

# Cerium(IV)–sorbose-initiated polymerization of acrylamide and methacrylamide

Kunj Behari\*, Uma Agrawal and Rima Das

Polymer Laboratory, Chemistry Department, University of Allahabad, Allahabad 211002, India

(Received 28 May 1992; revised 18 January 1993)

The kinetics of the aqueous polymerizations of acrylamide and methacrylamide employing the cerium(IV) ammonium nitrate–sorbose redox pair under an inert atmosphere were studied. It was found that the rate of monomer disappearance is directly proportional to the concentration of sorbose and inversely proportional to the cerium(IV) ion concentration but depends on the square of the monomer concentration. The rate of cerium(IV) ion disappearance is directly proportional to the initial concentration of cerium(IV) ion and sorbose but independent of the monomer concentration. The effects of various additives, namely alcohols, inorganic salts and so on, on the rates of polymerization of acrylamide and methacrylamide were also studied. The viscometric average molecular weight  $\bar{M}_v$  decreases on increasing the concentration of monomer and sorbose. A plausible mechanism based on experimental results is proposed.

(Keywords: polymerization; acrylamide; kinetics)

## INTRODUCTION

The thermal and photochemical reactions involving quadrivalent cerium ion in vinyl polymerizations in aqueous solution have been the subject of considerable research. The graft copolymerization kinetics of dextran and chitin initiated by cerium(IV) ion have been reported by Wallace and Young<sup>1</sup> and Kurita *et al.*<sup>2</sup>. Many workers<sup>3,4</sup> have reported the kinetics of vinyl polymerizations initiated by cerium(IV) ion alone. A survey of the literature reveals that in the methyl methacrylate<sup>5</sup> polymerization initiated by the cerium(IV)–malonic acid redox pair the termination occurs by mutual combination of growing chain radicals. Contradictory reports regarding the mode of initiation and termination have prompted us to undertake a detailed kinetic study of acrylamide and methacrylamide polymerizations initiated by the cerium(IV)–sorbose redox couple.

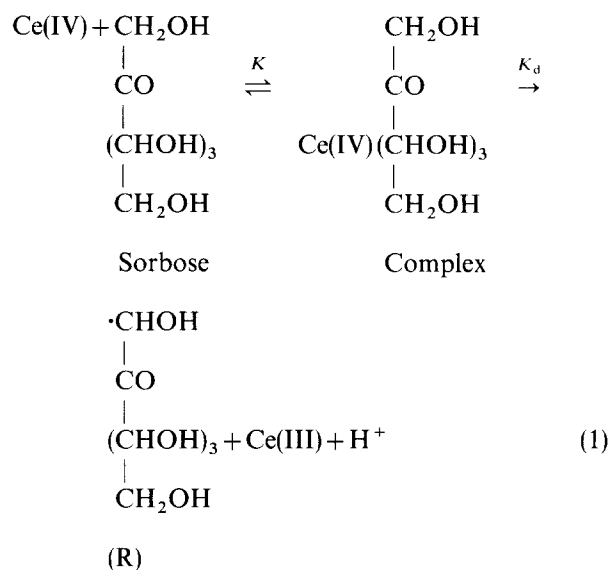
## EXPERIMENTAL

The purification of acrylamide and methacrylamide and the methods used for the measurement of polymerization rate and viscometric average molecular weight  $\bar{M}_v$  were reported in an earlier communication<sup>6</sup>.

## RESULTS AND DISCUSSION

Duke and Froist<sup>7</sup> have proposed the formation of free radicals from the decomposition of the complex between cerium(IV) and sorbose via a single-electron transfer process.

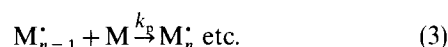
In the present study, the rate of polymerization decreased on increasing the cerium(IV) ion concentration, contrary to the results reported by Mino *et al.*<sup>8</sup> and Misra *et al.*<sup>9</sup>. The following sequence of reactions appears to be the most probable to explain our results.



Initiation

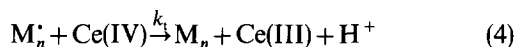


Propagation

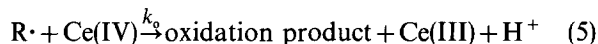


\* To whom correspondence should be addressed

Termination



Oxidative termination

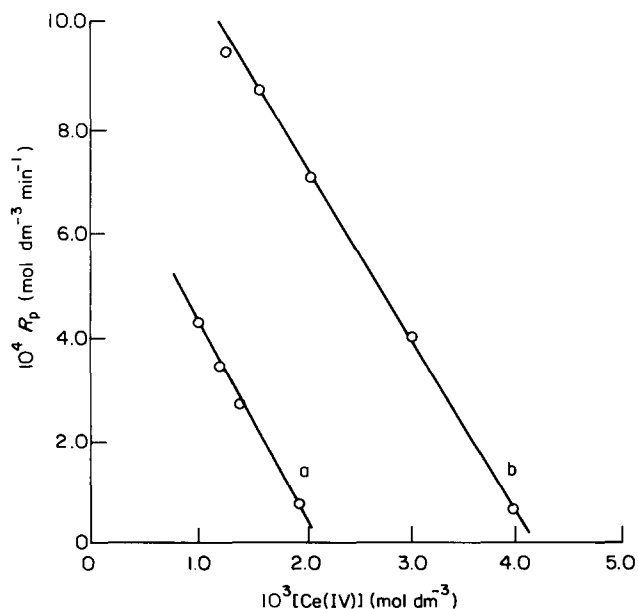


Effect of initiator concentration on the rate of polymerization and the molecular weight of the polymer

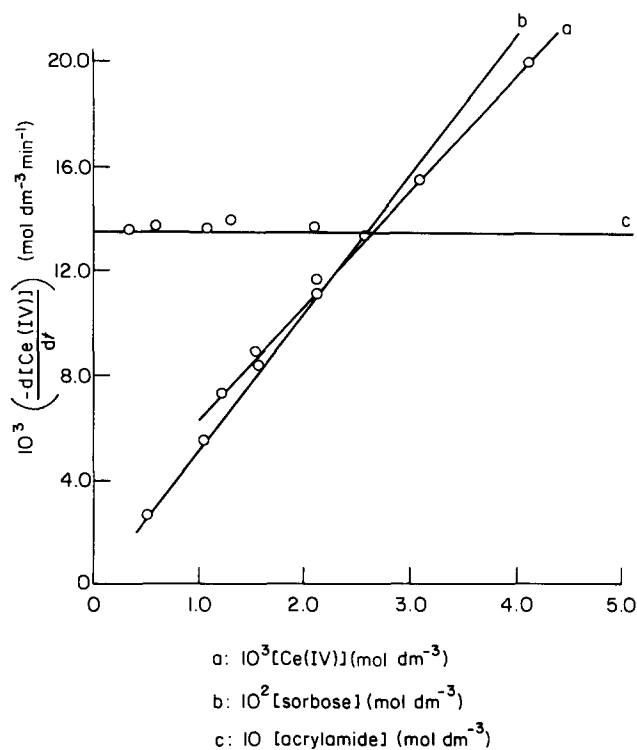
It was observed during the polymerization studies that the rate of polymerization decreases on increasing the concentration of cerium(IV) ion (Figure 1). This can be explained by assuming that the hydroxyalkyl free radical, which is extremely reactive towards cerium(IV), is oxidized in the termination and oxidative termination steps (equations (4) and (5)). Hence the rate of polymerization decreases as suggested by Collinson *et al.*<sup>10,11</sup>. The cerium(IV) ion does not participate in the initiation process directly but it forms a complex with sorbitol which on decomposition produces a primary free radical (R·) (equation (1)). The concomitant determination of cerium(IV) ion disappearance showed a direct proportionality to the initial concentration of cerium(IV) ion (Figures 2a and 3a), which leads to the conclusion that the cerium(IV) ion participates actively in the termination processes of the hydroxyalkyl free radical and the growing polymer chain radicals and excludes the possibility of initiation through cerium(IV). Table 1 clearly shows that the viscometric average molecular weight decreases on increasing the concentration of cerium(IV). This can be explained by the fact that increasing the concentration of cerium(IV) provides more chances for premature termination of the growing chain radicals, and hence the degree of polymerization is decreased.

Effect of activator concentration on the rate of polymerization and the molecular weight of the polymer

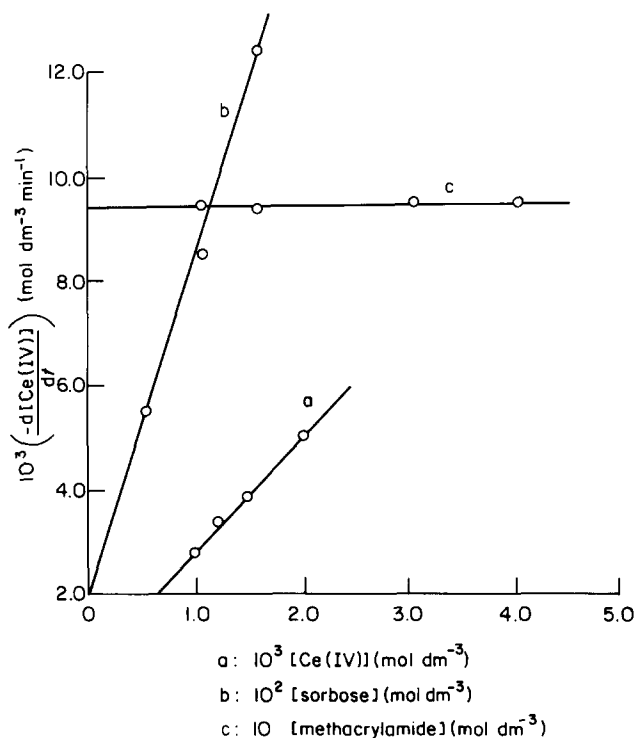
Figure 4 shows the unit order of reaction with respect to sorbitol for acrylamide and methacrylamide.



**Figure 1** Dependence of the rate of polymerization on [Ce(IV)]: (a) temperature = 30°C, pH = 1.60, [acrylamide] =  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ , [sorbitol] =  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ; (b) temperature = 40°C, pH = 1.30, [methacrylamide] =  $2.0 \times 10^{-1} \text{ mol dm}^{-3}$ , [sorbitol] =  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$



**Figure 2** Effect of variation of the initial concentration of cerium(IV) (a), sorbitol (b) and acrylamide (c) on the initial rate of cerium(IV) ion disappearance (temperature = 30°C, pH = 1.60): (a) [acrylamide] =  $1.25 \times 10^{-1} \text{ mol dm}^{-3}$ , [sorbitol] =  $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ ; (b) [Ce(IV)] =  $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [acrylamide] =  $1.25 \times 10^{-1} \text{ mol dm}^{-3}$ ; (c) [Ce(IV)] =  $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [sorbitol] =  $1.5 \times 10^{-2} \text{ mol dm}^{-3}$



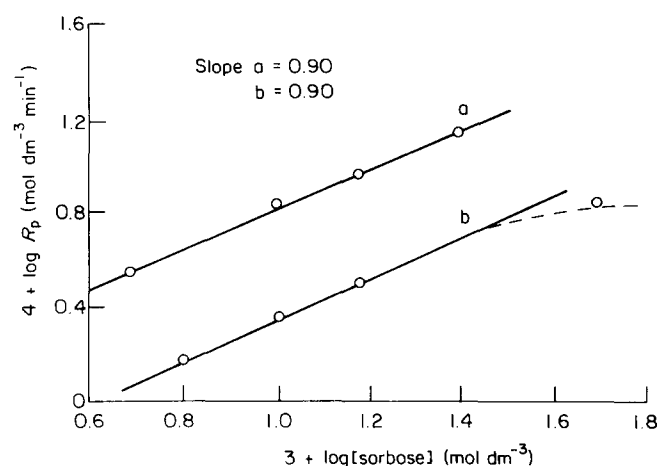
**Figure 3** Effect of variation of the initial concentration of cerium(IV) (a), sorbitol (b) and methacrylamide (c) on the initial rate of cerium(IV) ion disappearance (temperature = 40°C, pH = 1.30): (a) [methacrylamide] =  $1.5 \times 10^{-2} \text{ mol dm}^{-3}$ , [sorbitol] =  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$ ; (b) [methacrylamide] =  $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ , [Ce(IV)] =  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ; (c) [Ce(IV)] =  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ , [sorbitol] =  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$

**Table 1** Dependence of viscosity and molecular weight on initiator concentration

$10^3[\text{Ce(IV)}]$ (mol dm <sup>-3</sup> )		$10^2[\eta]$ (dl g <sup>-1</sup> )		$\bar{M}_v$	
A <sup>a</sup>	B <sup>b</sup>	A	B	A	B
4.0	2.0	68.02	2.60	35 080	2837
3.0	1.33	77.51	3.00	42 760	3680
2.0	1.20	88.40	3.52	52 240	4920
1.5	1.0	93.45	5.00	56 750	9315
1.2	-	100.00	-	62 950	-

<sup>a</sup> [Acrylamide] =  $1.25 \times 10^{-1}$  mol dm<sup>-3</sup>; [sorbse] =  $1.5 \times 10^{-2}$  mol dm<sup>-3</sup>; temperature = 30°C; pH = 1.60

<sup>b</sup> [Methacrylamide] =  $1.5 \times 10^{-1}$  mol dm<sup>-3</sup>; [sorbse] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>; temperature = 30°C; pH = 1.30



**Figure 4** Dependence of the rate of polymerization on sorbose concentration: (a) temperature = 30°C, pH = 1.60, [acrylamide] =  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup>, [Ce(IV)] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>; (b) temperature = 40°C, pH = 1.30, [methacrylamide] =  $2.0 \times 10^{-1}$  mol dm<sup>-3</sup>, [Ce(IV)] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>

**Table 2** Dependence of viscosity and molecular weight on activator concentration

$10^2[\text{Sorbse}]$ (mol dm <sup>-3</sup> )		$10^2[\eta]$ (dl g <sup>-1</sup> )		$\bar{M}_v$	
A <sup>a</sup>	B <sup>b</sup>	A	B	A	B
2.5	5.0	102	4.85	64 860	8810
2.0	1.5	92	3.50	55 460	4871
1.5	1.0	68	2.0	35 080	1760
1.0	0.5	62	1.28	30 480	782
0.5	-	48	-	20 700	-

<sup>a</sup> [Acrylamide] =  $1.25 \times 10^{-1}$  mol dm<sup>-3</sup>; [Ce(IV)] =  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>; temperature = 30°C; pH = 1.60

<sup>b</sup> [Methacrylamide] =  $2.00 \times 10^{-1}$  mol dm<sup>-3</sup>; [Ce(IV)] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>; temperature = 30°C; pH = 1.30

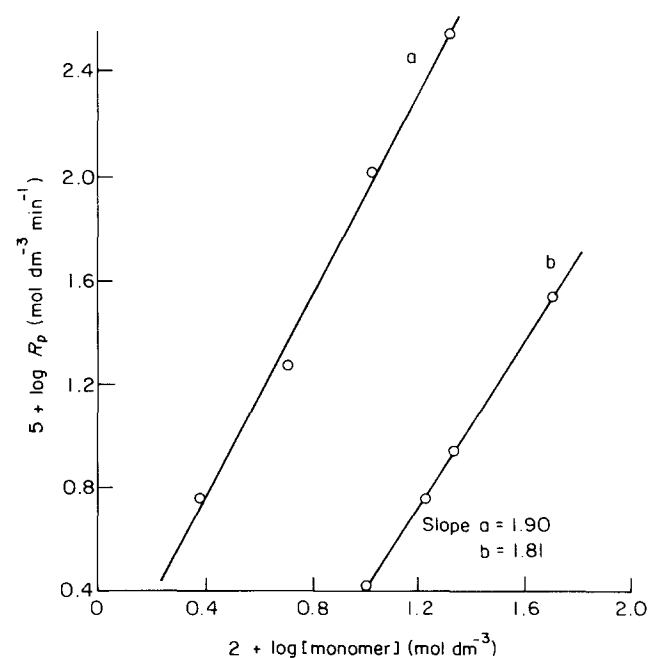
The rate of cerium(IV) ion disappearance increases linearly with increasing sorbose concentration (Figures 2b and 3b), which clearly indicates that cerium(IV) ions are participating in the oxidative termination of hydroxyalkyl free radicals.

The viscometric average molecular weight measurements (Table 2) reveal that on increasing the concentration of sorbose the molecular weight and intrinsic viscosity of polyacrylamide and polymethacrylamide increase, which

further rules out the possibility of termination by combination of growing chain radicals.

#### Effect of monomer concentration on the rate of polymerization and the molecular weight of the polymer

Figure 5 shows that the rate of polymerization depends on the square of the monomer concentration, which completely rules out termination by interaction of macroradicals<sup>4</sup>. This dependence on monomer concentration has also been reported by other workers<sup>4,12</sup>. The rate of cerium(IV) disappearance remains constant (Figures 2c and 3c) on varying the monomer concentration, which lends additional support to the conclusion that cerium(IV) does not participate in the initiation process. Termination by cerium(IV) has been observed by Dainton *et al.*<sup>13</sup> during the X-ray-initiated polymerization of acrylamide in the presence of cerium(IV). Table 3 clearly indicates that the intrinsic viscosity and the average molecular weight increase on increasing the concentration of acrylamide and methacrylamide, which is in accordance with equation (7).



**Figure 5** Dependence of the rate of polymerization on monomer concentration: (a) acrylamide, temperature = 30°C, pH = 1.60, [sorbse] =  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [Ce(IV)] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>; (b) methacrylamide, temperature = 40°C, pH = 1.30, [sorbse] =  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [Ce(IV)] =  $5.0 \times 10^{-3}$  mol dm<sup>-3</sup>

**Table 3** Dependence of viscosity and molecular weight on monomer concentration

$10[\text{Monomer}]$ (mol dm <sup>-3</sup> )		$10^2[\eta]$ (dl g <sup>-1</sup> )		$\bar{M}_v$	
A <sup>a</sup>	B <sup>b</sup>	A	B	A	B
2.0	4.0	98	4.32	61 080	7132
1.25	2.0	68	2.60	35 080	2837
1.0	1.5	48	2.18	20 710	2060
0.5	1.0	27	1.44	8664	969
0.25	-	15	-	3555	-

<sup>a</sup> Acrylamide: [sorbse] =  $1.5 \times 10^{-2}$  mol dm<sup>-3</sup>; [Ce(IV)] =  $4.0 \times 10^{-3}$  mol dm<sup>-3</sup>; temperature = 30°C; pH = 1.60

<sup>b</sup> Methacrylamide: [sorbse] =  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup>; [Ce(IV)] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>; temperature = 30°C; pH = 1.30

Effect of temperature on rate of polymerization

The energies of activation have been found to be 32.0 kJ mol<sup>-1</sup> and 53.0 kJ mol<sup>-1</sup> for acrylamide and methacrylamide, respectively (Figure 6). The higher energy of activation in the case of methacrylamide is owing to the lower rate of polymerization because of the presence of the methyl group. At higher temperatures the rate of polymerization increases, which may be caused by facile decomposition of the complex formed in equation (1) resulting in the production of more R•.

The decrease in the intrinsic viscosity of the solution at higher temperatures (Table 4) is caused by the free mobility of the growing chain radicals further leading to their efficient termination (equation (4)) and hence a decrease in the molecular weight of the polymer.

Effects of additives

The effects of various additives such as alcohols, inorganic salts, detergents and nitric acid on the rates of polymerization of acrylamide and methacrylamide have been studied and the results are given in Figures 7 to 10.

In both cases the rate of polymerization increases with increasing nitric acid concentration (Figure 10). It is well known that cerium nitrate forms many inactive

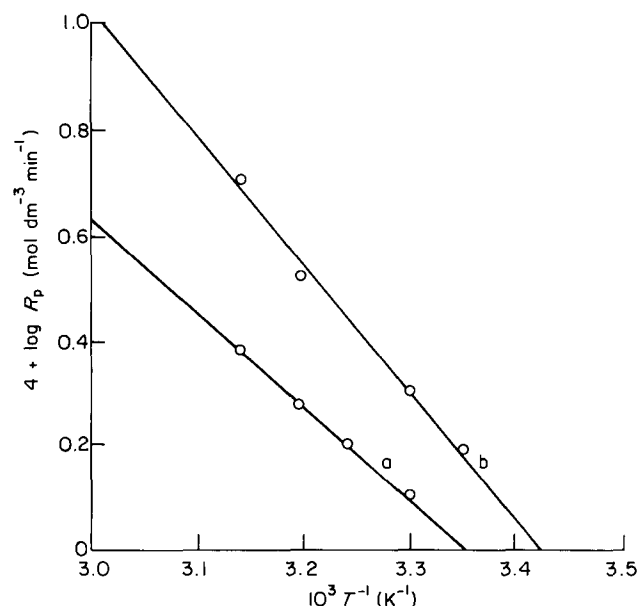


Figure 6 Dependence of the rate of polymerization on temperature: (a) pH = 1.60, [acrylamide] = 2.0 × 10<sup>-1</sup> mol dm<sup>-3</sup>, [sorbose] = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [Ce(IV)] = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; (b) pH = 1.30, [methacrylamide] = 2.0 × 10<sup>-1</sup> mol dm<sup>-3</sup>, [sorbose] = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [Ce(IV)] = 5.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>

Table 4 Dependence of viscosity and molecular weight on temperature

Temperature (°C)		10 <sup>2</sup> [η] (dl g <sup>-1</sup> )		M <sub>v</sub>	
A <sup>a</sup>	B <sup>b</sup>	A	B	A	B
25	30	89.0	4.50	52 770	7691
30	35	68.0	3.87	35 080	5842
40	40	47.0	2.60	20 060	2837
45	45	27.0	1.41	8664	928
-	50	-	1.05	-	545

<sup>a</sup>[Acrylamide] = 1.25 × 10<sup>-1</sup> mol dm<sup>-3</sup>; [sorbose] = 1.5 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [Ce(IV)] = 4.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; temperature = 30°C; pH = 1.60

<sup>b</sup>[Methacrylamide] = 1.5 × 10<sup>-1</sup> mol dm<sup>-3</sup>; [sorbose] = 2.5 × 10<sup>-2</sup> mol dm<sup>-3</sup>; [Ce(IV)] = 2.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>; temperature = 30°C; pH = 1.30

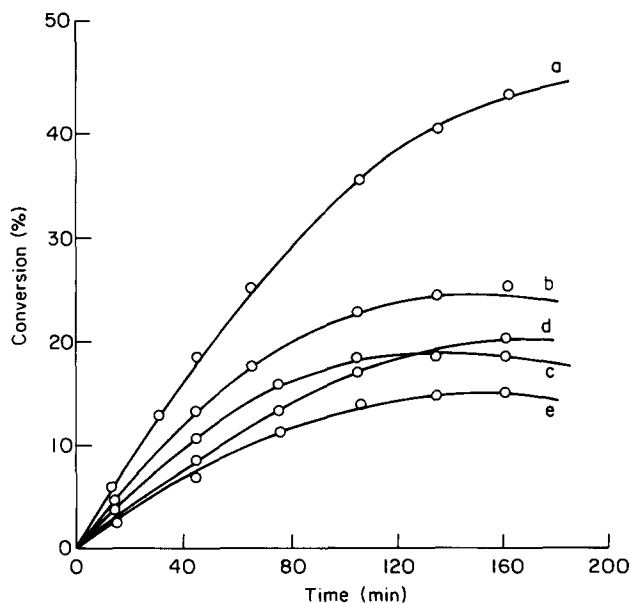


Figure 7 Effect of the addition of alcohols on conversion (temperature = 40°C, pH = 1.30, [methacrylamide] = 2.0 × 10<sup>-1</sup> mol dm<sup>-3</sup>, [sorbose] = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [Ce(IV)] = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [alcohols] = 1.0 mol dm<sup>-3</sup>): (a) blank; (b) methanol; (c) ethanol; (d) propanol; (e) butanol

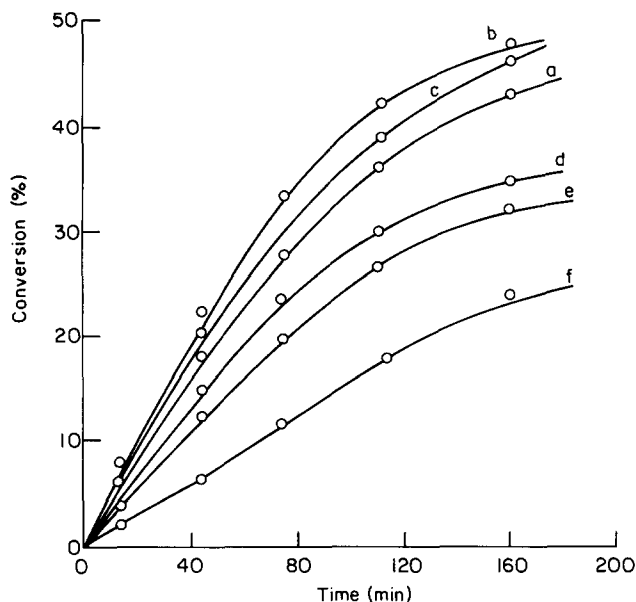


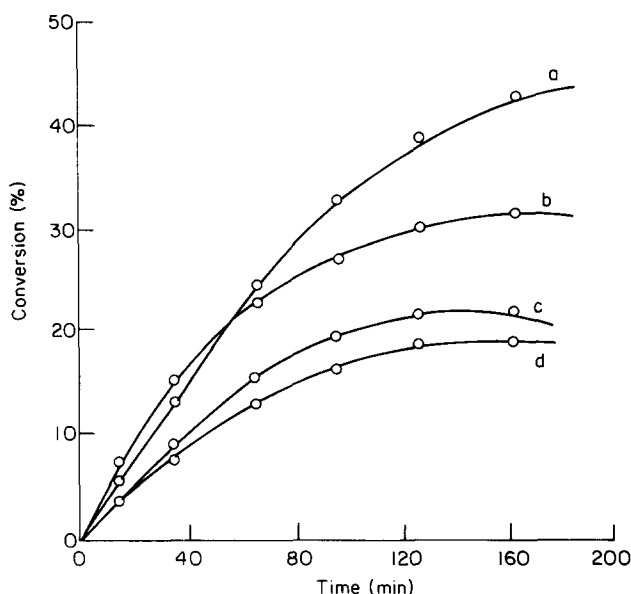
Figure 8 Effect of the addition of inorganic salts on conversion (temperature = 40°C, pH = 1.30, [methacrylamide] = 2.0 × 10<sup>-1</sup> mol dm<sup>-3</sup>, [sorbose] = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>, [Ce(IV)] = 2.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, [salts] = 2.0 × 10<sup>-2</sup> mol dm<sup>-3</sup>): (a) blank; (b) LiCl; (c) NaCl; (d) NH<sub>4</sub>Cl; (e) KCl; (f) Na<sub>2</sub>SO<sub>4</sub>

complexes with water molecules<sup>7</sup>, causing a decrease in the reactivity of cerium(IV). At higher concentrations of nitric acid it is less likely that these aquo complexes will form and hence the polymerization rate is increased.

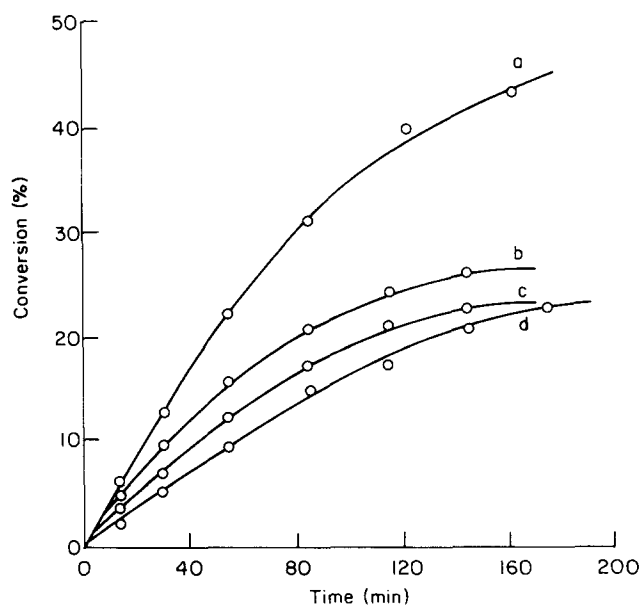
CONCLUSIONS

On the basis of the experimental results and considering the proposed reaction steps in equations (1) to (5) the following rate expression has been derived

$$R_p = \frac{Kk_p k_d [M]^2 [CH_2OHCO(CHOH)_3CH_2OH]}{k_t \{ [M] + (k_o/k_i) [Ce(IV)] \}} \quad (6)$$



**Figure 9** Effect of the addition of detergents on conversion (temperature = 40°C, pH = 1.30, [methacrylamide] =  $2.0 \times 10^{-1}$  mol dm<sup>-3</sup>, [sorbitose] =  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [Ce(IV)] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>): (a) blank; (b)  $4.0 \times 10^{-4}$  mol dm<sup>-3</sup> sodium oleate; (c)  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> CTAB; (d)  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup> CTAB



**Figure 10** Effect of nitric acid on conversion (temperature = 40°C, pH = 1.30, [methacrylamide] =  $2.0 \times 10^{-1}$  mol dm<sup>-3</sup>, [sorbitose] =  $2.0 \times 10^{-2}$  mol dm<sup>-3</sup>, [Ce(IV)] =  $2.0 \times 10^{-3}$  mol dm<sup>-3</sup>): (a) blank; (b)  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup> HNO<sub>3</sub>; (c)  $1.25 \times 10^{-2}$  mol dm<sup>-3</sup> HNO<sub>3</sub>; (d)  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> HNO<sub>3</sub>

and the kinetic chain length can be given as

$$v = \frac{k_p[M]}{k_t[\text{Ce(IV)}]} \quad (7)$$

The proposed reaction steps are further verified by considering the rate of cerium(IV) ion disappearance as follows

$$-\frac{d[\text{Ce(IV)}]}{dt} = 2K_d[\text{Ce(IV)}][\text{CH}_2\text{OHCO(CHOH)}_3\text{CH}_2\text{OH}] \quad (8)$$

Equations (6) to (8) explain all the experimental results which lead to the conclusion that cerium(IV) ions do not participate directly in the initiation process and termination occurs exclusively through oxidative termination of cerium(IV). The dependence on the square of the monomer concentration also rules out the possibility of mutual termination of growing chain radicals.

It is further concluded from the experimental results (Tables 1 to 4) and the energies of activation that acrylamide undergoes polymerization faster than methacrylamide owing to the steric hindrance caused by the presence of the methyl group in the latter. The intrinsic viscosity and average molecular weight are low in the case of methacrylamide.

#### ACKNOWLEDGEMENTS

The authors are grateful to CSIR, New Delhi and CST, Lucknow for financial assistance through the awards of SRF (R. D.) and JRF (U. A.)

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