Polymerization of Acrylonitrile Initiated by the Cerium(IV)-Glutamine Redox System: A Kinetic Study

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Polymerization of acrylonitrile monomer [M], initiated by the free radicals. formed *in situ* in cerium(IV)-glutamine [SH^+] redox system, was studied in aqueous sulphuric acid medium in the temperature range 30–50°C. The rate of polymerization (R_p) and the rate of cerium(IV) disappearance have been measured. The influence of varying [M], [SH^+] and [Ce^{4+}] was examined. The effects of some water miscible organic solvents and surfactants on the rate of polymerization were investigated. The temperature dependence of the rate was studied and the activation parameters were computed using Arrhenius and Eyring plots. A mechanism consistent with the experimental data involving cerium(IV)-glutamine complex formation which generates free radicals was suggested. The chain termination step of polymerization reaction was completed by mutual interaction of free radicals.

Key Words: Polymerization, Acrylonitrile, Cerium(IV), Glutamine, Redox, Kinetic.

INTRODUCTION

Redox polymerization of vinyl monomers initiated by transition metal ions in their higher oxidation states in an aqueous medium can provide valuable information regarding the mechanistic details of the elementary steps[1–9]. Cerium ion alone[10–17] or in conjunction with suitable reducing agents which include pinacol[18], amines[19], alcohols[20–29], thiourea[24–26], acetophenone[27], thiomalleic acid[28] and 2-mercaptoethanol[29].

The chemistry of glutamine has attracted the attention of many investigators due to its biological activities and synthetic applications. This paper reports a kinetic study of a polymerization reaction of acrylonitrile initiated by the cerium(IV)-glutamine redox system in aqueous sulphuric acid medium in the temperature range of 30–50°C. The anomalous kinetic behaviour associated with acrylonitrile polymerization in aqueous medium[30] and the importance of polyacrylonitrile in the fibre industry, have stimulated the choice of this study.

EXPERIMENTAL

Preparation of reagents: Acrylonitrile (Sisco-Chem, India) was purified by the method of Bamford and Jenkins[31]. Ceric ammonium sulphate was an E. merck

AR product. All other chemicals such as glutamine, sodium bisulphate, sulphuric acid, ferrous ammonium sulphate, sodium lauryl sulphate, cetyltrimethyl ammonium bromide and triton-X-100 were of analytical grade. Aqueous cerium(IV) stock solutions were freshly prepared by dissolving ceric ammonium sulphate in sulphuric acid with known concentration. Triply distilled water was used throughout the experiment. Pure nitrogen obtained by passing through a column of Fieser's solutions and distilled water, was used for the deaeration of all experimental systems.

Kinetic measurements: Reactions were performed under the inert atmosphere of nitrogen in pyrex glass vessels. In a typical kinetic run, a mixture of solutions containing requisite amounts of the acrylonitrile monomer [M], glutamine [SH$^+$], cerium(IV), the acid (sulphuric acid + sodium bisulphate to maintain a known acid concentration), sodium perchlorate (to maintain a constant ionic strength) and water (to keep the total volume constant) was thermally equilibrated in a water bath at a desired temperature. A wash bottle containing an aqueous solution of acrylonitrile, whose concentration is same as in the reaction vessel, was interposed between the nitrogen train and reaction vessel to avoid any loss of monomer due to deaeration. Oxygen free nitrogen was bubbled through the solution for given period (*ca.* 30 mins.) and then the solution of the oxidant, cerium (IV), was added. The reaction vessel was sealed with a rubber gasket.

Ceric ion estimation: Ceric ion concentrations at different intervals of time are determined by quenching the aliquots in suitable excess of ferrous ammonium sulphate, followed by back titration of the excess ferrous ions with ceric ammonium sulphate of known concentration using N-phenyl anthranilic acid as indicator. The rate of d [Ce(IV)]/dt is found to be first order with respect to [Ce(IV)] and also independent of monomer concentration. Earlier workers have shown that Ce(IV) does not form kinetically detectable complexes with amino acids.

Molecular weight determination: The molecular weights (M_v) of the purified samples of polyacrylonitrile product were determined by viscometry. A 0.1% solution of the polymer in DMF was filtered through a fritted glass filter and placed in an Ubbelhode type suspended level dilution viscometer. The intrinsic viscocity [η] for the reaction mixture was detemined and the M_v value was evaluated using the following Mark-Houwink equation given by Stockmayer and Cleland: [η] = $(3.335 \times 10^{-4})\ M_v^{0.72}$ at 30°C for polyacrylonitrile. The molecular weight of the polymer product, under standard conditions, was found to be 1.76×10^5. It increases with increase in monomer concentration and decreases with increase in [Ce^{4+}], [Glutamine] and temperature. This effect is attributed to the fact that the increase in [Ce^{4+}], [Glutamine] or temperature provides more chances for premature termination of growing chain radicals reducing the degree of polymerization.

RESULTS AND DISCUSSION

The polymerization of acrylonitrile initiated by cerium(IV)-glutamine redox

system takes place at a measurable rate at 40°C. Although no induction period was observed under deaerated conditions, there exists an induction period if the solution was not deaerated. Thus it is evident that the polymerization is initiated by free radicals formed *in situ* by the redox system. The steady state was attained within 180 minutes. The rate of disappearance ($-R_m$) was first order with respect to cerium(IV) and is independent of monomer concentration. It depends on the concentration of both cerium(IV) and glutamine. A plot of $-1/R_m$, *vs.* 1/glutamine is linear with an intercept on rate axis, indicating Lineweaver-Burk kinetics for complex formation[32].

Effect of monomer concentration: The effect of monomer concentration on the rate of polymerization (R_p) was studied in the range (0.3034–0.9103 mol dm^{-3}). The initial rate and percentage conversions were found to increase with the increase in monomer concentration. When the concentration of monomer increases, the availability of the monomer molecules in the propagation steps increases which obviously increases the rate of polymerization. The exponent with respect to the monomer concentration was found to be 1.5 [Fig. 2]. An order of the reaction higher then unity is indicative of the occurrence of cage effect[33].

Effect of cerium(IV) concentration: The initial rate as well as maximum conversion increases with increase in cerium(IV) concentration in the range [(2.5 to 12.5) × 10^{-3} mol dm^{-3}]. This is due to the fact that the increase in cerium(IV) concentration increases the rate of production of primary radicals and hence the number of propagating polymer radicals, which in turn increases the polymerization rate and the maximum conversion. The order with respect to cerium(IV) concentration was found to be one half from a plot of log R_p *vs.* log cerium(IV) [Fig. 1B], which clearly indicates that the termination occurs through a bimolecular interaction of growing polymer chain radicals. The M_v value decreases with the increase of cerium(IV) concentration is due to the fact that increasing concentration of cerium(IV) provides more chance for premature termination of growing chain radicals, which in turn reduces the degree of polymerization.

Effect of glutamine concentration: The initial rate, as well as the maximum conversion, increases with increase in the glutamine concentration in the range (0.01–0.09 mol dm^{-3}) . This is due to the fact that the increase in the glutamine concentration increases the production of primary radicals, and hence it leads to increase in R_p and also the maximum conversion. The exponent of glutamine concentration was found to be one half from the plot of log R_p *vs.* log [Glutamine] [Fig. 1A]. The decrease in M_v further supports the possibility of bimolecular termination by mutual interaction of growing polymer chain radicals.

Effect of H$^+$ ion concentration: Kinetic measurements were performed in sulphuric acid-sodium bisulphate solutions of different hydrogen ion concentrations in the range [0.1–0.5 M]. The effective hydrogen ion concentrations were evaluated from the calibration plot of Kemp and Waters[34]. The rate of polymerization decreases with increase in hydrogen ion concentration indicating that the hydrolyzed species of cerium (IV) is more reactive than the unhydrolyzed species, and also that the unprotonated form of glutamine is more reactive than the protonated form. The order with respect to hydrogen ion concentration was found to be one half from the plot of log R_p *vs.* log [H$^+$] [Fig. 3A].
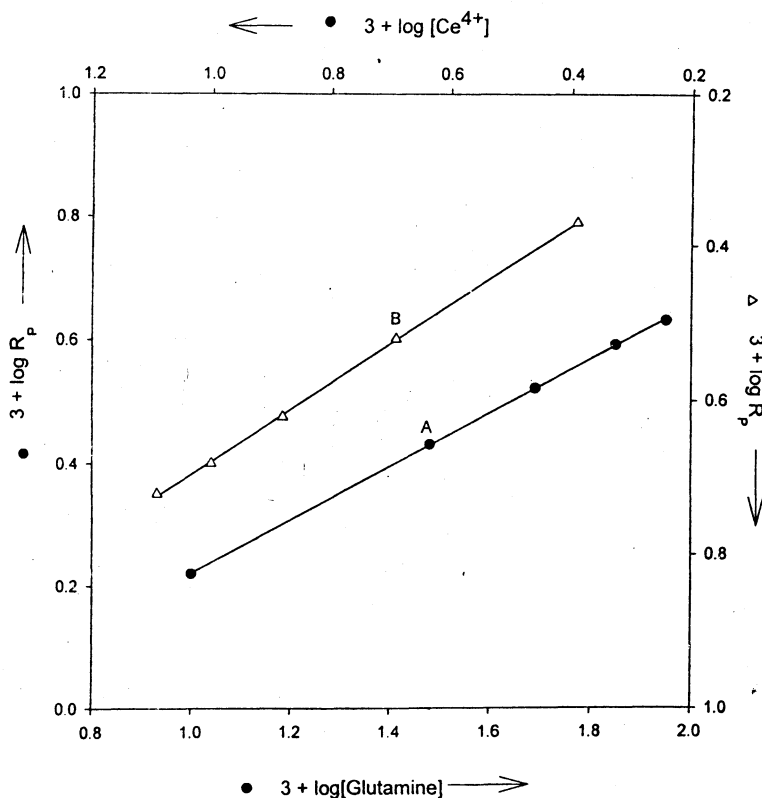
Fig. 1. [A] Plot of $3 + \log R_p$ vs. $3 + \log$ [Glutamine]. $[Ce^{4+}] = 0.005$ mol dm^{-3}, $[M] = 0.6068$ mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3}, Temperature = 313 K, $[I] = 0.5$ mol dm^{-3}, [Glutamine] $= 0.01, 0.03, 0.05, 0.07$ and 0.09 mol dm^{-3}. [B] Plot of $3 + \log R_p$ versus $3 + \log [Ce^{4+}]$. $[Ce^{4+}] = 0.0025, 0.005, 0.0075, 0.010$ and 0.0125 mol dm^{-3}, $[M] = 0.6068$ mol dm^{-3}, [Glutamine] $= 0.05$ mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3}, Temperature = 313 K, $[I] = 0.5$ mol dm^{-3}

Effect of Organic solvents: Addition of water-miscible organic solvents (5% v/v), such as DMF, methanol and isopropanol, to the reaction mixture depresses the initial rate as well as the maximum conversion. The R_p was found to be in the order: DMF > MeOH > isopropanol [Fig. 4]. This may be due to the following reasons:

(i) The chain transfer phenomenon, *i.e.*, abstraction of hydrogen atom by the propagating macro radical, resulting in the formation of alkoxy radical.

(ii) Decrease in the area of shielding of a strong hydration layer in the aqueous medium, resulting in the termination of the radical end of growing chain.

(iii) Increase in the regulated rate of production of primary radicals caused by the solvent, which renders the termination rate to be relatively fast as compared with the growing polymer chains.

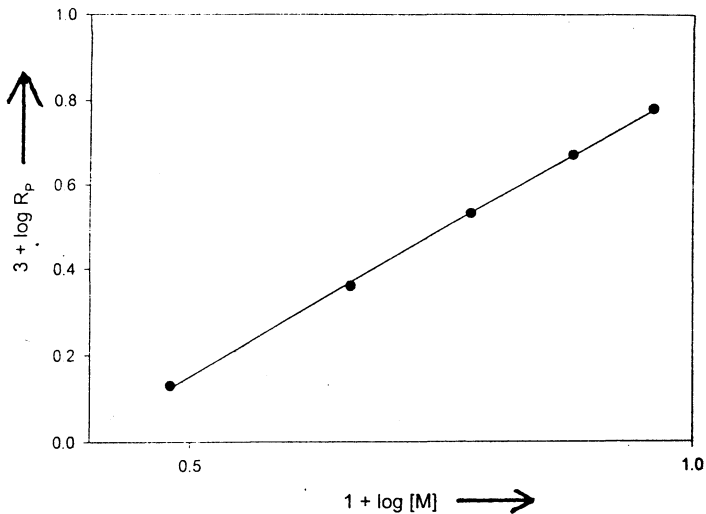(iv) Change in the termination rate arising from a change in the degree of occlusion of the radical.

Fig. 2. Plot of $3 + \log R_p$ vs. $1 + \log [M]$. $[Ce^{4+}] = 0.005$ mol dm^{-3}, [Glutamine] = 0.05 mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3}, Temperature = 313 K, [I] = 0.5 mol dm^{-3}, [M] = 0.3034, 0.4551, 0.6068, 0.7585 and 0.9103 mol dm^{-3}.

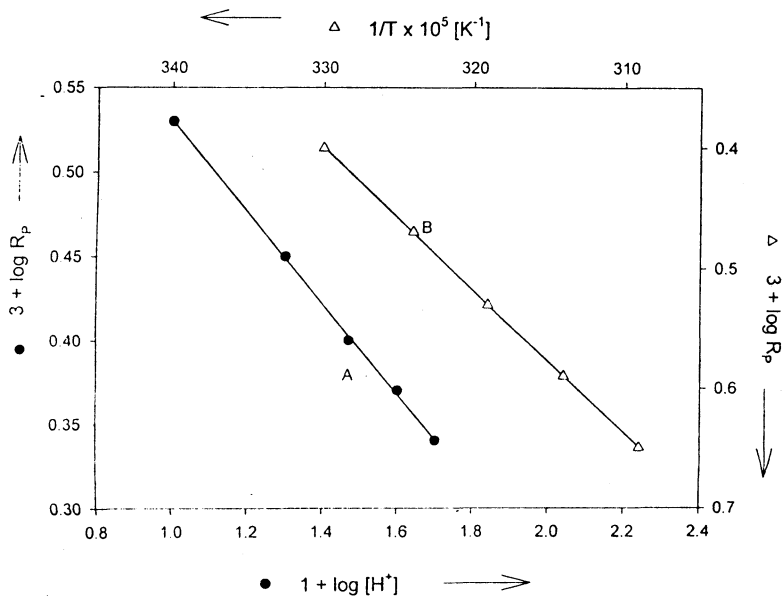
Fig. 3. [A] Plot of $3 + \log R_p$, vs. $1 + \log [H^+]$. $[Ce^{4+}] = 0.005$ mol dm^{-3}, [Glutamine] = 0.05 mol dm^{-3}, [M] = 0.6068 mol dm^{-3}, Temperature = 313 K, [I] ≠ 0.5 mol dm^{-3}, $[H^+]$ = 0.1, 0.2, 0.3, 0.4 and 0.5 mol dm^{-3}. [B] Plot of $3 + \log R_p$ vs. $1/T$. $[Ce^{4+}] = 0.005$ mol dm^{-3}, [Glutamine] = 0.05 mol dm^{-3}, [M] = 0.6068 mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3}, [I] = 0.5 mol dm^{-3}, Temperature = 303, 308, 313, 318 and 323 K.

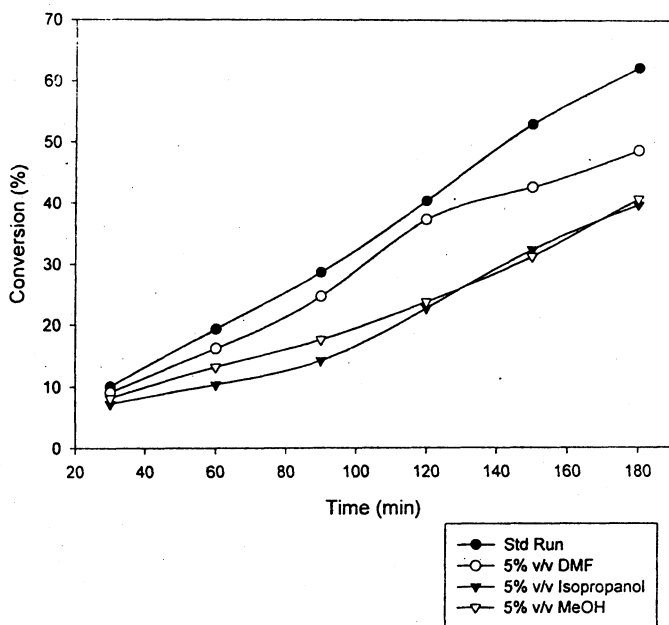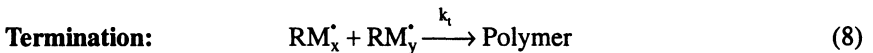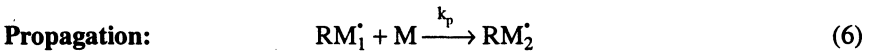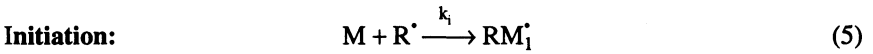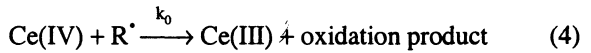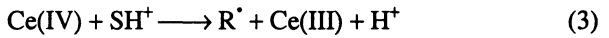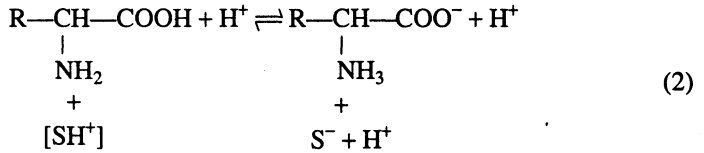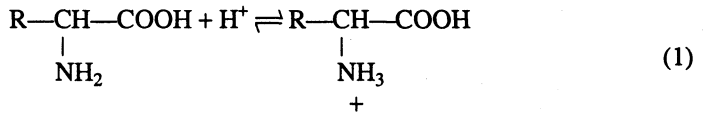Fig. 4. Plot of % conversion versus time. $[Ce^{4+}] = 0.005$ mol dm^{-3}, [Glutamine] = 0.05 mol dm^{-3}, [M] = 0.6068 mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3}, Temperature = 313 K, [I] = 0.5 mol dm^{-3}.

Effect of surfactants: Addition of anionic surfactant, sodium lauryl sulphate, increased the R_p above and below the CMC value. The cationic surfactants like cetyltrimethyl ammonium bromide decrease the rate above and below the CMC value. In contrast, the non-ionic surfactants like Triton-X-100 have no effect on the rate. The reason may be that ammonium bromide decreases the rate above and below the CMC value. In contrast, the non-ionic surfactants like Triton-X 100 have no effect on the rate. The reason may be attributed to the hydrophobic interactions, which are responsible for the enhancement or inhibition of the rate of polymerization.

Effect of temperature: The rate of polymerization and the percentage of conversion increases steadily with increasing temperature. At higher temperature the maximum conversion increases. The energy of activation as calculated from the Arrhenius plot of log R_p vs. 1/T in the temperature range 30–50°C was found to be 23.31 ± 0.5 kJ mol^{-1} [Fig. 3B]. The overall thermodynamic parameters were calculated and are found to be $\Delta H^* = 20.71$ kJ mol^{-1}, $\Delta G^* = 91.62$ kJ mol^{-1} and $\Delta S^* = -226.53$ J K^{-1} mol^{-1}.

Mechanism and the Rate Law

The following reaction mechanism may be used to explain satisfactorily the observed kinetic results.

$$R\text{—}CH\text{—}COOH + H^+ \rightleftharpoons R\text{—}CH\text{—}COOH$$
$$\quad | \qquad\qquad\qquad\qquad | $$
$$\quad NH_2 \qquad\qquad\qquad NH_3 \qquad (1)$$
$$\qquad\qquad\qquad\qquad\qquad\quad +$$

$$R\text{—}CH\text{—}COOH + H^+ \rightleftharpoons R\text{—}CH\text{—}COO^- + H^+$$
$$\quad | \qquad\qquad\qquad\qquad\quad | $$
$$\quad NH_2 \qquad\qquad\qquad\quad NH_3$$
$$\quad + \qquad\qquad\qquad\qquad + \qquad\qquad\qquad (2)$$
$$[SH^+] \qquad\qquad\qquad S^- + H^+$$

$$Ce(IV) + SH^+ \longrightarrow R^{\bullet} + Ce(III) + H^+ \qquad (3)$$

$$Ce(IV) + R^{\bullet} \xrightarrow{k_0} Ce(III) + \text{oxidation product} \qquad (4)$$

Initiation:
$$M + R^{\bullet} \xrightarrow{k_i} RM_1^{\bullet} \qquad (5)$$

Propagation:
$$RM_1^{\bullet} + M \xrightarrow{k_p} RM_2^{\bullet} \qquad (6)$$

$$RM_{x-1}^{\bullet} + M \xrightarrow{k_p} RM_x^{\bullet} \qquad (7)$$

Termination:
$$RM_x^{\bullet} + RM_y^{\bullet} \xrightarrow{k_t} \text{Polymer} \qquad (8)$$

Applying the steady state principles, we get

$$\frac{d[R^{\bullet}]}{dt} = k_1[Ce(IV)][SH^+] - k_0[Ce(IV)][R^{\bullet}] - k_i[M][R^{\bullet}] = 0 \qquad (9)$$

$$\Rightarrow \qquad k_1[Ce(IV)][SH^+] - k_0[Ce(IV)][R^{\bullet}] - k_i[M][R^{\bullet}] = 0$$

$$[R^{\bullet}] = \frac{k_1[Ce(IV)][SH^+]}{K_0[Ce(IV) + K_i[M]} \qquad (10)$$

$$R_p = k_p[RM^{\bullet}][M] \qquad (11)$$

$$R_i = k_i[M][R^{\bullet}] \qquad (12)$$

$$R_t = k_t[RM_x^{\bullet}][RM_y^{\bullet}] \qquad (13)$$

But, $\qquad\qquad\qquad R_i = R_t$

$$k_i[M][R^{\bullet}] = k_t[RM_x^{\bullet}]^2 \qquad (14)$$

$$[RM_x^{\bullet}] = [RM_y^{\bullet}]$$

$$[RM_x^{\bullet}]^2 = \left(\frac{k_i}{k_t}\right)[M][R^{\bullet}] \qquad (15)$$

$$= \left(\frac{k_i}{k_t}\right)[M] \times \frac{k_1[Ce(IV)][SH^+]}{k_0[Ce(IV)] + k_i[M]} \tag{16}$$

$$[RM_x^\bullet] = \left(\frac{k_i k_1}{k_t}\right)^{1/2}[M]^{1/2}\left\{\frac{[Ce(IV)][SH^+]}{k_0[Ce(IV)] + k_i[M]}\right\}^{1/2} \tag{17}$$

$$R_p = k_p\left(\frac{k_i k_1}{k_t}\right)^{1/2}\frac{[M]^{3/2}[Ce(IV)]^{1/2}[SH^+]^{1/2}}{\{k_0[Ce(IV)] + k_i[M]\}^{1/2}} \tag{18}$$

Thus, the dependence of R_p on $[M]^{1.5}$, $[Ce(IV)]^{1/2}$, $[SH^+]^{1/2}$, $[H^+]^{-1/2}$, all which observed are consistent with the experimental results.

The low energy of activation is an indication that the high reactivity of the initiator which provides direct experimental evidence of the existence of transient radical intermediate generated in redox reactions. It also enables the identification of these radicals as end group of the polymer. Further work on the kinetics of polymerization of various vinyl monomers initiated by the reaction of cerium(IV) and other transition metal ions with suitable reductants is in progress in our laboratories.

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