respect to Ce(IV) for MMA and AN polymerizations, respectively. The orders with respect to monomer are 1.60 and 1.50 for MMA and AN polymerizations, respectively, which supports the linear termination with Ce(IV) by growing chain as well as bimolecular termination of the growing chains. The higher exponent in the MMA polymerization also gives support to the complex nature of the initiation reactions involving monomer molecules as participating reactants to generate initiating free radicals [15]. The trend observed in the maximum conversion on increasing the temperature has also been reported in the literature [12, 16]. The overall activation energies under the present experimental conditions are 7.01 and 11.28 kcal/mol for MMA and AN polymerizations, respectively, which are of the same order as those found in other aqueous systems [12, 17, 18].

The following reaction scheme is found to explain satisfactorily the kinetic results obtained.

Primary radical formation:

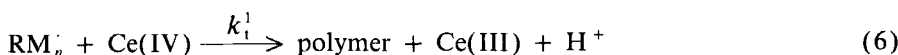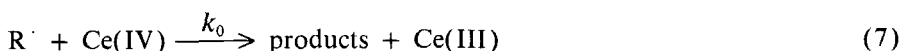$$Ce(IV) + EC \underset{\longleftarrow}{\overset{K}{\longrightarrow}} complex \tag{1}$$

$$Complex \xrightarrow{k_d} R^\cdot + Ce(III) + H^+ \tag{2}$$

Initiation:

$$R^\cdot + M \xrightarrow{k_i} RM_1^\cdot \tag{3}$$

Propagation:

$$RM_i^{\cdot} + M \xrightarrow{k_p} RM_2$$

$$\vdots$$

$$RM_n^{\cdot} + M \xrightarrow{k_p} RM_{n+1} \tag{4}$$

Bimolecular termination:

$$RM_n^{\cdot} + RM_m^{\cdot} \xrightarrow{k_t} polymer \tag{5}$$

Monomolecular termination with Ce(IV) (linear termination):

$$RM_n^{\cdot} + Ce(IV) \xrightarrow{k_t^1} polymer + Ce(III) + H^+ \tag{6}$$

Oxidative termination of primary radicals:

$$R^{\cdot} + Ce(IV) \xrightarrow{k_0} products + Ce(III) \tag{7}$$

Where $R^{\cdot}$ is a primary radical and $RM_n^{\cdot}$ is the growing primary radical. By applying the steady-state principle to the active intermediates $R^{\cdot}$ and $RM_n^{\cdot}$, and considering only the mutual type of termination as effective under our experimental conditions, the Eqs. (8) and (9) for R_p and R_{Ce} were derived:

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

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

Under the present experimental situation, if the condition $k_i[M] \gg k_o[Ce(IV)]_{eq}$ exists, then Eqs. (8) and (9) reduce to

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

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

Since the measured rate $-d[Ce(IV)]/dt$ applies to total $[Ce(IV)]$, and since $[Ce(IV)]_T = [Ce(IV)]_{eq}(1 + K[EC])$, one obtains

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

$$R_{Ce} = \frac{-d[Ce(IV)]}{dt} = k_d K \frac{[EC][Ce(IV)]_T}{(1 + K[EC])} \tag{13}$$

On the other hand, if under the present experimental conditions the situation is $k_o[Ce(IV)]_{eq} \gg k_i[M]$, then Eqs. (8) and (9) reduce to

$$R_p = (k_p/k_t^{1/2})(k_i/k_o)^{1/2}(k_d K)^{1/2}[EC]^{1/2}[M]^{3/2} \tag{14}$$

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

The molecular weight increased with the progress of polymerization and fell at 44.1% conversion in MMA polymerization, which is seen to be related to the loci of

polymerization. The polymerization of MMA in aqueous medium initially follows homogeneous polymerization kinetics, then follows emulsion polymerization kinetics for some period in the intermediate stage when the charge-stabilized discrete particles are dispersed in the aqueous phase where the monomer is soluble in the polymer and shifts to these particles, and finally reaches a pseudohomogeneous-type reaction when MMA is situated in the insoluble phase coarse particles. This type of kinetics can show an effect on the molecular weight of the polymer, which varies with the percent conversion. During the intermediate stage, polymerization inside the charge-stabilized discrete particles to which most of the monomer has transferred from the aqueous medium, the biomolecular termination rate is slow between the growing primary radicals because their availability in these particles is less. Polymerization takes place inside particles that bear a single radical and that are permeable to regulated diffusion of primary radicals from the aqueous medium. When these particles reach a certain critical size and number, they coagulate to coarse particles, and these are large enough to permit the coexistence of more than one primary radical inside the particle, which brings down the molecular weight. The polymerization of AN in water shows many apparently erratic features. These stem from its monomer–polymer incompatibility. The monomer remains mostly in the aqueous phase even after the separation of the polymer, be it a sol or a precipitate. Therefore, the locus of polymerization resides mainly in the aqueous phase throughout the reaction. In this system there is the possibility of long-lived radicals becoming occluded in the suspended phase [16].

Evaluation of Rate Constants

The experimental results indicate that both polymerizations have the condition $k_i[M] \gg k_o[Ce(IV)]_{eq}$ because the exponents of $[Ce(IV)]$ are 0.41 and 0.48 for MMA and AN polymerizations, respectively.

Then Eq. (13) can be rearranged in the form

$$\frac{-d[Ce(IV)]}{[Ce(IV)]_T} = \frac{k_d K[EC]}{(1 + K[EC])} dt \tag{16}$$

Assuming $[EC]$ is constant and integrating Eq. (16):

$$-d(\ln[Ce(IV)]_T/dt)^{-1} = (k^1)^{-1} \tag{17}$$

where

$$k^1 = \frac{k_d K[EC]}{(1 + K[EC])} \tag{18}$$

From the plot of $\log[Ce(IV)]_T$ vs time at different $[EC]$ (Figs. 12 and 13), straight lines with a slope of $(k^1/2.303)$ are obtained, with k^1 the pseudo-first-order rate constant for ceric ion consumption. Then Eq. (18) is rearranged in the form

$$\frac{1}{k^1} = \frac{1}{k_d K[EC]} + \frac{1}{k_d} \tag{19}$$

and by plotting $1/k^1$ vs $1/[EC]$ the values of K and k_d can be obtained from the straight line graph (Fig. 5, Table 2).
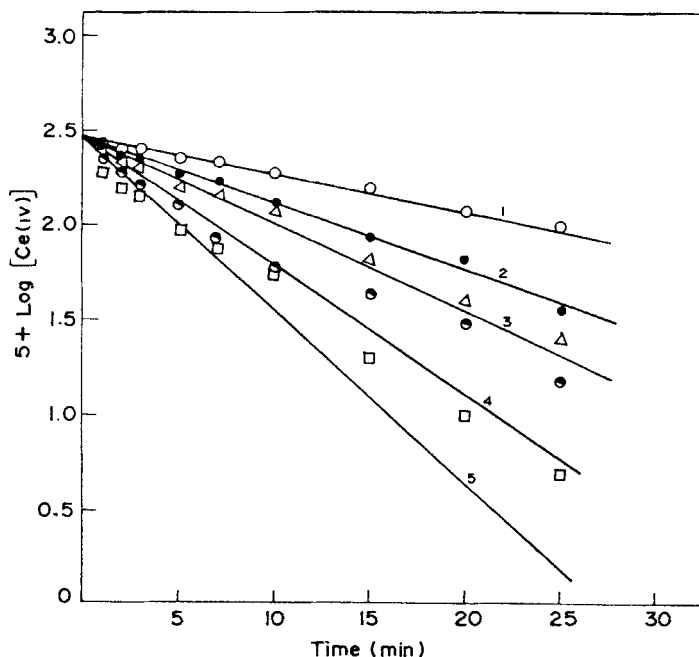
FIG. 12.   Log [Ce(IV)] vs time at different [EC]. [Ce(IV)] = 0.003 M, [MMA] = 0.1084, [HNO$_3$] = 0.2 M, T = 30°C. [EC]: (1) 0.05 M, (2) 0.1 M, (3) 0.2 M, (4) 0.3 M, (5) 0.4 M.

When there is a dependence of R_p on [Ce(IV)], Eq. (8) can be rearranged to

$$[M]^2/R_p^2 = \frac{k_t}{k_p^2}\left(\frac{1}{k_d K[EC]} + \frac{1}{k_d}\right)\frac{1}{[Ce(IV)]_T} + \frac{k_t}{k_p^2}\left(\frac{k_o}{k_i k_d K[EC][M]}\right) \qquad (20)$$

By plotting ([M]^2/R_p^2) vs 1/[Ce(IV)]$_T$, the rate constant ratios k_i/k_0 and $k_p/k_t^{1/2}$ could be evaluated (Fig. 14, Table 2). The values of the rate constants are comparable with the values already reported in the literature [12, 19–21].

CONCLUSIONS

The results in the present experimental conditions show the consumption of Ce(IV) is first order with respect to ceric ion concentration, and the points at higher and lower concentrations show deviations in the graph. The proportionality between $(k^1)^{-1}$ and [EC]$^{-1}$ supports complex formation between Ce(IV) and EC, which is further supported by spectrophotometric observations. The lower orders with respect to [EC] for the polymerization of MMA and AN are considered to be due to the premature termination of growing radicals by primary radicals, and also due to the rise of oxidative termination rate at relatively higher values at higher concentrations of EC than at lower concentrations of EC. The addition of ammonium nitrate
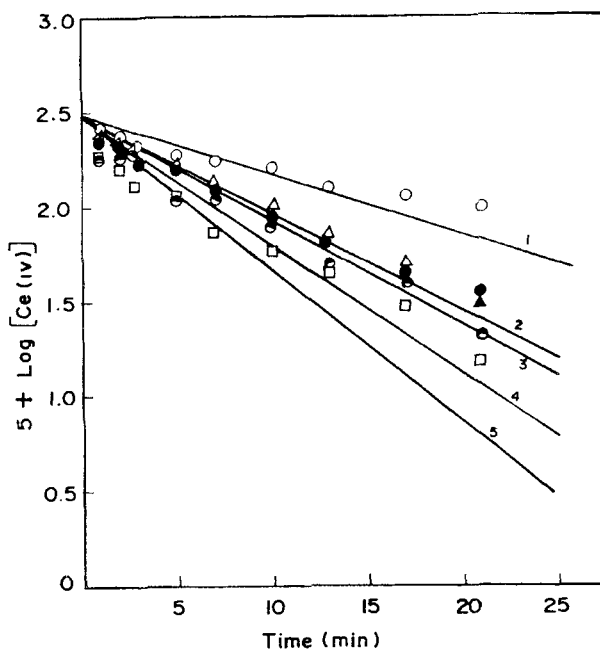
FIG. 13. Log [Ce(IV)] vs time at different [EC]. [Ce(IV)] = 0.003 M, [AN] = 0.1748 M, [HNO$_3$] = 0.2 M, T = 30°C. [EC]: (1) 0.05 M, (2) 0.1 M, (3) 0.2 M, (4) 0.3 M, (5) 0.4 M.

to the reaction medium to maintain constant [NO$_3^-$] could bring down the rate of polymerization. The orders with respect to monomers support linear termination with Ce(IV) by growing chains as well as biomolecular termination of the growing chains. The molecular weight variation with percent conversion shows the dependence on the loci of polymerization for MMA polymerization, which is due to

TABLE 2. Rate Parameters for the Polymerization of MMA and AN by Ammonium Ceric Nitrate–Ethyl Cellosolve Redox System at 30°C

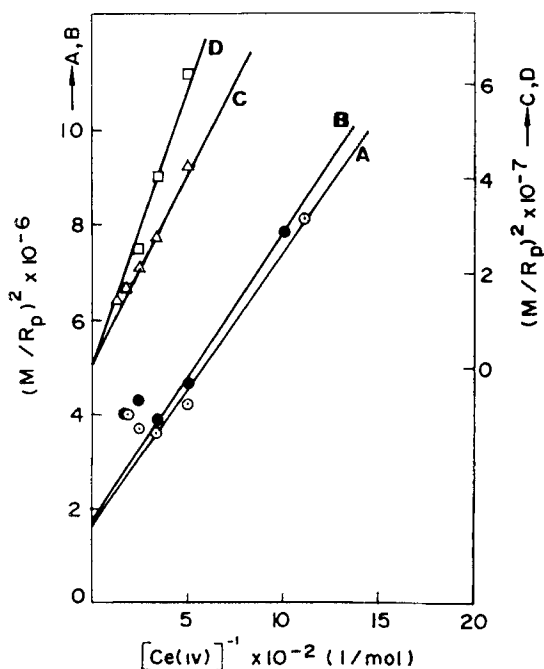| Polymer system	K, 1/mol	k_i/k_0	$k_d \times 10^3$ s^{-1}	$k_p/k_t^{1/2}$ L$^{1/2}$/(mol$^{1/2}\cdot$s$^{1/2}$)
MMA	3.571	0.0189	5.000	0.2882
MMA with constant [NO$_3^-$] in the reaction medium	5.990	0.0146	3.130	0.3106
AN	12.420	0.2686	3.333	0.0717
AN with constant [NO$_3^-$] in the reaction medium	7.930	0.4916	3.704	0.0629

FIG. 14. $([M]/R_p)^2$ vs $[Ce(IV)]^{-1}$ ($\odot$, $\bullet$) [MMA] = 0.1084 M, ($\triangle$, $\square$) [AN] = 0.1748 M, [EC] = 0.2 M, [HNO$_3$] = 0.2 M, ($\bullet$, $\square$) [NO$_3^-$] = 0.233 M, T = 30°C.

monomer–polymer compatibility. On the other hand, in AN polymerization the molecular weight variation with percent conversion shows many apparently erratic features due to its monomer–polymer incompatibility. The overall energies of activation for MMA and AN polymerizations in the temperature range 27–40°C are in accordance with literature values.

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