

Aqueous Polymerization of Methyl Methacrylate Initiated by Ceric Ion Reducing Agent Systems in Sulfuric Acid Medium

G. VENKATARAMANA REDDY,^{1*} S. LUNA EUNICE,² R. KALAIARASI,² and R. SRIRAM²

¹Central Leather Research Institute, Madras 600 020, India, and ²Department of Chemistry, Coimbatore Institute of Technology, Coimbatore 641 014, India

SYNOPSIS

Polymerization of methyl methacrylate (MMA) was carried out in aqueous sulfuric acid medium at 30°C using ammonium ceric sulfate (ACS)/methyl ethyl ketone (MEK) and ammonium ceric sulfate/acetone as redox initiator systems. A short induction period was observed with both the initiator systems, as well as the attainment of limiting conversion for polymerization reactions. The rate of ceric ion consumption, R_{Ce} , was first order with respect to Ce(IV) concentration in the concentration range $(0.5-5.5) \times 10^{-3}M$, and 0.5 order with respect to reducing agent concentration in the concentration ranges (0.0480–0.2967M) and (0.05–0.3912M) for Ce(IV)–MEK and Ce(IV)–acetone initiator systems, respectively. A fall in R_{Ce} was observed at higher reducing agent concentrations. The plots of R_{Ce} versus reducing agent concentrations raised to the half power yielded straight lines passing through the origin, indicating the absence of complex formation between reducing agents and Ce(IV). The addition of sodium sulfate to maintain constant sulfate ion concentration in the reaction medium could bring down the R_{Ce} values in the present reaction systems. The rate of polymerization of MMA, R_p , increased with increase in Ce(IV), reducing agent, and monomer concentrations for the Ce(IV)–MEK initiator. The rate of polymerization of MMA is independent of Ce(IV) concentration and increased with an increase in reducing agent and monomer concentrations for the Ce(IV)–acetone initiator. At higher concentrations of reducing agent (0.4–0.5M), a steep fall in R_p values was observed with both the initiator systems. The orders with respect to Ce(IV), MEK, and MMA using the Ce(IV)–MEK initiator were found to be 0.23, 0.2, and 1.29, respectively. The orders with respect to Ce(IV), acetone, and MMA using the Ce(IV)–acetone initiator were found to be zero, 0.42, and 1.64, respectively. Maintaining constant $[SO_4^{2-}]$ in the reaction medium could bring down R_p values for the Ce(IV)–MEK initiator system. On the other hand, a rise in R_p values with an increase in $[Na_2SO_4]$ could be observed when constant $[SO_4^{2-}]$ was maintained in the reaction medium for the Ce(IV)–acetone initiator system. A kinetic scheme involving direct attack of Ce(IV) on reducing agent, production of radicals, initiation, propagation, and termination of the polymeric radicals by bimolecular interaction is proposed. An oxidative termination of primary radicals by Ce(IV) is also included. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Many oxidation-reduction reactions produce radicals that can be used to initiate polymerization. The prime advantage of redox initiation is that

radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system, including initiation at moderate temperatures of 0–50°C and even lower. Ceric salts show a high reactivity in aqueous media¹ and have been used either alone² 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

* To whom correspondence should be addressed.

free radicals from reducing agents.⁶ 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 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 sulfuric and nitric acid media.⁷⁻¹⁰

Studies have been made in the recent past on ceric ion initiation of polymerization of vinyl monomers, including graft and block copolymerization in aqueous acid media, in the literature using various types of reducing agents,¹¹⁻²² and in graft and block copolymerization the substrate itself can be oxidized²³⁻²⁵ by Ce⁴⁺ to initiate the polymerization. Attempts have also been made to study the effect of organic additives on the kinetics of polymerization initiated by ceric salt reducing agent systems in aqueous acid media.^{11,26}

This article describes the study of kinetics of polymerization of methyl methacrylate (MMA) in aqueous sulfuric acid under nitrogen atmosphere initiated by ammonium ceric sulfate/methyl ethyl ketone and ammonium ceric sulfate/acetone redox pairs.

EXPERIMENTAL

Materials

The monomer MMA (LR, Burgoyne Burbidges and Co., India) was purified by washing with 5% sodium hydroxide followed by distilled water and dried over anhydrous sodium sulfate. The washed monomer was further purified by vacuum distillation under nitrogen atmosphere. Acetone (LR, Fischers Inorganic and Aromatics, India), methyl ethyl ketone (MEK) (LR, S. D. Fine Chemical Ltd., India), and methanol (LR, Fischer Inorganic and Aromatics, India) were purified by the standard procedure. Ferrous solution (AR, S. D. Fine Chemical Ltd., India), ammonium ceric sulfate (ACS) (LR, Sarabhai M. Chemicals Ltd., India), ammonium ferrous sulfate (AR, S. D. Fine Chemical Ltd., India), and sodium sulfate (LR, S. D. Fine Chemical Ltd., India) were used as supplied without further purification.

Methods

A mixture of monomer and reducing agent in the required concentration in aqueous solution was

taken in a 50-mL reaction tube (Pyrex) provided with an inlet and an outlet for the passage of nitrogen, and the reaction tube was maintained at 30°C in a thermostatic water bath. The oxidant solution of ammonium ceric sulfate in sulfuric acid medium was also deaerated before adding it to the aforementioned reaction mixture maintained at constant temperature in the thermostatic water bath. The polymerization reaction in this reaction tube was arrested at the required time interval by adding a slight excess of ammonium ferrous sulfate to the reaction mixture in this reaction tube. Thus, the polymers formed for different time intervals were separated by filtration in sintered crucibles and 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 the percent conversions of monomer into polymer at different time intervals were computed from the weights of these dried polymers. The initial rate of polymerization, R_p , was calculated from the slope of the steady-state zone of the plot, percent conversion versus time.

Determination of Ceric Ion Concentration

The concentration of ceric ion in the reaction was 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 neutralize the Ce(IV) in the reaction medium. The excess ammonium ferrous sulfate was back-titrated with a standard ammonium ceric sulfate solution. The initial rate of ceric ion disappearance, R_{Ce} , was calculated from the initial slope of the plot, percent consumption of Ce(IV) versus time.

Molecular Weight Determination

The molecular weights of the purified polymers at different percent conversions were determined by measuring their intrinsic viscosities with an Ubbelohde suspended level dilution viscometer in a thermostatic water bath, which could regulate the temperature within $\pm 0.01^\circ\text{C}$. The following Mark-Houwink relationship was employed for poly(methyl methacrylate) at 30°C in acetone to compute molecular weights²⁷:

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

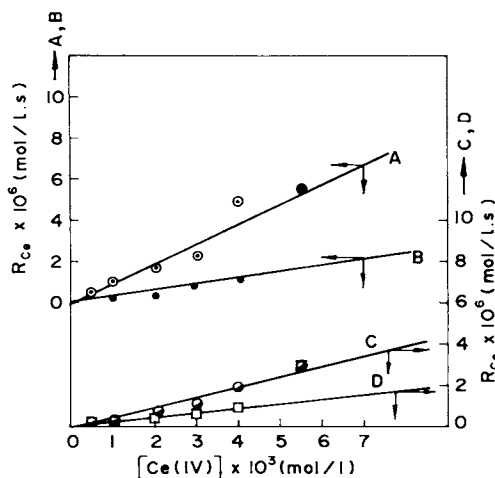


Figure 1 R_{Ce} versus $[Ce(IV)]$. $[MMA] = 0.08788M$, $[MEK] = 0.29665M$, $[acetone] = 0.3032M$, $[H_2SO_4] = 0.1M$, $T = 30^\circ C$. (\odot , \bullet) $Ce(IV)$ -MEK initiator system; (\square , \blacksquare) $Ce(IV)$ -acetone initiator system; (\bullet , \square) $[SO_4^{2-}] = 0.122M$.

RESULTS

Rate of Ceric Ion Disappearance

In the absence of reducing agent, there was no polymerization even after long periods (60 min) and no reduction of $Ce(IV)$.

Dependence on $Ce(IV)$ Concentration

$[Ce(IV)]$ was varied in the range $(0.5-5.5) \times 10^{-3}M$ with all other parameters in each system remaining constant. It was found that the ceric ion consumption increases with increasing $Ce(IV)$ concentration. Figure 1 shows that the rate of ceric ion reduction is first order with respect $[Ce(IV)]$. In the present study, R_{Ce} falls with the addition of sodium sulfate to maintain constant $[SO_4^{2-}]$ in the reaction medium (Fig. 1).

Dependence on Reducing Agent Concentration

The dependence of $Ce(IV)$ reduction on reducing agent concentration was investigated at a ceric ion concentration of $3 \times 10^{-3}M$. The concentration of reducing agent was varied in the range 0.048–0.601M for the $Ce(IV)$ -MEK initiator system and 0.05–0.593M for the $Ce(IV)$ -acetone initiator system; all other parameters in each system remained constant. The rate of ceric ion consumption increased with increasing reducing agent concentration up to 0.2967M for the $Ce(IV)$ -MEK system and up to 0.303M for the $Ce(IV)$ -acetone system, showing 0.5 order dependence on reducing agent concentration. At higher concentrations the rate fell with the re-

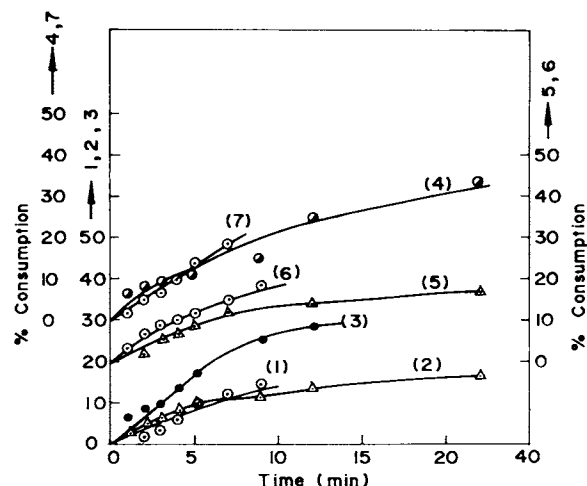


Figure 2 Ceric ion consumed versus reaction time at different $[MEK]$. $[Ce(IV)] = 0.003M$, $[MMA] = 0.08788M$, $[H_2SO_4] = 0.1M$, $T = 30^\circ C$, $[MEK]$: (1) 0.04811M, (2) 0.10022M, (3) 0.20044M, (4) 0.29665M, (5) 0.40089M, (6) 0.4971M, (7) 0.6013M.

ducing agent concentration for both the systems, respectively (Figs. 2, 3, and 6). An absence of complex formation between reducing agent and ceric ion was revealed by the straight-line plot of the rate of ceric ion consumption against the square root of the reducing agent concentration passing through the origin (Fig. 6). Under present study, R_{Ce} falls with the addition of sodium sulfate to maintain constant $[SO_4^{2-}]$ in the reaction medium (Figs. 4, 5, and 6).

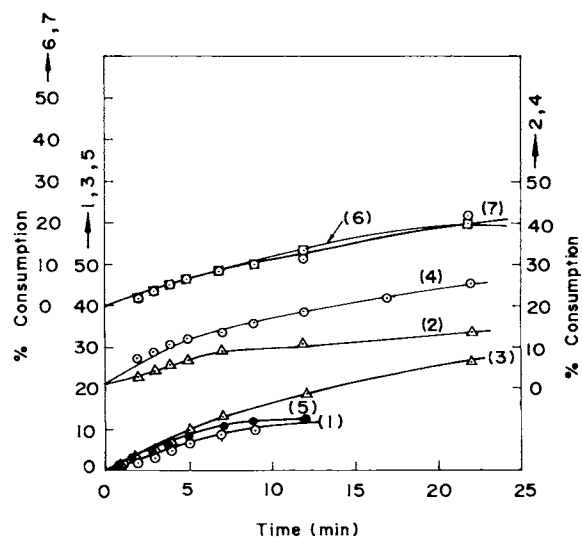


Figure 3 Ceric ion consumed versus reaction time at different $[acetone]$. $[Ce(IV)] = 0.003M$, $[MMA] = 0.08788M$, $[H_2SO_4] = 0.1M$, $T = 30^\circ C$, $[Acetone]$: (1) 0.05M, (2) 0.09781M, (3) 0.1956M, (4) 0.3032M, (5) 0.3912M, (6) 0.4988M, (7) 0.5931M.

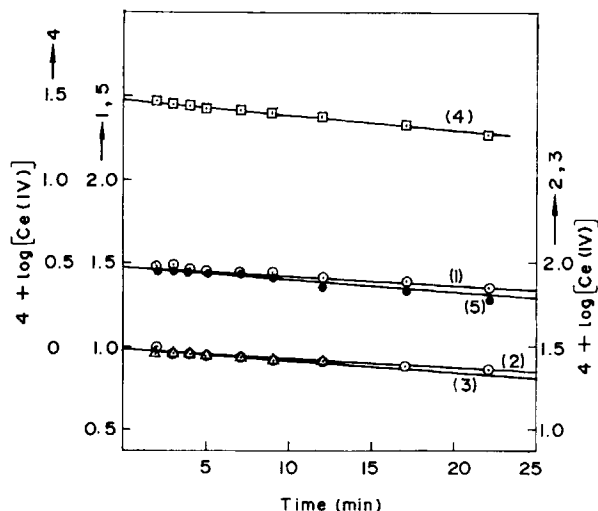


Figure 4 $\log[\text{Ce(IV)}]$ versus time at different $[\text{MEK}]$. $[\text{Ce(IV)}] = 0.003M$, $[\text{MMA}] = 0.08788M$, $[\text{H}_2\text{SO}_4] = 0.1M$, $[\text{SO}_4^{2-}] = 0.122M$, $T = 30^\circ\text{C}$. $[\text{MEK}]$: (1) $0.10022M$, (2) $0.20044M$, (3) $0.29665M$, (4) $0.40089M$, (5) $0.4971M$.

Rate of Polymerization

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

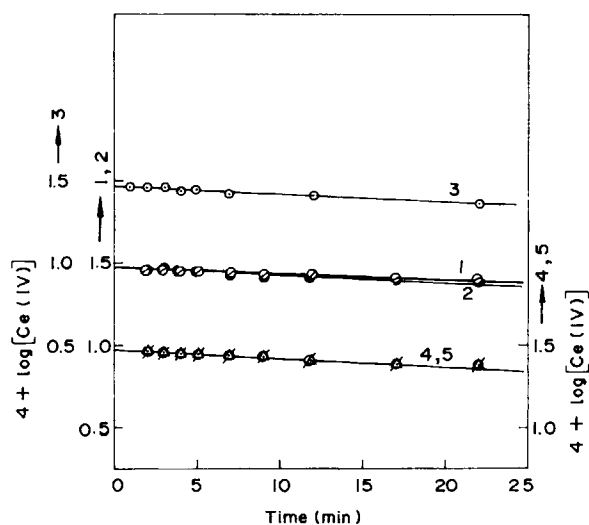


Figure 5 $\log[\text{Ce(IV)}]$ versus time at different $[\text{acetone}]$. $[\text{Ce(IV)}] = 0.003M$, $[\text{MMA}] = 0.08788M$, $[\text{H}_2\text{SO}_4] = 0.1M$, $[\text{SO}_4^{2-}] = 0.122M$, $T = 30^\circ\text{C}$, $[\text{Acetone}]$: (1) $0.0978M$, (2) $0.1956M$, (3) $0.3032M$, (4) $0.3912M$, (5) $0.4805M$.

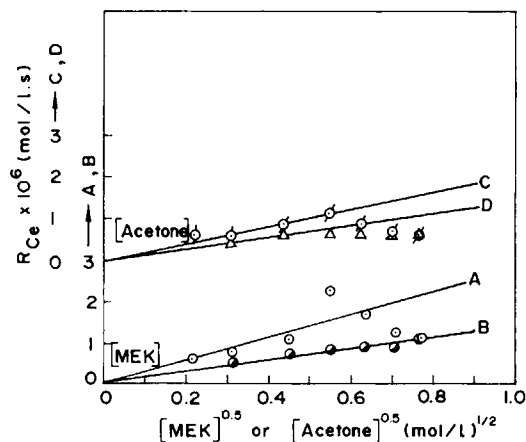


Figure 6 R_{Ce} versus $[\text{reducing agent}]^{0.5}$ $[\text{Ce(IV)}] = 0.003M$, $[\text{MMA}] = 0.08788M$, $[\text{H}_2\text{SO}_4] = 0.1M$, $T = 30^\circ\text{C}$. (\odot , \ominus) Ce-MEK initiator system; (ϕ , \triangle) Ce(IV)-acetone initiator system; (\ominus , \triangle) $[\text{SO}_4^{2-}] = 0.122M$.

Dependence on Ce(IV) Concentration

Ceric ion concentration was varied in the range $(1-5.5) \times 10^{-3}M$ with all other parameters in each system remaining constant. The same polymerization reactions were also carried out at constant $[\text{SO}_4^{2-}]$ in the reaction medium. The initial rate of polymerization with Ce(IV)-MEK as the initiator for MMA polymerization increased up to $0.003M$ concentration, and later the rate remained constant up to $0.0055M$ concentration of Ce(IV) (Fig. 7). Under present experimental conditions, the rate is dependent on $[\text{Ce(IV)}]^{0.23}$ (Fig. 7). There was a fall in the rate of polymerization when $[\text{SO}_4^{2-}]$ was maintained

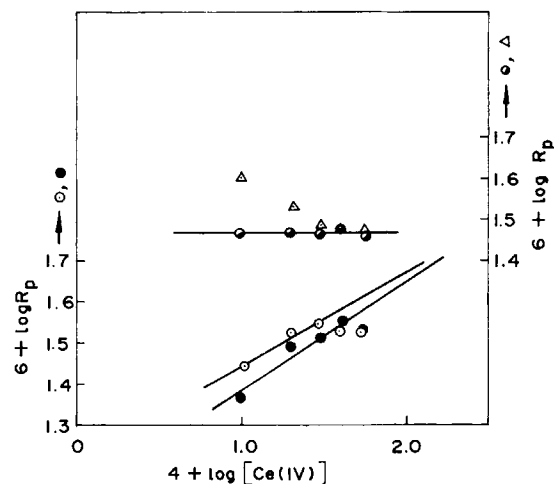


Figure 7 $\log R_p$ versus $\log[\text{Ce(IV)}]$. $[\text{MMA}] = 0.08788M$, $[\text{MEK}] = 0.29665M$, $[\text{acetone}] = 0.3032M$, $[\text{H}_2\text{SO}_4] = 0.1M$, $T = 30^\circ\text{C}$. (\odot , \bullet) Ce(IV)-MEK initiator system; (\ominus , \triangle) Ce(IV)-acetone initiator system; (\bullet , \triangle) $[\text{SO}_4^{2-}] = 0.122M$.

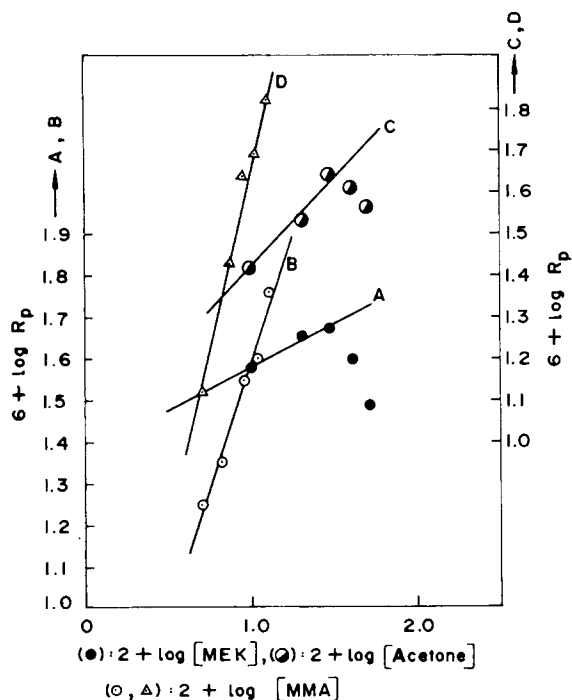


Figure 8 $\log R_p$ versus $\log[\text{reducing agent}]$ and $\log R_p$ versus $\log[\text{MMA}]$ plots. $[\text{Ce(IV)}] = 0.003M$, $[\text{H}_2\text{SO}_4] = 0.1M$, $T = 30^\circ\text{C}$. (●, ○) $[\text{MMA}] = 0.08788M$, (○) $[\text{MEK}] = 0.29665M$, (△) $[\text{acetone}] = 0.3032M$.

constant in the reaction medium for the Ce(IV)–MEK initiator system, and the rate was dependent on $[\text{Ce(IV)}]^{0.27}$ (Fig. 7). The initial rate of polymerization with Ce(IV)–acetone as the initiator for MMA polymerization remained constant in the concentration range of Ce(IV) studied (Fig. 7). When the experiments were carried out with constant $[\text{SO}_4^{2-}]$ in the reaction medium, there was a rise in R_p at lower concentrations of Ce(IV) ($\leq 0.003M$), and at higher concentrations of Ce(IV) the rate remained constant (Fig. 7).

Dependence on Reducing Agent Concentration

The reducing agent concentration was varied for Ce(IV)–MEK as the initiator in the range 0.1002–0.4971M and for Ce(IV)–acetone as the initiator in the range 0.0978–0.4988M. The maximum conversion increased for the Ce(IV)–MEK initiator system up to MEK concentration, 0.2004M, and for the Ce(IV)–acetone initiator system up to acetone concentration, 0.401M. A decrease in maximum conversion was observed above these concentrations. The initial rate of polymerization of MMA using Ce(IV)–MEK as the initiator increased with an increase in $[\text{MEK}]$ up to 0.2967M. At higher concentrations of MEK the rate fell with an increase in

$[\text{MEK}]$, and the order with respect to $[\text{MEK}]$ was found to be 0.2 (Fig. 8). The initial rate of polymerization of MMA using Ce(IV)–acetone as the initiator increased with an increase in $[\text{acetone}]$ up to 0.3032M. At higher concentrations of acetone the rate fell with an increase in $[\text{acetone}]$, and the order with respect to $[\text{acetone}]$ was found to be 0.42 (Fig. 8).

Dependence on Initial Monomer Concentration

Polymerizations were always carried out within the solubility range of monomer. MMA concentration was varied in the range 0.0507–0.1284M. The R_p was found to increase with monomer concentration in the concentration range studied for both the initiators. The initial rates of polymerizations for MMA polymerization using Ce(IV)–MEK and Ce(IV)–acetone as initiators were found to depend on $[\text{MMA}]^{1.29}$ and $[\text{MMA}]^{1.64}$, respectively (Fig. 8).

Molecular Weight

The molecular weights of the polymer samples obtained at different percent conversions are reported in Table I. The molecular weight increased with percent conversion for MMA polymerization using Ce(IV)–MEK as the initiator up to 52% conversion. A decrease beyond this point was observed with percent conversion (Fig. 12). The molecular weight increased with percent conversion for MMA polymerization using Ce(IV)–acetone as the initiator up to 47% conversion, and a decrease beyond this point was observed (Fig. 12).

Effect of Temperature

The effect of temperature on the polymerization rates of MMA using Ce(IV)–MEK and Ce(IV)–acetone initiator systems was investigated over the temperature range 27–40°C. A short induction period was detected in the 27–40°C range with both the initiator systems and was found to decrease with the rise in temperature. The rate of polymerization increased with an increase in temperature, and the breadth of the steady-state zone decreased with an increase in temperature (Figs. 9 and 10). The overall activation energies of polymerizations, (E_{overall}), as calculated from the Arrhenius plots (Fig. 11) for MMA polymerization using Ce(IV)–MEK and Ce(IV)–acetone as initiators, were found to be 3.80 and 10.17 kcal/mol, respectively.

Table I Determination of Energies of Activation, E_{overall} , and Molecular Weights of Polymer Samples with Percent Conversion for MMA Polymerization

Sample No.	Temp. (°K)	Ce(IV)-MEK	Ce(IV)-Acetone	Ce(IV)-MEK Initiator System		Ce(IV)-Acetone Initiator System	
		Initiator System $R_p \times 10^5$ (mol L s)	Initiator System $R_p \times 10^5$ (mol L s)	(% Conversion)	$\bar{M}_w \times 10^{-5}$	(% Conversion)	$\bar{M}_w \times 10^{-5}$
1	300	3.296	3.515	13.0	7.10	7.4	3.42
2	303	3.515	4.394	22.0	7.31	23.0	8.65
3	308	3.735	5.273	31.8	7.52	41.9	7.55
4	313	4.321	7.616	40.7	9.30	46.7	9.07
				51.8	12.17	51.1	8.09
		$E_{\text{overall}} = 3.80$	$E_{\text{overall}} = 10.17$	54.7	12.09	61.4	5.99
		kcal/mol	kcal/mol	63.7	10.23	65.2	5.86
				72.9	4.25	68.7	5.03

DISCUSSION

There is no evidence of complex formation between ceric ion and reducing agents, and the oxidation of reducing agents appears to proceed by direct attack of the ceric species on the reducing agents.^{6,10} The linear plots of R_{Ce} versus [reducing agent]^{0.5} pass through the origin, clearly indicating the absence of complex formation between Ce(IV) and reducing agents. The fall of R_{Ce} at higher reducing agent concentrations might be due to the cage effect.^{10,28}

A short induction period is observed with every polymerization system and is found to vary inversely with the rate of initiation. From the results obtained at different MEK concentrations, it is deduced that

with the increase in MEK concentration the primary radical production increases as R_p increases regularly up to 0.2967M, and at higher concentrations of MEK the R_p falls with an increase in [MEK] (Fig. 8). The order with respect to MEK for MMA polymerization under the present experimental conditions is 0.2. Similar observations are also made with acetone as the reducing agent. The rate increases with acetone concentration when acetone is used as a reducing agent up to 0.3032M and falls at higher concentrations of acetone with an increase in [acetone]. The order with respect to [acetone] for MMA polymerization under the present experimental conditions is 0.42. These reduced orders with respect to reducing agents compared to theoretical

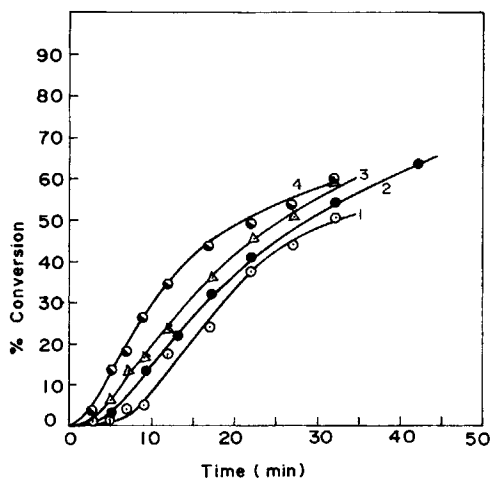


Figure 9 % conversion versus time plots for MMA polymerization using Ce(IV)-MEK initiator system at various temperatures. [Ce(IV)] = 0.003M, [MMA] = 0.08788M, [MEK] = 0.29665M, [H₂SO₄] = 0.1M, T: (1) 27°C, (2) 30°C, (3) 35°C, (4) 40°C.

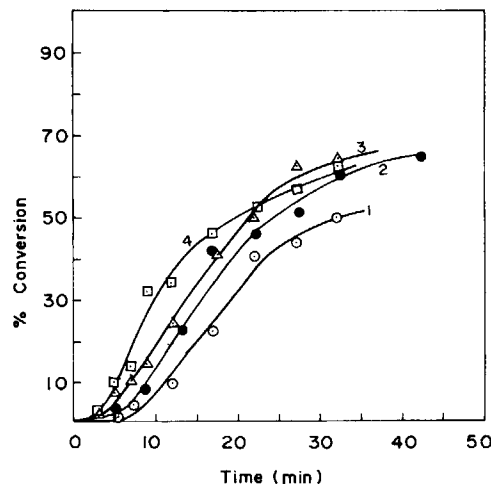


Figure 10 % conversion versus time plots for MMA polymerization using Ce(IV)-acetone initiator system at various temperatures. [Ce(IV)] = 0.003M, [MMA] = 0.08788M, [acetone] = 0.3032M, [H₂SO₄] = 0.1M, T: (1) 27°C, (2) 30°C, (3) 35°C, (4) 40°C.

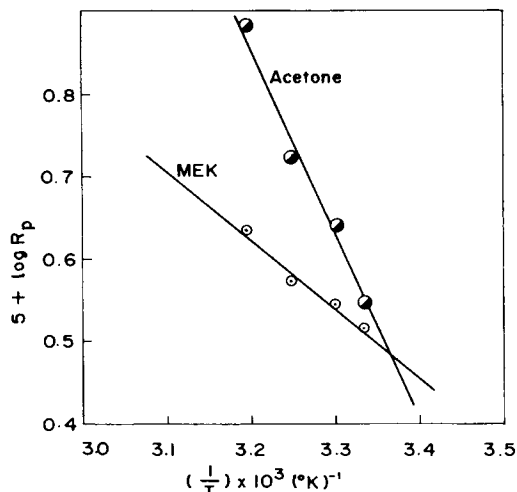


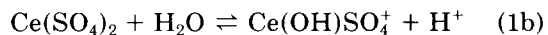
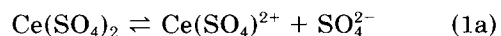
Figure 11 $\log R_p$ versus $(1/T)$ plot for the determination of overall energy of activation. $[\text{Ce(IV)}] = 0.003M$, $[\text{MMA}] = 0.08788M$, $[\text{H}_2\text{SO}_4] = 0.1M$, (○) $[\text{MEK}] = 0.2966$, (●) $[\text{acetone}] = 0.3032M$.

value (0.5) under the present experimental conditions can be attributed to the generation of an excess of primary radicals, which leads to premature termination of the growing chains and furthermore causes the oxidative termination rate of primary radicals by Ce(IV) to be relatively higher than at lower concentrations of reducing agents. The steep fall of R_p at higher concentrations of reducing agents may be due to the cage effect,^{10,28} which is also observed with R_{Ce} at higher reducing agent concentrations (Figs. 6 and 8).

In the present study the order with respect to Ce(IV) for MMA polymerization using the Ce(IV)–MEK initiator system is found to be 0.23. 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.²⁹ Addition of sodium sulfate to the reaction medium to maintain constant SO_4^{2-} concentration can bring a fall in R_p in the aforementioned reaction system, and the reaction rate under such conditions is proportional to $[\text{Ce(IV)}]^{0.27}$ (Fig. 7). The rate for MMA polymerization when Ce(IV)–acetone is used as the initiator is found to be independent of $[\text{Ce(IV)}]$ (Fig. 7), which indicates that the rate of initiation is negligible compared to the rate of oxidative termination in this reaction system. Addition of sodium sulfate to maintain constant $[\text{SO}_4^{2-}]$ in the reaction medium can bring about an increase in R_p up to the concentration of Ce(IV) $\leq 0.003M$ for the reaction system using Ce(IV)–acetone as the initiator. At higher

concentrations of Ce(IV) the rate remains constant (Fig. 7).

In solution of ceric ammonium sulfate in sulfuric acid (0.1M), the ceric species might be the covalently bound neutral ceric sulfate molecule, $\text{Ce}(\text{SO}_4)_2$, and the following equilibria are recognized^{10,30}:



The increase of rate with increase of $[\text{Na}_2\text{SO}_4]$ may be due to an increase in the concentration of $\text{Ce}(\text{SO}_4)_2$ by operation of the equilibria of Eqs. (1a) and (1b). Hence, the rise in R_p for the Ce(IV)–acetone system for MMA polymerization could be obtained. With the Ce(IV)–MEK initiator for MMA polymerization the addition of sodium sulfate to maintain constant $[\text{SO}_4^{2-}]$ in the reaction medium could bring about decrease in R_p values. This deviation in observation may be due to the specific solvent interactions caused by the reducing agents in these reaction systems.

The order with respect to monomer for MMA polymerization using Ce(IV)–MEK as the initiator is found to be 1.29, indicating that initiation is more pronounced than oxidative termination of primary radicals. The order with respect to $[\text{MMA}]$ using Ce(IV)–acetone as the initiator is 1.64, which supports the linear termination of growing chains as well as bimolecular termination of the growing chains. The higher order with respect to monomer also gives support to the complex nature of the initiation reactions involving monomer molecules as participating reactions to generate initiating free

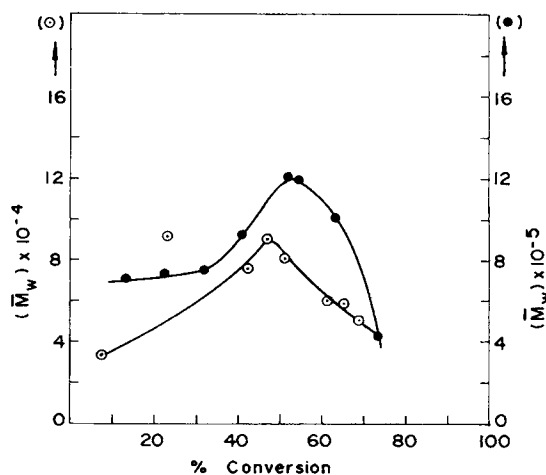
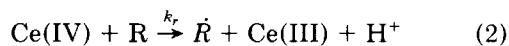


Figure 12 \bar{M}_w versus % conversion. $[\text{Ce(IV)}] = 0.003M$, $[\text{MMA}] = 0.08788M$, $[\text{H}_2\text{SO}_4] = 0.1M$, (●) $[\text{MEK}] = 0.2966$, (○) $[\text{acetone}] = 0.3032M$, $T = 30^\circ\text{C}$.

radicals.³¹ The overall activation energies, E_{overall} , under the present experimental conditions for MMA polymerization are found to be 3.80 and 10.17 kcal/mol with Ce(IV)–MEK and Ce(IV)–acetone as initiator systems, respectively; these are of the same order as those found in the literature.^{20,21,29,32–34}

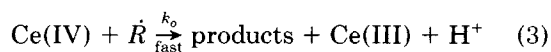
The following reaction scheme explains satisfactorily the kinetic results obtained:

Reaction of ceric ion with reducing agent

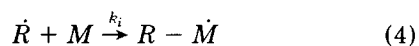


where R is the reducing agent and \dot{R} is a primary radical.

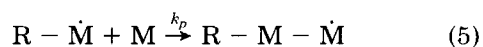
Reaction of primary radical with Ce(IV) to give the product



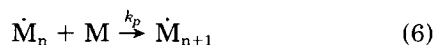
Initiation



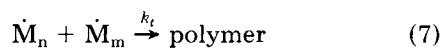
Propagation



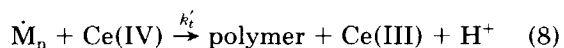
⋮



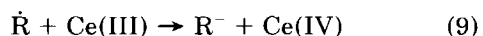
Bimolecular termination



Monomolecular termination with Ce(IV) (linear termination)



A possible alternative to Eq. (3)



Equation 9 may arise especially from a consideration of products of Eq. (2) still in the solvent cage, which means competition for \dot{R} between Ce(IV) and Ce(III). Occurrence of such a step would mean a decrease in the rate of ceric ion disappearance with time, which is the case at higher concentrations of reducing agents in the present study (Figs. 2, 3, and 6).

Making the usual assumptions for the steady-state concentrations of free radicals (primary and chain) and with the rate constants being indepen-

dent 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 were derived:

$$R_{\text{Ce}} = \frac{-d[\text{Ce(IV)}]}{dt} = k_r[\text{Ce(IV)}][\text{R}] \quad (10)$$

$$R_p = \frac{-d[\text{M}]}{dt} = \frac{k_p[\text{M}]^{3/2}}{k_t^{1/2}} \left\{ \frac{k_i k_r [\text{R}][\text{Ce(IV)}]}{k_i[\text{M}] + k_o[\text{Ce(IV)}]} \right\}^{1/2} \quad (11)$$

Under the present experimental situation, if the condition $k_i[\text{M}] \gg k_o[\text{Ce(IV)}]$ obeys, then eq. (11) reduces to

$$R_p = k_p(k_r/k_t)^{1/2}[\text{Ce(IV)}]^{1/2}[\text{R}]^{1/2}[\text{M}] \quad (12)$$

On the other hand, if under the present experimental conditions the situation is $k_o[\text{Ce(IV)}] \gg k_i[\text{M}]$, then eq. (11) reduces to

$$R_p = (k_p/k_t^{1/2})(k_i/k_o)^{1/2}k_r^{1/2}[\text{R}]^{1/2}[\text{M}]^{3/2} \quad (13)$$

Molecular weight increased with the progress of polymerization and fell at higher conversions, after 51.8 and 46.7% conversions using Ce(IV)–MEK and Ce(IV)–acetone as initiator systems, respectively. The polymerization of MMA in aqueous medium initially follows homogeneous polymerization kinetics, situated in the aqueous medium; then emulsion polymerization kinetics for some period 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 pseudohomogeneous-type reaction situated in the insoluble phase, with coarse particles. The aforementioned type of kinetics can have an effect on the molecular weight of the polymer, which varies with percent conversion. During the intermediate stage for the polymerization inside the charge-stabilized discrete particles to which most of the monomer transferred from the aqueous medium, the bimolecular termination rate is slow between the growing primary radicals because their availability in these particles is lower. 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 become coagulated to coarse particles. These are large enough to permit the coexistence of more than one

primary radical inside the particle; hence, the termination rate is higher, which can lower the molecular weight. In the present study the degree of polymerization with the Ce(IV)–MEK initiator system is higher than with the Ce(IV)–acetone initiator system (Fig. 12, Table I), which indicates that bimolecular termination is taking place more with the Ce(IV)–MEK initiator system compared to Ce(IV)–acetone initiator system. This may also be due to the premature termination of growing chains by primary radicals with the latter initiator system.

Evaluation of Rate Constants

In the present study, $R_{Ce} = k_r[\text{Ce(IV)}][\text{R}]^{0.5}$. By plotting R_{Ce} versus $[\text{Ce(IV)}]$, we can get $k_r[\text{R}]^{0.5}$ as the slope from which k_r is evaluated (Fig. 1, Table II). When there is a dependence of R_p on $[\text{Ce(IV)}]$, Eq. (11) can be rearranged in the following form:

$$[\text{M}]^2/R_p^2 = \frac{k_i}{k_p^2 k_r [\text{R}][\text{Ce(IV)}]} + \frac{k_i k_o}{k_p^2 k_i k_r [\text{R}][\text{M}]} \quad (14)$$

and plotting $[\text{M}]^2/R_p^2$ versus $1/[\text{Ce(IV)}]$, the rate constants ratio (k_i/k_o) and ($k_p/k_i^{1/2}$) can be evaluated (Fig. 13, Table II). The values of rate constants for MMA polymerization using Ce(IV)–MEK as the initiator are comparable with the values already reported.^{10,29,35}

CONCLUSIONS

In the present study the rate of ceric ion consumption shows first-order dependence on $[\text{Ce(IV)}]$ and 0.5-order dependence on reducing agent concentration. An absence of complex formation between Ce(IV) and reducing agent is observed with both the initiator systems, Ce(IV)–MEK and Ce(IV)–acetone, in the present study. A fall in R_{Ce} values is observed at higher concentrations of reducing agents for both the initiator systems. This fall in R_{Ce} is

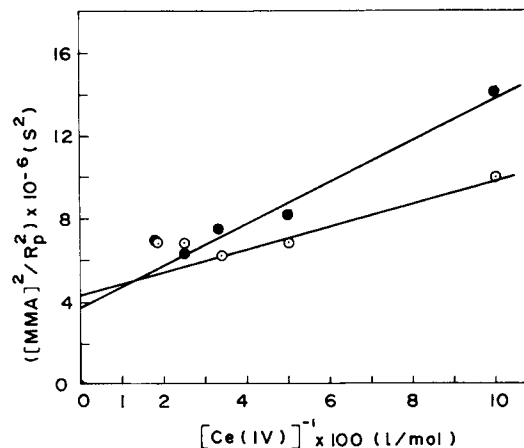


Figure 13 $([\text{MMA}]^2/R_p^2)$ versus $[\text{Ce(IV)}]^{-1}$. $[\text{MMA}] = 0.08788M$, $[\text{MEK}] = 0.29665M$, $[\text{H}_2\text{SO}_4] = 0.1M$, (●) $[\text{SO}_4^{2-}] = 0.122M$, $T = 30^\circ\text{C}$.

attributed due to cage effect at higher concentrations of reducing agents. The lower order (0.23) with respect to $[\text{Ce(IV)}]$ for MMA polymerization using the Ce(IV)–MEK initiator system is attributed to the simultaneous effect of ceric ion on the initiation rate and on the oxidative termination rate of primary radicals. Addition of sodium sulphate to the reaction medium to maintain constant $[\text{SO}_4^{2-}]$ could cause a fall in R_p values in the aforementioned reaction system. Zero-order dependence on $[\text{Ce(IV)}]$ for MMA polymerization using the Ce(IV)–acetone initiator system is observed. The lower order with respect to $[\text{MEK}]$ (0.20) and $[\text{acetone}]$ (0.42) may be due to the premature termination of growing radicals by primary radicals, and also to the rise in the oxidative termination rate at higher concentrations of reducing agents. The steep fall in R_p at higher concentrations of reducing agents is attributed to the cage effect. The higher order with respect to monomer (1.64) when Ce(IV)–acetone is used as the initiator may be due to simultaneous occurrence of linear termination as well as bimolecular termination. The molecular weight variation with percent conversion shows dependence on the loci of polymerization.

Table II Rate Parameters for the Polymerization of MMA at 30°C

Initiator System	$k_r \times 10^3$ (L mol s)	(k_i/k_o)	$(k_p/k_i^{1/2})$ ($\text{L}^{1/2} \text{mol}^{1/2} \text{s}^{1/2}$)
Ce(IV)–MEK	1.7485	0.0130	0.6067
Ce(IV)–MEK, with constant $[\text{SO}_4^{2-}]$ in the reaction medium	0.540	0.0299	0.7901

Initially, homogeneous polymerization takes place in the aqueous phase; in the next stage polymerization occurs in charge-stabilized discrete particles similar to emulsion polymerization. Finally, pseudohomogeneous-type polymerization takes place in coarse suspension. This type of polymerization can bring a change in molecular weight with percent conversion. The molecular weight of the polymer obtained with the Ce(IV)-MEK initiator system is higher than that of the polymer obtained with the Ce(IV)-acetone initiator system. This may be due to the occurrence of more bimolecular termination with the Ce(IV)-MEK initiator system compared to the Ce(IV)-acetone initiator system. The energies of activation for MMA polymerization using Ce(IV)-MEK and Ce(IV)-acetone initiator systems under the present experimental conditions in the temperature range 27–40°C are in accordance with the literature values.

REFERENCES

1. T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).
2. V. S. Ananthanarayanan and M. Santappa, *J. Appl. Polym. Sci.*, **9**, 2437 (1965).
3. G. Renders, G. Broze, R. Jerome, and Ph. Teyssie, *J. Macromol. Sci., Chem.*, **A16**(8), 1399 (1981).
4. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polym. Sci.*, **38**, 393 (1959).
5. A. A. Katai, V. K. Kulshrestha, and R. H. Machessault, *J. Polym. Sci., Part C*, **2**, 401 (1963).
6. T. A. Turney, *Oxidation Mechanisms*, Butterworths, London, 1965, p. 42.
7. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959).
8. J. Shorter, *J. Chem. Soc.*, 1868 (1962).
9. G. G. Guilbault and W. H. McCurdy, *J. Phys. Chem.*, **67**, 283 (1963).
10. S. V. Subramanian and M. Santappa, *J. Polym. Sci., Part A*, **1**, 493 (1968).
11. M. D. Fernandez and G. M. Guzman, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 2427 (1989).
12. F. M. B. Coutinho, M. J. O. C. Guimaraes, and A. S. Gomes, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 2131 (1986).
13. K. Qiu, X. Guo, D. Zhang, and X. F. Chin, *J. Polym. Sci.*, **9**(2), 145 (1991).
14. A. Goemen and B. Basaran, *Acta Polym.*, **42**(12), 675 (1991).
15. E. S. Lee, J. H. Shin, and S. Mah, Han'guk Somyu Konghakhoechi, **24**, 1 (1987); *Chem. Abstr.*, **107**, 134722y.
16. N. K. Chakrabarty and A. K. Chaudhuri, *J. Macromol. Sci., Chem. Ed.*, **A22**, 1691 (1985).
17. M. D. Fernandez and G. M. Guzman, *Br. Polym. J.*, **21**, 413 (1989).
18. M. D. Fernandez and G. M. Guzman, *Br. Polym. J.*, **22**, 1 (1990).
19. M. D. Fernandez and G. M. Guzman, *Makromolek. Chem. Macromolec. Symp. (International Symposium Polymer Materials, 1987)* **20/21**, 91 (1988).
20. G. V. Ramana Reddy, M. V. Vmamaheeswari, V. Vidya, and V. Krishnaswamy, *Polym. International*, **34**, 279 (1994).
21. G. V. Ramana Reddy, R. Chandraganthi, K. Vasanthi, and R. Sriram, *J. Macromol. Sci., Pure Appl. Chem.*, **A32**(12), 1997 (1995).
22. C. M. Patra and B. C. Singh, *J. Appl. Polym. Sci.*, **52**(11 & 12), 1557 (1994).
23. M. Gurruchaga, I. Goni, M. Valero, and G. M. Guzman, *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 21 (1984).
24. M. Gurruchaga, I. Goni, M. B. Vazquez, M. Valero, and G. M. Guzman, *J. Polym. Sci., Part C*, **27**, 149 (1989).
25. S. Nagarajan and K. S. V. Srinivasan, *Eur. Polym. J.*, **30**(1), 113 (1994).
26. H. K. Das and B. C. Singh, *J. Appl. Polym. Sci.*, **49**(6), 1107 (1993).
27. S. Krause and K. E. Cohn-Ginsberg, *J. Phys. Chem.*, **67**, 1479 (1963).
28. M. S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).
29. M. D. Fernandez and G. M. Guzman, *J. Polym. Sci., Polym. Chem.*, **27**, 3703 (1989).
30. S. S. Muhammed and K. Vijayachander Rao, *Bull. Chem. Soc. Japan*, **36**, 944 (1963).
31. G. Odian, *Principles of Polymerization*, John Wiley & Sons, New York, 1981, p. 205.
32. W. M. Thomas, E. H. Gleason, and G. Mino, *J. Polym. Sci.*, **24**, 43 (1957).
33. D. H. Grant and N. Grassie, *Trans. Faraday Soc.*, **55**, 1042 (1959).
34. D. Pramanick and A. K. Chatterjee, *Eur. Polym. J.*, **17**, 239 (1981).
35. A. Jayakrishnan, M. Haragopal, and V. Mahadevan, *J. Polym. Sci., Polym. Chem.*, **19**, 1147 (1981).

Received September 12, 1995

Accepted March 11, 1996