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Polymerization of Acrylonitrile Initiated by Ce^{4+}-Isopropyl Alcohol Redox System in the Presence and Absence of Ag^+: A Kinetic Study

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ABSTRACT

Polymerization of acrylonitrile (AN) initiated by Ce^{4+} isopropyl alcohol (IPA) has been carried out in the presence and absence of Ag^+ ions. In the absence of Ag^+ ions the order with respect to [IPA], [Ce^{4+}], and [AN] was found to be 0.4, 0.1, and 1.55, respectively. A mechanism involving primary radical production by the reaction of Ce^{4+} with IPA, which initiates polymerization of AN and mutual termination of growing polymer radicals, is envisaged. In the presence of Ag^+ ions the order with respect to [Ag^+], [AN], [Ce^{4+}], and [IPA] is found to be 0.4, 1.4, 0.3, and 0.15, respectively. Formation of an Ag^+-IPA adduct which is oxidized to radicals by Ce^{4+} via an intermediate Ag^{2+}-adduct is assumed. The initiation of polymerization by primary radicals as well as by Ag^{2+}-adduct and mutual termination of growing polymer radicals are proposed to explain the kinetic data.

Ceric salts alone [1] or in combination [2, 3] with reducing agents act as initiators for vinyl polymerization. It is known that, in redox initiated polymerizations, metal ions like Ag^+, Cu^{2+}, and Mn^{2+} can activate [4] or retard [5] the rate of polymerization depending upon the type of redox system used and the conditions employed. Earlier [6] in our laboratory it was shown that Ce^{4+} oxidation of isopropyl alcohol (IPA), which involves formation of free radicals, is catalyzed [7] by Ag^{+} ions. In view of this, we have chosen this system for carrying out the polymerization of acrylonitrile (AN) to understand the role of Ag^{+} ions in the polymerization process.

EXPERIMENTAL

All chemicals used in this work were of the BDH AnalaR grade. The monomer AN was purified by distilling at low pressure under N_2 atmosphere after washing with 5% NaOH and 3% H_3PO_4. The polymerization experiments were conducted in the dark under deaerated conditions at constant ionic strength. The time-average kinetics was followed and assumed as steady-state kinetics. The rate of monomer disappearance was followed gravimetrically and that of ceric disappearance titrimetrically. The detailed experimental procedure is given in an earlier paper [8].

RESULTS AND DISCUSSION

Oxidation

In the Ce^{4+} oxidation [6] of IPA the rates of oxidation were found to increase with increase in both [Ce^{4+}] and [IPA]. The order with respect to [IPA] and [Ce^{4+}] were found to be one each. At high [IPA] the order in [IPA] was fractional. The rate of oxidation decreased with an increase in [H^{+}] when the ionic strength was not constant. But at constant ionic strength the rates increased with an increase in [H^{+}]. These were explained by assuming neutral $Ce(SO_4)_2$ as the reactive species and an outer sphere reaction between IPA and Ce^{4+}.

Polymerization

The polymerization of AN with Ce^{4+} alone was extremely slow. The polymerization of AN was carried out with the Ce^{4+} - IPA redox system in H_2SO_4 medium at 45° C. The nature of the initiating species has been confirmed from the IR spectra of polyacrylonitrile which showed the typical peak of the $\rangle$C–OH group at 3600 cm^{-1}, suggesting C–H bond rupture during oxidation and formation of the $(CH_3)_2\dot{C}{-}OH$ radical.

The order with respect to [IPA] was found to be 0.4 in the concentration range 0.4 to 3.2 M and decreased at higher concentrations (Fig. 1A). The order in [Ce^{4+}] was found to be fractional (0.1) in the concentration range 6×10^{-4} to 5×10^{-3} M and independent of [Ce^{4+}] at higher concentrations (Fig. 1C). The order with respect to monomer was found to be 1.55 (Fig. 1B). The fractional orders in [initiator]

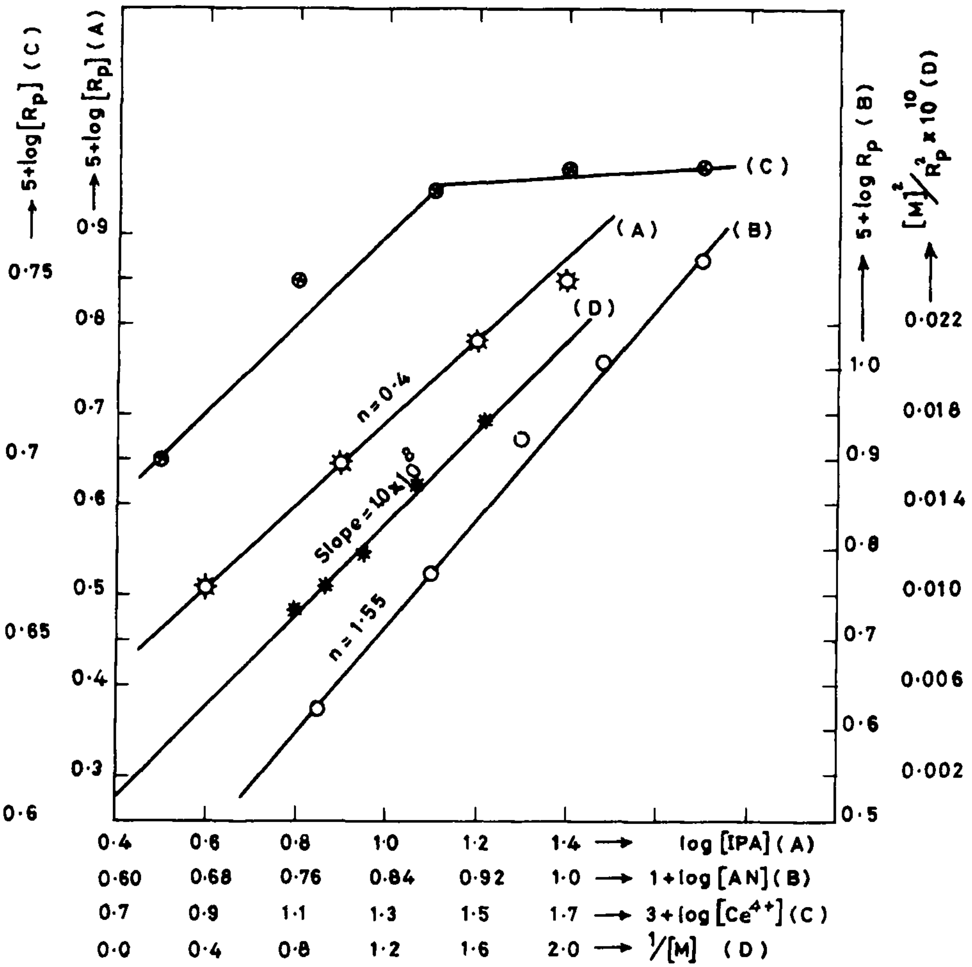

FIG. 1. (A) Plot of $5 + \log R_p$ vs $\log [\mathrm{IPA}]$: $[\mathrm{Ce}^{4+}] = 5.00 \times 10^{-3}$ M, $[\mathrm{H}^+] = 1.00$ M, $[\mathrm{AN}] = 0.760$ M, temperature = 46° C. (B) Plot of $5 + \log R_p$ vs $1 + \log [\mathrm{AN}]$: $[\mathrm{IPA}] = 1.60$ M, $[\mathrm{Ce}^{4+}] = 5.00 \times 10^{-3}$ M, $[\mathrm{H}^+] = 1.00$ M, temperature = 46° C. (C) Plot of $5 + \log R_p$ vs $3 + \log [\mathrm{Ce}^{4+}]$: $[\mathrm{H}^+] = 1.00$ M, $[\mathrm{AN}] = 0.760$ M, $[\mathrm{IPA}] = 1.60$ M, temperature = 46° C. (D) Plot of $[\mathrm{M}]^2/R_p^2$ vs $1/[\mathrm{M}]$: Conditions same as in B.

and 1.55 order in [monomer] strongly suggest mutual termination. This is similar to what has been reported by Rao et al. [2] earlier in the Ce^{4+} + diacetone alcohol + AN system. The dependence of the rate of ceric disappearance on [Ce^{4+}] and [IPA] was the same in the absence of monomer.

On the basis of the above results, the mechanism proposed is

$$Ce^{4+} + IPA \xrightarrow{k_1} R^{\bullet} + Ce^{3+} + H^{+} \tag{1}$$

$$R^{\bullet} + Ce^{4+} \xrightarrow{k_0} \text{products} \tag{2}$$

$$R^{\bullet} + M \xrightarrow{k_i} M_1^{\bullet} \tag{3}$$

$$Ce^{4+} + M \xrightarrow{k_i'} M_1^{\bullet} \tag{4}$$

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet} \tag{5}$$

• • • • • • • •

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_t} \text{polymer } (M_{n+m}) \tag{6}$$

Neglecting the small contribution of k_i' under our experimental conditions and applying the steady-state principle to the active intermediates, the rate law comes out to be

$$R_p = \frac{k_p}{k_t^{1/2}} \left[\frac{k_i k_1 [Ce^{4+}][IPA]}{k_i[M] + k_0[Ce^{4+}]} \right]^{1/2} [M]^{3/2} \tag{7}$$

$$-\frac{d[Ce^{4+}]}{dt} = k_1[Ce^{4+}][IPA] \tag{8}$$

The above rate law explains well all our experimental results at a low concentration range of IPA and Ce^{4+}. Squaring and taking the reciprocal of Eq. (7) for R_p, we get

$$\frac{[M]^2}{R_p^{\,2}} = \frac{k_t k_0}{k_1 k_i k_p^{\,2}[M][IPA]} + \frac{k_t}{k_1 k_p^{\,2}[Ce^{4+}][IPA]} \tag{9}$$

The values of the composite constants, i.e., $k_p^{\,2}k_1/k_t$ and k_0/k_i, have been evaluated from the slope and intercept values of the linear plot of $[M]^2/R_p^{\,2}$ vs $1/[M]$ (Fig. 1D) and found to be 11.4×10^{-6} and 2.0×10^{3}, respectively. Taking into account the fact that $k_0[Ce^{4+}] \gg k_i[M]$ at high $[Ce^{4+}]$, the expression for R_p reduces to

$$R_p = k_p(k_i k_1/k_t k_0)^{1/2}[M]^{3/2}[IPA]^{1/2} \tag{10}$$

The independence of R_p on $[Ce^{4+}]$ at high $[Ce^{4+}]$ can be explained from the above equation. Several [9] such instances are known in the literature, and these have been explained by considering $k_0[Ce^{4+}] \gg k_i[M]$. The decrease in order in [IPA] at high [IPA] is probably due to the increased regulated rate of production of primary radicals which renders the termination rate relatively fast compared to the growing polymer chain rate.

Water-soluble solvents such as acetic acid and acetonitrile depress the rate of polymerization considerably. The increase in percentage of acetic acid and acetonitrile from 0 to 20 (v/v) decreased the rate of polymerization from 5×10^{-5} to 3.8×10^{-5} and 2.0×10^{-5}, respectively (Table 1). This behavior can be interpreted by assuming that the presence of solvents increases the regulated rate of production of primary radicals which renders the termination rate relatively fast compared to the growing polymer chain rate and can also decrease the area of shielding of the strong hydration layer in aqueous medium, resulting in termination of growing chains, in accordance with the view of Kern et al. [10]. Addition of Cu^{2+} ions decreased the rate of polymerization, probably by trapping the radicals, a property for which Cu^{2+} is now well known [11] (Table 1).

In the Presence of Ag^+

Oxidation

The presence of trace amounts of Ag^+ was found to catalyze [7] the oxidation of IPA by Ce^{4+}. The order in $[Ce^{4+}]$ and $[Ag^+]$ were found to be one each and fractional in [IPA]. The catalysis was explained by assuming adduct formation between IPA and Ag^+. The latter reacts with Ce^{4+} to give Ag^{2+}-adduct. This was then assumed to disproportionate to give free radicals in a fast step.

TABLE 1. Effect of Varying Solvents and [Cu^{2+}] on Rate of Polymerization (R_p) ([Ce^{4+}] = 5.00 × 10^{-3} M, [IPA] = 1.60 M, [AN] = 0.760 M, [H^+] = 1.00 M, temperature = 45° C)

% of acetic acid (v/v)	$R_p \times 10^5$	% of acetonitrile (v/v)	$R_p \times 10^5$	[Cu^{2+}] × 10^2	$R_p \times 10^5$
0.00	6.00	0.00	6.00	0.00	6.00
5.00	5.30	5.00	5.00	0.500	5.80
10.0	4.50	10.0	3.90	1.00	5.40
15.0	4.10	15.0	2.80	2.00	5.20
20.0	3.80	20.0	2.00	4.00	5.00

Polymerization

In the presence of Ag^+ the polymerization rate was significantly higher at a very low concentration of IPA than under uncatalyzed conditions. This can also be seen from the plot of time vs percent conversion in the presence and absence of Ag^+ (Fig. 2A and 2B). The maximum percent of conversion was also increased from 75 to 90 in the presence of Ag^+. The order with respect to [IPA], [Ce^{4+}], [Ag^+], and [M] was found to be 0.15, 0.3, 0.4, and 1.4, respectively (Fig. 3). The order in [IPA], however, decreased significantly at high [IPA]. The dissimilarities in kinetic parameters and catalytic activity of Ag^+ can be explained as follows.

The promoting action of Ag^+ is probably due to some facile reaction path through the intermediacy of a new redox system formed by added Ag^+ ion. Ag^+ ions are known to form colorless adducts with IPA, and evidence for the formation of such an adduct was obtained from IR and NMR studies [7]. The decrease in order with respect to [IPA] could be due to adduct formation between IPA and Ag^+. The 0.3 order with respect to [Ce^{4+}] can be explained by assuming participation of the Ag^{2+}-adduct in the initiation step in addition to the primary radicals produced by the disproportionation of the Ag^{2+}-adduct. The catalytic activity of Ag^+ is also probably due to Ag^{2+}-adduct initiation rather than to an increase in the production of radicals at a higher rate. If the initiation is only by primary radicals, the rate of polymerization should increase gradually with increasing [IPA], [Ce^{4+}], or [Ag^+]. It was observed that the rate increased with an increase in [Ag^+] and not with an increase in [IPA] and [Ce^{4+}]. The supporting Ag^{2+}-adduct also participates in initiation. The dependence of rate of ceric disappearance on [Ce^{4+}], [Ag^+], and [IPA] was

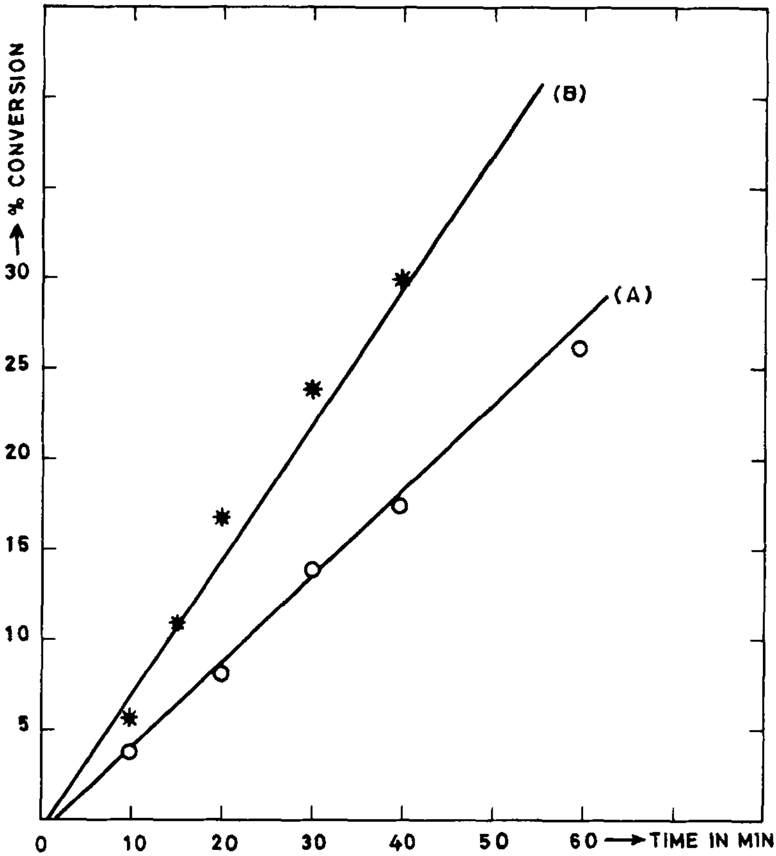

FIG. 2. (A) Plot of percent conversion vs time: [Ce^{4+}] = 5.00 × 10^{-3} M, [H^+] = 1.00 M, [IPA] = 1.60 M, [AN] = 0.760 M, temperature = 46°C. (B) Plot of percent conversion vs time in the presence of 0.01 M Ag^+: Conditions same as in A.

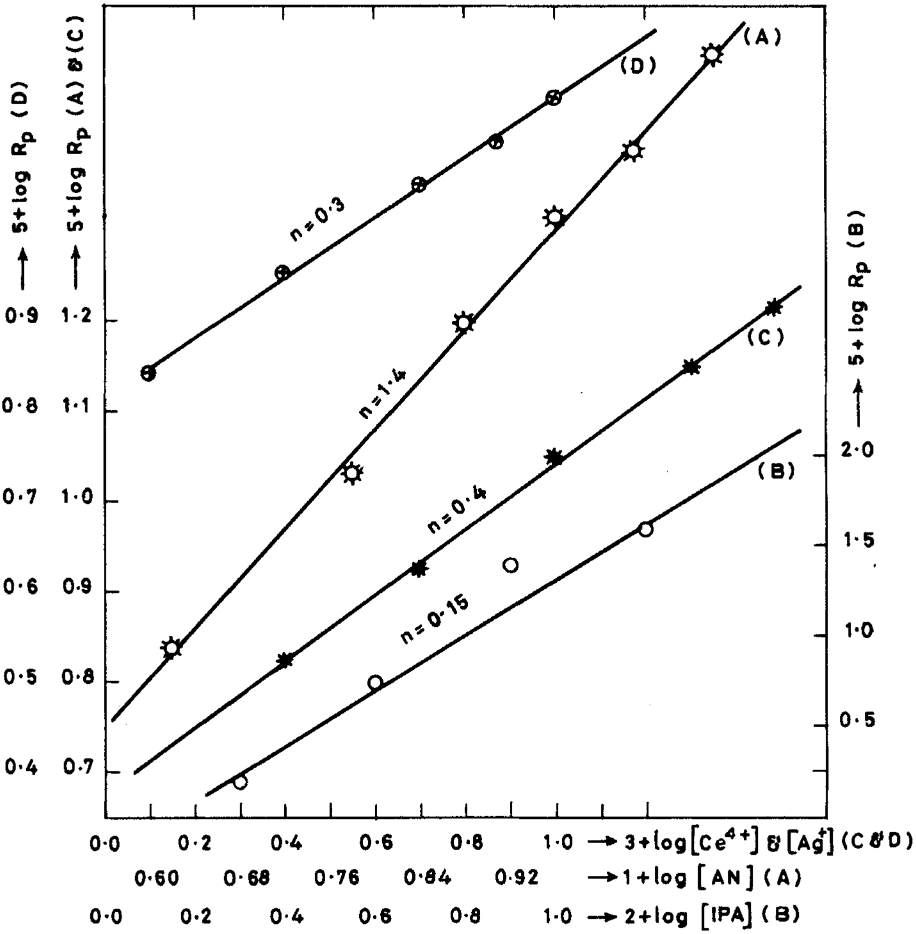

FIG. 3. (A) Plot of 5 + log R_p vs 1 + log [AN]: [Ce^{4+}] = 5.00 × 10^{-3} M, [IPA] = 1.60 M, [H^+] = 1.00 M, [Ag^+] = 1.00 × 10^{-2} M, temperature = 46° C. (B) Plot of 5 + log R_p vs 2 + log [IPA]: Conditions same as in A. (C) Plot of 5 + log R_p vs 3 + log [Ag^+]: Conditions same as in A. (D) Plot of 5 + log R_p vs 3 + log [Ce^{4+}]: Conditions same as in A.

the same as in the absence of monomer, and an increase in [M] did not produce any appreciable change.

On the basis of the above discussion the following mechanism is proposed for polymerization in the presence of Ag^+:

$$Ag^+ + IPA \xrightleftharpoons{K} (adduct)^+ \tag{11}$$

$$Ce^{4+} + (adduct)^+ \xrightarrow{k_2} Ag^{2+}\text{-adduct} \tag{12}$$

$$Ag^{2+}\text{-adduct} + M \xrightarrow{k_i} M^{\bullet} + Ag^+\text{-adduct} \tag{13}$$

$$Ag^{2+}\text{-adduct} \xrightarrow{k_3} R^{\bullet} + Ag^+ + H^+ \tag{14}$$

$$R^{\bullet} + M \xrightarrow{k_i'} M^{\bullet} \tag{15}$$

$$R^{\bullet} + Ce^{4+} \xrightarrow{k_0} \text{products} \tag{16}$$

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet} \tag{17}$$

$$\cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot$$

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_t} M_{n+m}\text{polymer} \tag{18}$$

Applying steady-state treatment to the reactive intermediates, the rate laws obtained are

$$R_p = \frac{k_p[M]^{3/2}}{k_t^{1/2}} \left[\frac{Kk_2[IPA][Ag^+]}{(k_i[M] + k_3)(1 + K[Ag^+] + K[IPA])} (k_i[Ce^{4+}] + \frac{k_i'k_3}{k_0}) \right]^{1/2} \tag{19}$$

$$-\frac{d[Ce^{4+}]}{dt} = \frac{Kk_2[Ce^{4+}][Ag^+][IPA]}{1 + K[Ag^+] + K[IPA]} \tag{20}$$

The above rate laws explain well all our experimental results in the presence of Ag^+.

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