POLYMERIZATION OF ACRYLAMIDE WITH CERIC ION–PHENYL ALANINE REDOX SYSTEM – A KINETIC STUDY

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ABSTRACT

The polymerization of acrylamide (AM) in aqueous sulphuric acid medium initiated with ceric ammonium sulphate (Ce(IV)) – phenyl alanine (PA) redox system was investigated in the temperature range 30–50° C. The rates of polymerization (R_p) and of cerium (IV) disappearance were measured. The influence of varying [AM], [PA] and [Ce(IV)] and the effects of organic solvents on the rate of polymerization were examined. The temperature dependence of the rate was also studied and the activation parameters were calculated using Arrhenius and Erying plots. The initiation was caused by the free radical generated by the decomposition of the complex formed between Ce (IV) and PA. The chain termination step of polymerization reaction occurred by the mutual interaction of free radicals.

Key words: Polymerization, Acrylamide, Cerium (IV), Phenyl alanine, Redox, Kinetic.

INTRODUCTION

The polymerization of vinyl monomers initiated by transition metal ions in their higher oxidation states in aqueous medium has been well documented[1–4]. The combined usage of a metal ion and a reducing substance in polymerization studies has been proposed to provide information regarding the mechanistic details of the elementary steps.[5–18] Cerium ion alone[1–4] or with reducing substances such as carboxylic acids,[9,10] alcohols,[11] aldehydes,[12] ketones,[13] thiourea,[14] acetophenone,[15] thiomaleic acid,[16] iminodiacetic acid[17] and amino acids[18] were used in the redox system. The reducing agent is well known to be the initiator fragment in the initiation reaction. The mechanistic studies reveal that the reducing agent reacts with the metal ion to form a complex intermediate, which subsequently decomposes to give the free radical, thus initiating the polymerization. This paper reports a kinetic study of polymerization reaction of acrylamide initiated by cerium (IV) – phenyl alanine redox system in aqueous sulphuric acid medium in the temperature range of 30–50°C. The anomalous kinetic behaviour associated with acrylamide polymerization has stimulated the choice of this study.

EXPERIMENTAL

Preparation of reagents: Acrylamide (s.d. fine) was purified by two recrystallizations from methanol. Ceric ammonium sulphate, phenyl alanine and sulphuric acid (all AR or equivalent grades) were used as such. Aqueous cerium (IV) stock solutions were freshly prepared by dissolving ceric ammonium sulphate in sulphuric acid. Triply distilled water was used throughout the experiment. Pure nitrogen obtained by passing the commercial gas through the columns of Fisher's solution and distilled water was used for the deaeration of all experimental systems.

Kinetic measurements: Reactions were performed under the inert atmosphere of nitrogen gas in pyrex glass. In a typical kinetic run, a mixture containing solutions of sulphuric acid, the monomer acrylamide, Ce (IV) and phenyl alanine were thermally equilibrated in a water bath at a desired temperature. During polymerization, the rate of monomer disappearance is followed by bolometric method and the rate of disappearance of Ce (IV) volumetrically with Fe (II) using ferroin indicator. The studies are carried out by varying monomer, Ce (IV), phenyl alanine and sulphuric acid concentrations and also by varying the temperature.

RESULTS AND DISCUSSION

The polymerization of acrylamide was carried out with Ce (IV) in the absence of the reducing substance and it was observed that no polymerization occured for 30 min. However, in the presence of PA, the polymerization of acrylamide proceeds without any induction period. The polymerization of acryamide by Ce (IV)–PA redox system occurred at a measurable rate at $400^\circ C$. No induction period was observed under deaerated condition, but there existed an induction period, when the solutions were not deaerated; thus, it is evident that the polymerization was initiated by free radicals formed by the redox system.

Effect of monomer concentration: The polymerization reaction was investigated at different initial concentrations of the AM from 0.04 to 0.24 mol dm^{-3} keeping the concentrations of other reactants constant (Table 1). The initial rate and percentage conversions were found to increase with increase in monomer concentration. When the concentration of monomer was increased, the availability of monomer molecules in the propagation step increases, which obviously increases the rate of polymerization. The plot between log [M] and log R_p is linear with a slope value of 1.42, thus establishing that the order of the reaction with respect to the monomer concentration is 1.5. An order higher than unity indicates the occurrence of a cage effect.[19]

Effect of cerium (V) concentration: The initial rate and maximum conversion increased with increase in the concentration of Ce (IV) in the range from 0.004 to 0.024 mol dm^{-3} (Table 1). An increase in the concentration of Ce (IV) increases the rate of production of primary radicals and hence, initial rate and maximum conversion increases. The order with respect to

[Ce(IV)] was found to be 0.5. A plot of log R_p versus log [Ce (IV)] indicates that the termination occurs through a bimolecular interaction of growing polymer chain radicals.

Effect of phenyl alanine concentration: The initial rate as well as the maximum conversion increased with increase in the concentration of PA in the range from 0.004 to 0.024 mol dm^{-3} (Table 1). This is due to the fact that the increase in the concentration of PA increases the production of primary radicals. The activator component was found to be one half from the plot of log R_p versus log [PA].

Table 1. Dependence of rate on [AM], [Ce (IV)] and [PA]

10^1[AM] mol dm^{-3}	10^2 [Ce(IV)] mol dm^{-3}	10^2 [PA] mol dm^{-3}	10^5 R_p mol dm^{-3} s^{-1}
0.4	0.2	0.2	0.201
0.8	0.2	0.2	0.467
1.2	0.2	0.2	0.941
1.6	0.2	0.2	1.504
2.0	0.2	0.2	2.042
2.4	0.2	0.2	2.655
1.6	0.4	0.2	1.933
1.6	0.8	0.2	2.734
1.6	1.2	0.2	3.348
1.6	1.6	0.2	3.866
1.6	2.0	0.2	4.322
1.6	2.4	0.2	4.735
1.6	0.2	0.4	1.576
1.6	0.2	0.8	2.229
1.6	0.2	1.2	2.730
1.6	0.2	1.6	3.152
1.6	0.2	2.0	3.524
1.6	0.2	2.4	3.860

Solvent: 10% (v/v) aqueous sulphuric acid, [H$^+$] = 0.1 mol dm^{-3}, Temp. = 313 K

Effect of H$^+$ ion concentration: Kinetic studies were carried out in different hydrogen ion concentrations in the range from 0.02 to 0.12 mol dm^{-3} (Table 2). The rate of polymerization decreased with increase in hydrogen ion concentration. This is due to the formation of highly sulphated complex of ceric ion, which predominates at higher sulphuric acid concentrations, thereby rendering the Ce (IV) ions inactive towards initiating the polymerization.

Table 2. Effect of [H$^+$] and temperature on the polymerization of acrylamide

[AM] = 0.16 mol dm^{-3} · [Ce (IV)] = 0.002 mol dm^{-3}, [PA] = 0.002 mol dm^{-3}, Solvent = 10% (v/v) aqueous sulphuric acid

[H$^+$] mol dm^{-3}	Temperature K	10^5 R$_p$ mol dm^{-3} s^{-1}
0.1	313	1.602
0.2	313	1.437
0.3	313	1.257
0.4	313	1.008
0.5	313	0.798
0.1	303	1.245
0.1	308	1.280
0.1	313	1.593
0.1	318	1.929
0.1	323	2.258

Effect of temperature: The rate of polymerization and the percentage of conversion increased steadily with increasing temperature (Table 3). At higher temperatures, the conversion was maximum. The energy of activation was calculated from the Arrhenius plot of log R$_p$ versus 1/T and was found to be 60.74 kJ/mol.

Effect of organic solvents: Addition of 10% (v/v) water–miscible organic solvents, such as methanol, DMF and isopropanol to the reaction mixture depressed the initial rate and maximum conversion (Table 3 and Figure 1). This may be due to the following factors.

Table 3. Effect of organic solvents

[AM] = 0.16 mol dm^{-3}, [Ce (IV)] = 0.002 mol dm^{-3}, [PA] = 0.002 mol dm^{-3}, [H$^+$] = 0.1 mol dm^{-3}, Temp. = 313 K

Time min.	% Conversion			
	Std. Run	10% (v/v) aq. DMF	10% (v/v) aq. MeOH	10% (v/v) aq. Isopropanol
20	9.53	9.01	8.72	8.17
60	20.13	15.33	10.45	9.23
100	31.16	24.76	13.25	11.47
120	40.12	33.28	20.62	14.25
160	54.26	40.37	26.52	19.32
180	62.72	48.27	34.22	24.57

(i) Solvent molecules may decrease the area of shielding of the strong hydration layer in an aqueous medium and results in premature termination of the radicals and the growing chain.

(ii) The abstraction of hydrogen atom by the propagating macro radical, resulting in the formation of alkoxy radical.

(iii) The solvents may increase the regulated rate of production of primary radicals, which renders the termination rate to be relatively fast as compared with the growing polymer chains.
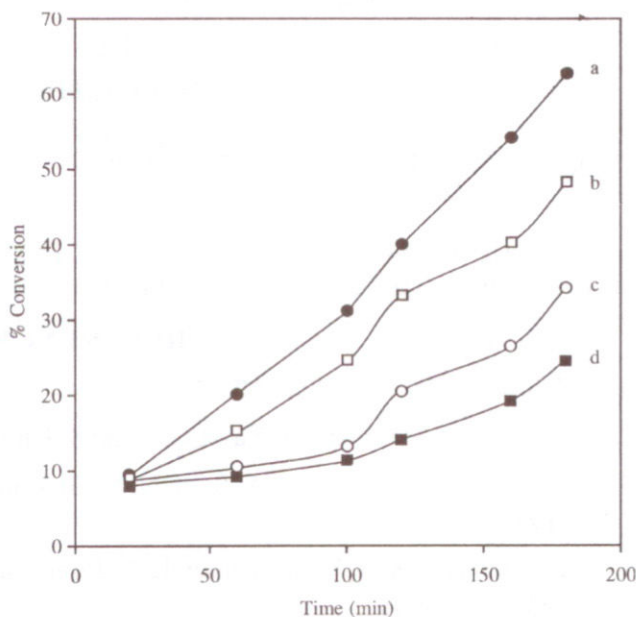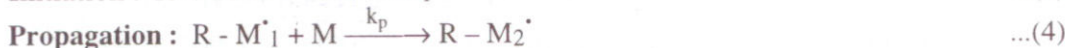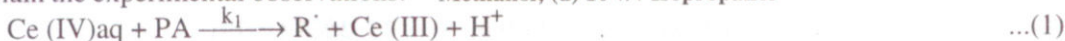

Figure 1. Plot percentage conversion versus time in various organic solvens (a) Std. run; (b) 10 v/v DMF; (c) 10 v/v Methanol; (d) 10 v/v Isopropanol

Mechanism and the rate law: The following reactions scheme is found to explain the experimental observations.

$$Ce\,(IV)aq + PA \xrightarrow{k_1} R^{\bullet} + Ce\,(III) + H^+ \qquad \text{...(1)}$$

$$Ce\,(III) + R^{\bullet} \xrightarrow{k_0} Products \qquad \text{...(2)}$$

Initiation : $R^{\bullet} + M \xrightarrow{k_i} R - M_1^{\bullet}$ \qquad ...(3)

Propagation : $R - M_1^{\bullet} + M \xrightarrow{k_p} R - M_2^{\bullet}$ \qquad ...(4)

$$R - M_{x-1}^{\bullet} + M \xrightarrow{k_p} R - M_x^{\bullet} \qquad \text{...(5)}$$

Termination : $R - M_x^{\bullet} + R - M_y^{\bullet} \xrightarrow{k_t} Polymer$ \qquad ...(6)

Applying steady state approximation, we get

$$\frac{d[R^{\bullet}]}{dt} = k_1[Ce(IV)][PA] - k_0\,[Ce(IV)][R^{\bullet}] - k_i[M][R^{\bullet}] = 0 \qquad \text{...(7)}$$

$$[R^{\bullet}] = \frac{k_1[Ce(IV)][PA]}{k_0[Ce(IV)] + k_i[M]} \qquad \text{...(8)}$$

$$R_p = k_p\,[RM^{\bullet}][M]; \quad R_i = k_i[R^{\bullet}][M] \qquad \text{and} \qquad R_t = k_t[RM_x^{\bullet}][RM_y^{\bullet}]$$

But $R_i = R_t$

$$k_i[R^{\bullet}][M] = k_t[RM_x^{\bullet}][RM_y^{\bullet}]; \quad [RM_x^{\bullet}] = [RM_y^{\bullet}]; \quad k_i\,[R^{\bullet}][M] = k_t\,[RM_x^{\bullet}]^2$$

$$[RM_x^{\bullet}]^2 = \left(\frac{k_i}{k_t}\right)[R^{\bullet}][M]$$

Substituting the value of [R˙], we get,

$$[RM_x^{\cdot}] = \left(\frac{k_i}{k_t}\right)^{1/2} [M]^{1/2} \left[\frac{[Ce(IV)][PA]}{k_0[Ce(IV)] + k_i[M]}\right]^{1/2} \qquad ...(9)$$

$$R_p = k_p \left(\frac{k_i k_1}{k_t}\right)^{1/2} \underline{[M]^{3/2}[Ce(IV)]^{1/2}[PA]^{1/2}} \qquad ...(10)$$

Thus, R_p depends upon $[M]^{3/2}$, $[Ce(IV)]^{1/2}$, $[PA]^{1/2}$ and all the experimental observations are consistent with the derived rate equation.

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