

## Kinetics of Vinyl Polymerization Initiated by Ceric Ion in Aqueous Solution

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### Synopsis

A systematic kinetic study of the thermal polymerization of methyl methacrylate, methyl acrylate, and acrylonitrile initiated by ceric ion in aqueous perchloric, nitric, and sulfuric acid solutions, has been made. The polymerization experiments were conducted in the dark at 35°C. under conditions of negligible oxidation of water by ceric ion. The polymerization was found to proceed without an induction period, and the steady-state rate was attained in a short time. The rate of monomer disappearance (followed by gravimetry) was found to bear a square dependence on monomer concentration and is independent of both the ceric and hydrogen ion concentrations. The rate of ceric disappearance (followed by titrimetry or spectrophotometry) was found to be directly proportional to the ceric, monomer, and hydrogen ion concentrations. The chain lengths of the polymers (determined viscometrically) were directly proportional to the monomer concentration and inversely to the ceric and hydrogen ion concentrations. Initially added cerous ion had negligible effect on the rates. Increase in ionic strength caused a slight increase in the rates. From experiments conducted at different temperatures, the activation energies for the various processes in the reaction were calculated. Most of the experimental results were suitably explained by a kinetic scheme involving initiation and termination by ceric ion in the unhydrolyzed  $Ce^{4+}$  form.

### INTRODUCTION

The thermal and photochemical reactions involving quadrivalent cerium in aqueous solution have been the subject of considerable research. Ceric salts have been employed for the oxidation of a wide variety of inorganic as well as organic substrates. That ceric ions also initiate polymerization of vinyl monomers has been reported by Bacon.<sup>1</sup> Saldick<sup>2</sup> has made a qualitative study of the initiating capacities of ceric ion in different acid media. Venkatakrisnan and Santappa<sup>3</sup> have studied to some extent the kinetics of ceric ion-initiated polymerization of methyl acrylate. The ceric-alcohol redox systems have been used for studies on kinetics of vinyl polymerization by Lalitha and Santappa.<sup>4</sup> Mino, Kaizermann, and Rasmussen<sup>5</sup> have studied the kinetics of polymerization of acrylamide using the ceric nitrate-3-chloro-1-propanol redox system. More recently, the kinetics of polymerization of acrylonitrile initiated by the ceric sulfate-ethylene glycol redox system has been investigated by Katai, Kul-

shrestha, and Marchessault.<sup>6</sup> The radicals produced by decomposition of the ceric-alcohol complex have been shown to be responsible for initiating the polymerization in these redox systems. However, studies on polymerization by ceric ions alone with no reducing agent, have been scanty. One may even generalize that these studies on vinyl polymerization initiated by oxidizing agents alone have received little attention. Apart from their practical applications, such studies, it is obvious, have a fundamental importance in understanding the reactions of the oxidizing agents, especially the metal ions, in solution. With this end in view, we carried out a systematic kinetic study of thermal polymerization of methyl methacrylate, methyl acrylate, and acrylonitrile initiated by ceric ion in various acids, perchloric, nitric, and sulfuric. A brief account of this study was recently reported by the authors.<sup>7</sup>

## EXPERIMENTAL

### Reagents

Methyl methacrylate and methyl acrylate monomers were Rohm and Haas products while acrylonitrile was obtained from American Cyanamid Co. The monomers were purified by standard methods, distilled repeatedly in an atmosphere of nitrogen, and stored at 5°C. Water which had been doubly distilled over alkaline permanganate in a Pyrex all-glass set-up and passed through the ion exchange resin Biodiminrolit, was used for the preparation of reagents and solutions. Ceric perchlorate was obtained from G. Frederick Smith Chemical Company (U.S.A.), as a 0.65*M* solution in 2*M* perchloric acid. Cerous perchlorate was prepared from cerous carbonate supplied by the Atomic Energy Establishment, Trombay, India. Ceric ammonium nitrate and ceric ammonium sulfate were B. D. H. Analar products. Perchloric acid was E. Merck, Guaranteed Reagent grade containing ca. 60% HClO<sub>4</sub>, while nitric and sulfuric acids were A. R. grades from Basic Synthetic Chemicals, India. Sodium perchlorate used for adjustment of ionic strength in perchloric acid solutions was prepared by mixing equimolar volumes of perchloric acid and A.R. sodium hydroxide. Sodium nitrate and sodium hydrogen sulfate, A.R. grades, were used in nitric and sulfuric acid media, respectively, for adjusting ionic strength. Other reagents like ferrous ammonium sulfate, *o*-phenanthroline, brucine, sodium thiosulfate, potassium hydrogen phthalate etc., were mostly B. D. H. Analar or E. Merck G. R. products. Solvents, such as benzene, acetone, dimethylformamide, and methanol, were distilled before use. Deaeration of the system was done either by high vacuum or by nitrogen freed from oxygen by Fieser's solution.

### Estimations

Ceric ion concentration ( $>5 \times 10^{-3}M$ ) in stock ceric solution was estimated by titration against standardized ferrous sulfate solution. For lower ceric concentrations ( $5 \times 10^{-5}$ – $5 \times 10^{-3}M$ ), an excess of ferrous

sulfate was added to the ceric solution and the  $\text{Fe}^{3+}$  produced ( $\equiv\text{Ce}^{4+}$ ) estimated by its absorption at  $304\text{ m}\mu$  with the use of a Hilger Uvispek spectrophotometer, H-700. The brucine method<sup>8</sup> was employed for estimation of low ceric ion concentration, especially in studying the effects of hydrogen ion concentration, ionic strength etc., on the rate of ceric disappearance. The acid content of the ceric solution was estimated with standard alkali after reduction and removal of the ceric ion as cerous oxalate. Cerous salts were estimated after oxidation to the ceric state.

### Experimental Set-Up and Procedure

The reaction vessel was a 100-ml. Pyrex conical flask fitted with a B-24 socket carrying a B-24 cone with an inlet and outlet tube for nitrogen. The inlet tube was provided with a B-14 socket at its end, while the outlet tube carried a B-14 cone, so that two vessels could be deaerated side by side, the first vessel containing a blank solution of the same monomer concentration (but without the initiator) as in the reaction mixture contained in the second. This served to minimize any loss of monomer from the reacting mixture during deaeration.

In a typical experiment, the reaction mixture consisting of the appropriate quantities of monomer, acid, ceric solution, and the neutral salt solution, was deaerated in the dark for 20–30 min. under ice-cold conditions. The reaction vessel was then disconnected from the duplicate vessel, after closing the outlet and inlet tubes by means of Pyrex vacuum stopcocks and kept inside a thermostat ( $35 \pm 0.1^\circ\text{C}$ . maintained by a toluene regulator and a Sunvic hot wire vacuum switch relay). The thermostat was a circular glass trough (12 in. diameter, 6 in. depth) standing on a magnetic stirrer and housed in a dark chamber. (The induction period in all cases was found negligible.) After the specified time, the reaction was arrested by addition of excess ferrous solution; the polymer was filtered off, washed well with water, and dried to constant weight under vacuum or in an air oven at  $50\text{--}60^\circ\text{C}$ ., and from the weight of the polymer, the rate of monomer disappearance was calculated.

The rates by gravimetric method and by bromometric method of estimation of the residual monomer concentration were identical within limits of experimental error. The rate of ceric disappearance was calculated from the final concentration of the ceric ion (determined by titrimetry or spectrophotometry or colorimetry) in the filtrate after removal of the polymer. The chainlengths of the purified polymers were determined viscometrically by using the appropriate Mark-Houwink relationships. The viscosity measurements were made with the P.C.L.-Ubbelohde suspended level dilution viscometer in Kreb (U.S.A.) viscometric bath with a temperature control of  $\pm 0.01^\circ\text{C}$ . For the unfractionated polymers eqs. (1)–(3) were employed.

For poly(methyl methacrylate) in benzene,  $25^\circ\text{C}$ .:<sup>9</sup>

$$n = 2.81 \times 10^3 [\eta]^{1.32} \quad (1)$$

For poly(methyl acrylate) in acetone, 25°C.:<sup>10</sup>

$$n = 11.2 \times [\eta]^{1.22} \quad (2)$$

For poly(acrylonitrile) in dimethylformamide, 25°C.:<sup>11</sup>

$$[\eta] = 2.34 \times 10^{-4} (\bar{M}_v)^{0.75} \quad (3)$$

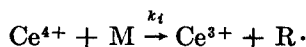
## RESULTS AND DISCUSSION

The polymerization was inhibited by oxygen, hydroquinone, and phenol, thus indicating the free radical nature of the reaction. The rates did not vary with the type of vessel used, showing the absence of any heterogeneous effects. The rates were enhanced markedly if the system was exposed to diffused daylight. Rates of polymerization in the three acid media increased in the order  $\text{HClO}_4 > \text{HNO}_3 > \text{H}_2\text{SO}_4$ , and therefore ran parallel to oxidation potentials of the  $\text{Ce}^{4+}$ - $\text{Ce}^{3+}$  couple in the respective acids, viz., 1.71, 1.61, and 1.44. The experiments with methyl methacrylate and acrylonitrile were carried out under stirred conditions, while with methyl acrylate, firm adherence of the polymer on to stirring element necessitated our adopting unstirred conditions only. With the former two monomers, the rates under unstirred conditions were found to be greater than those under stirred conditions. This may be due to the greater probability of encounters between the chain radicals and the terminating agent under the stirred conditions. The polymerization was found to take place without an induction period, and the steady-state rate was attained within a short time. A preliminary study of the oxidation of water by ceric ion was made under diverse conditions of ceric ion concentration, acidity, temperature etc., so as to arrive at conditions under which there is negligible oxidation of water and production of hydroxyl radicals, which would complicate the polymerization reaction initiated by ceric ions. It is to be noted that a wide variety of species can exist in solutions of ceric ion, depending on the experimental conditions.<sup>12-14</sup> The majority of our experiments were carried out in perchloric acid medium under conditions of low ceric and high acid concentrations, where, according to Hardwick and Robertson,<sup>12</sup> only  $\text{Ce}^{4+}$  and  $\text{Ce}^{4+}\text{OH}^-$  species are considered to be present. A few experiments were carried out in nitric and sulfuric acid media for comparison purposes.

### Kinetic Scheme

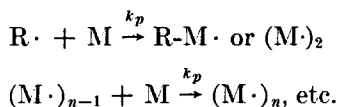
The following sequence of reactions appears to be the most probable to explain our results.

Initiation:

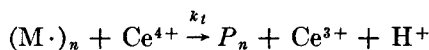


(where  $\text{R} \cdot$  may be a radical ion)

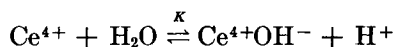
Propagation:



Termination:



The hydrolytic equilibrium:



Using the steady-state assumption for the radical concentrations and also the principle of nonvariation of the rate constants with the size of the polymer radical, we arrive at the equations (4), (5), and (6) for rate of ceric disappearance, rate of monomer disappearance, and chain length  $n$ , respectively.

$$-d[\text{ceric}]/dt = 2k_t[M][Ce^{IV}]_T[H^+]/(K + [H^+]) \quad (4)$$

where

$$[Ce^{IV}]_T = [Ce^{4+}]_{\text{eq}} + [Ce^{4+}OH^-]_{\text{eq}}$$

= total ceric concentration

$$-d[M]/dt = (k_t k_p / k_i) [M]^2 \quad (5)$$

$$n = (k_p / k_t) ([M] / [Ce^{IV}]_T [H^+]) (K + [H^+]) \quad (6)$$

### Rate of Ceric Disappearance

In conformity with eq. (4), it was experimentally observed that the rate of ceric disappearance was directly proportional to ceric, monomer, and hydrogen ion concentrations in the case of all the three monomers in perchloric and nitric acid media. The changes in rates in sulfuric acid medium were too low to be accurately determined. The plots of rate versus ceric concentration are linear (Fig. 1.). The first-order dependence on ceric concentration precludes the possibility of the dimeric or polymeric ceric species like  $(Ce-O-Ce)^{6+}$ ,  $(OH-Ce-O-Ce-OH)^{4+}$  etc., having any significant role in the reaction, since higher orders should be expected in such cases. The order with respect to monomer concentration was found to be unity, as seen from the linear plots of rate versus monomer concentration  $[M]$  (Fig. 2). For methyl acrylate and acrylonitrile, the intercepts of the lines on the  $y$  axis are negligible; for methyl methacrylate however, the intercept is found to be rather large. This may arise due to any one of the following reasons: (a) simultaneous initiation by hydroxyl radicals; (b) a side reaction involving oxidation of the monomer by ceric ion, the reaction being assumed to be independent of monomer concentration; (c) a side reaction involving oxidation of the impurities in the mono-

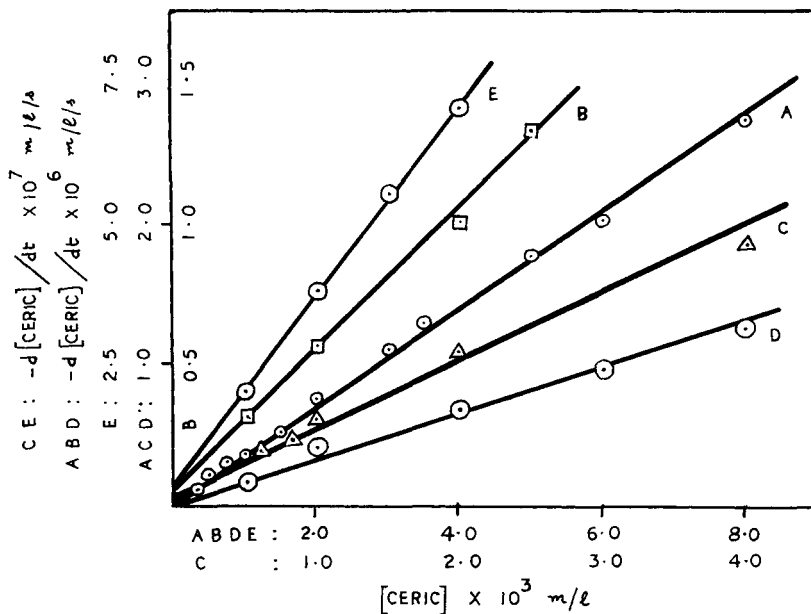


Fig. 1. Dependence of rate of ceric disappearance on ceric ion concentration: (A) methyl acrylate, perchloric acid medium,  $[\text{M}] = 0.221$  mole/l.; (B) methyl acrylate, nitric acid medium,  $[\text{M}] = 0.442$  mole/l.; (C) acrylonitrile, perchloric acid medium,  $[\text{M}] = 0.745$  mole/l.; (D) methyl methacrylate, perchloric acid medium,  $[\text{M}] = 0.094$  mole/l.; (E) methyl methacrylate, nitric acid medium,  $[\text{M}] = 0.1128$  mole/l.

mer by ceric ion. Under our experimental conditions, there is practically no oxidation of water by ceric ion and hence production of hydroxyl radicals by this means is negligible. Further, initiation by hydroxyl radicals would require the presence of hydroxyl endgroups in the poly(methyl methacrylate) obtained, for which we have only negative evidence from the dye-partition test<sup>15</sup> as well as the infrared spectrum of the polymer. There seems to be no considerable oxidation of the monomer by ceric ion, since both gravimetric and volumetric determinations of the rates of polymerization were found to agree within limits of experimental error. The possibility of oxidation of the impurities in the monomer by ceric ion receives some support from the evidences in literature<sup>16,17</sup> where impurities present in the polymerization systems have been shown to affect the determination of reaction rates. However, the magnitude of the intercept in Figure 2 for methyl methacrylate is rather too great to be explained by this argument alone. The fact that the rate in the case of all the three monomers increased with monomer concentration goes strongly against initiation by hydroxyl radicals (from water oxidation), which would require the rate to be independent of the monomer concentration. We may therefore conclude that the initiation takes place by a direct reaction between the monomer and ceric ion. This may probably involve an electron transfer

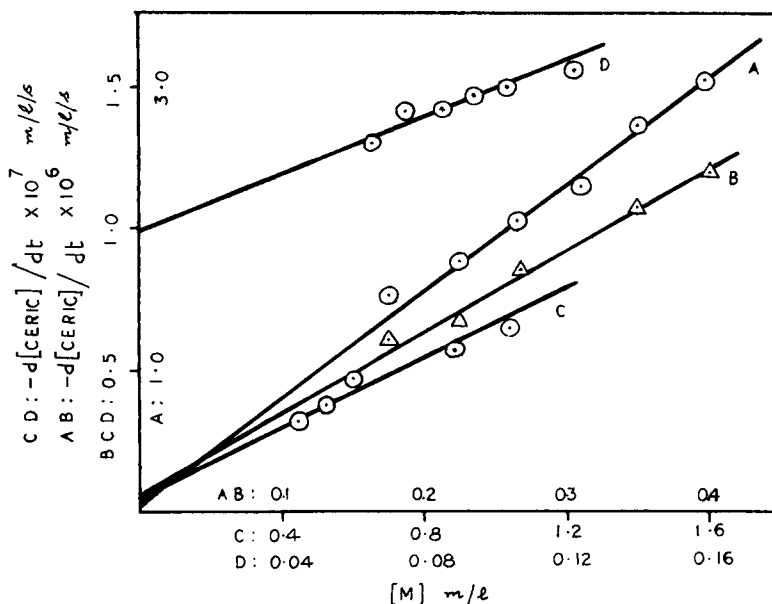


Fig. 2. Dependence of rate of ceric disappearance on monomer concentration: (A) methyl acrylate, perchloric acid medium,  $[\text{ceric}] = 5 \times 10^{-3}$  mole/l.; (B) methyl acrylate, nitric acid medium,  $[\text{ceric}] = 5 \times 10^{-3}$  mole/l.; (C) acrylonitrile, perchloric acid medium,  $[\text{ceric}] = 1 \times 10^{-3}$  mole/l.; (D) methyl methacrylate, perchloric acid medium,  $[\text{ceric}] = 1 \times 10^{-3}$  mole/l.

from the former to the latter, producing a radical-ion of the type  $\dot{\text{C}}\text{H}_2 - \dot{\text{C}}\text{HX}$ , which is similar to the one proposed by Bawn and Sharp<sup>18</sup> in the oxidation of olefins by cobaltic ion. The direct dependence of the rate on monomer concentration has also been observed in the studies with ceric-reducing agent redox systems.<sup>4,6</sup> An insight into the nature of the ceric species which is responsible for initiation can be had from the manner of dependence of the ceric rate on hydrogen ion concentration. If  $\text{Ce}^{4+}$  is the active species, the reciprocal rate should be linear with respect to reciprocal  $[\text{H}^+]$  [eq. (4), Fig. 3], whereas the rate is inversely proportional to the hydrogen ion concentration if  $\text{Ce}^{4+}\text{OH}^-$  initiates. The increase in the rate with increasing hydrogen ion concentration has also been reported in many oxidation<sup>19,20</sup> as well as polymerization<sup>3,5,6</sup> reactions involving ceric ions.

### Rate of Monomer Disappearance

The rate of monomer disappearance was found to bear a square dependence on the monomer concentration (Fig. 4) and to be independent of either the ceric ion ( $1 \times 10^{-2}$ – $1 \times 10^{-3}M$ ) or hydrogen ion (0.1–1.6M) concentration in the case of all the three monomers in perchloric, nitric, and sulfuric acid media. A second-order dependence of the rate on

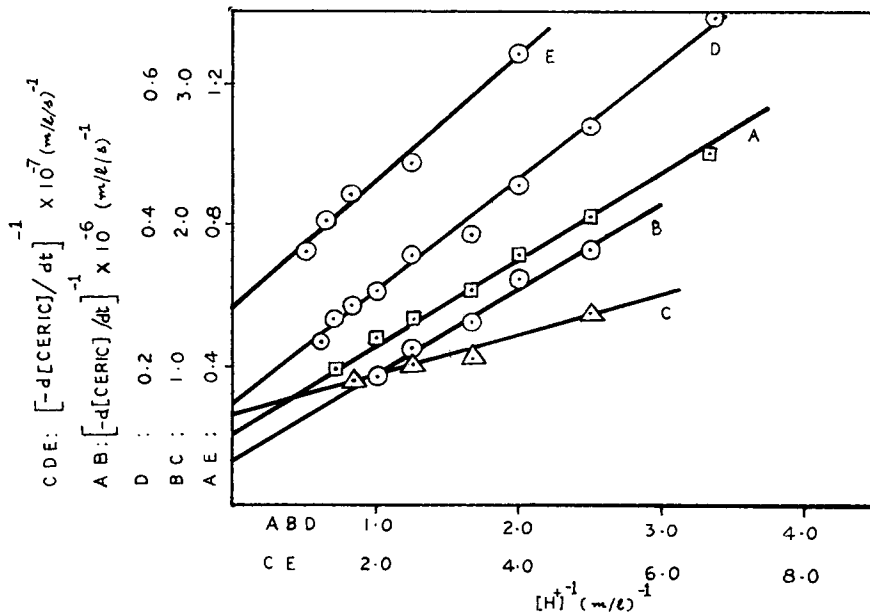


Fig. 3. Effect of hydrogen ion concentration on rate of ceric disappearance: (A) methyl acrylate, perchloric acid medium, [ceric] =  $5 \times 10^{-3}$  mole/l.; [M] = 0.221 mole/l.; (B) methyl acrylate, nitric acid medium, [ceric] =  $5 \times 10^{-3}$  mole/l.; [M] = 0.354 mole/l.; (C) acrylonitrile, perchloric acid medium, [ceric] =  $1 \times 10^{-3}$  mole/l., [M] = 0.745 mole/l.; (D) methyl methacrylate, perchloric acid medium, [ceric] =  $1.34 \times 10^{-3}$  mole/l., [M] = 0.1128 mole/l.; (E) methyl methacrylate, nitric acid medium, [ceric] =  $5 \times 10^{-4}$  mole/l., [M] = 0.1128 mole/l.

monomer concentration was observed at both low ( $5 \times 10^{-4}M$ ) and high ( $5 \times 10^{-3}M$ ) ceric ion concentrations. This fact is of great significance, since it completely rules out the case of termination in our system by mutual type which would require an order of three halves for the monomer concentration. On the other hand, if the initiation and termination processes are effected by ceric ions, as assumed in the kinetic scheme given, the second-order dependence is easily reconciled. Having established earlier the initiation by  $Ce^{4+}$  ions, if now the termination of the radicals is by the  $Ce^{4+}OH^{-}$  species, the rate of monomer disappearance should increase with hydrogen ion concentration, whereas it should be independent of the latter when  $Ce^{4+}$  ion acts as the terminating agent. The experimental findings, therefore, support initiation and termination by the  $Ce^{4+}$  ion. The nondependence of the rate on the ceric ion concentration lends additional support to this conclusion. Termination by metal ions, in complete preference to the mutual type, has been observed in many similar cases of polymerization reactions.<sup>5,6,21-23</sup> In particular, termination by ceric ion has been proved by Dainton and co-workers<sup>23</sup> in the  $\alpha$ -ray-initiated polymerization of acrylamide in the presence of ceric ion, by Mino et al.<sup>5</sup> in the ceric nitrate-3-chloro-1-propanol-acrylamide system, and by Katai et al.<sup>6</sup> in the ceric sulfate-ethylene glycol-acrylonitrile system.



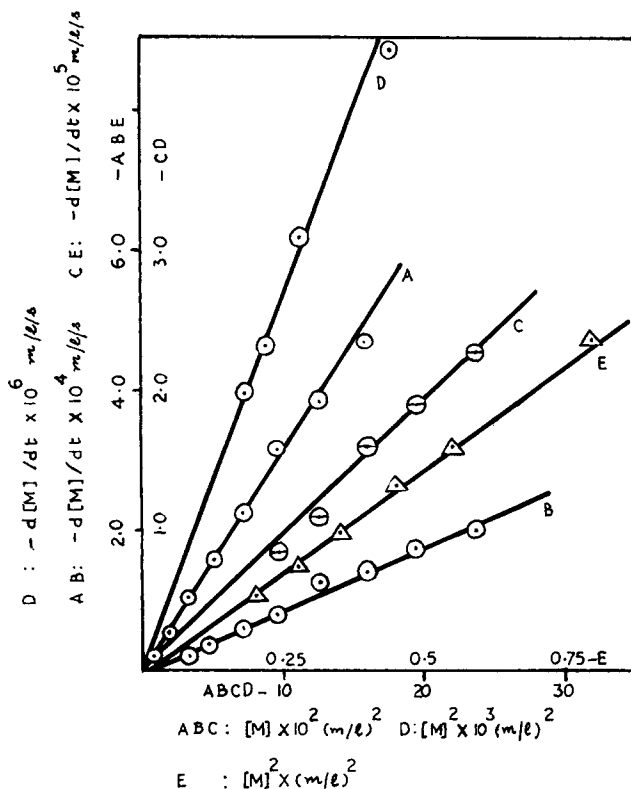


Fig. 4. Dependence of rate of monomer disappearance on monomer concentration: (A) methyl acrylate, perchloric acid medium,  $[\text{ceric}] = 5 \times 10^{-3}$  mole/l.; (B) methyl acrylate, nitric acid medium,  $[\text{ceric}] = 5 \times 10^{-3}$  mole/l.; (C) methyl acrylate, sulfuric acid medium,  $[\text{ceric}] = 5 \times 10^{-3}$  mole/l.; (D) methyl methacrylate, nitric acid medium,  $[\text{ceric}] = 2 \times 10^{-3}$  mole/l.; (E) acrylonitrile, perchloric acid medium,  $[\text{ceric}] = 1 \times 10^{-3}$  mole/l.

The effect of initially added cerous ion on the rates of ceric and monomer disappearance was studied up to a  $[\text{cerous}]/[\text{ceric}]$  ratio of 10. No significant change in either of the rates was noticed, indicating the negligible effect of  $\text{Ce}^{4+}-\text{Ce}^{3+}$  redox equilibrium. Increase in the ionic strength of the medium over a range of 0.5–1.6M was found to cause a slight increase in both the rates. This observation is similar to that by Mino et al.<sup>5</sup> However, it is difficult to attribute this increase to any specific reason in view of the complicated nature of the system under study. The rates of monomer and ceric disappearance were measured at different temperatures (25–45°C.) under various monomer and hydrogen ion concentrations and the values of  $k_t$  and  $k_p/k_t$  calculated in each case by use of eqs. (4)–(6). These values at 35°C. for the three monomers are collected in Table I, while the values for  $E_t$  and  $E_p-E_t$  are given for methyl methacrylate and methyl acrylate in Table II.

TABLE I  
 Rate Constants

Monomer	Medium	Tempera-	$k_i$	$k_p/k_t$
		ture, °C.		
Methyl acrylate	HClO <sub>4</sub>	35	$1.886 \times 10^{-3}$	1.697
" "	HNO <sub>3</sub>	35	$6.59 \times 10^{-4}$	1.109
Methyl methacrylate	HClO <sub>4</sub>	35	$3.12 \times 10^{-3}$	0.144
" "	HNO <sub>3</sub>	45	$1.591 \times 10^{-3}$	0.1797
Acrylonitrile	HClO <sub>4</sub>	35	$6.087 \times 10^{-6}$	54.21

 TABLE II  
 Effect of Temperature (Medium: Perchloric Acid)

Monomer	Temper-	$k_i$	$k_p/k_t$	$E_i$	$E_p - E_t$
	ature, °K.				
Methyl methacrylate	308	$3.12 \times 10^{-3}$	0.1351	14.88	6.866
" "	313	$4.728 \times 10^{-3}$	0.1692		
" "	318	$7.092 \times 10^{-3}$	0.1928		
Methyl acrylate	298	$1.065 \times 10^{-3}$	1.643	10.86	6.545
" "	303	$1.508 \times 10^{-3}$			
" "	308	$1.886 \times 10^{-3}$	1.697		

The poly(methyl methacrylate) obtained by ceric initiation was tested for the presence of cerium by the ammonia-hydrogen peroxide test<sup>24</sup> after purification and ignition of the polymer. There was no residue left on ignition, and the test for cerium was negative. This is contrary to the observation by Norrish and Edgecombe<sup>25</sup> that polymers obtained by ceric ion initiation contain cerium in them. From their analysis of endgroups in poly(methyl methacrylate) obtained by initiation with ceric sulfate in sulfuric acid, Ghosh, Mukherjee, and Palit<sup>26</sup> concluded that initiation takes place only by the agency of hydroxyl radicals in the ceric-vinyl monomer systems. However, our kinetic data as well as endgroup and infrared analysis of the polymer provide convincing evidence against initiation by hydroxyl radicals. Direct initiation by the attack of ceric ion on the monomer has also been found by Katai et al.<sup>6</sup> to explain their kinetic data obtained in the ceric sulfate-ethylene glycol redox-initiated polymerization of acrylonitrile.

### Chain Lengths

The chain lengths of the polymers obtained in perchloric and nitric acid media [also in sulfuric acid medium for poly(methyl acrylate)] were calculated from viscometric data. Generally, the chain lengths in the three acid media increased in the order H<sub>2</sub>SO<sub>4</sub> > HNO<sub>3</sub> > HClO<sub>4</sub>. The chain lengths were found to increase with the monomer concentration and de-

crease with the ceric and hydrogen ion concentrations (Table III). These findings are in agreement with the requirements of the kinetic scheme.

TABLE III  
Variation of Chain Length with [M], [Ceric], and [H<sup>+</sup>]  
(Monomer Methyl Acrylate; Temperature 35°C.)

Monomer concn., mole/l.	Ceric concn. $\times 10^3$ , mole/l.	H <sup>+</sup> concn., mole/l.	Chain length, <i>n</i>
0.265	5.0	1.0 <sup>a</sup>	3,678
0.354	5.0	1.0 <sup>a</sup>	4,482
0.398	5.0	1.0 <sup>a</sup>	5,069
0.442	5.0	1.0 <sup>a</sup>	5,745
0.530	5.0	1.0 <sup>a</sup>	6,393
0.221	1.0	0.5 <sup>b</sup>	25,850
0.221	2.0	0.5 <sup>b</sup>	25,650
0.221	4.0	0.5 <sup>b</sup>	22,380
0.221	6.0	0.5 <sup>b</sup>	21,030
0.221	10.0	0.5 <sup>b</sup>	17,200
0.221	5.0	0.2 <sup>c</sup>	5,357
0.221	5.0	0.4 <sup>c</sup>	3,695
0.221	5.0	0.6 <sup>c</sup>	2,359
0.221	5.0	0.8 <sup>c</sup>	1,364

<sup>a</sup> HNO<sub>3</sub> medium.

<sup>b</sup> H<sub>2</sub>SO<sub>4</sub> medium.

<sup>c</sup> HClO<sub>4</sub> medium.

### Rate Constants

Table I gives the rate constants for the three monomers at 35°C. The value of the initiation rate constant  $k_t$  for each monomer was obtained from the corresponding plot in either Figure 1, 2, or 3; the values obtained from these plots agreed within themselves in the limits of experimental error. In evaluating  $k_t$  from the plots in Figure 1 or 2, the value for the hydrolytic constant  $K$  has been substituted from the slope by intercept ratio in Figure 3. The value for  $k_p/k_t$  was obtained from Figure 4 for each monomer. These values could also be obtained from the plots of chain length against either the monomer concentration or the reciprocal of the ceric or hydrogen ion concentration. The values obtained thus, however, did not agree with those from Figure 4, probably because the chain length measurements were made on unfractionated polymers and the calculations using the viscosity-molecular weight relationships may involve some error. The values obtained for  $k_p/k_t$  were quite high when compared to those obtained in other types of polymerizations involving the mutual type of termination of chain radicals. As pointed out by Katai et al.,<sup>6</sup> this indicates that the propagation and the termination reactions in the present system are similar processes. In the case of acrylonitrile, the value obtained by us for  $k_p/k_t$  ratio was found to be of the same order of magnitude as that reported by

Katai et al.,<sup>6</sup> who have extrapolated their data in the presence of the reducing agent to a zero concentration of the latter.

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### References

1. Bacon, R. G. R., *Trans. Faraday Soc.*, **42**, 140 (1946).
2. Saldick, J., *J. Polymer Sci.*, **19**, 73 (1956)
3. Venkatakrishnan, S., and M. Santappa, *Makromol. Chem.*, **27**, 51 (1958).
4. Lalitha, J., and M. Santappa, *Vignana Parishad Anusandhan Patrika*, **4**, 139 (1961).
5. Mino, G., S. Kaizermann, and E. Rasmussen, *J. Polymer Sci.*, **31**, 242 (1958).
6. Katai, A. A., V. K. Kulshrestha, and R. H. Marchessault, *J. Polymer Sci.*, **C2**, 403 (1963).
7. Ananthanarayanan, V. S., and M. Santappa, *Indian J. Chem.*, **2**, 330 (1964).
8. Sandell, E. B., *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1944, p. 186.
9. Baxendale, J. H., S. Bywater, and M. G. Evans, *J. Polymer Sci.*, **1**, 237 (1946).
10. Fuhrman, M., and R. B. Mesrobian, *J. Am. Chem. Soc.*, **76**, 3281 (1954).
11. Stockmayer, W. H., and R. L. Cleland, *J. Polymer Sci.*, **17**, 473 (1955).
12. Hardwick, T. J., and E. Robertson, *Can. J. Chem.*, **29**, 818, 828 (1951).
13. Duke, F. R., and A. A. Forist, *J. Am. Chem. Soc.*, **71**, 2790 (1949).
14. Blaustein, B. D., and J. W. Gryder, *J. Am. Chem. Soc.*, **79**, 540 (1957).
15. Palit, S. R., and P. Ghosh, *J. Polymer Sci.*, **58**, 1225 (1962).
16. Kolthoff, I. M., and A. I. Medalia, *J. Am. Chem. Soc.*, **71**, 3777, 3784 (1949).
17. Santappa, M., *Current Sci. (India)*, **23**, 145 (1954).
18. Bawn, C. E. H., and J. A. Sharp, *J. Chem. Soc.*, **1957**, 1854, 1866, 2026.
19. Hargreaves, G., and L. H. Sutcliffe, *Trans. Faraday Soc.*, **51**, 1105 (1955).
20. Higginson, W. C. E., D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discussions Faraday Soc.*, **29**, 49 (1960).
21. Bamford, C. H., A. D. Jenkins, and R. Johnston, *Nature*, **177**, 992 (1956).
22. Collinson, E., F. S. Dainton, and G. S. McNaughton, *Trans. Faraday Soc.*, **53**, 487 (1957).
23. Collinson, E., F. S. Dainton, D. R. Smith, G. J. Trudel, and S. Tazuke, *Discussions Faraday Soc.*, **29**, 188 (1960).
24. Feigl, F., *Spot Tests, Inorganic Applications*, Elsevier, Amsterdam, 1956, p. 197.
25. Norrish, R. G. W., and F. H. C. Edgecombe, *Nature*, **197**, 282 (1963).
26. Ghosh, P., A. R. Mukherjee, and S. R. Palit, *J. Polymer Sci.*, **A2**, 2817 (1964).

### Résumé

On a effectué une étude cinétique systématique de la polymérisation thermique du méthacrylate de méthyle, de l'acrylate de méthyle, et de l'acrylonitrile, initiée par l'ion cérique en solutions aqueuses d'acides perchlorique, nitrique et sulfurique. Les expériences de polymérisation ont été effectuées à 35°C et à l'obscurité et dans des conditions d'oxydation négligeable d'eau par l'ion cérique. On a trouvé que la polymérisation s'effectuait sans période d'induction, et que la vitesse de l'état stationnaire était atteinte après une courte période. La vitesse de disparition du monomère (suivie par gravimétrie) dépend du carré de la concentration en monomère et était indépendante des concentrations en ion cérique et en ion hydrogène. La vitesse de disparition de l'ion cérique (suivie par titrimétrie ou spectrophotométrie) est directement proportionnelle aux con-

centrations en ion cérique, en monomère et en ion hydrogène. On a observé que les longueurs de chaîne des polymères (déterminées par viscosimétrie) sont directement proportionnelles à la concentration en monomère et inversement proportionnelles aux concentrations en ions cérique et hydrogène. L'addition initiale d'ion céreux à un effet négligeable sur les vitesses. L'augmentation de la force ionique provoque une légère augmentation des vitesses. À partir d'expériences effectuées à différentes températures, on a calculé les énergies d'activation des différents processus de la réaction. On a trouvé que la plupart des résultats expérimentaux pouvaient s'expliquer d'une façon convenable par un schéma cinétique faisant intervenir une initiation et une terminaison par l'ion cérique dans la forme non hydrolysée  $Ce^{4+}$ .

### Zusammenfassung

Eine systematische kinetische Untersuchung der thermischen, durch Cerionen in wässrigen Perchlor-, Salpeter- und Schwefelsäurelösungen gestarteten Polymerisation von Methylmethacrylat, Methacrylat und Acrylnitril wurde durchgeführt. Die Polymerisationsversuche wurden bei 35°C im Dunkeln bei vernachlässigbarer Oxydation des Wassers durch Cerionen ausgeführt. Die Polymerisation verläuft ohne Induktionsperiode, und die stationäre Geschwindigkeit wird in kurzer Zeit erreicht. Die Geschwindigkeit des Monomerumsatzes (gravimetrisch bestimmt) zeigt eine quadratische Abhängigkeit von der Monomerkonzentration und war von der Cer- und Wasserstoffionenkonzentration unabhängig. Die Geschwindigkeit des Cerverbrauchs (titrimetrisch oder spektrophotometrisch bestimmt) ist der Cer-, Monomer- und Wasserstoffionenkonzentration direkt proportional. Die Kettenlänge der Polymeren (viskosimetrisch gemessen) ist der Monomerkonzentration direkt und der Cersowie der Wasserstoffionenkonzentration umgekehrt proportional. Anfänglich zugesetzte Cerionen haben keinen merklichen Einfluss auf die Geschwindigkeit. Erhöhung der Ionenstärke verursacht eine schwache Zunahme der Geschwindigkeit. Aus Versuchen bei verschiedenen Temperaturen wurde die Aktivierungsenergie für die verschiedenen Prozesse berechnet. Die Mehrzahl der Versuchsergebnisse kann durch ein kinetisches Schema mit Start und Abbruch durch Cerionen in der nichthydrolysierten  $Ce^{4+}$ -Form erklärt werden.

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