Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Misra, G. S. , Bassi, P. S. and Abrol, S. L.(1985) 'Polymerization of Methacrylamide Initiated by Ceric Ion-Citric Acid Redox System', Journal of Macromolecular Science, Part A, 22: 8, 1167 — 1175
To link to this Article: DOI: 10.1080/00222338508063322
URL: http://dx.doi.org/10.1080/00222338508063322

J. MACROMOL. SCI.–CHEM., A22(8), pp. 1167-1175 (1985)

Polymerization of Methacrylamide Initiated by Ceric Ion-Citric Acid Redox System

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ABSTRACT

Homogeneous polymerization of methacrylamide initiated by the ceric ammonium sulfate-citric acid (CA) redox pair has been investigated and reported at 35 ± 0.2°C under nitrogen atmosphere. The initiation was caused by the free radical generated by the decomposition of the complex formed between ceric ion and citric acid. The rate of monomer disappearance was found to be proportional to $[\mathrm{CA}]^{0.4}$, $[\mathrm{Ce}^{4+}]^{0.65}$, and $[\mathrm{Monomer}]^{1}$. The rate of ceric ion disappearance was directly proportional to the ceric ion concentration but independent of the monomer concentration. The initial rate was independent of $[H_2SO_4]$. The activation energy of the system was found to be 21.4 kJ/mol.

INTRODUCTION

The polymerization kinetics of acrylamide initiated by various redox systems has been extensively studied [1-3]. However, the polymerization of methacrylamide (MA) has not been studied as much. Furthermore, a literature survey reveals a lot of controversy existing about the mode of initiation as well as termination in redox polymeri-

0022-233X/85/2208-1167$3.50/0

zation. To elucidate these facts, a new system, the citric acid-ceric ion redox system, was used to polymerize MA in aqueous medium.

EXPERIMENTAL

Purification of methacrylamide (BDH) was by repeated recrystallization from methanol and subsequent drying under vacuum. Ceric ammonium sulfate (Loba), citric acid (Sarabhai M, AR), and sulfuric acid (AR) were used as received. Conductivity water was used as the solvent in all experiments. The apparatus and technique were the same as those used by Misra et al. [4]. Estimation of ceric ion concentration in the polymerization system was done by cerimetry.

RESULTS AND DISCUSSION

Rate of Monomer Disappearance (R_p)

The initial rate and maximum conversion increased with increasing concentration of Ce(IV) from 5×10^{-4} to 30×10^{-4} mol/L. The catalyst exponent was found to be 0.65, indicating a bimolecular termination mechanism. The rate increased with increasing concentration of citric acid from 2.5×10^{-3} to 20×10^{-3} mol/L. The citric acid exponent of 0.4 indicated a bimolecular termination mechanism. Increasing the concentration of monomer from 5×10^{-2} to 25×10^{-2} mol/L increased the rate and maximum conversion. The monomer exponent was found to be unity, confirming a bimolecular termination mechanism (Fig. 1 and Table 1). Increasing the reaction temperature from 25 to 45°C increased the initial rate and maximum conversion. Both decreased at 50°C, which is due to some side reactions of the primary radicals with ceric ion or, more probably, primary radical termination occurs at higher temperatures. The activation energy was found to be 21.43 kJ/mol. The initial rate remained almost unaltered with an increase in $[H_2SO_4]$ but the maximum conversion decreased.

Rate of Ceric Ion Disappearance ($-R_{Ce(IV)}$)

The rate increased with increasing [CA] and [Ce(IV)]. A plot of rate^{-1} vs $[CA]^{-1}$ gave a straight line with a considerable intercept on the ordinate, thereby showing complex formation between ceric ion and citric acid (Fig. 2 and Table 2) which was isolated and subjected to various studies. The rate of ceric ion disappearance was directly proportional to the ceric ion concentration (Fig. 3 and Table 3). The complex was found to be insoluble in such organic solvents as acetone and

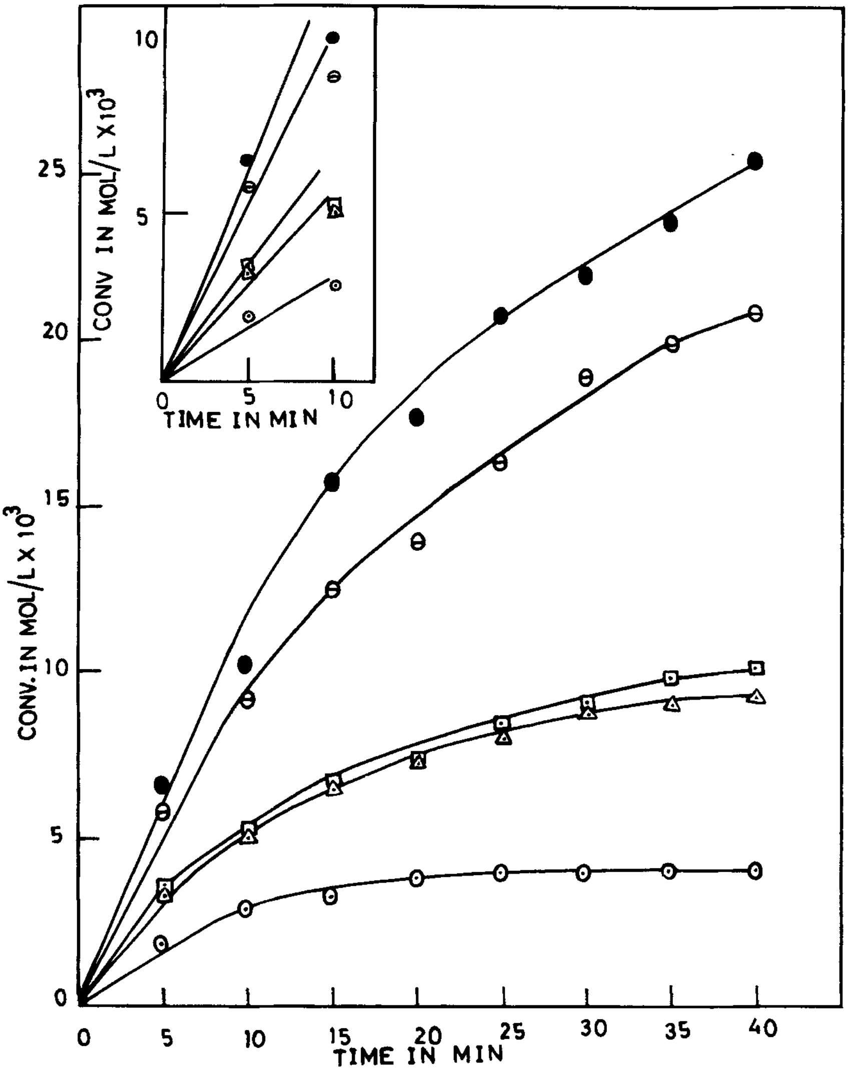

FIG. 1. Polymerization of methacrylamide with varying initial concentrations of monomer at constant [CA] = 20 × 10^{-3} mol/L, [Ce^{4+}] = 10 × 10^{-4} mol/L, [H_2SO_4] = 0.125 mol/L, 35 ± 0.2°C. [MA] values: ○ 5 × 10^{-2} mol/L, ▲ 10 × 10^{-2} mol/L, ▣ 15 × 10^{-2} mol/L, ⊖ 20 × 10^{-2} mol/L, ● 25 × 10^{-2} mol/L.

TABLE 1. Aqueous Polymerization of Methacrylamide with Varying Initial Concentrations of Monomer at Fixed Concentrations of [CA] = 20×10^{-2} mol/L, [H_2SO_4] = 0.125 mol/L, [Ce^{4+}] = 10×10^{-4} mol/L, 35 ± 0.2°C

Experiment	[MA] × 10^2 mol/L	Extent of conversion in mol/L × 10^3 with reaction time in minutes								R_{INI} × 10^6 mol/L/s	6 + Log R_{INI}	2 + Log [MA]
		5	10	15	20	25	30	35	40			
1	5	1.9	2.85	3.3	3.8	4.0	4.0	4.0	4.0	5.098	0.7074	0.6990
2	10	3.33	5.11	6.44	7.33	7.99	8.66	9.1	9.3	10.98	1.0406	1.0
3	15	3.42	5.18	6.60	7.31	8.25	8.96	9.66	10.13	11.85	1.0737	1.1761
4	20	5.9	9.2	12.5	13.92	16.28	18.88	19.82	20.76	16.67	1.2219	1.3010
5	25	6.6	10.15	15.83	17.7	20.78	21.95	23.6	25.5	21.43	1.3310	1.3979

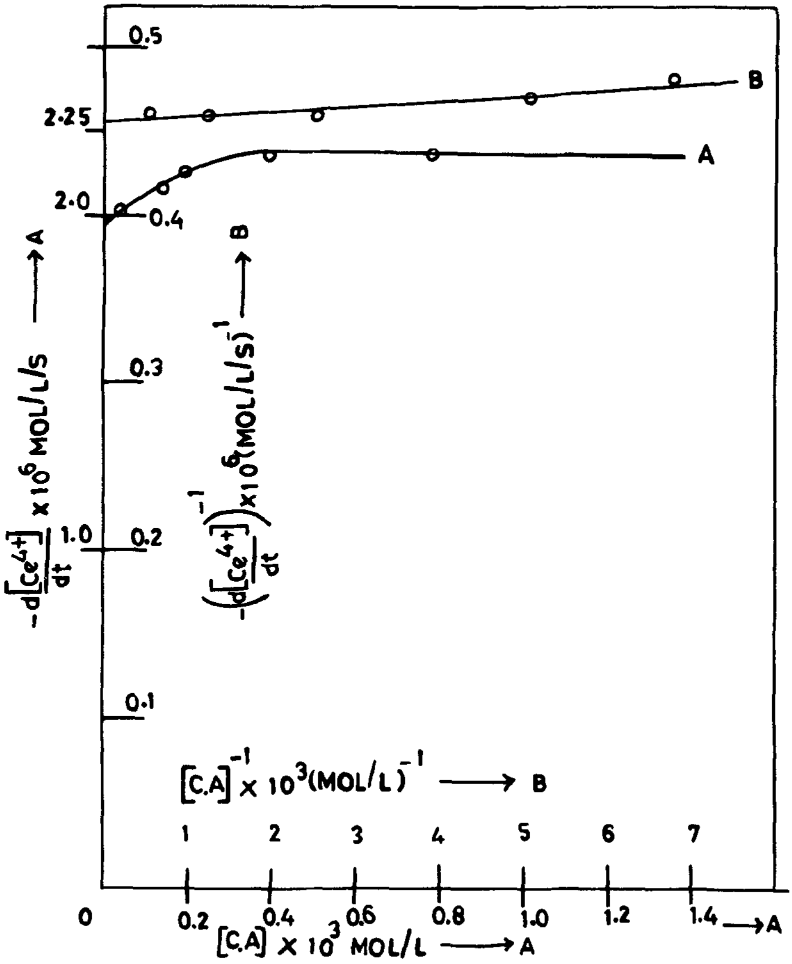

FIG. 2. Aqueous polymerization of methacrylamide. (A) Plot of rate of ceric ion disappearance versus citric acid concentrations. (B) Plot of $[\text{rate}]^{-1}$ vs $[\text{CA}]^{-1}$ at constant [monomer] = 10.59 × 10^{-2} mol/L, $[\text{Ce}^{4+}]$ = 14.55 × 10^{-4} mol/L, $[\text{H}_2\text{SO}_4]$ = 0.585 mol/L, 35 ± 0.2°C.

TABLE 2. Rate of Ceric Ion Disappearance with Varying Citric Acid Concentrations at Constant [MA] = 10.59 × 10^{-2} mol/L, $[H_2SO_4]$ = 0.585 mol/L, $[Ce^{4+}]$ = 14.55 × 10^{-4} mol/L, 35 ± 0.2°C

Experiment	[CA] × 10^3 mol/L	$[CA]^{-1} \times 10^3$ $(mol/L)^{-1}$	$-d\frac{[Ce^{4+}]}{dt} \times 10^6$ mol(L·s)	$\left(-d\frac{[Ce^{4+}]}{dt}\right)^{-1} \times 10^6$ (L·s)/mol
1	0.04915	20.346	2.013	0.497
2	0.1474	6.784	2.081	0.481
3	0.1966	5.086	2.126	0.470
4	0.3932	2.543	2.178	0.459
5	0.7864	1.272	2.178	0.459
6	0.9660	0.509	2.178	0.459

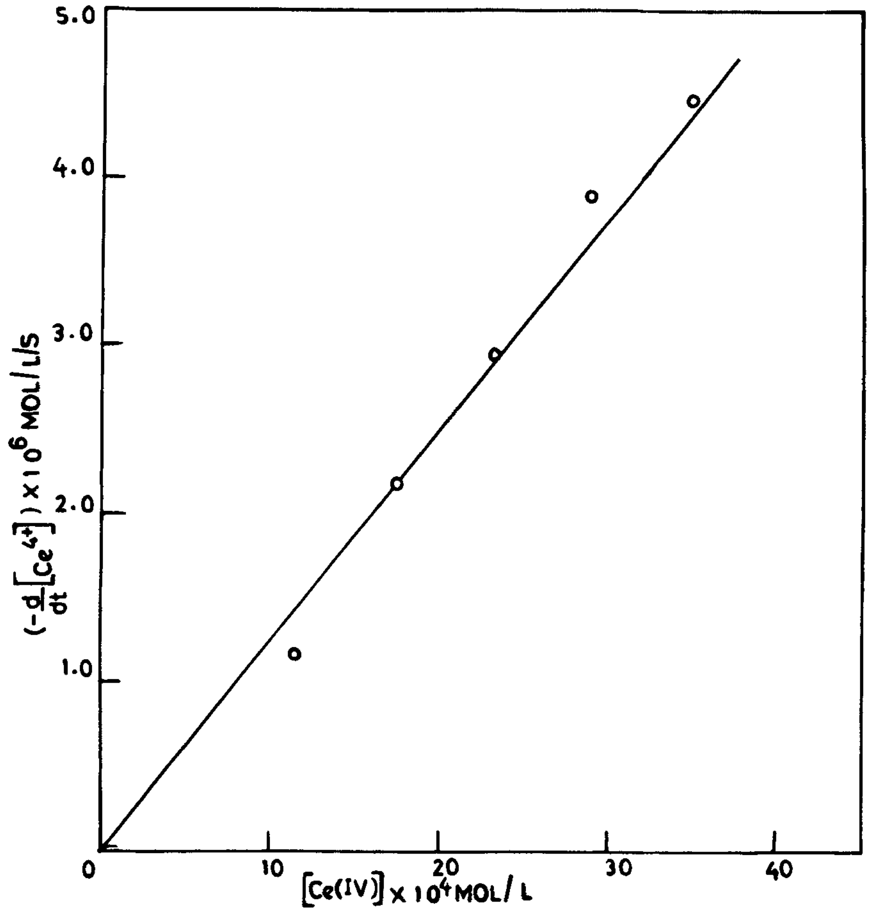

FIG. 3. Aqueous polymerization of methacrylamide. Plot of ceric ion (rate of disappearance) vs concentration of ceric ion at constant [monomer] = 11.90 × 10^{-2} mol/L, [CA] = 20 × 10^{-3} mol/L, [H_2SO_4] = 0.585 mol/L, 35 ± 0.2°C.

TABLE 3. Rate of Ceric Ion Disappearance with Varying Cerium Concentrations at Fixed Concentrations of [MA] = 11.90 × 10^{-2} mol/L, [CA] = 20 × 10^{-3} mol/L, [H_2SO_4] = 0.585 mol/L, 35 ± 0.2°C

Experiment	$[Ce^{4+}] \times 10^4$ mol/L	$-d\frac{[Ce(IV)]}{dt} \times 10^6$ mol/L/s
1	11.64	1.17
2	17.46	2.18
3	23.28	2.95
4	29.10	3.92
5	34.92	4.46

TABLE 4. Rate of Ceric Ion Disappearance with Varying Monomer Concentrations at Constant [Ce(IV)] = 14.55 × 10^{-4} mol/L, [CA] = 20 × 10^{-3} mol/L, [H_2SO_4] = 0.585 mol/L, 35 ± 0.2°C

Experiment	$[MA] \times 10^2$ mol/L	$-d\frac{[Ce(IV)]}{dt} \times 10^6$ mol/L/s
1	7.44	1.77
2	10.488	1.73
3	22.32	1.73
4	29.76	1.70
5	37.20	1.77

methanol, but dissolved in a strong acidic medium. The rate was found to be independent of monomer concentration (Table 4), thereby showing that the ceric ion participates only in the redox reaction to generate free radicals.

KINETIC SCHEME AND RATE EXPRESSION

The following reaction scheme can be postulated to explain the experimental observations:

$$\mathrm{Ce(IV)} + \mathrm{CA} \overset{K}{\rightleftharpoons} \text{complex} \tag{1}$$

$$\text{complex} \xrightarrow{k_r} \mathrm{R^{\cdot}} + \text{products} \tag{2}$$

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

$$\mathrm{RM^{\cdot}_{n-1}} + \mathrm{M} \xrightarrow{k_p} \mathrm{RM_n^{\cdot}} \tag{4}$$

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

On the basis of above postulated mechanism, the following two rate expressions have been derived:

$$-\frac{d[M]}{dt} = R_p[M]\left[\frac{Kk_r[CA][Ce(IV)]}{k_t}\right]^{\frac{1}{2}} \tag{6}$$

and

$$-R_{Ce(IV)} = \frac{Kk_r[Ce(IV)]_{total}[CA]}{1 + K[CA]} \tag{7}$$

All the experimental observations can be satisfactorily explained on the basis of these two rate expressions.

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